

April 10, 2007

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Dear Mike:

Subject: Final Report for Task 2b, "Methods Testing for Measurement of Mercury Speciation for High-Reactive Dust"; Agreement No. A85811; EERC Fund 9301

Enclosed is the final report for the testing that was done at Keewatin Taconite facility to develop a method that would accurately measure speciated mercury in highly reactive dust scenarios. The test was done at the inlet to the scrubber where previous results clearly indicated mercury conversion as a result of reactive dust collecting on a filter. The tests were conducted October 25–30, 2006.

If you have any questions or comments, I can be reached by phone at (701) 777-5138, by fax at (701) 701-5181, or by e-mail at dlaudal@undeerc.org.

Sincerely,

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Enclosure

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METHODS TESTING FOR MEASUREMENT OF MERCURY SPECIATION FOR HIGH-REACTIVE DUST

Final Report

(for the period of March 1, 2006, through June 30, 2007)

Prepared for:

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EERC Fund 9301

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METHODS TESTING FOR MEASUREMENT OF MERCURY SPECIATION FOR HIGH-REACTIVE DUSTS

1.0 INTRODUCTION

Previous work at both coal-fired power plants and taconite facilities have shown that reactive dust collected on a filter prior to a mercury measurement method can result in either adsorption of mercury or conversion of mercury across the filter. The dust that is being generated as a result of the taconite processes and being removed by the scrubber consists of a material that has a very high iron concentration. Therefore, this material has the potential to catalyze a wide range of chemical reactions including those of mercury.

Based on tests conducted at Keewatin Taconite (Keetac) by the Coleraine Minerals Research Laboratory in August of 2006 using the Flue-gas Adsorbent Mercury Speciation (FAMS) Method (shown in Table 1), it is clear that conversion of mercury is occurring since the elemental mercury (Hg^0) concentration measured at the scrubber outlet is greater than that measured at the inlet. This can be a result of two mechanisms. The first is that the filter used in front of the FAMS tube is collecting dust and the high level contact between the flue gas and the dust on the filter is resulting in oxidation of the mercury across the filter. As a result, there is a measured high bias for oxidized mercury (Hg^{2+}) or low bias for Hg^0 . In this mechanism, the actual Hg^{2+} in the flue gas is, as expected, captured by the scrubber leaving primarily Hg^0 .

The second mechanism that could explain the results shown in Table 1 is that there was substantial mercury reemission across the scrubber. In this mechanism, the scrubber inlet mercury speciation results are correct; however, a portion of the Hg^{2+} collected by the scrubber is reemitted as Hg^0 . This has been shown to be a result of SO_2/SO_3 reactions. This is unlikely as the scrubbers used in the taconite industry are not typical SO_2 scrubbers but are modified venturi particulate scrubbers. In addition, the SO_2 and, therefore, the SO_3 concentrations entering the scrubber are very low (<75 ppm).

The Minnesota Department of Natural Resources (MDNR) contracted with the Energy & Environmental Research Center (EERC) to test a method that can accurately measure speciated mercury at the inlet to the scrubber.

Table 1. FAMS Mercury Speciation Results at Keetac (8/22/06)

Hg Species	Scrubber Inlet*		Scrubber Outlet*	
	Avg, $\mu g/m^3$	St. Dev., $\mu g/m^3$	Avg, $\mu g/m^3$	St. Dev., $\mu g/m^3$
Hg (part.)	0.35	0.10	0.29	0.11
Hg^{2+}	8.77	1.53	0.61	0.22
Hg^0	1.12	0.61	4.61	1.18
Hg (total)	10.24	1.02	5.51	1.50

* Three tests were conducted.

2.0 PROJECT OBJECTIVES

It was the objective of the project to develop a method that will accurately measure speciated mercury at the inlet of the scrubbers at taconite facilities. Other objectives are as follows:

- The method should be relatively simple to use.
- Evaluate which of the two mechanisms discussed in the introduction is occurring.
- Determine if sorbent traps using an inertial separation probe (ISP) can be used to accurately speciate mercury.

