# CHEMICAL IDENTIFICATION AND ORGANOLEPTIC EVALUATION OF IODINE AND IODINATED DISINFECTION BY-PRODUCTS ASSOCIATED WITH TREATED SPACECRAFT DRINKING WATER

by

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(Abstract)

Aboard the International Space Station, potable water will likely be produced from recycled wastewater. The National Aeronautic and Space Administration (NASA) plans to use iodine as a disinfectant, and, consequently, the formation of iodinated disinfection by-products (IDBPs) requires investigation. Objectives of this research were to determine possible precursors of IDBPs, identify IDBPs formed, and apply flavor profile analysis (FPA) as a tool to evaluate water quality. Experiments were performed by separately reacting iodine with each of the following organic compounds: methanol, ethanol, 1-propanol, 2-propanol, 1-methoxy-2-propanol, acetone, and formaldehyde. NASA previously identified all of these compounds in wastewater sources under consideration for recycling into potable water. Experiments were performed at pH 5.5 and 8, iodine concentrations of 10 and 50 mg/L, and organic compound concentrations of 5 and 50 mg/L. Gas chromatography/mass spectrometry was used to identify and monitor the concentrations of organic species. Spectrophotometry was used to monitor the iodine concentration. Acetone was the only compound identified as an IDBP precursor and it reacted to produce iodoacetone and iodoform. Concentrations of iodoform from 0.34 mg/L to 8.637 mg/L were produced at conditions that included each pH level, iodine concentration, and acetone concentration. The greatest iodoform concentration was produced at pH 8 from 50 mg/L of iodine and acetone. FPA indicated that the odor threshold concentration (OTC) of iodoform was 1.5 μg/L and the OTC of iodine was 500 μg/L. Both iodine and iodoform have medicinal odors, making it difficult to distinguish each compound when present in a mixture.

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# CHAPTER I:  INTRODUCTION

Among the many challenges of space exploration is the need to provide safe drinking water for the crews. For many years, the National Aeronautics and Space Administration (NASA) has generated water from the $H_2$ and $O_2$ fuel cells aboard the Space Shuttles (Sauer *et al*., 1991). The water is then disinfected with iodine to give a residual of approximately 4 mg/L $I_2$. The use of iodine has worked well for the Shuttle missions, which last approximately one week and use the fuel cells to generate power as well as water.

At this time, NASA is planning for the permanent manning of the International Space Station early in the 21st Century. The Space Station will be using solar panels instead of fuel cells. In addition, the launching of water from the earth is very expensive; thus NASA is prohibited from constantly resupplying the Space Station's water during its proposed 30 years of operation. For these reasons, NASA plans to recycle waste water aboard the Space Station. Water will be recycled from urine, cabin condensate, shower water, and water used to wash hands and clothes (Sauer *et al*., 1991). Iodine will still be used for disinfection, but the combination of iodine and recycled water has led to concern about possible health issues from the formation of iodinated disinfection by-products (IDBPs).

Based on results from preliminary test, NASA believes that small, water-soluble organic molecules may be difficult to remove from the recycled water (Straub II *et al*., 1995). Little is known about the formation of iodinated disinfection by-products or the health risks they may pose (Bull, 1987); therefore, NASA does not know which of these organic compounds are likely to react with iodine to form IDBPs.

Another concern for NASA is the ability to monitor water quality aboard the Space Station. Analytical instruments must be custom-designed and manufactured to be compact and operate in the microgravity of space; thus, the amount of equipment NASA is able to put on the Space Station is constrained by cost, size, and weight. If applicable, organoleptic evaluation by crew members may be a useful tool because additional equipment is not required.

Flavor Profile Analysis (FPA) has been used successfully for many years by water utilities on earth to monitor water quality. Iodine and many known iodinated organic molecules produce distinctly medicinal odors (Bruchet *et al.*, 1989). If astronauts could be trained to use FPA to detect levels of iodine and IDBPs, it may be a good supplemental tool for monitoring water quality on the Space Station.

Objectives of this research were to:

1) determine if iodine can react with selected organic compounds expected to be present in recycled Space Station water,
2) identify and quantify IDBPs that are formed by the reaction of iodine and specific organic compounds expected to be in Space Station drinking water, and
3) explore the possibilities of using FPA to monitor iodine and IDBPs in drinking water.

# CHAPTER II:  LITERATURE REVIEW

## IODINE CHEMISTRY AND DISINFECTION

Starting in the late 1960's, disinfection by-product formation became an important topic in the water industry.  Since that time, voluminous amounts of research have been conducted on chlorinated by-products, more specifically trihalomethanes (THMs), produced by chlorination of water containing natural organic matter.  Disinfectants such as ozone and chlorine dioxide are now beginning to receive more attention, while less-frequently-used disinfectants such as bromine and iodine have been largely ignored.

Iodine has been used by the military, travelers in underdeveloped countries, communities in emergency situations, NASA, and in other limited situations (Cooney and Chura, 1990; Sobsey *et al.*, 1991).  Even with iodine's continued use as a disinfectant, little is known about iodinated disinfection by-products.  The majority of the known iodine chemistry deals with iodine's disinfecting abilities.

An aqueous iodine solution is a very complex system.  Seven ions and molecules of iodine can exist in one solution, of which two exhibit strong germicidal properties: molecular iodine ($I_2$) and hypoiodic acid (HOI).  The iodine cation ($[H_2OI]^+$), triiodide ion ($I_3^-$), hypoiodite ion ($OI^-$), iodide ion ($I^-$), and iodate ion ($IO_3^-$) do not significantly add to the germicidal property of iodine (Black *et al*., 1968).  Molecular iodine is believed to penetrate the cell wall of microorganisms (Chang, 1971).  Gottardi (1983) stated that iodine, once inside the cell wall, reacts with N-H groups, S-H groups, and phenolic groups, prohibiting the normal functions of many amino acids.  According to Apostolov (1980), $I_2$ has such a strong affinity for carbon-carbon double bonds that it may react with unsaturated fatty acids, and, for this reason, can inhibit membrane-bound viruses by inducing changes in the lipid bilayer.  Sobsey *et al*., (1991) studied the disinfecting power of iodine for Hepatitis A virus, poliovirus type one, and echovirus type one. The research indicated that "virus inactivation was generally more effective at higher pH, in cleaner water, at higher temperature and at higher iodine dose." At higher pH levels, HOI is more prevalent than $I_2$, but while HOI tends to be a stronger virucide, $I_2$ tends to be a more efficient disinfectant for bacteria and cyst (Chang, 1958).

Another interesting reaction is that of iodine with powdered drink mixes. During space flights the astronauts reconstitute powdered drink mixes with water prior to consumption. Cooney and Chura (1990) found that compounds such as ascorbic acid and tannic acid, commonly found in drink mixes, may interfere with iodine's disinfecting abilities. These compounds converted $I_2$ to $I^-$, rendering the solution ineffective as a disinfectant. Cooney and Chura concluded that iodine must be given adequate time to disinfect drinking water before a drink mix is added.

## HALOGENATION REACTIONS

The lack of knowledge of iodinated DBPs is due in part to the difficulties associated with studying halogenation reactions that result in only trace amounts of products. Certain organic chemicals react with halogens, including iodine and iodide, the extent of the reaction being dependent on the characteristics of the organic molecule, halogen species, and reaction conditions. Most organic chemical reactions have been investigated under conditions that involve molar concentrations of reactants which should favor product formation. This is not generally the situation in spacecraft potable water where the reactants are expected to be micromolar to millimolar aqueous concentrations.

Alkanes can be halogenated in free-radical reactions that require initiation by ultraviolet radiation. The order of reactivity is: $F_2 > Cl_2 > Br_2 > I_2$ ; iodine is the least reactive halogen and generally very low yields of products are observed (March, 1977). Either primary, secondary, or tertiary alcohols can be converted to the corresponding alkyl halides. Halogen acids or inorganic acid halides; and not molecular chlorine, bromine, or iodine; participate in the reaction. Reactions involving HI sometimes result in alkane formation because HI will cause reduction to the alkyl iodide (March, 1977). Iodine ($I_2$) can be used for the dehydration of alcohols to form alkenes. Phenols can readily be halogenated in the ortho and para-positions by molecular chlorine or bromine; molecular iodine will also react, but it is the least reactive of the halogens (March, 1977). Heating ethers with concentrated HI or HBr will result in the formation of an alkyl halide and alcohol. Ethers containing methoxy groups will form methyl iodide (March, 1977).

Aldehydes and ketones can readily be halogenated in the α-position by molecular chlorine, bromine, or iodine. The α-hydrogens are replaced by halogens in reactions that are either acid or base catalyzed. The purpose of the acid or base catalyst is to enhance formation of the corresponding enol or enolate. The enol or enolate ion, not the aldehyde or ketone, is actually halogenated (March, 1977). Halogenation of the aldehydic hydrogen to form acyl chlorides can occur for aldehydes that do not contain α-hydrogens. The reaction is not very useful; halogenation at the α-position is preferred (March, 1977)

The well-known haloform reaction, which involves halogenation of a methyl ketone or acetaldehyde, is base-catalyzed and results in halogenation of the methyl group to form the corresponding trihalomethane and carboxylic acid (March, 1977; Fuson and Benton, 1934). Alcohols, if first oxidized to a ketone, are susceptible to the haloform reaction. Several parameters, such as pH, temperature chemical structure, and composition of the water matrix, affect the haloform reaction. Each haloform also has a slightly different reaction to each parameter (Dore *et al*., 1982). The best known IDBP is iodoform. Iodoform is produced by the reaction of iodine with a ketone (Seelye and Turney, 1959).

$$RCOCH_3 + OH^- \longrightarrow RCOCH_2^- + H_2O \quad (1)$$

$$RCOCH_2^- + HIO \longrightarrow RCOCH_2I + OH^- \quad (2)$$

The electron withdrawing inductive effect of iodine expedites the iodination to $RCOCI_3$

$$RCOCI_3 + OH^- \longrightarrow RCOO^- + CHI_3 \quad (3)$$

The $HOI/I^-$ redox potential is very low, and unlike chloroform and bromoform, iodoform is produced before iodine reacts with other compounds in the water. This coupled with the ease with which iodoform can be measured has led to the recommendation that iodoform be used to test the potential of a water supply to produce THMs (Dore *et al*., 1982; Reckhow and Edzwald, 1991).

## REGULATIONS FOR DRINKING WATER

Under the Safe Drinking Water Act, the United States Environmental Protection Agency (USEPA) regulates disinfectants and disinfection by-products in drinking water. During the 1990's, much discussion focused on revising the drinking water regulations. USEPA plans in the future to have lower limits for more disinfection by products than in previous decades (USEPA, 1994).

Since 1979, USEPA has regulated trihalomethanes in drinking water. The THMs typically monitored in chlorinated drinking water are chloroform, dichlorobromomethane, dibromochloromethane and bromoform. Iodoform is also a member of this class of compounds. The present standard is 0.10 mg/L total THMs, but, this level will likely be reduced to 0.080 mg/L total THMs. Another important class of disinfection by-products that are likely to be regulated during the late 1990's are the mono-, di-, and tri- haloacetic acids (HAAs). The proposed regulatory standard for the sum of five specified HAAs is expected to be 0.060 mg/L (USEPA, 1994).

Other DBPs which have been increasingly scrutinized are haloketones (HKs) and haloacetonitriles (HANs). On May 14, 1996, the USEPA promulgated the Information Collection Rule (ICR). The ICR requires that concentrations of certain DBPs be collected monthly for 18 months by water treatment facilities, starting July 1997 (EPA, 1997). The collected information will be used by EPA as the basis of new regulations. Two haloketones were on the list to be monitored: 1,1-dichloropropanone and 1,1,1-trichloropropanone. The suggested method for monitoring the haloketones was the USEPA Method 551 which is a liquid-liquid extraction coupled to gas chromatography for detection (Pontius, 1996).

## TREATMENT AND PURIFICATION OF SPACECRAFT WATER

To understand the formation of IDBPs, one must know what reactants are in the water. This begins with the purification system. NASA's approach has been to produce distilled, deionized, disinfected water for potable use by astronauts. As with most treatment, NASA's first line of defense against IDBPs is by the removal of organics from the recycled water.

