

**Preliminary Study of a Prototype Methyl-Mercury Monitor for
In-Field Pore Water Sample Analyses – 11559**

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ABSTRACT

This study involves proof-of-concept research for an innovative, low-cost, and portable methylmercury (MeHg) monitor to be utilized at Oak Ridge Reservation (ORR) creek beds. The MeHg monitor comprises three primary steps: (1) chemical derivatization; (2) preconcentration using the purge-and-trap (P&T) method; and (3) sensing using Quartz Crystal Microbalance (QCM) sensors. This preliminary study deals with the measurement of only inorganic mercury (Hg) (e.g. Hg²⁺) which was measured using a modified version of the U.S. Environmental Protection Agency's (U.S. EPA) Method 1631, Revision E for chemical reduction using stannous chloride (SnCl₂). Preconcentration was handled using a gold trap in the P&T method and Hg was released employing a variable voltage controller and heating coil at 450°C. Sensing was managed via utilization of QCM sensors functionalized with gold, which causes amalgamation when Hg comes into contact with the gold surface. This causes a change in mass on the sensor's surface, thereby translating to a resonant frequency shift. The characteristics of both polished and etched surface QCM sensors were studied in measuring inorganic Hg at different flow-rates (18 and 50 mL/min). The polished surface QCM sensors yielded linear ranges of detection of 5 mg/L to 10 mg/L and 1 mg/L to 10 mg/L with regression values of 0.9987 and 0.9736 for 18 mL/min and 50 mL/min respectively. The etched surface QCM sensors gave linear ranges of detection of 1 mg/L to 10 mg/L and 1 mg/L to 10 mg/L with regression values of 0.9888 and 0.9864 for 18 mL/min and 50 mL/min respectively. An etched surface QCM sensor with a flow-rate of 18 mL/min will be used for organic Hg determination due to it having at least 5 times the frequency response compared with other variations at higher flow-rates or utilizing polished surface QCM sensors. Regeneration of polished and etched surface QCM sensors was also investigated with microscopic imaging. The optimal settings of these integrated techniques were found and will be utilized in further experiments measuring concentrations of organic Hg.

INTRODUCTION

There are many ongoing efforts to develop simple techniques and devices for quick and easy determination of mercury (Hg). These include portable devices such as sensors [1] [2] and probes [3] as well as mobile instrumentation that can be deployed in the field [4] [5]. However, these devices and techniques can rarely be used for methylmercury (MeHg) analysis. In fact, even for total Hg (THg) analysis, these devices and techniques have limited application for environmental samples because the sensitivity of most of these methods is insufficient for detecting environmentally relevant concentrations of Hg. It is more difficult for these methods to be employed for MeHg analysis because (1) MeHg concentration in the environmental matrix (other than in biological samples) is much lower (about 10-100 times lower) than THg; (2) MeHg coexists with inorganic Hg species (which contributes to the dominant fraction of THg); and (3) most of these methods are unable to differentiate MeHg from inorganic Hg. However, MeHg is the most toxic Hg species that can be bioaccumulated in fish through the food chain and then enter the human body through fish consumption. In addition, the mechanisms for the methylation and de-methylation of Hg are not well understood and vary in different ecosystems. Current methods used for MeHg analysis involve field sample collection, sample transport to and storage in the laboratory, sample pretreatment, and instrumental analysis. The disadvantages of these methods include time-consuming, tedious, and sometimes troublesome work in order to preserve and isolate MeHg species from the environmental matrix during sample treatment, which results in the high cost of MeHg analysis of environmental samples. For these reasons, the development of a MeHg monitor for rapid measurement of many samples of pore water in the field at a greatly reduced cost would considerably expand the number and complexity of experiments in Hg contaminated areas around the world, particularly at Oak Ridge Reservation (ORR).

