Surface Acoustic Wave Continuous Emissions Monitor for Total Mercury

Joshua J. Caron (jcaron@srdcorp.com; 207-866-0100)
Sensor Research and Development Corporation
5 Godfrey Drive
Orono, ME 04473

Introduction

Mercury (Hg) is a ubiquitous environmental pollutant found in a variety of chemical and physical forms throughout the biosphere. Because it bioaccumulates, concentrations increase substantially moving up the food chain from plankton to insects to fish. Thus, mercury concentrations in eagles, loons, and other animals that eat primarily fish can be as much as a million times higher than the mercury concentration in the surrounding environment. Mercury is extremely toxic to humans and animals, adversely affecting the nervous system, even at relatively low concentrations. At high concentrations it can poison nearly every organ or system in the body. Furthermore, mercury is a teratogen, having much more pronounced effects on fetuses and developing children. Compounded with its bioaccumulative nature, mercury pollution has significantly disrupted reproduction in countless species, and has been shown to substantially affect reproductive health and neurological function in human societies where fish is a substantial part of the diet.

Waste incinerators (i.e. hazardous waste incinerators, municipal waste incinerators, medical waste incinerators, and sewage sludge incinerators) are among the most prolific anthropogenic emitters of mercury into the atmosphere. In order to better understand mercury emission sources, transport throughout the biosphere, and environmental and societal impacts continuous emissions monitors (CEMs) for mercury concentration measurements at each source are imperative. However, purchase and operating expenses associated with most commercially available CEMs are far too high for most emitters. Furthermore, commercially available instrumentation is typically based upon fragile atomic absorption or fluorescence spectrophotometry and lacks the robustness required for many CEM applications. Many doubt that use of this instrumentation by the myriad small- and medium-sized emitters will ever by economically feasible. Thus, new technology must be developed which is less expensive, simpler to maintain, and more robust.

Microwave acoustic devices, such as thickness shear mode (TSM) resonators and surface acoustic wave (SAW) delay lines, offer a promising new approach to detection of environmental pollutants. By incorporating a thin film which selectively chemically sorbs a target measurand (e.g. mercury), electrical and mechanical changes in the thin film are manifested as alterations in the resonant frequency of the acoustic wave device. Thus, by coating a SAW delay line with a gold film which efficiently sorbs mercury, a highly sensitive mercury vapor sensor can be realized.

Objective

The overall objective of this work has been to demonstrate the feasibility of a SAW mercury vapor sensor and to incorporate the technology into a prototype CEM for use in a hazardous waste incinerator.

Approach

In order to demonstrate feasibility, the sensing element had to be rigorously designed. This process included prolific empirical measurements in order to determine the most appropriate film and operating parameters (film thickness, adhesion layer, temperature) for detecting and measuring gaseous mercury, as well as a rigorous theoretical and empirical design process for the SAW delay line oscillator. With the sensing element designed and constructed, feasibility as a mercury sensor was to be assessed through a series of laboratory-based experiments wherein the oscillation frequency of the device was measured as a function of exposure to gaseous mercury.

Next, the sensing element was incorporated into a prototype CEM. In addition to two individual sensing elements, this instrument included the mechanical and electrical components for gas sampling, oscillator and frequency measurement electronics, temperature control electronics, a notebook computer with the user interface, and all other electronics and systems necessary for autonomous operation.

Early testing of the instrument indicated that the sensing elements could be fouled by acid gases. Therefore, the approach has been modified to incorporate a gas sampling and preconditioning system under development by the Energy and Environmental Research Center (EERC) at the University of North Dakota. This system is designed to remove SO_2, HCl, and water vapor from the incoming gas stream, thereby minimizing the poisoning effects of those gases.

