

# DEMONSTRATION OF A CONTINUOUS EMISSION MONITOR FOR TOTAL MERCURY MEASUREMENTS AT THE DOE OAK RIDGE TSCA INCINERATOR FACILITY

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## ABSTRACT

This paper details the results of a six week field test program to document the ability of the Perkin Elmer MERCEM continuous emission monitor to meet EPA's Draft Performance Specification 12 for total mercury emissions. The tests were conducted at the U. S. Department of Energy (DOE) Toxic Substances Control Act (TSCA) mixed waste incinerator in Oak Ridge, Tennessee. Results from the Relative Accuracy Test Audit (RATA - Method 101A), Calibration Error, Calibration Drift and Interference tests are presented. Calibration techniques utilizing elemental mercury permeation tube and compressed cylinder gases were investigated over the duration of testing. The analyzer's unique gold amalgamation technique and HgCl<sub>2</sub> reduction method employing a SnCl<sub>2</sub> reactor are also discussed.

## INTRODUCTION

Revised regulations by the U.S. Environmental Protection Agency (EPA) for the burning of hazardous wastes in incinerators and boilers and industrial furnaces on April 19, 1996 (1). dealt in part with mercury emissions. The proposed regulations outlined the eventual requirement of advanced continuous emissions monitors (CEMs) for some hazardous air pollutants (HAPs) or surrogates for HAPs and encouraged the use of CEMs for other HAPs or HAP surrogates. In support of these monitoring requirements, the EPA and the U.S. Department of Energy (DOE) formed a joint program to identify and test commercially available CEMs to meet the proposed requirements. As result of a request for proposals, an extended duration test of three total mercury CEMs was conducted at a commercial hazardous waste burning cement kiln at Holly Hill, South Carolina, in 1996-97 timeframe (2). It is believed that failure of the CEMs was due to emission characteristics of the kiln, specifically the combination of high particulate matter, moisture, and acid gases (3). Understanding that a DOE mixed waste incinerator would present less adverse conditions and thus allow a total mercury CEMS to operate successfully, the DOE Office of Science and Technology Characterization, Monitoring and Sensor Technology Crosscutting Program and the Mixed Waste Focus Area elected to conduct a follow-up total mercury CEMS investigation at the TSCA Incinerator. The MERCEM manufactured by Perkin Elmer and represented by Aldora Technologies was selected for that further evaluation at the DOE Toxic Substances Control Act (TSCA) Incinerator located at the East Tennessee Technology Park (ETTP), formerly K-25 Site, in Oak Ridge, Tennessee.

## Objectives

The objectives of this field study were focused in three areas of evaluation and assessment:

- Performance of the MERCEM continuous emissions monitoring system against EPA draft Performance Specification 12 (PS 12) for mercury CEMS
- Calibration methods and quality assurance techniques with reference concentrations of mercury utilizing a permeation device and compresses gas cylinders
- Long-term endurance of the MERCEM under wet stack conditions of a mixed waste incinerator

## **Overview**

A technical approach and scope were developed to meet the project objectives within budgetary and time constraints. Site modifications to accommodate proposed testing were determined to be minimal with logistics and services to support the project readily available.

The four elements of EPA Draft Performance Specification 12 (PS12) (4), for which this field performance testing was specifically designed to address are:

- Calibration error test
- 7-day calibration and zero drift test
- Relative accuracy test
- Interference test

The overall scope of the project was carried out over approximately a two-month period from September through October 1998.

## **Organization**

The project was funded by the DOE Office of Science and Technology Characterization, Monitoring and Sensor Technology (CMST) Crosscutting Program and the DOE Mixed Waste Focus Area (MWFA). The TSCA Incinerator is owned by DOE.

The test program participants consisted of five organizations, which directly contributed to the project.

- Lockheed Martin Energy Systems, Inc. -Oak Ridge, Tennessee  
responsible for test planning and reporting, and Method 101A testing.
- Bechtel Jacobs Company LLC -Oak Ridge, Tennessee  
provided overall coordination of the test program and managed the operation of the TSCA Incinerator.
- Aldora Technologies - League City, TX & Hartsdale, NY  
provided the MERCEM system hardware and operated the CEMS during the performance test
- Perkin Elmer, Environmental & Process Control Division - Meersburg, Germany  
provided the MERCEM system hardware and operated the CEMS during the performance test
- Spectra Gases Inc. - Alpha, New Jersey  
provided mercury calibration gas cylinders for calibrations and calibration error testing

## **DESCRIPTION OF HOST FACILITY AND THE MERCEM ANALYZER**

### **General Facility Description : TSCA Incinerator**

The DOE TSCA Incinerator is permitted by the State of Tennessee and the EPA for storing and thermally treating polychlorinated biphenyl (PCB) contaminated radioactive and hazardous (mixed) waste. The incinerator, which is operated by Bechtel Jacobs Company LLC, is located at the ETPP in Oak Ridge, Tennessee. By virtue of the unique combination of nine permits and approvals held by the facility, the TSCA Incinerator is the only incinerator in the country that has regulatory approval for treating PCB contaminated mixed wastes. Over 23,000,000 lbs. of waste in the form of solids and organic and aqueous liquids have been treated since routine operations commenced in April 1991.

