

Tests and Comparison of Two Mobile Industrial Analytical Systems for Mercury Speciation in Flue Gas

Karel Borovec, Jerzy Gorecki, Tadeas Ochodek

Abstract—Combustion of solid fuels is one of the main sources of mercury in the environment. To reduce the amount of mercury emitted to the atmosphere, it is necessary to modify or optimize old purification technologies or introduce the new ones. Effective reduction of mercury level in the flue gas requires the use of speciation systems for mercury form determination. This paper describes tests and provides comparison of two industrial portable and continuous systems for mercury speciation in the flue gas: Durag HM-1400 TRX with a speciation module and the Portable Continuous Mercury Speciation System based on the SGM-8 mercury speciation set, made by Nippon Instruments Corporation. Additionally, the paper describes a few analytical problems that were encountered during a two-year period of using the systems.

Keywords—Mercury determination, speciation, continuous measurement, flue gas.

I. INTRODUCTION

THE main source of the environment contamination with mercury (Hg) compounds is combustion of solid fuels [1]-[6], especially coal in which Hg may exist in the form of several compounds [7], [8]. While burning coal, Hg compounds are decomposed and Hg is released from coal as elemental Hg. In the flue gas, Hg can exist in some forms: as elemental Hg, oxidized Hg and particulate-bound Hg [9]-[13]. Hg⁰ is insoluble in water and may remain in the atmosphere for many months. Hg²⁺ is water soluble and in water reservoirs (bottom sediment) could be transformed into methylmercury chloride, highly toxic and most dangerous for living creatures [14], [15]. The above properties of Hg made the European Community introduce several regulations aimed at reducing emissions of Hg (Integrated Pollution Prevention and Control Directive 96/61/WE, Large Combustion Plant Directive - 2001/80/WE, National Emission Ceilings Directive - 2001/81/WE). The above regulations impose an obligation of pollution monitoring (for combustion installations with a nominal power > 50 MW). In addition, in 2010 an Industrial Emissions Directive (IED) was issued by the European Parliament (2010/75/EU). It requires at least one measurement of total Hg per year (for coal-burning emission sources of a nominal power > 100 MW). For many years, the Ontario Hydro Method has been the most common tool for the flue gas Hg speciation [16]-[18], but its flaws such as the analytical

problems, the inability to perform on-line and continuous measurements or the difficulty of its use in the industrial conditions, all make continuous measurement systems increasingly popular. Nowadays, there are several industrial systems for continuous Hg speciation in the flue gas in the market, for instance: Sir Galahad II (PS Analytical), Tekran 3300, Mercury Freedom System (Thermo scientific), Durag HM-1400 RTX [19]-[22]. In contrast to the determination of total Hg, the Hg speciation in the flue gas enables more precise control or modification of the combustion process to reduce the Hg emission. However, the measurement of Hg in the flue gas itself and, to an even greater extent, its speciation is a very difficult task from analytical point of view. Hg speciation in the variable conditions, that occur during a test or modification of combustion processes, can cause analytical problems. Especially in the case of the use of automated analytical systems generally designed for stable condition. One purpose of this paper is to provide the reader with information on constructing, tests and industrial use of two portable continuous system for Hg speciation in the flue gas: Durag HM 1400 TRX (with a speciation module) and the Portable Continuous Mercury Speciation System (PCMSS) based on the Nippon Instrument Corporation (NIC) speciation set: SGM-8. Another objective of the article is to present a few analytical problems related to Hg speciation in the flue gas that the authors encountered during several years of using the described speciation systems.

II. MATERIALS AND METHODS

A. Apparatus

In the described study, two portable continuous systems for Hg speciation in flue gas were used: Durag HM 1400 TRX (Durag) with a speciation module and the PCMSS based on SGM-8, a NIC set. According to the authors, this is the first industrial use of the speciation version of Durag HM 1400 TRX. The PCMSS system used in this study was designed in the Department of Coal Chemistry and Environmental Sciences, Faculty of Energy and Fuels, AGH University of Science and Technology in Cracow (Poland).

1. Construction and Operation of the PCMSS

The idea and the test of the PCMSS based on the use of two SGM-8 Hg speciation sets, made by NIC, was described in detail in [23].

Briefly, the PCMSS system (Fig. 1) consists of: a heated probe (N1) (ZAM Kęty, Poland) equipped with a fly ash filter

Karel Borovec, Jerzy Gorecki, and Tadeas Ochodek are with the Energy Research Center, VŠB - Technical University of Ostrava, Listopadu 15/2172, 708-33 Ostrava - Poruba, Czech Republic (e-mail: karel.borovec@vsb.cz, gorecki@agh.edu.pl, tadeas.ochodek@vsb.cz).

