Semi-Annual Technical Progress Report

For the months of October, 1997 through March, 1998

Document Number: DE-AR26-97FT34316-002.12

Surface Acoustic Wave Mercury Vapor Sensor

Work Performed Under Contract:

DE-AR26-97FT34316

Issued: 2 June, 1998

Submitted By:

**Sensor Research and Development Corporation
5 Godfrey Road
Orono, Maine 04473**

Program Manager: Carl J. Freeman

Phone Number: 207-866-0100

Fax Number: 207/866-2055

Principal Investigator/Author: Joshua Caron

Phone Number: 207/866-0100

Fax Number: 207/866-2055

Submitted To:

**U. S. Department of Energy
Morgantown Energy Technology Center
Morgantown, West Virginia
COR: James Huemrich**

Disclaimer

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Abstract

Sensor Research and Development Corporation (SRD) has been contracted to develop and deliver a prototype instrument capable of the *in situ* detection and measurement of low levels of gaseous mercury for use in thermal treatment process control applications and continuous emissions monitoring. The goal is to develop a fast, simple, inexpensive and reliable *in situ* sensor instrument for detecting and monitoring vaporized mercury that should be able to react to extremely low (< 200 ppb) levels of mercury vapor, should be site deployable and provide continuous data on either cumulative mercury exposure or instantaneous concentration.

To date, a delivery system for gaseous mercury has been designed and constructed, sensor responses have been measured and analyzed for a wide range of sensing film thicknesses and operating temperatures, a microheater and temperature control circuitry and software have been designed and implemented, and a contract modification, which has received initial approval from DOE, to include measurement of total mercury (both in elemental and reacted forms) has been drafted.

Table of Contents

Executive Summary.....	4
Introduction.....	4
Results and Discussion	5
Gas Delivery System	5
Microheater Development	6
Gas Testing.....	7
Contract Modification.....	8
Conclusion	8
List of Acronyms and Abbreviations	9

Executive Summary

Sensor Research and Development Corporation (SRD) is currently undergoing a project to develop and deliver a prototype instrument capable of the *in situ* detection and measurement of low levels of gaseous mercury for use in thermal treatment process control applications and continuous emissions monitoring. The goal is to develop a fast, simple, inexpensive and reliable *in situ* sensor instrument for detecting and monitoring vaporized mercury that should be able to react to extremely low (< 200 ppb) levels of mercury vapor, should be site deployable and provide continuous data on either cumulative mercury exposure or instantaneous concentration.

The tasks embodied in the proposed work support the fundamental objective of achieving the design and fabrication of a prototype thermal treatment process control instrument for the detection and measurement of gaseous mercury. The work begins with the determination of the optimum operating temperature and film thickness for the sensing element. At this point, the sensing element will be designed and fabricated. Next, the sensing element will be rigorously tested in a laboratory environment to ensure that it meets certain reasonable success criteria. The next phase of the work involves the design and fabrication of a prototype instrument based around the mercury sensing element. When the instrument is completed, it will be tested in both the laboratory and in real-world applications to verify its operational capabilities.

Technical progress to date on the project include the following: A delivery system for gaseous mercury has been designed and constructed. Sensor responses have been measured and analyzed for a wide range of sensing film thicknesses and operating temperatures. A microheater and temperature control circuitry and software have been designed and implemented. A contract modification, which has received initial approval from DOE, to include measurement of total mercury (both in elemental and reacted forms) has been drafted.

Introduction

This technical report for the period of October, 1997 through March, 1998 is an update on the technical progress to date of SRD's project for the development and delivery of an instrument for *in situ* measurement of gaseous mercury in thermal treatment processing facilities. The underlying sensing mechanism for gaseous mercury is based upon surface acoustic wave (SAW) technology with a thin gold film. A SAW delay line is used as an ultrasensitive microbalance. By coating the delay line with a thin gold film and configuring it as an RF oscillator, mass changes in the film can be measured by monitoring the oscillation frequency. Because of gold's strong interaction with mercury (amalgamation), this configuration can be used to sensitively detect gaseous mercury. Mercury can be driven from the film by heating it to a high temperature. Furthermore, by operating the device at an elevated temperature, the reaction kinetics of mercury amalgamation and desorption can be balanced so that an equilibrium surface mass can be quickly realized. The oscillation frequency then becomes a direct measure of the instantaneous mercury concentration.

