ZEEMAN AAS AS UNIVERSAL METHOD FOR MERCURY DETERMINATION IN COMBUSTION PLANTS

A. Kuznetsov, N. Mashyanov, S. Sholupov, J. Siperstein

Lumex-marketing, Russia; Ohio Lumex, USA

INTRODUCTION

Mercury (Hg) is considered as a global pollutant. In particular, mercury is released into the atmosphere from various industrial processes. According to the UN Environment assessment, artisanal and small-scale gold mining, coal combustion, non-ferrous metals smelting and cement production are the main sources of mercury emissions into the atmosphere. Coal combustion is the second largest source of anthropogenic mercury on a global scale, giving 474 (304 - 678) tons annually, and is a dominant source of mercury emissions in India [1, 2].

The mercury concentration in coal varies in a very wide range from 1 ppb to 300 ppm (more than 5 orders of magnitude) with the world's average of 100 ppb. 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, 4]. 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 [3 - 5].

The problem of reducing mercury emissions from industry, primarily coal-combustion power plants, is one of the most urgent and discussed environmental problems in recent years. To address mercury-related issues globally, the United Nations Environmental Programme has developed the Minamata Convention on Mercury (the Convention) which had been enforced on August 16th, 2017. Article 8 of the Convention addresses controlling and, where feasible, reducing emissions of mercury and mercury compounds to the atmosphere from the point sources in categories listed in Annex D to the Convention. The list of point source categories in Annex D includes coal-fired power plants, coal-fired industrial boilers, non-ferrous metals smelting and roasting processes, waste incineration plants, and cement clinker production plants.

MERCURY IN COAL AND COAL COMBUSTION PRODUCTS

Due to the variability of the mercury content in coal deposits, and even within coal layers, a big uncertainty still exists in assessment of mercury resources in coal basins and in calculated emissions.

Monitoring of mercury content at all stages of coal preparation and combustion is necessary to optimize technologies of reducing emission of mercury into the atmosphere and discharge with sewage. Total mercury in flue gas is the sum of elemental, oxidized, and particle-bound mercury. Oxidized mercury is soluble in water and deposits locally whereas volatile elemental mercury is insoluble in water, and can travel thousands of kilometers, making mercury emissions a global concern.

Mercury content is measured in flue gases to calculate mercury emissions into the atmosphere. To optimize the technology of flue gas cleaning processes, it is required to measure the mercury species in flue gases (the ratio of ionic and elemental mercury). The mercury content has also to be measured in scrubber water, condensate, waste water, treated wastes, liquid fuels, solid fuels, ash, sorbents, sludge, gypsum and other types of liquid and solid samples. Therefore, most universal analytical approach to the measurements of the mercury concentrations in gas, liquids and solids is required.

ZEEMAN AAS AS A UNIVERSAL TOOL FOR MERCURY DETERMINATION

Atomic absorption spectroscopy with Zeeman background correction (Zeeman AAS) makes it possible to determine mercury in all media, such as air and gases, liquids and solids. This suggests the sought universal analytical tool to be comprised of RA-915M Zeeman AA spectrometer coupled with a pyrolysis attachment. The highest selectivity of measurement is provided by Zeeman Effect, that is, splitting of the resonance mercury line to several components in a strong magnetic field.

A radiation source (mercury lamp) of the analyzer is placed in permanent magnetic field H (Fig.1). The mercury resonance line $\lambda=254$ nm is split into three polarized Zeeman components (π, σ- and σ+, respectively). When radiation propagates along the direction of the magnetic field, a photodetector detects only the radiation of the σ - components, one of those falling within the absorption line profile and another one lying outside. When mercury vapor is absent in the analytical cell, the radiation intensities of both σ - components are equal. When absorbing atoms appear in the cell, the difference between the intensities of the σ- components increase as the mercury vapor concentration grows. The σ - components are separated by the polarization modulator. The spectral shift of the σ-components is significantly

