

***Tekran Comments regarding:
Final Technical Report, ICCI Project Number: 10/6A-1***

**“DETERMINING THE VARIABILITY OF CONTINUOUS MERCURY MONITORS (CMMS)
AT LOW MERCURY CONCENTRATIONS”**

Rev 1.03 June 16, 2011

Executive Summary

This study, conducted by the Energy and Environmental Research Center (EERC) and jointly funded by EPRI and the ICCI, was designed to test the responses of commercially available continuous mercury monitors (CMMs) to mercury concentrations in the sub-microgram per cubic meter range. This is a vitally important study since the proposed MACT regulations will require that many, if not all, US coal fired power plants reduce their emissions to this level. The study is definitive and will become an important reference for years to come. It provides a great service to industry and accurately measured the performance of CMMs during exposure to low mercury levels.

EERC took great care in the conduct of the study and Tekran greatly appreciates the attention to detail exhibited throughout the experimental phase. The resultant report should adequately reflect this high level of professionalism and must be technically irrefutable and free of errors. We believe that EERC, ICCI and EPRI are open to a collaborative review to improve the end result of this vital study. We offer the following comments to help ensure that the final report will remain an expression of the high quality of the experimental work performed. The current version of the report is available on the ICCI website at: <http://www.icci.org/reports/10Laudal6A-1.pdf>

The major issues are:

- The title is misleading. The study could not assess the variability of the CEM systems since the variation in output concentrations produced by the test facility greatly exceeded the instruments' variability.
- Accuracy. The uncertainty (accuracy) of the reference method should be assessed since, in the absence of the usual regulatory acceptance criteria (e.g. 20% ± 0.8 µg/m³), some sort of error bounds on the reference method must be given. Calculating the precision of replicate runs is not the same thing as assessing the uncertainty of the analytical results.
- Some of the statistical methods used are invalid since they directly compare the analytical uncertainty of replicate analyses against a time varying series of concentrations.
- Some of the crucial summary plots contain significant errors and omit data.
- At least one of the daily graphs uses an incorrect data set and at least one table has the CMM supplier names interchanged.
- We believe that the minimum quantifiable level (MQL) determination for the Tekran CMM is incorrect. The Tekran CMM was routinely measuring background levels in the pilot scale combustor that were a fraction of the MQL stated in the report.

Introduction

The above noted report, written by the Energy and Environmental Research Center (EERC), discusses the results of a study conducted in April 2010 where the CMM systems of Tekran Instruments Corporation and Thermo Fisher Scientific were subjected to a number of tests at low levels of mercury ($<1 \mu\text{g}/\text{m}^3$) in a pilot scale combustion facility.

The study was well conducted and many of the conclusions of the report are valid. However, there are some significant errors in data analysis and some editorial comments must be corrected.

Title of the Study [Page 1]

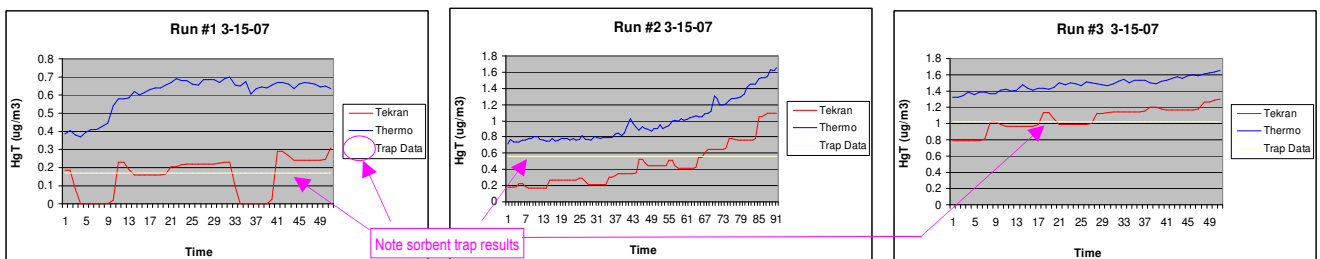
Although the title may have been determined very early on, even before the study was funded and approved, it is nevertheless inaccurate and misleading. This study could simply not determine “the variability” of either CMM evaluated since the variability of the concentrations generated by the mercury injection source were far larger than the instruments’ variability. This high simulator variability is acknowledged in several places later in the report (e.g. page 18, para 2).

The study was, in fact, more about determining the accuracy of results under various low level conditions.

Abstract [Page 1]

The final line states “...*the Thermo Scientific Instrument did not perform as well as expected*”. This phrase is repeated several more times within the report. Surely the investigators should have been open and unbiased regarding the potential performance of either instrument and should not have developed a priori expectations on how well they would work.

