RELATIVE ACCURACY TESTING OF AN X-RAY BASED CONTINUOUS MERCURY MONITOR

Contract No. DACA42-03-P-0239
(TASK 2)

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R5-2014-0104710000621

FINAL REPORT

Prepared for

U. S. Army Corps of Engineers
Engineer Research and Development Center
Construction Engineering Research Laboratory

Submitted By

Cooper Environmental Services
10170 SW Nimbus Ave Suite H5
Portland, Oregon 97223

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B.E. Johnsen, J.A. Cooper, M.Nakanishi, S. Fry, D. Barth, P. Ginochio
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11120 SW 124th Place
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Submitted to

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P. O. Box 9005, CN-E, Champaign, IL 61826-9005

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EXECUTIVE SUMMARY

Mercury has been identified by the EPA as their air toxic of greatest concern (EPA, 2000). Accordingly, the EPA and Bush administration have proposed legislation such as the Clear Skies Act and Utilities MACT which have focused on mercury reduction and monitoring. To date, however, limited success with mercury Continuous Emissions Monitors (CEMs) has been achieved. Cooper Environmental Services (CES) was contracted by the U.S. Army Corp of Engineers to test their *Xact* continuous mercury monitor during an EPA sponsored test at a coal-fired power plant (CFPP). The Xact extracts a representative emissions sample which is then drawn through a reactive filter. The filter is advanced to an x-ray fluorescence analyzer where total mercury mass is determined. Results are reported every 20 to 30 minutes with detection limits of better than 0.1 micrograms per dry standard cubic meter.

For the tests, CES first evaluated the filter trapping efficiency and precision using a Mercury Speciation Cassette (MSC). The MSC consists of a stack of filters which measures oxidized and elemental mercury. The MSC tests were designed to compare the capabilities of the filter based approach relative to the EPA's standard Ontario-Hydro (OH) method for measuring mercury.

In general, the *Xact* and MSC performed very well relative to the OH, showing accuracy and precision that were on the same order as the standard method. Test results showed that:

1) The *Xact* total mercury relative accuracy was 25%, which was essentially the same as the 22% RA between duplicate OH test runs.
2) The MSC total mercury relative accuracy was 12% relative to the OH method, substantially less than the 20% required for method equivalency.
3) The MSC fractional mercury speciation was in excellent agreement with OH results showing an average of only 4% difference in the percent elemental mercury for all 12 OH runs.
4) The MSC relative precision was 30% better than the precision listed in the OH method for measurements less than 3 μg/dscm.

This first Xact unit did develop cold spots which caused occasional water condensation and inconsistent results. This problem is being mitigated with more uniform heating.

One of the largest problems for all candidate methods was the limited accuracy and precision of the EPA standard method at low mercury concentrations. Concentrations for all but one OH run were below 3 μg/dscm. The OH has a listed precision of 34% under these low concentrations (ASTM, 1999) limiting its ability to evaluate the relative accuracy of the mercury CEMs. In addition, mercury was almost exclusively in the elemental form for all but one run. Since many CEM approaches are severely impacted by oxidized mercury, the tests have limited applicability for CFPP which have significant concentrations of oxidized mercury. Although additional testing is needed at varying mercury concentrations and speciation levels, the EPA tests demonstrated the feasibility of the *Xact* filter based approach to measure mercury in coal-fired power plant emissions.

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During the MRI tests, CES conducted a series of grab-sample test runs using its Mercury Speciation Cassette (MSC). The purpose of the MSC testing during the first phase was to evaluate CES' proprietary filter for trapping and speciating capabilities as well as its use as an alternative to the EPA standard method (OH). During the second phase, CES conducted precision testing of the MSC and tested its *Xact* mercury monitor relative to the OH reference method. The *Xact* is a true continuous emissions monitor (CEM) for mercury and reports total mercury concentrations every 20 to 30 minutes.

This report summarizes the performances of CES' MSC and *Xact* relative to the EPA standard Ontario-Hydro method.