The ORR is owned by the United States Department of Energy (U.S. DOE) which is located in Oak Ridge, Tennessee. ORR was established in the early 1940s as part of the Manhattan Project, which helped produce materials for the first atomic bomb. Throughout the following years, many changes have occurred at ORR to help meet U.S. needs in defense, energy, and other areas of research. There are currently three major operating sites: Oak Ridge National Laboratory (ORNL), East Tennessee Technology Park (formerly the K-25 Site), and the Oak Ridge Y-12 National Security Complex [6]. The Y-12 is the major area of concern as this facility formally produced components for various nuclear weapons systems in the 1950s and early 1960s. Hg was used at Y-12 as a key element to capture enriched lithium by separating lithium isotopes. As a result, Hg has become a key contaminant in soil, sediment, surface water, groundwater, buildings, drains, and sumps [7] throughout ORR. Research results have discovered that concentrations of Hg in Upper East Fork Poplar Creek (UEFPC) watershed (soil) range from 0.01 to 7,700 mg/kg [8]. Measurements taken at UEFPC sediments and Lower East Fork Poplar Creek show Hg peaking at 40 mg/kg (depth of 10-20 cm) and 15 mg/kg (depth of 40-60 cm) [9]. Measured values of Hg concentrations are much greater than U.S. Environmental Protection Agency's (U.S. EPA's) standard of 1 mg/kg [10]. This large amount of Hg has the potential of converting to MeHg through the methylation process which poses a serious issue at ORR. This makes it imperative to find a cost-effective, field-deployable technique for measuring MeHg.

The development of such a technique will not be an easy task due to the extremely low concentration of MeHg in the environment ($\mu\text{g/L}$ to ng/L range in natural waters). In order to detect MeHg, the method/technique used must: (1) employ the use of a Hg detector (e.g., atomic fluorescence spectroscopy (AFS) or various sensors) with a relatively low detection limit; and (2) be selective toward MeHg rather than inorganic Hg species (or these Hg species are separated in a separate step). Since the sensitivity of currently available instruments or sensors is insufficient for direct measurement of MeHg in environmental samples, a preconcentration step is needed.

This research will develop an innovative, low-cost, and portable Hg monitor platform that will measure MeHg in water in the field. The proposed technique will involve three key steps: 1) derivatization using a chemical reagent; 2) preconcentration using on-line purge-and-trap (P&T); and 3) detection using Quartz Crystal Microbalance (QCM) sensors. This approach exploits the proven high preconcentration factor and effective cleanup associated with the chemical separation techniques employed in this study and followed by P&T concentration. QCM sensors yield a significant resonant-frequency shift as its loading mass is subjected to a small change. QCM sensors are simply functionalized with gold, which efficiently adsorbs Hg^0 (elemental Hg).

The rest of this document is organized as follows:

- Background.
- Experiments.
- Analyses and Results.
- Conclusions.
- Future Work.
- Acknowledgements.
- References.

BACKGROUND

In order to fully grasp the significance of this research, reviews on environmental Hg, traditional methods of measuring MeHg, and QCM sensors were performed.

Mercury

Hg, a toxic element present in the environment, is used for a variety of different applications including auto parts, batteries, fluorescent bulbs, medical products, thermometers, and thermostats [11]. It occurs in three oxidation states: Hg(0) (elemental Hg), Hg(I) (Hg^+), and Hg(II) (Hg^{2+}). Hg^{2+} can be converted to MeHg via the methylation process. It should be noted that MeHg is considered approximately 100-1,000 times more toxic to organisms than the inorganic species [12]. Exposure to this and other forms of Hg is extremely

hazardous to humans and can result in Hg poisoning, which can cause severe neurological disorders. Symptoms include deterioration of the nervous system, impaired hearing, speech, vision and gait. Involuntary muscle movements, skin and mucus membrane corrosion, and difficulty chewing and swallowing can also occur [13]. The risk of Hg poisoning in humans is significantly increased via consumption of fish in which Hg has been bioaccumulated. Bioaccumulation occurs as a result of Hg uptake in small fish and subsequent concentration/biomagnification up the food chain as large amounts of small fish are eaten by larger fish, which are then ultimately consumed by humans. The primary large, edible species of fish that act as carriers of Hg for humans include swordfish, shark, and ahi tuna [14].

The Hg cycle which transfers Hg throughout the environment, is also very important. The first step involves the release of Hg in its gaseous form from rock, soils, water, volcanoes, and human activities [15]. These Hg emissions are then transported through the atmosphere and can be deposited in two forms: dry and wet. Dry deposition is where non-soluble Hg settles from the atmosphere, whereas wet deposition, which takes place more rapidly, occurs through different types of precipitation such as rain and snow. Once deposited, Hg is available for methylation and then can be bioaccumulated in the food chain. Hg in sediments can be returned to the atmosphere through volatilization and then recycled as described above.

