EM TASK 24 – DEVELOPMENT OF AN IN SITU INSTRUMENT FOR MEASURING MERCURY IN A GAS STREAM

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TASK 24 – DEVELOPMENT OF AN IN SITU INSTRUMENT FOR MEASURING MERCURY IN A GAS STREAM

1.0 INTRODUCTION

As part of its overall Environmental Management Program, the U.S. Department of Energy (DOE) has developed thermal and incineration processes for treating hazardous mixed wastes. These mixed wastes often contain mercury that is released into the atmosphere during the incineration process. The U.S. Environmental Protection Agency (EPA), as well as many states, clearly views mercury emissions from incinerators and combustion systems as a potential human health problem (1). Although validated batch measurement methods such as EPA Method 29, the Ontario Hydro mercury speciation method, and EPA Method 101A exist for total and speciated mercury, they are difficult and costly to perform. In addition, the data are not available for use until several days later. Continuous emission monitors (CEMs) are a very attractive option because the data are in near real-time, allowing the data to be used as feedback control for mercury control strategies. Also, a properly designed analyzer should require minimal operator input. However, based on the current state of the art, mercury CEMs are not without problems, as demonstrated in recent field tests (2). In addition, they are often bulky and costly to purchase.

Sensor Research and Development Corporation (SRD) was contracted by DOE's National Energy Technology Laboratory (formerly the Federal Energy Technology Center [FETC]) to develop a prototype instrument for thermal treatment process continuous emission monitoring applications. The work by SRD for DOE on the mercury CEM was conducted under two different contracts. Work under the first contract began October 1, 1997, and ended June 2000, with a second contract continuing until June 2001. The SRD process has the potential to be the basis for a very low-cost mercury CEM. The initial cost estimates provided by SRD are an order of magnitude lower than any other proposed mercury CEM. Although the instrument will be low-cost, it still has the potential to detect low limits of mercury and, therefore, has a wide range of possible uses. In addition, the instrument will be very portable.

The underlying technology upon which this project is based can be categorized as microwave acoustics. A high-frequency surface acoustic wave (SAW) delay line is coated with a thin sorbent film. Gaseous mercury that comes into contact with this film is absorbed through amalgamation. The resulting perturbations to the electrical and mechanical properties of the film then cause a corresponding change in the SAW velocity. By configuring the device into a radio frequency (RF) oscillator, these velocity perturbations are manifested as alterations in the oscillation frequency. The entire device is solid state, with simple RF electronics and frequency counters. Therefore, the technology has an immediate advantage over other available technologies that typically rely upon more expensive and less robust atomic absorbance or fluorescence spectrophotometric techniques. The oscillation frequency is sensitive to several properties of the substrate, including the following:

- Coatings or films on its surface
- Mass
- Elasticity (stiffness)
- Electrical conductivity
- Surface temperature

A schematic showing the basic premise of the SAW device is shown in Figure 1. Figure 2 is a photograph showing the very small size of the device.

As part of the Environmental Management Cooperative Agreement with DOE, the Energy & Environmental Research Center (EERC) was asked to be a consultant to SRD to provide it with information to help it design, build, and test a prototype instrument that will be as versatile as possible. Also, the EERC was to help SRD understand the types of problems that can occur in measuring mercury in gas streams such as those produced from thermally treating mixed wastes or incinerating hazardous waste materials.

2.0 OBJECTIVES

As part of its Environmental Management Cooperative Agreement with DOE, the EERC was asked to serve as a consultant to SRD. The overall goal of the project (for both SRD and the EERC) is to provide an inexpensive, reliable analyzer that can measure total mercury under a variety of flue gas conditions. There are four specific objectives for EERC participation in the project:

- Provide SRD with information to help it design and build a prototype instrument that will be as versatile as possible.
- Help SRD understand what types of problems can occur in measuring mercury in gas streams such as those produced from thermally treating mixed wastes or incineration of hazardous waste materials.