(N2) (ALF, Poland), a transfer line (N3) (JCT, Austria), a T - connector (N4) (ALF, Poland), two scrubber sets (N5, N6), and two CV AAS EMP-2 detectors (N7, N8) equipped with flow controllers and pressure gauges.

The principle of operation of the PCMSS system is a continuous, simultaneous measurement of Hg_{tot} and Hg^0 forms of Hg. In the first SGM-8 set (first scrubber), the Hg^{2+} is reduced to Hg^0 using a wet method (10% $SnCl_2$ solution). Then, the sum of Hg^0 is determined by means of the first EMP-2 detector. The second SGM-8 set is responsible for determination of Hg^0 only. Before Hg determination by the second EMP-2 detector, Hg^{2+} is removed from the flue gas by using a 10% KCl solution (first scrubber). Concentration of Hg^{2+} in the flue gas is calculated from the difference of total Hg concentration and concentration of Hg at the zero-oxidation state. Interfering substances (e.g. HCl , SO_2) are removed from the flue gas with a 10% KOH solution (second scrubber), the moisture is removed by the third scrubber, whose temperature is reduced to 5 °C. The solutions in the scrubbers may be discharged and replaced automatically at a specified time. At determined intervals (typically every 60 s), the EMP-2 detector controls the background level using a gold trap which removes Hg from the flue gas and corrects the analytical signal.

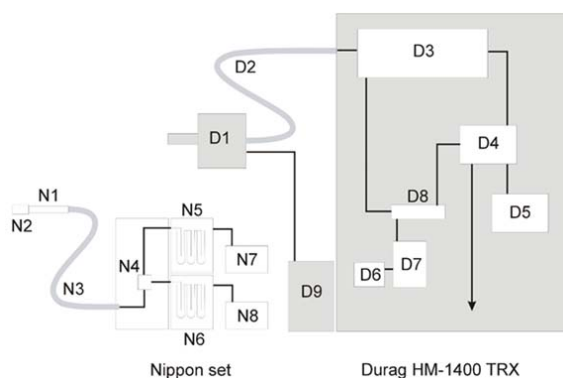


Fig. 1 The Hg speciation systems: PCMSS and Durag

Dimensions of the ready-to-use system are: 800x300x600 mm, the probe and the transfer line are 1 m and 1.5 m long, respectively. The weight of the system is about 50 kg (five separate boxes). Time to prepare the system to work is about 2 hours.

The measurement range of the EMP-2 detector is from 0.1 to 999.9 $\mu g/m^3_N$. The detector performs one measurement per second. The EMP-2 detector works in two measurement modes: mobile and stable. In the mobile mode, the resolution of the EMP-2 detector is 1 $\mu g/m^3_N$ and in the stable mode 0.1 $\mu g/m^3_N$. LOD is 0.3 $\mu g/m^3_N$.

Measurement data are collected on two SD cards and are processed in an Excel sheet that automatically generates a final report with an average concentration of Hg^0 and Hg^{2+} forms.

2. Construction and Operation of the Portable Hg Analyzer Durag HM-1400 TRX

Durag HM 1400 TRX is a commercially available system for Hg determination in the flue gas and process gases [22]. The system used in this study was equipped with a by-pass that enables speciation of Hg in the flue gas.

The Durag HM 1400 TRX (Fig. 1) consists of the following main parts: a probe with a fly ash filter (D1), a transfer line (D2), a thermo-catalytic reactor (D3), a flue gas cooler (D4) and a dual beam UV CVAAS photometer (D5). The unit can be additionally equipped with a module allowing to speciate Hg. The module consists of a pump (D6), a KOH solution container (D7) and a reaction chamber (D8). Automatic calibration is possible thanks to an independent calibration module (D9) which is responsible for introducing the calibration gas into the probe. Typically, calibration is done once a day. In Durag HM 1400 TRX, total Hg determination is performed by conversion of Hg^{2+} to Hg^0 in a thermo-catalytic reactor. The same thermo-catalytic reactor is responsible for removing SO_2 from the flue gas before Hg determination. After Hg reduction, the cleaned flue gas is dried in the cooler and transferred into the detector. To realize speciation of Hg, the system is optionally equipped with a speciation module. Since the analyzer is equipped with one detector only, speciation analysis (Hg^0 determination) is performed periodically (typically once per 15 minutes). The oxidized form of Hg is calculated as the difference between total and elemental Hg. To determine the concentration of the oxidized form (Hg^{2+}), in the periods between the real determination of Hg^0 form, it is assumed that there is a constant ratio between total and elemental Hg for 14 minutes.