For example Tekran has seen these high biases at low level stacks several times before. (See March 2007 test data from actual power plant site, below). To us, the other system performed “as expected”. (We apologize for the poor choice of color for the trap results.)



CMM Operation [page 14]

The report states the following:

..... The Thermo Scientific CMM was designed and programmed to provide a data point every minute. In addition, both total and elemental mercury data are provided simultaneously. The Tekran CMM uses gold traps that must be desorbed, and therefore, the instrument was programmed to provide a data point every 2.5 minutes. The Tekran CMM can provide either total or elemental mercury data but not both simultaneously.

This is incorrect. Both CMM systems feature only one detector and can measure only one variable at a time. In both cases, a valve switches between the Hg^{T} and an Hg^{O} sample stream. A sample and hold arrangement is used to hold the most recent averaged reading of the two variables and a subtraction is then performed to determine HgCl_2 . All three species are displayed simultaneously on both systems although the analysis is sequential on each.

Sorbent Trap Accuracy

Throughout the entire document, frequent reference is made to the precision of duplicate or quad trap results taken simultaneously. This is then used to determine a λ (95%) “confidence interval”. This leads to a mistaken belief that the sorbent traps must be “correct” within this interval. However, everyone knows that there is a large difference between accuracy and precision. There is no doubt that the EERC results were precise, but there has been no attempt to calculate the uncertainty of Method 30B results. In matters of regulation, this might be excused since the reference method may be deemed by law to be “correct” despite any innate errors. However, regulations include both absolute and relative tolerances to acknowledge the potential uncertainty of both the reference method and the instrument. Staff at the US EPA have privately conceded that they consider Method 30B to be “a $\pm 10\%$ method”.

However, in a research study, an attempt *must* be made to determine the uncertainty (accuracy) of the reference readings.

Data Analysis: Sorbent Traps vs. CMM

Inappropriate data analysis is used throughout the report, but is particularly evident in Tables 8, 9 and 12. In these tables, each set of CMM results is a varying time series of combustor concentrations. Given that the concentrations vary over time, not only randomly but often with a discernable trend, the standard deviation is not necessarily an indication of instrument “noise”. It is likely that the instrument(s) are measuring legitimate fluctuations in the background concentrations.

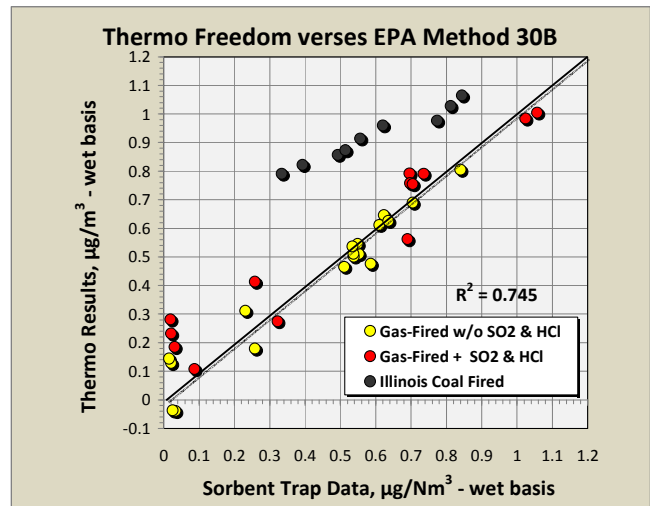
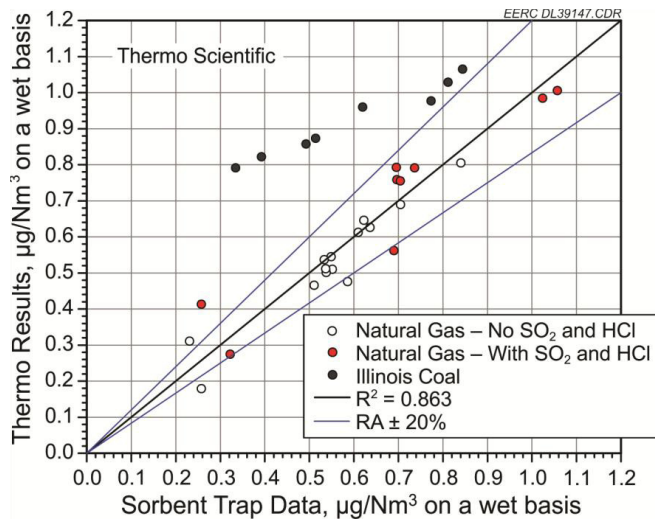
By contrast, each trap result is a single integrated value. Replicate trap results, taken over the same time period, would be expected to yield absolutely identical results and the lambda confidence interval would be a valid statistic. (Although an actual result uncertainty would be a more useful indicator.) For example the report states: “Overall, the reproducibility for the quad sorbent trap sampling ($\sigma = 3.6\%$) contributes to a high level of confidence ...” [page 24, para 2].