Traditional Methods of Quantifying Hg Concentrations

There are many techniques currently available for measurement of Hg at a variety of different sensitivity levels such as: (1) Atomic Absorption Spectroscopy (AAS) [16]-[19]; (2) Atomic Emission Spectroscopy (AES) [20]; (3) Atomic Fluorescence Spectroscopy (AFS) [21]; (4) Inductively Coupled Plasma Mass Spectrometry (ICPMS) [22]; (5) Potentiometric Detection (PD) [23]; Voltammetric Detection (VD) [24]; and several types of mass-based sensors.

Quartz Crystal Microbalance Sensors

There is much research that deals with mass-based sensors such as QCM sensors, Surface Acoustic Wave (SAW) sensors, Acoustic Plate Mode (APM) sensors, and others. A dual delay line SAW sensor was developed in [25] for gaseous Hg by using the interaction between a gold film and Hg, which forms an amalgam. The resulting increase in film mass is manifested as a decrease in oscillation frequency. Responses of this sensor to gaseous Hg concentrations are in the $\mu\text{g/L}$ range. APM sensors are studied in [26] which are capable of detecting relevant concentrations of aqueous Hg while withstanding typical environmental conditions. This piezoelectric sensor protects the electronics from potentially corrosive aqueous fluids in the environment while providing significant interaction with the fluid. Gold films are employed to accumulate Hg via surface amalgamation. The added mass is measured as a change in the resonant frequency of the piezoelectric element.

SAW chemical sensors based either on gallium arsenide (GaAs) or gallium nitride (GaN) structures are presented in [27] to measure low concentrations of gaseous Hg. The design of the acoustic part of the sensor, including the structure for the generation and reception of the SAW and the chemo-selective coating made of gold is described in detail.

A quartz resonator is used in a piezoelectric sorption sensor [28] to determine the concentration of Hg vapor in the air. A maximum sensitivity of 3 ng/L can be attained. A built-in microheater is also used with the quartz resonator to regenerate the sensor without dismounting it from the equipment. The temperature used for regeneration is 150°C.

Gold-coated piezoelectric crystals without substrates were initially tested in [29] to measure the concentration of Hg vapor using three generation techniques to produce standardized vapors: (1) saturation; (2) syringe dilution; and (3) use of a permeation tube. Later, using a permeation tube as a source of metal, some substances were investigated as possible substrates capable of interaction with Hg vapor. The best material found was a mixture of Pd(II) chloride solution (saturated in acetone) and tetrahydroxyethyl-ethylenediamine (THEED) in acetone.

An automatic micro gravimetric screening system based on piezoelectric detection and the use of acidic SnCl_2 as a reductant was developed in [30] for the fast detection and determination of total Hg in water. Reduced Hg is detected as an amalgam by using a gold-coated piezoelectric crystal, the sensor subsequently being regenerated by passing it through a peroxydisulfate solution. The detector exhibits good sensitivity, allowing the determination of Hg at sub- $\mu\text{g/L}$ concentration levels (0.30 – 1.00 $\mu\text{g/L}$).

EXPERIMENTS

There are three key steps in creating an integrated process for measuring MeHg concentrations (i.e., developing a MeHg monitor). These include: (1) derivatization; (2) preconcentration using the P&T method; and (3) sensing using QCM sensors. Gold is used to functionalize the sensor where amalgamation causes the Hg to bond to the gold surface. This causes a change in mass, thereby translating to a resonant frequency shift. Measurement of inorganic Hg (e.g., Hg^{2+}) and the regeneration of QCM sensors were studied by using a micro-heater, which is described in this section.

Stage #1 Experiments

Fig. 1 displays the initial experimental setup to quantify inorganic Hg. The setup measures the concentration of Hg^{2+} in water. U.S. EPA's Method 1631 was employed to analyze the Hg^{2+} which was reduced to Hg^0 by utilizing SnCl_2 in acidic solution. Hg^0 was then purged from the solution in the bubbler using N_2 gas at 350 mL/min for 20 min and trapped on a gold trap. The Hg^0 was released from the trap by heating to 450°C for 10 minutes using a heating coil connected to a variable voltage controller. Hg^0 vapor then travels to the QCM flow cell where different flow rates were tested (18 and 50 mL/min). Initially, different concentrations of HgCl_2 were utilized to determine a calibration curve (0, 1, 2, 5, and 10 mg/L). Resonant frequency shifts were monitored using an oscillator chip, frequency counter, General Purpose Interface Bus (GPIB), and Personal Computer (PC) with Laboratory Virtual Instrumentation Engineering Workbench (LabVIEW). These experiments were repeated using both polished and etched surface QCM sensors to determine which type produced better results.