Initially NASA planned to have separate systems for hygiene and potable water, but due to other changes in the Space Station design, the hygiene and potable systems have been combined (Sauer *et al*., 1991). As of 1996, NASA's water purification system consisted of four steps. The urine will be distilled by vapor compression then combined with the other waste water. In the second step, organic and inorganic compounds will be removed by multifiltration beds that contain cation and anion exchange media plus granulated activated carbon (Muckle *et al*., 1993). These multifiltration beds were designed and produced by Umpqua Research Company. Granulated activated carbon is present to remove non-polar, poorly water soluble organic compounds. Cations exchange resins are present to remove ammonium ions, sodium, calcium, magnesium, and amines. Anion exchange resins are included to remove negatively charged ions such as conjugate bases of organic acids. Questions have been raised as to how the material in the bed will behave in microgravity. If enough of the bed's media shrink, channels will form, decreasing the bed's efficiency. For this reason, the media is packed into canisters that are then spring-loaded (Straub II *et al*., 1995).

Certain low-molecular-weight, nonionic, polar organics (e.g., methanol, ethanol, acetone, and propanols) are not removed well by the multifiltration bed. In order to remove these compounds, catalytic oxidation has been installed to oxidize the small compounds to carbon dioxide and the corresponding aldehyde or organic acid. These compounds will then ideally be removed by multifiltration sorption media (Straub II *et al*., 1995). The final step in the water purification system is the addition of iodine as a disinfectant. Solid iodinated anion exchange resins called microbial check valves will be used to add sufficient iodine to maintain a residual of 1-4 mg/L. In order to limit microbial growth in the multifiltration beds, the check valves may also be installed prior to distillation (Sauer *et al*., 1991; Atwater *et al*., 1992).

The purification system will be required to produce water of a very high standard. Many of the life science experiments that will be on the Space Station will need as few variables between earth and the Space Station as possible; thus, the initial standards set are similar to standards set by EPA (Table 1). Monitoring will be very important to maintain these standards. The water purification method is such a small, closed system that increases in contaminants will occur quickly if not well guarded (Sauer *et al*., 1991).

Table 1: Comparison of Specific EPA and Space Station Water Quality Standards

| Quality Parameter | EPA Standards | Space Station Standards |
|---|---|---|
| Total Solids (mg/L) | 500 | 100 |
| Color (pt/co units) | 15 | 15 |
| Taste (TTN) | — | 3 |
| Odor (TON) | 3 | 3 |
| pH | 6.5-8.5 | 6.0-8.5 |
| Turbidity (NTU) | 1 | 1 |
| Total Acids (µg/L) | — | 500 |
| Total Hydrocarbons (mg/L) | 0.1 | 10 |
| Total alcohols (µg/L) | — | 500 |
| Total Organic Carbon (µg/L) | — | 500 |

## ORGANIC COMPOUNDS IN SPACECRAFT WATER

Although the water purification system was designed to comprehensively remove cationic, anionic, and neutral species, preliminary test have shown that some organic compounds are still appearing in the final product. The cabin condensate is considered to be a major source of organic compounds that will contaminate the water. Compounds exhaled by humans; including methane, carbon dioxide, ethanol, water, methanol, acetone, and acetaldehyde; can build up in the cabin if not removed by condensing the cabin gases (National Research Council, 1992). Untreated condensate samples from Space Shuttle missions STS-45 and STS-47 and Spacelab missions revealed that total organic carbon reached up to 229 mg/L in the Space Shuttle and 230 mg/L in Spacelab, with alcohols and glycols accounting for much of the TOC. Ethanol reached levels of 132 mg/L, 2-propanol reached 60 mg/L, methanol 12 mg/L, and 1,2-propanediol reached levels of 128 mg/L (Muckle *et al*., 1993). These compounds should be removed from the water to make it potable.

Space Shuttle condensate from mission STS-68 was treated by the multifiltration beds. Analysis revealed that the low-molecular weight compounds (methanol, ethanol, 2-propanol, formaldehyde, and 1,2-propanediol) were not removed very well by the multifiltration bed. Ethanol (16.6 mg/L to 122.4 mg/L), 2-propanol (0.9 mg/L to 48.9 mg/L), and 1,2-propanediol (18.9 mg/L to 42.8 mg/L) were the most prevalent organic compounds in the treated water. The concentration ranges for the other compounds were 1.5 mg/L to 3.2 mg/L for methanol and 2.6 mg/L to 6.4 mg/L for formaldehyde (Straub II *et al*., 1995). These data support the assumption that the multifiltration bed alone is unable to remove all of the organic compounds. Unpublished data from test run by NASA on earth using the full purification system indicated that even with catalytic oxidation, small organic compounds such as ethanol, 1-propanol, and acetone may still be poorly removed by the proposed water purification system. A membrane may be included as an additional treatment step.

## REACTION OF IODINE WITH ORGANIC COMPOUNDS IN SPACECRAFT WATER

Atwater *et al*. (1992) studied the reactions of iodine in urine distillate and humidity condensate collected from Space Shuttle missions. The results showed that the predominant reaction was between iodine and formic acid, producing carbon dioxide and iodide anion, yet the study suggested that other unknown competing reactions were occurring. Atwater *et al*. hypothesized that the compounds involved in the reactions might be phenol or benzoic acid. Atwater *et al*. believed that the pH was too low for the iodoform reaction to occur. If organic compounds were reacting with iodine, the products were in the part per billion range or lower. While at first this might seem trivial, the possibility of small amounts of water soluble organic compounds slipping through the purification system and reacting with iodine in the final product may prove to be problematic. Iodinated disinfection by-products, even in the part per billion range may cause problems, especially in a small closed system where the concentrations may be intensified.

Symons and Muckle (1990) studied the reaction of iodine with several compounds found in humidity condensate. A mixture resembling Space Shuttle cabin condensate was treated with iodine, before and after the multifiltration bed, using iodinated anion exchange resins (IR). Symons and Muckle (1990) monitored " the amount of iodide released from a known amount of IR in contact with a specific organic compound" . These by-products were called iodine-substituted organic compounds (IOX). The IOX that formed before the multifiltration bed was removed very efficiently by the activated carbon, but some organic compounds passed through the multifiltration bed and then reacted with the iodine added after the bed. These reactions were believed to be temperature and pH dependent. Precursors were characterized into two categories: those that reacted to form by-products at pH $<7$ and those that reacted at pH $\geq 7$. The $<7$ category included phenol, lysine, and sodium formate. The $\geq 7$ were acetone, acetaldehyde, and ethanol. The products of these reactions were not identified. A later study by Barkley *et al*., (1992) looked at reactions of iodine with single compounds and mixtures of likely IDBP precursors. Most of the analysis was done using gas chromatography with electron capture detection (GC/ECD). New products were detected but could not be identified. Although not conclusive, this research did indicate a need for further investigation with analysis techniques such as gas chromatography/mass spectrometry (GC/MS) to identify the by-products.

FLAVOR PROFILE ANALYSIS

As the previous research has shown, when DBP formation occurs it results in very small concentrations, normally in the μg/L range.  Gas chromatography (GC) has been needed to analyze concentrations this small, yet the practicality of putting a GC on the Space Station makes this option unlikely.  The careful and regular monitoring of the recycled water is essential, but certain constraints, such as microgravity, limit the equipment available.  For these reasons, flavor profile analysis (FPA) has been suggested as an additional method for monitoring the water aboard the Space Station.

Flavor profile analysis was initially developed to be used by the food, beverage, and pharmaceutical industries (Cairncross and Sjostrom, 1950).  In the early 1980's, the FPA technique was modified for use in the water industry (Krasner, 1985).  Since that time, FPA has been used successfully by many utilities to control or explain taste and odor problems (Anselme *et al*., 1988; Dietrich *et al*., 1995; Mallevialle and Suffet, 1987; Meng and Suffet, 1992; Rashash *et al*., 1996; Rashash *et al*., 1997; Suffet *et al*., 1988).  FPA, as described by the 18th edition of *Standard Methods for the Examination of Water and Wastewater* (1992), is a technique that uses a trained panel to characterize and assign intensities to tastes and odors. A panel of approximately five people are trained to recognize taste and odors that are common problems to water utilities.  When monitoring odors, each panel member will make an individual assessment of a set of samples.  Each assessment consist of a descriptor and an intensity rating on a scale of 1 to 12 with 12 being the strongest.  The group will then discuss their opinions.  If at least 50% of the panel agrees on a description, an average is calculated. An intensity of zero is used in the average for any panel member whose description did not agree with the majority.  The standard method does not outline any further analysis, but many utilities use a Weber-Fechner plot to visualize the data.  In a Weber-Fechner plot, the average intensities assigned to samples are plotted against the log of the concentration for each sample. The odor threshold concentration (OTC) is the concentration where the average intensity is two (Krasner, 1988; Suffet *et al*., 1988). Examples of case studies that have successfully utilized FPA include a study in Philadelphia of odors produced by geosmin in drinking water (Burlingame *et al*., 1986) and the use of FPA by a suburban Philadelphia water treatment plant for identification of odors (Preti *et al*., 1993).

Iodine and many iodinated organic compounds have distinct medicinal odors and tastes. Bruchet *et al*. (1989) found that the odor threshold of iodoform in water is “close to 1 microgram per liter”. With the human nose being able to detect an IDBP at such a small concentration, FPA may prove to be a valuable tool to the astronauts.

# CHAPTER III: METHODS AND MATERIALS

In this chapter, details will be given about the methods used for chemical analysis of reactions between iodine and specific organic compounds that were expected to be present in recycled water in the Space Station. Details will be given also about the methods used for organoleptic evaluations of IDBPs that were likely to form and the data analysis.

## GLASSWARE

All glassware was cleaned with chromic acid and rinsed five times with distilled-deionized water, unless otherwise noted.

## CHEMICALS

NASA expects to iodinate distilled deionized water; therefore, distilled deionized water was used as the matrix of all experiments. All reagent water was produced by a MilliQ® reagent water system, which uses anion, cation, and granular activated carbon (GAC) columns to purify water. Iodomethane (CAS # 74-88-4), chloroiodomethane (CAS # 593-71-5), diiodomethane (CAS # 75-11-6), iodoform (CAS # 75-47-8), iodoethane (CAS # 75-03-6), 1-iodopropane (CAS # 107-08-4), 2-iodopropane (CAS # 75-30-9), iodoacetic acid (CAS # 64-69-7), formaldehyde (CAS # 50-00-0), 1-methoxy-2-propanol (CAS # 107-98-2), and PFBOA (CAS # 57981-02-9) were purchased from Aldrich Chemical Company. Ethanol (CAS # 64-17-5), methanol (CAS # 67-56-1), 1-propanol (CAS # 71-23-8), isopropyl alcohol (CAS # 67-63-0), and sodium sulfate (CAS # 7757-83-7) were purchased from Fisher Scientific. The leuco crystal violet chemical 4, 4′, 4′′-methylidynetris (N, N-dimethylaniline) was purchased from Eastman.

## EXPERIMENTAL DESIGN

Although the NASA water purification system was designed to produce distilled, deionized and disinfected water for potable use, officials working for NASA and NASA-contractors found that several organic compounds routinely passed through the purification system during preliminary test (unpublished data). Seven of these prevalent organic compounds were chosen for this study: methanol, ethanol, 1-propanol, isopropanol (2-propanol), 1-methoxy-2-propanol, acetone, and formaldehyde.

As of 1996, when this research was performed, the exact amount of iodine that would normally be added to Space Station potable water was unknown, but the NASA standards required a 1-4 mg/L iodine residual. At times when the water supply would need to be replenished, water would be iodinated on Earth then transported by the Space Shuttle to the Space Station. This water could be in storage for a month or more before being transported; therefore, amounts greater than 4 mg/L of iodine may be necessary. Increased amounts of iodine may also be added if breakdowns occur in the purification system during space flight. For these reasons, 10 mg/L and 50 mg/L $I_2$ were chosen as the low and high concentrations that might be applied to potable water for Space Station use.

High and low concentrations of each of the seven organic compounds were reacted with $I_2$ to determine how the organic concentration affected the reaction. The concentrations needed to be large enough that the products would be detectable, so for this reason, 5 mg/L and 50 mg/L in water were chosen as concentrations for the organic compounds.

Symons and Muckle (1990) found iodinated reactions to be pH dependent. Thus acidic and basic conditions were investigated. A pH of 5.5 was chosen for the acidic condition to simulate the pH of distilled deionized water, the expected product of the Space Station purification system. A pH of 8 was chosen for the basic condition.

