WSRC-MS-97-0214
CONF-970677--13

Joint EPA/DOE Demonstration Program for Total Mercury Continuous Emissions Monitors

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A document prepared for AIR AND WASTE MANAGEMENT ASSOCIATION at Toronto, , Canada from 6/8/97 - 6/13/97.

DOE Contract No. **DE-AC09-96SR18500**

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For Presentation at the Air & Waste Management Association's 90th Annual Meeting & Exhibition, June 8-13, 1997, Toronto, Ontario, Canada

97-WP72B.09

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Introduction

Continuous emissions monitoring of mercury from hazardous waste thermal treatment processes is desired for verification of emission compliance, process control, and public safety perception. Continuous real-time monitoring of mercury would permit actual measurement of mercury emissions and permit measurement of real-time (actual) mercury emissions and allow accurate (realistic) human risk assessment from hazardous thermal treatment facility operation. The U.S. Environmental Protection Agency (EPA) has proposed regulations that require the use of total mercury continuous emissions monitors (CEMs) on incinerators, boilers, and industrial furnaces that burn hazardous waste. These proposed regulations also include draft performance specifications for mercury CEMs. This paper describes an ongoing joint EPA/DOE program to identify and demonstrate commercially available mercury CEMs that can meet the proposed EPA performance specification and includes initial instrument test results obtained. The complete demonstration consists of a six month performance test of several commercially available total mercury CEMs at a commercial cement kiln that co-fires hazardous waste. During the performance test, several indicators of CEM performance will be evaluated (as required in the proposed performance specification), including; zero and calibration drift, relative

accuracy through comparison to EPA manual Reference Methods, calibration error through testing with calibration standards, and specific interference tests. The results of this extensive test program will be used to either confirm availability of mercury CEMs that meet the requirements in the proposed EPA performance specification, provide the necessary data for revision of the proposed mercury CEM performance specification, or reveal the need for further instrument development prior to deployment.

Technology Requirements

The U.S. Environmental Protection Agency (EPA) regulates the burning of hazardous waste in both incinerators and boilers and industrial furnaces. The agency has recently proposed revised regulations for incineration of these wastes (See 61 FR 17358, April 19, 1996). Included in this proposed regulation are requirements for the use of total mercury continuous emissions monitors (CEMs) and the draft performance requirements for these instruments. The draft specification outlines eight requirements for a mercury CEM. These requirements are summarized below.

1. Relative Accuracy (RA)

The RA is the absolute mean difference between the pollutant concentration determined by the CEM and the value determined by the manual Reference Method (RM), plus an error coefficient, divided by the mean of the RM tests or the applicable emission limit. The RA of the CEM must be no greater than 20% of the mean value of the Reference Method test data, or 10% of the applicable standard, whichever is greater.

2. Calibration Error (CE)

The CE is assessed using standards for Hg (0) and $HgCl_2$. The mean difference between the CEM and the reference standard should be no greater than 15% of the reference standard concentration.

3. Calibration Drift (CD)

The CEM calibration may not drift or deviate from the reference value of the calibration standard by more than 10% of the applicable emission limit.

4. Zero Drift (ZD)

The CEM zero point shall not drift by more than 5% of the applicable emission limit.

5. Sampling and Response Time

The CEM shall sample the stack effluent continuously. The CEM response time should not exceed two minutes to achieve 95% of the final stable value.

6. CEMs Interference Response

Interference is the difference between the CEM response with the listed interfering components present and absent. The components include carbon monoxide, carbon dioxide, oxygen, sulfur dioxide, nitrogen dioxide, water vapor, hydrogen chloride, and chlorine. The sum of the interferences with all components must be less than 10% of the applicable emission limit.

7. Calibration Source Error

A series of three injections of the same calibration gas shall produce results which do not vary by more than 5% from the mean. Failure to attain this precision indicates a problem in the CEM calibration system.

Mercury CEM Technologies

In support of these proposed monitoring requirements and instrument performance requirements, the EPA and DOE formed a joint program to identify and test commercially available mercury CEMs to verify that instruments are available that can meet the proposed requirements. A request for proposals was published in the Federal Register (See 61 FR 7232, February 27,1996) for mercury CEM vendors to participate in extended instrument durability testing to the proposed EPA requirements. As a result of this process, three mercury CEM vendors were identified to participate in the program. The participating vendors and a brief description of their system is described below.