smaller than the widths of molecular absorption bands and scattering spectra, hence the background absorption by interfering components does not affect analyzer's readings.
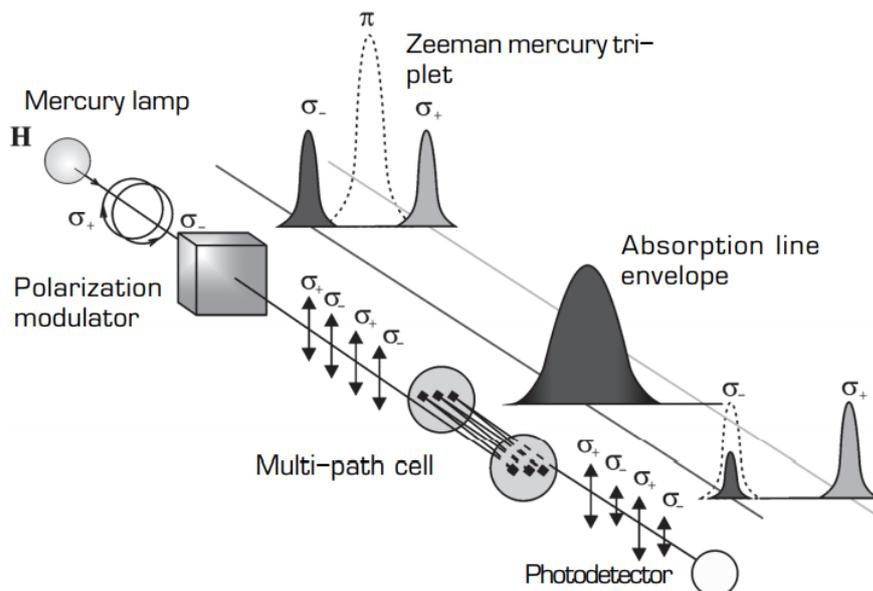

Fig. 1. – Principle of operation of the RA-915M Zeeman AAS mercury analyzer

The PYRO-915+ attachment is used for rapid analysis of solid and liquid samples. The attachment consists of the double-chamber atomizing system combined with the heated analytical cell (Fig. 2).
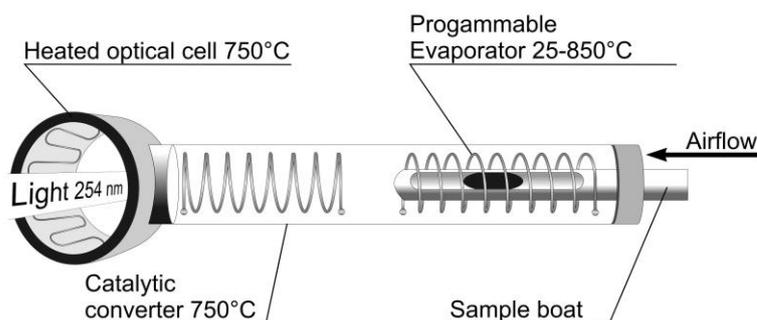

Fig. 2. – Pyrolysis system: PYRO-915+ double-section atomizer and heated analytical cell.

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 $750^{\circ}C$ 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 $850~^{\circ}C$. 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 thermoscanning option enables fast determination of mercury species having different binding energy to solid matrix of coal and coal combustion products and thereby to enhance the efficiency of coal pre-combustion treatment: washing, mild pyrolysis, sulphides removal [5].

The Zeeman background correction provides high selectivity of the mercury determination in samples with complex matrices [6]. Real-time measurement enables fast recording of the process of 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 in order to detect possible interferences. 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. It means that no sample preparation, additional oxidizers, gold trap and carrier gases (e.g. oxygen, argon) are required. The real-time recording of D makes it possible to qualitatively control processes of the matrix decomposition.

Such set is widely used at combustion plants for mercury determination in ambient air, stack gas, coal, coal combustion products, sludge, gypsum, waste waters, etc.

MERCURY MEASUREMENT IN STACK GAS

Several methods are available to measure Hg emissions. These methods differ in level of complexity, application conditions, and their ability to speciate Hg (ability to differentiate the elemental form of Hg from oxidized form of Hg).