Gas chromatography (GC) was the method used to separate and quantify the different components of each reaction. As previous research showed, mass spectrometry (MS) was needed to determine the identity of the by-products. Unfortunately, water as a matrix causes large solvent peaks that can mask or interfere with detection of trace amounts of $C_1$-$C_3$ compounds when using GC/MS. The products of these reactions were also expected to be in the part per billion range; thus, the Selective Ion Monitoring (SIM) mode was used to improve the detection limits. The ions selected were those indicative of the organic compounds studied and IDBPs likely to be produced. For selected IDBPs, liquid-liquid extraction with methylene chloride and GC/MS were used to determine the amount of by-product.

EXPERIMENTAL PROCEDURE FOR DILUTE AQUEOUS REACTIONS

A set of eight experiments was conducted with each of the seven organic compounds studied. The experimental conditions were as follows:

| Condition | pH | Organic concentration (mg/L) | Iodine concentration (mg/L) |
|---|---|---|---|
| 1 | 5.5 | 5 | 10 |
| 2 | 8.0 | 5 | 10 |
| 3 | 5.5 | 5 | 50 |
| 4 | 8.0 | 5 | 50 |
| 5 | 5.5 | 50 | 10 |
| 6 | 8.0 | 50 | 10 |
| 7 | 5.5 | 50 | 50 |
| 8 | 8.0 | 50 | 50 |

The iodine solutions were made by stirring a one liter solution of reagent water with 100 mg of solid iodine for a minimum of five hours. The pH of this solution was typically 5.5. The pH of the reagent water and the iodine solution was increased to pH 8 by adding sodium hydroxide. Each reaction was performed at room temperature then stored in 40 mL amber glass vials with Teflon® septa, headspace free. The concentrations of organics, concentrations of iodine, and the production of IDBPs were measured multiple times for each reaction. The number and timing of the measurements varied.

Sufficient volumes of reaction conditions that produced IDBPs were prepared so that the FPA panel could evaluate the reaction mixture and liquid-liquid extraction could be performed to measure the amount of iodoform produced. Amber bottles, 1L in size, were prepared and allowed to react for 35 days. At the end of the 35 day period, 200 mL of each solution as removed, and warmed to 45° C, and immediately presented to the FPA panel. The remaining 800 mL of each solution was immediately extracted with 3 X 50 mL of methylene chloride using 2 L separatory funnels. The methylene chloride extracts were injected into the GC/MS and iodoform was measured.

## EXPERIMENTAL PROCEDURE FOR CONCENTRATED REACTIONS OF IODINE AND ORGANICS

Concentrated solutions of iodine and the pure organic compounds were reacted in order to investigate the possible reactions of iodine with the selected organic compounds and to generate substantial quantities of iodinated disinfection by-products and any intermediate compounds. A volume of 1-2 mL of methanol, ethanol, 1-propanol, 2-propanol, acetone, or 1-methoxy-2-propanol was added to an amber glass autosampler vial. One or two crystals of solid iodine were added and dissolved. A volume of about 100 uL of this mixture was placed in another amber glass autosampler vial and capped. A second portion of about 100 uL was removed and diluted 1:10 with reagent water and placed in another amber glass autosampler vial and capped. The IDBPs in these vials were monitored over time.

The materials in these vials were monitored by GC/MS in the SIM and full scanning modes. Because of concerns about too much $I_2$ on the GC columns, only the gas phase above the vials containing 100 uL of concentrated iodine/organic were sampled. Either gas phase or aqueous phases of reactions in water were sampled; only a limited number of direct aqueous injections were performed with these solutions to avoid placing large amounts of iodine on the column.

DETERMINATION BY GC/MS

The concentrations of the reactions with isopropanol, acetone, and 1-methoxy-2-propanol were measured by a Hewlett-Packard 5890 series II GC and a Hewlett-Packard 5971 MSD operated in SIM mode. The GC/MS used to measure 1-propanol and formaldehyde was a Hewlett-Packard 5970 MSD in SIM mode. The concentrations of methanol and ethanol were measured by GC/FID. The column used was an HP INNOWAX (30 m x 0.25 mm x 0.25 µm). The GC procedure used for all of the organic compounds was as follows:

| | |
|---|---|
| Injection port temperature | 200° C |
| Injection mode | split (approximately 90:1) |
| Initial column temperature | 60° C |
| Initial column temperature held | 4.5 minutes |
| Temperature ramp (60° - 95°) | 35 C/min |
| Temperature ramp (95° - 100°) | 5 C/min |
| Temperature ramp (100° - 150°) | 20 C/min |
| Final Temperature held | 1 minute |

All organic compounds except formaldehyde were measured directly by GC/MS. An o-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine (PFBOA) derivative of formaldehyde was extracted with hexanes and then measured by GC/MS. In the SIM mode, m/z 136, 181, 195, and 127 were monitored. Detailed instructions of the PFBOA derivatization method for the detection of formaldehyde was provided by Ms. Judy Svoboda of KRUG..

IDBPs were monitored by GC/MS using an HP5 (30 m x 0.25 mm x 0.25µm). The procedure was as follows:

| | |
|---|---|
| Injection port temperature | 200° C |
| Initial column temperature | 60° C |
| Initial column temperature held | 3 minutes |
| Temperature ramp | 25 C/min |
| Final temperature | 240° C |
| Final temperature held | 4.20 minutes |

The presence of IDBPs was monitored using both SIM mode and full scanning GC/MS (50-420 amu). For experimental conditions 1-8, aliquots of the dilute aqueous sample were directly injected into the GC/MS and only SIM was utilized. Preliminary research had indicated that the quantities of IDBPs formed were below the detection limits of full scanning. For reactions in which concentrated iodine was reacted with pure organics, both SIM and full scanning GC/MS were utilized.

Formaldehyde containing solutions were evaluated for the presence of the IDBPs listed in Table 2. Additionally, if an iodinated aldehyde formed, then this compound would likely have reacted with PFBOA to form derivatives. Any PFBOA derivatives analyzed by MS yields m/z 181 which is associated with the PFBOA moiety. Because m/z 181 was monitored when the PFBOA derivative of formaldehyde was measured by GC/MS, then iodinated aldehydes would have been detected.

Mass spectra for the monitored iodinated compounds can be found in the WILEY-NBS mass spectral database. Retention times were determined for all compounds for which pure standards were available; these included iodomethane, chloroiodomethane, diiodomethane, triiodomethane, iodoethane, 1-iodopropane, 2-iodopropane, and iodoacetic acid. In the SIM mode, the following ions were monitored (Table 2).

Table 2: Mass spectral information for the IDBPs monitored in this research

| IDBP | Molecular Ion | Major m/z values that were monitored | Possible Source for this IDBP |
|---|---|---|---|
| Iodomethane | 142 | 142, 141, 127 | Iodination of 1-methoxy-2-propanol or methanol |
| Chloroiodo-methane | 176 | 176, 127 | Iodination of methylene chloride |
| diiodomethane | 268 | 268, 127 | Iodination of methanol |
| triiodomethane (iodoform) | 394 | 267, 140, 127 | Iodination of primarily acetone but also any other organic |
| Iodoethane | 156 | 156, 127 | Iodination of ethanol |
| 1-Iodopropane | 170 | 170, 141, 127 | Iodination of 1-propanol |
| 2-Iodopropane | 170 | 170, 127 | Iodination of isopropanol |
| Iodoacetone | 184 | 184, 141, 127 | Iodination of acetone |
| Iodoacetic acid | 186 | 186, 127 | Iodination of acetone |

DETERMINATION OF IODINE

The concentrations of iodine in the experiments containing 1-propanol or formaldehyde were determined by the lueco crystal violet method according to section 4500-$I^-$ B, *Standard Methods for the Examination of Water and Wastewater* (1992). Iodine was measured directly with lueco crystal violet, and total iodine was measured by adding oxone before the addition of lueco crystal violet. The intensity of the blue product was measured at 592 nm with a spectrophotometer. The concentration of iodine in the experiments containing acetone, isopropyl alcohol, and 1-methoxy-2-propanol were analyzed by the lueco crystal violet method and a method developed at Johnson Space Center utilizing UV/VIS. The Johnson Space Center method involved the use of either a 1 cm or 10 cm cell for concentrations of 50 mg/L or 10 mg/L respectively. Absorbance was measured at 700 nm, 462 nm, 352 nm, and 288 nm and the pH was also measured. The absorbances at these wavelengths and sample pH were entered into a computer program that calculated the amounts of $I^-$, HOI, and $I_2$ based on thermodynamic equilibrium reactions. The method was not valid when solution pH was greater than 8.

ORGANOLEPTIC EVALUATION

The organoleptic evaluations were conducted according to Section 2170 B, Flavor Profile Analysis, *Standard Methods for the Examination of Water and Wastewater* (1992); only odor was evaluated. The containers were 500 mL Erlenmeyer flasks with ground-glass stoppers, and the samples were heated to 45° C in a water bath. The panel consisted of three women and four men. Two were faculty members, four were students, and one was a visiting faculty member from Brazil. The panel was trained by Dr. Diana Rashash over a two day period. The panel met weekly and evaluated four to five samples per meeting. Primarily iodine and iodoform were evaluated. Acetone was also evaluated, but not as thoroughly.

## DATA ANALYSIS

For experiments with sufficient data, the concentration of organic and the concentration of total iodine/iodide were plotted versus time. A regression analysis of the slope of each line was performed using the data analysis function in an Excel spreadsheet.

Flavor profile analysis data were presented in a Weber-Fechner plot. The odor threshold concentration was determined by the concentration that had an average intensity of two.

# CHAPTER IV: RESULTS

## REACTIONS OF IODINE AND ORGANICS AT HIGH CONCENTRATIONS

In an attempt to generate substantial concentrations of IDBPs for detection and identification by full scanning GC/MS, crystals of iodine were mixed with the pure organic compound; an aliquot of this mix was diluted 1:10 with reagent water. Reacted samples were stored at room temperature in autosampler vials. Vapors from both the aqueous and nonaqueous reaction were analyzed by GC/MS by sampling the headspace above approximately 200 uL of solution. Only the aqueous solution was injected directly on the column. A chromatogram of the IDBPs monitored in this research is shown in Figure 1. All these iodoalkanes were detectable at 100 μg/L using SIM-GC/MS.

More iodinated and non-iodinated reaction products of acetone were detected by direct aqueous injection than by injection of either vapor sample. This could have resulted from the low vapor pressures and low vapor concentrations of the reaction products. The reactions which contained water appeared to produce more types and higher concentrations of iodinated products than those with only pure iodine and organic compound. The indication was that water was a necessary component of the iodination reaction.

Reaction time was also a factor in the production of iodinated by-products of acetone. After four hours of reacting acetone and $I_2$ in water, several products formed and were seen as shown in the full scan GC/MS chromatogram in Figure 2. The selected ion monitoring chromatogram for this same sample is shown in Figure 3. As can be seen from these two chromatograms, the major iodine-containing component eluted at 4.714

minutes. Interpretation of the full scanning mass spectrum, which is presented in Table 3 and Figure 4, indicates that this component was iodoacetone. Iodoacetone is an expected intermediate in the haloform reaction. It was identified on the basis of interpretation of the mass spectrum and a reasonable retention time compared to the other pure iodoalkanes that were shown in Figure 1. At a reaction time of 45.5 hours, only a trace of iodoacetone appeared, as indicated by a trace of m/z 184 at 4.71 minutes using SIM.

Table 3: Interpretation of mass spectrum of Iodoacetone

| m/z Value of Major Ions | Interpretation | Formula of Ion |
|---|---|---|
| 184 | molecular ion | $C_3H_5OI^{+\cdot}$ |
| 169 | loss of $CH_3$ | $C_2H_2OI^+$ |
| 141 | loss of $C_2H_3O^{\cdot}$ | $CH_2I^+$ |
| 127 | $I^+$ cation | $I^+$ |

.

Iodoform, which should have eluted at 8.3 minutes, was not detected as a product in the reaction of concentrated aqueous acetone and iodine at either 4 or 45.5 hours. As indicated in Figure 2 and 3, other products, not all of which were iodinated compounds, were detected; SIM GC/MS indicated that the compounds with retention times of 6.19, 7.45, and 8.65 minutes did not contain iodine. The compound eluting at about 3.62 minutes appeared to be $I_2$ because the base peak was m/z 127 and the m/z 254 peak occurred at 50 percent intensity; no ions greater than m/z 254 were observed. The compound eluting at 4.2 minutes was not identified.