Monitor Labs, representing Verewa

The Verewa HM-1400 continuous total mercury analyzer was provided and supported by Monitor Labs. This monitor is designed to measure total mercury: elemental, mercury compounds, and particulate matter (PM) bound mercury, on a continuous weight/volume basis (µg/dscm). A gas sample is extracted non-isokinetically at a constant sample rate of two (2) l/min from the stack through a resistance heated, polytetrafluoroethylene (PTFE) lined probe. The sample is transported to the analyzer through a PTFE sample line heated to 120°C. In the analyzer, the sample gas first passes through an oven where it is heated to 800°C. This vaporizes any mercury present in the particulate and partially dissociates mercury compounds. The sample is then mixed with hydrochloric acid (HCl) at 70°C to transform all mercury compounds to $HgCl_2$. This solution then reacts with sodium borohydride ($NaBH_4$) at 10°C to reduce all the mercury to the elemental form. A gas-liquid separator at 2°C strips the gas phase mercury vapors out of solution. The mercury vapor is then detected in an ultraviolet (UV) photometer at 253.7 ηm. The photometer uses a double-beam configuration. Mercury sample flows through one beam, is then scrubbed of mercury and passes through the second beam. This technique eliminates most potential interferences. The differential in signals is due to any interfering substances detected by the photometer, minus the mercury fraction. However, its effectiveness depends on the selectivity of the scrubbing. Finally, the sample gas is dried and the volume flow rate measured so that the instrument output can be reported on a dry basis.

Periodic zero checks are completed every 2 hours by switching the sample stream through a zero air scrubber (iodized charcoal) to remove mercury. The analyzer output was automatically adjusted for zero drift based on the instrument response during this sequence. An automatic calibration check is not normally performed by this instrument; however, Monitor Labs will perform a biweekly manual analyzer calibration procedure to calculate calibration drift using a standard reagent to generate controlled amounts of elemental mercury.

EcoChem, representing Seefelder Messtechnik.

The Seefelder Messtechnik Hg-Mat 2 continuous total mercury analyzer was provided and supported by EcoChem Technologies. This monitor is designed to measure total mercury: elemental, mercury compounds, and PM bound mercury. Analyzer output is on a continuous weight/volume basis (µg/dscm) as mercury. A gas sample is extracted non-isokinetically at a constant sample rate of 1.5 l/min from the stack through a heated stainless steel probe and transported to the analyzer through a

PTFE sample line heated to 200°C. In the analyzer, the sample gas passes through two reactors where it is cooled and all speciated mercury is converted to the elemental form. PM bound mercury is also desorbed in the reactors. The elemental mercury is carried in the vapor phase (separated from the liquid by a demister) to a UV photometer operating at 253.7 ηm. Finally, the sample gas is dried and the volume flow rate measured so that the instrument output can be reported on a dry basis.

Daily zero and calibration checks are completed automatically at preselected intervals. Periodic auto zeroing of the analyzer is done on an hourly basis. The analyzer output is automatically adjusted for zero drift based on the instrument response during this sequence. A calibration check sequence is completed once daily. Zero gas passes over a temperature controlled mercury permeation cell that generates an air and mercury calibration gas (non-certified value) that is injected into the reaction chamber.

Wheelabrator Clean Air Systems (now U.S. Filter), representing Perkin-Elmer;

The Perkin-Elmer MERCEM continuous total mercury analyzer was provided and supported by Wheelabrator Clean Air Systems. This monitor is designed to measure total mercury: elemental and mercury compounds, on a weight/volume basis (μg/dscm). A gas sample is extracted non-isokinetically at a constant sample rate of about 17 l/min from the stack through a heated platinum probe equipped with two heated sintered metal filters. The sample is transported to the analyzer through a PTFE sample line heated to 185°C. At the analyzer, a small portion of the sample flow (about 0.5 l/min) enters a reactor in which mercury compounds are reduced to elemental mercury by a tin (II) chloride ($SnCl_2$) solution. The sample gas containing vapor phase elemental mercury is separated from the reaction chamber liquid and enters a thermo-electric cooler, where it is cooled and dried to a dew point of 5°C. The dried sample then enters an amalgamation unit during a continually cycling batch operation. Mercury vapor is collected on a cool gold/platinum trap. At the end of the batch collection time, the trap is purged with instrument air, and the photometer baseline is determined. Then the trap is heated to 750°C to thermally desorb the mercury, which is released into the nitrogen carrier gas flow and measured in the photometer. Sample flow rate is measured so that the mercury concentration can be reported on a dry basis.