Figure 1. Schematics illustrating the basic operation of the SAW sensor.

Figure 2. Photograph of the SAW sensor illustrating size.

- Systematically test the prototype instrument at both the bench- and pilot-scale level.
- Help SRD locate potential field demonstration sites.

3.0 APPROACH

The approach to proving the SRD technology was twofold. First was the developmental work being done by SRD. Once a prototype instrument was completed, testing was done at the EERC.

3.1 Summary of the SRD Development Work

The SRD work over the past several years has focused on optimizing the device's operational parameters for the application requirements and on constructing a prototype instrument to be tested in several field locations. Parameters such as film thickness and operating temperature were varied in order to optimize the device's response to gaseous mercury and mercuric chloride in the low parts per billion ($\mu\text{g}/\text{m}^3$) range. Advantages and disadvantages in all operational and functional aspects were carefully weighed in the selection of these operating parameters. Further device-oriented engineering efforts were focused on precise temperature control of the sensing element.

One of the first criteria for SRD was to design and construct a custom RF electronics package with an integrated heating element, along with the incorporation of precise temperature transducers on the SAW device. These units were required to have the ability to operate and maintain the sensing element within 0.03°C of its prescribed operating temperature.

The first prototype instrument based upon this technology included a gas sampling and filtration system, complete with a prefilter pressure transducer and backflushing capability, as well as all necessary sensor support, control, display, communications, and data logging instrumentation. However, after the initial bench-scale testing was done, it was clear that additional development work was necessary.

Using the results obtained from previous tests, an instrument was built that allows simultaneous testing of up to four SAW dual-delay-line sensors. Each sensor element has independent temperature control, and since much of the testing required can be done with a single SAW delay line, rather than with a dual-delay line setup with a reference channel, up to eight sensing films can be used. Labview software controls the operation of the sensors such that the eight SAW delay lines can be used either sequentially or simultaneously to measure mercury emissions. In addition, a preconcentrating step was added. In this way, the sensitivity of the instrument was improved. A photograph of the new instrument in operation during the EERC test is shown in Figure 3.

3.2 EERC Program

The bench-scale test rig used by the EERC was designed so that almost any gas can be added to the system. This includes both elemental and HgCl_2 vapor. Depending on the nature of the gas and the process, either or both of these mercury vapors can be produced. Gold-mercury amalgam techniques such as those used in the SRD instrument may give different results, depending on the design of the instrument and the other constituents in the gas stream. Therefore, it was important to test the instrument using both mercury species. A schematic of the bench-scale system is shown in Figure 4.

The gases and concentrations to be used for the simulated flue gas that was to be tested by the SRD instrument are shown in Table 1. The full factorial design test matrix is shown in

Figure 3. A photograph showing the new instrument in operation during an EERC test.

Figure 4. Schematic of the EERC bench-scale test rig.

Table 1. Gas Concentration for Original Bench-Scale Tests

Gas	Concentration
O ₂	5%
H ₂ O (vapor)	10%
CO ₂	15%
Hg ⁰	50 µg/Nm ³
HgCl ₂	50 µg/Nm ³
SO ₂	0 or 500 ppm
NO/NO ₂	0 or 600/30 ppm
HCl	0 or 500 ppm
Organics ^{1,2}	0 or 5 ppb of each organic
N ₂	Balance

¹ An example of an organic gas stream is Scott Speciality Gases Blend 3. This gas contains contains 100 ppb each of benzene, toluene, *o*-xylene, chlorobenzene, and *m*-dichlorobenzene.

² 100 ppb in the cylinder will result in ~5 ppb of each in the bench-scale gas stream.

Table 2. Both a Semtech Hg 2000 and a PS Analytical Sir Galahad mercury CEM were used for comparison. Both of these instruments have been shown to give accurate results in previous bench-, pilot-, and full-scale tests (3). However, as will be discussed in Section 4, the SRD instrument was unable to complete this testing as a considerable amount of development work needed to be done.