The incinerator consists of a rotary kiln and a secondary combustion chamber (SCC) followed by a wet off-gas cleaning system. Organic liquids, aqueous, and solid wastes can be fed into the rotary kiln. Permits only allow high heat value organic liquid wastes to be fed to the SCC. The rotary kiln and SCC each have an auxiliary burner that utilizes natural gas to control incineration temperatures. Auxiliary systems servicing the incinerator include a tank farm containing fifteen storage and feed tanks with a combined storage capacity of 90,000 gal, a kiln ash removal system, and sumps for managing scrubber water blowdown.

The off-gas cleaning system consists of a quench chamber, venturi scrubber, packed bed scrubber, two ionizing wet scrubbers (IWS) in series, induced draft fan, and exhaust stack. The APC devices cool and saturate the combustion gases, neutralize the acidic gas components such as hydrochloric acid (HCl), and remove particulate matter from the off-gas. Both mercury stack emissions and mercury feed rate to the incinerator rate are currently restricted to 0.48 pounds per day.

### **MERCEM Analyzer Description**

The MERCEM monitor is designed to measure total mercury emissions from hazardous waste combustors. Fig. 2 shows a flow diagram of the MERCEM system. A gas sample is extracted in a non-isokinetic fashion from the stack at 1000 L/h and transported to the analyzer through a probe, filter, and sample line. All components in contact with the stack gas are properly heated to 185°C to avoid condensation and corrosion. The sample gas is reduced to 35 L/h at the analyzer before entering a reactor where mercuric chloride is reduced to elemental mercury by a stannous chloride (SnCl<sub>2</sub>)

solution. The sample gas containing vapor phase elemental mercury passes through a two stage cooler where the gas sample is dried and the volume flow rate measured so that instrument output can be reported on a dry basis. The sample gas then enters a gold trap where mercury forms an amalgam with the gold. The trap is purged with nitrogen at the end of the collection period and the analyzer baseline is established. Mercury is then driven from the unit by heating the trap and swept to the photometer where it is measured using atomic absorption spectrometry. An advantage of the amalgamation step is that optical interferences from other stack gas components are eliminated. Additionally, the system sensitivity can be varied by using different sample collection periods. The entire cycle time is on the order of 3 minutes. Replenishment of reagents and removal of waste solutions are required about every three months. The reagents used in the analyzer are stored in the CEM enclosure and pumped continuously into the reactors. The MERCEM has been published as an certified instrument in Germany by the TUV Rheinland Sicherheit und Umweltschutz GmbH (5). A flow chart for illustrating the sample path is shown in Fig 1.