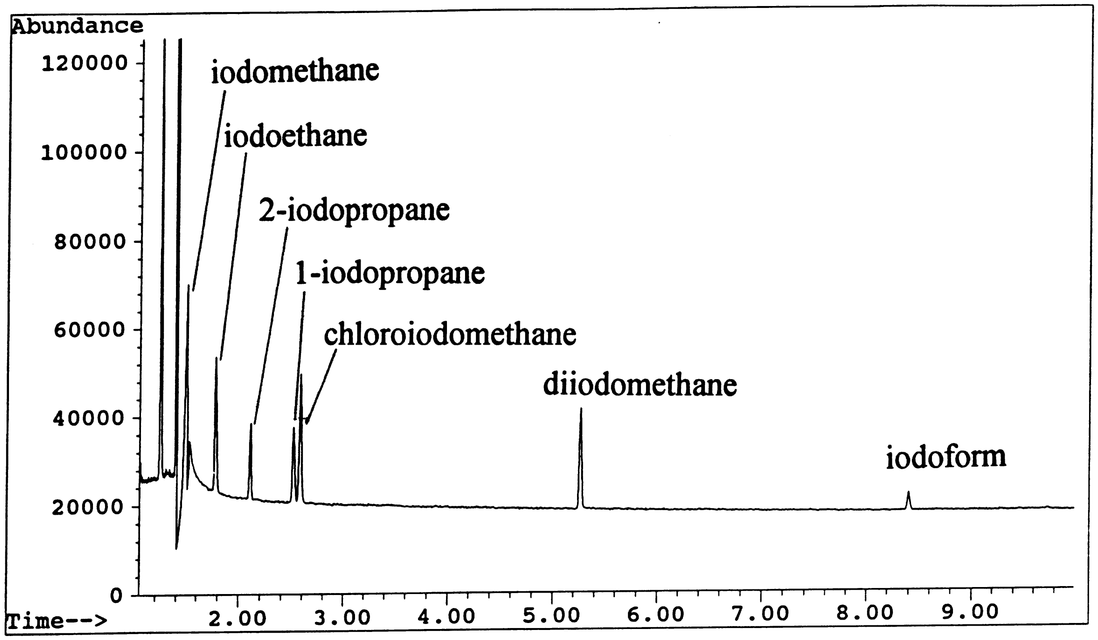


**Figure 1:** Selected ion monitoring chromatogram for a 1000 µg/L solution of the six iodoalkanes and chloroidomethane which were selected as IDBPs that were likely to be produced. Shown is the total ion chromatogram for all ions that were monitored (m/z 127, 140, 141, 156, 170, 176, 184, 186, 267, 268).

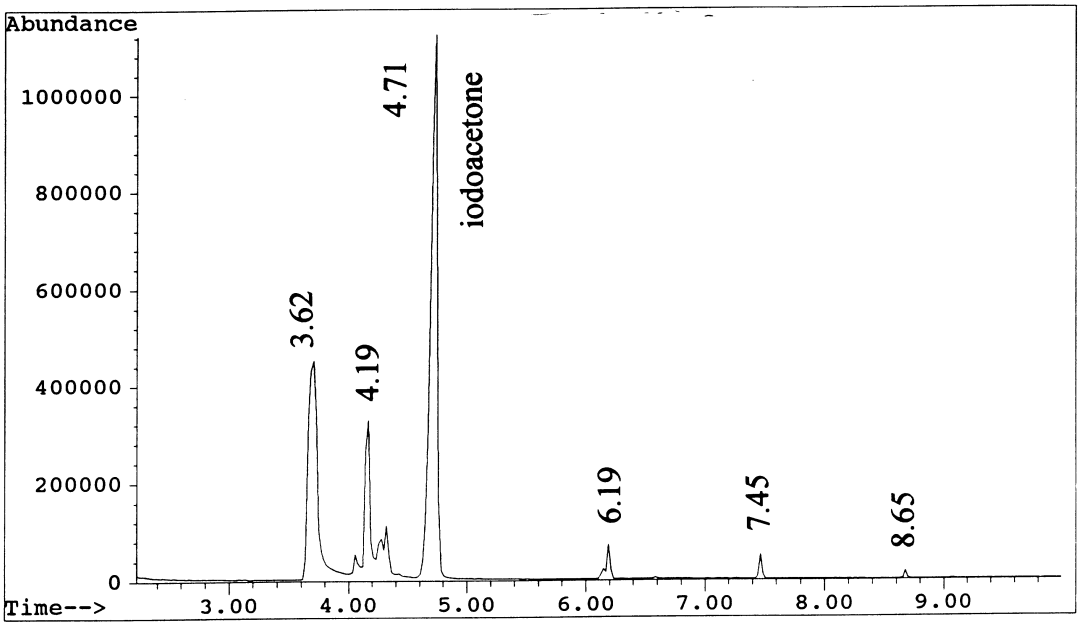


**Figure 2:** Full scanning GC/MS chromatogram (m/z 50-420) of the products from the reaction of acetone and iodine in a 1:10 dilution with water. The reaction time was 4.06 hours at room temperature. The total ion chromatogram is plotted.

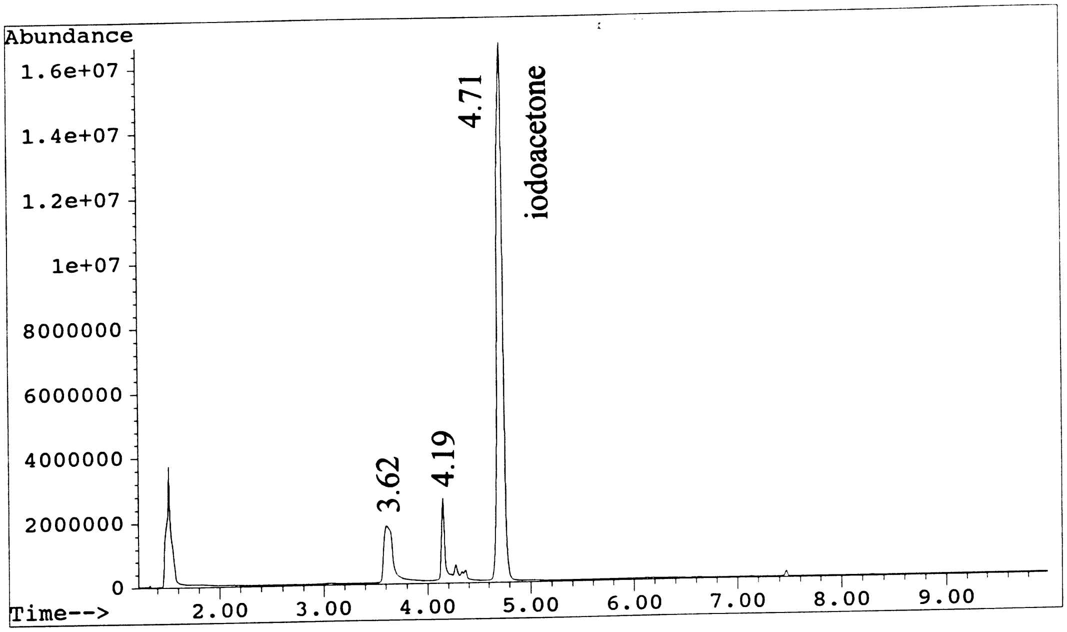


**Figure 3:** Selected ion monitoring GC/MS chromatogram (showing the total ion chromatogram for m/z 127, 140, 141, 156, 170, 176, 184, 186, 267, 268) of the products from the reaction of acetone and iodine in a 1:10 dilution with water. The reaction time was 3.82 hours at room temperature.

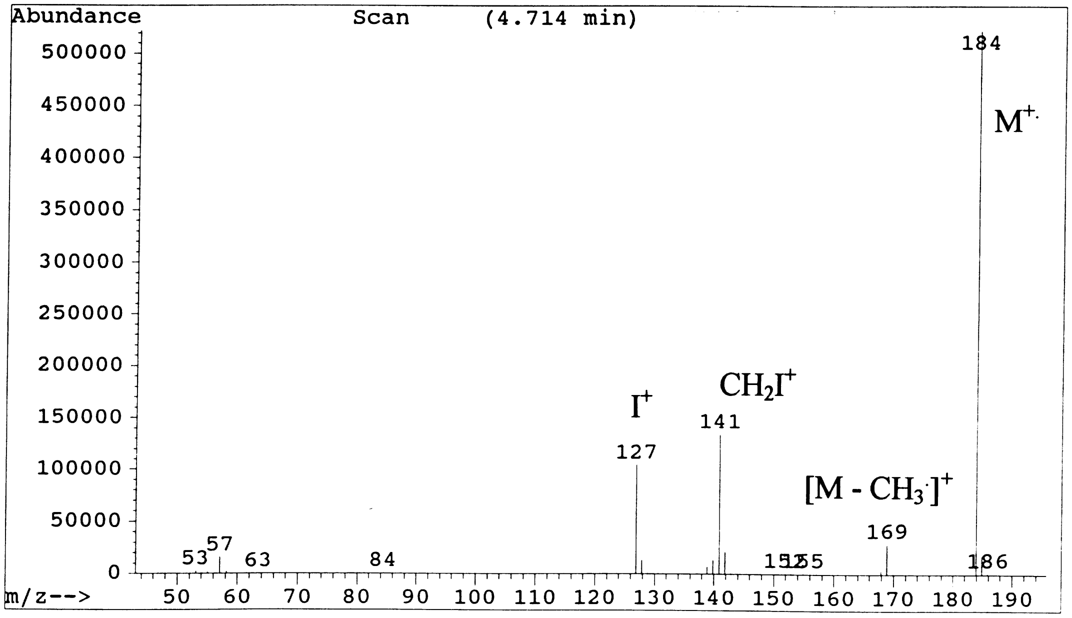


**Figure 4:** Mass spectrum of iodoacetone (MW 184) which was produced from the reaction of acetone and iodine in a 1:10 dilution with water. The reaction time was 4.06 hours at room temperature.

Concentrated methanol, ethanol, 1-propanol, 2-propanol and 1-methoxy-2-propanol were reacted with iodine. Samples of the vapors from the reactions, both alcohol and iodine and alcohol-iodine diluted 1:10 with water, were taken at about 1 hour and 24 hours and investigated using SIM GC/MS. No iodinated by-products or other products were detected at the m/z values monitored.

## REACTIONS IN DILUTE AQUEOUS SOLUTIONS

### *SUMMARY COMMENTS*

For results presented in Figures 7-40 and Tables 4-8, the following background data are provided which will assist in interpreting the data.

Variability in measuring concentrations of organics by direct aqueous injection on the GC/MS was determined by monitoring standard solutions of acetone over 13 days. The acetone standards, at a concentration of 5 mg/L, had a variation of plus or minus 9.0%. The variability in measuring formaldehyde by GC/MS was larger than the variability in measuring the other organics, due in part to the increased number of steps. The PFBOA derivatization method used to measure formaldehyde by GC/MS involved reacting formaldehyde with PFBOA, extracting with hexane, drying with sodium sulfate, then several transfer steps before being injected into the GC/MS.

Organic concentrations were generally averages of two or more injections. The error bars on the graphs represent the range. For some data, the range is very narrow and not apparent. For other samples, only one datum was available. Some chromatograms generated when monitoring the concentrations of organics appeared abnormal and were attributed to bad injections. The data for these bad injections were thrown out. In two other cases, internal standard disappeared for no known reason. On the graphs, the initial data points for measured concentrations of organic compounds were plotted at time zero. All samples were measured on day zero when the experiments were prepared. The measurements occurred at approximately 12 hours, but there was some slight variation for individual samples because of processing by the GC autosampler.

Initially, the spectrophotometric method developed at NASA was used to measure $I^-$, HOI, and $I_2$. This method required measurement of pH and absorbance at four wavelengths; these data were entered into a computer program that calculated $I^-$, HOI, and $I_2$. This method was used to measure the first two sets of iodine concentration for acetone and the initial iodine concentration for isopropanol. The method was later abandoned and replaced with the leuco-crystal violet method. The reason for the abandoning the spectrophotometric method was that it did not work well for basic solutions because the mathematical algorithm resulted in negative concentrations. In addition, the pH meter gave unstable readings for the poorly buffered pH 5.5 and pH 8 reaction mixtures and this lead to inaccuracies. The low initial iodine readings for the acetone and isopropanol data may be due to the use of the spectrophotometric method.

The pH was generally stable. For pH 8 solutions, pH measurements after several weeks did not decline more than 0.5 pH units. For pH 5.5 solutions, pH measurements after several weeks did not decline more than 0.2 pH units. Due to the time involved in the setup of reactions, measuring organic and iodine concentrations, the iodine concentrations were not always measured at time zero.