The basic parameters of the Durag HM 1400 TRX system, according to the manufacturer, are as follows: measuring ranges: 0-45 and 0-500 $\mu g/m^3_N$, accuracy: <1% of measuring range, dimensions: 1800x600x500 mm, weight 220 kg, detection limit: <1 $\mu g/m^3_N$. Time to prepare the system to work is around 2 hours. The particular Durag equipment used in these studies was equipped with rollers for equipment transportation.

B. Materials

All reagents and standards were of an analytical grade or higher. A 10% $SnCl_2$ solution for Hg^{2+} reduction was prepared from $SnCl_2$ powder (Avantor Performance Materials Poland S.A.). KCl powder (Chempur S.A.) was used to prepare a 10% KCl solution for Hg^{2+} absorption. Concentrated 95-98% H_2SO_4 (Aldrich) was used to acidify the $SnCl_2$ solution. 70% HCl (J.T.Baker) was used to acidify the KCl solution. Concentrated 69% HNO_3 (J.T.Baker) was used for equipment cleaning. The Hgo standard gas was prepared in 10 dm³ Tedlar bags (Supelco) by means of the MB-1 gas box (NIC) and the PS-4 sampler unit (NIC). The thermo-catalytic reactor cartridge was delivered by Durag (Germany).

III. RESULTS

The data presented below are the results of two years of Hg measurements in power stations in the Czech Republic.

A. Comparison of Hg Speciation with PCMSS and Durag HM 1400 TRX

Comparing the results of Hg speciation (using both speciation systems) was held under the large-laboratory and industrial conditions. In the large-laboratory test, the furnace SCB was used as a source of the flue gas containing Hg forms. SCB is an automatic boiler combusting bituminous coal with heating output of 25 kW. There was only one socket in the installation, so the speciation systems were connected in succession. The furnace SCB worked in the low power mode (8 kW) during the test. Preceding the measurements, the furnace worked for several hours to get the stable level of flue gas composition. During the test, both systems used a heated probe with a fly ash filter connected to the heated transfer line. At first, the PCMSS system was connected to the flue gas line socket. Then, the Durag system was connected to the outlet of the same sample line. In both cases, speciation of Hg was carried out for 60 minutes. The results of measurements are listed in Table I.

TABLE I
RESULTS OF HG SPECIATION IN THE FLUE GAS FROM FURNACE SCB

PCMSS	$\mu\text{g}/\text{m}^3_{\text{N}}$	SD	n
Total Hg	1.9	0.5	64
Elemental Hg	1.6	0.5	64
Oxidised Hg	0.3	0.1	64
Durag HM-1400 RTX			
Total Hg	2.7	0.8	45
Elemental Hg	2.3	0.7	45
Oxidised Hg	0.4	0.6	45

In the case of the PCMSS and DURAG systems, the total levels of Hg concentration were: $1.9 \pm 1.2 \mu\text{g}/\text{m}^3_{\text{N}}$ ($n=64$ $p=0.05$) and $2.7 \pm 1.6 \mu\text{g}/\text{m}^3_{\text{N}}$ ($n=45$ $p=0.05$), respectively. Apparently, the result uncertainty intervals overlap, but the T-test of the difference between two means shows that there is a high statistically significant difference between the mean values ($t_{\text{cal}}=6.26$ and $p<0.001$). In the case of elemental Hg determination, the result uncertainty intervals overlap too, but the results of the T-test are similar ($t_{\text{cal}}=5.42$ and $p<0.001$). However, when analyzing the results of the experiment, the fact that measurements were taken one by one must be taken into account. This was due to the limitations of the measuring stand (one socket). Secondly, the concentration of Hg in the flue gas was at the low level. LOD of PCMSS was defined as $0.3 \mu\text{g}/\text{m}^3_{\text{N}}$, so LOQ defined as $6 \times \text{LOD} = 1.8 \mu\text{g}/\text{m}^3_{\text{N}}$ which is at the level of obtained results. In case of Durag LOQ is $< 6 \mu\text{g}/\text{m}^3_{\text{N}}$, so the results obtained can be considered as quite consistent. The second test was performed in the industrial conditions. The comparison measurements were performed before the chimney in the flue gas tract of a 60 MW boiler, burning brown coal with NaCl addition (Hg reduction test). During the measurements, both measuring systems (PCMSS and Durag) were placed in a measurement car. Two heated transfer lines, 20 m long, were connected to two measuring sockets. Before the comparison, both systems were compared