Results and Discussion

Gas Delivery System

The first major accomplishment of this project was the design and construction of a system for quickly delivering gaseous mercury at any desired concentration within the ranges specified in this contract (1 ppb to 1 ppm). The system was designed around a permeation oven containing multiple flow paths with various mercury permeation tubes. When held at a constant temperature, the permeation tubes outgas mercury at a known rate. By varying the flow rate of air across the permeation tubes, the concentration of mercury in this gas stream can be precisely controlled. Three different permeation tubes (with permeation rates of ~ 10 , ~ 100 and ~ 1000 ng/min at 100°C) are used so that concentration can be varied over three orders of magnitude with only a one order of magnitude dynamic range in the flow rate. A schematic of the gas delivery system is shown in Figure 1.

The system utilizes four flow paths through the permeation oven, each with a mass flow controller (MFC) to set the carrier gas flow rate. The oven is maintained at $100 \pm 0.1^\circ\text{C}$. The carrier gas in each path is channeled through a U-shaped glass tube within the permeation oven. One half of the U-tube is filled with glass beads to evenly heat the carrier gas as it enters. In three of the U-tubes the other half contains the permeation tube. The fourth U-tube is left without a permeation tube and is used to generate gas without mercury while mimicking the same temperature and pressure conditions as the other three channels. Two-way normally closed solenoid valves are placed in line with the gas stream on either side of each U-tube containing mercury. These valves are wired directly to the MFC circuitry so that they open automatically whenever a non-zero flow signal is given to the MFC. Otherwise, the valves remain closed. These prevent mercury from leaking from the U-tube when it is not in use or during a power outage. Downstream from each mercury-containing U-tube is a three-way valve which can direct the gas stream either into the system's gas manifold or out to the exhaust. In this way, a flow can be set up through one of the tubes for a few minutes before that gas actually is delivered to the sensor. This allows the high-concentration gas which has been sitting inside the U-tube to be purged out without passing it over the sensor. Thus, gas delivery can be quickly switched from among the three tubes without a disruption in flow or a concentration spike. A four-way valve is used downstream from the gas manifold to direct either the clean gas or the mercury gas over the sensor. The other gas, in either case, is directed out the exhaust.

Figure 1. Schematic of mercury gas delivery system.

Surface Acoustic Wave Mercury Vapor Sensor

In order to keep small temperature and pressure fluctuations from affecting the sensor response, the gas flow over the sensing element must remain at a relatively constant rate. Because of the gross flow variations required to generate wide ranges of concentrations, flow through the sensor is limited to 50 cm³/min using a mass flow controller downstream from the sensor. The excess gas is exhausted through a restricted opening upstream from the sensor. Eventually, this setup may be replaced with a sampling pump. A photograph of the mercury gas delivery system is shown in Figure 2.

Figure 2. Photograph of the mercury gas delivery system.

The permeation tubes within the mercury gas delivery system have been gravimetrically calibrated to within $\pm 5\%$ of their indicated permeation rate at $100 \pm 0.1^\circ\text{C}$. The MFCs are calibrated to within $\pm 2\%$ the flow setpoint. Since these are the only two parameters which grossly affect the gas concentration, the system delivers gas at concentrations quite close to the setpoint. In order to verify this, however, as well as get some measure of the dynamics of the delivery system, a cold vapor atomic fluorescence spectrophotometer will be placed just downstream from the sensor in the same gas stream. This instrument has been ordered and is due to arrive in April.