The detection limits for the measurements of iodine and total I were 0.05 mg/L. The detection limit for the measurement of IDBPs was approximately 0.1 mg/L, and the detection limit for the organic measurements were 0.5 mg/L.

*IODINE CONTROLS*

Iodine controls were monitored for concentrations of iodine and total iodine/iodide (Figures 5 and 6). The iodine concentrations did not significantly change with time for the reactions at pH 5.5. The iodine concentrations for the controls at pH 8 declined rapidly between initiation of the reaction and the initial measurements (within two hours). The iodine concentrations of the pH 8 controls continued to decrease, but not as rapidly. The total iodine/iodide concentrations did not significantly vary over time for pH 5.5 or pH 8 controls.

*ACETONE*

In two separate experiments, in 40 mL vials, reactions of acetone with iodine consistently produced iodoform under reaction conditions 2, 5, and 8. Presence of iodoform and other IDBPs were monitored after 21 days and 38 days for all the pH 5.5 reaction conditions and after 9 and 26 days for all the pH 8 reaction conditions. The average concentration of iodoform produced by condition 2 over several weeks was 3.49 mg/L, the average for condition 5 was 1.34 mg/L, and the average for condition 8 was 5.36 mg/L (Figure 7). Figures 8 and 9 present plots of the concentration of acetone versus time. Regression analysis indicated that the concentration of acetone did not significantly vary over the 30 day time period for all conditions. Although changes in acetone concentration can be seen, probability (P) values (Table 4) indicated that the slope of the lines were not significantly different from zero at an alpha of five percent.

Iodine concentrations and total iodine/iodide concentrations were measured to certify that iodine was present and to monitor the relative amounts of iodine and iodide. Note from Figure 10 and 12 that condition 2 is the only one to have an iodine concentration below 3 mg/L by the twelfth day. The iodine concentrations at pH 8 have larger initial decreases than those at pH 5.5 (Figures 11 and 13). The data for iodine and total iodine/iodide reflect the data for the iodine controls.

Table 4: Regression Data for Acetone Concentrations vs. Time

| Experimental Design | | | | Regression Statistics for Acetone | | |
|---|---|---|---|---|---|---|
| Condition | pH | $I_2$ mg/L | acetone mg/L | slope | Std. error | P value |
| 1 | 5.5 | 10 | 5 | -0.004 | 0.012 | 0.7563 |
| 2 | 8.0 | 10 | 5 | -0.027 | 0.020 | 0.2372 |
| 3 | 5.5 | 50 | 5 | 0.006 | 0.007 | 0.4290 |
| 4 | 8.0 | 50 | 5 | -0.074 | 0.028 | 0.0564 |
| 5 | 5.5 | 10 | 50 | -0.038 | 0.143 | 0.8057 |
| 6 | 8.0 | 10 | 50 | 0.100 | 0.219 | 0.6773 |
| 7 | 5.5 | 50 | 50 | -0.194 | 0.089 | 0.1182 |
| 8 | 8.0 | 50 | 50 | 0.078 | 0.094 | 0.4545 |