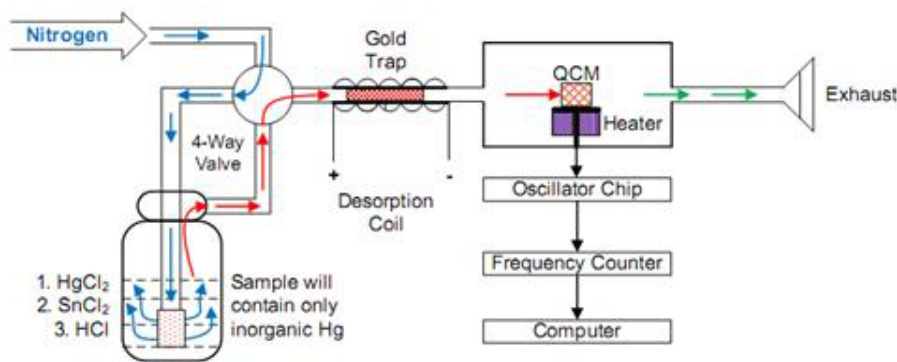


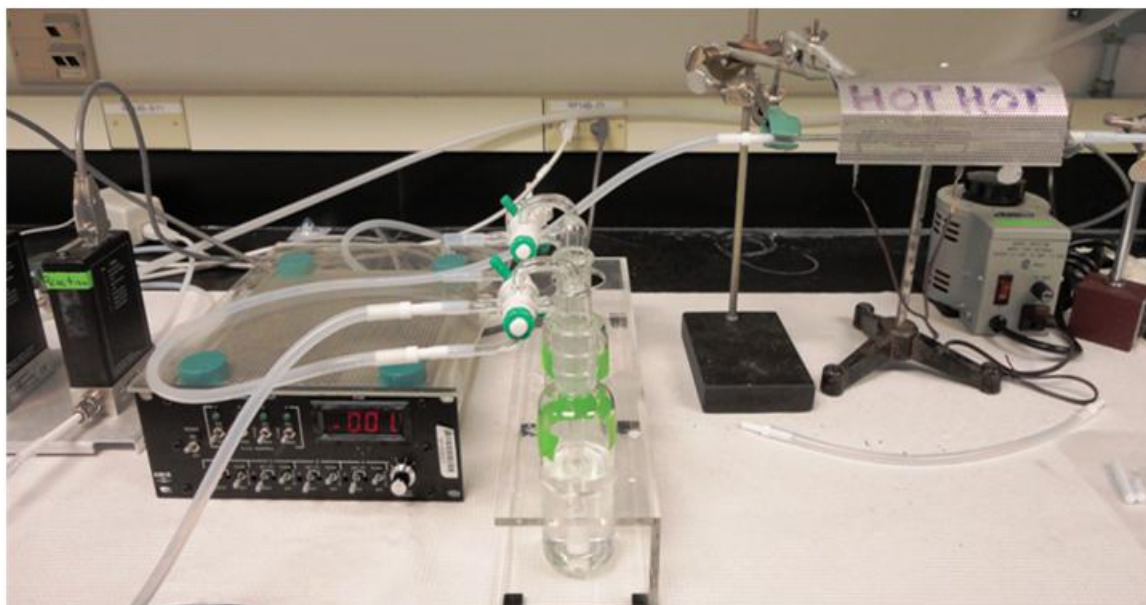
Fig. 1. Experimental plan of measuring inorganic Hg.