**Flowchart**

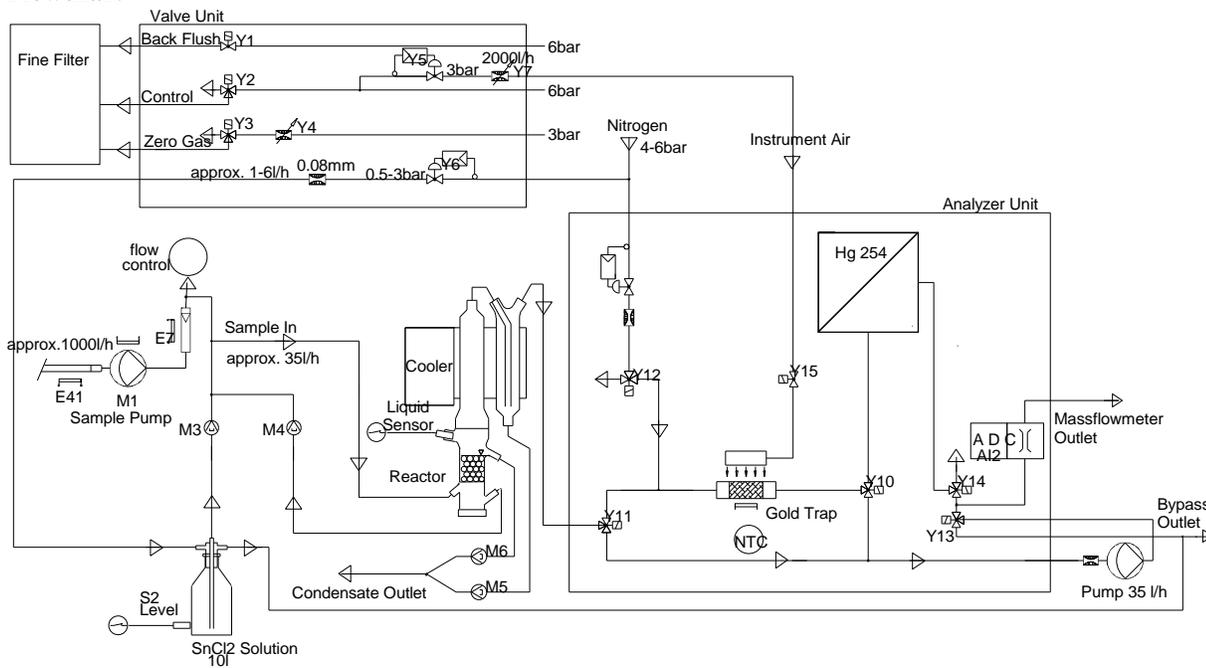


Fig 1. MERCEM Flow Chart

**Photometric Concentration Determination & Cycle Time**

Together with the nitrogen the mercury is conducted into the cell; the absorbance of the peak range is determined by photometric measurement. After calculation of the sample gas volume and the absorbance, the concentration is displayed on a LCD panel. The concentration is also available as a 4-20 mA signal. Once the gold trap has been purged and cooled down by a strong air stream the gold trap is prepared for the next sample.

**Cycle Time**

The typical cycle time of a measurement (i.e. with a measuring range of 0 - 100 µg/m3) is 180 sec. As shown in Fig 2. The measurement cycle is comprised of the following:

- Cooling: approx. 30 sec.
- Collecting period: 10 sec.
- Baseline: approx. 50 sec.
- Heating and Measurement: approx. 90 sec.

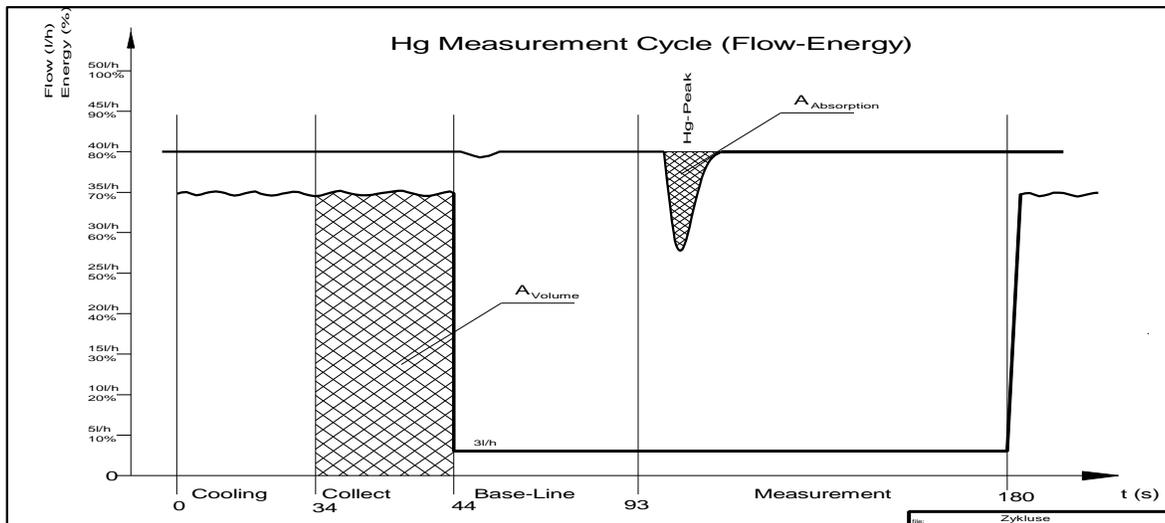


Fig 2. Profile of a Measurement Cycle

### Sampling Locations

The TSCA Incinerator stack is 1.36 meter inside diameter and has two stack platforms used for sampling and monitoring emissions from the air pollution control system. Both are accessible by ladders from the ground. The lower platform is approximately 10 meters from the ground. One port at this location is dedicated to a probe that extracts stack gas analyzed for CO, CO<sub>2</sub>, and O<sub>2</sub> by facility CEMs. Other ports at this level are used for experimental CEM testing and compliance testing for gaseous pollutants. The upper platform is approximately 15 meters from ground level and contains ports for continuous radionuclide and metals sampling systems, reference methods requiring particulate sampling traverses, and experimental CEM testing. Ports on the upper platform meet ideal regulatory sampling location requirements for particulate traverses at least eight equivalent duct diameters downstream and more than two upstream from any flow disturbance. Ports on the lower platform are four equivalent diameters downstream of the fan discharge. The sampling probe for the MERCEM analyzer was installed in a port on the lower sampling platform. A heated sample line approximately 40 meters long transported the gas sample directly to the MERCEM analyzer in a laboratory trailer on the ground. The probe of the reference method sampling train was co-located (at the same elevation and within 15 cm) with the MERCEM probe and remained fixed (i.e., not traversed).