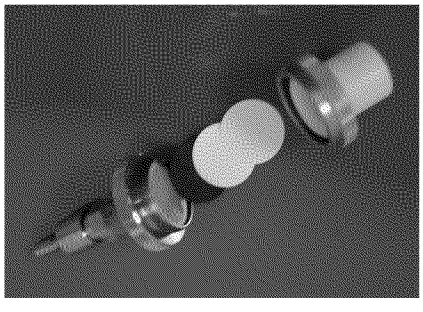
MERCURY SPECIATION CASSETTE TESTING

The MSC consists of a filter stack within a Teflon coated stainless steel filter holder (Figure 1). The first filter traps particulate and gas phase reactive mercury. This filter is followed by a filter for trapping elemental mercury and a back-up carbon impregnated filter to ensure that breakthrough was not occurring. The cassettes are small enough to fit in the palm of an operator's hand and can be inserted directly into the stack through a port that is 3 inches or larger in diameter. For this test, an in-stack approach was used since the stack temperature was about 180° F.

Table 1. MRI Test Arrangement

Phase	Date	CES Test	MRI Test
I	May-03	MSC-RA	12 OH Runs
II	Jul-03	*Xact*	12 OH Runs
II	Jul-03	MSC-Prec.	--

Figure 1. Mercury Speciation Cassette



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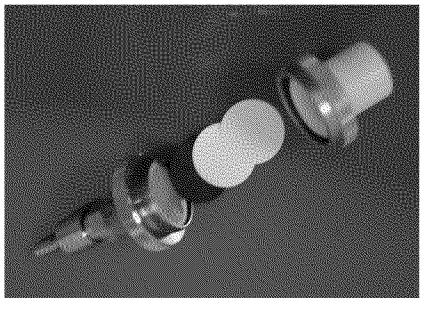
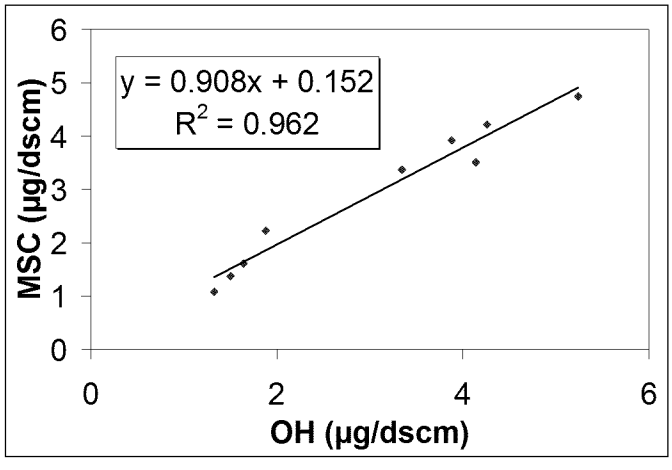


The MSC approach offers a number of advantages over traditional standard methods including:

- Detection limits of better than 0.1 micrograms/dscm for 50 minutes of sampling
- Sampling, analysis and sample recovery are completed without chemicals
- Sampling can be conducted by one operator
- Cassettes can be changed within five minutes
- Filter samples can be sent via FedEx for next day analysis
- Low per-run analysis cost
- Routine analysis turn-around-time is typically less than one week
- Potential exists for in-field XRF analysis for same day results
- XRF analysis is non-destructive, so filters can be archived and reanalyzed at a later date

The results of the MSC testing during phase 1 are illustrated in the regression plot shown in Figure 2 and listed in Table 2. A total of 12 OH runs were conducted with each run lasting two hours. For each OH run, two 50 minute MSC samples were collected by CES. In general, the MSC and OH were in very good agreement with a relative accuracy of about 12% (nine valid runs), well within the 20% criteria for alternative methods specified by EPA's proposed Performance Specification 12. Three of the 12 OH test runs were omitted from all candidate method comparisons. Runs 2 and 6 were omitted because of poor OH replication (>40% difference) and run 8 was omitted due to a plant upset and highly variable mercury concentrations. For 11 of the 12 runs, the total mercury concentration ranged from about one to five µg/m³ with 90% in the form of elemental mercury. During run number 8, the stack gas temperatures increased significantly, total mercury increased to over 20 µg/m³ and averaged about 14 µg/m³ during the two hour OH test run. During this upset period, the elemental mercury concentration dropped from about 4 µg/m³ to about 2 µg/m³, but the oxidized mercury concentration increased about 300 fold; i.e., from about 0.04 µg/m³ to about 12 µg/m³, and represented about 85% of the total mercury. The high correlation ($r^2 = 0.962$) and low intercept of the MSC with the OH for the nine valid runs indicates good agreement between the two methods.

