

# **Proof-of-Concept Development of a Microfabricated Tuning-Fork Based Sensor for Disinfection By-products in drinking water**

Prof. Paul Westerhoff  
ASU Civil and Environmental Engineering

Prof. Nongjian Tao  
ASU Electrical Engineering

Prof. Roberto Guzman  
UA Chemical Engineering

KC Kruger  
ASU Civil and Environmental Engineering

Francis Tsow  
ASU Electrical Engineering

Dr. Erica Forzani  
ASU Electrical Engineering

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## **CHAPTER 1 INTRODUCTION AND PROJECT OBJECTIVES**

Addition of disinfectants during water treatment forms disinfection by-products (DBPs), which are carcinogenic, due to reaction between the chemical disinfectants (e.g., chlorine) with precursors (e.g., organic matter). Several classes of disinfection by-products (e.g., trihalomethanes) are currently regulated in drinking water systems, and others may be regulated in the future. Currently the burden of manual sampling, coupled with external laboratory sample analysis, data input, and interpretation of DBP data is not responsive to the regulatory intent and provides no real-time feedback to operators to improve system performance (e.g., minimize DBP formation). Development of in-line DBP sensors could greatly aid in the ability to optimize treatment processes (e.g., alum chemical dosages at water treatment plants) and operations (e.g., hydraulic residence time in water distribution systems) and lower DBP levels at the consumers tap. Additionally, chloroform (one of the regulated trihalomethanes) is a groundwater pollutant and sensors are needed for groundwater monitoring and treatment.

The USEPA is responsible for providing regulations for water treatment facilities across the nation in order to safe guard public health and minimize the adverse health impacts of drinking water contaminants. The concentration of various chemicals, metals, viruses, and bacteria allowed in public drinking water supplies all fall under federal guidelines set forth by the EPA and applies to drinking water systems of all sizes in the United States.

THMs are a class of regulated disinfection by-products (DBPs) which primarily form in drinking water when chlorine reacts with organic matter in water. The four regulated THM's are chloroform, bromodichloromethane, dibromochloromethane, and bromoform. These chemicals are suspected carcinogens and when ingested, have the potential to lead to liver, kidney, bladder and central nervous system problems.

### **CURRENT REGULATION**

Under the current regulations implemented by the Stage 1 disinfectant/disinfectant by-product (D/DBP) rule, the sum of the four regulated THM's should not exceed 80 parts per billion (ppb). These regulations are set such that DBP's are measured and municipalities must maintain DBP levels below this maximum contaminate level (MCL) based on a running annual average of quarterly averages of the entire distribution system. With this method of monitoring THM's certain areas of a distribution system may exceed the MCL so long as the average of quarterly samples of the entire distribution system is below 80 ppb. The system as a whole is not in violation of EPA DBP rules due to the averaging with other samples of lower DBP concentrations elsewhere in the distribution system. This regulation is currently undergoing a transition to provide superior monitoring and prevent high THM concentrations in a distribution system.

Upon adoption of the Stage 2 D/DBP rule, the regulatory limit of THMs will remain at 80 ppb but the sampling sites and method of averaging concentrations will differ greatly. Municipalities will be required to conduct an Initial Distribution System Evaluation (IDSE) in which they must identify locations throughout the distribution system that are prone to high DBP concentrations.

These locations will then be the sampling points for DBP monitoring to ensure Stage 2 D/DBP compliance. The new regulation will be based on the locational running annual average (LRAA). The LRAA is the average of four quarters of data from a single distribution system location instead of the average of the entire distribution system. This new regulation is intended to reduce the DBP concentrations in areas of a distribution system that historically may have exceeded the MCL for DBPs.

The current regulatory procedure of DBP monitoring required of municipalities is based on quarterly or other periodic sampling. However THM formation during water treatment can vary more frequently based on open water sources as water quality parameters affecting THM formation can change. These changes may be due to weather events, changes in water sources or other natural cycles. For larger cities with in-house laboratories, THM concentrations may be available to operators within 2 days of the sample being collected. For cities requiring the use of external labs, the turnaround can be greater than 2 weeks. These delayed THM results do not provide real-time data which can be helpful in the optimization of a WTP.

## **STATEMENT OF NEED**

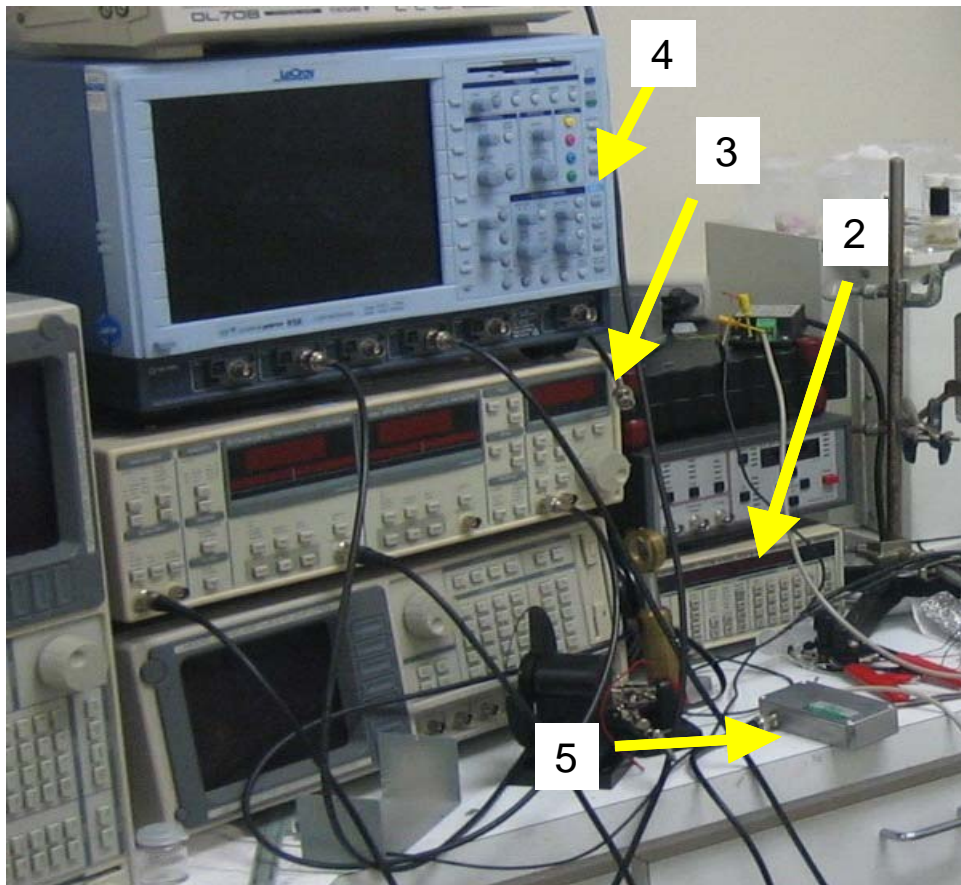
Drinking water treatment systems and distribution systems must comply with new USEPA regulations (Stage II) that require THM concentrations to average less than 80 µg/L at multiple points in the water distribution systems. Many cities are having difficulty meeting this regulation and are doing multiple sampling per week at numerous locations in distribution systems to better manage DBP formation. This requires a lot of man-power for sampling, transport to centralized laboratories, laboratory analysis, data reduction, and data interpretation. For cities with their own centralized lab the turnaround time can be as short as two days, but is >2 weeks when commercial labs are used. Having a near real-time sensor located in the field that provides autonomous data back to the water treatment plant would allow real-time (< 1 hour) management of water quality. Therefore, the largest stakeholder for this project are cities and ADEQ who oversee the drinking water regulations. In addition, this technology would revolutionize laboratory studies on DBPs for which there are many. Another application of this device is to detect chloroform at groundwater remediation sites, and may be suitable to measure chloroform in various industrial workplaces. Beyond the specific application of the sensor technology to chloroform, we hope to build the technical capacity among researchers at different universities to pursue external funding for similar sensors capable of detecting a wide range of environmental pollutants. The research should demonstrate proof-of-concept for a THM sensor device which would be commercialized.

