

06-March-2015

### **Re: PUBLIC COMMENTS:**

"National Emissions Standards for Hazardous Air Pollutants from Coal- and Oil-Fired Electric Utility Steam Generating Units" Docket ID No.: EPA-HQ-OAR-2009-0234 (NESHAP/MATS action)

Dear Sirs:

Tekran Instruments Corporation provides, herein, our perspectives on the subject NESHAPS Docket, with particular focus on the proposed tolerances on the Relative Accuracy Test Audits results.

Tekran Instruments Corporation is a supplier of electronic Continuous Emissions Mercury Monitoring Systems (HgCEM Systems) and Services as well as trace-level laboratory analytical and ambient mercury monitoring systems.

### Proposed Amendment to the EPA Draft RATA Tolerance

Based on the body of evidence available to Tekran Instruments Corporation at this point in time, we will argue below that we could support a RATA tolerance of  $\pm 0.4 \ \mu g/m^3$  for RATA's conducted at concentrations less that the regulatory limit of 1.5  $\mu g/m^3$ . After the first years of operations under the EGU MATS, and after reviewing additional data, there may a case for lowering this tolerance further. In the interim, the levels proposed by EPA do not seem to be in alignment with the level of uncertainty that can be expected using the current technology and Method 30B at the regulatory mercury levels. Thus, the current proposed RATA tolerances are considered overly restrictive and present undue hardship on both owner/operators and electronic HgCEM Systems suppliers.

In providing the above recommendation for RATA tolerances, it is noted that many coalfired power plants have and will be making substantial investments in capital equipment and operating costs (e.g. for Activated Carbon Injection, chemicals for coal and scrubber treatment, etc.) From the perspective of the end-user, we appreciate, and are sensitive to, the motive that tighter tolerances would result in economic benefits to the owner-operator.

### Background

In anticipation of monitoring and compliance associated with EPA's NESHAP/MATS regulations, a number of electric utilities have chosen electronic HgCEM Systems for compliance monitoring. These systems will, in many cases, also be employed to monitor and control mercury abatement technologies in order to achieve compliance and optimize mercury emissions control costs. EPA has stipulated Relative Accuracy Test Audit (RATA) tolerances of  $\leq 20.0\%$  when the average Hg concentrations are  $\geq 50\%$  of the emissions limits – or on the order of  $0.75 - 1.5 \ \mu g/m^3$ . Assuming nominal controlled levels of Hg on the order of  $1.0 \ \mu g/m^3$ , the Relative Accuracy of the HgCEM System versus EPA 30B Sorbent Trap reference method must be  $\leq \sim 0.2 \ \mu g/m^3$ . This new level is one fifth of the current Relative Accuracy tolerance of  $\pm 1.0 \ \mu g/m^3$  for concentrations less than 5.0  $\mu g/m^3$ .



# Position Support Discussion -and Proposed Amendment to the HgCEM System RATA Tolerance

# Measurement Uncertainties, Limits of Detection (LOD) and Limits of Quantification (LOQ).

For perspective, it is important to point out that the MATS regulated total mercury concentrations are extremely low and must be selectively and accurately measured in a complex matrix of gases and particles. For reference, a 0.1 ug/m<sup>3</sup> difference measured between a Method 30B and HgCEM System RATA is just 11 parts per trillion (pptv) volume-to-volume basis. The limit of detection (LOD) and lower limit of quantification (LLOQ) must be considered when setting the criteria for a reference accuracy test. Furthermore, the expanded uncertainty of a measurement method may also be relevant. It seems that the proposed new RATA tolerances have not considered the expected range of uncertainty of low level measurements below the LLOQ for the HgCEM and Method 30B. Commonly, the LLOQ is 10x the standard deviation  $(S_0)$  at the blank level [1] and will have a defined uncertainty of  $\pm 30\%$  at the 95% confidence level [2]. In practical application, EPA Method 30B using a direct thermal method of analysis and electronic HgCEM Systems may be making total mercury measurements at or near their LLOQs during a RATA test (e.g.  $0.5 \text{ ug/m}^3$ ). If this were the case, then it could be statistically improbable that the proposed new RATA criteria could be achieved. It would be easy to assume that a simple solution would be to lower the Method 30B and HgCEM LLOQ to decrease the uncertainty of the measurement. However, Method 30B does not require knowledge or attainment of a specified on-site LOD or LLOQ and even the best RATA testing groups will nominally collect the shortest sample possible, likely below the LLOQ, and still meet the method requirements. In addition, the on-site LOD and LLOQ of Method 30B is likely a function of many variables, each adding to the overall uncertainty such as trap blanks, sample flow rate, sample volume, sorbent trap technology, analyst experience and the analytical methodology used for analysis of collected Hg. This is depicted in the figure below.