Figure 2. Correlation of MSC with OH During MRI Phase 1 Testing



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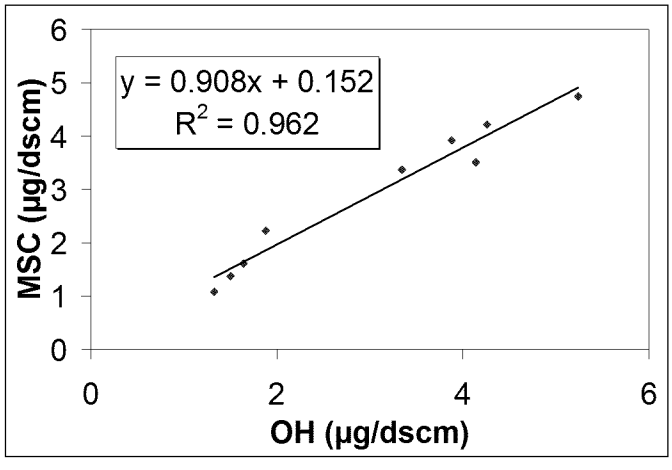

Table 2. Reported MSC and Ontario-Hydro Results for Phase 1 Testing

OH RUN	MSC RUN	DATE	TIME		MSC (µg/dscm)				OH				Percent Hg°		
			START	STOP	OXID[a]	ELEM.	TOT.	AVG.	OH-1	OH-2	AVG.	Valid[b]	MSC	OH	% Diff
1	1A	1-May	13:20	14:15	<0.03	0.74	0.74	1.08	1.36	1.29	1.33	Yes	>95.9	94.2	2.6
	1B	1-May	14:26	15:19	<0.04	1.42	1.42						>97.2		
2	2A	2-May	10:20	11:11	0.12	2.77	2.89	2.75	5.34	3.05	4.20	**No**	96.0	99.5	-3.1
	2B	2-May	11:20	12:10	<0.08	2.59	2.61						>96.9		
3	3A	2-May	14:41	15:31	0.10	1.63	1.74	1.61	1.64	--	1.64	Yes	94.0	99.0	-8.4
	3B	2-May	15:40	16:30	0.19	1.30	1.49						87.4		
4	4A	5-May	10:00	10:50	<0.04	1.38	1.38	1.38	1.50	1.50	1.50	Yes	>97.1	98.6	-1.6
	4B	5-May	--	--	--	--	--						NM		
5	5A	5-May	14:10	14:50	<0.05	1.75	1.75	2.23	1.88	--	1.88	Yes	>97.1	98.9	-1.0
	5B	5-May	15:00	15:50	<0.04	2.70	2.70						>98.5		
6	6A	6-May	9:28	10:18	<0.04	4.58	4.58	4.39	6.91	4.22	5.57	**No**	>99.1	99.4	-0.3
	6B	6-May	10:27	11:17	<0.04	4.19	4.19						>99.0		
7	7A	6-May	15:27	16:17	<0.04	3.35	3.35	3.51	4.14	--	4.14	Yes	>98.8	99.2	-0.4
	7B	6-May	16:26	17:16	<0.04	3.67	3.67						>98.9		
8	8A	7-May	15:21	16:06	19.46	3.62	23.08	19.00	14.27	--	14.27	Yes	15.7	15.2	20.3
	8B	7-May	16:13	17:03	11.80	3.12	14.91						20.9		
9	9A	8-May	9:20	10:10	0.54	4.39	4.93	4.75	5.24	--	5.24	Yes	89.1	94.1	-3.5
	9B	8-May	10:17	11:07	0.34	4.22	4.56						92.5		
10	10A	8-May	12:21	13:06	0.29	3.84	4.13	4.22	4.26	--	4.26	Yes	93.0	96.5	-3.5
	10B	8-May	13:16	14:06	0.29	4.01	4.30						93.2		
11	11A	9-May	9:22	10:12	0.12	3.41	3.53	3.37	3.33	3.36	3.35	Yes	96.5	99.1	-3.6
	11B	9-May	10:21	11:11	0.18	3.04	3.21						94.5		
12	12A	9-May	13:50	14:40	<0.08	3.57	3.57	3.92	3.88	--	3.88	Yes	>97.8	99.2	-2.4
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a) Includes particulate and vapor phase oxidized Hg
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The MSC relative mercury speciation results (% Hg°) were also in excellent agreement with the OH results as shown in Table 2. The 12-run average unsigned mean difference in the % Hg° from the two methods was 4.2%. The largest oxidized mercury concentration was observed during Run 8 in which the dominating oxidized mercury concentration was changing rapidly. In addition, the OH and MSC were both stopped in the middle of the run due to the plant upset and the MSC runs covered only 100 of the 120 minutes of the OH run during which the mercury concentration was changing rapidly. Thus, the MSC clearly demonstrated its responsiveness to changing relative mercury speciation and demonstrated a high degree of accuracy in the relative species apportionment.