The goal of this project is to take advantage of inter-university expertise in drinking water (Westerhoff), sensors (Tao) and polymers (Guzman) to develop a proof-of-concept prototype trihalomethane (THM) sensor which could lead to external funding and eventual commercialization. The sensor platform is based upon an inexpensive wristwatch tuning fork across which a polymer is stretched. The polymer interacts with the target compound (e.g., chloroform) and affects the resonance of the tuning fork. The basic tuning fork sensor technology has been developed, patented, and published by Dr. Tao. Now direct applications of the basic technology need to be developed.

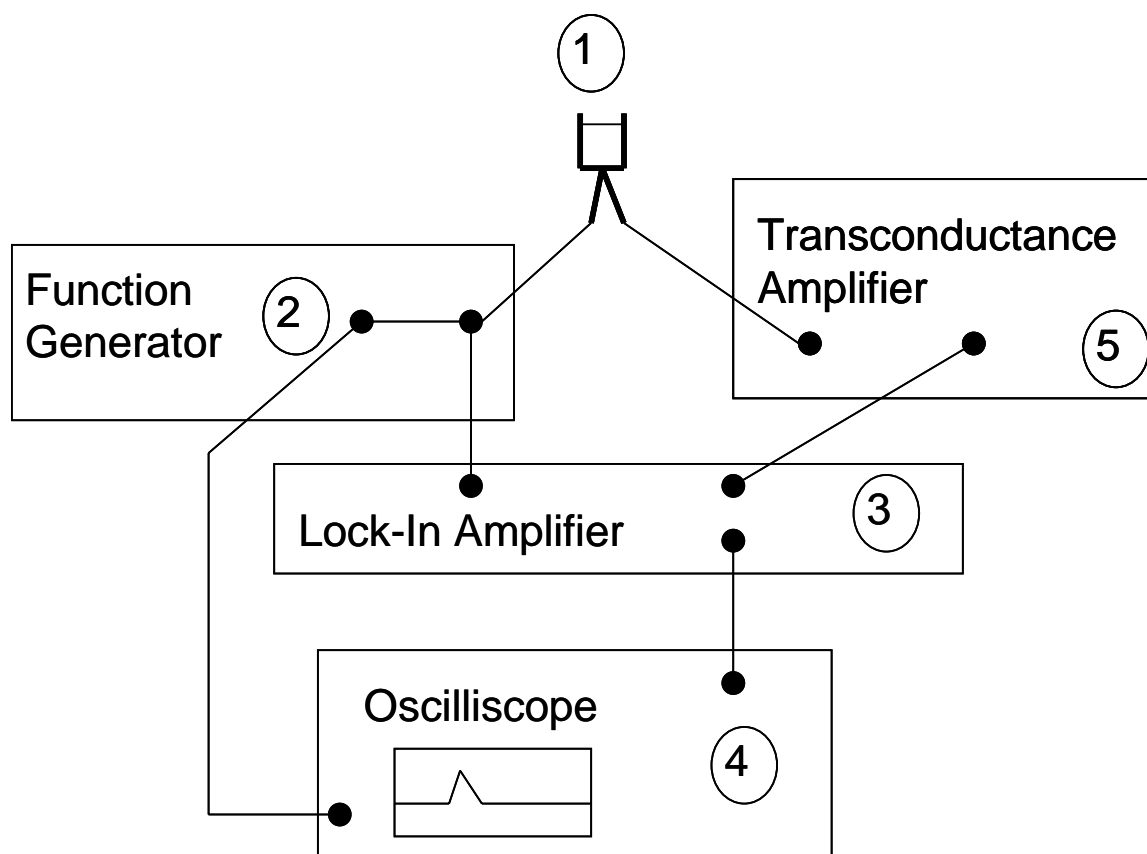
## CHAPTER 2 METHODS

### QUARTZ TUNING FORKS

Each quartz tuning fork (QTF) is modified differently with one of several polymers. The QTF's are purchased from Newark Electronics and have dimensions of (4 x 0.25 x 0.6) mm<sup>3</sup>. Each is modified by bridging a polymer solution across each tine and allowed to dry overnight. The polymer solutions are prepared by dissolving a given polymer in a solvent, toluene or chloroform. After a 24 hour drying period, each QTF is tested to check that the resonant frequency is higher than that of a bare QTF in a vacuum, 32.768 kHz. The instrumental setup used to test the resonant frequency is the same used during chemical sensing and is illustrated in Figures 2.1 and 2.1.



**Figure 2.1** Photograph of the QTF electrical set up. (2) Function generator, (3) Lock-In Amplifier, (4) Oscilloscope, and (5) Transconductance Amplifier.



**Figure 2.2 Schematic of the setup used to monitor the resonant frequency of the polymer modified QTF's. The lines between each instrument indicate an electrical connection.**

The QTF (1), from Newark Electronics, is electrically connected to the function output of the Stanford Research Systems DS345 30 MHz synthesized function generator (2). This function output is then connected to the reference input of the Stanford Research Systems Model SR830 DSP lock-in amplifier (3). The channel 1 output of the lock-in amplifier is connected to the channel 1 input of the LeCroy Wavepro 950 1 GHz Oscilloscope (4), where the frequency data is displayed and recorded. The transconductance amplifier (5) was made in the lab and is connected to the output of the lock-in amplifier. The transconductance amplifier is also connected to the free terminal of the QTF to close the circuit.

When using the modified tuning forks to sense chloroform in the gas phase, a stock bag of gas phase chloroform is prepared by injecting known volumes of Mallinckrodt brand 100% pure chloroform into air filled tevlar bags of various sizes (Custom Sensor Solutions, Oro Valley, AZ). Different concentrations of gas phase chloroform are created by diluting the stock bag of chloroform with chloroform free, air filled tevlar bag using a model 1010 precision gas diluter (Custom Sensor Solutions, Oro Valley, AZ). The advantage of the gas diluter is that it produces a gas stream with a chloroform concentration that can be controlled to any fraction of the stock chloroform concentration.

When preparing aqueous solutions of chloroform, all standards were prepared with distilled water filtered through a Barnstead nanopure laboratory water system with a resistivity of no less than 18.2 megohm per centimeter.

## ANALYTICAL METHODS

### Liquid-Liquid Extraction of THMs for Chlorination Tests

After the addition of ammonium chloride and phosphate buffer to the chlorination test samples, 8 grams of sodium chloride and 5 mL of pentane are added to each 40 mL vial containing the water samples and shaken vigorously for exactly 2 minutes ensuring a disassociation of all salts and proper contact between the pentane and the water. Once the pentane is allowed to separate from the water, approximately 1.5 mL of pentane is placed in a septa crimped sealed auto sample vial. Using an auto sampler, 2  $\mu$ L of each sample are separately injected into a Hewlett Packard 5890 Series 2 Gas Chromatograph with a linearized Electron Capture Detector. A Supelco SPB-1 fused silica capillary column is used to divide the separate chemicals. Approximate elution times for the individual compounds are in Table 2.1.