Zero and calibration checks are completed automatically at preselected intervals. A zero check is completed with each measurement cycle. The analyzer output is automatically adjusted for zero drift based on the instrument response during this sequence. Calibration checks are completed once daily using a mercury permeation device (non-certified). The calibration gas is introduced into the gold trap. This is an internal check that verifies the proper performance of the analyzer.

Test Facility

The site selected for this mercury CEMs demonstration was Kiln number 2 at the Holly Hill, Inc. cement manufacturing facility located in Holly Hill, South Carolina. This cement kiln co-fires hazardous waste with various other fossil and waste fuels. This facility was selected for several reasons. First, a cement kiln represents a reasonable worst-case test for the Hg CEMs, relative to a hazardous waste incinerator because they have relatively high mercury emissions. A target mercury emission range from 15 to 30 μg/dscm was chosen as being representative of a typical facility processing mercury waste. This is also consistent with the proposed HWC MACT emission limit of 50 μg/dscm. Also, cement kilns have higher particulate matter (PM) emissions, relative to incinerators. In addition, PM emissions may contain mercury since the PM is derived in large part from the raw meal and the raw meal, in turn, can be a significant source of the mercury fed into the kiln. Thus, the possibility exists for significant

mercury bound to PM, which represents a worst case test for the Hg CEMs. And cement kilns air pollution control systems typically control only PM. Other pollutants are uncontrolled and may be present in high concentrations. Since these pollutants, such as SO_2 and NO_2, may cause interference with the measurement of mercury, this once again is a worst case situation for the mercury CEMs.

The Holnam wet process kiln is 18'6" in diameter and 580' long, with a design capacity of 2,100 tons per day. The main raw materials in the portland cement manufacturing process are limestone, providing calcium, and clay, providing silica, alumina, and iron. The hot end of the kiln is equipped with a 600 mm Btu/hr multi-fuel burner, with coal being the primary fuel. The burner is also fired with supplemental liquid hazardous waste fuel. The average feed rate for hazardous waste fuel is approximately 7.5 tons/hr. The offgasses from the kiln are passed though electrostatic precipitators, then out the facility stack. All three CEMs probes are installed in a transfer duct between the ESP and the stack. At this point in the process, the gas temperature averages 180°C and has a moisture content of approximately 37%. The manual Reference Method samples will be taken both at a point in the transfer duct (co-located with the CEMs) and at the normal sampling location in the facility stack. The location in the stack meets all Reference Method sampling location requirements (distance from both upstream and downstream flow disturbances), unlike the point in the transfer duct. Limitations in the allowable CEM sample line lengths prevented CEM installation in the facility stack.

Test Method

The CEM demonstration will be designed and conducted to assess each instrument for the following performance characteristics:

Calibration and Zero Drift

Calibration Drift (CD) is defined as the difference in the CEMs signal output while measuring an established reference value (of mercury only) after a stated period of operation during which no unscheduled maintenance, repair, or adjustment took place. Zero Drift (ZD) is the calibration drift determined at the zero level. Calibration and zero drift will be evaluated once daily over a 7-day period. Zero calibrations will be completed automatically by all three CEMs. Zero drift is determined by introducing a zero gas into the analyzer portion of the CEM. High level calibrations will be conducted automatically by a permeation tube technique for the MERCEM and Hg-Mat 2 CEMs, and by manual calibration with mercury solutions for the Verewa CEM.

Calibration Error Test

Calibration Error (CE) is the difference between the concentration indicated by the CEM and the known concentration generated by a calibration source when the entire CEM sample system is challenged. The CE test is conducted by challenging the CEM with concentrations of elemental mercury (Hg^0) and mercuric chloride ($HgCl_2$) generated using a permeation tube apparatus. The CE was carried out separately for both Hg^0 and $HgCl_2$. The calibration system introduces a quantity of gas phase Hg^0 or $HgCl_2$ in nitrogen to the sampling system of the Hg CEMS, upstream of all filters, scrubbers, and other gas conditioning. In each case, the target CE test concentrations is 0%, 40-60%, and 80 - 120% of the emission limit (50 µg/dscm). The challenge will be conducted three times non-consecutively at each level. The gas concentrations were verified by a simultaneous measurement during each challenge using a Method 101A verification train.

