

**Hg Continuous Emissions Monitoring
Significant Technical Issues From The Utility Industry Perspective**

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Introduction

There are a number of Hg emission measurement issues raised by the Environmental Protection Agency's (EPA) final Hg electric utility rules. Until the inevitable litigation is concluded we will assume that the Hg control program will be a cap and trade program. So, once again we will not be just measuring emissions; we will be measuring money. Unfortunately, the technical support documentation in the rule dockets and information available from industry research clearly shows that mercury measurement technology is not commercially available at the level of reliability, accuracy and cost needed for a trading program. This fact has recently been confirmed by the most recent EPA field test of Hg monitors. You will hear more from other speakers at this conference on the results of the EPA field study. Please do not let the positive spin by the various speakers give you whiplash. It is a simple fact that we are still not at the point where there are viable continuous Hg monitors available that will meet all of the requirements of the Hg control regulations.

EPA appears to recognize that there are significant impediments to the commercial application of Hg continuous monitoring technology. As you may have heard, EPA has been conducting an extensive dual site evaluation project to define and refine the continuous Hg monitoring technology. Three different EPA groups are involved: (1) Office of Air Quality Planning and Standards (OAQPS), (2) Clean Air Markets Division (CAMD), and (3) Office of Research and Development (ORD). This paper is a summary of major technical issues associated with Hg continuous emissions monitoring technology from the utility industry perspective. It is critical that the EPA and industry research projects not only resolve the major technical issues associated with Hg CEMS but also demonstrate the reliable, continuous operation of Hg CEMS.

Technical Discussion of Issues Related to the Evaluation Projects

There are a number of major technology issues associated with Hg monitoring that include:

- The precision, accuracy and time lag associated with the Ontario Hydro wet chemical reference test method
- Availability and demonstration of an instrumental reference method for Hg
- Availability and demonstration of continuous Hg monitor calibration techniques for elemental and oxidized Hg
- Demonstration of oxidized Hg converter performance
- Demonstration of calibration drift and linearity of the continuous Hg monitors
- Quantification of lower measurement limit for continuous Hg monitors
- Reliability and operability of Hg monitoring systems
- Performance of Hg carbon traps (Method 324) relative to other measurement methods

Many of these issues are interrelated as discussed below.

Issue 1 - The precision, accuracy and time lag associated with the Ontario Hydro wet chemical reference test method

While we may disagree, it is generally accepted by the research and development community that the Ontario Hydro (OH) wet chemical test method is reasonably accurate and precise at Hg concentrations above approximately 1 microgram/m³. Little is known, however, about its accuracy and precision at lower concentrations. If the Hg control program is implemented as is presently thought, many utility boilers will be emitting Hg at levels lower than 1 microgram/m³ - especially those firing Eastern bituminous coals. Since the OH method will likely be the EPA Reference Method for Hg measurements, it is important that the method be evaluated for accuracy and precision at low levels. It should also be noted that various OH field tests indicate that measurement precision may be a problem. The source of this variable performance may lie with the sampling or analytical procedures; however, at this point the source of the problem is not clear.

We are also very concerned about the amount of time it takes to conduct a Hg continuous monitor Relative Accuracy Test Audit (RATA) using the OH test. A RATA test period of 6-7 days can be anticipated. In addition, obtaining the analytical results can require from 3-6 weeks and we believe this time lag is unacceptable because in the interim it is not known whether the continuous monitor has passed the RARA or not.

For example, during a recent EPA test site certification test series it was four weeks before the OH test results were available and we assume these samples were on an expedited analysis schedule. In addition, this certification test was *unsuccessful* because 4 of the 12 paired OH samples did not pass the relative deviation criteria (<10%)¹ for the paired trains.

