PILOT-SCALE TESTING EVALUATING THE EFFECTS OF BROMINE ADDITION ON CMMs AT LOW MERCURY CONCENTRATIONS

EXECUTIVE SUMMARY

Under consent decree, the U.S. Environmental Protection Agency (EPA) finalized a National Emission Standard for Hazardous Air Pollutants (NESHAPs) for the utility industry in December 2011. The floor for mercury emissions was determined using the maximum achievable control technology (MACT) basis under Section 112 of the 1990 Clean Air Act Amendments. As a result, many plants both in the eastern and western parts of the United States will be required to control and continuously measure mercury concentrations at less than 1.0 microgram per cubic meter ($\mu g/m^3$) of gas. It is expected that many of the plants burning Wyoming Powder River Basin (PRB) coal will be required to use either brominated compounds or bromine-impregnated activated carbons (BACs) to comply with the MACT standard. There appears to be some evidence that bromine in the flue gas can result in interferences, biasing continuous mercury monitor (CMM) results (1, 2). As a result, the University of Wyoming School of Energy Resources, the Electric Power Research Institute (EPRI), the U.S. Department of Energy (DOE), and the Energy & Environmental Research Center (EERC) Center for Air Toxic Metals® (CATM®) funded a project at the EERC to evaluate the two CMMs most widely used by the utility industry: the Tekran Model 3300 and the Thermo Scientific Mercury Freedom system.

Objectives

The primary goal of the project was to determine the effects of bromine on the accuracy and precision of CMMs at mercury concentrations <1.0 $\mu g/Nm^3$. Specific objectives of the project are as follows:

- Verify the accuracy of carbon trap measurements via quadtrain sampling and spiked traps while sampling bromine-laden flue gas for mercury.
- Determine the accuracy and variability of the CMM measurements while natural gas is burned, with mercury and bromine added under controlled conditions.
- Determine the accuracy and variability of the CMM measurements while Wyoming PRB coal is burned, with mercury control to levels <1.0 $\mu g/m^3$.

To accomplish these objectives, pilot-scale tests were conducted, and the accuracy of the instruments was determined by comparison to the reference method EPA M30B (sorbent traps). The project also required that the variability of the sorbent trap sampling be determined. Therefore, to assess the precision of the sorbent traps, quadtrain samples were taken. In addition, spiked and blank samples were analyzed.

All of this required a very high level of quality control/quality assurance (QA/QC) to ensure that all equipment (the pilot-scale combustor, the mercury-spiking systems, the hydrogen bromide [HBr] injection system, the sorbent trap-sampling equipment, the Ohio Lumex sorbent trap analyzer, and the CMMs) was calibrated properly and operating optimally during the testing phase of the project.

Approach

The overall approach to determining the effect of bromine on CMMs at mercury concentrations <1.0 $\mu g/Nm^3$ was to compare the CMM results to those obtained based on a reference method (EPA M30B). To do this, three primary tasks were completed. The first task was the initial preparation of the equipment, and the other two tasks were pilot-scale tests. Task 1 was designed to ensure that all the equipment (spiking systems, combustor, sorbent trap-sampling systems, Ohio Lumex sorbent trap analyzer, and CMMs) was operating at the highest level.

The second task was to complete 1 week of pilot-scale testing firing natural gas and adding mercury and bromine using the spiking systems that were developed at the EERC. The third task was to complete 1 week of testing firing a Wyoming PRB coal in the EERC pilot-scale combustor while utilizing HBr and/or BACs to reduce the mercury concentration to <1.0 μg/Nm^3. The test plans for each of the pilot-scale tests are shown in Tables ES-1 and ES-2.

Table ES-1. Test Plan Firing Natural Gas

Test Condition	Spiked Hg Location	AC	HBr Injection, ppmv	Nominal Hg Conc., μg/Nm^3
NG1	Baghouse outlet	None	5	0.25
NG2	Baghouse outlet	None	5	0.75
NG3	Baghouse outlet	None	25	0.25
NG4	Baghouse outlet	None	25	0.75
NG5	Combustor	Hg-LH[1]	None	0.25
NG6	Combustor	Hg-LH	None	0.75
NG7	Combustor	Hg[2]	5	0.75
NG8	Combustor	Hg	5	0.25
NG9	Combustor	Hg	25	0.25
NG10	Combustor	Hg	25	0.75

[1] Norit America DARCO® Hg-LH (BAC).
[2] Norit America DARCO Hg (AC).