Interference Test

Interference Response is defined as the sum of the differences between the CEMs response to a calibration source with each of eight (8) individual gaseous components present and absent. The interference testing will be conducted following the CE test at the high concentration level for both Hg^0 and $HgCl_2$. As with the CE testing, calibration gases will be generated with a permeation tube device, and the concentration verified with a modified Method 101A verification train. After the CEMS response to each high level calibration gas is recorded, the interference test gases will be substituted for the nitrogen dilution gas flow used in the CE test. The response of the Hg CEMS will be recorded and compared with that from the Hg^0 and $HgCl_2$ individually to calculate the interference as described in the performance specification. Each interference test gas is introduced singly.

Relative Accuracy Test Audit (RATA)

The relative accuracy (RA) test will be conducted by comparing simultaneous CEM and reference method measurements. The reference methods used in this demonstration will be the proposed draft Method 101B (M101B) train for speciating mercury and a standard Method 29 (M29) sampling train. The draft M101B is being used to measure the concentrations of both Hg^0 and $HgCl_2$. The standard M29 procedure gives only a total mercury value, not the concentrations of each species. Initially, the reference method measurements will be conducted at two locations: the standard stack sampling location, and on the transfer duct co-located with the Hg CEMS. The stack measurements will utilize both M101B and M29 trains with a full traverse of the stack. The transfer duct measurements will be made at a fixed point with a single M101B sampling train. Nine runs will be made at both locations. RA will be calculated according to the draft performance specification for each individual method and location. During the RA testing, the feedstreams (meal, fuel, and hazardous waste) will be sampled by Holnam according to standard EPA protocol and analyzed for mercury and chlorine. Plant operating conditions will be compared with the mercury measurements established during the testing.

Endurance Testing

This phase of the demonstration test will involve a six months CEM endurance test. The proposed regulations require Relative Accuracy Test Audits (RATAs) every 3 years and quarterly checks of calibration error, called an Absolute Calibration Audit (ACA). During the endurance test, RATAs and ACAs will be performed monthly. In addition, the reliability and maintenance requirements of the mercury CEMs will be documented. The elements of the endurance test will therefore consist of:

- Monthly RATAs (comparison to Reference Method measurements);
- Monthly calibration error checks (ACAs);
- Continuous recording of Hg CEMS data for up to one year;
- Documentation of daily calibration and zero checks;
- Documentation of all maintenance and adjustments performed on the Hg CEMS; and
- Documentation of data availability and the reasons why data was not available.

Discussion of Test Results

The initial mercury CEM performance test has been completed. Currently, the six month endurance test is ongoing. The initial RATA testing was conducted following a three week conditioning period and a calibration error test. During the conditioning period, the CEMS must analyze effluent stack gas. The

conditioning period demonstrates the CEM is able to operate reliably at stack gas conditions before continuing with further performance specification procedures.

The RATA testing procedures used two reference methods, EPA Method 29 (M29) and proposed draft Method 101B (M101B), developed to speciate between elemental and oxidized forms of mercury. The M101B sample train consists of a standard M29 sampling train with the following modification: the first acidified peroxide impinger is replaced with two (2) impingers containing distilled water. The water captures oxidized forms of mercury (Hg^{2+}) while elemental mercury passes through the solution. The remaining acidified peroxide impinger captures SO_2 to prevent interference with the capture of elemental mercury (Hg^0) in the permanganate impingers. Laboratory testing has shown that >99% of Hg^{+2} is retained in the water impingers (testing with $HgCl_2$ only), and >99% of Hg^0 is retained in the acidified permanganate.

The reference method measurements were conducted at the two locations described previously, at the stack sampling location, and on the transfer duct co-located with the CEMs. The stack measurements were completed with both a M101B sampling train and a M29 sampling train, utilizing a full 20 point traverse, as required by the method.

The transfer duct measurements were completed from a single sample point with M101B. The M101B data from the duct were used to evaluate the relative accuracy of the three CEMS at the CEMS sampling location. This data was also compared to the M101B data obtained at the stack to assess the relationship between the mercury measured at the duct location and the mercury measured at the stack location. Finally, a comparison was made between the total emissions measured at the stack by M29 and M101B as a check on the validity of the modified manual reference method [A full Method 301 validation was conducted on the draft M101B. The results of this effort is presented in a separate paper in these conference proceedings] .

Summary of Reference Method Data

All reference method data is summarized in Table 1. From this data, it can be seen that the mercury concentrations measured by both the draft M101B and the standard M29 at the stack location were very consistent from run to run. M101B (Train A) averaged 25.3 µg Hg /dscm at the stack location, while M29 (Train B) averaged 21.9 µg Hg /dscm.