Referring to the above figure:

- The 30B mercury coming from field blank, trap blank and particulate are always positive and must always be included in the 30B Total Hg.
- For the HgCEM, mercury scrubbing by the flyash on the filter may cause a negative bias.
- Dual 30B trap difference and analytical for both can cause positive or negative bias.
- Worst case is 0.38 ug/m<sup>3</sup> difference between methods that pass all QA criteria.

Regarding the electronic HgCEM Systems, independent research reported an estimated LOD of 0.01 ug/m<sup>3</sup> and 0.04 ug/m<sup>3</sup> for the Tekran and Thermo HgCEM Systems, respectively [**3**]. However, from a practical perspective, owner-operators are likely to have a LOD 5 times higher than this careful laboratory study. Thus, the LLOQ could easily reach levels approaching 0.17 and 0.66  $\mu$ g/m<sup>3</sup> for the Tekran and Thermo HgCEM Systems respectively. In short, at MATS levels of compliance, and Method 30B as currently written and practically applied in the field, the new proposed RATA criteria are not in alignment with the statistical limitations of measuring near the LOD and LLOQ. Thus, since Method 30B is the reference method, the concern becomes that failed RATAs using the stricter proposed RATA criteria may unnecessarily impugn the HgCEM accuracy, due to the inherent uncertainty of Method 30B below the LLOQ. As an example, please review the results of a comparison of sorbent traps and other extractive methods (e.g. Ontario Hydro Method) for measurement of relatively high levels of total mercury as depicted in the figure below as reported in Reference 4.





Figure E-5: Sorbent Trap Bias Error With Respect To OHM

The above Figure was extracted from Reference [4]. Mercury concentrations during the test campaigns ranged from approximately  $7 - 27 \ \mu g/m^3$ . As such, biases of just 1 percent represent significant differences in absolute mercury concentrations.

Method 30B and Electronic HgCEM Systems Measure Different Hg Species – EPA MATS Rules stipulate measurement of vapor-phase mercury, Method 30B sorbent traps measure elemental (Hg<sup>0</sup>) and oxidized mercury (Hg<sup>2+</sup>), as well as particulate-bound mercury (Hg<sup>P</sup>). To the extent that significant levels of Hg<sup>P</sup> are present in the flue gas, the Sorbent Traps will read higher than the electronic HgCEM System, which only measure vapor-phase mercury. The amount of particulate-bound Hg in the Armstrong Study [4] ranged from <0.1 µg/m<sup>3</sup> to as high as 0.66 µg/m<sup>3</sup>.

### Example Data from Relative Accuracy Test Audits (RATA)

The graph below presents data from 15 different RATAs conducted on Tekran HgCEM Systems. The HgCEM Systems were and are well maintained by the owner/operators. For the most part, the plants were running with emissions at or below the limits of the EGU MATS. Further, the RATA test teams were experienced, with reasonable quality control and assurance protocols.





Each of the test values shown in the figure above represent the average of nine (9) 30B samples (paired traps) and corresponding averages of the electronic HgCEM Systems for the sampling periods. The average difference for all tests was  $0.22 \,\mu g/m^3$  and the average percentage difference was 22%. While not always the case based on Tekran's broader experience, note that all of the Electronic HgCEM Systems' readings averaged less than the 30B Sorbent Trap readings. In addition to the prospect of particulate-bound mercury contributing to the low bias, it is noted that Method 30B has no provision for developing Field Blanks (AKA "Procedural Blanks"), another contributing factor to low-bias and difference in the results from the two methods of measurement.

#### Summary Comments

The proposed RATA tolerances in the February 17, 2015 Docket ID No.: EPA-HQ-OAR-2009-0234 (NESHAP/MATS) are considered overly restrictive and are not supported by field data and analyses and the experiences of Tekran Instruments Corporation. An alternative approach, with empirical bases, has been proposed herein.

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#### REFERENCES

[1] U.S. EPA Detection Limit / Quantitation Limit Summary Table - <u>http://www.epa.gov/fem/pdfs/MDLMQL-ToolBox-Final-Oct2010.pdf</u>

[2] "Quality Assurance of Chemical Measurements", pp. 79-82, J. K. Taylor, Lewis Publisher, 1987

[3] – "Determining the Variability of Continuous Mercury Monitoring Systems (CMMS) at Low Mercury Concentrations", Energy and Environmental Research Center Final Technical Report, January 1, 2010 – March 31, 2011. Co Researchers – Electric Power Research Institute and the EERC Center for Air Toxic Metals.

[4] Armstrong Project – Evaluation and Comparison of U.S. and EU Reference Methods for Measurement of Mercury, Heavy Metals, PM 2.5 and PM10 emissions from Fossil-Fired Power Plants, Final Report, Dr. Nenad Sarunac, Energy Research Center, Lehigh University, February, 2007, Report No. 07-400-02.