Project Description

The technology embodied in this project is based upon a surface acoustic wave (SAW) dual delay line oscillator. The device consists primarily of a piezoelectric substrate, transducers which excite and measure an acoustic wave, a chemical sensing film which perturbs the acoustic wave in the presence of mercury, and radio frequency (RF) electronics (amplifiers, couplers, mixers, etc.) to sustain a measurable oscillation. The substrate, due to its piezoelectric nature, is mechanically strained by the application of an electric field. An interdigital transducer (IDT), a metallic structure on the substrate surface which resembles a ladder or comb, can therefore be used to electrically generate a mechanical wave which propagates across the surface of the substrate. A second IDT can be used to receive this mechanical wave and convert it back into an electrical signal. This structure is called a delay line. By amplifying the output electrical signal and feeding it back into the input, a circuit is realized which self-oscillates at the resonant frequency of the device. This resonant frequency is determined primarily by the velocity of the mechanical wave across the surface of the substrate. By placing a material across the substrate which alters the velocity of the propagating wave, the resonant frequency of the device changes, thereby changing the frequency at which the circuit oscillates. Furthermore, after this material is in place, the circuit will continue to be sensitive to electrical and mechanical perturbations to that material which can continue to alter the surface wave velocity. Thus, by depositing a film (i.e. gold) which sorbs mercury onto the surface of the device, a mercury sensor is realized. Sorption of mercury adds mass to the film, elastically stiffens the film, and decreases electrical conductivity, all of which change the acoustic wave velocity and are, therefore, manifested as changes in oscillation frequency. Inclusion of a second delay line oscillator on the same substrate without a sensing film allows other extraneous effects (e.g. temperature changes) which can alter oscillation frequency of both delay lines to be cancelled out. A schematic of the device is shown in Figure 1. A photograph is shown in Figure 2.

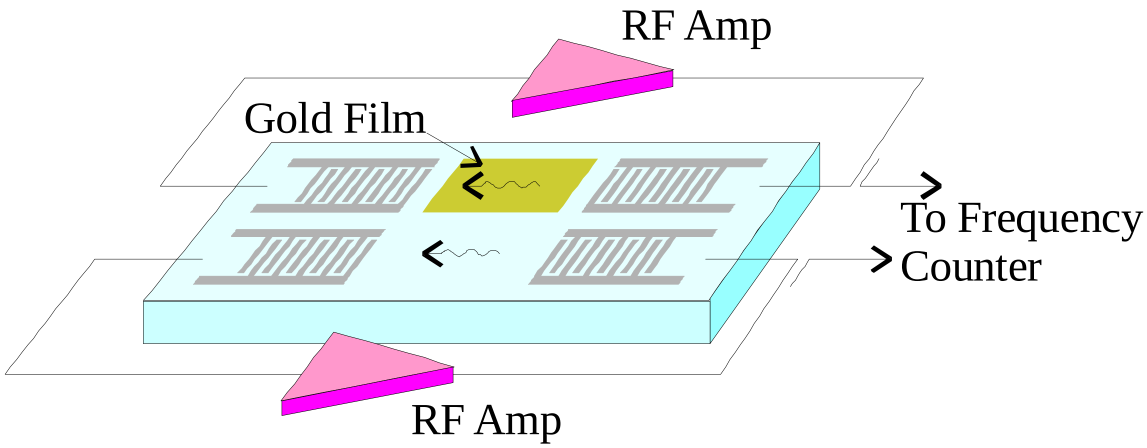

Figure 1. The dual delay line SAW mercury sensor consists of a reference delay line (bottom) and sensing delay line (top) coated with a gold film.

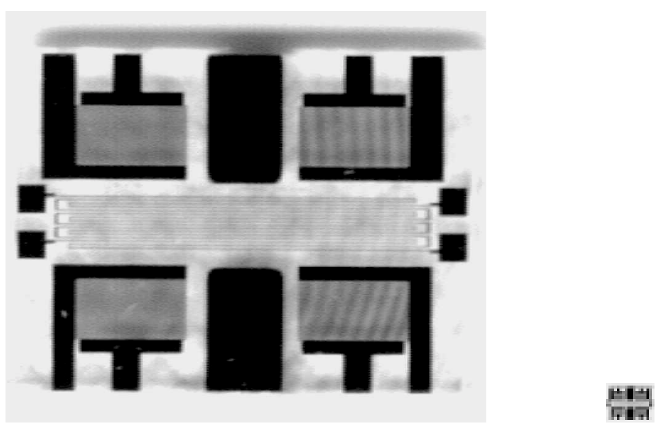

Figure 2. Micrograph of the sensing element. The device is shown actual size on the right.

Feasibility of the technology for the detection of gaseous elemental mercury has already been demonstrated and documented in previous papers[1]. Therefore, the next step was to integrate the device into a self-contained prototype CEM. The instrument was designed to utilize two SAW sensors, operated alternately such that one collects mercury while the other is purged. Upon saturation of the first device, the operation is switched so that the second device takes over

[1] See, for example, J. Caron and R. Wright, “Continuous Emissions Monitor for Total Mercury Based Upon Surface Acoustic Wave Technology”, Federal Energy Technology Center, United States Department of Energy, Proceedings of the 1999 Industry Partnerships to Deploy Environmental Technology Conference, http://www.netl.doe.gov/publications/proceedings/99/99em/caron.pdf

measurement of mercury, while the first device is purged. Upon saturation of the second sensor, the operation is switched back, the now-regenerated first sensor again collects mercury, and the process repeats.