In addition to the stack tests, a series of runs were made comparing the MSC results to a direct injection of elemental mercury from a Spectra Gases mercury canister (Table 3, Figure 3). The first two tests were conducted using a known concentration of 8 µg/dscm with MSC reported concentrations of 8.1 and 8.2 µg/dscm respectively. The MSC results are well within the Spectra Gases listed uncertainty of 20%. Following the initial tests, another series of three blind (unknown) tests were conducted by MRI with no CES personnel present. These blind tests used equivalent certified concentrations of 8, 19 and 19 µg/dscm respectively with the MSC results closely correlated at 8.4, 18.3, and 17.9 µg/dscm. The mean MSC recovery for the three blind tests was 98.4% with a standard deviation of 5.4% and a range from 94 to 105%. Again, the small percentage difference was well within the listed 20% uncertainty of the Spectra canisters.

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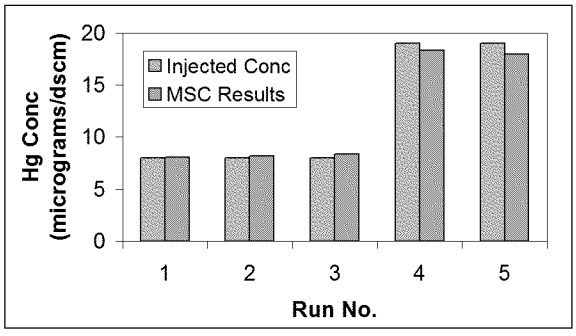
Table 3. Comparison of MSC Reported Mercury Concentrations with Certified Spike Concentrations.

Injection Type		Date	MSC	Std.	% Recovery
			µg/dscm	µg/dscm	
STD.	Known	1-May	8.1	8.0	101.0
STD.	Known	1-May	8.2	8.0	102.5
STD.	Blind	8-May	8.4	8.0	104.6
STD.	Blind	8-May	18.3	19.0	96.4
STD.	Blind	8-May	17.9	19.0	94.3
Average					99.8
Standard Deviation					4.3

Figure 3. MSC vs. Certified Mercury Concentrations for Spike Injection



A second series of 11 test runs were conducted using a pair of MSCs during phase 2 of the MRI tests (Table 4). Since the May tests had indicated good agreement with the standard method for the MSC, the July tests were limited to demonstration of the MSC precision relative to the typical OH test run. According to the OH standard operating procedure, the OH has an 11% precision when concentrations are above 3 µg/dscm and a 34% precision when concentrations are less than 3 µg/dscm. Since only two MSC test runs during phase 2 were above 3 µg/dscm and all concentrations were below 3.3 µg/dscm, MSC precision could not be determined for high mercury concentrations. The MSC precision for the 8 runs below 3 µg/dscm ranged from 0 to 37% with an average of 24%, significantly better than the OH listed precision. It is believed that the MSC precision can be improved to about 5% with refinement.

Table 4. MSC Precision Tests During Phase 2 Testing

Table 3. Comparison of MSC Reported Mercury Concentrations with Certified Spike Concentrations.

Injection Type		Date	MSC	Std.	% Recovery
			µg/dscm	µg/dscm	
STD.	Known	1-May	8.1	8.0	101.0
STD.	Known	1-May	8.2	8.0	102.5
STD.	Blind	8-May	8.4	8.0	104.6
STD.	Blind	8-May	18.3	19.0	96.4
STD.	Blind	8-May	17.9	19.0	94.3
Average					99.8
Standard Deviation					4.3