Issue 2 - Development of a Hg Instrumental Reference Method

It is imperative that an Instrumental Reference Method for Hg be developed. No air emissions cap-and-trade program, can be expected to deal with a difficult wet chemical reference method that has 3-6 weeks turn around before the source knows the results of a monitor certification, RATA or QA audit. Given our present knowledge about the OH method that has been specified as the reference method for the Hg control program, it is estimated that a single RATA will require 6-7 days of on-site testing and may require the performance of 15-18 paired train sampling runs. This was our estimate a year ago and, considering the recent *certification failure* experience in the EPA field test program, our estimate has not changed. As clearly demonstrated by the EPA experience, this extreme effort will be necessary to ensure that the source has collected enough data to have nine or more valid paired train values, especially at low Hg concentrations. Of course, it is possible that there will still not be enough valid samples resulting in the source being out of control and having to repeat the test. Not only is this a very expensive testing exercise but unit load will need to be blocked for long periods of time potentially resulting in significant "off economic" generation expenses. When one considers the risk and amount of substitute data (substitute data can basically be considered high biased measurements)

¹ Relative deviation, as defined by "EPA math," is half what would normally be considered relative difference. In other words, 10% relative deviation between the paired OH trains is really 20% relative difference.

associated with this wet chemical reference method approach, it is obviously an untenable situation.

Therefore, development of an instrumental reference method for Hg is essential. I am pleased to report that EPA agrees with this assessment and that development of an instrumental reference method has been a part of the EPA field test program. Development of the instrumental reference method will be done as a normal course of the overall Hg monitoring evaluation project. Some of that work has been completed and, hopefully, will be reported in this conference. Unfortunately, the original draft of the Hg instrumental reference method appears to be very complicated and restricted to very specific Hg analyzer systems. We hope that EPA and initial users can determine ways to simplify the instrumental reference method.

Issue 3 - Evaluation of Hg Monitor Calibration Procedures

Daily calibration of CEMS has been a hallmark of all past emission monitoring programs in the United States. Virtually all optical instruments exhibit calibration drift over time. While daily calibration may not be absolutely necessary, some periodic calibration check process is certainly desirable. Daily calibration has also been shown to be a valuable maintenance indicator for when there might be a pending problem with an analyzer. There are a number of calibration techniques available for calibrating Hg monitors with elemental Hg. Examples of these techniques include Hg calibration gas cylinders, permeation tubes, head space devices and direct injection. All of these techniques need to be further evaluated in a daily use environment rather than a research environment. We initially expected elemental Hg calibration using gas cylinders to be the basis for any daily requirement, however, head space devices appear to be gaining ground. Let us not lose sight of the fact that NIST traceability is required by the rule and it is not clear how this traceability will be established or in what time frame. This is an area that needs further work. In other words, NIST needs to get their act together and develop appropriate protocols. Use of Hg calibration gas cylinders is the obvious preferred option² and further work is needed at lower concentrations. When Hg emissions are in the 1 microgram/m³ range, calibration gases approaching 3-5 micrograms/m³ are needed. Hopefully, such low level calibration gases can be developed and provided at a reasonable price.³

Issue 4 - Demonstration of Oxidized Hg Converter Performance

Since all Hg monitors must measure oxidized Hg as well as elemental Hg, some kind of converter will be necessary for the conversion of oxidized Hg to elemental Hg. These converters have been **problematic** in past research efforts exhibiting limited life and poor performance. The problems with Hg converters were highlighted by the recent vendor experiences in the EPA field demonstration programs. Obviously, considerable research is needed on the fundamentals of practical converter design and operation.

In addition, periodic quantification of the converter performance will be necessary for both reference method testing and routine monitoring. At present, there appear to be two

² This is not to say that other options do not hold promise.

³ It should be noted that Hg calibration cylinders are very low concentration since 8 µg/m³ Hg concentration is approximately equal to 1 ppbv.

devices/processes that allow for the injection of oxidized Hg - the Hovacal and the Mercal. Both have been used in the past in research applications but neither has been used on a production basis. The accuracy and precision of the calibration devices is unknown and should be quantified. Again, we believe that a NIST protocol is required.