However, the M101B data at the duct location was more variable. Results for Run 1 of Train C show a mercury concentration of 55.7 µg /dscm, or almost three standard deviation units from the mean. Comparison of this data with the simultaneous runs at the stack location shows that this concentration is more than twice the average of the other trains during the same time period. Therefore, Run 1 of Train C is considered an outlier, and has been excluded from further statistical analysis. Run 9 of Train C is also unusually low, due to a leak during testing caused by a cracked U-tube in the back half of the sample train. This run has also been excluded from the data set. A summary of M101B data, adjusted for outliers, is shown in Table 2.

The adjusted M101B data for Train C is very consistent, with a standard deviation of 1.54, and a mean of 21.5 µg /dscm. While this only leaves seven (7) data points for the purposes of relative accuracy determination, the low standard deviation (7.1% of the mean value) indicate excellent precision between the remaining data. The precision of all three measurement trains indicate stable mercury concentrations over the duration of the sampling period.

TABLE 1. SUMMARY OF REFERENCE METHOD DATA

		Reference Method Concentrations		
Location:		Stack	Stack	Transfer Duct
Measurement Type:		Method 101B	Method 29	Method 101B
Measurement Units:		(ug/dscm)	(ug/dscm)	(ug/dscm)
Date:	Run #:	Train A	Train B	Train C
8/28/96	1	26.557	20.268	** 55.683
8/28/96	2	27.548	20.708	22.610
8/28/96	3	23.837	21.661	21.073
8/29/96	4	26.510	24.183	22.307
8/29/96	5	26.424	25.747	21.230
8/29/96	6	24.568	23.433	22.997
8/29/96	7	25.562	23.236	21.731
8/30/96	8	20.962	18.646	18.383
8/30/96	9	25.976	19.115	** 10.847
Statistical Analysis				
Average		25.327	21.888	24.096
Minimum		20.962	18.646	10.847
Maximum		27.548	25.747	55.683
n		9	9	9
St. Deviation		1.980	2.414	12.427

Note: Data flagged with ** indicates results that are considered outliers in the data set.

TABLE 2. METHOD 101B DATA, ADJUSTED FOR OUTLIERS

		Reference Method Concentrations		
Location:		Stack	Stack	Transfer Duct
Measurement Type:		Method 101B	Method 29	Method 101B
Measurement Units:		(ug/dscm)	(ug/dscm)	(ug/dscm)
Date:	Run #:	Train A	Train B	Train C
8/28/96	1	26.557	20.268	***55.683***
8/28/96	2	27.548	20.708	22.610
8/28/96	3	23.837	21.661	21.073
8/29/96	4	26.510	24.183	22.307
8/29/96	5	26.424	25.747	21.230
8/29/96	6	24.568	23.433	22.997
8/29/96	7	25.562	23.236	21.731
8/30/96	8	20.962	18.646	18.383
8/30/96	9	25.976	19.115	***10.847***
Statistical Analysis				
Average		25.327	21.888	21.476
Minimum		20.962	18.646	18.383
Maximum		27.548	25.747	22.997
n		9	9	7
St. Deviation		1.980	2.414	1.535

Note: ***Italicized bold*** data indicates results that are outliers in the data set that have not been used for statistical analysis.