by means of Hg^0 calibration gases. The tests gases were prepared in a 10 dm^3 Tedlars bag by means of an Hg^0 MB-1 gas generator (NIC). The volume of 10 dm^3 was appropriate to perform one check with both detectors. The results of check were as follows: for the PCMSS $\text{Hg}_{\text{tot}}=18.3 \mu\text{g}/\text{m}^3_{\text{N}}$ and $\text{Hg}^0=18.1 \mu\text{g}/\text{m}^3_{\text{N}}$, for Durag $\text{Hg}_{\text{tot}}=18.3 \mu\text{g}/\text{m}^3_{\text{N}}$. The results of measurements are listed in Table II. Regarding the total levels of Hg concentration, it was $13.9 \pm 0.5 \mu\text{g}/\text{m}^3_{\text{N}}$ ($n=24$ $p=0.05$) for the PCMSS and $13.0 \pm 1.5 \mu\text{g}/\text{m}^3_{\text{N}}$ ($n=18$ $p=0.05$) for Durag. The result uncertainty intervals overlap, but the T-test of the difference between two means shows that there is a statistically significant difference between mean values ($t_{\text{cal}}=2.7$ and $p=0.05$). In the case of elemental Hg determination, the results of test are $t_{\text{cal}}=5.42$ and $p<0.001$ which means that there is a high statistically significant difference between mean values. In the case of comparison of total Hg measurements, the result obtained is at the boundary of the relevant and irrelevant difference. In the case of elemental Hg determination, the results of test are worse ($t_{\text{cal}}=19.39$ and $p<0.001$). The difference may be due to the different ways of Hg^0 concentration obtaining by the PCMSS and Durag systems. In the case of the PCMSS, measurement is continuous (two independent CV AAS detectors, one measurement per second). In the case of Durag, Hg^0 concentration is measured every 15 minutes. Between the real Hg^0 concentration measurements, the Hg^0 concentration is proportionally increased or decreased according to the changes of total Hg concentration. The manufacturer of Durag assumes that the $\text{Hg}^0/\text{Hg}^{2+}$ ratio is stable within 15 minutes.

TABLE II
RESULTS OF HG SPECIATION IN THE FLUE GAS FROM 60 MW BOILER

PCMSS	$\mu\text{g}/\text{m}^3_{\text{N}}$	SD	n
Total Hg	13.9	0.2	24
Elemental Hg	9.3	0.4	24
Oxidised Hg	4.5	0.4	24
Durag HM-1400 RTX			
Total Hg	13.0	0.7	18
Elemental Hg	6.8	0.4	18
Oxidised Hg	6.0	0.5	18

Regarding the flue gas composition instability, this assumption may be a source of measurement errors. Fig. 2 shows the changes in the $\text{Hg}^0/\text{Hg}^{2+}$ real concentration ratio in case of Hg speciation in the flue gas containing higher amount of HCl (brown coal with NaCl addition). As one can see, the changes in the $\text{Hg}^0/\text{Hg}^{2+}$ concentration ratio are significant, which may mean that in unstable conditions up to 93% (13/14) of Hg^{2+} results generated by the Durag equipment may not be consistent with reality. Another problem with the described measurements was in low temperature which caused dropping in case of the PCMSS. The problem described in [23] caused instability of the results. Unfortunately, during the described measurements, the anti-dropping system specially designed for PCMSS (constant SnCl_2 solution flow in the first scrubber) was not used.

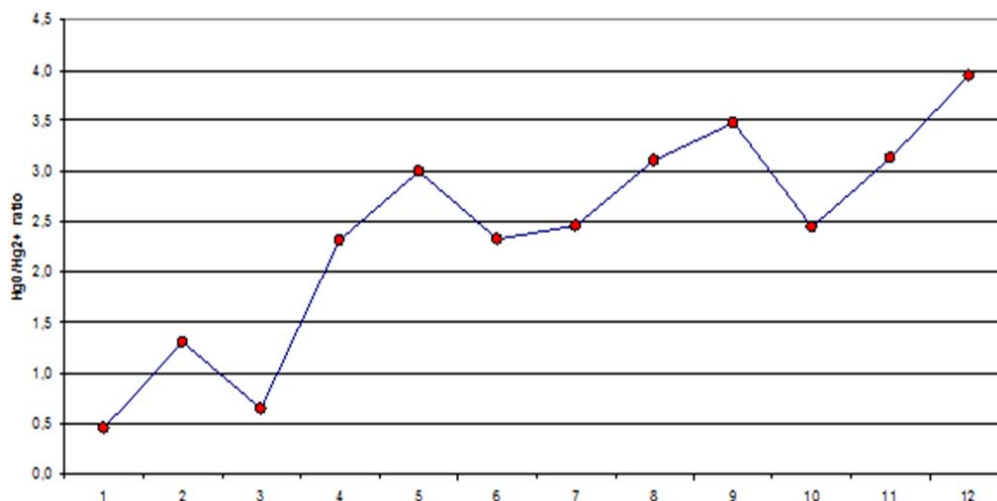


Fig. 2 Changes of ratio of $\text{Hg}^0/\text{Hg}^{2+}$ concentrations in case of Hg measurement in the flue gas containing high amount of HCl

Conclusions from the comparison measurements are as follows: in order to perform a valid comparative test of speciation systems, stable measurement conditions (constant ratio of Hg forms) and appropriate level of oxidized form are required. Meeting the above requirements is very difficult in the industrial conditions. Therefore, to test the speciation systems properly, it is necessary to have a suitable test stand. Perhaps, the system based on the Durag HM-1400 TRX calibrator unit or Hg^{2+} generator [24] would be useful in this case.