Issue 5 - Calibration and Linearity Drift of Hg Continuous Monitoring Systems

This issue is obviously related to Issue 3 because the problem of how to calibrate Hg monitors has to be solved first. Once it is, then the stability of Hg monitors should be evaluated. It should be noted that previous EPA reports indicated that some Hg monitors were not designed for daily calibration in accordance with the rule. Since the daily calibration requirement is to be a part of Performance Specification 12A and the final rule, any monitor that cannot perform daily calibrations should not be allowed into the program.

With respect to linearity and converter checks, we do not believe it is necessary to check linearity with both elemental Hg and oxidized Hg on a routine basis. A high level test of the converter should be adequate, however, this decision can be made later based on the results of tests conducted for Issue 3.

Issue 6 - Reliability and Operability of Hg Continuous Monitoring Systems

Past Hg CEMS projects have indicated that the analyzer systems are not as reliable as the typical SO₂ and NO_x CEMS. This is to be expected given the infant stage of technology development. The infant stage of development has been evident in the EPA field evaluation programs since all of the Hg monitors are exhibiting “teething” problems, especially on the scrubber-equipped source. It will be important for both sources and EPA to have an understanding of the reliability and operability of the Hg CEMS in a normal production environment. Consequently, it is believed that the instruments should, to the extent possible, be operated and maintained as if they were installed in a production environment for compliance purposes. Careful zero and span drift records as well as maintenance records should be kept in electronic format. All CEMS readings should also be maintained in electronic format.

In past field evaluations, EPA has conducted “test campaigns” whereby the evaluation was focused on short-term testing periods. During periods when specific tests were not being conducted, the Hg monitors were either shutdown or simply allowed to operate unattended. We believe that realistic day-to-day operation should be the approach during the new evaluation programs.

The information developed in these demonstration projects will be essential for sources that have to select and purchase systems and we believe that this is a very important component of the evaluation program.

Issue 7 - Quantification of Lower Measurement Limit for Hg CEMS

Recent data indicate that some (perhaps many) SCR+scrubber-equipped units have extremely low (below 1 microgram/m³) Hg emissions. In fact, the Hg emissions may be too low to

measure with present day Hg monitors except on a semi-continuous basis. This issue will likely have an impact on future EPA policy regarding how to monitor/measure very low emitting sources. Certainly, it makes no sense to install a monitor on a source where the Hg emissions are below the detection limit or measurement capability of the monitor or reference method. This issue is of lower importance at this point in time because it is not clear how prevalent the problem might be. Clearly, more data are needed concerning the total actual and potential source population and perhaps a population study is the correct near-term course of action.

Issue 8 - Performance of Carbon Traps Relative to Other Measurement Methods

The carbon trap method (Method 324) is a very promising method, especially for low Hg emitting sources where use of a continuous monitor may be impossible. Existing data also indicate that it performs on par with Hg CEMS; however, the database needs to be expanded and reinforced. This method has been performed by RMB on a periodic basis during the entire Hg CEMS evaluation program. There have been some problems with the sampling equipment and freezing due to very low temperatures. Solutions to these problems appear to be straightforward. The traps were run as paired trains so that precision can be further quantified. There were also quad train comparisons performed to evaluate spiking and alternative Hg analytical procedures. Alternative analytical procedures should be evaluated to quantify the precision and error probability.⁴ Unfortunately, there were a variety of problems with the carbon trap tests during the EPA test program. These problems were generally related to spiking, trap manufacture and analytical procedures. Specifications for the traps should be developed and alternative analysis approaches should be further developed and evaluated. There is still considerable work required to evaluate the carbon trap method.

Summary

Addressing the issues identified above is critical in ensuring the successful implementation of a Hg continuous emissions monitoring program under either the present cap-and-trade rule. The EPA evaluation/demonstration project should be further structured to not only develop the measurement technology and procedures, but to also demonstrate continuous operation of the Hg CEMS in a production environment. In addition, the electric utility industry needs to bring to bear resources to answer those questions that EPA cannot or will not.

⁴ The analytical procedures specified for the carbon traps are reasonably complex. In addition, it has been suggested that these procedures require extensive sample dilution, which can introduce measurement error.