## TECHNICAL APPROACH

### Test Planning and Execution

In addition to determining the sampling locations and equipment layout and the site support and logistical considerations of the project, radiological control, health and safety, and incinerator feed operation were addressed during test planning and execution. To ensure that the MERCEM left the TSCA Incinerator site in a radiologically clean state, health physics (HP) technicians directly surveyed the stack probe and filter. In addition the sample line was rinsed with nitric acid, and the rinse solution was sampled and analyzed for total activity. The condensate removed from the gas processed by the analyzer was sampled and analyzed for total activity. As deemed necessary by HP technicians, tubing connections inside the analyzer cabinet were disconnected to survey analyzer internal surfaces. Other radiological contamination control measures included return of that portion of the stack gas not processed for analysis back to the stack, filtering the exhaust of the processed gas sample, and return of liquid condensates to a sump for treatment.

Ensuring the health and safety of individuals participating in the project was of utmost importance and of top priority during test planning. The project was conducted following the guidelines embodied by the DOE Integrated Safety Management Program. Normal incinerator operation during testing was planned with actual waste streams containing mercury with no additional spiking. MERCEM performance data were obtained while incinerating liquids only as well as both liquids and bulk solids.

### Performance Testing Method Selection Criteria

The performance test plan was based on PS12 including a relative accuracy test series. Since available data on mercury emissions from the TSCA Incinerator indicated that most of the mercury has previously been vapor phase as elemental

mercury, a performance evaluation addressing speciated mercury was determined to be beyond the scope of the project. Accordingly, EPA Method 101A (6) was selected as a cost-effective alternative to Method 101B (7) and the Ontario-Hydro method for speciated mercury or Method 29 (8) for metals including mercury.

Relative accuracy commonly used as a criterion for accepting or rejecting CEMS systems, is a regulatory statistic in PS 12 expressed as the deviation of the CEMS from the reference method relative to the emission levels occurring at the time of the test, was determined by comparing MERCEM and Method 101A measurements. Nine one-hour runs were conducted during each performance test period. The runs were scheduled during a consistent set of operating conditions for the incinerator to the extent possible.

Only gas phase elemental mercury was used to assess calibration error and calibration drift. Aldora Technologies investigated both the use of calibration gases of known mercury vapor concentrations supplied in gas cylinders and the generation of a gas phase mercury standard using a permeation tube device.

#### **Application of a Calibration Correction Factor (Response Factor (rf))**

Although the MERCEM system was calibrated at the factory, the need was considered to conduct an initial series of reference method tests to develop a site-specific response factor to adjust MERCEM output readings before any measurements to determine relative accuracy. Such a measure was recognized to have merit particularly in cases in which reference materials are unavailable or unreliable. However, due to the short-term schedule of the project, no preliminary reference method testing was performed prior to the Phase I RATA.

The use of calibration correction factors was not defined in PS 12. However, there has been discussion of the validity of this pragmatic approach. When mercury CEMS are used for applications in Germany, the CEMS are factory calibrated before installation, then compared against a series of wet chemistry tests similar to EPA's current reference method. The MERCEM can use a supplemental permeation tube or calibration gas as a reference value for the purpose of daily calibration checks, but it does not currently adjust the output concentration on the basis of the response to these daily span checks. The CEMS' responses to the initial RATA test during the six-month evaluation testing at Holly Hill, SC (7) were used to derive a calibration adjustment factor. This response factor was applied to adjust the output of the CEM for all subsequent testing. A similar approach was used for evaluating portions of the calibration drift data utilizing the Phase I RATA data set conducted within the first two weeks of the test program.

The response factor is defined as a simple ratio of the average reference method response over the average CEM response. This approach assumes linear response across the entire measurement range. Applying this technique, the MERCEM response factor is calculated to be 0.87 .

### **PERFORMANCE SPECIFICATION 12 (PS12)**

#### ***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 system, including the sampling interface, is challenged. PS12 prescribes that the CEM be challenged three non-consecutive times at each measurement point and that the responses be recorded. The measurement levels are specified as a zero level (0-20% of the emission limit), mid-level (40-60% of the emission limit, and high-level (80-120% of the emission limit). According to PS12, calibration error is to be assessed using standards for both mercury and mercuric chloride and that the mean difference between the indicated CEM concentration and the reference concentration value at all test levels shall be no greater than  $\pm 15\%$  of the reference concentration at each level.

For this project, the CE challenge test was performed at the available nominal concentrations of 0, 20, 70, and 300  $\mu\text{g}/\text{m}^3$ . The available cylinders of calibration gas had to be rationed over the duration of the program with priority given to daily calibrations. CE was assessed only for elemental mercury in an abbreviated format.