B. Analytical Problems during Hg Speciation in the Industrial Conditions

This section discusses analytical problems that appear during Hg speciation in the flue gas, associated with the use of the discussed speciation systems. At this point, it is important to mention that getting the correct results of Hg speciation in the industrial conditions is very difficult. It is, among other things, the result of a breakdown of the production line, weather conditions (particularly low temperature and rain), difficult access to the samples, failure of measuring devices exposed to vibrations and transport shocks, long periods of stabilization of the composition of the flue gas (e.g. after the change of the boiler power) and variability in fuel composition.

1. Analytical Problems during Hg Speciation in the Industrial Conditions

In May 2017, the system Durag HM 1400 TRX was used to speciate Hg in the flue gases from the combustion of brown coal with the addition of NaCl. The aim of the test was to determine what percentage of the Hg can be oxidized. Duration of the measurement of the flue gas with high HCl content was four days. The measurements were performed before the chimney in the flue gas tract of a 60 MW boiler. At the end of the measurement period, the results generated by the Durag equipment were additionally monitored using the PCMSS system. The results of comparison were as follows:

for Durag $\text{Hg}_{\text{tot}} = 6.8 \pm 0.4 \mu\text{g}/\text{m}^3_{\text{N}}$ ($n=20$ $p=0.05$), $\text{Hg}^0 = 1.8 \pm 0.4 \mu\text{g}/\text{m}^3_{\text{N}}$ ($n=20$ $p=0.05$), $\text{Hg}^{2+} = 5.0 \pm 0.4 \mu\text{g}/\text{m}^3_{\text{N}}$ ($n=20$ $p=0.05$) for PCMSS $\text{Hg}_{\text{tot}} = 6.1 \pm 1.0 \mu\text{g}/\text{m}^3_{\text{N}}$ ($n=20$ $p=0.05$), $\text{Hg}^0 = 4.3 \pm 0.4 \mu\text{g}/\text{m}^3_{\text{N}}$ ($n=20$ $p=0.05$), $\text{Hg}^{2+} = 1.9 \pm 1.0 \mu\text{g}/\text{m}^3_{\text{N}}$ ($n=20$ $p=0.05$). So, Durag showed 26% of Hg^0 form and 74% of Hg^{2+} form and PCMSS showed 70% of Hg^0 form and 30% of Hg^{2+} form. At the end of the measurements, both systems were checked with an Hg^0 calibration gas. The tests gases were prepared in a 10 dm³ Tedlars bag by means of an Hg^0 MB-1 gas generator (NIC). The purpose of this check was to find whether the Durag did not oxidize elemental Hg. The results of the test were as follows: the PCMSS showed 98% of Hg^0 form and 2% of Hg^{2+} form. Durag showed 62% Hg^0 form and 38% of Hg^{2+} form in the case of concentration $46 \mu\text{g}/\text{m}^3_{\text{N}}$ and 49% Hg^0 form and 51% of Hg^{2+} form in the case of concentration $14 \mu\text{g}/\text{m}^3_{\text{N}}$. The PCMSS performed measurements in the flue gas containing HCl for about 6 hours and Durag for 100 hours. The advantage of the PCMSS system is the possibility to quickly clean the filter, probe and transfer line. Depending on the degree of contamination, cleaning can be done by heating, washing with hot HNO_3 or replacement of the PTFE system components.

The result of the test clearly shows the possibility of oxidation of elemental Hg in the flue gas by the filter and transfer lines contaminated with HCl. When analyzing the above situation, it can be stated that in the case of Hg speciation in the flue gas containing oxidizers (such as HCl), long-term measurements (several days) can cause large measurement errors.

