Continuous Emissions Monitor for Total Mercury Based Upon Surface Acoustic Wave Technology

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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. While such CEMs have been used for several years in Europe, 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 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 elemental mercury and mercuric chloride ($HgCl_2$), 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, as well as several potential interferent gases. Incorporation of the sensing element into a prototype CEM is the next major objective. Accomplishing this involves several sub-objectives, including designing an adequate gas sampling system and creating the electronic "brains" to measure frequency, control gas flow and sensor operating temperatures, and translate the sensor responses into a useful output format (i.e. μg/dscm).

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.

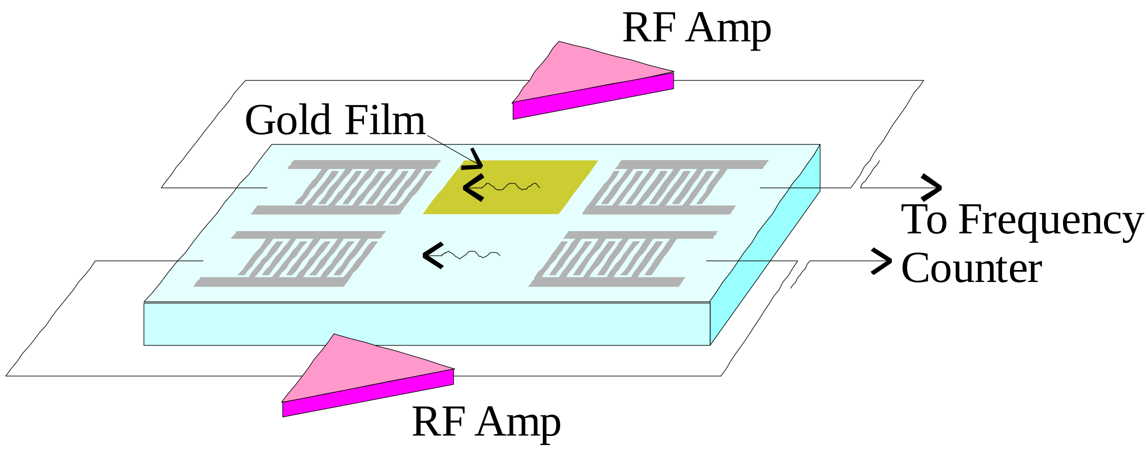

Figure 1. The dual delay line SAW mercury sensor consists of a reference delay line (bottom) and sensing delay line (top) coated with a gold film.

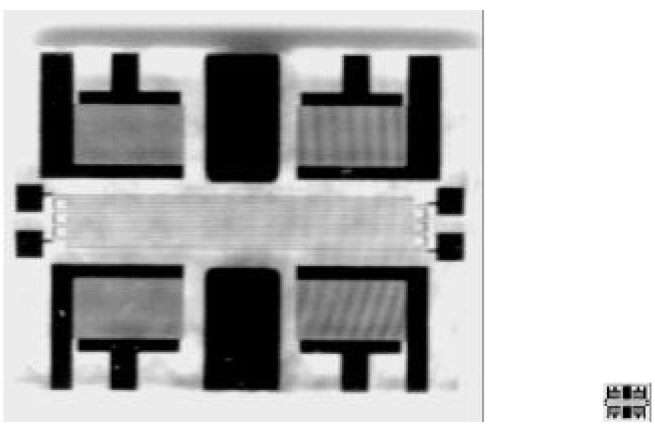

Figure 2. Micrograph of the sensing element. The device is shown actual size on the right.

Integration of the sensor into a CEM instrument is ongoing. In the current design, gas is sampled from the emissions source through 1/16” OD tubing and a 10µ particulate filter. The flow path from input to sensor will be heated to minimize interactions between the gas-phase mercury and the tubing. Two separate sensing elements are used, and the sampled gas is split into two paths. In one path an activated charcoal filter is used to remove the gaseous mercury. The other path contains a .2µ particulate filter, but otherwise leaves the gaseous constituents unchanged. A dual three-way valve directs the flow of the two gas streams to either of the two sensors. This allows the sensor not being exposed to mercury to desorb periodically to a level below saturation, and then respond again when the gas streams are switched. At most operating temperatures of interest, the sensor acts as an integrating device for the first few minutes of exposure, and the switching of gas flow paths periodically constitutes a slow mechanical “chopping” which is commonly used in integrating detectors.

An additional feature of the instrument is the ability to back-flush the particulate filters if the pressure drop across them is too high. Measurement of this pressure drop, valve control, temperature control of the sensors, flow rate control, back-flushing, data collection, data storage, concentration correlation, and communication to the outside world are all performed via microprocessor. Remote control of the instrument can be performed from a distance of several hundred feet using a Category 5 Ethernet line or a wireless link to a laptop computer. Remote control can also be performed from virtually anywhere in the world using a modem.

A photograph of the current prototype instrument is shown in Figure 3. The majority of the volume is consumed by gas handling and control electronics. The prototype was sized to fit in a commercial hard sided shipping container (not shown). A commercial version could be dramatically smaller.

Figure 3. Photograph of the prototype mercury CEM instrument.