#### ***Interference Response Test***

Interference response testing is prescribed by PS12 during the CE test at the high concentration level. After the CE measurements are made, the interference test gases are substituted for a portion of the nitrogen dilution gas flow. The response of the CEM is recorded and compared three times alternately to that with the mercury challenge alone. Each interference gas is introduced singly. The interference test gases are injected into the sampling system in a manner to undergo all the conditioning of an actual sample. The prescribed interference test gas concentrations are: 500 $\pm$ 50 ppm carbon monoxide, 10 $\pm$ 1 percent carbon dioxide, 20.9 $\pm$ 1 percent oxygen, 500 $\pm$ 50 ppm sulfur dioxide, 250 $\pm$ 25 ppm nitrogen

dioxide, 50±5 ppm hydrogen chloride, 10±1 ppm chlorine, and 25±5 percent water vapor.

Interference response testing was performed near the end of the project by blending interference gases at a 1:1 ratio with mercury vapor calibration gas. According to PS-12, the sum of the interferences shall be less than 10% of the emission limit value.

#### ***Calibration and Zero Drift Test***

Calibration drift (CD) is defined as the difference in CEM output readings from the established reference value after a stated period of operation during which no maintenance, repair, or adjustment took place. Zero drift (ZD) is similarly defined for zero input. PS12 is designed to allow calibration of CEMs by use of a calibration standard that challenges the pollutant analyzer part of the CEM and as much of the whole system as possible, but not necessarily the entire system and the sampling interface.

CD and ZD were evaluated daily for a seven-day period. ZD was determined by exposing the CEM to zero gas. CD was evaluated by challenging the CEM with elemental mercury only. According to PS12, the CEM calibration shall not drift or deviate from the reference value of the calibration standard by more than 2% of the reference value, and the zero point shall not drift by more than 2% of the emission standard.

The April 19, 1996, EPA proposal provided for an emission standard for mercury of 50 µg/dscm corrected to 7% oxygen. A subsequent notice of data availability and request for comment on May 2, 1997, changed the proposed emission limit for mercury to 40 µg/dscm corrected to 7% oxygen (9). An emission standard of 50 µg/dscm has been assumed for purposes of evaluating data from this field test.

#### ***Relative Accuracy Test***

Relative accuracy (RA) is defined in PS12 as the absolute mean difference between the pollutant concentration determined by the CEM and the value determined by the reference method (RM) plus the 2.5 percent error confidence coefficient of a series of tests with that result then divided by the mean of the RM tests or the applicable emission limit.

The RA test was conducted by comparing simultaneous MERCEM and RM measurements. The selected RM was EPA Method 101A. The RM measurements were performed with a sampling probe co-located with the MERCEM probe at a fixed point (i.e., not traversed). Nine one-hour runs were conducted during each performance test period with a target gas sample volume for each of 30 dry standard cubic feet. During each run, a gas sample was obtained for measurement of oxygen and carbon dioxide by classical Orsat analysis. The runs were scheduled during a consistent set of operating conditions for the incinerator to the extent possible.

In EPA Method 101A, particulate and gaseous mercury emissions are withdrawn isokinetically from the source and collected in acidic potassium permanganate (KMnO<sub>4</sub>) solution. During sample analysis, the mercury collected (in the mercuric form) is reduced to elemental mercury, which is then aerated from the solution into an optical cell and measured by atomic absorption spectrophotometry. For this project, the sampling nozzle and the probe liner were constructed from quartz glass and the optional filter was omitted. Glassware preparation followed the cleaning procedure of EPA Method 29. The liquid impingers of the sampling train were recovered along with a rinses of the sampling train glassware with fresh acidic permanganate solution and deionized water. Remaining deposits were recovered by rinsing with 8 normal hydrochloric acid, which was analyzed separately for mercury. The results for both the MERCEM and the reference method were corrected to 7% oxygen using Orsat data from the reference method.

#### **Mercury Vapor Calibration Gas**

Spectra Gases supplied cylinders of elemental mercury calibration gas. Aldora Technologies also furnished an elemental mercury permeation tube calibration device controlled by an isothermal bath with nominal range of 0-150 µg/m<sup>3</sup>. Two of the initially prepared cylinders were sent to Energy and Environmental Research Center of University of North Dakota (EERC), in Grand Forks, North Dakota, for verification prior to use in the field at Oak Ridge. The measurements for each cylinder were made in duplicate using a full-scale EPA Method 101A. All of the cylinders supplied by Spectra Gases as well as output from the permeation tube device were sampled by Lockheed Martin technicians after the second relative accuracy test using a modified train, minus the probe and filter, with midget impingers arranged in the same configuration as Method 101A. This modified impinger train configuration was previously used during the joint EPA/DOE demonstration (10).

