Group G

Review of proposal, "Proposal to Analyze Volatile...."

Overall Evaluation: Excellent (Range includes Outstanding, Excellent, Very Good, Good, Fair, and Poor); Percentile Rank = 10% (top 10%).

This is a very nice proposal on VOCs in drinking/surface water. The proposal is well organized, is clearly written, and is easy to follow. The major weakness of the proposal is the lack of a discussion on the mechanism of formation of the chlorinated compounds and how the mechanism is dependent on pH, [Cl2] or other chlorine-containing materials, [organic], sunlight, etc. The proposal could be improved by addressing the following.

1. Use spell check.

2. Hypothesis should be more fully stated in Abstract.

3. Mechanism of formation needs to be placed into hypothesis.

4. Why was Jefferson Parish chosen? Environment, etc.?

5. A comparison as to why P&T GC/MS was chosen is in order.

6. Need to discuss more fully the previous work of Clark and Garcia-Villanova.

7. What is free chlorine? total chlorine?

Grade = 93%

G-2

Proposal to Analyze Volatile Organic Compounds In Drinking Water

by

Group G

Abstract:

Contamination of drinking water with volatile organic compounds (VOCs) is a major environmental concern. Organic compounds that undergo chlorination produce chloroorganics through free radical halogentation of alkanes and substitution or addition reactions of alkenes [1]. Most of these compounds are a major health hazard upon chlorination since they are carcinogenic. We will identify and quantify these VOCs using a purge and trap gas chromatography mass spectrometry (P&T GC/MS) analysis. Samples will be collected daily in Jefferon Parish and analyzed by P&T GC/MS within 14 days of collection. The concentration of free and total chlorine will also be determinated on a daily basis. We will analyze samples collected over a 15-20 day period and record the concentration variation of the identified VOCs. Also, the relationship between the chlorine concentration and VOC concentrations will be established.

Introduction:

During past decades, environmental pollution has become a major concern in our every day lives [2]. An appreciable portion of our environmental contamination problems is attributed to volatile organic compounds (VOCs) in surface waters as well as drinking water supplies. The existence of VOCs in our drinking water has undoubtedly invaded our health since some of them are toxic. In order to gain a better insight about the quality of drinking water that we consume daily, we propose to study qualitatively and quantitatively the VOCs in the drinking water of Jefferson Parish. Our hypothesis is the concentrations of VOCs will vary from time to time and this variation is directly proportional to the concentration of chlorine in drinking water. The major forms of chlorine that are present in drinking water are molecular free chlorine, hypochlorous acid and hypochlorite ion [3]. To verify our assertion, we will study the water samples collected daily by identifying the VOCs and their concentrations using purge and trap gas chromatography mass spectrometry (P&T GC/MS). The VOCs in the drinking water will first be purged, in which the VOCs will be extracted from the aqueous phase into the vapor phase and these VOCs will then be trapped using a sorbent trap. Next, the trap will be heated and these VOCs will be sent to a GC column in which the VOC mixture will be separated using temperature programming. Finally, the individual VOCs will be identified using the mass spectrometer. Also, the correlation between chlorine content and VOC content will be studied by measuring the daily concentration of chlorine in the water.

VOCs are a variety of compounds primarily composed of carbon and hydrogen. Many VOCs also contain chlorine, fluorine, and/or bromine. The halogenated VOCs are predominantly used as solvents, degreasers, cleaning solutions, dry cleaning fluids, and components of pesticides and plastics [4]. These chemicals are described as volatile because of their tendency to evaporate. They generally enter drinking water systems through spills and improper disposal. Public drinking water systems are required to monitor for VOCs in the water because of various health concerns including cancer, organ damage, blood disorders and nervous system disorders. VOCs can get into water supplies in various ways. Many VOCs are products of industrialization and

may get into water supplies through various means, such as leakage of storage tanks, accidental spills, or illegal dumping of toxic wastes [2]. Other VOCs of concern are disinfection byproducts (DBPs), such as trihalomethanes (THM's) which are methane molecules that contain 3 halogen atoms. These by-products get into the water supply as a result of the disinfection process (usually chlorination) which makes our water potable [2]. Almost every region in the U.S. has VOCs in their drinking water supplies. Urban areas may get VOCs from industrial waste, and rural areas may get VOCs from agricultural waste. Also, 90% of U.S. drinking water is chlorinated and most likely contains disinfection byproducts; thus, VOCs are practically everywhere [4]. Primary drinking water standards, also known as maximum contamination levels (MCLs), have been established to monitor the contents of VOCs in drinking water. For example, the maximum contamination level for trihalomethanes is 100ppb [5].

