AGH UNIVERSITY OF SCIENCE AND TECHNOLOGY

Faculty of Energy Research and Fuels

Department of Coal Chemistry and Environmental Sciences

Ms. Ref. No.: **FUPROC-D-16-00310**

Old title: Online mobile system for mercury speciation in flue gas from coal combustion

New title: A portable, continuous system for mercury speciation in flue gas and process gases

Reviewers' comments:

Reviewer #2: This is a good note and excellent work; I recommend publication after minor revisions.

1. Introduction - add the following
"Mercury is present within untreated coal-derived flue gases at trace levels of around 1 ppb. At the high temperatures within the boiler, the mercury is liberated from the coal as elemental mercury. As heat is extracted from the combustion process, mercury can exist within the flue gas as elemental mercury, oxidized mercury (compound form, often assumed to be mercuric chloride), and particulate-bound mercury [reference A, B, C, D, E]. The low concentration makes distinguishing between the three forms very difficult. Further complicating the analysis is the fact that mercury can readily convert between these three species, and because of the low concentrations, also be readily lost due to adsorption on tube walls [reference A, B, C, D, E]. In addition, various surfaces such as tube walls can catalyze the oxidation of mercury [references C, D, F]."
The Introduction was updated.

References
A. Novel Sorbents for Mercury Removal from Flue Gas, Evan Granite, Henry Pennline, and Richard Hargis, Industrial & Engineering Chemistry Research, vol. 39, pp. 1020-1029, April 2000.
B. Photochemical Removal of Mercury from Flue Gas, Evan Granite and Henry Pennline, Industrial & Engineering Chemistry Research, vol. 41, pp. 5470-5476, October 2002.
C. Critical Review: Survey of Catalysts for Oxidation of Mercury in Flue Gas, Albert A. Presto and Evan J. Granite, Environmental Science & Technology, 40(18), 5601-5609, September 2006.

University of Science and Technology | Faculty of Energy and Fuels
al. A. Mickiewicza 30, 30–059 Kraków,
tel. +48 12 617 22 93, fax +48 12 617 23 99
gorecki@agh.edu.pl

D. Noble Metal Catalysts for Mercury Oxidation in Utility Flue Gas, Albert A. Presto and Evan J. Granite, Platinum Metals Review, 52(3), 144-154, July 2008.
E. Impact of Sulfur Oxides on Mercury Capture by Activated Carbon, Albert A. Presto and Evan J. Granite, Environmental Science & Technology, 41(18), 6579-6584, September 2007.
F. A Kinetic Approach to the Catalytic Oxidation of Mercury in Flue Gas, Albert A. Presto, Evan J. Granite, Andrew Karash, Richard A. Hargis, William J. O'Dowd, and Henry W. Pennline, Energy & Fuels, 20(5), 1941-1945, September 2006.
The literature was updated.

Reviewer #3: This manuscript describes the construction of an apparatus designed to facilitate mobile measurement of mercury from coal combustion flue gas.

The essential shortcoming of this manuscript lies in weaknesses in its comparison of existing technologies to the described apparatus. Specifically, the manuscript describes the Lumex RA-915+ as one of the "rare" examples of mobile mercury monitoring systems, which are (according to the manuscript) often not suited for sampling from flue gas. Sorbent traps such as those sold by Ohio Lumex are commonly used by electric utilities in the U.S. to conduct quarterly (four times per year) compliance testing, thereby avoiding the need for continuous mercury monitors. The U.S. EPA has built a mobile mercury monitoring toolkit that uses the sorbent trap method. The toolkit, operated by Dr. Jeff Ryan at EPA, has been dispatched globally to benchmark mercury emissions from sources in the host country issuing the invitation. Thus, the claim in this manuscript that mobile mercury monitors are either rare or not suited for sampling from flue gas is demonstrably not true, based on the
experiences of U.S. utilities and the U.S. EPA.
In the text there was an error resulting from an oversight. Our intention was to write that the number of mobile and **continuous** measurement systems is rather limited. We read carefully the information on the Lumex trap system and we find it very useful. Recently we use successfully sorbent-carbon traps for mercury speciation in the process gases in the coke industry. The trap system (such as Lumex) is very efficient, but it is not possible to determine mercury continuously (1 measurement/second) with it.

A few words on why we decide to construct our own system. Before we start working on constructing our system we try to buy the complete small and portable mercury speciation system for continuous measurement of Hg in flue gas. We need such a system to measure Hg it in a demo installation for mercury removal from flue gas (Knowledge and Innovation Community InnoEnergy (KIC SE) Project "CoalGas"). We could not find a system that met our requirements, so we decided to adapt the EMP-2 WLE-8 Nippon Instrument Corporation system which is most appropriate for us. By the way, it appeared that there is no information on the construction of such a system in the literature.
In our opinion, this paper delivers important information on the construction of a portable, continuous, scientific system for mercury speciation in flue gas. The confirmation of the lack of this type of information is associated with the problems with the commercial system for Hg speciation in the flue gas made by Nippon Instrument Corporation SGM-8.