#### **Calibration Gas Verification**

At the conclusion of the testing, the gas cylinders originally tested by EERC were reanalyzed in duplicate using EPA

Method 101A. The mercury calibration gases used in several performance tests underwent final laboratory analysis to examine the stability of the gases over a five month period. The results indicate a variation in measurements performed at different times and potential sampling and analytical difficulties with the modified midget impinger train. The cylinder concentration values used for comparison consisted of the average of the four (two pre-test August 1998 and two post-test February 1999) wet chemistry analyses by EERC.

## **PROJECT CHRONOLOGY**

The MERCEM arrived at the host facility on September 8, 1998. After a four day period of analyzer commissioning, optimization, and fine-tuning, the first calibration error and 7-day calibration and zero drift testing was conducted. The initial relative accuracy tests began on September 16 and concluded on September 17. A four-week operational test period proceeded without continuous on-site support by Aldora and Perkin Elmer personnel until the week of October 19. A single visit was made on October 8 to conduct a calibration and mid-operational period inspection. A second relative accuracy test was performed on October 22 and 23, along with interference response testing and a second calibration error and 7-day calibration and zero drift test during the timeframe. The field activities concluded shortly thereafter with attempts to verify the mercury vapor calibration reference materials by sampling and analysis and with decontamination, decommissioning, and shipment of the MERCEM from the host facility.

An itemized chronology of key events during execution of the project was as follows:

### Installation & Commissioning

Day 1	September 8	Equipment arrival on site
Day 2-3	September 9-10	MERCEM analyzer commissioning
Day 4-7	September 11-14	Analyzer optimization and fine-tuning

### Phase I Performance Testing

Day 4-11	September 11-18	First 7-day calibration and zero drift test
Day 8	September 15	First calibration error test
Day 9-10	September 16-17	First relative accuracy test
Day 11-41	September 18- October 18	Operational testing
Day 31	October 8	Mid-Operational testing period inspection

### Phase II Performance Testing

Day 42-46	October 19 - 23	Second 7-day calibration and zero drift test
Day 43	October 20	Second calibration error test
Day 45	October 22-23	Second relative accuracy test
Day 46	October 24	Interference response testing
Day 47	October 25	Decontamination and decommissioning
Day 57	November 4	MERCEM analyzer shipped from facility

## **MERCEM Installation and Commissioning**

A major issue that arose during installation and commissioning was the potential for transient spikes of mercury to be released into the flue gas during the feeding of bulk solids in discrete charges introduced by the ram feeder system for the rotary kiln. Although the feed operating conditions were within hourly and daily limits established in regulatory approvals, the temporarily elevated stack concentrations on occasion over-ranged the MERCEM and required manual intervention for recovery and resumption of reliable unattended operation. A decision was made to operate only with liquid waste during the first relative accuracy test and to leave the MERCEM in standby when feeding solids containing more than 1 µg/g of mercury during the four weeks before the second relative accuracy test.