Determining Hg^{2+} Concentration using EPA's Method 1631

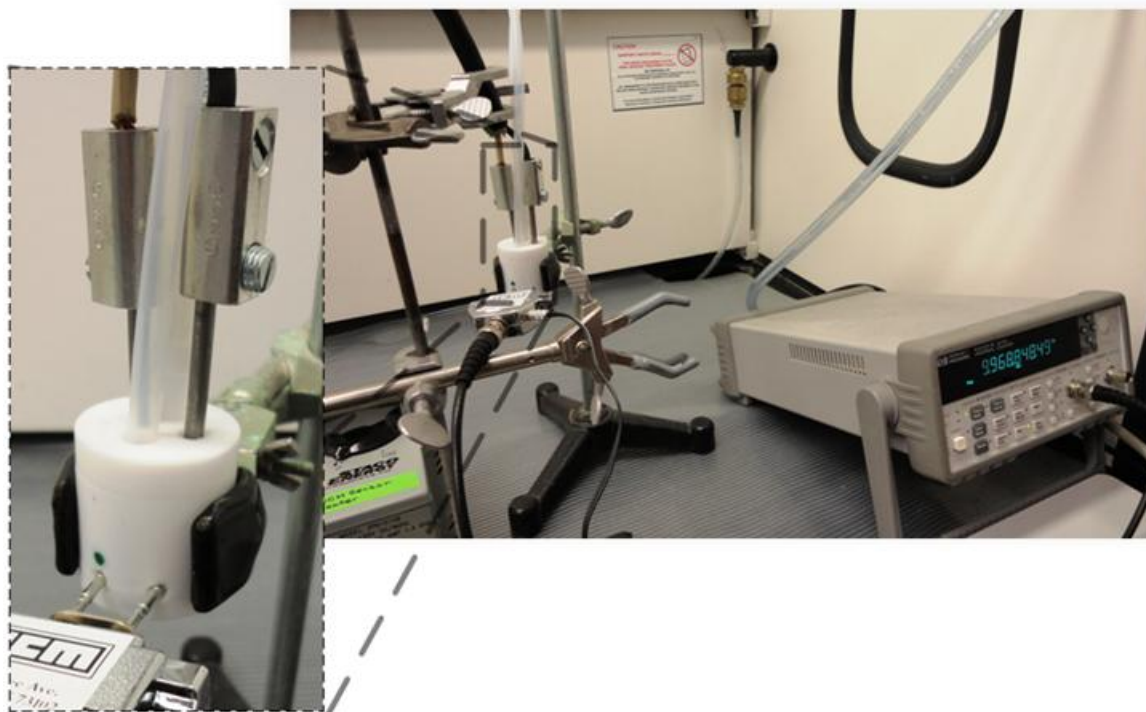
The experimental setup is shown in Fig. 2 (a) which used EPA's Method 1631 Revision E [31]. This was accomplished by mixing 100 mL of deionized (DI) water, 0.5 mL of SnCl_2 solution, and the corresponding concentration of HgCl_2 standard needed for each experiment in a 200 mL bubbler. The solution was then purged at 350 mL/min with N_2 for 20 minutes and Hg^0 was transferred into a gold trap shown in Fig. 2 (a). The gold trap was then heated to 450°C for 5 minutes using a heating coil connected to a variable voltage controller from Starco Energy Products Company (Model # 3PN1010B). During this time, N_2 gas was flowing at either 18 or 50 mL/min to transport the inorganic Hg being released by the gold trap to the QCM sensor.

Sensing using QCM Sensors

Hg measurements were made using a QCM sensor, shown in Fig. 2 (b). The QCM sensors utilized in this research were purchased from International Crystal Manufacturing (ICM) Co. Inc. All had a resonant frequency of 10 MHz with polished and etched surfaces. The flow-cell used in these experiments was also from ICM and was a static cell (ID # 35368) made of Teflon.



(a) Chemical Derivatization



(b) Sensing

Fig. 2. Experimental setup of inorganic Hg detection (a) Chemical Derivatization and (b) Sensing.

Flow Control and Data Acquisition

In order to control the flow rate of N₂ gas into the experimental setup, the MKS 247C 4-Channel Readout was utilized with MKS Flo-Controllers (Model # 1479A13CS1AM). A universal counter from Hewlett Packard (Model # 53131A) was used to measure the resonant frequency from QCM sensors in the experiments. The universal counter was connected to a PC via a GPIB connection for data communication. Data acquisition was handled using the LabVIEW program.

Experimental Plan and Procedures

The experimental test matrix which included both polished and etched surface QCM sensors, and flow-rates of 18 and 50 mL/min using a 100 mg/L HgCl₂ standard is exhibited in Table I. The five different concentrations that were tested aided in determining the linearity of the system.