Microheater Development

Another major accomplishment of the work to date was the development of a serpentine microheater for precise temperature control of the SAW sensing element. The device is comprised of a 1 micron thick chrome meander line on a polished alumina substrate. It is suspended by wires within a hole in the RF electronics circuit board. Aluminum wires are then ultrasonically bonded to make from the circuit board to small bond pads on the heater in order to

make electrical contact. The SAW sensing element is then glued onto the top of the heater. This apparatus, together with a thermocouple glued to the SAW delay line surface, is capable of heating the sensing element to temperatures greater than 500°C and maintaining a constant temperature within $\pm 0.05^\circ\text{C}$. The entire apparatus is then sandwiched between two halves of a Telfon gas chamber with makes an airtight seal against the circuit board. A schematic of the setup without the gas chamber is shown in Figure 3.

Figure 3. Schematic of serpentine microheater apparatus.

Gas Testing

With the gas delivery system and testing apparatus in place actual gas testing was begun. Gold films of 50Å, 150Å, 500Å, 1000Å and 2000Å thickness were sputtered onto SAW devices with a 50Å tungsten adhesion layer. Each of these devices was exposed to 500 ppb mercury at temperatures ranging from 25°C to 400°C in 25°C increments (total of 16 different exposures for each of the 5 devices). Each test began with a quick temperature ramp to 500°C to drive any residual mercury out of the film. This temperature was maintained for 5 minutes, at which point the temperature was lowered to the desired setpoint (25-400°C). After 15 minutes of baseline measurement (no mercury), a 500 ppb gas stream was introduced. This gas concentration was injected for a period of twenty minutes, at which time clean air was reintroduced. Twenty more minutes of baseline were then measured. Thus, each test required one hour. The frequencies of both SAW delay lines were measured at 10 second intervals throughout each test. A few sample responses are plotted in Figures 4 and 5.

Figure 4. Response of a 500Å gold film to 500 ppb of mercury at 50°C. Notice there is a large response but relatively little recovery of the film after removal of the mercury at this low temperature.

Figure 5. Response of a 2000Å gold film to 500 ppb of mercury at 150°C. While the response magnitude is smaller than at lower temperatures, the film recovers to its original baseline after removal of the mercury.

The next major Task involving gas testing will begin after data from the first round of testing is analyzed, an appropriate film thickness and operating temperature are chosen, and a new sensing element and test apparatus are designed and constructed. Because the majority of the design and construction of the new apparatus does not require knowledge of the specific film thickness and operating temperature to be used, that portion of the work is presently ongoing. In the interim, further testing is being performed to investigate the effects of a chrome adhesion layer or no adhesion layer on the gold film. When operating temperature and thickness must be chosen in order for the design and construction effort to continue, the two parameters will be selected based upon all of the data collected up to that point (including the data from the adhesion layer tests). This added testing should allow a more optimal film composition/thickness/temperature choice without delaying any of the design and construction effort.

Contract Modification

In addition to the work already discussed, a modification to the existing contract is planned. The planned modification would extend the existing contract to include work on the detection and measurement of reacted mercury species (e.g. HgCl_2). Measurement of total mercury is much more relevant to DOE than measurement of only elemental mercury. The modified work plan has already been drafted and will be submitted to DOE in late April or early May.

Conclusion

Work to date, according to the work plan submitted in 9/97 remains on schedule. Work on Task 1 is essentially complete, other than making the choice of final film thickness and operating temperature. This choice will be made as required for the last steps of Tasks 2 and 3, which are continuing as planned. While the original schedule shows that Task 2 to be completed, the design and fabrication efforts are, in fact, concurrent operations and will start and end at approximately the same time. With the expected contract modification, several tasks will be affected, and some start/end dates may be altered. However, no problems or delays are foreseen completing either the original contract or the anticipated modification on time and within budget.

The original contract is to complete over the next six months the design, fabrication and operational verification of a new sensing element for elemental mercury. The expected contract modification, however, may affect this plan. The initial plan will be completed as contracted, with some additional work to be performed in order to create a sensing element for elemental mercury, as well as reacted species. The contract modification is expected to be approved in June and implemented in July.

List of Acronyms and Abbreviations

cm ³ /min	Cubic centimeters per minute
MFC	Mass flow controller
ng/min	Nanograms per minute
ppb	Parts per billion
ppm	Parts per million
RF	Radio frequency
SAW	Surface acoustic wave