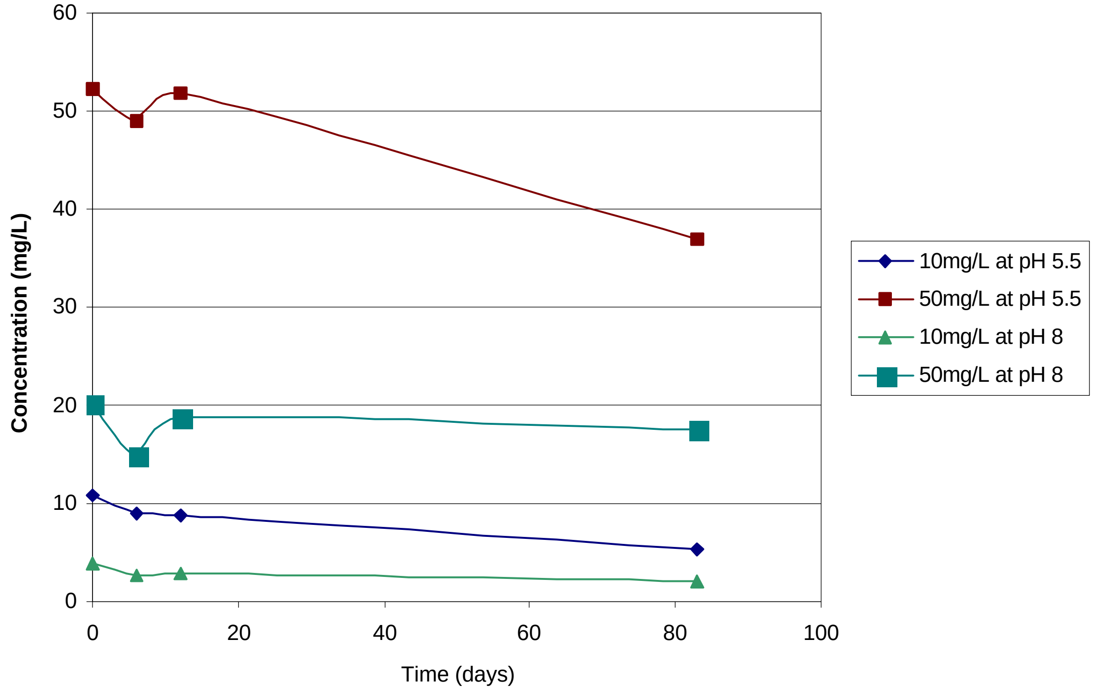


**Figure 5: Iodine ($I_2$ and HOI) Measurements for Iodine Controls**

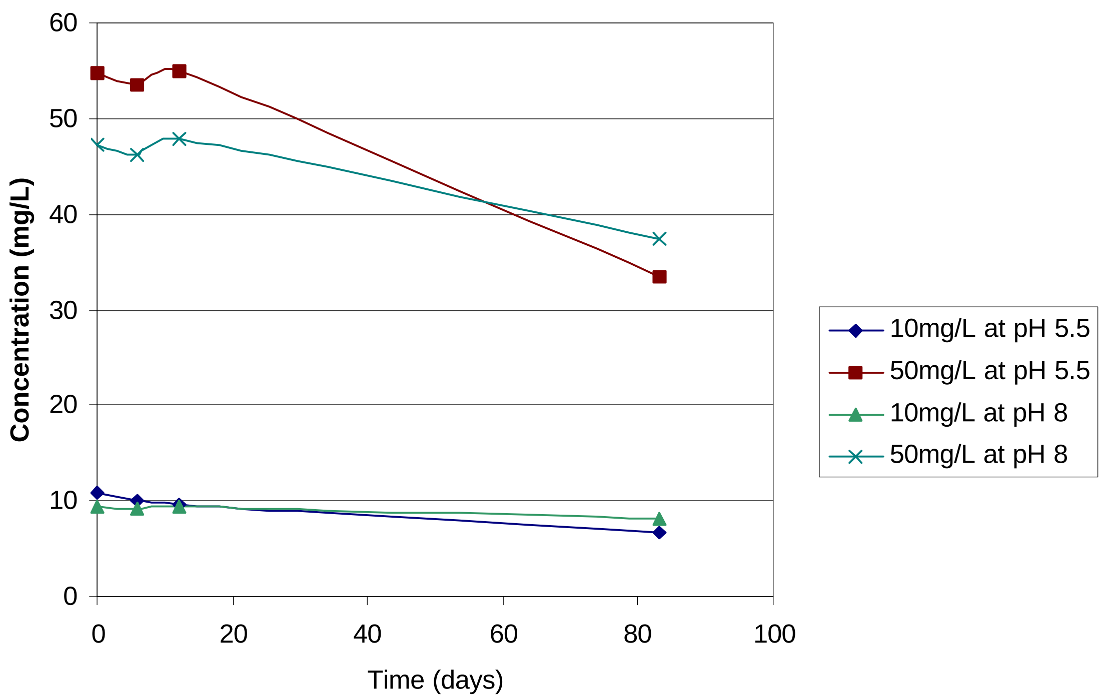


**Figure 6: Total ($I_2$, HOI, $I^-$) Measurements for Iodine Controls**

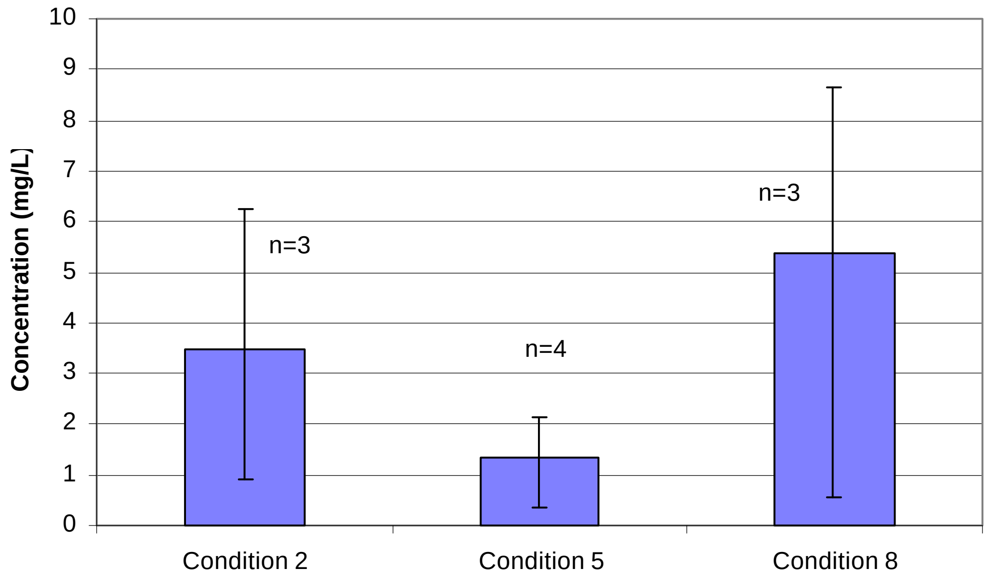


**Figure7: Iodoform Concentrations Produced by Acetone and Iodine**

**Condition 2: pH 8, 5 mg/L acetone, 10 mg/L iodine**

**Condition 5: pH 5.5, 50 mg/L acetone, 10 mg/L iodine**

**Condition 8: pH 8, 50 mg/L acetone, 50 mg/L iodine**

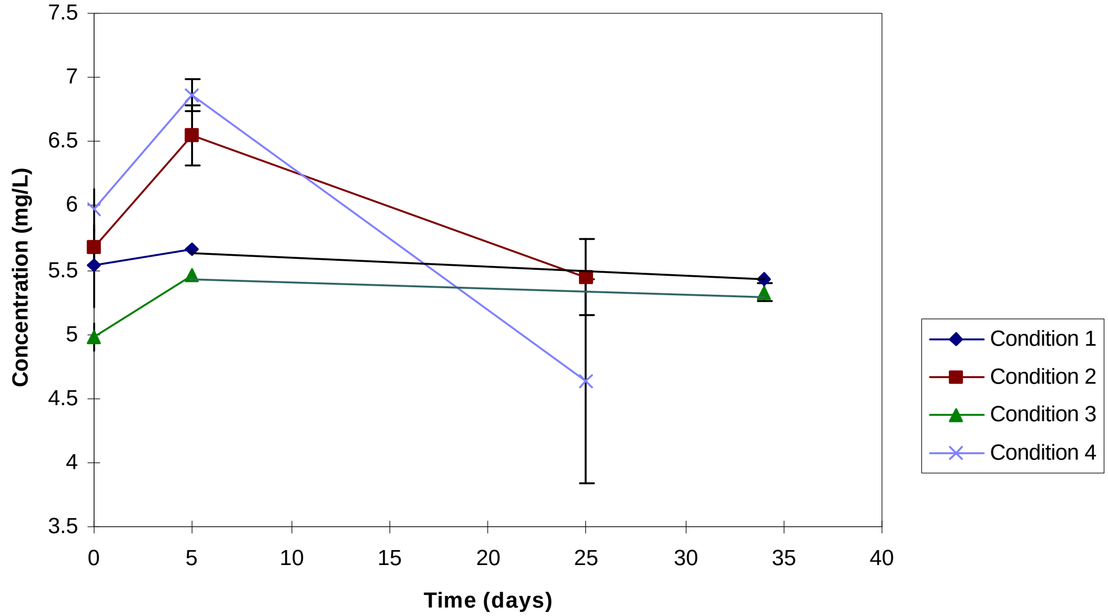


**Figure 8: Acetone Measurements for Conditions 1-4**

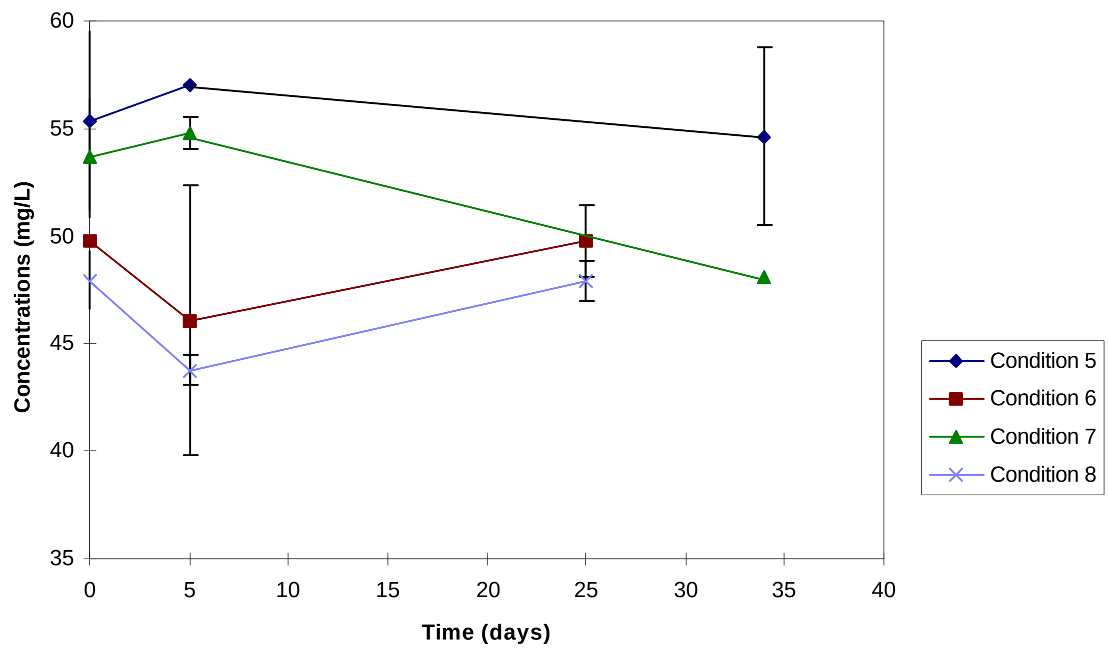


**Figure 9: Acetone Measurements for Conditions 5-8**

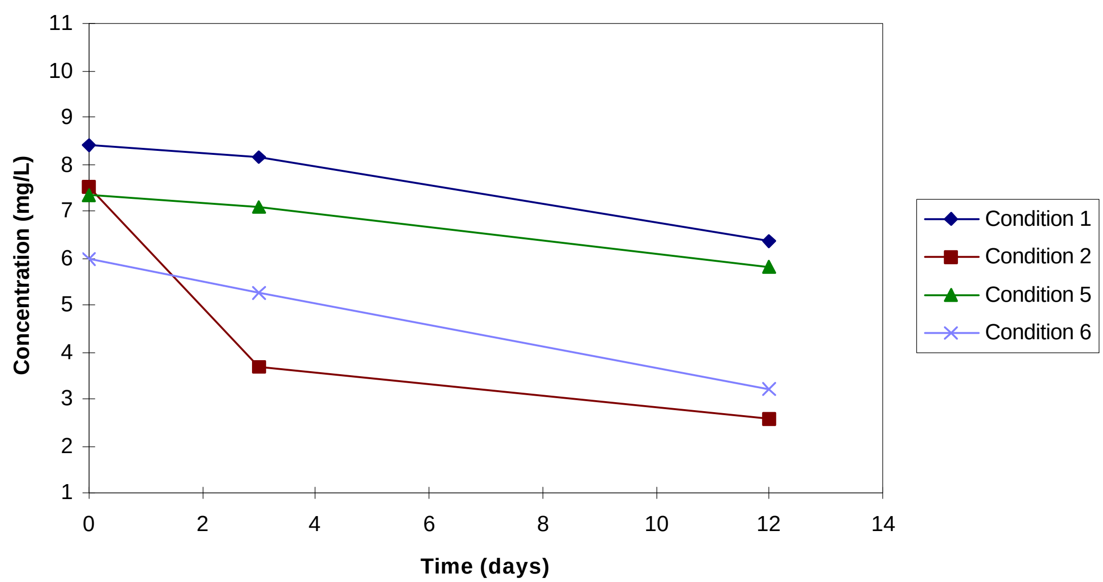


**Figure 10: Iodine ($I_2$ and HOI) Measurements for Acetone Conditions 1,2,5, and 6**

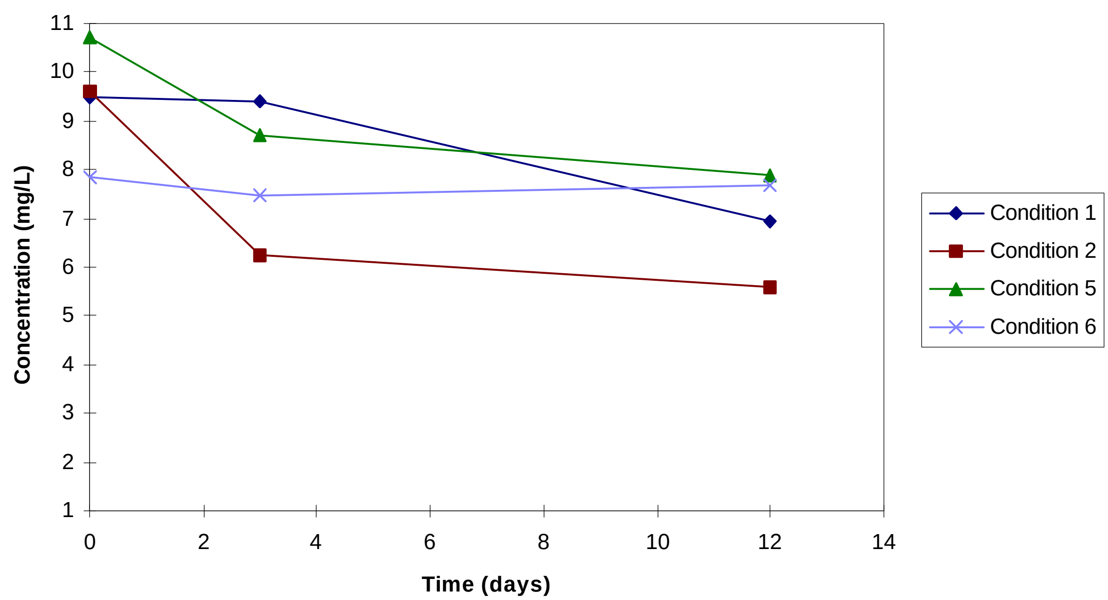


**Figure 11: Total Iodine/Iodide ($I_2$, HOI, and $I^-$) Measurements for Acetone Conditions 1,2,5, and 6**

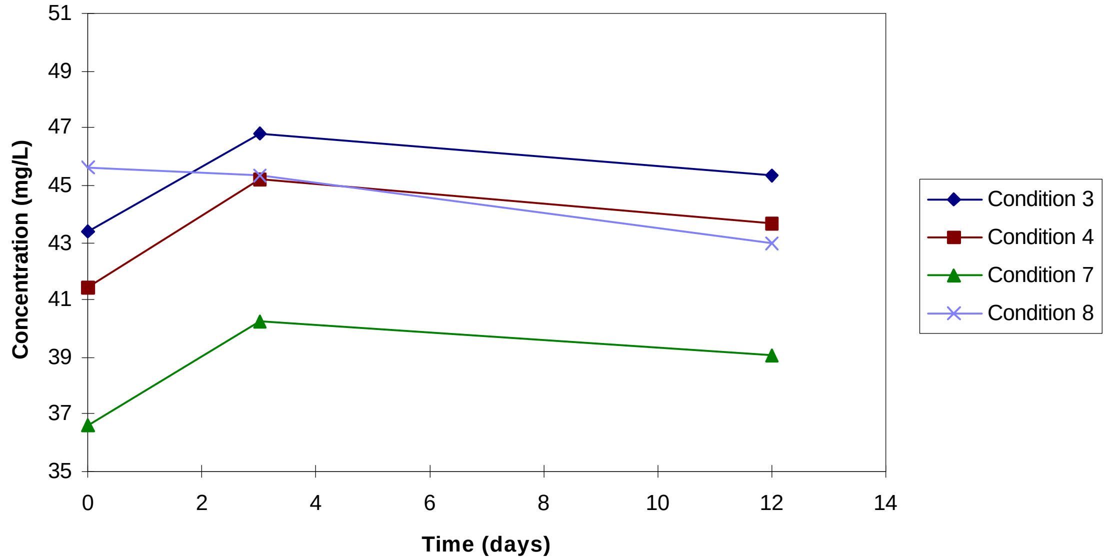


**Figure 12: Iodine ($I_2$ and HOI) Measurements for Acetone Conditions 3,4,7, and 8**

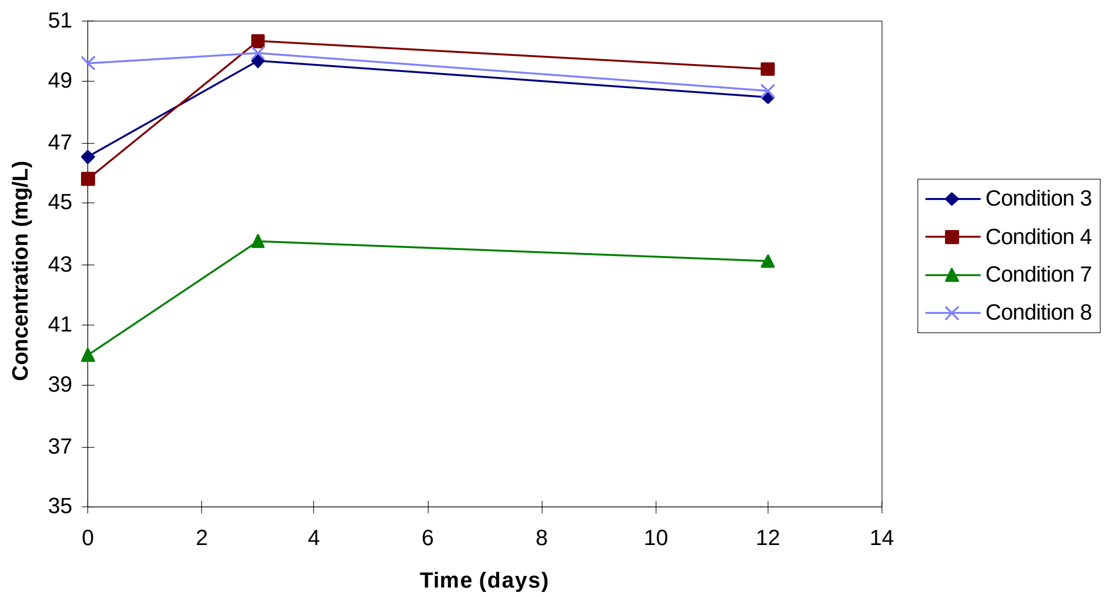


**Figure 13: Total Iodine/Iodide ($I_2$, HOI, and $I^-$) Measurements for Acetone Conditions 3,4,7, and 8**

For the experiments involving reactions of acetone and iodine, a small amount of iodoacetone, estimated to be about 100 μg/L, and also iodoform, were detected after 48 hours under conditions 7 and 8. About 100 μg/L iodoacetone and 1000 μg/L iodoform were detected at 4 days under reaction condition 8; no iodoacetone or iodoform was detected for condition 7. No iodoacetone was detected under experimental condition 7 or 8 when the reaction time was extended to 38 or 26 days, respectively. Iodoacetone was never detected under condition 1-6. Thus, iodoacetone appeared to be an intermediate product that forms but does not accumulate.

One liter volumes of conditions 2, 5, and 8 solutions were allowed to react for five weeks in an attempt to produce large volumes of reaction mixtures that could be evaluated by the FPA panel and by GC/MS after liquid-liquid extraction. The FPA panel evaluated 200 mL of the sample and the remaining 800 mL were liquid-liquid extracted and evaluated by the GC/MS. The reaction under condition 8 was the only one to produce detectable amounts of iodoform and the measured concentrations was approximately 4 mg/L.