2. Hg Speciation in High Fly Ash Concentration

The purpose of the measurements was to check the effectiveness of the fabric filter as an element of installation to reduce the Hg concentration in the flue gas. The measurements were performed before the fabric filter in the flue gas tract of two (circulated fluid bed) boilers combusting 70% of lignite and 30% of biomass. The concentration of the fly ash in the flue gas was about $30 \text{g}/\text{m}^3$. The concentration of

SO₂ was 130 mg/m³_N. The measurement with the PCMSS lasted about 30 minutes. During the measurement the total Hg concentration decreased (Fig. 3) from the value 20.5±0.6 µg/m³_N (n=50 p=0.05) to the value 6.4±0.4 µg/m³_N (n=50 p=0.05), which is 31% of the initial value and elemental Hg decreased from the value 16.2±0.6 µg/m³_N (n=50 p=0.05) to the value 4.9±0.2 µg/m³_N (n=50 p=0.05) which is 30% of the initial value. In fact, the concentration of all Hg forms decreased drastically during the measurement. Decrease in the Hg concentration was caused by deposition of the fly ash on

the fly ash filter and adsorption of Hg on the ash layer. The initial faster rate of decline in Hg concentration (Fig. 3 400-700s) is due to the coverage of an initially pure filtering surface by the first portion of ash. The slower rate of decrease in concentration (Fig. 3 700-1900s) results from the detachment of ash fragments from the horizontally arranged ash filter. Applications for this measurement probe were equipped with a filter with a 37-mm filtering insert. For larger diameter filters or backflow purge filters, the Hg concentration drop during the measurement will be probably lower.

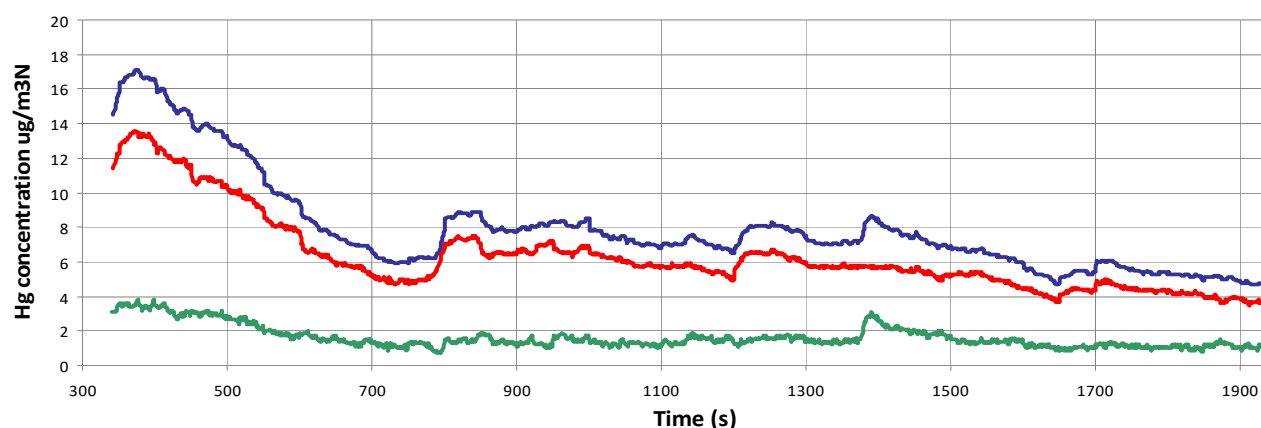


Fig 3 Speciation of Hg, before the fabric filter, with PCMSS

On the same day, there were three Hg speciation measurements performed with the Ontario Hydro (OH) method. The results of the measurements are listed in Table III. The mean value of total Hg concentration was 12.1±3.8 µg/m³_N which is close to the mean value of total Hg concentration in case of the PCMSS measurement 9.8±2.8 µg/m³_N. In the case of the first OH measurement, the total Hg concentration of 16.5 µg/m³_N was quite close to the initial total Hg concentration measured by means of the PCMSS (20.5±0.6 µg/m³_N). The next two measurements were about 50% lower. As in the case of decreasing in the results of the PCMSS measurements, the fly ash cumulating in the OH sampling line may be responsible for reducing the results in the case of the OH method. The superiority of the systems for continuous measurements over the scrubbing systems results from a significant increase in the amount of data: for OH two measurements per hour, for PCMSS 4000 measurements per hour. For optimization and non-stable conditions, the continuous measurement systems are more useful.

TABLE III
RESULTS OF HG SPECIATION IN THE FLUE GAS FROM FURNACE SCB

Sampling point	Total Hg [µg/m ³ _N]	Hg ²⁺ [%]	Hg ⁰ [%]
Before FF	16.5	52.6	47.5
Before FF	10.3	70.5	29.5
Before FF	9.6	67.5	32.5

3. Hg Measurements in High SO₂ Concentration

For longer measurements of Hg which are performed in the flue gases with high SO₂ content, a problem with the thermal-

reactor efficiency may appear. The appearance of SO₂ in the purified flue gas increases the analytical signal obtained from CV AAS detectors. In the case of the PCMSS, the above problem does not exist, because the PCMSS uses the analytical signal flue gas, from which the Hg is removed with a gold trap. To check whether the thermal reactor is working properly, the calibration gas containing SO₂ could be used. The results of the test with a calibration gas containing SO₂ in an amount of 250 µg/g are as follows: before the thermal reactor exchange, the result of the measurement was 4.7±0.6 µg/m³_N (n=3 p=0.05), after thermal-reactor exchange 0.0±0.0 µg/m³_N (n=3 p=0.05). Unfortunately, Durag HM-1400 TRX does not have automatic thermal-reactor control and the test procedure with SO₂ calibration gas must be done manually.