To determine mercury in flue gases, the US EPA (US Environmental Protection Agency) certified method for direct measurements of mercury content in flue gas (US EPA Method 30A – Determination of Total Vapor Phase Mercury Emissions From Stationary Sources [Instrumental Analyzer Procedure]) and a method for sampling on the sorbent traps and subsequent laboratory analysis (US EPA Method 30B – Determination of Total Vapor Phase Mercury Emissions from Coal-Fired Combustion Sources Using Carbon Sorbent Traps) [7, 8]. Both methods are designed to determine the total content of mercury in flue gases. The difference between these two methods is illustrated in Fig. 3.
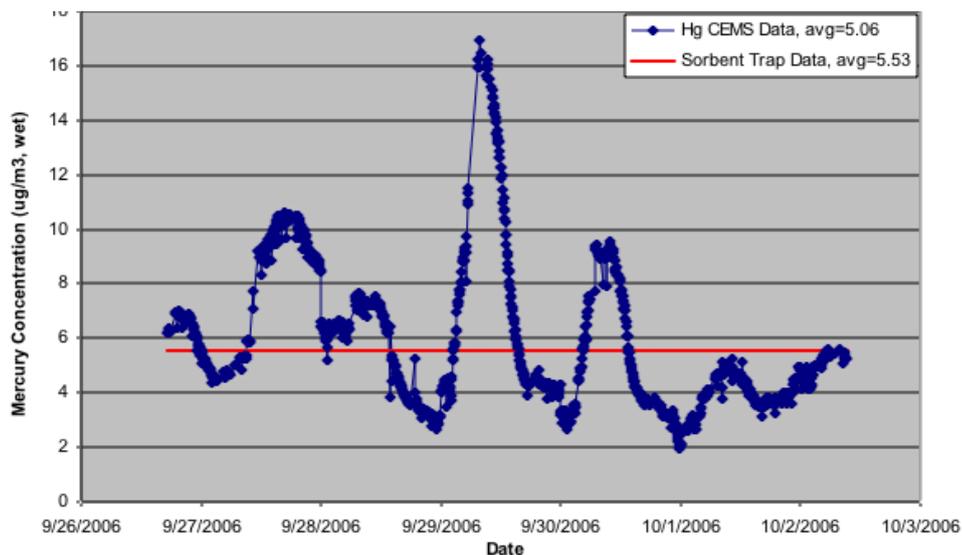

Fig. 3 – Parallel measurements of mercury content in the flue gas of USA coal-fired power plant. Continuous recording (method 30A) and average value per period (method 30B).

The advantage of method 30A is the real-time data acquisition; the disadvantages are the high cost and complexity of equipment and maintenance, the need for external control by reference methods.

The advantages of method 30B are lower cost of equipment and maintenance as compared to that of continuous monitoring. The method provides an embedded quality control of results therefore the reliability of data is much higher. This allows using method 30B as a reference method for relative accuracy test audits (RATAs) of continuous emission monitoring systems operating under the method 30A. The only drawback of the method is non-real-time data acquisition, which imposes restrictions on the scope of its application. Method 30B is used for long-term emissions control. To solve the problems of developing and optimizing technologies for flue gas cleaning processes, more sophisticated sorbent tubes have been developed to determine the mercury species in flue gases.

Method 30B is widely used in the US to control mercury emissions from coal-fired power plants, cement kilns, industrial boilers and other stationary sources of emissions. It facilitates short- and long-term measurements needed to develop plant-specific emissions factors, support development of emissions inventories, assess impacts on mercury emissions of different coal types and control configurations, collect data needed to develop mercury emissions control and monitoring programs, and potentially validate emission inventories and compliance approaches. Method 30B is implemented in a so-called US EPA Mercury Measurement Toolkit [7]. The Toolkit is used to measure mercury emissions in the UNEP pilot project to demonstrate and implement BAT/BEP (Best Available Techniques / Best Environmental Practices) in China, Russia, South Africa, Vietnam, Indonesia, Thailand, and other countries.

The US EPA Toolkit includes the equipment and procedures necessary to measure stack gas mercury concentration and other necessary plant operational parameters: sorbent traps, sampling probes, flow meters, a direct combustion system to analyze mercury in solid samples, other auxiliary equipment, and sampling and measurement protocols. The toolkit combines the use of sorbent traps and

direct thermal analysis to provide a cost effective and powerful tool for measuring mercury content in samples [8].