*ISOPROPYL ALCOHOL*

Iodinated disinfection by-products were not detected in any of the isopropyl alcohol experiments. IDBPs were monitored after 38 days for the pH 5.5 reaction conditions and 26 days for the pH 8 reaction conditions. Figures 14 and 15 present plots of the concentration of isopropyl alcohol versus time. Regression analysis (Table 5) indicated that concentrations of isopropyl alcohol significantly decreased in conditions 2, 3, and 6. The large disappearance of internal standard in condition 8 led to an inaccurate measurement of the isopropyl alcohol in this sample, thus condition 8 was omitted from this graph. Note from Figures 16 and 18 that by day 3, reactions under conditions 1 and 2 had concentrations of iodine less than 3 mg/L.

Most of the iodine concentrations behaved similarly to the iodine controls. The reaction under condition 1 (pH 5.5) decreased more than 50%. This was not seen in the controls.

Table 5: Regression Data for Isopropyl Alcohol Concentrations vs. Time

| Experimental Design | | | | Regression Statistics for Isopropyl Alcohol | | |
|---|---|---|---|---|---|---|
| Condition | pH | $I_2$ mg/L | IPA mg/L | Slope mg/L/day | Std.error | P value |
| 1 | 5.5 | 10 | 5 | -0.163 | 0.225 | 0.5444 |
| 2 | 8.0 | 10 | 5 | -0.206 | 0.063 | 0.0462 |
| 3 | 5.5 | 50 | 5 | -0.241 | 0.055 | 0.0477 |
| 4 | 8.0 | 50 | 5 | -0.019 | 0.024 | 0.4823 |
| 5 | 5.5 | 10 | 50 | -0.723 | 0.251 | 0.1019 |
| 6 | 8.0 | 10 | 50 | -3.179 | 0.298 | 0.0087 |
| 7 | 5.5 | 50 | 50 | 0.792 | 0.618 | 0.3284 |