The standard deviations and the confidence intervals of the CMMs versus the sorbent traps results are totally different measurements and cannot be compared in any meaningful way.

Summary Plot of Results – Thermo [Fig 10]

The summary plot in the report is misleading and biased. When evaluating any instrument, its response to a zero concentration of the analyte is one of the most essential items of information an evaluator needs to know. These zero responses are valid readings and are always used to calculate the response curve of an instrument. In virtually all cases, the instrument’s response to zero gas may be below the “detection limit” of the analyzer, but this does not invalidate their use. Yet, all of the low level response points have been omitted from the Thermo plot!

The graph on the left is from the EERC report. The graph on the right shows the same data set including the omitted readings.

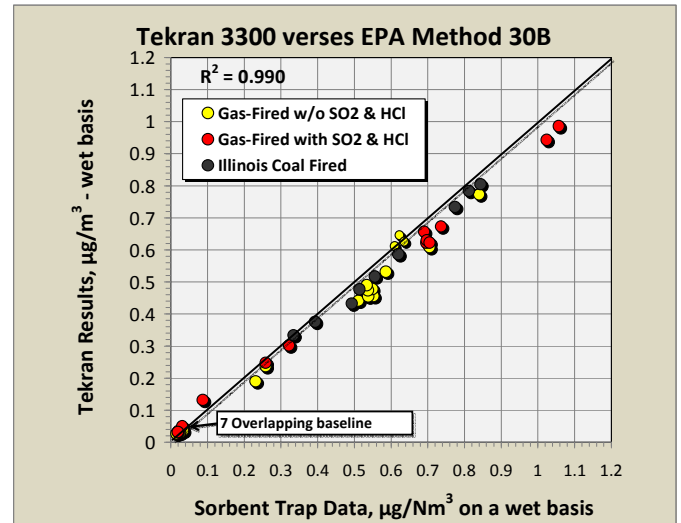
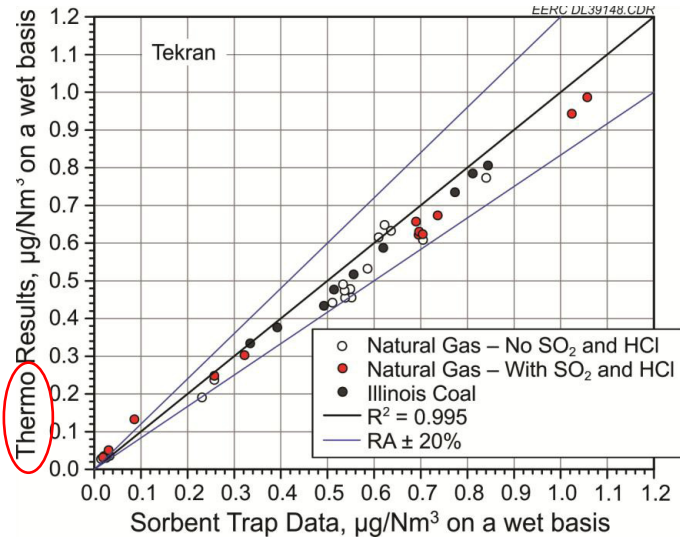


The R^2 value shown on the EERC graph is also incorrect. The **0.863** value is actually R for the entire data set (including the omitted points), not R^2 . (This error was pointed out to EERC several times.) The actual R^2 of the full data set is **0.745**. Also, it should be noted that the legend on the EERC graph gives the impression that the dark inclined line is the *regression line* for the data set. In actuality, this is the 1:1 line showing where the points would lie if the measurements were identical.

Summary Plot of Results – Tekran [Fig 11]

The Y axis label mistakenly says “Thermo”, not “Tekran”. The R^2 value shown on the EERC graph for Tekran incorrect. The 0.995 is actually R , of the full data set, not R^2 . The actual R^2 of the full data set is 0.990.

The graph on the left is from the EERC report. The graph on the right shows the correct R^2 value. Once again, the dark line is the 1:1 line, not the regression line.



Sorbent Trap Exact Start and End Times Required

A table should be added (or Tables 6 and 8 modified) to provide the *exact* start and end times for each sorbent trap test. Given the variability of the concentrations, this information is essential to allow proper averaging of the CMM data results over the appropriate time period.