**Table 2.1 Typical elution times for the individual THMs.**

Compound	Time (min)
CHCl <sub>3</sub>	3.11
CHBrCl <sub>2</sub>	4.69
CHBr <sub>2</sub> Cl	6.81
CHBr <sub>3</sub>	8.82

The injector and detector temperatures are held at 120 °C and 290 °C respectively throughout each sample run. The oven temperature program consists of 3 temperature ramp stages with and uncontrolled cool down. The step profile is listed in Table 2.2.

**Table 2.2 Oven temperature profile of the GC during a sample run**

Initial Temperature	40 °C for 3 min
Initial Ramp	15 °C / min
Final Temperature	63 °C
Hold Time	1.5 min
Ramp 2	15 °C / min
Final Temperature	100 °C
Hold Time	1 min
Ramp 3	40 °C / min
Final Temperature	180 °C
Hold Time	2 min

The carrier flow rate of ultra high purity (UHP) Helium is set between 50 and 60 mL/min, the back pressure is 12 psi, and the makeup gas of UHP nitrogen is approximately 40 mL/min. Prior

to each analysis, the septa at the injection port is changed and the oven temperature is set to 280 °C for 45 min to ‘bake out’ any residual chemicals in the column.

### Manual Injection Measurements of THMs for Polymer Screening

The polymer selection process requires testing the polymers ability to absorb/adsorb the analyte to be detected, chloroform in this instance. The initial polymer screening process involves attempting to dissolve each individual polymer in pure chloroform. If a polymer does not react with the chloroform in its purest form, there is no reason for it to do so in a dilute system and the polymer is no longer a good candidate for the modified tuning fork application. Initially, approximately 0.5 grams of polymer were placed in a test tube with 5 mL of chloroform. Adequate contact between the polymer and chloroform was ensured by mixing for 15 seconds using a vortex mixer. To find the most reactive polymer, the process was repeated using 0.5 mL of chloroform.

The subsequent polymer screening process involves placing 0.06 grams of polymer into a 40 mL glass vial and sealed with a Teflon coated septa cap. Each of the vials, including empty vials as controls, are prepared in triplicate. Using a 500 µL GASTIGHT® syringe from the Hamilton Company, 200 µL of a 100 ppmV stock bag of chloroform is manually injected thru the septa and into each vial. The stock bag of chloroform gas is prepared by injecting 1.34 µL of pure chloroform into an air filled 4 L tevlar bag. The chloroform gas and polymer are allowed to react for 24 hours. Using a separate 500 µL GASTIGHT® syringe, 200 µL of the headspace from each vial are separately and manually injected into the GC. As noted in Table 3.3, the elution time for chloroform is only 3.11 min. Each run took approximately 3.5 min at 40 °C without any temperature ramps. Injection and detector temperatures, gas flow rates and back pressure settings are identical to the liquid-liquid extractions.

### STANDARD METHODS

It is necessary to measure several parameters to confirm the WTP model. Table 2.3 lists the parameter measured, the method, and the instrument used to measure each individual parameter.

**Table 2.3 List of the parameters measured using each instrument and method.**

Parameter	Method	Instrument
DOC	5310 <sup>a</sup>	Shimadzu TOC-V <sub>CSH</sub> carbon analyzer
TDN	<sup>b</sup>	Shimadzu TNM-1 total nitrogen measuring unit
pH	4500-H <sup>+</sup> <sup>a</sup>	YSI 60 pH and temp instrument
UVA <sub>254</sub>	5910 <sup>a</sup>	Shimadzu Multi-Spectrometer 1501
Alkalinity	2320 <sup>a</sup>	HACH Digital Titrator Kit
Bromide	4110 <sup>a</sup>	Dionex DX-120 Ion Chromatography system
THM's	EPA 551.1	Hewlett Packard 5890-2 Gas Chromatograph with Electron Capture Detector
Ammonia	HACH 10205	HACH DR/5000 spectrophotometer
Turbidity	HACH 8237	HACH DR/2000 spectrophotometer

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Chlorine Residual	HACH 8021	HACH DR/5000 spectrophotometer
Jar Test	<sup>c</sup>	Phips and Bird PB-901 Programmable Jar Tester

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<sup>a</sup>(*Eaton, Clesceri et al. 1995*)

<sup>b</sup> *Chemiluminescence Detection (Lee and Westerhoff 2005)*

<sup>c</sup> (*USEPA 1999*)

## CHAPTER 3 QUARTZ TUNING FORK DEVELOPMENT FOR CHLOROFORM SENSING

The purpose of this research is to develop a proof of concept prototype chemical sensor with the intent of detecting THMs in drinking water. The sensor is based on a polymer modified quartz tuning fork (QTF) commonly found in analogue wristwatches. The premise of this work is that a polymer wire is used to bridge the tines of a tuning fork with a very well known resonant frequency. This bridged wire creates and increases tension in the QTF, which in turn causes a shift in the resonant frequency. Upon exposure of the polymer wire to the analyte, in this case chloroform, the physical properties of the polymer are altered, causing a change in the tension imposed on the QTF. This will induce a frequency shift in the QTF, which can be translated into a chloroform concentration.

### CHLOROFORM PARTITIONING

Chloroform is a volatile organic chemical meaning that when present in an aqueous solution, a fraction of the chemical concentration will partition into the gas phase. The fraction of the chemical that will eventually partition into the gas phase is dependent on a property of the chemical known as Henry's constant ( $K_H$ ). This constant will vary on several parameters including temperature and the ratio of water and gas volumes the chemical is in. Henry's constant for a volatile chemical can be calculated using equation 3.1 (Washington 1996). Once Henry's constant is known, the concentration of the chemical that will partition into the gas phase headspace above the aqueous solution can be calculated using equation 3.2 (Sanders 2002).

$$\ln K_H = \frac{-\Delta H_r^\theta}{RT} + \frac{\Delta S_r^\theta}{R} \quad (3.1)$$

$$C_{air} = C_{water} \frac{K_H V_{water}}{K_H \times V_{air} + V_{water}} \quad (3.2)$$

Where

$K_H$  is the dimensionless Henry's law constant

$-\Delta H_r^\theta$  is the standard state enthalpy of the chemical (kJ / mol)

$R$  is the universal gas constant (0.082054 L-atm / deg-mol)

$T$  is the temperature (K)

$\Delta S_r^\theta$  is the standard state entropy (J / mol-K)

$C_{air}$  is the molar concentration of the chemical in the gas phase (mol / L)

$C_{water}$  is the molar concentration of the chemical in aqueous solution (mol / L)

$V_{air}$  is the volume of air above the liquid (liters), and

$V_{water}$  is the volume of aqueous solution containing chemical (liters).

The modified QTF's are incredibly sensitive to small changes in the environment in which they are operating. Changes in temperature, humidity, pressure, and chemical concentrations in its surrounding environment will induce a noticeable resonant frequency shift. For this reason initial chloroform measurements were made in the gas phase, or headspace directly above the water sample. In order for the measurements to be made in the liquid phase, the depth the QTF would be submerged in the water would have to be minimized and replicated to the exact depth for each sample. This is due to the fact that as the QTF becomes submerged in a more viscous liquid, the energy recovered by the QTF is reduced and the quality factor (Q) is lowered resulting in a reduction of sensitivity.

Chloroform was chosen as the THM to focus on because it is the most volatile of the four regulated THM's and will be the most present in the headspace of a typical chlorinated surface water. In the headspace, temperature, humidity and pressure can all be controlled over time.

Stock samples of a known gas phase chloroform concentration are needed in order for polymer testing, creating calibration curves, and testing the modified QTFs reaction to gas phase chloroform. Stock gas phase standards of chloroform were prepared in tevlar bags using equation 3.3.

$$ppmV = \frac{mg}{L} \times (10^3) \times \frac{1}{MW_{chloroform} [g / mole]} \times 0.08205 \left[ \frac{L \cdot atm}{mol \cdot K} \right] \times \frac{T_{air} [K_H]}{P_{air} [atm]} \quad (3.3)$$

The molecular weight of chloroform ( $MW_{chloroform}$ ), is approximately 119 grams per mole. The density of pure liquid chloroform is approximately 1.498 micrograms per milliliter.