Table ES-2. Test Plan Firing Wyoming PRB Coal

Test Condition	AC	HBr Injection, ppmv	Nominal Hg Conc., μg/Nm^3
C1	Hg	None	0.75
C2	Hg	None	0.25
C3	Hg-LH	None	0.75
C4	Hg-LH	None	0.25
C5	Hg	5	0.75
C6	Hg	5	0.75
C7	Hg	25	0.25
C8	Hg	25	0.75

As stated previously, the overall approach for the pilot-scale test was to compare the results obtained using the Tekran and Thermo Scientific CMMs and those obtained using the sorbent trap reference methodology (EPA M30B). The sorbent traps that were done for each of the tests are shown in Tables ES-3 and ES-4. The actual mercury concentrations shown are based on the sorbent trap results. Sorbent trap analysis was completed by the EERC using the Ohio Lumex sorbent trap analyzer.

Table ES-3. Sorbent Traps Test-Firing Natural Gas

Test Condition	No. Standard Traps	No. Speciation Traps	Sample Time, hr	Nominal Hg Conc., $\mu g/Nm^3$	Actual Hg Conc., $\mu g/Nm^3$
NG1	2		3	0.25	0.258
NG2	2		3	0.75	0.707
NG3	2		3	0.25	0.168
NG4	2		3	0.75	0.602
NG5	2		3	0.25	0.047
NG6	2		3	0.75	0.565
NG7	2		3	0.75	1.13
NG8	2		3	0.25	0.159
NG9	2	2	3/2*	0.25	0.266
NG10	4	2	3/2*	0.75	0.757

*3/2 represents 3 hours for the standard trap and 2 hours for the speciation trap.

Table ES-4. Sorbent Traps Test-Firing Wyoming PRB Coal

Test Condition	No. Standard Traps	No. Speciation Traps	Sample Time, hr	Nominal Hg Conc., $\mu g/Nm^3$	Actual Hg Conc., $\mu g/Nm^3$
C1	4		3	0.75	0.929
C2	4		3	0.25	0.573
C3	4		3	0.75	0.773
C4	4		3	0.25	0.364
C5	4		3	0.75	0.638
C6	4		3	0.25	0.371
C7	4		3	0.75	1.26
C8	4	2	3/2*	0.25	0.768

*3/2 represents 3 hours for the standard trap and 2 hours for the speciation trap.

Results and Discussion

Previous testing showed that, without the use of HBr and/or BAC injection, both instruments performed very well for a range of sulfur dioxide, hydrogen chloride, and oxygen gas conditions when either natural gas or coal was fired (3). The Tekran instrument did provide a lower quantitation limit compared to the Thermo Scientific instrument: 0.01 $\mu g/Nm^3$ compared to 0.04 $\mu g/Nm^3$. The results are summarized in Figures ES-1 and ES-2.

Testing under this contract, with the University of Wyoming School of Energy Resources, EPRI, DOE, and the EERC CATM Affiliates Program, showed an impact of bromine addition on the Tekran CMM while natural gas was fired, resulting in a calculated relative accuracy (RA) of 57% compared to the sorbent trap method. The firing of Wyoming PRB coal limited the effects, resulting in a RA of 19%. The results for the Tekran data are summarized in Figures ES-3 and ES-4. As shown in Figure ES-5 and ES-6, the results obtained with the Thermo Scientific instrument results were similar to the previous testing without bromine addition, giving an overall RA of 10%. It should be noted that the greatest deviation was for bromine injection levels of >10 ppmv. This is a substantially higher concentration than what would be injected in a full-scale application.

Conclusions and Observations

Based on the results from these tests, the following conclusions and observations can be made:

- Overall, the CMMs operated very reliably, with very few problems encountered. The CMMs were operated continuously over the 3 weeks, including the time when the particulate test combustor (PTC) was not being operated (CMMs sampled ambient air), with very little input from EERC personnel.