Sorbent traps collect a mercury sample in accordance with EPA Method 30B. The extraction of a known volume of flue gas is performed through paired, in-stack sorbent tubes at an appropriate fixed flow rate. After the sampling period, the sorbent is removed and analyzed for mercury content. Quality assurance and quality control requirements are included to assure that the data collected is of known and acceptable quality. An emission test uses three sets of measurements with a minimum sample time of thirty minutes for each set. The test can also determine the portion of mercury in oxidized and elemental forms. A typical sampling system consists of a trap probe, sorbent traps, dry gas meters, and pumps. The dry gas meter sampling box is used to quantify the volume of gas collected through the tubes, control the sampling flow rate, and control the probe temperature.

The sorbent traps media is configured in a trap with at least two distinct sections that can be tested separately. Section 1 is designated for the primary capture of gaseous mercury. Section 2 is designated as a backup section for determination of vapor phase mercury breakthrough. The sorbent media may be any collection material (e.g., carbon, chemically-treated filter) capable of quantitatively capturing and recovering mercury for subsequent analysis. Sorbent traps can be supplied with an additional spiked section intended for the Analytical Bias Test. Dedicated sorbent traps can include a section for acid gases removal and additional two sections for speciation analysis [9].

CONCLUSION

A universal analytical set based on Zeeman atomic absorption spectrometry enables rapid selective mercury determinations in solid, liquid and gaseous samples encountered in combustion plants: ambient air, coal, co-fired fuels, fly ash, gypsum, sludge, waste water, etc.

Based on this analytical solution, the US EPA's Mercury Measurement Toolkit is widely used for rapid and cost-effective measurements of mercury, including its speciation, in stack gases (US 30B sorbent traps method), coal, fly ash, and other matrices. The Toolkit has been widely used for UN Environment-sponsored projects to conduct on-site testing to determine the mercury content in stack gases.

REFERENCES

1. Global Mercury Assessment 2013: Sources, Emissions, Releases and Environmental Transport. UNEP Chemicals Branch, Geneva, Switzerland. UNEP, 2013. – 32 p.

2. L.L. Sloss. Coal in the Indian energy future – emissions and policy considerations. IEA Clean Coal Centre, 2015. – 42 p.

3. Ozerova N.A. Mercury in Geological Systems. In: W. Baeyns, R. Ebinghaus, O. Vasiliev, editors. Global and Regional Mercury Cycles: Sources, Fluxes and Mass Balances. Kluwer Acad Publ; 1996: 463-474.

4. Yudovich Y.E., Ketris M.P. Mercury in coal: a review Part 1, 2. Geochemistry. Int J Coal Geology 2005; 62: 107– 134.

5. N. Mashyanov, S. Pogarev, E. Panova, N. Panichev, V. Ryzhov. Determination of mercury thermospecies in coal. Fuel 2017, 203: 973-980.

6. S. Sholupov, S. Pogarev, V. Ryzhov, N. Mashyanov, A. Stroganov. Zeeman atomic absorption spectrometer RA-915 for direct determination of mercury in air and complex matrix samples// Fuel Processing Technology. – 2004. – V. 85:, – pp. 473-485.

7. R. Forte, J.V. Ryan, T.P. Johnson, P.H. Kariher. The United States Environmental Protection Agency's Mercury Measurement Toolkit: An Introduction // Energy&Fuels, ACS. – 2012. – 26. – pp. 4643-4646.

8. J. Siperstein, J.E. Wright, V. Schmidt, N. Mashyanov, S. Sholupov. U.S. EPA Compliance Mercury Monitoring at Coal – Fired Power, Cement producing Plants and Industrial Boilers. Proc 11-th International Conference "Mercury as a Global Pollutant" Edinburgh, 28 July – 2 August, 2013. http://www.mercury2013.com/index

9. Manual for Determination of the Mercury Concentration in Stack Gas Using Sorbent Traps. Scientific Research Institute for Atmospheric Air Protection, Saint-Petersburg, Russia; United Nations Environment Programme, Geneva, Switzerland. 2017. 44 p.