The experimental procedures for polished and etched surface QCM sensor experiments in Stage #1 are conveyed in Table II and Table III respectively. Different procedures for the different surfaces of QCM sensors are needed because etched surface QCM sensors take a greater amount of time in reaching equilibrium. Constant monitoring was needed until equilibrium was obtained to ensure that no irregularities in that time interval occurred. The difference in recording times of frequency response data for polished and etched surface QCM sensors was 50 and 240 minutes respectively. The “Count” and “Total Count” columns of Table II and Table III signify the variable utilized in the LabVIEW program for defining the amount of time needed to record.

Table I. Experimental Plan.

mg/L	µg/L	Hg (mg)	100 mg/L Standard (µL)	100 mg/L Standard (mL)
9.05	9050	1	10000	10
4.74	4740	0.5	5000	5
1.95	1950	0.2	2000	2
0.98	9800	0.1	1000	1
0	0	0	0	0
* Performed at 18 and 50 mL/min at room temperature				
** Performed using 100 mg/L standard				
*** Performed for both polished and etched QCM sensors				

Table II. Experimental Procedure for Polished Surface QCM Sensors.

<i>Step</i>	<i>Time (min)</i>	<i>Total Time (min)</i>	<i>Purpose</i>
0	-	-	Warm up QCM oscillator chip until obtaining a stable resonant frequency. There is no gas running to the sensor.
1	20	20	Purge bubbler for 20 min at 350 mL/min using nitrogen or argon gas. The bubbler is connected to the gold trap, which is not connected to the QCM sensor.
2	2	22	Adjust flow to the gold trap to the needed flow rate and connect the outlet of the gold trap to the QCM sensor.
3	5	27	Heat gold trap to 450°C.
4	10	37	Keep gas flow w/o heat on gold trap.
5	13	50	Turn gas off and let QCM sensor obtain equilibrium.

Table III. Experimental Procedure for Etched Surface QCM Sensors.

<i>Step</i>	<i>Time (min)</i>	<i>Total Time (min)</i>	<i>Purpose</i>
0	-	-	Warm up QCM oscillator chip until obtaining a stable resonant frequency. There is no gas running through the sensor.
1	20	20	Purge bubbler for 20 min at 350 mL/min using nitrogen or argon gas. The bubbler is connected to the gold trap, which is not connected to the QCM sensor.
2	2	22	Adjust flow to the gold trap to the needed flow rate and connect the outlet of the gold trap to the QCM sensor.
3	5	27	Heat gold trap to 450°C.
4	10	37	Keep gas flow w/o heat on gold trap.
5	203	240	Turn gas off and let QCM sensor obtain equilibrium.

Quartz Crystal Microbalance Sensor Regeneration

Sensor regeneration was accomplished by following the procedure shown in Table IV. The QCM sensor was heated to 150°C [27] [33] [34] to desorb Hg from the sensor's surface.

Table IV. QCM Sensor Regeneration Procedure.

<i>Step</i>	<i>Time (min)</i>	<i>Total Time (min)</i>	<i>Purpose</i>
1	5	5	Heat QCM sensor to 150°C with a flow of N ₂ gas at 50 mL/min. ^a
2	5	10	Continue with N ₂ gas flow at 50 mL/min. ^a
3	470	480	Monitor resulting frequencies.

RESULTS AND ANALYSES

Inorganic Hg was quantified using EPA's Method 1631 Revision E. Both polished and etched surface QCM sensors were tested at flows of N₂ of 18 and 50 mL/min. The behavior of polished and etched QCM sensors during regeneration was also examined through frequency response and using microscopy.

Stage #1 Experiments

Table V presents the negative frequency shift of the various Hg concentrations shown in Table I for polished and etched surface QCM sensors at 18 and 50 mL/min. The calibration curves of all four cases are shown in Fig. 3. The regression values of all four calibration curves are acceptable ranging from 0.9570 to 0.9987 with slopes ranging from 2.54 to 43.3. The case with the best sensitivity however was using etched surface QCM sensors at an 18 mL/min flow rate, which resulted in a range of frequency shifts between 20 to 421 Hz. Etched surface QCM sensors gave larger frequency shifts because the etched surface has much more surface area compared to the polished surface, which provides a higher Hg binding capacity. The slower flow rate of 18 mL/min compared to 50 mL/min gave greater frequency shifts because Hg has more time to bind to the gold surface with a lower flow rate. The case of etched surface QCM sensors at 18 mL/min would be the best choice for proceeding experiments dealing with organic Hg (e.g. MeHg) detection.