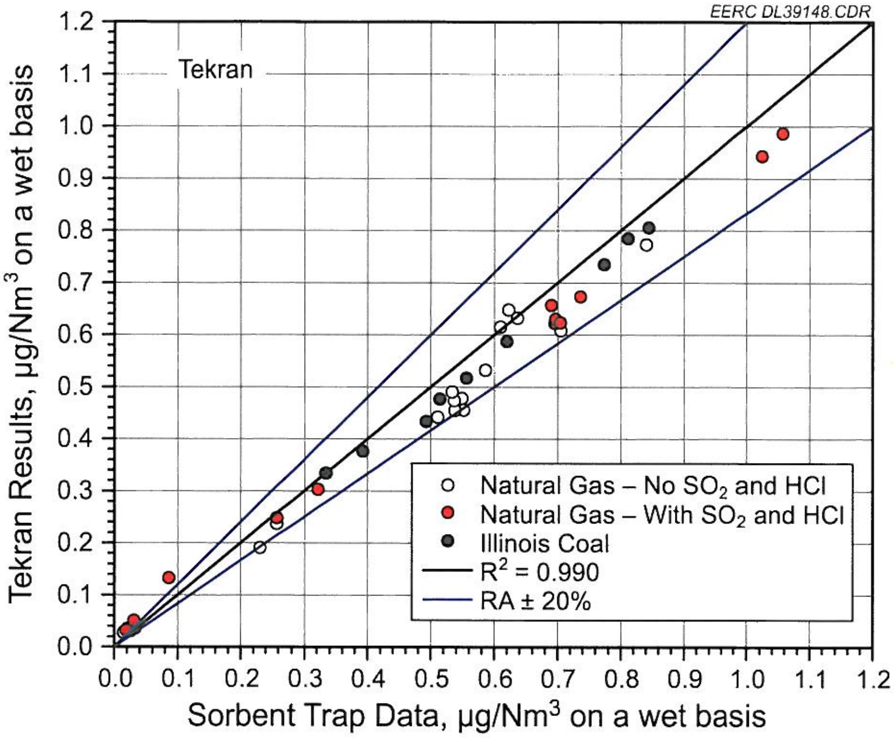

Figure ES-1. Summary of baseline Tekran CMM.

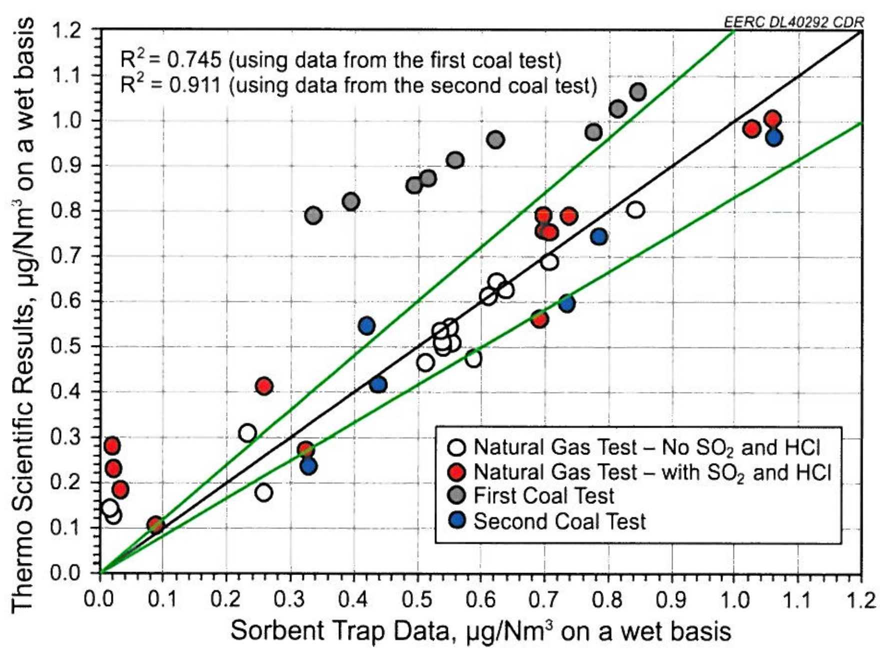

Figure ES-2. Summary of baseline Thermo Scientific CMM results.