Figure 3. MSC vs. Certified Mercury Concentrations for Spike Injection

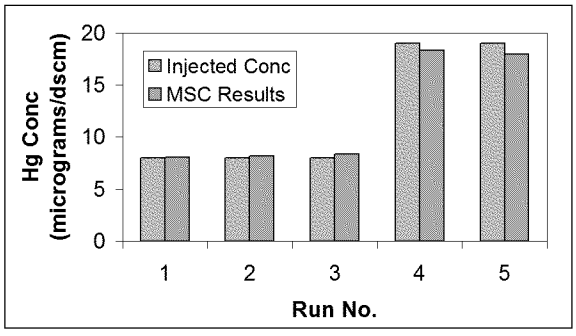


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Table 4. MSC Precision Tests During Phase 2 Testing

MSC RUN	Total (µg/m³)	% Diff.
1A	2.22	0.4
1B	2.21	
2A	2.16	--
2B*	--	
3A	2.87	16.7
3B	2.43	
4A	1.57	35.5
4B	2.25	
5A	2.10	37.3
5B	3.06	
6A	3.29	8.8
6B	3.01	
7A	2.79	14.9
7B	3.24	
8A	2.33	17.5
8B	2.77	
9A	2.02	23.0
9B	2.55	
10A	1.95	25.0
10B	2.51	
11A	2.05	34.6
11B	2.90	
Avg. (all)		**21.4**
Avg. (< 3 µg/dscm)		**23.8**

* 2B Omitted due to water contamination

MSC RUN	Total (µg/m³)	% Diff.
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5B	3.06	
6A	3.29	8.8
6B	3.01	
7A	2.79	14.9
7B	3.24	
8A	2.33	17.5
8B	2.77	
9A	2.02	23.0
9B	2.55	
10A	1.95	25.0
10B	2.51	
11A	2.05	34.6
11B	2.90	
Avg. (all)		**21.4**
Avg. (< 3 µg/dscm)		**23.8**

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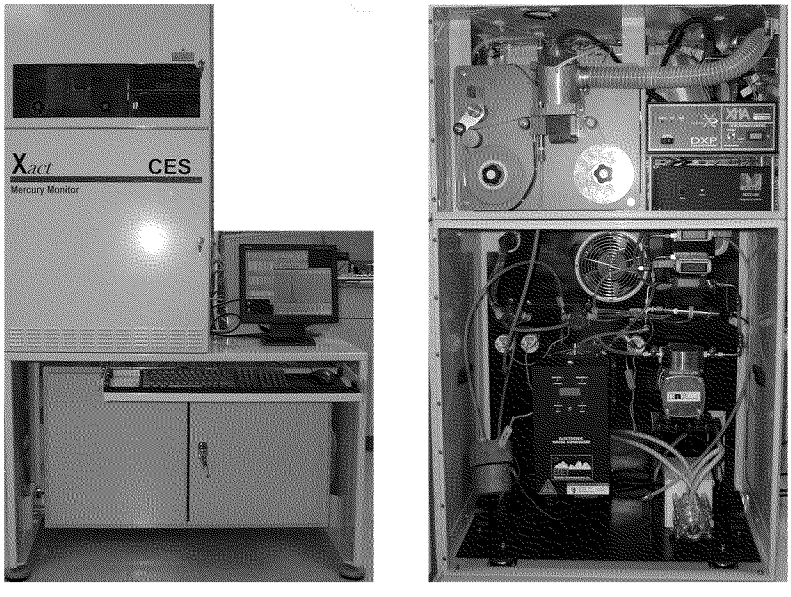
Overall, the MSC had better precision than the standard OH method under low mercury conditions, was able to effectively speciate the mercury concentrations, measured the standard gases to within 6%, and had a relative accuracy of 12% compared to the OH method. However, since the MRI test site had limited opportunities to measure speciated mercury and rarely had mercury concentrations above 3 µg/dscm, further testing under a variety of stack conditions is recommended.

Xact TESTING

The *Xact* mercury monitor is designed to continuously measure total mercury concentrations and report data every 20 to 30 minutes with a detection limit of better than 0.1 µg/dscm (Figure 3). The monitor extracts a representative gas sample and concentrates the mercury on a reactive filter. The filter deposit is then advanced to an x-ray fluorescence (XRF) analyzer which determines mass concentrations. Minimal stack gas pretreatment is required, which greatly simplifies the approach. Other advantages of the *Xact* include:

- Collection of total Hg including particulate, oxidized and elemental fractions
- Introduction of a fresh filter with each sample – no memory or blank bias
- Since XRF is non-destructive, filters can be archived
- Solid-phase Hg calibration minimizing use of expensive calibration gases
- Since XRF is non-destructive, results can be independently verified by another method
- Multi-element sensor allows for option of simultaneous monitoring for chromium, manganese, iron, cobalt, nickel copper, zinc, arsenic, selenium, bromine, and lead as well as mercury.
- Smoothly varying theoretically predictable sensitivities as a function of atomic number provides additional quality assurance.