## POLYMER SCREENING

Thousands of different polymers exist that may be selected for the QTF, and thousands of different modifications can be made to each one of these polymers that may alter the properties and make it more or less selective to chloroform. In order to create a modified QTF that is selective to sensing chloroform, the proper polymer must be used to form the wire across the tines of the QTF. A polymer that is more reactive to chloroform will be a better candidate for the QTF wire as it is more likely that a shift in its physical properties will occur in the presence of chloroform. The polymers that were selected for screening were mostly in house polymers that were readily available for testing. A three step polymer screening process has been developed to determine the best candidate polymer.

1. The first stage of the polymer screening process is to determine if the polymers can dissolve in pure chloroform. If the polymer would not dissolve or otherwise noticeably react to the chloroform in its purest form, it would not do so in a very dilute system. This reaction is the basis of the detection platform. Following the first polymer screening, a more quantitative screening is necessary in order to determine which polymer is most reactive in the presence of chloroform.
2. Equal amounts of the remaining polymers are weighed out and placed in 40 mL amber vials and capped with Teflon lined septa. A stock bag of 100 ppmV chloroform gas is prepared by injecting 0.33  $\mu$ L of pure chloroform into a 1 L sealed bag with a septa lined cap. Once the liquid chloroform is completely volatilized, 200  $\mu$ L from the stock chloroform bag are injected into the sealed vials containing the polymers. After a 24 hour

waiting period, equal volume samples of headspace from the vials is injected into a gas chromatograph equipped with a linearized electron capture detector in order to measure the residual chloroform concentration remaining in the headspace. Several vials containing no polymer are prepared in the same way as controls. This experiment would demonstrate which polymer would absorb the most chloroform, indicating a reaction with the chemical.

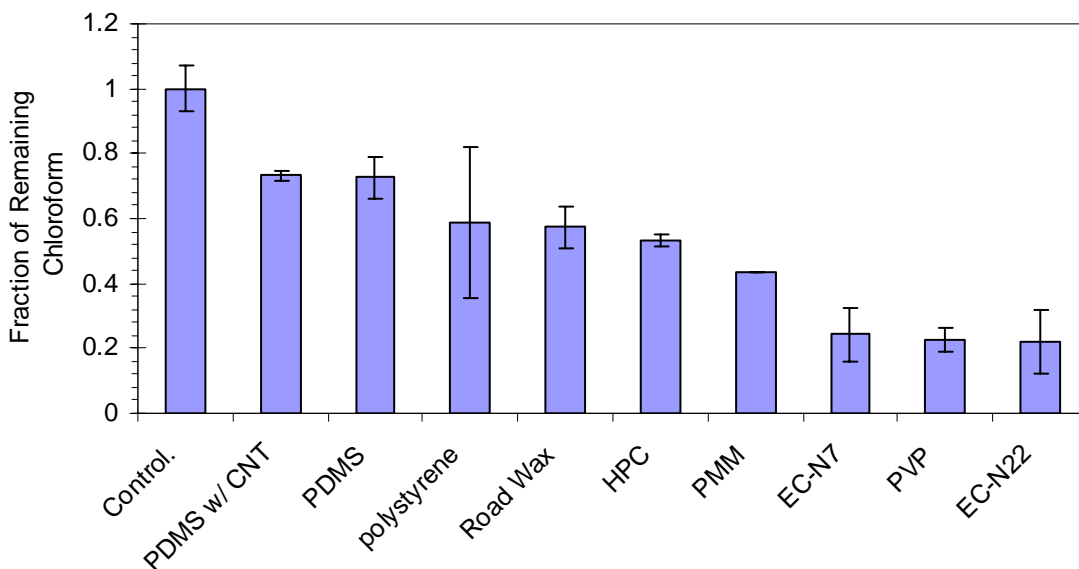
- After steps 1 and 2, the several best candidate polymers have been selected due to their reactivity to chloroform. Step 3 is necessary in order to determine if a polymer solution can bridge the tines of a QTF. A polymer solution is then made by dissolving of the polymer in a solvent, in this case chloroform. A drop of the solution is placed on each of the two tines using a hypodermic needle. As the solution begins to dry, the needle is used to bridge a wire between the two drops. If the polymer solution cannot form a wire, the polymer will not be useful for this application and the next best polymer is selected.

**Table 3.1 List of selected polymers tested for their ability to detect chloroform on a modified QTF.**

<b>Abbreviation</b>	<b>Name</b>	<b>Characteristics</b>
EC-T10	Ethyl cellulose	Cellulose ether with Ethoxyl content of 49.6 – 51.5 %
PMM		n/a
Wax	Apiezon ®	n/a
PVP	Polyvinylpyrrolidone	n/a
CMC	Sodium carboxymethyl cellulose	n/a
PVC	Polyvinyl chloride	Polymerized vinyl chloride monomers
HEC	Hydroxyethylcellulose	Cellulose based polymer
EC-N7	Ethyl cellulose	Cellulose ether with Ethoxyl content of 48.0 – 49.5 %
EC-N22	Ethyl cellulose	Cellulose ether with Ethoxyl content of 48.0 – 49.5 %
HPC	Hydroxypropyl cellulose	n/a
PANI	Polyaniline	Emeraldine salt average MW > 15,000
PVS	Poly(vinylsulfonic acid, sodium salt)	n/a
PAA	Poly(acrylic acid)	Average MW >250,000
PVA	Polyvinyl alcohol	n/a
PS	Polystyrene	MW: 250,000
PVP w/ 2% DVB	Polyvinyl Piridine w/ 2% divinylbenzene	n/a
PEI	Polyethylenimine	Average MW: 25,000
PAM	Polyacrylamide	n/a
PDMS	Poly(dimethylsiloxane)	n/a

## POLYMER SCREENING RESULTS

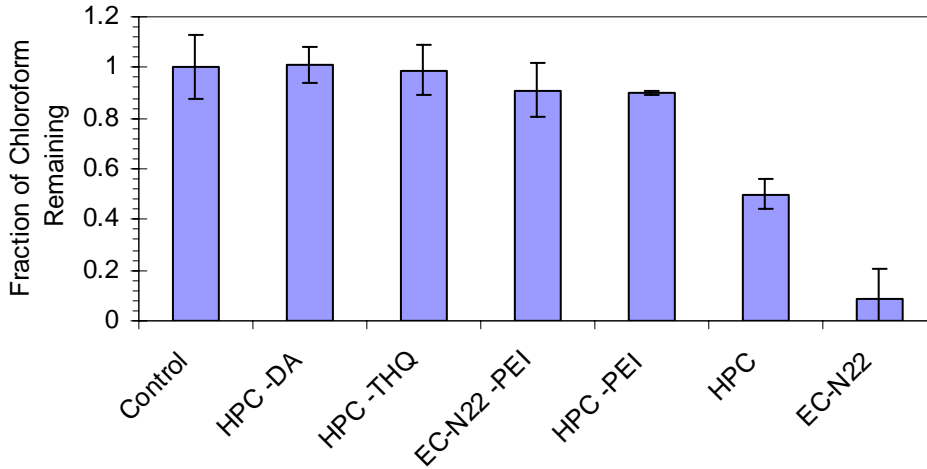
The initial testing of the polymers, to check for solubility in chloroform, shows that 10 polymers are not soluble in chloroform, reducing the number of candidate polymers. PEI, PAM, PVA, and PVS are polymers that could not form wires on the tuning forks. Data from the second screening process is displayed in figure 3.1. The PDMS w/ CNT is PDMS containing carbon nano-tubes (CNT). Figure 3.1 indicates that the CNTs have no affect on the ability to absorb chloroform.