Results

The prototype CEM is currently undergoing characterization testing at SRD's laboratory facilities in Orono, Maine. For purposes of testing the gas handling and control strategies and for the development of signal processing routines, the instrument is currently being tested without the heated input lines using only elemental mercury gas streams. Future testing will incorporate mercuric chloride.

Difference frequency data from an early test of the prototype CEM showing the individual detector responses to approximately 27 μg/dscm elemental Mercury in dry nitrogen is contained in Figure 4. The effect of "chopping" the gas stream is evident in the plots, as is the integrating effect of the sensor elements. Note that detector B was exposed first. Later, as the gas flows are switched, detector B recovers while detector A responds. Current testing will establish the correct combination of slope and trend information which will be processed to provide a continuous concentration output at update rates greater that 1 per minute.

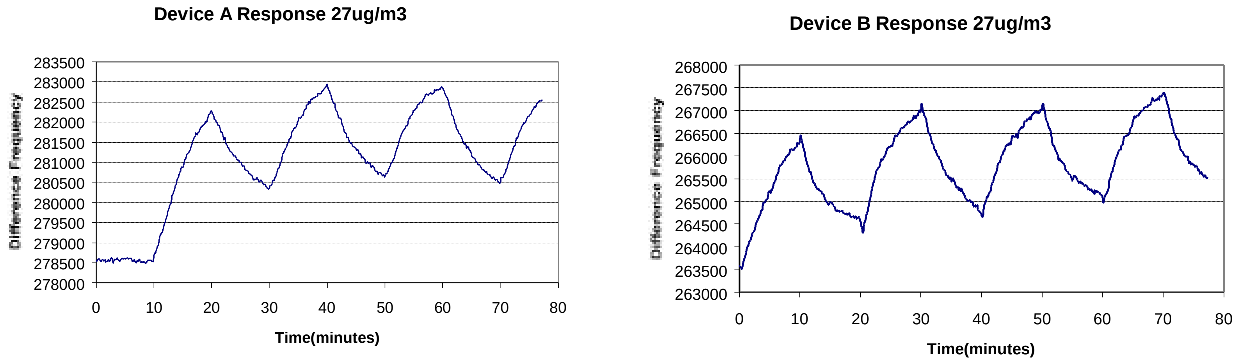

Figure 4. Unprocessed frequency data

For hazardous waste incineration applications, concentrations of interest are relatively high (~50µg/m^{3}) and the slope response of the sensor elements dominates. Figure 5 shows the slope for both detector elements based on the response data contained above. Testing has also shown a strong correlation between concentration and peak response slope, as shown in Figure 6. By measuring the envelope of the response slope, it may be possible to accurately correlate to concentration. Current signal processing software development efforts are concentrated on calculating and interleaving peak slope responses from the two detector elements in real time.

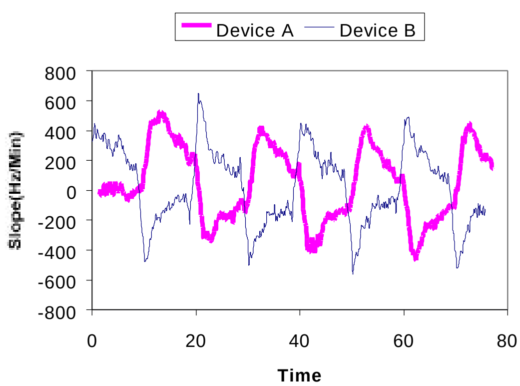

Figure 5. Raw slope data.

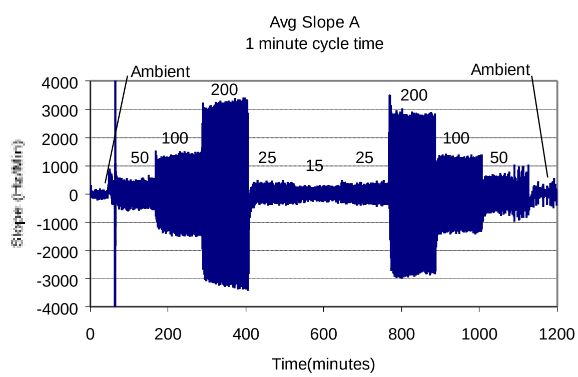

Figure 6. Slope envelope for several concentrations. The approximate concentrations being delivered (mg/dscm) are indicated by the numbers.

Applications requiring greater sensitivities such as coal-fired utility emissions monitoring and ambient air monitoring are also thought to be practical using the inherent high sensitivity of the sensor element trend (DC) response in addition to slope response.

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

Testing and development of signal processing algorithms will continue at SRD facilities using elemental mercury gas streams. In parallel, a second prototype instrument is being developed with integral heated gas flow path that will be characterized using both elemental and oxidized mercury species. The instrument will be tested at the Energy and Environmental Research Center (EERC) at the University of North Dakota in the presence of interfering gases and against current manual standard methods. Final testing of the CEM will take place at an operating Hazardous Waste Incinerator (HWI).

Theoretical work is currently under way at SRD to extend the technology developed under this effort to liquid phase detection of Mercury.

Acknowledgements

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