Measurement of Particulate Bound Mercury

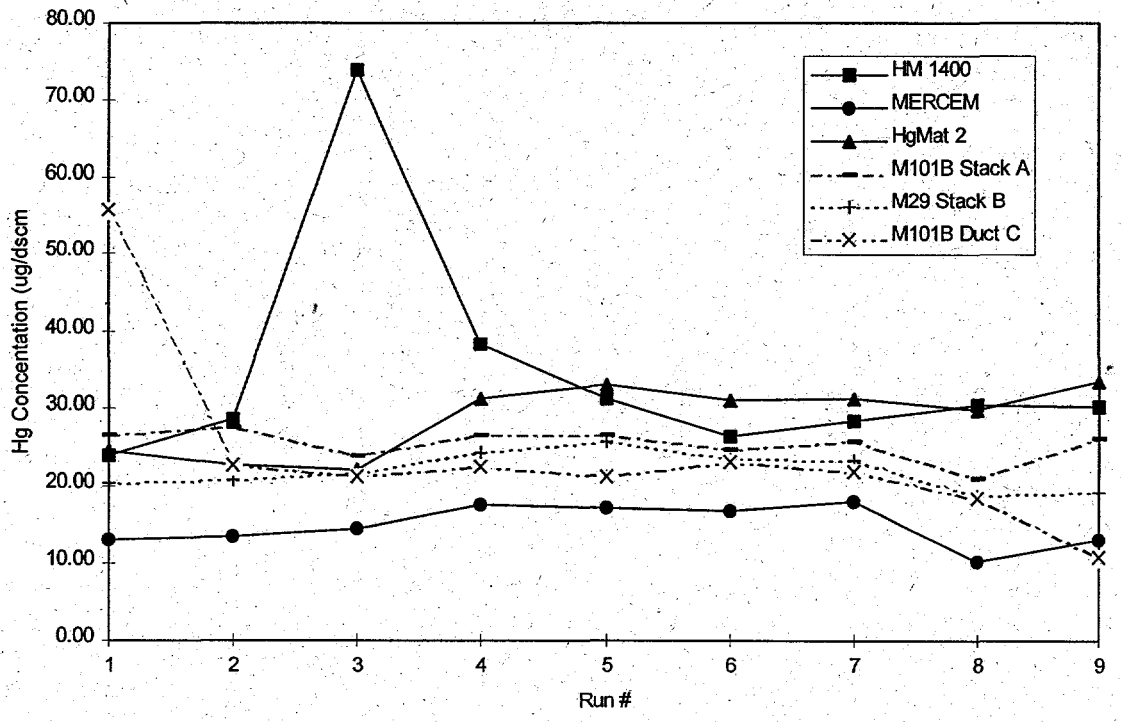
The limitations associated with limited sample line lengths and CEM installation requirements required the placement of the CEMs sample probes in the transfer duct location, yet this location does not meet EPA requirements for distance from upstream and downstream flow disturbances for particulate sampling. However, available data and experience indicate that the concentration of particulate bound mercury should not be significant. To validate this assumption, the analysis of each reference method sample was conducted such that the particulate-bound mercury was measured separate from the gas-phase mercury. The particulate-bound mercury concentrations were measured by combining the front half rinse and filter catch. The average concentration of particulate-bound mercury for all three sample trains (27 total runs) was .025 µg/dscm, or less than .2% of the average concentration of total mercury species detected during these sample run. The value of particulate-bound mercury measured by M101B

at both the stack and duct locations was .022 and .034 µg/dscm respectively. These data support two assumptions made in the design of the testing approach. First, the particulate bound mercury is not a significant fraction of the total mercury in this stack gas effluent. And second, the transfer duct location measurements are representative of the particulate bound mercury measured at the stack.

Relative Accuracy Test Results

The RATA results represent the initial performance of the CEMS as compared to M101B, (train C, duct location). At this time, only the RATA data has been analyzed. Data for the other measures of CEM performance (CE, CD, ZD, etc.) are still undergoing analysis. The RATA results for each CEM have been summarized in Tables 3, 4, and 5 and Figure 1. Each Table includes the average of the CEM reading during the time the reference method sample was taken. The CEM mercury concentration result is compared to both the reference method value obtained in the stack and in the transfer duct. Seven (7) of the nine reference method runs were used for the calculation of relative accuracy in comparing the transfer duct reference method data since Runs 1 and 9 were eliminated as outliers from the reference method data set.

FIGURE 1: CEM RATA Results



Relative accuracy of the Verewa HM-1400 is shown in Table 3. Run 3 was not considered in the calculations. The response from this run was over twice the average response for the other 8 runs. The analyzer exhibited a large drift in zero response immediately preceding this time period, and was adjusted for this drift problem before run 4 the next day. The relative accuracy was calculated for six runs (2, 4, 5, 6, 7, and 8). Although one less run was used for the RA calculation than for the other to CEMs, the increase in the standard deviation in the data if run 3 had been used would have a greater negative impact on the results than the use of a lesser t-factor. The relative accuracy of the Verewa compared to M101B, train C, was 66.8%, with a standard deviation of the difference from the reference method data of 4.958. The magnitude of the RA was influenced by large differences from the reference method during runs 4, 5, and 8. The variability of the CEMs response is reflected in the standard

deviation of the CEMS data. The positive bias of the Verewa response appears to be related to consistent zero drift difficulties with the analyzer due to "fogging" of the optical bench windows. Verewa has implemented modifications to this CEM to eliminate this drift characteristic.

