DIRECT AA **MERCURY** DETERMINATION IN COAL

ASTM D6722-01(2006)
EPA 7473

INTRODUCTION

Mercury is one of the most toxic trace contaminant naturally occurring in the coals. During the coal combustion process at the coal-fired power plants mercury is released from its bound state into the environment. To manage effectively the stack gas cleaning process, it is necessary to know a comprehensive pattern of mercury content in the fossil fuel, stack gases, and liquid and solid waste (fly ash, bottom ash, boiler slag, FGD products). Getting this information is a complicated analytical problem, because the mercury content in coals and combustion products may vary greatly. In some regions of Russia, China, USA, India, and other countries, there exist coal-fields with anomalous high content of mercury (up to 15 ppm).

Standard methods of mercury determination in coal using atomic absorption spectrometry (ASTM D6414-01 (2006) and ISO 15237:2003) involve preliminary digestion of the sample that takes from 0.5 to 8 hours depending on the digestion conditions, followed by the quantitative measurement using Cold Vapor AAS.

Alternative methods for coal analysis (ASTM D6722-01(2006) and EPA 7473) propose a simpler analysis procedure, namely, thermal decomposition of the sample combined with catalytic conversion, amalgamation and quantitative determination by AAS.

The use of an **RA-915+/RA-915M analyzer** with a **PYRO-915+ pyrolytic attachment** provides direct determination of mercury in coal without digestion and intermediate amalgamation.

MEASUREMENT METHOD

This method of mercury determination in coal is based on the atomization of mercury contained in the sample in a **PYRO-915+** attachment and subsequent mercury determination by flameless AAS in a mercury analyzer **RA-915M/RA-915+**.

The two-section atomizer **PYRO-915+** consists of evaporator, in which evaporation of liquid samples and pyrolysis of solid samples are carried out, and of the heated reactor, in which catalytic destruction of the sample matrix compounds proceeds. After the furnace, the gas flow heated to 700 ^{O}C enters directly the analytical cell, which is heated up to 750 ^{O}C. The interference from the remaining impurity compounds is eliminated due to the high selectivity of the **RA-915M/RA-915+** analyzer with the Zeeman background correction. The analysis procedure has been developed by LUMEX engineers.

ANALYSIS FEATURES

The proposed method of analysis by pyrolysis shows the following advantages as compared to the common two-stage mercury determination (digestion + AAS):

- High analysis throughput (3–5 minutes per sample).
- No need for reagents that bring about toxic waste, no need for carrier gas.
- Systematic errors of analysis are reduced.

MEASUREMENT RANGE

Detection limit for mercury determination in coal is **1 µg/kg (1 ppb)**.

The upper limit for analysis is **500 mg/kg (500 ppm)**.

EQUIPMENT AND REAGENTS

The following equipment and materials are used for analysis:

- Mercury analyzer RA-915M or RA-915+ with PYRO-915+ attachment;
- Computer with the installed dedicated software;
- SRM of mercury (SRM of soil (290 ± 20 ppb) SDPS-3, NIST 1630a Trace Mercury in Coal SRM (105± 23 ppb) or any other certified SRM).

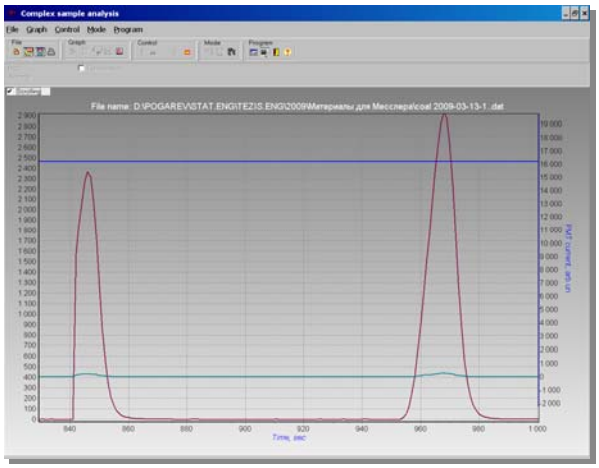
PREOPERATIONAL PROCEDURES

Sample preparation is done in accordance with the ISO 5069-2:1983 standard; a 0.5–1-mm size fraction from a homogenized coal sample is taken for analysis.

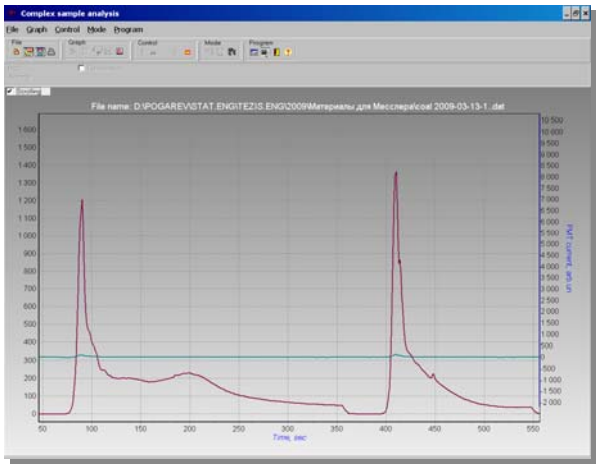
MEASUREMENT PROCEDURE

Depending on the expected concentration of mercury in the sample, an appropriate heating mode of the PYRO-915+ attachment is selected (slow or fast heating). The sample (50–500 mg) is placed into a quartz dosing spoon, then mercury is thermally atomized in the PYRO-915+ attachment, and the concentration of mercury is measured by flameless Zeeman AAS with RA-915+/RA-915M mercury analyzer using a pre-calculated calibration line. The analyzer is calibrated using a solid SRM or calibration solutions.

EXAMPLES OF ANALYSIS



Sample: SRM of soil (290±40 ppb; m = 135 mg)
Measurement results: 290±3 ppb



Sample: coal sample (m = 305 mg)
Measurement results: 305±16 ppb