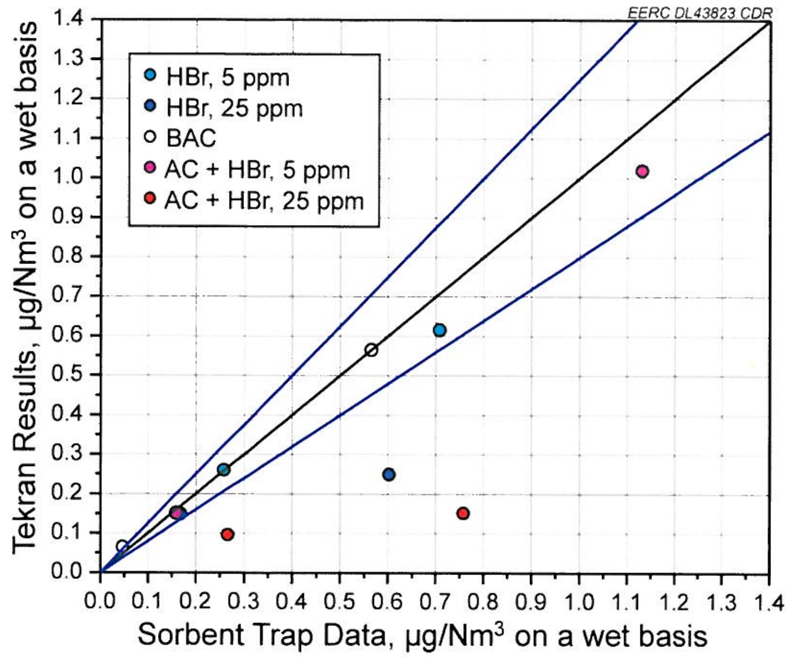

Figure ES-3. Summary of Tekran CMM results when natural gas with bromine addition was fired.

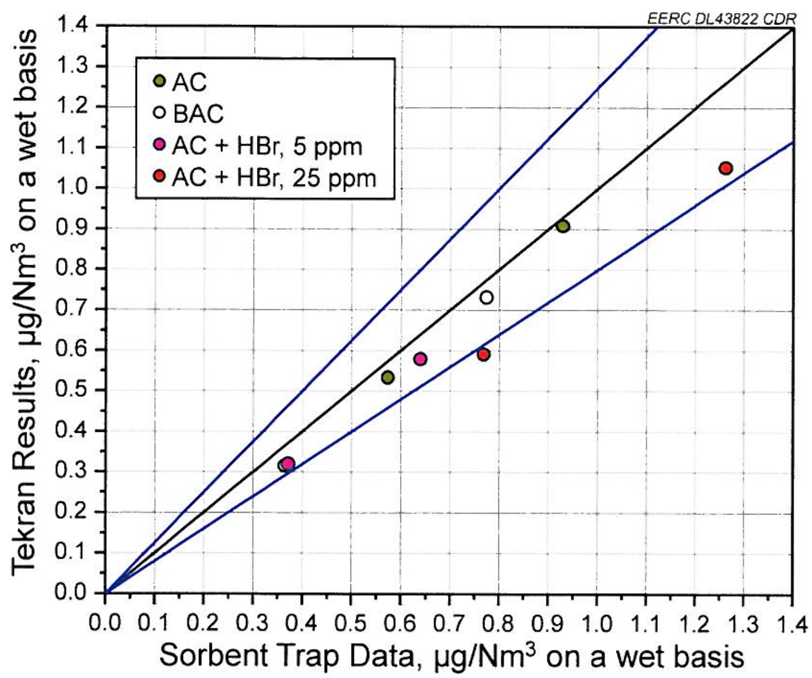

Figure ES-4. Summary Tekran CMM results when Wyoming PRB coal with bromine addition was fired.

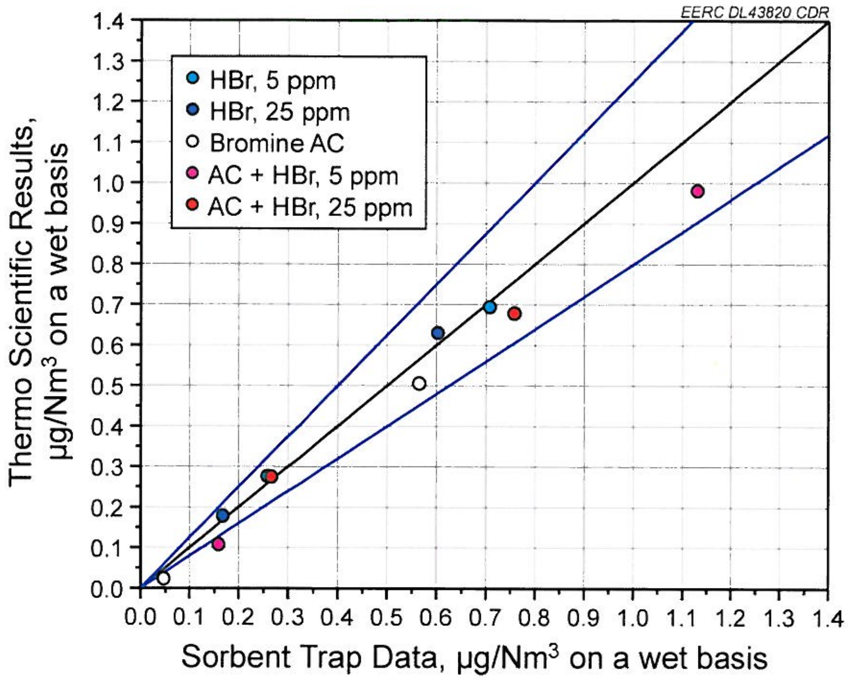

Figure ES-5. Summary of Thermo Scientific CMM when natural gas with bromine addition was fired.