It was originally planned that pilot-scale tests would be completed once the bench-scale tests were successful. Because of the problems encountered, a new bench-scale test plan was developed. The tests are shown in Table 3. This test series was eventually pared down so that the final bench-scale tests included a series of spikes (e.g., gold trap) measurements and continuous sampling, starting with just O₂, CO₂, and H₂O and then continuing with the acid gases (SO₂ and NO_x).

It is now known that an interaction between HCl and NO_x results in erroneous mercury results for any mercury CEM that uses gold amalgam to collect the mercury (3). The SRD instrument uses a thin gold film to catch the mercury on its SAW chip. It is highly likely that the ability of the SAW device to accurately measure mercury will be greatly diminished if HCl and NO_x are present in the gas stream. Both of these gases are present in most types of combustion systems, whether fossil fuel or mixed-waste incinerators. Therefore, it is expected that some type of preconditioning treatment for the gas stream will be necessary before the SRD instrument can be used.

During the past several years, the EERC has been working on such a pretreatment system. The pretreatment cell is able to remove the HCl and reduce Hg²⁺ to Hg⁰ without removing any mercury from the gas stream. In this way, a mercury CEM can be used to speciate mercury by difference. A schematic of the pretreatment system is shown in Figure 5. A solid alkali-based sorbent is used to remove the acid gases (HCl and SO₂), and stannous chloride solution is then used to convert Hg²⁺

Table 2. Bench-Scale Test Matrix to Evaluate the SRD Mercury CEM

Test No	SO ₂	NO/NO ₂	HCl	Organics
1	500	600/30	500	5
2	0	600/30	500	5
3	500	0	500	5
4	0	0	500	5
5	500	600/30	0	5
6	0	600/30	0	5
7	500	0	0	5
8	0	0	0	5
9	500	600/30	500	0
10	0	600/30	500	0
11	500	0	500	0
12	0	0	500	0
13	500	600/30	0	0
14	0	600/30	0	0
15	500	0	0	0
16	0	0	0	0

to Hg⁰. Once the pretreatment system was built and the next generation of SRD mercury analyzer was built, a new bench-scale test program was completed at the EERC. The pretreatment system was used as part of these tests.

4.0 RESULTS AND DISCUSSION

4.1 Test Series I

In November 1999, the first attempt was made to complete the bench-scale tests. However, several problems occurred that prevented the test matrix from being completed. The most serious problem was that the SRD mercury CEM was damaged during shipping. Attempts were made to fix the problems; however, the measurements were extremely variable and inaccurate. It was decided that some modifications to the instrument to improve its sensitivity would be made and that SRD would then return to the EERC to complete the test matrix. The first modification was to reduce the sample volume, and the second was to provide a complete second set of SAW devices to the instrument (measurement and reference). Prior to shipping the CEM to the EERC, the instrument was calibrated using dry N₂ and Hg⁰. It appeared that both sensors were responding with minimum detection of <1 ppb.

Table 3. Systematic Interferent Testing¹

Test	O ₂ , %	CO ₂ , %	H ₂ O, %	SO ₂ , ppm	NO, ppm	NO ₂ , ppm	Hg ⁰ , ppm
1				Nitrogen only			
2	0	0	0	0	0	0	80
3				Nitrogen only			
4	0	0	0	50	0	0	0
5	0	0	0	50	0	0	80
6				Nitrogen only			
7	0	0	0	100	0	0	0
8	0	0	0	100	0	0	80
9				Nitrogen only			
10	0	0	0	250	0	0	0
11	0	0	0	250	0	0	80
12				Nitrogen only			
13	0	0	0	500	0	0	0
14	0	0	0	500	0	0	80
15				Nitrogen only			
16	0	0	0	0	50	0	0
17	0	0	0	0	50	0	80
18				Nitrogen only			
19	0	0	0	0	100	0	0
20	0	0	0	0	100	0	80
21				Nitrogen only			
22	0	0	0	0	250	0	0
23	0	0	0	0	250	0	80
24				Nitrogen only			
25	0	0	0	0	500	0	0
26	0	0	0	0	500	0	80
27				Nitrogen only			
28	0	0	0	0	0	30	0
29	0	0	0	0	30	80	
30				Nitrogen only			
31	5	0	0	0	0	0	0
32	5	0	0	0	0	0	80
33				Nitrogen only			
34	0	15	0	0	0	0	0
35	0	15	0	0	0	0	80
36				Nitrogen only			
37	0	0	10	0	0	0	0
38	0	0	10	0	0	0	80