Acknowledging the existence of a competing technology is a relatively easy modification to the manuscript. However, with this acknowledgment it becomes

University of Science and Technology | Faculty of Energy Research and Fuels
al. A. Mickiewicza 30, 30–059 Kraków,
tel. +48 12 617 22 49, fax +48 12 617 23 99
gorecki@agh.edu.pl

incumbent on the authors to demonstrate that the apparatus described in the manuscript has performance and/or features that meet or exceed those of existing, competing technologies. This requires much more detailed performance data than exists in the manuscript in its current form.

The following additional information and changes were introduced to the paper:
- a new title which precisely defines the basic features of our system
- information about the US EPA Mercury Measurement Toolkit and its use [line 64]
- 9 new references: 9-13, 17, 23, 24, 30
- new Table: Table 2 – "Results of mercury determination in flue gases obtained with the Standard Addition Method procedure".
- four new pictures (e.g. fly ash construction, tee connector construction) [fig 2, fig 3, fig 6, fig 7]
- new chapter - description of continuous measurement of Hg with our system during low thermal pyrolysis of coal [start: line 327]
- new chapter - the latest (04.2016) comparison with Durag HM 1400 TRX [start: line 298]
- new chapter - data on the Standard Addition Method application and matrix effect [start: line 255]
- a description of the latest method used to avoid acid condensation inside the $SnCl_2$ scrubber in low temperatures [line 354]

Less significant and minor changes that are needed:

1. All acronyms should be defined at or prior to first use.

Done.

2. Additional schematics showing more detail are needed, beyond the overall schematic shown in Figure 1.

A picture of the fly ash filter construction and a picture of tee connector construction were added [fig 2, fig 3]

3. Liquid-filled impingers are used in both the Ontario Hydro method and the subject apparatus. This commonality makes it difficult to convince the reader that the subject apparatus does in fact offer any benefits over the O-H method.

Impingers are practically the only common parts in OH and our system. The OH method is a portable, but not continuous. To help the reader understand the idea of our system the introduction to the system description has been extended [line 86].

4. The need for heat-traced sampling lines and the existence of measurement artifacts caused by interferences from collected fly ash are well-known challenges in mercury measurement from flue gas. To report them here as "lessons learned" actually detracts from arguments that the results described in the manuscript represent technological advances.

We agree. This part was removed from manuscript.

5. (Line 36) Because there are several Clean Air Acts (CAAs) that are in effect in different countries, need to be specific as to which country's CAA is being referenced.

Done.

University of Science and Technology | Faculty of Energy Research and Fuels
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tel. +48 12 617 22 49, fax +48 12 617 23 99
gorecki@agh.edu.pl

6. (Line 39) If concentrations are to represent part per billion-level concentrations then the Greek letter mu is conventionally used, rather than "m", to represent micro (10^-6).
We agree. It was a mistake. It was changed.

7. (Line 44) References to citations 238 through 241 must be typos, since there are not this many citations in the list of references.
We agree. It was a mistake. We removed these references.

8. It is questionable to assert that the most common method of mercury measurement is Ontario Hydro. OH has a long history, but its difficulties have been well-documented and CEMs/CMMs are arguably the preferred approach.
We checked the frequency of the OH method use in ScienceDirect and indeed the popularity of this method had been declining in recent years. Therefore the text about the OH method was modified [line 69]. Nevertheless, the big advantage of the OH method (used as a reference method – especially in Poland) is its availability. Our data shows (Mercury conference in Gdynia, Poland in 05/2016 and personal contacts with distributors of mercury analyzers) that in Poland there are currently only a few systems for mercury speciation in the flue gas: Tekran 3300 (Institute of Chemical Processing of Coal), our PC-AGH and 5 sets of SGM-8 NIC (Bełchatów power plant). However, the SGM-8s in the Bełchatów Power Plant are still being tested and modified.

9. (Line 65) For an introductory and essential description of a proposed new apparatus or technology such as this, supporting data should be included here, not left to the reader to search and find in other documents.
Line 65 was removed from the manuscript.
We tested the SGM-8 Nippon Instrument Corporation in the Bełchatów Power Plant and in Ostrava (Trebovice Power Plant) and we found out that in its current form the SGM-8 is not ready for the speciation of mercury in the flue gas (huge problems with condensation: water in the transfer line, problems with the probe and tee connector construction and lack of pressure measurement). The official information from Nippon Instrument Corporation said that SGM-8 is ready for speciation of mercury in the flue gas. We checked that it is not true, but we have no experimental data to prove it. The Nippon Instrument Corporation has the full information on our system and if they want they can improve the SGM-8 set even before the publication of this article. Therefore we decided not to present our negative opinion on the SGM-8 in this paper.

10. (Line 103) Where much emphasis is placed on details such as the temperature setting of the fly ash filter, values should be provided, rather than left until later in the manuscript to be specified.
Additional information was added to this section of the article [line 123].

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al. A. Mickiewicza 30, 30–059 Kraków,
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gorecki@agh.edu.pl