Table V. Frequency Shifts of Polished and Etched Surface QCM Sensors at 18 mL/min and 50 mL/min Flow Rates.

	Polished – 18 mL/min	Polished – 50 mL/min	Etched – 18 mL/min	Etched – 50 mL/min
Conc. (mg/L)	ΔF (Hz)	ΔF (Hz)	ΔF (Hz)	ΔF (Hz)
0	7	4	-14	-4
1	3	10	20	6
2	6	16	83	27
5	14	50	170	40
10	26	73	421	85

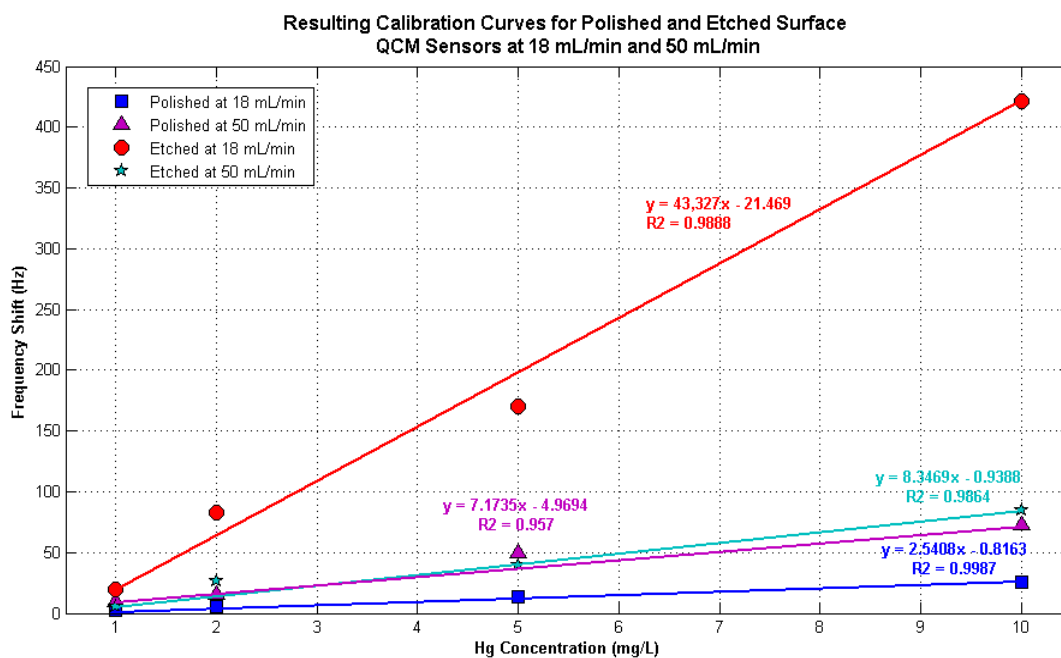


Fig. 3. Calibration curves for polished and etched surface QCM sensors at 18 mL/min and 50 mL/min flow rates.

Quartz Crystal Microbalance Sensor Regeneration

Regeneration of polished and etched surface QCM sensors was performed using the procedure presented in Table IV. The expected reaction was an increase in the resonant frequency once Hg was desorbed. The opposite occurred however, where the resonant frequency decreased by 5,111 Hz and 5,161 Hz for polished and etched surface QCM sensors respectively. Images taken from an x10 microscope (Nikon 1002908 with Pixelink camera) showed that Hg was successfully desorbed. These images are shown in Fig. 4. It is shown for both polished and etched surface QCM sensors for the used case that amalgam was formed, which is represented by black splotches. The regenerated images show less black splotches in the case of the polished surface QCM sensor and no black splotches for the etched surface QCM sensor.