¹For all tests, the balance gas is nitrogen.

Figure 5. Schematic of the EERC pretreatment/conversion system.

4.2 Test Series II

The next attempt to do systematic bench-scale testing (as outlined in Table 2) at the EERC was in March 2000. However, during the first test, designed to establish a baseline with dry N_2 and an Hg^0 concentration of 5 ppb, it was clear that the CEM had very poor sensitivity. In addition, there was a factor of about 1.8 difference in calibration when comparing the EERC tests to those performed at the SRD facility. The source of that error was later determined to be an incorrect flow rate measurement at SRD. Although the bench-scale tests could not be completed as planned, SRD did several other bench-scale tests as part of the instrument development effort. These included testing two separate sensor packages in the presence of high concentrations of a variety of interfering gases. Testing was performed without any pretreatment of the gas stream and presented the CEM with a challenging environment. Initial exposure of the sensors to the base gas (5% O_2 , 15% CO_2 , 10% H_2O vapor, balance N_2) caused some erratic behavior in the output, reducing overall sensitivity to mercury by about 50%.

Next, SO_2 was added to the mixture at a concentration of 500 ppm (100,000 times the Hg concentration). This concentration of SO_2 caused a relatively large negative response and had an apparent long-term poisoning effect on the gold film. A similar response was observed upon exposure to high concentrations of NO , although SO_2 poisoning from the previous exposure rendered these data inconclusive. Likewise, because of this poisoning effect, introduction of organic vapors following delivery of the above gases also gave inconclusive results.

The second sensor platform was set up and exposed to a concentration of 500 ppm HCl , another extremely acid gas. Again, the sensor demonstrated a relatively large negative response and appeared to be poisoned.

The data collected through these tests proved to be extremely valuable. Previous testing at SRD had shown the effects of NO and SO₂ to be negligible. However, these tests were performed with relatively high mercury concentrations (50 ppb) under low-humidity conditions. Results obtained at EERC indicate showed that these gases were problematic for the sensing element. Therefore, it became evident that a gas pretreatment system was necessary. Also, the EERC suggested to SRD that some form of preconcentrating of the mercury may help improve instrument sensitivity. This was done using an inverse dilution approach. The mercury was adsorbed on a gold trap, and the exact flue gas flow rate in and out of the trap was measured. The mercury was then thermally desorbed from the trap and recaptured on the SAW gold film and measured.

SRD then proceeded to do additional development work and testing of the CEM at its facility. SRD developed an interface to the EERC preconditioning unit. As part of the development work, SRD decided to use the CEM in two monitoring modes. The first is to preconcentrate the mercury onto a gold trap and then desorb it to the instrument (spiking mode). The advantage is that instrument sensitivity is greatly enhanced. However, sampling becomes less real time compared to the second mode, continuous sampling.

4.3 Test Series III

In April 2001, the final test series at the EERC was completed using both modes of monitoring. The first test series completed was a series of spike (e.g., gold trap) measurements using the preconcentration system developed by SRD. The second test series was continuous sampling directly from the preconditioner. These tests started with just O₂, CO₂, and H₂O followed by tests with the acid gases (SO₂, HCl, and NO_x).