3.0 APPROACH

3.1 Plant Description

The tests were conducted at the Keetac facility owned and operated by United States Steel Corporation. Keetac has 1 grate kiln furnace that has a production rate of 700 long tons per hour. A new scrubber system and coal handling system were installed this year so that the furnace could burn coal. Powder River Basin (PRB) coal is used as the induration fuel. The new scrubber is a recirculating scrubber with lime treatment so the SO₂ removal efficiency is about 70%, which is a higher removal efficiency than most other taconite wet scrubbers. It should be noted that there is a multiclone located prior to the scrubber. Also, based on experience, the dust generated from the burning PRB coal is not very reactive toward mercury.

The plant produces standard (acid) pellets but at times adds approximately 1% limestone to increase pellet strength for shipping purposes. The annual production rate of Keewatin Taconite is 5.5 million long tons of pellets.

3.2 Continuous Mercury Monitor (CMM) Description

All CMMs essentially consist of three sections. These are the probe, pretreatment/conversion system, and the analyzer. The primary equipment that was used for the test includes the following:

- Two modified PS Analytical conversion systems
- Three PS Analytical Sir Galahad mercury analyzers
- One ISP
- FAMS sampling equipment

3.2.1 PS Analytical Conversion Systems

The function of the pretreatment/conversion system is to remove any potential interference gases and to convert all the mercury present in the flue gas to Hg⁰ so that the monitor can

analyze the mercury. A modified wet chemistry PS Analytical pretreatment conversion system was used for this test to ensure accurate speciated mercury measurements were being made. The system is shown in Figure 1. In this system SnCl_2 in a sodium hydroxide solution is used to convert all the mercury to Hg^0 to provide a total mercury concentration. The second half of the system uses a KCl solution to strip out the Hg^{2+} giving the concentration of Hg^0 (the difference between the two values is the concentration of Hg^{2+}).

3.2.2 PS Analytical Sir Galahad Mercury Analyzers

The PS Analytical (PSA) is based on the principle of atomic fluorescence which provides an inherently more sensitive signal than atomic absorption. The system uses a gold-impregnated silica support for preconcentrating the mercury and separating it from potential interferences that degrade sensitivity.

The Sir Galahad requires a 4-step process to obtain a flue gas mercury measurement. In the first step, 2 L of flue gas is pumped through a gold trap which is maintained at a constant temperature. Before the mercury is desorbed from the gold trap, a flushing step is initiated to remove any flue gas that may be present, because it has a damping effect on the mercury fluorescence. When this is completed, the analysis step begins. The heating coil is activated, and the gold trap is heated to approximately 500°C . This desorbs the mercury from the trap, and the mercury is carried into the fluorescence detector. The gold trap is cooled rapidly by pumping argon over it, in preparation for the next sample. The total time for the entire process is about 5 minutes.

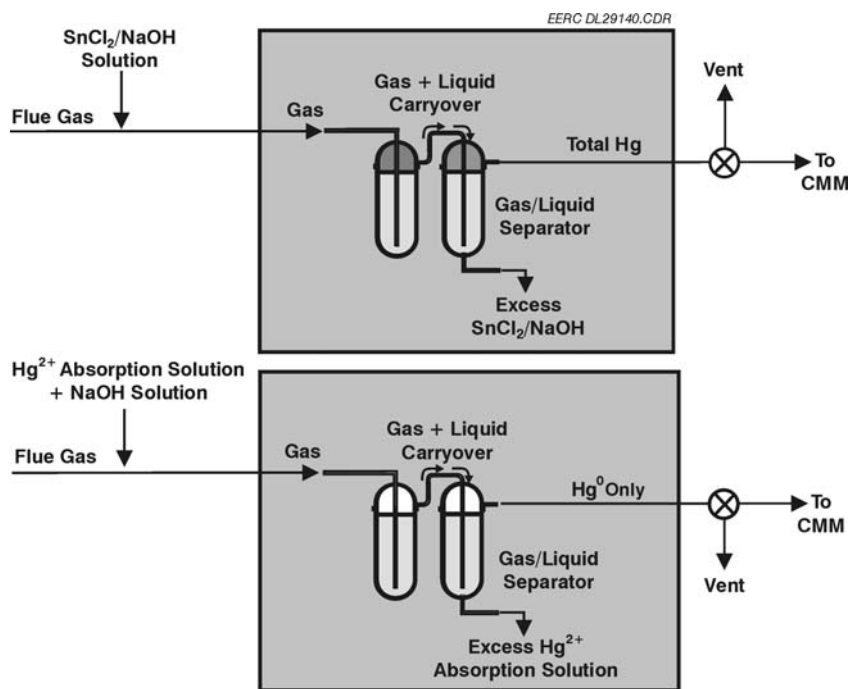


Figure 1. Schematic of the modified PS Analytical pretreatment/conversion system.