Figure 3. *Xact* Mercury Monitor



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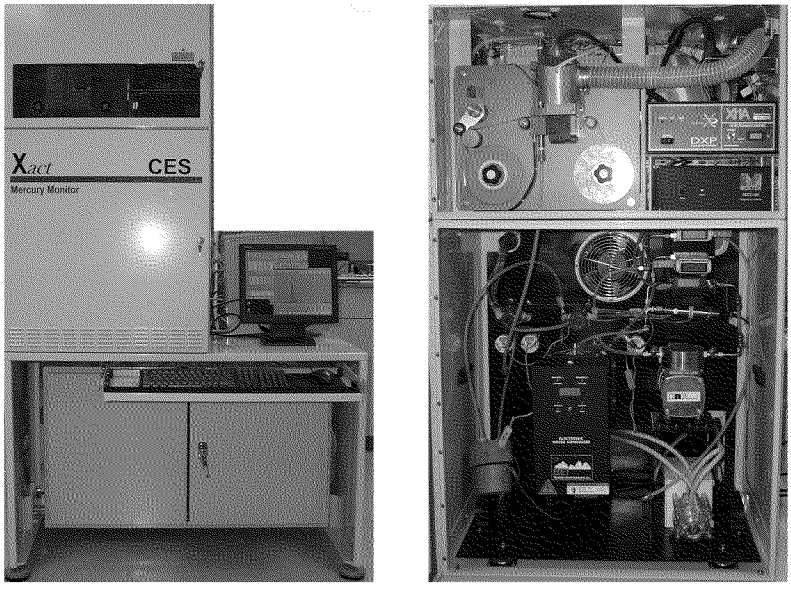

Xact Performance

During phase 2 testing, typical measured concentrations for both the *Xact* and the OH ranged from one to three micrograms per dry standard cubic meter (µg/dscm). Overall, the instrument's relative accuracy (RA) compared to the OH was 25%, slightly higher than the 20% relative accuracy criteria set forth in the proposed performance specification (Table 5) and similar to the other CEMs tested by MRI which had RA ranging from 15 to 40%.

MRI used duplicate OH trains for all phase 2 testing. On average, the OH duplicate trains differed from each other by about 25% with three runs showing a difference of greater than 50%. According to the standard method, the OH precision is typically about 34% when the mercury concentrations are below 3 µg/dscm range so the MRI precision results were typical or slightly better than historical OH precision levels. The magnitude of this imprecision, however, is on the same order as the desired relative accuracy. Thus, a large uncertainty exists in determining the relative accuracy results. For example, the RA of the OH duplicate trains compared to each other was 22%. **Any approach being compared to the OH could not expect to have a RA better than that of the OH trains relative to each other.**

The *Xact* reported concentrations for 10 out of the 12 OH runs conducted during phase 2 tests. During run 1, the *Xact* experienced heater problems and developed a leak which was not repaired until the run had been completed. During run 7, the instrument was behaving appropriately prior to the run and following the run, but was turned off during the run. It is not known why the instrument was turned off; however, it was located centrally in a very crowded room and could have been accidentally turned off by a bystander.

Table 5. Reported *Xact* and Ontario-Hydro Results for Phase 2 Testing

Run	Date	Time	Xact (µg/dscm)	OH-1 (µg/dscm)	OH-2 (µg/dscm)	OH-Avg. (µg/dscm)
1	7/24/2003	1010-1210	--	1.44	1.32	1.38
2	7/24/2003	1420-1620	1.61	3.39	3.38	3.39
3	7/25/2003	0950-1150	2.07	2.27	2.38	2.33
4	7/25/2003	1425-1625	1.61	1.83	2.19	2.01
5	7/28/2003	1120-1320	1.27	1.53	1.26	1.40
6	7/28/2003	1525-1725	1.18	1.79	0.99	1.39
7	7/29/2003	0920-1120	--	1.46	0.82	1.14
8	7/29/2003	1320-1520	1.69	1.56	1.24	1.40
9	7/30/2003	0915-1115	1.55	1.24	2.25	1.75
10	7/30/2003	1340-1540	1.51	1.17	1.63	1.40
11	7/31/2003	0915-1115	2.30	1.51	1.32	1.42
12	7/31/2003	1325-1525	1.72	1.25	1.20	1.23
Avg.			**1.65**	**1.70**	**1.67**	**1.68**