One of the most important steps in VOC analysis in aqueous samples is the quantitative separation of all VOCs from the sample matrix. Many different methods have been utilized to perform this process. Some of the conventional approaches are purge and trap, hollow fiber membrane module (HFM) and vacuum distillation. All these methods have their own features and their capability highly depends on the method of sampling, the location of the sample and the experimental purpose of the analysis.

same P+T?? Not clear!

The purge and membrane mass spectrometry (PAM MS) is one of the most selective and sensitive on-site and online methods for VOC analysis [6]. This method involves purging the VOCs from water samples with an inert gas in which the stream is directed through a sheet of membrane module, which selectively extracts the VOCs from the matrix. These organics then pervaporate through the membrane into the ion source of a mass spectrometer. This on-site method is best suited for its high sensitivity, in which it can detect concentration levels below 1 ppb, but is unreliable for direct collection of VOCs from samples that have solid materials. [6]

In an experiment done by Hiatt, a vacuum distillation method is used to determine the concentration of VOCs in environmental samples [7]. The sample is first evacuated in which the water vapors are collected on a condenser column and the distillates that are being studied are collected in a cryloop, which is kept at –196C in liquid nitrogen. Then, the nitrogen bath is replaced with a hot water bath to volatilize the distillates. These distillates are then transferred into a GC. Surrogate compounds are utilized to measure the matrix effects relating boiling point and relative volatility to the concentration of the target analytes. The accuracy of this method allows the analytes of the standard solutions to be used for the determination of analytes in different matrices as well as different sample sizes without affecting the usefulness of the data.[7]

The third approach is to use a hollow fiber membrane module (HFM), which is shown to be a simple, efficient and inexpensive alternative for quantitative extraction of VOCs from water in a solvent-free environment [8]. The extraction process is done under a condition in which the flow rate of water is relatively low. The contaminated water sample is first pumped through the center of the fiber, while an inert gas from the GC flows countercurrently around the exterior of the fiber. As a result, the flow rate of the gas through the HFM is equivalent to the flow rate of the carrier gas to the column of the GC. This membrane is made of a piece of silicone hollow fiber sealed with epoxy in a glass capillary tube. Since silicone is hydrophobic and nonporous, the water is not allowed to pass through the membrane and the VOCs will diffuse from the feed solution into the stripping gas, which is interfaced to a GC. [8]

which is best? why?

Experimental Approach:

In this section, we will outline the details of our hypothesis and experimental method that will be employed in our study.

A) Details of our hypothesis and claim

The purpose of this proposal is to study the identity and the quantity of VOCs in the drinking water supplied by the Mississippi River to the community of Jefferson Parish. We predict that the VOC composition and concentration will vary on a periodic basis. The chemical makeup of surface waters is constantly changing due to normal environmental changes as well as irresponsible chemical and biological discharges. Thus, VOCs are introduced into these waters at various concentrations and eventually make their way into drinking water supplies.. The amount of VOCs entering surface waters, temperature, pH and the volume of the surface water are some of the factors that can contribute to the concentration variation of VOCs. Upon chlorination of the river water, we also expect to see a correlation between the chlorine content and the VOC content. Hence, we will use this fluctuation to draw a relationship between the chlorine concentration and VOC concentration.

B) Prediction from References [9], [10]

In a paper by Garcia-Villanova and etc. (1997), the formation, evolution and modeling of trihalomethanes in the drinking water of the city of Salamanca, Spain were studied [9]. They found that there is a strong statistical correlation between the concentration of trihalomethanes with the chlorination dosages in treatment plants, distances run by the water and the concentration of residual free chlorine and total chlorine in the water [9]. In another paper by Clark ~~and etc.~~ et al. (1998), the authors develop a mathematical model based on pH, temperature and the initial concentration of chlorine, to predict chlorine residuals and the formation of total trihalomethanes (TTHMs) in drinking water [10]. The experimental data showed that initial chlorine residual level is one of the parameters that is proportional to the content of TTHMs in the drinking water, and the formation of TTHMs is a direct result of the consumption of chlorine [10]. These two studies clearly support our claim about the content of VOCs in our samples.