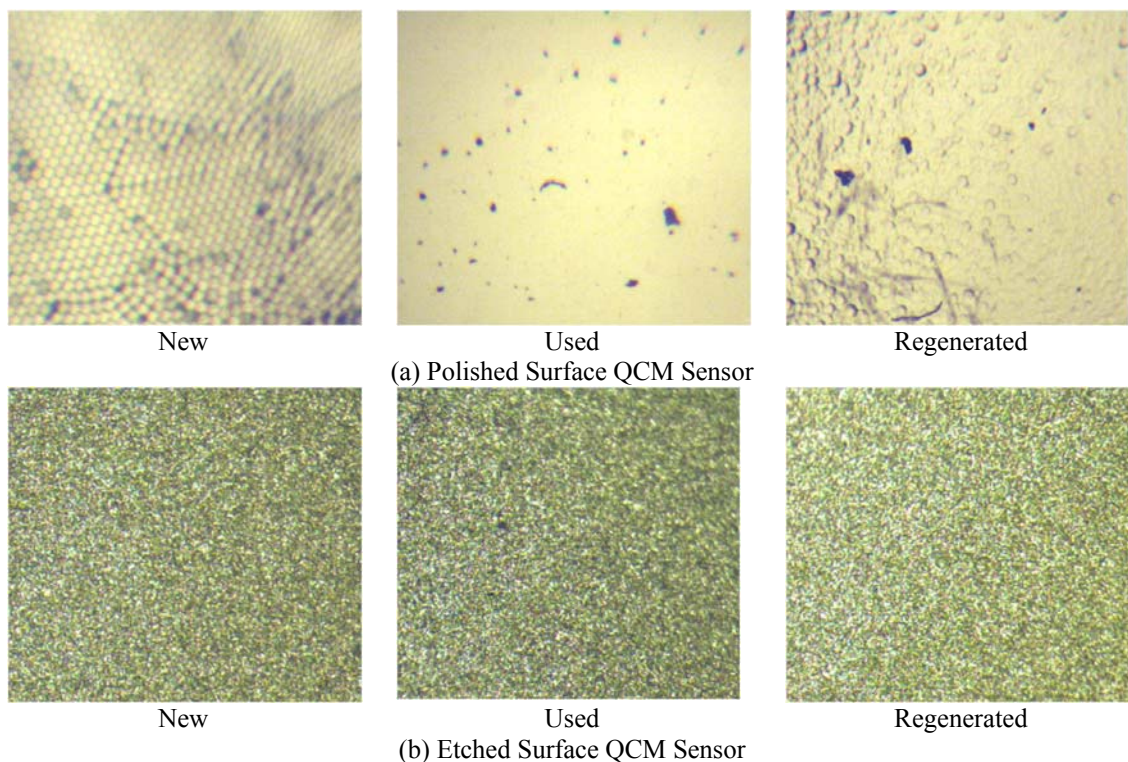


Fig. 4. Regeneration of polished and etched surface QCM sensors: (a) Polished Surface QCM Sensor and (b) Etched Surface QCM Sensor.

CONCLUSIONS

The focus of this research was a proof-of-concept Hg monitor using chemical derivatization, the P&T method, and QCM sensors in order to measure Hg in pore water samples at ORR creek beds. Experiments were performed using both polished and etched surface QCM sensors for inorganic Hg determination at different flow rates (e.g., 18 and 50 mL/min). The variation that produced the best results was etched surface QCM sensors at 18 mL/min, which will be utilized in future experiments dealing with organic Hg detection. QCM sensor regeneration was also investigated for both polished and etched surface QCM sensors. Adsorbed Hg on the sensor's surfaces was removed by heating to 150°C. However, further investigation is needed to determine the reason behind the resonant frequency decrease instead of the expected increase.

Research results generated in this research depict a successful proof-of-concept Hg monitor which uses a chemical derivatization, the P&T method, and QCM sensors for inorganic Hg detection which gave a detection range of 1 mg/L to 10 mg/L. Future research will deal with improving the detection limit for inorganic Hg and the detection of organic Hg using the optimal case (etched surface QCM sensors at 18

mL/min) found in this study. The argument can be made, however, that the resulting mg/L range of detection is inadequate compared with what is required for the detection of MeHg in environmental samples, which is in the ng/L range. Another issue was that the experimental setup using QCM sensors took far too long to reach equilibrium after injecting Hg into the flow cell. Future work is needed to resolve these issues. It was determined that these different techniques could be successfully integrated. Another step for future research would be to integrate the inorganic and organic Hg detection into experiments currently being planned. Afterwards, other sensing mechanisms such as microcantilever sensors, must be incorporated into this research to achieve lower ranges of detection that can one day be utilized to quickly detect ng/L levels of MeHg in environmental samples.

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