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In addition to the leak in run 1, the instrument experienced problems with heat tracing throughout the tests. The inlet tube immediately prior to the tape was heat traced but not thoroughly insulated due to its close proximity to the x-ray tube. The water content of the stack was higher than expected which led to periodic condensation in the tube with a resultant drop forming on the filter. Since the filter tape is hydrophilic, the droplet would result in temporary severe pressure drops and flow control issues. Although the droplets impact on pressure was severe, it is not certain that the condensation impacted the tape collection efficiency. However, the condensation on the walls could be a potential sink for oxidized mercury. For this reason, any future *Xact* design needs to include a more thorough heat tracing of the inlet tube.

Upon initial installation, a series of seven blind mercury standard gas tests were run with the *Xact*. The *Xact* reported concentrations were within one percent of the certified standard concentration. Following OH testing, the *Xact* was again injected with the calibration gas, but the *Xact* response was significantly lower than expected. It is believed that the *Xact* may have experienced some problems with the calibration gas due to a heat tracing problem. On occasion, the *Xact* also reported blank concentrations of up to one µg/dscm. The high blank values could not be duplicated when the instrument was returned to CES and are currently being investigated.

Overall, the prototype *Xact* was able to effectively measure the mercury for 10 of the 12 runs with a relative accuracy of 25%, approaching that of the replicate OH sample trains relative to each other (22%). The delivered unit was able to accurately measure the calibration gas and overall reported results correlated within uncertainty limits of the OH results. It is recommended, however, that the *Xact* be refined to improve transport and temperature control. It is also recommended that further reference method testing be conducted at a source with higher mercury concentrations to better evaluate the *Xact* capabilities and potential accuracy.

CONCLUSION AND RECOMMENDATIONS

The MSC was able to effectively measure mercury concentrations with a relative accuracy of 12% compared to EPA's standard reference method. The MSC precision was better than the OH for the low concentrations present in the stack and the MSC was able to consistently determine concentrations to within 10% of the gas canister standards. Although only one OH run was present with significant oxidized mercury concentrations, the MSC and OH percentages of oxidized mercury were in good agreement for that run. Overall, the MSC appears to be able to give comparable results to the OH at a fraction of the cost and effort.

The *Xact* mercury CEM had a relative accuracy of 25% in comparison to the OH method. Since the OH method's precision for the test was also on the order of 25%, the *Xact* RA uncertainty is limited by the uncertainty in the OH method. The *Xact* was able to accurately measure the Spectra gas standard upon initial installation and was able to track changes in total mercury concentrations relative to the OH method throughout the test.

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1) The MSC total mercury relative accuracy was 12%, substantially less than the 20% required for equivalency.
2) The MSC fractional mercury speciation was in excellent agreement with OH results showing an average of only 4% difference for all 12 OH runs.
3) The MSC relative precision was 30% better than the precision listed in the OH method for measurements less than 3 µg/dscm.
4) The Xact total mercury relative accuracy was 25%, which was essentially the same as the 22% RA between duplicate OH test runs.

This first *Xact* unit did develop cold spots which caused occasional water condensation and inconsistent results. This problem is being mitigated with more uniform heating.

One of the largest problems for all candidate methods was the limited accuracy and precision of the EPA standard method at low mercury concentrations. Concentrations for all but one OH run were below 3 µg/dscm. The OH has a listed precision of 34% under these low concentrations (ASTM, 1999) limiting its ability to evaluate the relative accuracy of the mercury CEMs. In addition, mercury was almost exclusively in the elemental form for all but one run. Since many CEM approaches are severely impacted by oxidized mercury, the tests have limited applicability for CFPP which have significant concentrations of oxidized mercury.

Although the MSC and *Xact* performed well during the MRI tests, it is recommended that they be retested at a site that will provide high enough concentrations for precise OH measurements. It is further recommended that:

- The MSC be reengineered for use in higher temperature stacks.
- The MSC undergo testing at a stack with significant quantities of both elemental and oxidized mercury.
- The MSC undergo testing at a stack with mercury concentrations greater than 3 µg/dscm.
- The *Xact* inlet should be reengineered for improved heat tracing and transport.
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