C. Advantages and Disadvantages of the Described Speciation Systems

Using the speciation systems described in this study over two years enables evaluation of their capabilities. Table IV summarizes the most important practical comments on these speciation systems.

IV. SUMMARY

The tests and comparison of two industrial portable and continuous systems for Hg speciation in the flue gas, Durag HM-1400 TRX with a speciation module and the PCMSS, were performed. The results of Hg speciation are quite consistent. By comparison of the two systems, it was found that the results generated by the Durag may not be consistent with reality in unstable conditions up to 93% of Hg²⁺. The

PCMSS system should be permanently equipped with an anti-dropping system. To perform a valid comparative test of speciation systems, a stand providing stable measurement conditions (constant ratio of Hg forms) and appropriate level of oxidized form are required. Some analytical problems that appear during Hg speciation in the flue gas, associated with the use of the above speciation systems, were discussed. The results of the Durag and the PCMSS test with the flue gas containing high level of HCl show the possibility of oxidation of elemental Hg by the filter and transfer lines contaminated

with HCl. In the case of Hg speciation with the PCMSS in the high level of fly ash, the concentration of all Hg forms of Hg decreased drastically during the measurement. Decrease in the Hg concentration was caused by deposition of the fly ash on the ash filter and adsorption of Hg on the ash layer. The results of the Durag HM 1400 TRX thermal-reactor control with SO₂ calibration gas were described. As a practical outcome, the advantages and disadvantages of the described speciation systems were summarized.

TABLE IV
ADVANTAGES AND DISADVANTAGES OF THE SPECIATION SYSTEMS

Field	Durag	PCMSS
Portability	Usually working in a measurement car with a long transfer line. The ability to move is limited (220 kg), but possible. Time to prepare the system for work - 2hrs	Small and light. Can be used in tight, hard-to-reach places. Time to prepare the system for work - 2hrs
Calibration	Automatic (calibration module) uses HgCl ₂ solution. External calibration system is required.	Manual calibration with use of Tedlar bags - not very practical in the industrial conditions. Difficult in the changing temperature.
Speciation	One detector. Hg _{tot} - one measurement per minute. Hg ⁰ is measured every 15 minutes - not a proper way from analytical point of view.	Two independent detectors. Fast response. One measurement of Hg _{tot} and Hg ⁰ per second. Good for quick tests and variable conditions.
Removing the SO ₂ interference effect	Thermo-catalytic reactor. Reactor should be controlled by means of a calibration gas containing SO ₂ . Quite easy exchange of reactor. Uncertain results of speciation without SO ₂ influence control.	10% KOH solution and by-pass with gold trap (zero check procedure). Scrubber system - not very practical in the industrial conditions.
Data acquisition	Automatic – Excel file.	Complicated - two independent SD carts. Need for manual pressure correction.
Cleaning in case of contamination	Quite complicated and long-term.	Heating, washing or fast replacement of PTFE parts (ash filter, probe, transfer line).

ACKNOWLEDGMENT

This work was prepared within the project „Innovation for Efficiency and Environment – Growth“, identification code LO1403 with the financial support from the Ministry of Education, Youth and Sports in the framework of the National Sustainability Programme I.