**Fig. 3.1. Fraction of remaining chloroform in headspace of 40 mL vials containing polymer. The polymer samples with the lowest residual chloroform concentrations are the best candidates for the modified QTFs.**

Table 3.1 clearly shows that the different polymers exhibit a range of affinities to chloroform. The polymers with lower fractions of chloroform remaining are more suitable candidates as they absorb more chloroform than the polymers with a higher chloroform residual.

This initial polymer screening was conducted with in-house polymers that were readily available for testing. This does not necessarily mean they are the best polymers to use for this application. The list of polymers available on the market is extensive with an equally extensive range of modifications that can be made to create new polymers. Polymers can also be synthesized in the lab resulting in an extremely large selection of polymers to choose from. Samples of the in house cellulose based polymers were modified with one of three chemicals; tetrahydroxyquino (THQ), Dodecyl amine (DA), or polyethylenimine (PEI). The ability of these modified polymers to absorb chloroform was then tested to note the effect the modification had on the absorptive capacity of the polymer. The results are available in figure 3.2.



**Fig. 3.2. Modified cellulose based polymers reaction to gas phase chloroform. The two polymers on the right side of the graph were HPC – hydroxypropyl cellulose and EC-N22. The other polymers were modified with DA – Dodecyl amine, THQ – tetrahydroxyquino, or PEI – polyethylenimine.**

Figure 3.2 shows that the modifications of the polymers had the opposite of the desired effect on chloroform adsorption. Unmodified HPC and EC-N22 removed an average of 50 and 90 percent of the gas phase chloroform. The polymers modified with PEI removed approximately 10 percent and the THQ and DA modified polymers did not remove any chloroform. This indicates that the unmodified polymers are better candidates to use on the QTFs.

## MODIFIED TUNING FORK SELECTION

The standard resonant frequency of an unmodified QTF in the vacuum of its packaging is 32.768 kHz as defined by the manufacture. When the polymer solution is added to the QTF, the mass loading of the polymer causes the resonant frequency of the QTF to decrease. As the polymer wire dries, a tension is applied between the two tines of the QTF causing the resonant frequency of the QTF to shift up.

This detection platform is based on a frequency shift induced by the presence of a chemical that will alter the physical characteristics of the polymer wire strung across the tines of a tuning fork. Equation 3.4 shows how the resonant frequency of the QTF can change. Where  $f_o$  is the resonant frequency of the QTF sensor,  $k$  is the spring constant which is influenced by the tension in the polymer wire, and  $m$  is the mass of the tuning fork including the additional mass of the polymer wire.

$$f_o = \frac{1}{2\pi} \sqrt{\frac{k}{m}} \quad (3.3)$$

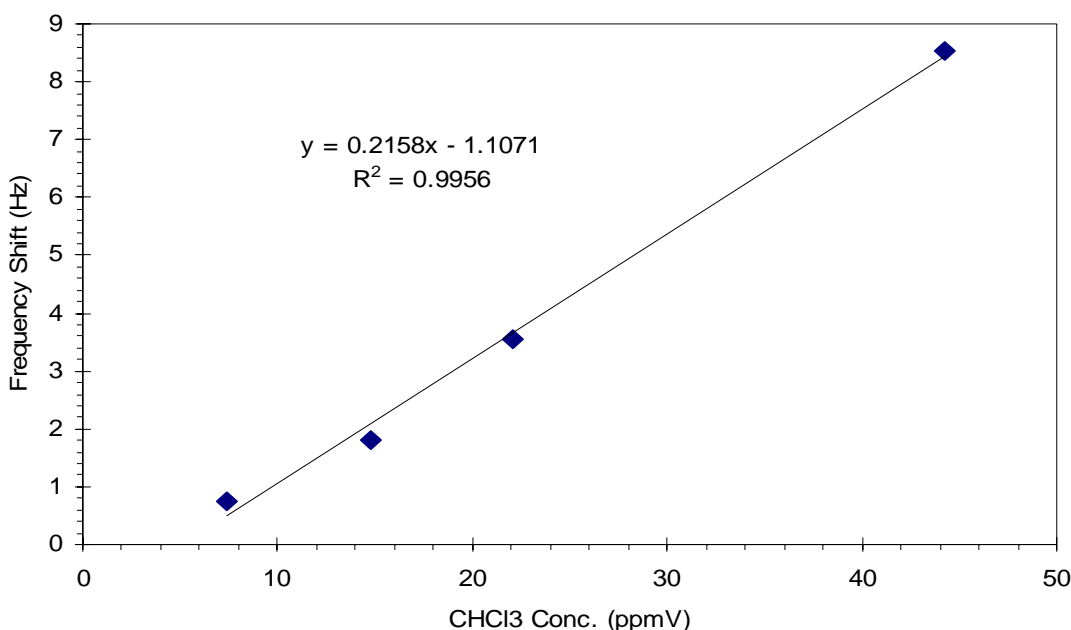
Ideally, the tension of the wire is at its greatest in the absence of chemicals that will compromise the wire. As the polymer is exposed to a chemical, the polymer wire is partially dissolved,

typically resulting in a resonant frequency reduction. To ensure adequate sensitivity, the frequency shift caused by the tension of the wire must be greater than the frequency reduction caused by the mass loading due to the polymer. After a polymer is selected to modify the QTFs, at minimum a dozen QTFs need to be modified and allowed to dry. A fairly large batch of modified QTFs needs to be prepared because only the modified QTFs with a resonant frequency higher than that of a bare QTF can be used. The resonant frequency can only be measured after the polymer has completely dried.

### QTF GAS PHASE DETECTION

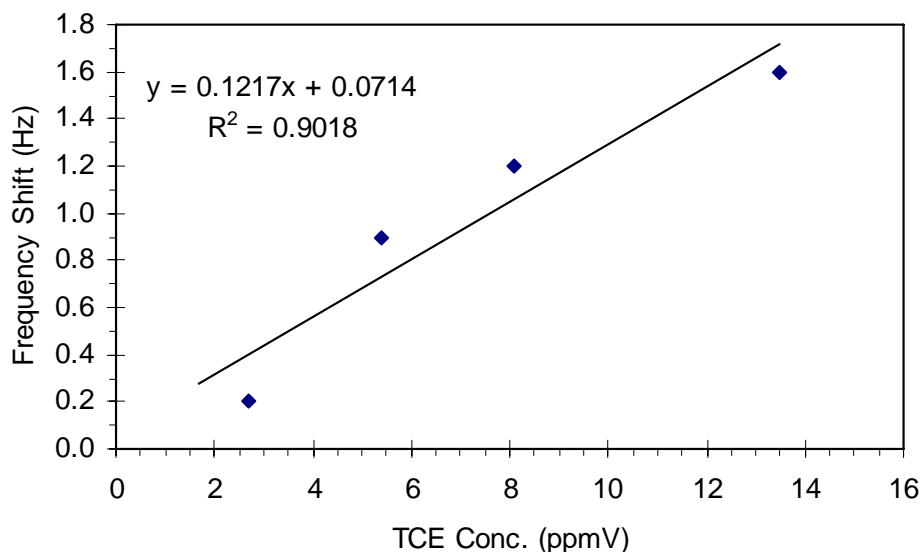
With the polymer selection complete and the modified QTFs created, it was necessary to determine if the QTFs had the ability to sense chloroform. Minimization of parameters that can affect the performance of the modified QTF was necessary for initial experiments in order to ensure that a frequency shift was due to the chloroform and not another parameter such as humidity or pressure change.