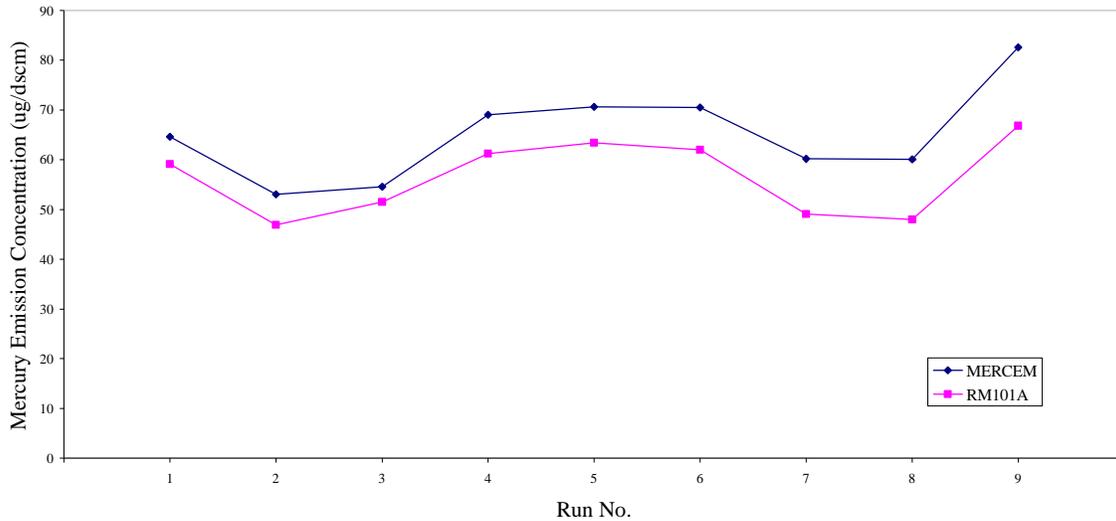
## **Phase I Performance Test Results**

### ***Calibration Error, Calibration Drift and Zero Drift Tests***

The interpretation of calibration error test results was made complicated by uncertainty in reference values for mercury calibration gas. Except for that uncertainty, the results appeared sufficiently consistent to reveal no other issue in assessing performance against PS12 guidelines. Likewise, the interpretation of calibration drift results was complicated by uncertainty in reference values for mercury calibration gas. The interpretation of zero drift results was complicated by uncertainty in a final emission limit value that may be proposed by EPA. The calibration drift results for the Phase I period with the response factor applied ranged from -4.8 to +8.8% at a concentration of 72.9 µg/m<sup>3</sup> and ranged from -8.2 to +7.2% at a concentration of 47.2 µg/m<sup>3</sup> both based upon an emission limit value of 50 µg/m<sup>3</sup>.

### Relative Accuracy Test

During the first relative accuracy test, the incinerator was operated only with liquid wastes being fed to the secondary and aqueous waste feed systems. Results from the first relative accuracy test are summarized in Fig 4. The calculated relative



accuracy for the first performance test was 20%, which is considered acceptable by PS 12.

Fig 4. Trend of MERCEM and Method 101A measurements during Phase I performance test while feeding liquid wastes only.

Both sets of measurements were corrected to 7%O<sub>2</sub>. The average mercury concentration measured by Method 101A was 56 µg/dscm while the MERCEM data averaged 65 µg/dscm. As seen from the graph, the MERCEM data was biased high but trended the Method 101A results very well.

### Operational Test Results

The MERCEM remained installed and collecting data intermittently during the four weeks between each performance test to provide a qualitative assessment of long-term operational issues. There were significant periods during which bulk solids being fed to the incinerator were greater than the conservatively established control point of 1 µg/g of mercury and the MERCEM was placed in standby.

Adjustments to the probe backpurging frequency (with instrument air) were refined as a result of this site specific operating experience. In addition, the programmed threshold value which automatically placed the MERCEM in standby in the event of a significant excursion was also optimized. To minimize the potential for this type of interruption, a 1.5 liter accumulator was evaluated to address the spiking nature of the mercury concentrations while feeding solid wastes.

### Phase II Performance Test Results

#### Interference Response Test

According to PS12, percent interference is calculated as a difference in response while measuring a reference concentration with and without the interference gas present relative to a reference value. With uncertainty in establishing a reference value, it may be as valid to redefine percent interference more simply as a percent change in response while measuring a level of mercury not intentionally varied. This approach is consistent with reporting of data from the EPA demonstration (11). Interference response testing results totaled 7.04% change (absolute).

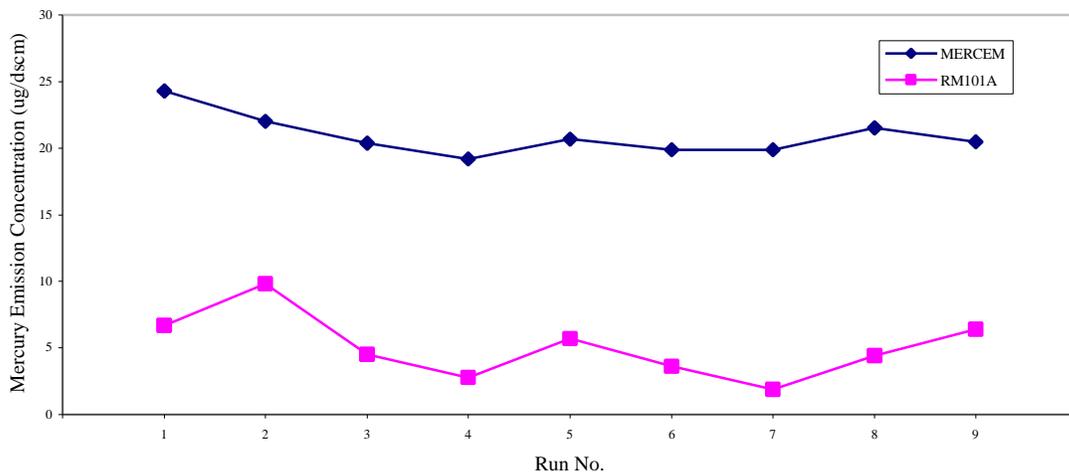
#### Calibration Error, Calibration Drift and Zero Drift Tests

Again interpretation of results was made complicated by uncertainty in reference material values and in the final emission limit that might be proposed by EPA. The calibration error tests did confirm the integrity of the entire sampling system

with zero gas deviations about  $2 \mu\text{g}/\text{m}^3$  and other measurements in range of 2% of the nominally prepared reference concentrations. Due to limited quantities of calibration gases, a full set of tests were not conducted during Phase II so as to preserve sufficient quantities in each cylinder for post test wet chemistry re-analysis.