TABLE 3. VEREWA HM-1400 RELATIVE ACCURACY

CEMS RELATIVE ACCURACY							
CEMS:		Verewa HM-1400					
Measurement Type:		M 101B			M 101B		
Location:		Stack			Duct		
Measurement Units:		(ug/dscm)			(ug/dscm)		
Date:	Run #:	Train A	CEMS	di	Train C	CEMS	di
8/28/96	1	26.5569	23.8537	2.7032	***55.6828***	***23.8537***	***31.8291***
8/28/96	2	27.5478	28.4311	-0.8833	22.6104	28.4311	-5.8208
8/28/96	3	***23.8368***	***73.8674***	***-50.0306***	***21.0733***	***73.8674***	***-52.7942***
8/29/96	4	26.5103	38.3198	-11.8095	22.3072	39.4227	-17.1155
8/29/96	5	26.4237	31.1700	-4.7463	21.2303	31.3766	-10.1463
8/29/96	6	24.5677	26.2874	-1.7197	22.9969	26.2874	-3.2905
8/29/96	7	25.5621	28.2698	-2.7077	21.7312	28.5307	-6.7995
8/30/96	8	20.9621	30.2725	-9.3104	18.3829	30.2725	-11.8896
8/30/96	9	25.9759	30.2053	-4.2293	***10.8473***	***30.2053***	***-19.3579***
Statistical Analysis							
Arithmetic Mean		25.5133	29.6012	-4.088	21.543	30.720	-9.177
n		8.000	8.000	8.000	6.000	6.000	6.000
sd		2.031	4.250	4.648	1.671	4.605	4.958
t		2.365	2.365	2.365	2.571	2.571	2.571
RELATIVE ACCURACY			**31.26%**			**66.75%**	

Note: ***Italicized bold*** data indicates results that are outliers in the data set that have not been used for statistical analysis.

The relative accuracy of the Perkin Elmer MERCEM is shown in Table 4. The relative accuracy was calculated for seven runs (2 through 8). The relative accuracy of the MERCEM compared to M101B, train C, was 37.3%. The standard deviation of the difference from the reference method data for the MERCEM (2.887) was the lowest of the three CEMS. The average response was also the lowest.

Perkin Elmer redesigned the reaction chamber design of this CEM after these tests in order to eliminate the negative bias of the measurements. Results of the modification should be reflected in the performance of the monitor during the endurance tests.

TABLE 4. PERKIN ELMER MERCEM RELATIVE ACCURACY

CEMS RELATIVE ACCURACY							
CEMS:		Perkin Elmer MERCEM					
Measurement Type:		M 101B			M 101B		
Location:		Stack			Duct		
Measurement Units:		(ug/dscm)			(ug/dscm)		
Date:	Run #:	Train A	CEMS	di	Train C	CEMS	di
8/28/96	1	26.5569	12.9688	13.5881	***55.6828***	***12.9688***	***42.7140***
8/28/96	2	27.5478	13.4338	14.1141	22.6104	13.4338	9.1766
8/28/96	3	23.8368	14.4518	9.3850	21.0733	14.4518	6.6215
8/29/96	4	26.5103	17.5927	8.9176	22.3072	18.3438	3.9634
8/29/96	5	26.4237	17.1027	9.3209	21.2303	17.0916	4.1387
8/29/96	6	24.5677	16.7570	7.8107	22.9969	16.7570	6.2398
8/29/96	7	25.5621	17.8571	7.7050	21.7312	17.5365	4.1947
8/30/96	8	20.9621	10.1757	10.7864	18.3829	10.1757	8.2072
8/30/96	9	25.9759	13.0819	12.8940	***10.8473***	***13.0819***	***-2.2346***
Statistical Analysis							
Arithmetic Mean		25.3270	14.8246	10.502	21.476	15.399	6.077
n		9.000	9.000	9.000	7.000	7.000	7.000
sd		1.980	2.645	2.465	1.535	2.887	2.091
t				2.306			2.447
RELATIVE ACCURACY			**48.95%**			**37.30%**	

Note: ***Italicized bold*** data indicates results that are outliers in the data set that have not been used for statistical analysis.

Relative accuracy of the Seefelder Hg-Mat 2 is shown in Table 5. The relative accuracy was calculated for seven runs (2 through 8). The relative accuracy of the Hg-Mat 2 compared to M101B, train C, was 54.4%, with a standard deviation of the difference from the reference method data of 4.815. As with the Verewa CEMS, the variability of the Hg-mat 2 CEMS response is reflected in the standard deviation of the CEMS data. EcoChem suspects that the positive bias of the Hg Mat 2 response is due in part to the known positive interference response to SO_2. In response to this problem, Seefelder has installed an SO_2

scrubber before the reaction chamber in order to reduce the SO_2 bias. Results of the modification should be reflected in the performance of the monitor during the endurance tests.