In order to create an experimental set up void of humidity and pressure differences, two 40 liter tevlar bags were inflated from the same air supply. One bag was injected with a known volume of pure chloroform. The two bags were then connected to a model 1010 precision gas diluter where any variation of blends of the two bags could be made. The effluent gas stream was then routed to a 60 mL syringe which houses the QTF array. A ventilation port was drilled in the side of the syringe downstream of the QTF array in order to ensure the chloroform gas stream passes over the sensors. Any frequency shift induced by humidity or pressure change occurs only initially and would not affect the performance of the QTF once the system reaches steady state. Injection times were 1 minute of gas phase chloroform and purged with chloroform free air for 3 minutes before the next concentration was pumped across the QTF.



**Fig. 3.3. Frequency shift of an N-22 modified QTF in the presence of chloroform at various gas phase concentrations.**

Trichloroethylene (TCE) is a groundwater contaminant that, when present, can be at much higher concentrations than what is typically found in drinking water systems. For this reason it was decided to determine if TCE could be detected in a similar fashion and at similar concentrations. The same experimental set up was used to monitor the frequency shift of the modified QTFs in the presence of TCE. The gas phase stock solution of TCE is prepared in the same manner as the chloroform stock using equation 3.3. The results of initial experiments are presented in figure 3.4.



**Figure 3.4. Frequency shift of a wax modified QTF in the presence of TCE at various concentrations.**

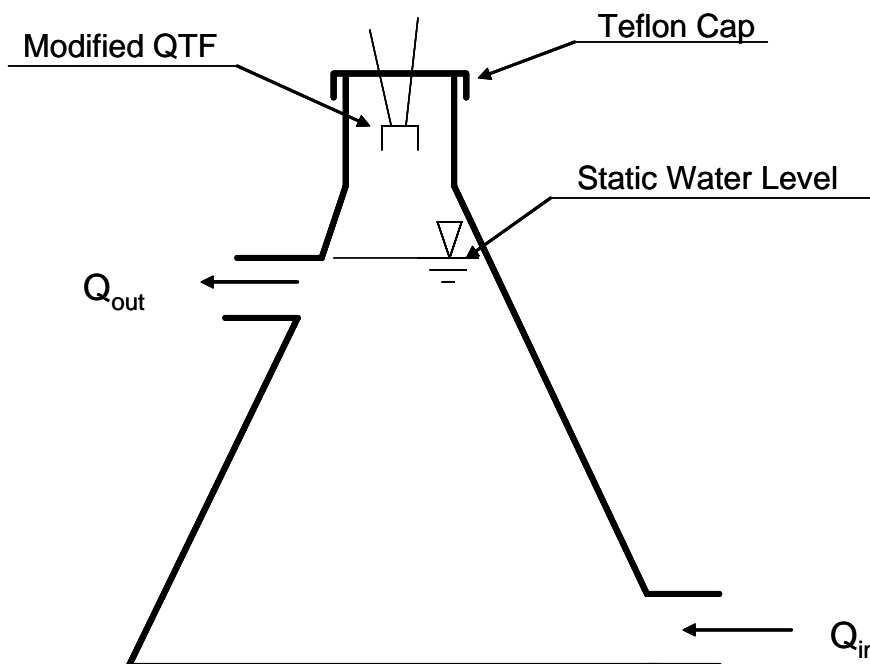
The selected polymers were not previously screened for their affinity to adsorb chloroform. The response to TCE was not linear, but a frequency shift of approximately 0.2 Hz was recorded at the lowest concentration of 2.7 ppmV of TCE.

### **QTF REACTOR DEVELOPMENT**

The initial detection method of chloroform in the gas phase was not applicable for detection in drinking water systems in which the gas stream would contain more humidity resulting in interference. With the initial polymer screening process complete, the next step was to introduce the QTFs to a water sample containing chloroform. A reactor was built and several modifications were made in order to expose the QTF to an environment more conducive to that of a distribution system.

The experimental set up was designed to be a flow through system that mimics the environment an on-line THM sensor would experience while in operation on a distribution system. Reactor #1 was designed such that valves were attached to the lower and upper end of a standard 250 mL Erlenmeyer flask. The valve on the upper end of the flask was placed approximately 2 cm below the top of the flask. This allowed for a headspace in which the QTF is placed in order to detect

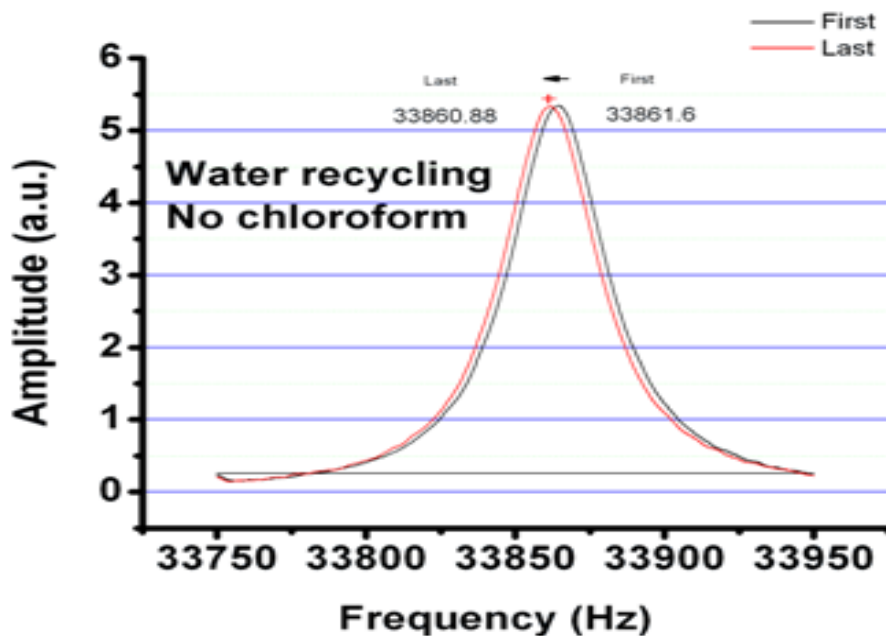
gas phase chloroform. Water can be pumped in through the lower valve and pumped out of the upper valve such that the gas in the headspace would be confined in the flask.