Data Errors

A closer inspection of some of the graphs and tables showed a number of serious errors. It is not known whether these errors propagated throughout the analyses or were localized to each actual chart or table. The following is an example only and not a complete list of possible errors.

Table 9. Thermo and Tekran or Data Interchanged

Upon examining the four **Baseline** results, it appears that the Thermo and Tekran results are interchanged. Please examine all data and correct this table!

MDL / MQL Calculations [page 26-27]

The report acknowledges that the simulator was noisy, particularly when generating mercury chloride and that most of the variation seen was due to combustor noise, not instrument noise. We do not believe that *any* of the test conditions gave sufficiently constant concentrations to enable a meaningful determination of the Tekran instrument's detection limit. It was a valiant attempt, but impossible, given the simulator conditions. Despite this, we believe that the MDL (0.01 µg/m³) calculated by EERC turned out to be a reasonable estimate.

However, the limit of quantification is not correct. While 0.1 ug/m³ is not a bad sounding quantitation value, the Tekran CMM was routinely measuring (and quantitating) background Hg levels in the 0.025 to 0.050 ug/m³ range every night between tests. The EERC method of simply taking an estimated MDL and multiplying it by a factor of 10 to create an MQL is not correct. In standard practice, the MDL is defined as *three* times the “noise” of a dataset of replicate observations. The MQL (also called Practical Quantitation Limit, PQL, or Limit of Quantitation LOQ) is *ten* times the noise of the dataset. (Not ten times the MDL!) Thus, based on EERC's own determination of the MDL, the MQL would be ~0.033 ug/m³ not 0.1 ug/m³.

Excerpt from: http://www.epa.gov/fem/pdfs/Env_Measurement_Glossary_Final_Jan_2010.pdf

Limit of Detection (LOD)/Limit of Quantification (LOQ) – The LOD and LOQ concentrations are calculated by applying the compound's calibration curve to the noise response of a sample to obtain a value which is then multiplied by a factor of 3 for LOD (3 times of noise) and 10 for LOQ (10 times of noise). The responses of the analytes are not considered in this approach. Only the noise level is included in the calculation. In some cases, the concentration of the lowest calibration standard is treated as the LOQ. The LOD is not defined in this case, although the LOD is often assumed to be 1/3 of the LOQ.

In addition, many of the assumptions inherent in the EPA standard MDL/MQL determination are not met here.

- 1) MDL determination requires replicate measurements of a *constant* concentration, close to the estimated detection limit. This type of gas was not available here, either during combustor idle periods (where the ambient levels still varied) or during tests.
- 2) The Tekran system has a quantitation limit much closer to the detection limit than conventional “continuous” analyzers. The implicit assumptions in the EPA MDL analyses is that an analyzer produces a continuously varying (analog) output with normally distributed values about some mean. The MDL is the minimum value of analyte that would produce a statistically significant shift in the output readings. The Tekran CMM integrates peaks, so does not produce the usual “normally distributed” output. Quantitation is reliable at values just slightly larger than the minimum detectable area.

The Tekran was operated in “speciating” mode throughout the tests. The data availability requirements of any proposed regulation will likely require that the CEM operate in **Hg^T** only mode, with an occasional switch to **Hg⁰** mode if the operator is interested in speciation. The switching between sample streams increases noise. Systems operated primarily in one mode will have even lower noise than exhibited by the test system.

Data Variability During HgCl₂ Injection

The graph below shows the results of the Tekran CEM for April 27th, Test Conditions 4 and 5: HgCl₂ injections. (see EERC graphs: B-2, B-8, B-9). This graph shows speciated readings from the Tekran CMM, rather than only the Total Hg readings. The following is evident from the graph.

- 1) The zero period (03:00-07:30, shows a decided downward trend as the simulator recovers from the previous day's activities. Thus the Standard Deviation of the Tekran system cannot be used as a determinant of instrument noise. Further, even in the absence of a well defined trend, the variations during background periods are legitimate. Tekran has been monitoring ambient air levels since 1993 and this type of variation is not unusual, especially in an industrial environment.
- 2) The periods of injection exhibit quite variable concentrations. Most of the variation occurs in the HgCl₂ levels. The elemental values are much more consistent.
- 3) The fact that the HgCl₂ readings exhibit lower variability than the HgT numbers is an artifact of how they are calculated. The HgCl₂ numbers are determined by subtracting a 5 minute Hg⁰ average from a 5 minute Hg^T average. This averaging reduces the variability, which indicates that most of the combustor variation is short term, rather than long term.
- 4) The Tekran CMM is measuring Total Hg values of from 0.013 to 0.04 µg/m³ during the background period of 03:00 to 07:30. This is only 13% to 40% of the report's calculated MQL, yet the readings appear to be perfectly valid!