The system is calibrated using vapor-phase Hg^0 injections as the primary standard. The Hg^0 is contained in a closed vial which is held in a thermostatic bath. The temperature of the mercury is monitored, and the amount of mercury is measured using vapor pressure calculations. Typically, the calibration of the unit has proven stable over a 24-hour period.

3.2.3 Inertial Separation Probe

The function of the ISP is to remove particulate matter from the gas stream with minimum interaction between the dust and the mercury. This is done by using a sintered metal filter and a very high velocity gas flow that continuously scours the filter. A small portion of the gas that is to be analyzed by the instrument is drawn through the filter with the remainder of the gas being put back into the duct. A diagram of an ISP is shown in Figure 2.

3.3 Sampling Approach

The EERC tested four mercury measurement methods at the inlet to scrubber. The first method was to use two CMMs with a PS Analytical conversion system. To ensure that accurate speciation measurements were being made, several modifications to the system were made for this test. First, the two sides of the conversion system were separated and two analyzers used. This resulted in continuous measurement of total mercury and Hg^0 rather than switching back and forth. Second, the solutions were injected at the probe tip, and no filter was used. Although this method would not be practical as a permanent measurement technique, it does ensure there is little if any biases as a result of the highly reactive dust.

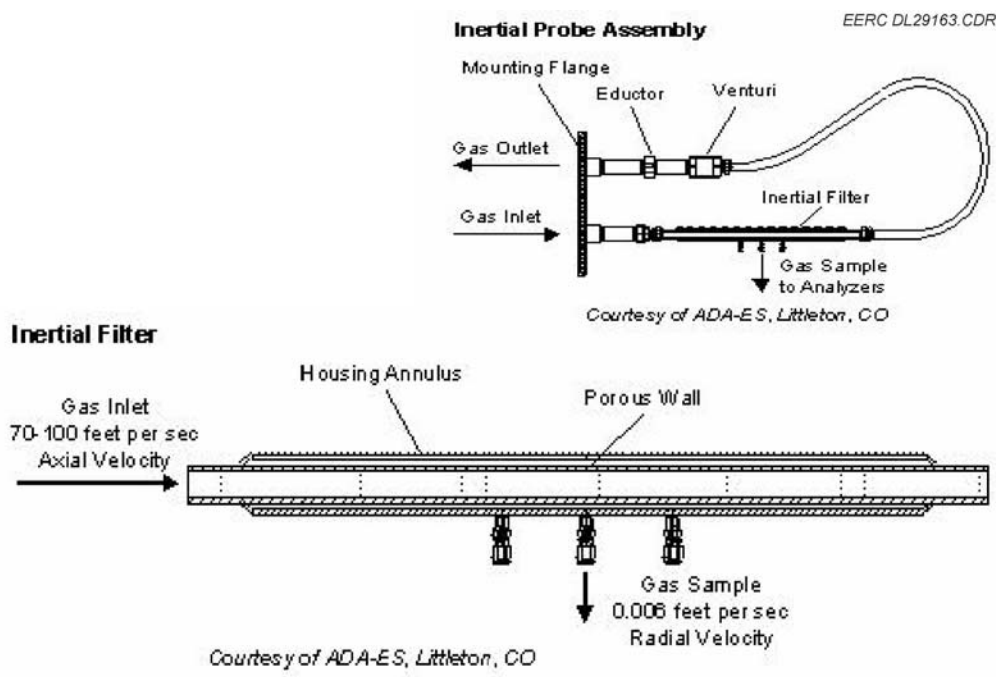


Figure 2. Diagram of an ISP.

The second method was to use an ISP with a CMM. This is the method typically used for coal-fired systems. Although the contact between the dust and the mercury across the filter is minimized, the method is not perfect, and there was concern that the highly reactive nature of the dust of the taconite facility would still impact the mercury speciation. By comparing this result to those obtained using the modified pretreatment/conversion system, the effectiveness of the ISP could be determined.