C) Chlorine Determination

Chlorine is widely used in the waters to destroy or deactivate the disease-producing microorganisms in order to improve the quality of drinking water. The chlorine added to the water is usually in molecular form and undergoes hydrolysis to form free chlorine, hypochlorous acid and hypochlorite ion [3]. The determination of residual chlorine in water that contains VOCs is difficult because chlorine is not stable in water and its content in water changes unpredictably. Exposure to light and agitation can reduce the chlorine concentration [3]. As a result, the concentration of total and free chlorine will be determined immediately after the water is collected using a HACH colorimeter test kit. The range for the free chlorine and total chlorine determination of the test kit are 0 to 3.5 mg/L and 0 to 0.7 mg/L respectively.

The test kit consists of a color comparator box, which has two compartments, one for the blank and one for the sample. The DPD total chlorine reagent powder pillows and the DPD free chlorine reagent powder pillows are added for total and free chlorine determination respectively. These DPD reagent powder pillows contain N,N-diethyl-p-phenylenediamine (DPD), ethylenediaminetetraacetic acid, a phosphate buffer and potassium iodide. Reactions are pH dependent. Hypochlorous acid, hypochlorite and free chlorine oxidize DPD causing a magenta color. This measures free chlorine. After this reaction is completed the combined forms of chlorine, such as chloroamines, react with the iodide and form iodine. The iodine reacts with the DPD just like chlorine. This reaction measures total chlorine. In order to find the free and total

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chlorine content in the sample, a color disc is used to compare the color of the sample to the color of the scaled sample disc.

D) Samples Collection, Preservation and Handling

40ml amber prewashed vials with PFTE faced silicone septa will be used to collect samples. These samples will be collected in Jefferson Parish. Each jar will contain approximately 25mg of ascorbic acid to remove residual chlorine because we do not want reactions taking place in the container [11]. Also, 2 drops of 1:1 HCL will be added during collection to lower the pH and prevent any microbial degradation of the volatile compounds [11]. The water tap will flow for about 10 minutes before collection to ensure a true homogenous representative sample. The sample will be filled to the top of the vial so that a concave appearance over the top of the vial is evident. Each vial will be capped and shaken for 1 minute. Each vial will be turned upside down to ensure that no air bubbles exist. Three samples will be collected each day, stored in a refrigerator and picked up every 7 days. During transport back to the lab, the samples will be kept at 4 degrees in an ice chest. Samples will be collected and analyzed over a 15-20 day period.

E) Instrumentation [11]

The method that we will be using is P&T GC/MS. Purge and Trap GC (P&T GC) was developed to overcome the limitations of existing techniques of GC, in which P&T GC has better sensitivity and can tolerate water injections. In P&T GC, the sample is purged with an inert gas, causing the volatile compounds to be swept out of the sample. The volatile compounds are then captured on an adsorbent trap. These volatile compounds are desorbed by heating the trap and are injected into a GC by backflushing the trap with GC carrier gas. The separation and detection are then accomplished by normal GC and MS operations. [11]

The amount of sample purged is proportional to its vapor pressure and solubility in the sample. In the process of purging, the system is no longer at equilibrium due to the fact that the volatile compounds, which are in the vapor phase, are constantly being removed by the inert gas. As a result, more volatile compounds migrate into the vapor phase. This means the volatile compounds can be removed more efficiently.

Now, we introduce the instrument that we will be using in our drinking water analysis:

1) *Purge and Trap*

We will use a Tekmar ALS2016 autosampler that uses 25ml needle sparging glassware (purge tubes) combined with a Tekmar LSC2000 concentrator. The autosampler, purge and trap concentrator and the GC/MS are connected together with 1/16 inch of nickel tubing transfer lines that are lined with fused silica. Sample is purged with helium at a flow rate of 40ml/min, sweeping the VOC's through the nickel transfer line connecting the autosampler to the concentrator and onto the adsorbent trap, which is at room temperature for 11.0 minutes. A 20ml sample is purged instead of 5ml so that trace quantities can be concentrated thus lowering our detection limit. The trap is a VOCARB 3000, which is composed of CarbopackB/Carboxen 1000 & 1001. Trap dimensions are 0.123" outside diameter x 12"long x 0.010" wall thickness. The trap is set to dry purge mode for 4 minutes, which removes water vapor off of the trap. In dry purge mode the purge vessel is bypassed. A moisture control module (MCM) is placed in line that thermoelectrically traps water. Then, the trap is heated to 250°C by using a thermocouple so that the adsorbed components move through the heated transfer line connected to the GC as a vapor plug and enters the injection port of the gas chromatograph. The desorb time is 4 minutes. Next, the trap is baked out for 16 minutes at 260°C. Also, the MCM is baked out at 85°C to remove water. This ensures that the trap is cleaned and ready for the next sample that will be purged on the autosampler.