TABLE 5. SEEFELDER HG-MAT 2 RELATIVE ACCURACY

CEMS RELATIVE ACCURACY							
CEMS:		Seefelder Hg-Mat 2					
Measurement Type:		M 101B			M 101B		
Location:		Stack			Duct		
Measurement Units:		(ug/dscm)			(ug/dscm)		
Date:	Run #:	Train A	CEMS	di	Train C	CEMS	di
8/28/96	1	26.5569	24.3901	2.1668	***55.6828***	***24.3901***	***31.2927***
8/28/96	2	27.5478	22.5672	4.9806	22.6104	22.5672	0.0431
8/28/96	3	23.8368	21.9746	1.8622	21.0733	21.9746	-0.9014
8/29/96	4	26.5103	31.1406	-4.6303	22.3072	31.4147	-9.1075
8/29/96	5	26.4237	32.8878	-6.4641	21.2303	33.0019	-11.7716
8/29/96	6	24.5677	31.0406	-6.4729	22.9969	31.0406	-8.0437
8/29/96	7	25.5621	31.2005	-5.6384	21.7312	31.2238	-9.4926
8/30/96	8	20.9621	29.6380	-8.6759	18.3829	29.6380	-11.2551
8/30/96	9	25.9759	33.4439	-7.4679	***10.8473***	***33.4439***	***-22.5965***
Statistical Analysis							
Arithmetic Mean		25.3270	28.6982	-3.371	21.476	28.694	-7.218
n		9.000	9.000	9.000	7.000	7.000	7.000
sd		1.980	4.472	4.983	1.535	4.499	4.815
t				2.306			2.447
RELATIVE ACCURACY			**28.43%**			**54.35%**	

Note: ***Italicized bold*** data indicates results that are outliers in the data set that have not been used for statistical analysis.

In addition to not meeting the 20% RA criteria, all three CEMs experienced operational problems during and after the initial RATA test (plugging, corrosion, etc.). In response to these problems, all three CEMS have been modified or upgraded to minimize the effects of the sample gas matrix. In general, these problems were associated with the content of the stack gas matrix associated with a cement kiln, and it's effect on sample transport, zero drift, and interference response. The CEMs evaluated for this

program were designed to be used in applications where the stack gas has been scrubbed of acid gases and that has low non-condensable particulate concentrations, neither condition of which exists at this test facility. These modifications were made to enhance the performance of the CEMS, and increase long term availability of the CEMS.

Conclusions

Continuous emissions monitoring of mercury from hazardous waste thermal treatment processes is desired for verification of emission compliance, process control, and public safety perception. The U.S. Environmental Protection Agency (EPA) has proposed regulations that require the use of total mercury continuous emissions monitors (CEMs) on incinerators, boilers, and industrial furnaces that burn hazardous waste. These proposed regulations also include draft performance specifications for mercury CEMs. This ongoing joint EPA/DOE program identified three different mercury CEMs ready to be tested for compliance with the proposed performance specifications. The instruments have been in operation at a commercial cement kiln that co-fires hazardous waste. The first phase of CEM testing revealed that all three instruments were not able to meet the EPA proposed performance standards. After a review of the test results, all three instrument vendors implemented system modifications to improve instrument performance. The effectiveness of these modifications will be assessed during the long-term endurance test.

In addition to the initial CEM RA test results, the data revealed several additional important observations. First, the CEMs were installed in a location that prevented meeting all Reference Method sampling location requirements (distance from both upstream and downstream flow disturbances). This could have a detrimental impact on performance if there was a significant quantity of particulate-bound mercury in the stack gas. The test data confirmed the assumption that particulate bound mercury is not a significant fraction of the total mercury in the stack gas effluent. Second, the data confirmed that CEM installation location in the facility transfer duct allows extraction of representative offgas samples as compared to the facility stack. Third, the proposed M101B proved to be very consistent with the standard EPA mercury reference method (M29) in measuring total mercury in the facility offgas. And fourth, the test facility selected for this instrument demonstration has a relatively stable mercury concentration in the stack gas, which confirms the selection of this facility for this type of testing.