**Fig. 3.5. Drawing of reactor #1 used to test modified QTFs reactions to chloroform in a humid flow thru system.**

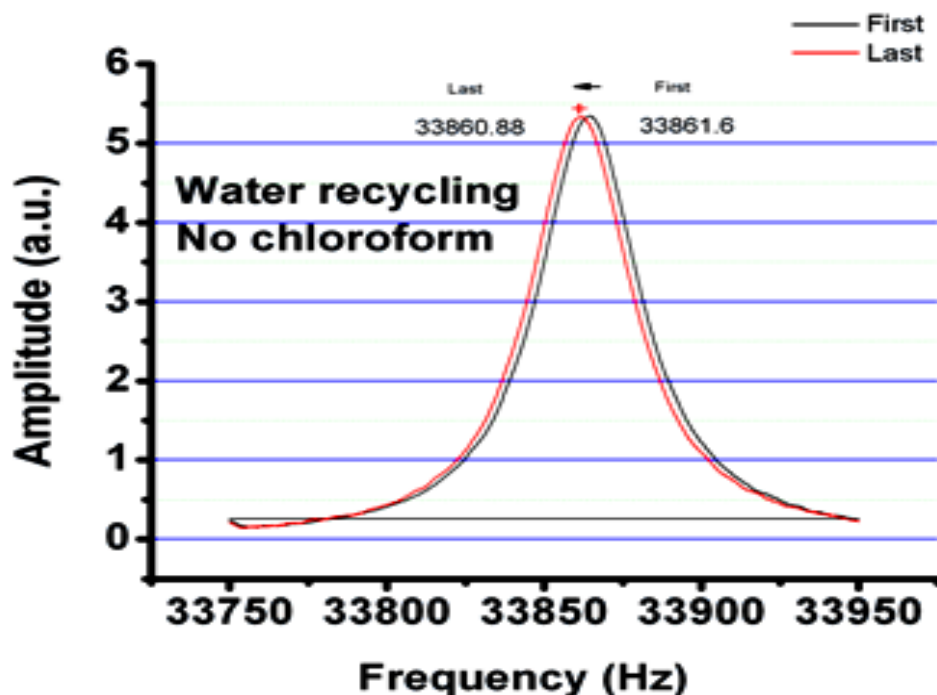
This system allows the chloroform to partition from the aqueous to the gas phase in an isolated area in which a QTF is placed. Unfortunately the moisture content in the gas phase is saturated and water begins to condense onto the QTF. A mass loading of water molecules onto the QTF causes a frequency shift much greater than the shift that expected from the chloroform. In order for this flow through system to function properly, it is necessary to remove the moisture before chloroform detection can occur.

The same Erlenmeyer flask as that in figure 3.5 was modified by placing a steel screen between the QTF and water level so a commercial desiccant could be set in place to remove the moisture from the air before it reaches the QTF. Granular form Drierite brand calcium sulfate was used to remove the moisture from the air prior to it encountering the QTF.



**Fig. 3.6. Stability of the QTF in the headspace of the Erlenmeyer reactor with desiccant. Only a 0.72 Hz shift was recorded after exposure to moist air for 15 minutes. The “Water recycling No chloroform” indicates that the pump was recycling only nanopure water through the flask throughout the experiment.**

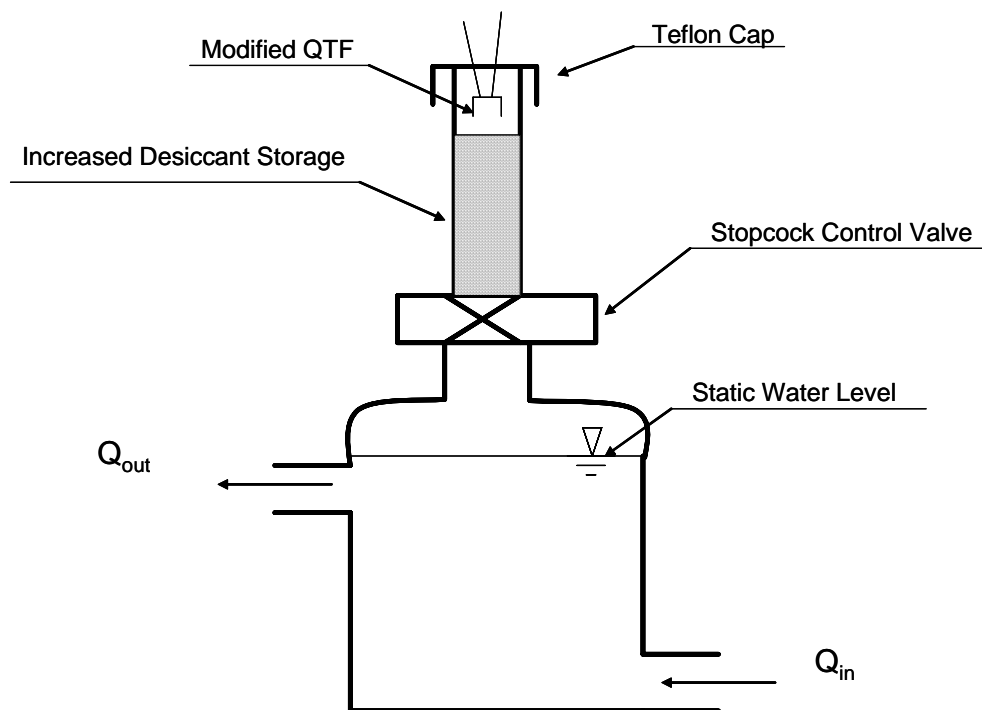
Figure 3.6 shows that after 15 minutes only a 0.72 Hz shift was detected in the QTF when nanopure water was pumped through the reactor. The quality factor of the QTF remained unchanged throughout the experiment indicating that there was minimal mass loading of water molecules on the QTF. The next step is to begin pumping nanopure water spiked with 10 ppm chloroform through the reactor.



**Fig. 3.7. Nanopure water containing 10 ppm of chloroform was pumped thru the reactor. The resulting shift was approximately 9 Hz after 15 minutes.**

Before the water containing 10 ppm of chloroform was pumped through the reactor, the desiccant was changed and the QTF was allowed to stabilize in order to more closely simulate the control experiment. Over the same time frame of 15 minutes, a 9 Hz resonant frequency shift was recorded in the presence of nanopure water containing 10 ppm chloroform. Unfortunately the same frequency shift was recorded every 15 minutes for the next hour. The gas phase chloroform was both steadily and partially dissolving the polymer wire. This suggests that the physical properties of the polymer wire were continuously being altered while in the presence of the gas phase chloroform. Therefore equilibrium was not yet reached.

A major drawback of reactor #1 is that a very limited amount of desiccant can be placed on the screen between the water level and the QTF due to special limitations. The result of this was that the small amount of desiccant became saturated with water vapor and needed to be changed frequently. The next reactor should be able to control moisture for an extended period of time.

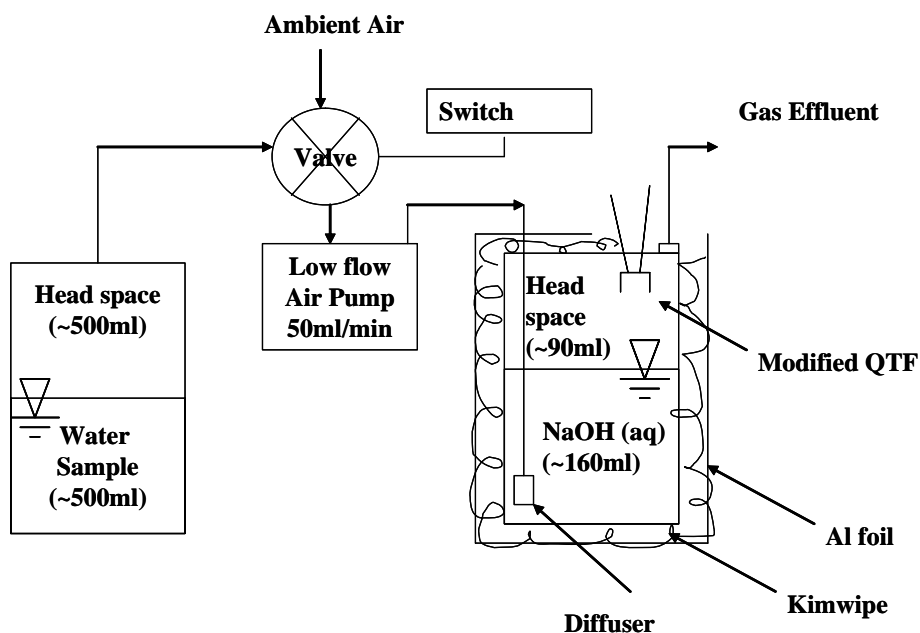


**Fig. 3.8. Drawing of reactor #2 used to detect gas phase chloroform from aqueous samples. The distance from water level to QTF is approximately 15 cm.**

The stopcock control valve was installed in order to allow the moisture and any volatile chemicals to reach equilibrium between the water level and the stopcock. This would allow the QTF to stabilize while simultaneously permitting a partitioning into the gas phase in preparation for experiments.