2) *Gas Chromatograph/Mass Spectrometer*

The Gas Chromatograph is a Hewlett Packard 5890 Series II with packed column injection port modified for a megabore column. The column is a DB-624 fused silica megabore column. The dimensions are 0.53 mm inside diameter x 75 m long with a 3 um film thickness. The stationary phase is 6% of cyanopropylphenyl and 94% of dimethylpolysiloxane and the flow rate is 10 ml/min before entering the jet separator (HP59913 jet separator) and 1 ml/min after exiting the jet separator. The jet separator provides the means to use a megabore column that is connected to a mass spectrometer. When the analyte mixture and the carrier gas exit the GC column and enter the low-pressure chamber of the jet separator, the lighter carrier gas molecules diffuse out of the chamber. However, the heavier sample molecules will pass through the chamber and flow into the mass spectrometer. Upon desorption of the purge and trap a relay switch activates the start time for the GC. This chromatogram is displayed through the software, which is the HP Colt-Chemstation-HPG1034C Version C. The GC oven temperature program will be initially set at the following conditions. Initially the oven temperature is set at 35°C and this temperature is maintained for 4 minutes. Then, the temperature will be raised at the rate of 8°C/minute to 200°C and this temperature is held for 5.0 minutes. If any detected compounds show signs of coelution, then the temperature program will be modified to better separate the peaks. The injection port and jet separator will be set at 250°C. The temperature for the GC/MS interface will be set at 280°C and the interface is followed by a mass spectrometer. The mass spectrometer will ionize molecules through electron impact, mass filtered with a quadropole mass filter and detected with an electron multiplier. The solvent delay will be set at 1.0 minutes and the scan rate and the scan range of the mass filter will be set at 1.8 scans/minute and from 25 amu to 300 amu respectively. The spectral library used will be the NIST54K library to identify unknown peaks

F) *Purge and Trap Sample Processing*

This is the process that limits the precision and accuracy of our result, so extra care is needed in order to minimize the loss of VOCs. 20 ml of each sample is placed in a 25ml gas-tight syringe with a luer tip valve. Internal standards (ISTD's) and surrogate compounds are injected into the sample before being placed in 25ml purge tubes. The ISTD's are bromochloromethane, 1,4-dichlorobutane and 2-bromo-1-chloropropane, while the surrogates are 4-bromoflurobenzene, fluorobenzene and pentafluorobenzene. All of these standards will be purchased through Accustandard. A 50ppb standard of all compounds will be prepared in 20ml of water by injecting 5ul of a 200ppm solution. The sample will be pushed into a purge tube and sealed. The sample will be purged at 40ml/min for 11.0 minutes. The concentrator will then move into dry purge mode for 4 minutes to remove water vapor. Then, the MCM will be set at 5 degrees. After that, the concentrator will move to desorb ready mode and heat the trap to 250 degrees. In order to strip compounds off of the trap into the injection port of the gas chromatograph, the concentrator will then move to desorb mode for 4 minutes. At the same time, the GC will automatically begin data analysis. Next, the concentrator will move to bake mode for 16 minutes at 260 degrees. Also, the MCM will bake off water at 85 degrees. Finally, the concentrator will move to purge ready mode waiting for the autosampler to begin purging the next sample.

G) Qualitative Analysis of VOC's

A drinking water sample will be analyzed using the GC/MS system. The NIST library will be used to identify the spectrum of each peak. A pure standard of all identified compounds will be purchased and analyzed separately. The GC retention time along with a matching mass spectrum of the original sample will be used for complete identification of each unknown peak.

Within 14 days of collection, drinking water samples will be analyzed. If we see different volatile compounds other than the original compounds detected in the first couple of samples, we will quickly order the new standard through Supelco. The fragmentation pattern of each spectrum will also be interpreted. → confirmation!