4.3.1 Spiking Mode

A series of mercury spikes ranging from 5 to 35 ng was loaded onto gold traps both directly from permeation tubes (i.e., traps were loaded with Hg⁰ only with N₂ as the carrier gas) and from the output of the sampling and preconditioner systems (traps loaded with Hg⁰ with the actual test gas used as a carrier). Figures 6 and 7 compare the results obtained by the SAW sensors and the Semtech mercury CEM.

The shift in frequency of the SAW sensor is used to obtain the mercury load on the gold trap from the calibration curve for each sensor. The Semtech CEM measurement is the average mercury concentration measured during the loading of the gold traps plotted against the frequency shift seen by the SAW sensors. As can be seen from these graphs, the results are in excellent agreement (within 5%). The results also indicate that, over a period of ~2 days, no poisoning effects were observed.

4.3.2 Continuous Mode

Following completion of the spike experiments, the SAW instrument was then coupled directly to the output of the EERC preconditioning system. The preconditioning system was set to run a Hg⁰ concentration of about 12 µg/dscm with only O₂, CO₂, H₂O, and N₂ flowing through the system. An immediate negative response was noted upon the introduction of a sample flow to the sensor.

Figure 6. A comparison of SAW Sensor 1 and the Semtech atomic absorption detector.

Figure 7. A comparison of SAW Sensor 2 and the Semtech atomic absorption detector.

Figure 8 gives a series of sensor responses as it was exposed initially (first three responses) to the preconditioned output. The slope was reduced from about 3000 to only 250 Hz/min. When all the test gases were added to the preconditioning system (O_2 , CO_2 , H_2O , N_2 , SO_2 , NO_x , and HCl), an additional reduction in slope was noted. As a result of the previous work, it was concluded that small amounts of interfering gas were exiting the preconditioning system and poisoning the sensors. Attempts were made to restore the sensors, but the poisoning was permanent.

The good results obtained previously from the spike tests indicated that the level of contaminants are sufficiently low as not to impact the results when using a preconcentration system. It appears that the large quantity of gold present in the gold trap compared to the gold film adsorbs the contaminants before they poison the gold film.

5.0 CONCLUSIONS AND RECOMMENDATION FOR FURTHER TESTING

It is clear that additional development work and testing are needed to fully understand the observations made during bench-scale testing. However, the second-generation prototype instrument appears to have potential. Although the system has become more complicated using preconditioning and preconcentration systems, the original advantages of the system remain. It should be a low cost and relatively portable instrument.

The following conclusions can be made based on the bench-scale tests that have been completed:

Figure 8. Frequency response of the SAW sensor during continuous sampling of the output from the UNDEERC preconditioner.

- The CEM has consistently detected Hg^0 concentrations of less than 5 ppb over exposure times of many hours in dry nitrogen (the original statement of work developed by SRD required detection of less than 200 ppb).
- Results to date show that the instrument can operate in the presence of some common stack gases (O_2 , CO_2 , organics, and H_2O). However, high concentrations of acid gases such as SO_2 and HCl have a negative effect on sensor response; therefore, a pretreatment system is necessary.
- HCl in particular appears to permanently poison the SAW device for mercury measurement.
- Additional testing is required to quantify the nonreversible effects of the acid gases.
- Pilot and/or full-scale testing is still needed.

6.0 REFERENCES

1. U.S. Environmental Protection Agency. *Mercury Study Report to Congress*; EPA-452/R-97-003, Dec 1997.
2. Rauenzahn, S. *Total Mercury CEMS Demonstration*; U.S. EPA Office of Solid Waste, Dec 1997.
3. Laudal, D.L.; Brown, T.D.; Chu, P. Testing of a Mercury Continuous Emission Monitor at Three Coal-Fired Electric Utilities. Presented at the Air & Waste Management Association's 92nd Annual Meeting & Exhibition; Paper 99-382, June 1999.