The third method was to again use the ISP, but rather than using the CMM, tests were conducted using the FAMS sorbent traps. These traps are being evaluated by MDNR for measuring mercury speciation at the various taconite facilities. Although in general the total mercury results have been reasonable, there have been questions as to the data validity. This has been especially true for mercury speciation data. The last method was to do the standard FAMS sampling.

4.0 RESULTS AND DISCUSSION

Table 2 and Figures 3–7 show the results comparing data collected from the two CMMS using the modified PSA conversion systems without a filter and the data collected using a CMM with an ISP. The results show that there is good agreement between the two methods for total mercury, but there was conversion of Hg^0 to Hg^{2+} across the sintered metal filter of the ISP. There also appeared to be more variability in the data when the ISP was used.

As stated previously, tests were conducted using the FAMS method in the standard mode and using an ISP. The results are shown in Table 3. The FAMS results were somewhat lower for total mercury compared to the CMMs. However, the percentage of Hg^0 was about the same comparing the standard FAMS results to those obtained using a CMM with an ISP. In both cases, there appeared to be a high bias for Hg^{2+} compared to the data collected for the CMM that was operated without any filter. The FAMS method did not work at all when used with an ISP. This may have been a result of the flow rates not matching properly or possible contamination in the ISP. The results are shown in Table 4.

Table 2. CMM Data

Date	CMMs without filter					CMM with ISP				
	Total Hg, $\mu\text{g}/\text{m}^3$	St. Dev., $\mu\text{g}/\text{m}^3$	Hg^0 , $\mu\text{g}/\text{m}^3$	St. Dev., $\mu\text{g}/\text{m}^3$	Hg^0 , %	Total Hg, $\mu\text{g}/\text{m}^3$	St. Dev., $\mu\text{g}/\text{m}^3$	Hg^0 , $\mu\text{g}/\text{m}^3$	St. Dev., $\mu\text{g}/\text{m}^3$	Hg^0 , %
10/25/2006	9.65	0.85	6.91	0.38	71.6	9.83	0.15	–	–	–
10/26/2006	8.54	1.18	5.97	0.6	69.9	7.04	0.88	6.05	2.69	85.9
10/27/2006	7.29	0.53	6.22	0.16	85.3	9.55	1.61	5.53	1.45	57.9
10/29/2006	6.36	0.44	5.61	0.21	88.2	6.48	0.85	4.31	0.28	66.5
10/30/2006	6.26	0.83	5.45	0.43	82.1	6.84	1.38	4.35	0.40	67.1