Several polymer modified QTFs were tested using the new reactor depicted in figure 3.8. The polymers tested were EC-N22, EC-T10, and Apiezon® wax. No concentration dependent shifts were noticed in the frequency of any of the modified QTFs. A frequency shift was initially noticed when the stopcock is opened, possibly due to a pressure difference. After this initial shift, the frequency stabilized and no shifts were noticed even after pumping a 100 ppm chloroform solution of water through the reactor for two hours.

The reason the QTFs could not detect the chloroform may have been due to the fact that the density of gas phase chloroform is more than 4 times that of air at standard pressure and temperature. There was no mechanism to cause air movement and mixing above the stopcock. Thus in order for chloroform to reach the QTF, diffusion is the transport mechanism. This is a prohibitively slow process especially in the presence of the desiccant which will physically slow the process. A reactor needed to be developed that would be able to remove moisture and help drive the chloroform gas to the QTF. Figure 3.9 illustrates the design of reactor #3.

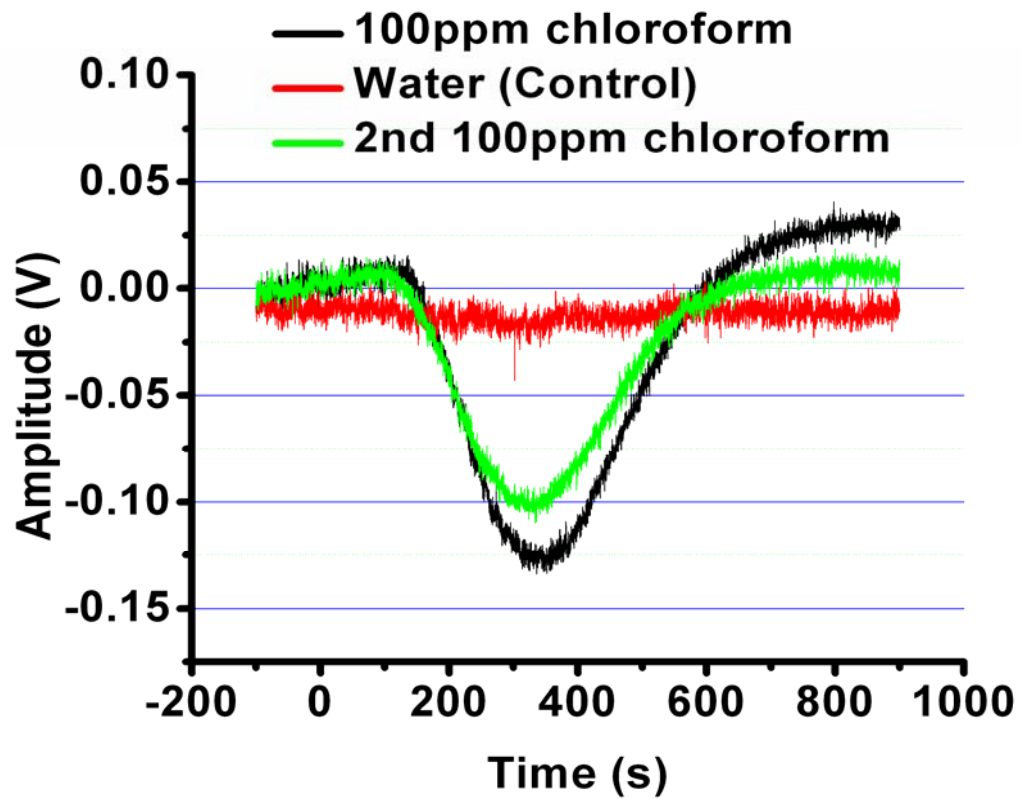


**Fig. 3.9. Schematic of reactor #3 for moisture control and mixing of chloroform laden air.**

Figure 3.9 illustrates reactor #3, a batch type method of chloroform detection. Several 1 liter bottles are half filled with water containing chloroform at various concentrations. The chloroform is allowed to partition into the gas phase overnight. The headspace gas is then bubbled through a NaOH solution via a stainless steel diffuser in order to reduce the relative humidity to approximately 5-6%. The constant pumping of air ensures adequate mixing of air in the headspace of the QTF housing bottle. The QTF housing bottle was wrapped first with a layer of Kimwipe brand lab tissue in order to minimize the effects of any outside mechanical motion, and secondly with a layer of commercially available aluminum foil to minimize any infrared radiation that might affect the performance of the QTF (Tsow and Tao 2007).

Reactor #3 was tested using an EC T-10 modified QTF. Three samples were prepared for the experiment. One bottle was half filled with nanopure water, as a control, and two others were half filled with nanopure water containing 100 ppm of chloroform. The bottles were filled, sealed, and allowed to sit overnight in order to allow the moisture and chloroform to reach equilibrium in the headspace. The air pumping sequence included an initial 100 seconds of pumping ambient air, followed by 300 seconds of sample headspace, and finally 600 seconds of ambient air to allow for QTF recovery.

No significant amplitude shift was measured when the headspace of the nanopure water was pumped thru the NaOH solution. Once pumping of the headspace from the 10 ppm chloroform solution began, a noticeable amplitude shift was recorded. The shift due to the first bottle was approximately 0.13 volts. The shift due to the second bottle was approximately 0.10 volts.



**Fig. 3.10.** Amplitude shift of an EC T-10 modified QTF in the presence of headspace gas from a 100 ppm solution of chloroform. The horizontal line is the control experiment to rule out any possible humidity interferences.

## CHAPTER 4 SUMMARY & RECOMMENDATIONS

The goals of this research were to develop a proof-of-concept prototype THM sensor and to validate the WTP model prediction for THM precursor removal and THM formation. The sensor development included:

- Developing polymer screening process
- Test modified QTFs response to gas phase chemicals
- Develop interface in transfer THMs from aqueous to gas phase and remove interferences such as humidity

Based on the research, the following conclusions were reached for QTF development:

1. A polymer screening process was successfully developed and is able to identify polymers with a high affinity to absorb gas phase chloroform.
2. Polymer modified QTFs are able to detect gas phase chloroform at sub 10 ppmV concentrations.
3. There exist many interferences in a drinking water system that would effect the performance of the modified QTFs including temperature, mechanical motion, and humidity.
4. Reactor #3 was developed to successfully remove interferences due to humidity by passing the air stream thru an aqueous solution of NaOH. A limitation of this system is that as the NaOH solution removes humidity from system, the solution becomes more dilute and will have to be changed to maintain consistent humidity.
5. This reactor allowed for detection of aqueous chloroform at concentrations of 100 ppm which is approximately 3 orders of magnitude above what might be expected in a typical drinking water system.

Improvements to the reactor are also possible. It is possible to control humidity in the sampling, but this involves purging the air stream thru a hazardous chemical. Further research is necessary to increase the gas phase THMs and reduction of other interferences. In order to detect THMs at regulatory concentrations the detection limit needs be reduced significantly. There are several ways this might be achieved, use a more selective polymer to modify the QTF and develop a new interface between the QTF and the water sample to more efficiently drive the THMs into the gas phase. The polymer selection process was effective at determining the best polymer out of a batch. Unfortunately, millions of polymers exist. A better understanding is necessary with regards to the property of a polymer that causes an affinity to chloroform. This can help determine what general type of polymer is more likely to react to chloroform, and the screening process can be performed on a series of modifications of these polymers to determine the best candidate.

## CHAPTER 5 REFERENCES

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