### Relative Accuracy Test

During the Phase II performance test, the incinerator was operated with organic liquid waste and containerized solids being fed to the rotary kiln. Results from the second test are summarized in Figure 5. A lower level of mercury emissions in the second performance test proved to be a more challenging set of conditions than experienced in the first test. The average emission level measured by Method 101A was  $5 \mu\text{g}/\text{dscm}$  while the MERCEM reported an average of  $21 \mu\text{g}/\text{dscm}$ . As in



the first test, the MERCEM data was biased high compared to the reference method values. The relative accuracy for the

Fig 5. Trend of MERCEM and Method 101A measurements during Phase II RATA performance test while feeding liquid and containerized solid wastes.

MERCEM was determined to be 339% compared to the reference method. An evaluation of the feed and operating data revealed that the MERCEM results were in close agreement with emission calculations assuming 100% partitioning of mercury in feeds to the stack gas. The results could indicate a potential bias of the reference method at low concentrations or merely be a coincidence from assignment of discrete values to parameter measurements with underlying uncertainty. The formal report presenting more thorough project details is currently in preparation (12).

### CONCLUSIONS

The two month evaluation of the MERCEM total mercury monitor from Perkin Elmer provided a useful venue in determining the feasibility of using a CEMS to measure total mercury in a saturated flue gas.

The MERCEM exhibited potential at a mixed waste incinerator to meet requirements proposed in PS12 under conditions of operation with liquid feeds only at stack mercury concentrations in range of proposed MACT standards.

Reliable performance under conditions of incinerating solids was not demonstrated for the operating conditions and configuration of the host facility. The reliability of available reference materials, particularly mercury calibration gas in cylinders, was not fully demonstrated to support, without further evaluation, their incorporation into routine procedures performed by operating facility personnel. It was possible to conduct the demonstration at a facility incinerating radioactively contaminated wastes and to release the equipment for later unrestricted use elsewhere.

Experience gained by this testing of CEMS at the TSCA Incinerator answered additional site-specific and general questions regarding the operation and maintenance of CEMS and their use in compliance monitoring of total mercury emissions from hazardous waste incinerators.

## REFERENCES

1. Environmental Protection Agency, *Federal Register*, "Revised Standards for Hazardous Waste Combustors," 61 FR 17358, April 19, 1996.
2. Burns, D.B.; Rauenzahn, H.S.; Stevens, F.M. "Joint EPA/DOE Demonstration Program for Total Mercury Continuous Emissions Monitors," 90th Air & Waste Management Association Annual Meeting and Exhibition, Toronto, Ontario, June 8-13, 1997.
3. Department of Energy, "Demonstration of Emerging Continuous Emissions Monitoring Technologies," Office of Technology Development, Technical Task Plan No. SR-17-C2-31, Rev. 1, May 5, 1998.
4. Environmental Protection Agency, April 19, 1996.
5. Institut für Umweltschutz und Energietechnik, *Report on the Aptitude Test of the Total Mercury Measuring Device "MERCER" Bodenseewerk Perkin-Elmer GMBH, Meersburg*, TUV Report No.:936/805012, Cologne, April 25, 1996.
6. Environmental Protection Agency, *Code of Federal Regulations*, 40 CFR 60, Appendix B, EPA Test Method 101A, "Determination of Particulate and Gaseous Mercury Emissions from Stationary Sources."
7. Environmental Protection Agency, *Site Specific Quality Assurance Test Plan, Total Mercury CEMS Demonstration, Holnam, Inc., Holly Hill, South Carolina Facility, Volume 1, Revision 1*, Office of Solid Waste, Arlington, Virginia, October 11, 1996.
8. Environmental Protection Agency, *Code of Federal Regulations*, 40 CFR 60, Appendix A, EPA Test Method 29, "Determination of Metals Emissions from Stationary Sources."
9. Environmental Protection Agency, *Federal Register*, "Revised Technical Standards for Hazardous Waste Combustion Facilities," 62 FR 24212, May 2, 1997.
10. Environmental Protection Agency, *DRAFT Mercury Continuous Emissions Monitor System Demonstration, Volume I: Holnam, Inc., Hazardous Waste Burning Kiln, Holly Hill, SC*, Office of Solid Waste and Emergency Response, Washington, D.C., March 1998.
11. Environmental Protection Agency, *Total Mercury CEMS Demonstration, Holnam, Inc., Holly Hill, South Carolina Facility, Draft Report, Revision 2, Volume 1*, Office of Solid Waste, Arlington, Virginia, April 8, 1997.
12. L.V. Gibson, Jr., J.E. Dunn, Jr., R.L. Baker, W. Sigl and I. Skegg, *Field Evaluation of Perkin Elmer MERCER System at Oak Ridge TSCA Incinerator*, in preparation.