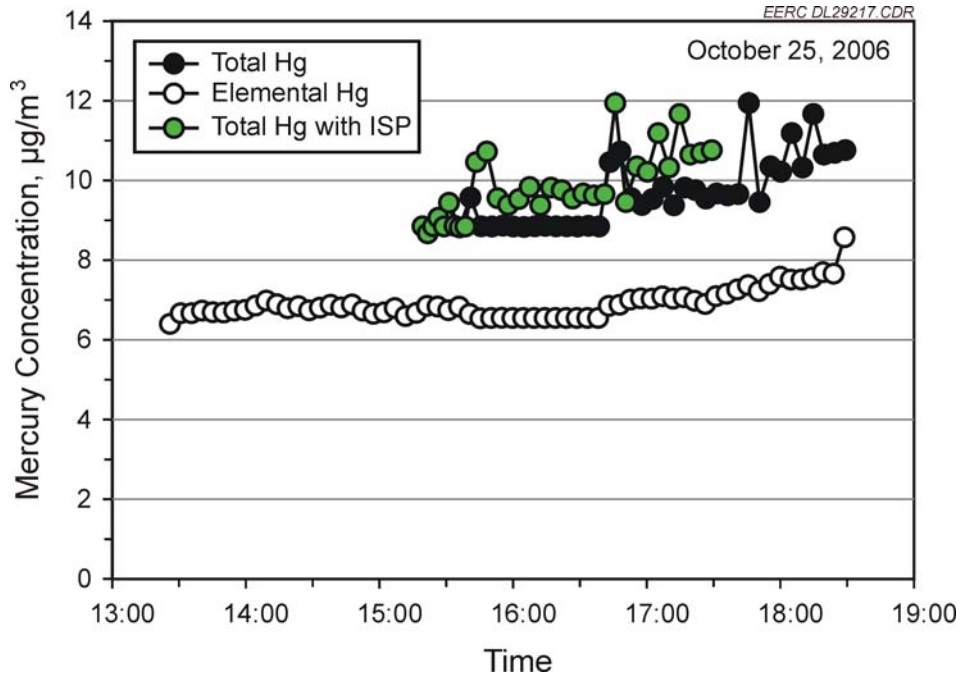


Figure 3. CMM results – October 25, 2006.

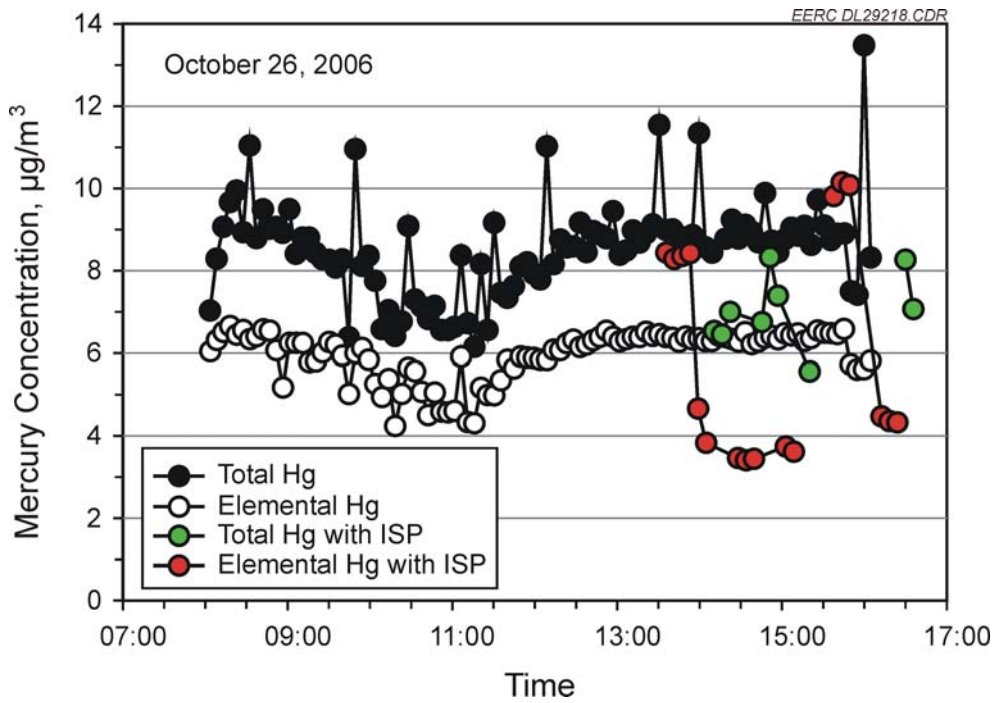


Figure 4. CMM results – October 26, 2006.