H) Quantitative Analysis of VOC's

A target ion for each compound will be chosen by inspecting the mass spectra of each compound and choosing the most abundant ion so that the detector will be very sensitive to the analyte of interest. An ion other than the most sensitive ion will only be chosen if two compounds have similar spectra and are very close to each other. Target ions will also be chosen for internal standards and surrogates in the same manner as analyte compounds. One or two qualifier ions for each compound will be chosen so that the data analysis system recognizes the spectra and quantifies using the target ion abundance of the spectra. A five-point calibration curve will be constructed for each VOC in the concentration range of the unknowns. Initially, a one-point curve will be constructed. A sample will be analyzed and quantified to determine an approximate concentration from this curve. Then a five-point curve will be established in the concentration range of the unknown. Three replicates of each standard will be analyzed and a least-squared method will be used to draw the best-fit line. The curve will be used to calculate the concentration of the unknowns.

I) Data Analysis and Reporting

A table showing the calibration curve data will be presented. The target ion abundance of each standard replicate will presented along with the average, standard deviation and 95%CI. The calibration curves of each compound will be presented along with the correlation coefficient for each curve. A graph showing the daily concentration of VOC's will be presented along with the daily concentration of chlorine. A table showing the daily concentration of chlorine will be presented. A table showing the target ion abundance, concentration, average concentration, standard deviation, and 95%CI will be presented for each compound each day of analysis. (Three samples will be analyzed for each day). The fragmentation pattern of each unknown spectra will be presented. Raw data will be handed in separately from the final report so that the documented data can be verified.

good

Application and Future Work:

Other than applying P&T GC/MS to explore the problems of environmental chemistry, P&T GC/MS has been used to study the flavor of food in food science and analysis of perfume. We hope that our project will strengthen the public awareness about environmental pollution, especially the contamination of drinking water with VOCs and their effects on our daily lives. By knowing the statistical variation of the concentrations of VOCs, we can undoubtedly begin to understand how the quality of our drinking water changes. Thus, if abnormal concentrations of VOCs are detected in drinking water, an emergency response can be taken immediately and effectively. If our claim about the proportionality between the contents of the chlorine and VOCs is true, we can have a better control over the concentration of VOCs in the drinking water by quantifying the amount of chlorine used in chlorination. Having this control can ensure that the people will consume a better quality of drinking water. In the future, we think that a study concerning the concentration of total organic compounds (TOCs) versus the concentrations of volatile organic compounds (VOCs) on a periodic basis will certainly enhance our understanding about the quality of our drinking water.

good

Project Timeline:

Week 1 (2/26/2000 to 3/4/2000):

Samples will be collected each day along with the analysis of free and total chlorine. We will analyze some samples and qualitatively determine the identity of the VOCs that make up the matrix and order the appropriate standards. The P&T GC/MS method parameters will be fine tuned, such as the temperature program, target and qualifier ion determinations for each identified VOC and integration parameters.

Week 2 (3/5/2000 to 3/11/2000):

The samples will be picked up on 3/5/2000. We will create calibration curves for each identified VOC. The sample replicates (total of 21 samples) from week 1 will be analyzed to obtain concentration values and begin a database. We will still collect the samples daily and determine the daily chlorine concentrations.

Week 3 (3/12/2000 to 3/18/2000):

The samples will be picked up on 3/12/2000. The sample replicates from week 2 will be analyzed to obtain concentration values. We will still collect the samples daily and determine the daily chlorine concentrations. We will begin to set up the correlation graphs of chlorine concentration and total VOC concentrations. Also, we will start to write the introduction of our final report.

Week 4 (3/19/2000 to 3/25/2000):

The samples will be picked up on 3/19/2000. The sample replicates from week 3 will be analyzed to obtain concentration values. We will still collect the samples daily and determine the daily chlorine concentrations. This will be the last week of our sample collection. We will update our database of total VOC and chlorine concentrations. Our database will be used to compare to cited references. Also, we will start to write the experimental section of our final report.

Week 5 (3/26/2000 to 4/1/2000):

The samples will be picked up on 3/26/2000. The sample replicates from week 4 will be analyzed to obtain concentration values. We will update our database of total VOC and chlorine concentrations. Also, we will begin to summarize our results by performing a statistical analysis on our data.

Week 6 to Week 8 (4/2/2000 to 4/22/2000)

We will complete and turn in our final report. We will also prepare for our oral presentation.

References:

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