REFERENCES

- [1] EPA. Air Pollution and the Clean Air Act. <http://www.epa.gov/air/caa/>. (accessed 16.09.2017).
- [2] EPA. Clean Air Mercury Rule. <http://www.epa.gov/camr/>. (accessed 16.09.2017).
- [3] EPA. Summary of the Clean Air Act. 10.03.2015; <http://www2.epa.gov/laws-regulations/summary-clean-air-act>. (accessed 16.09.2017).
- [4] V. M. Fthenakis, F. W. Lipferta, P. D. Moskowitz, L. Saroffb, “An assessment of mercury emissions and health risks from a coal-fired power plant”, *Journal of Hazardous Materials*, vol. 44 pp. 267–283 1995.
- [5] C. S. Wong, N. S. Duzgoren-Aydin, A. Aydin M. H. Wong, “Sources and trends of environmental mercury emissions in Asia”, *Sci Total Environ*, vol. 368 pp. 649-62. 2006.
- [6] Jun Lee, Seo YC, Jurng J, Hong JH, Park JW, Hyun JE, Gyu Lee T., Mercury emissions from selected stationary combustion sources in Korea, *Science of The Total Environment*, 325(1–3) (2004) 155–161.
- [7] L. Uruski, J. Gorecki, M. Macherzynski, T. Dziok, J. Golas, “The ability of Polish coals to release mercury in the process of thermal treatment”, *Fuel Processing Technology*. Vol. 140 pp. 12-20 2015.
- [8] Dziok T, Strugała A, Rozwadowski A, Macherzyński M., Studies on the correlation between mercury content and content of various form of sulfur in Polish hard coals. *Fuel*. 159 (2015) 206-213.
- [9] E. J. Granite, H. Pennline, “Novel Sorbents for Mercury Removal from Flue Gas”, *Industrial & Engineering Chemistry Research*. Vol. 39 pp. 1020-1029 2000.
- [10] E. J. Granite, H. Pennline, “Photochemical Removal of Mercury from Flue Gas”, *Industrial & Engineering Chemistry Research*. Vol. 41 pp. 5470-5476 2002.
- [11] A. A. Presto, E. J. Granite, “Critical Review: Survey of Catalysts for Oxidation of Mercury in Flue Gas. *Environmental Science & Technology*. Vol 40 pp. 5601-5609, 2006.
- [12] A. A. Presto, E. J. Granite, “Noble Metal Catalysts for Mercury Oxidation in Utility Flue Gas”, *Platinum Metals Review* vol. 52 pp. 144-154 2008.
- [13] A. A. Presto, E. J. Granite, “Impact of Sulfur Oxides on Mercury Capture by Activated Carbon”, *Environmental Science & Technology*. Vol. 41 () pp. 6579-6584 2007.
- [14] E. Kalisinska, J. Górecki, N. Lanocha, A. Okońska, J. B. Melgarejo, H. Budis, I. Rząd, J. Golas, “Total and methylmercury in soft tissues of white-tailed eagle (*Haliaeetus albicilla*) and osprey (*Pandion haliaetus*) collected in Poland”, *Ambio*. Vol. 43 pp. 858–870 2014.
- [15] E. Kalisinska, J. Gorecki, A. Okonska, B. Pilarczyk, A. Tomza-Marciniak, H. Budis, N. Lanocha, DI. Kosik-Bogacka, KM. Kavetska, M. Macherzynski, J. Golas, “Mercury and selenium in the muscle of piscivorous common mergansers (*Mergus merganser*) from a selenium-deficient European country”, *Ecotoxicology and Environmental* vol. 101 pp. 107–115 2014.
- [16] Q. Zhou, Y. F. Duan S. L. Zhao, C. Zhu, M. She, J. Zhang, SQ. Wang, “Modeling and experimental studies of in-duct mercury capture by activated carbon injection in an entrained flow reactor” *Fuel Processing Technology* vol. 140 pp. 304-311 2015.
- [17] Yu L. Yin L. Xu Q. Xiong Y. “Effects of different kinds of coal on the speciation and distribution of mercury in flue gas” *Journal of the Energy Institute*. Vol. 88 pp. 136-142 2015.
- [18] A. Fuente-Cuesta, M. Diaz-Somoano, M. A. Lopez-Anton, M. R. Martinez-Tarazona, “Oxidised mercury determination from combustion gas using an ionic exchanger”, *Fuel*, vol. 122 pp. 218-222 2014.
- [19] Online stack GAS/CEM Systems. <http://www.psanalytical.com/products/onlinestackgas.html>. (accessed 16.09.2017).
- [20] GmbH. S. M. MERCER Mercury Analysis System. file:///C:/Users/DOM/Desktop/Downloads/MERCER_en.pdf. (accessed 16.09.2017).
- [21] Scientific. T. Mercury Freedom System. <http://www.thermoscientific.com/content/tfs/en/product/mercury-freedom-system-1.html>. (accessed 16.09.2017).
- [22] Durag HM 1400 TRX continuous mercury analyser. <http://www.directindustry.com/prod/durag-group/product-9067-400797.html>. (accessed 02.04.2016).

- [23] J. Górecki, A. Łoś, M. Macherzyński, J. Gołaś, P. Burmistrz, K. Borovec, "A portable continuous system for mercury speciation in flue gas and process gases" *Fuel Processing Technology* vol. 154. pp. 44-51 2016.
- [24] J. Gorecki, A. Okonska, "The construction and testing of the portable Hg^{2+} ultrasonic calibrator for the control of mercury speciation systems" *Talanta*. Vol. 147 pp. 28-34 2016.