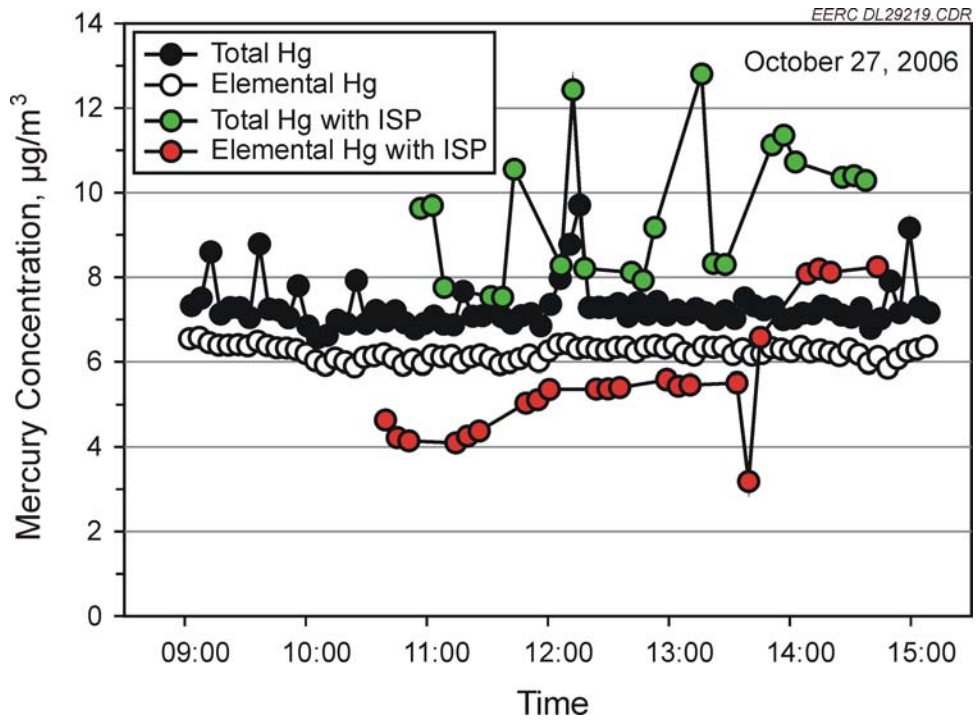


Figure 5. CMM results – October 27, 2006.

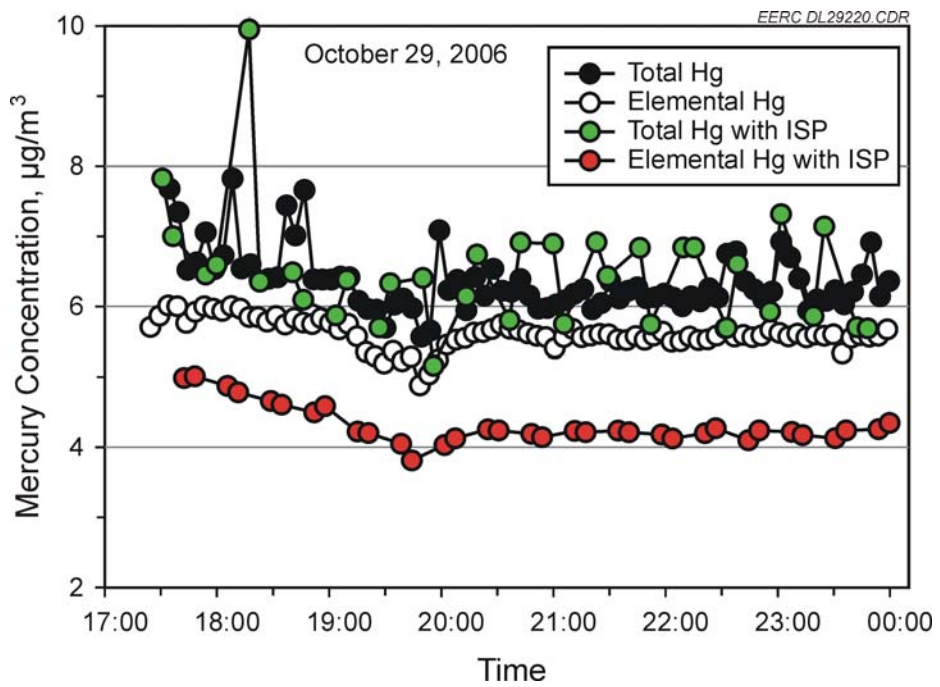


Figure 6. CMM results – October 29, 2006.