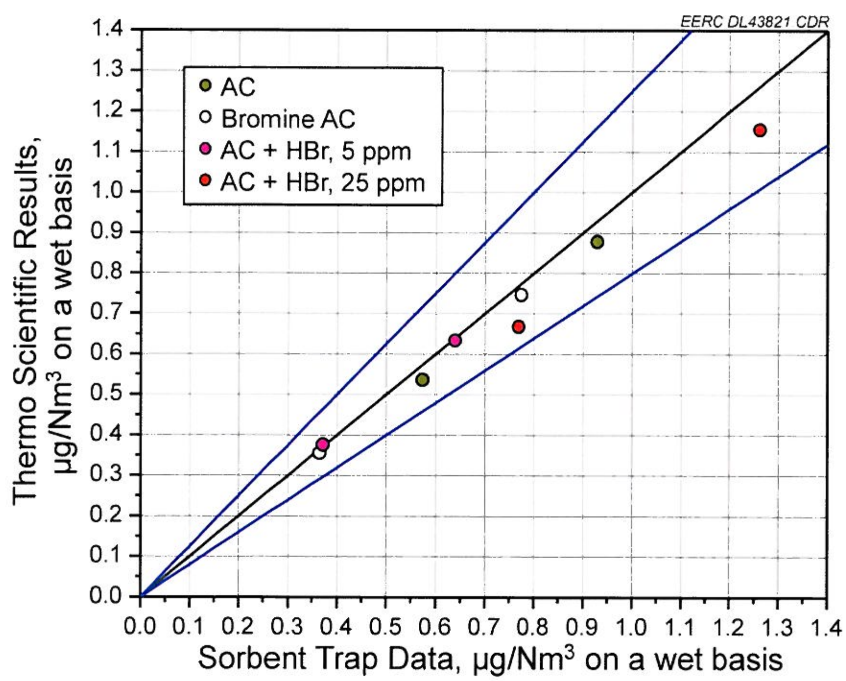

Figure ES-6. Summary of Thermo Scientific CMM results when Wyoming PRB coal with bromine addition was fired.

- The EERC mercury-spiking systems worked well and were consistent.
- Compared to the sorbent trap data, the Thermo Scientific CMM worked well when both natural gas and PRB coal were fired, with and without the addition of HBr. The Thermo Scientific CMM RA for the natural gas test was 14.6%, for the Wyoming PRB coal test was 10.4%, and for all 18 tests was 10.2%.
- The Tekran CMM showed a bias low when HBr was added to the flue gas as part of the test matrix. The bias was less severe when coal was fired. Compared to the sorbent trap data, the Tekran CMM RA for the natural gas test was 57.8%, 19.1%, for the coal test, and averaged 32.2% for all 18 tests. The difference between the sorbent traps and the Tekran CMM appears to be systemic in nature, as the CMM results were consistently lower than those measured using the sorbent traps when HBr was present.

References

1. Pavlish, J.H.; Thompson, J.S.; Martin, C.L.; Musich, M.A.; Hamre, L.L. *Field Testing of Activated Carbon Injection Options for Mercury Control at TXU's Big Brown Station*; Final Report (March 2, 2005 – March 31, 2008) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-05NT42305 and Luminant Power; EERC Publication 2008-EERC-01-05; Energy & Environmental Research Center: Grand Forks, ND, Feb 2008.
2. CATM Staff. *2008 Annual Report for the Center for Air Toxic Metals*. Energy & Environmental Research Center: Grand Forks, ND; www.undeerc.org/catm/pdf/area2/2008SamplingandAnalyticalMethods.pdf (accessed May 2008).

3. Laudal, D.L.; Thompson. J.S.; Subtask 4.10 – *Determining the Variability of Continuous Mercury Monitors (CMMs) at Low Mercury Concentrations*; Final Report (March 1, 2010 – June 30, 2011) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291; Energy & Environmental Research Center: Grand Forks, ND, 2011.