Because mercury and, especially, compounds thereof can be quite "sticky" at low temperatures, the majority of the wetted parts in the system were designed to be heated to 200°C. This requirement, as well as the desire for zero dead space within the flow path, dictated the use of a reversible pump to extract a gas sample, rather than a system of solenoid valves. A schematic of the instrument is shown in Figure 3.

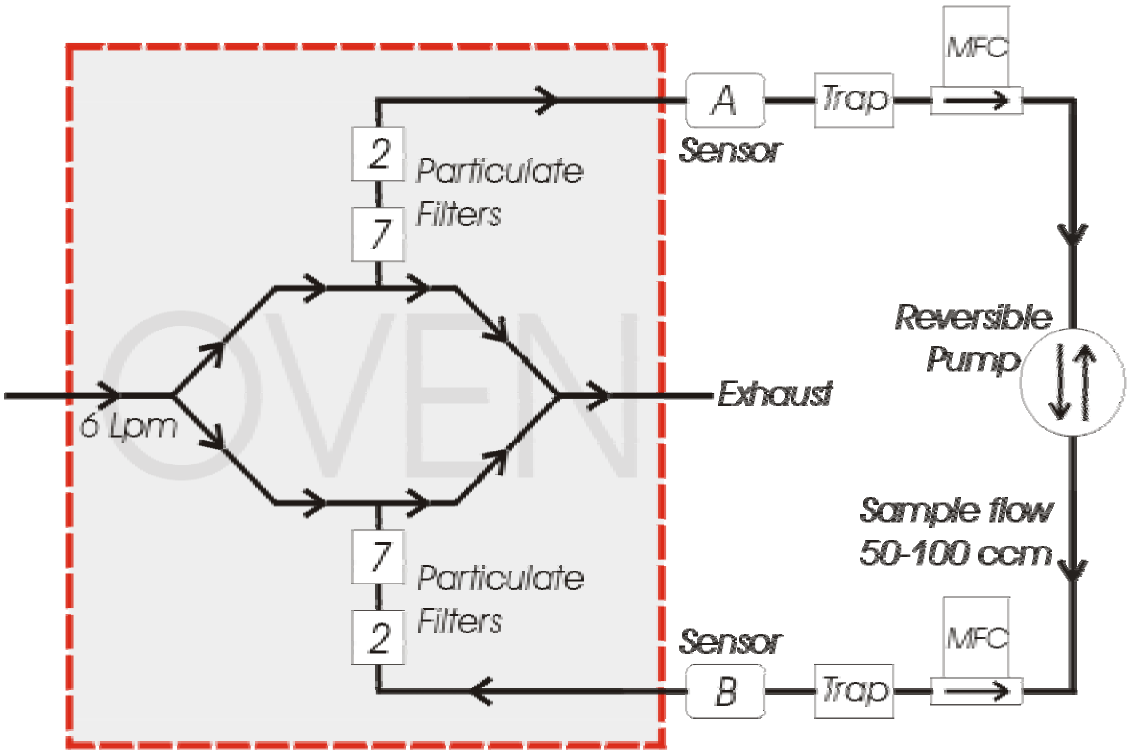

Figure 3. Schematic of the prototype mercury CEM.

As mentioned previously, the majority of the wetted parts in the system are designed to be heated. This section is shown in the schematic inside a gray box, designated "OVEN". Gas is sampled through the inlet at the left at a relatively high flow rate (several liters per minute). The flow is split into two paths (to minimize recycling of the gas through the sensors) and then reconverges and is exhausted through a carbon trap. From this gas flow, a closed-loop slip stream is sampled through some particulate filters at 50-100 cm^3/min. Depending on the direction of flow through the pump, either one of the sensors can be exposed to mercury while the other is purged. Carbon traps just downstream from each sensor remove mercury and prevent contamination of the mass flow controllers and pump, and they ensure that only mercury-free gas flows by the sensor which is being regenerated. Flow control, data acquisition, signal processing, and the user interface for the instrument are all handled by a notebook computer.

Results

Figure 4 shows a plot of the instrument's output for a varying concentration of elemental mercury. The dark solid line represents the delivered concentration, and the thin line is the output from the CEM.