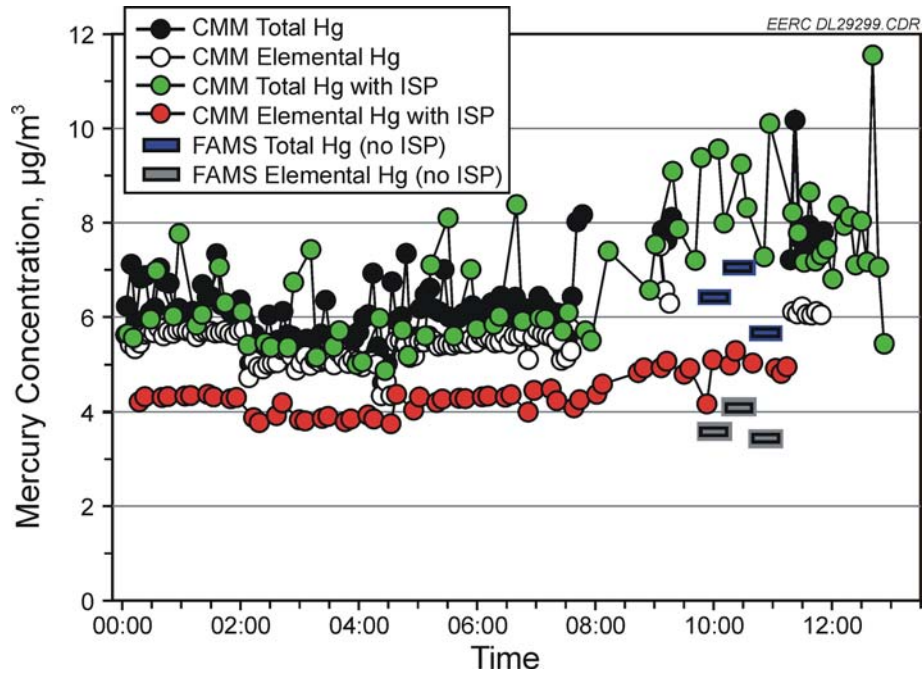


Figure 7. CMM results – October 30, 2006.

Table 3. Comparison of the Standard FAMS Data to the CMM Data

Time Start	FAMS Without ISP			CMMs With ISP			CMMs Without ISP*		
	Total Hg, $\mu\text{g}/\text{m}^3$	Hg^0 , $\mu\text{g}/\text{m}^3$	Hg^0 , %	Total Hg, $\mu\text{g}/\text{m}^3$	Hg^0 , $\mu\text{g}/\text{m}^3$	Hg^0 , %	Total Hg, $\mu\text{g}/\text{m}^3$	Hg^0 , $\mu\text{g}/\text{m}^3$	Hg^0 , %
9:48	6.42	3.59	55.9	8.98	4.75	53.4	8.11	6.29	77.6
10:13	7.04	4.11	58.4	8.52	5.10	60.7			
10:40	5.66	3.43	60.7	8.56	4.99	54.7	7.21	6.11	84.8
Average	6.37	3.71	58.3	8.69	4.94	56.2	7.66	6.20	81.2
St. Dev.	0.69	0.36		0.92	0.33				

* Instrument was not operating in this mode when FAMS samples were taken. Results shown are those just prior to the first FAMS sample and just after the last one.

Table 4. FAMS Results Using an ISP

Time Start	Total Hg, $\mu\text{g}/\text{m}^3$	Hg^0 , $\mu\text{g}/\text{m}^3$	Hg^0 , %
09:48	3.96	2.81	71.0
10:13	21.37	5.53	25.9
10:40	21.30	8.17	38.4
Average	15.54	5.50	45.1
St. Dev.	10.03	2.68	

5.0 CONCLUSIONS

Based on the results of the testing conducted under Task 2b, the following conclusions can be made:

- At Keetac, the use of a filtering device (ISP or filter) prior to the measurement device (CMM or FAMS) resulted in a high bias for Hg^{2+} at the inlet to the particulate scrubber. This was because of oxidation of some of the Hg^0 to Hg^{2+} across the filtering device.
- Compared to the previous testing (August 22, 2006) at Keetac, the results at the scrubber inlet clearly show oxidation of the mercury across the filter. When the CMM without a filter is used to measure the scrubber inlet mercury speciation concentrations, the scrubber outlet data in Table 1 makes more sense.
- Unbiased mercury results could be obtained using a PSA wet chemistry pretreatment/conversion system by completely separating the two sides of the system and injecting the oxidation and stripping solutions at the probe and not using a filter. Although for this test two monitors were used, the same type of data could be obtained by using one monitor and switching between the two sides of the pretreatment/conversion system.
- Compared to CMMs operated without a filter, the ISP resulted in a high bias for Hg^{2+} .
- Compared to the CMMs, FAMS total mercury results were somewhat low.
- Using the FAMS with an ISP did not give good results; however, tests were limited, and it is possible that good total mercury results could be obtained.