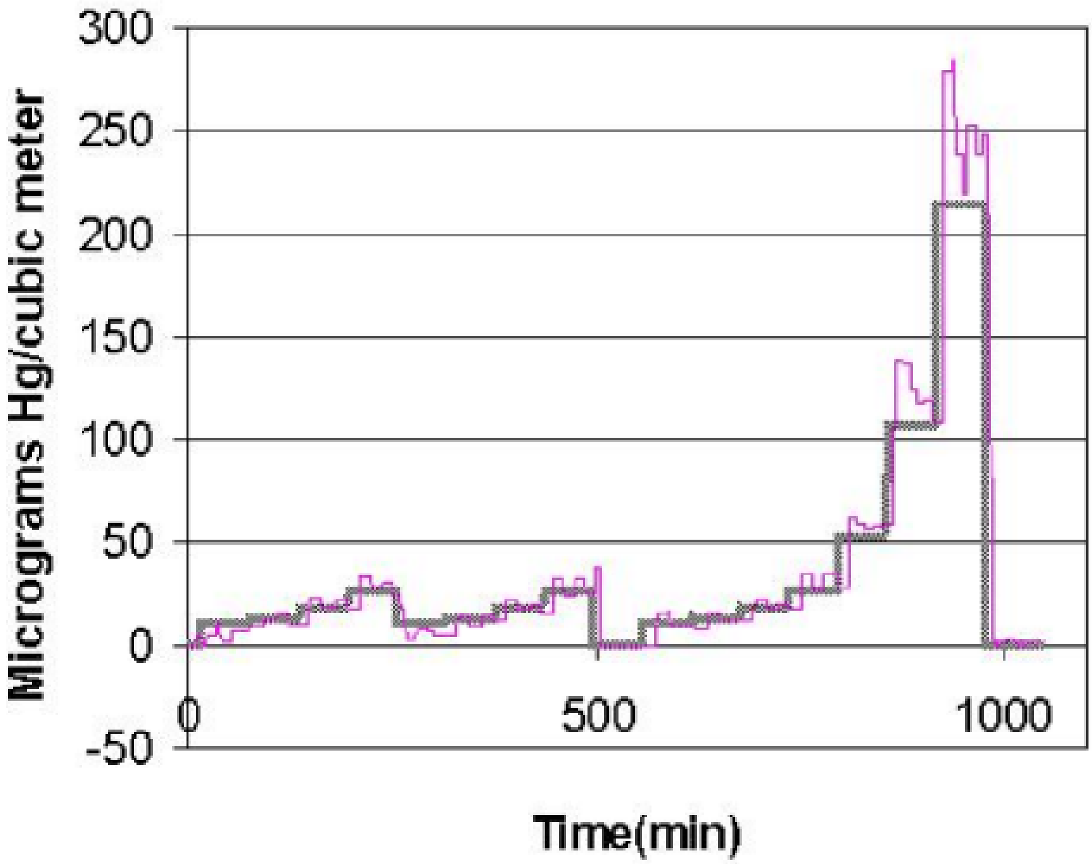

Figure 4. Measured CEM output (thin line) as compared to actual delivered concentration (thick line) of elemental mercury.

Though there is certainly some variability in the CEM output, and the reading is less accurate for higher concentrations, this initial data is very encouraging. It demonstrates that such an instrument is capable of not only detection, but also quantification of gaseous mercury.

Although the instrument showed promise for use in a laboratory environment, it was important next to determine how the instrument would perform in the real world. The first step in this process was to test the instrument with a variety of interferent gases. Many of the gases typically present in a thermal waste treatment exhaust stack were shown to have no adverse effects on the sensor performance. However, upon exposure to high concentrations of hydrochloric acid (HCl), a gas often found in incinerator exhaust streams, the sensor was severely poisoned. It was therefore determined that a gas preconditioning system would have to be included to remove this and other acid gases.

Such a preconditioning system is under development by researchers at the Energy and Environmental Research Center (EERC) at the University of North Dakota. Their system is designed to remove HCl, sulfur dioxide (SO_2), and water vapor. Furthermore, the system can be used to remove reacted mercury species (thereby only allowing the sensor to see that portion of the input which was elemental) or to reduce all species to elemental mercury (thereby allowing measurement of total mercury). The combination of these two features allows speciation by difference.

Benefits

The major advantage of the instrument under development over current CEM technology is cost. Both initial purchase cost and maintenance costs are expected to be significantly lower than those associated with currently commercially available technology. In addition, the small size and solid-state nature of the sensing element make it a good candidate for a truly portable CEM.

Future Activities

Development of the aforementioned gas preconditioning system at EERC is nearly complete, and integration into SRD's SAW mercury CEM will follow. The combination will then be rigorously tested to verify operation in gas streams containing HCl and other potential interferents. A calibration procedure will be developed for the instrument, and eventually it will be tested in a real thermal waste treatment environment.

Acknowledgements

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