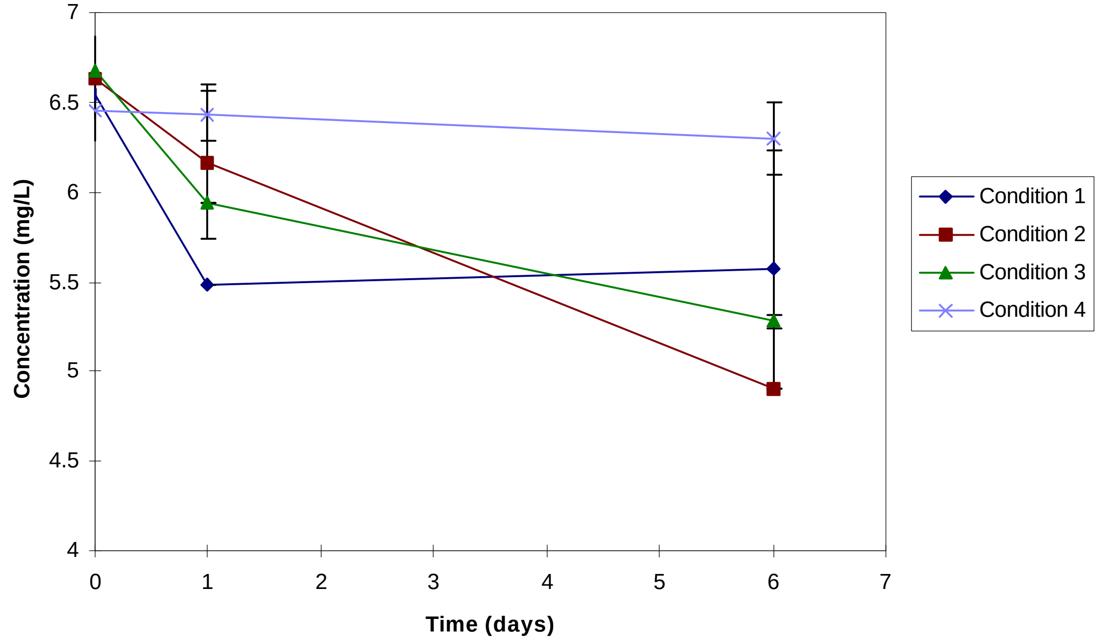


**Figure 14: Isopropyl Alcohol Measurements for Conditions 1-4**

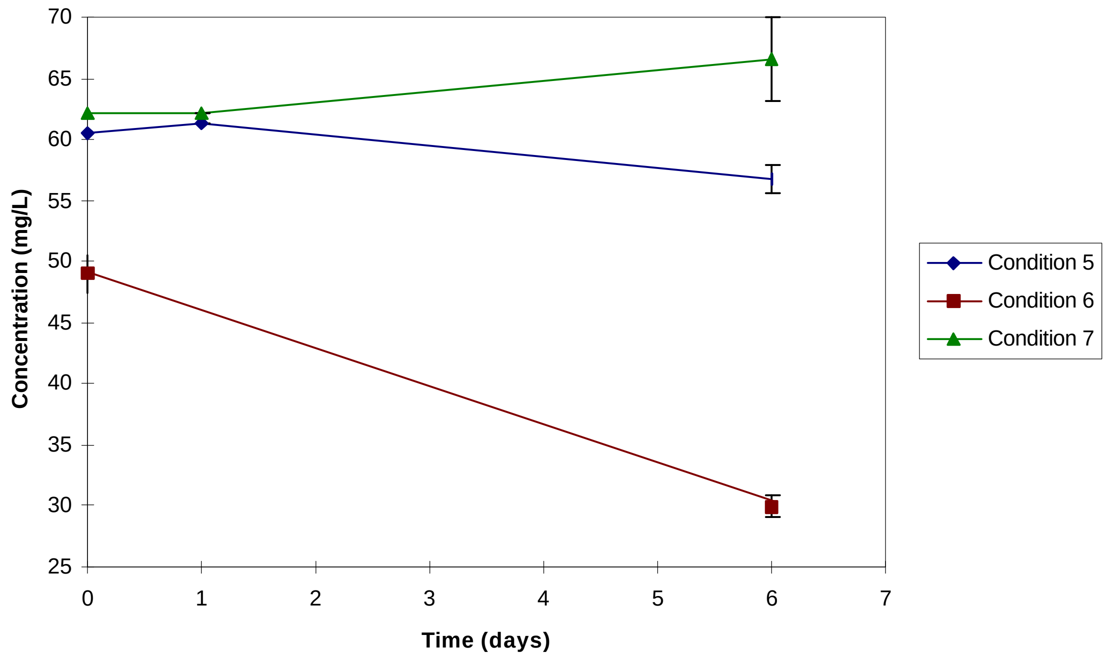


**Figure 15: Isopropyl Alcohol Measurements for Conditions 5-8**

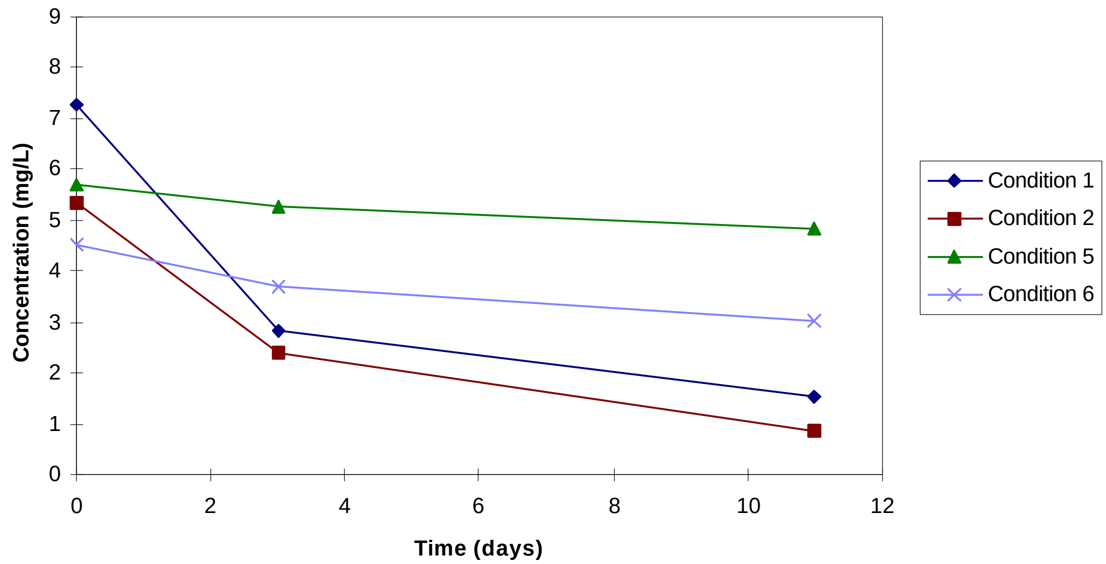


**Figure 16: Iodine ($I_2$ and HOI) Measurements for Isopropyl Alcohol Conditions 1,2,5, and 6**

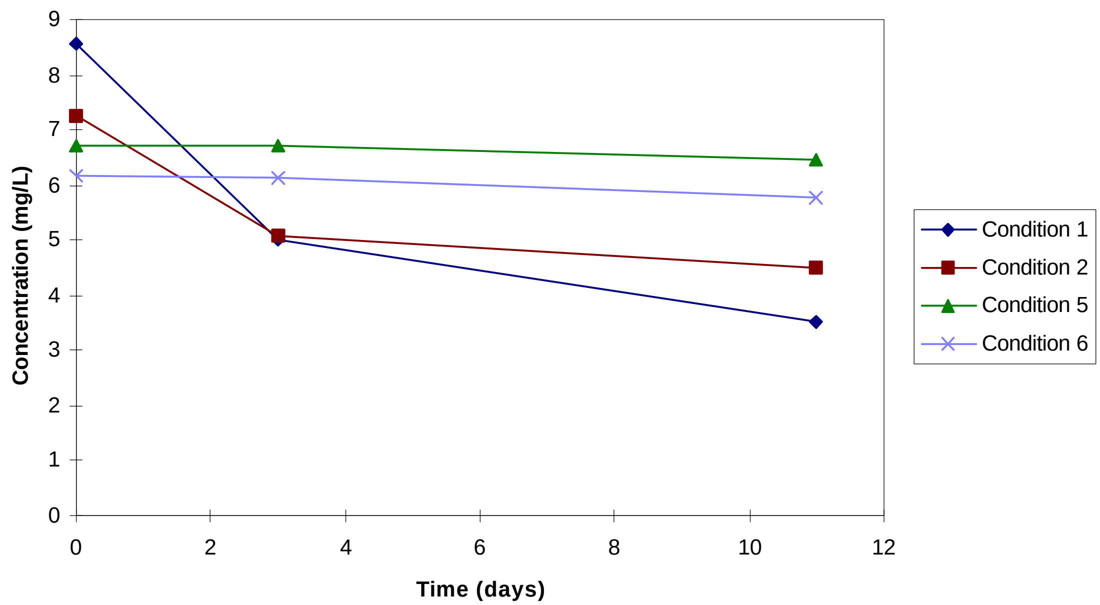


**Figure 17: Total Iodine/Iodide ($I_2$, HOI, and $I^-$) Measurements for Isopropyl Alcohol Conditions 1,2,5, and 6**

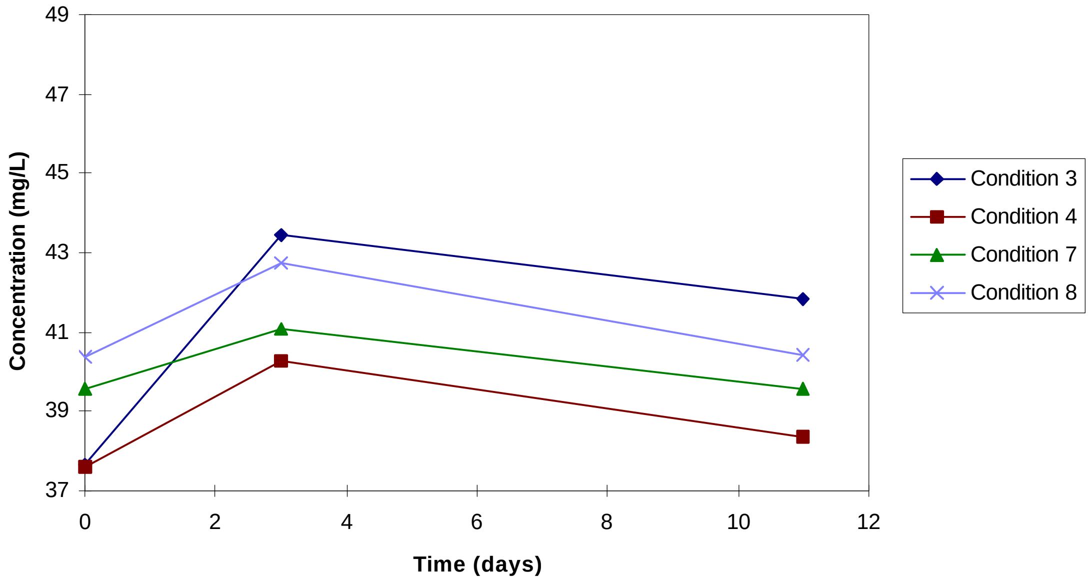


**Figure 18: Iodine ($I_2$ and HOI) Measurements for Isopropyl Alcohol Conditions 3,4,7, and 8**

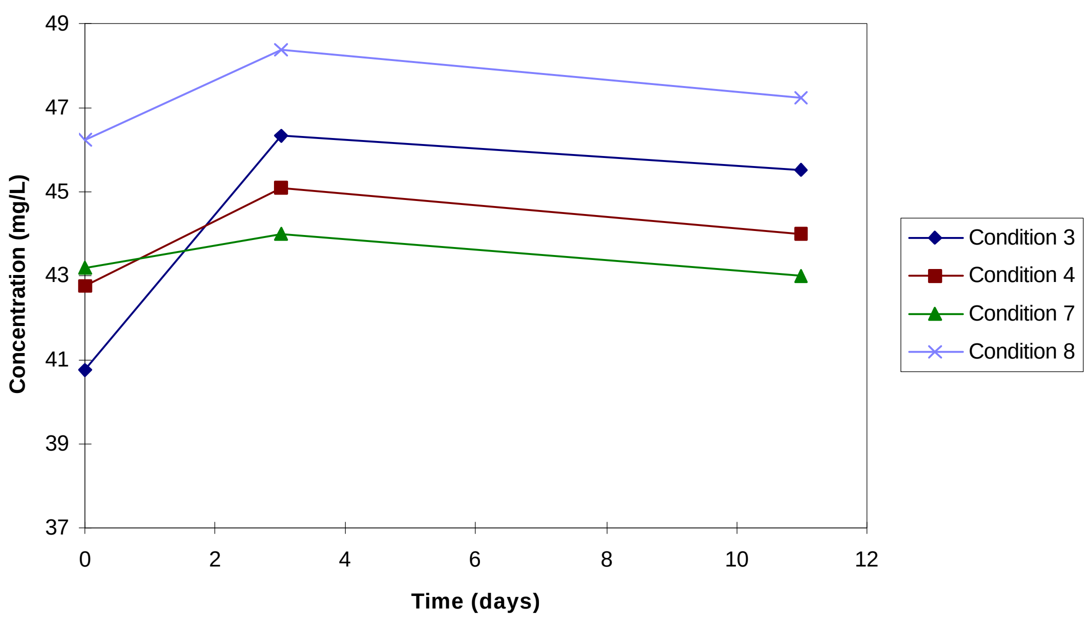


**Figure 19: Total Iodine/Iodide ($I_2$, HOI, and $I^-$) Measurements for Isopropyl Alcohol Conditions 3,4,7, and 8**

*FORMALDEHYDE*

Iodinated disinfection by-products were not detected in any of the formaldehyde experiments. Presence of iodoformaldehyde was measured on days 14, 28, and 42; presence of iodoalkanes was measured on day 70. Figures 20 and 21 present plots of the concentration of formaldehyde versus time. Regression analysis (Table 6) indicated that the concentration of formaldehyde significantly decreased in condition 1 and significantly increased in condition 4. Internal standard in condition 4 was noted to have decreased, thus causing the appearance of an increase. Note from Figures 22 and 24 that by day 60, reactions under conditions 2 and 6 had iodine concentrations less than 3 mg/L. Although statistical analysis was not performed on the iodine data due to the low number of data, large decreases in total iodine/iodide do not appear to have occurred. The largest decrease was in condition 4 from 22.58 mg/L to 17.39 mg/L.

Table 6: Regression Data for Formaldehyde Concentrations vs. Time

| Experimental Design | | | | Regression Statistics for Formaldehyde | | |
|---|---|---|---|---|---|---|
| Condition | pH | $I_2$ mg/L | formaldehyde mg/L | Slope | Std.error | P value |
| 1 | 5.5 | 10 | 5 | -0.040 | 0.016 | 0.0333 |
| 2 | 8.0 | 10 | 5 | 0.001 | 0.066 | 0.9918 |
| 3 | 5.5 | 50 | 5 | 0.006 | 0.051 | 0.9164 |
| 4 | 8.0 | 50 | 5 | 0.127 | 0.033 | 0.0081 |
| 5 | 5.5 | 10 | 50 | 0.066 | 0.318 | 0.8466 |
| 6 | 8.0 | 10 | 50 | 0.013 | 0.329 | 0.9709 |
| 7 | 5.5 | 50 | 50 | -0.136 | 0.205 | 0.5298 |
| 8 | 8.0 | 50 | 50 | -0.069 | 0.259 | 0.8040 |

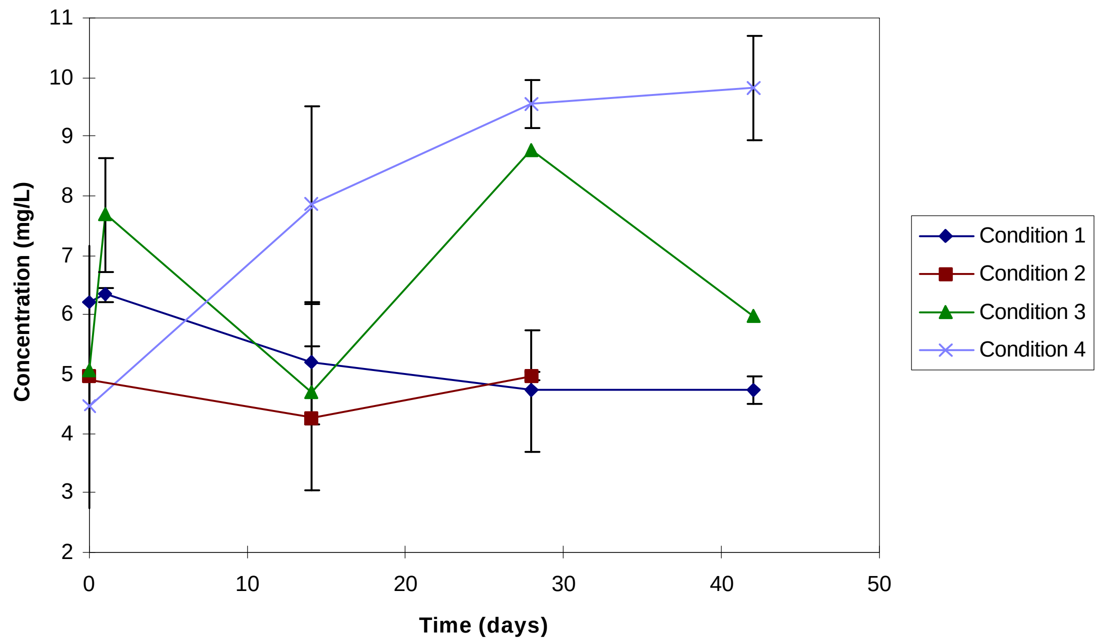


**Figure 20: Formaldehyde Measurements for Conditions 1-4**

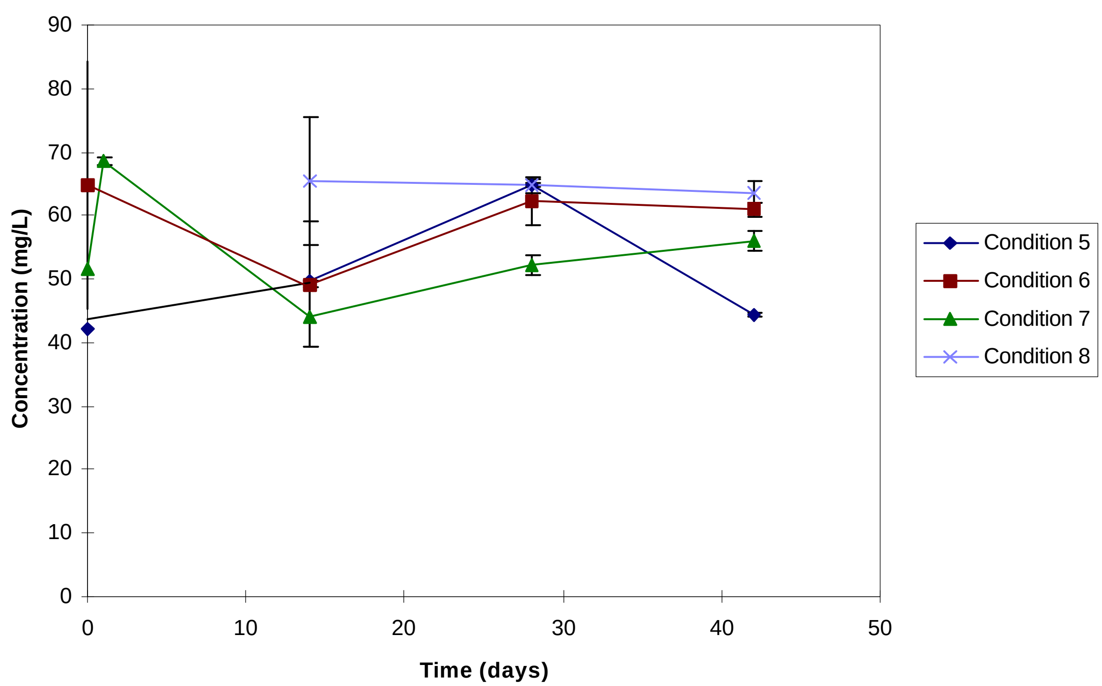


**Figure 21: Formaldehyde Measurements for Conditions 5-8**

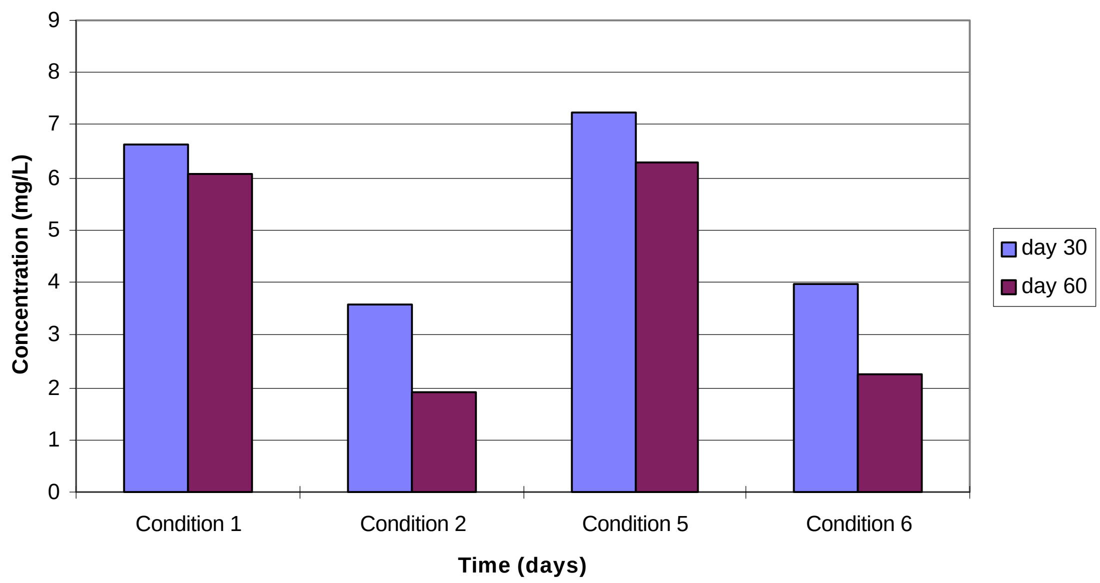


**Figure 22: Iodine ($I_2$ and HOI) Measurements for Formaldehyde Conditions 1,2,5, and 6**

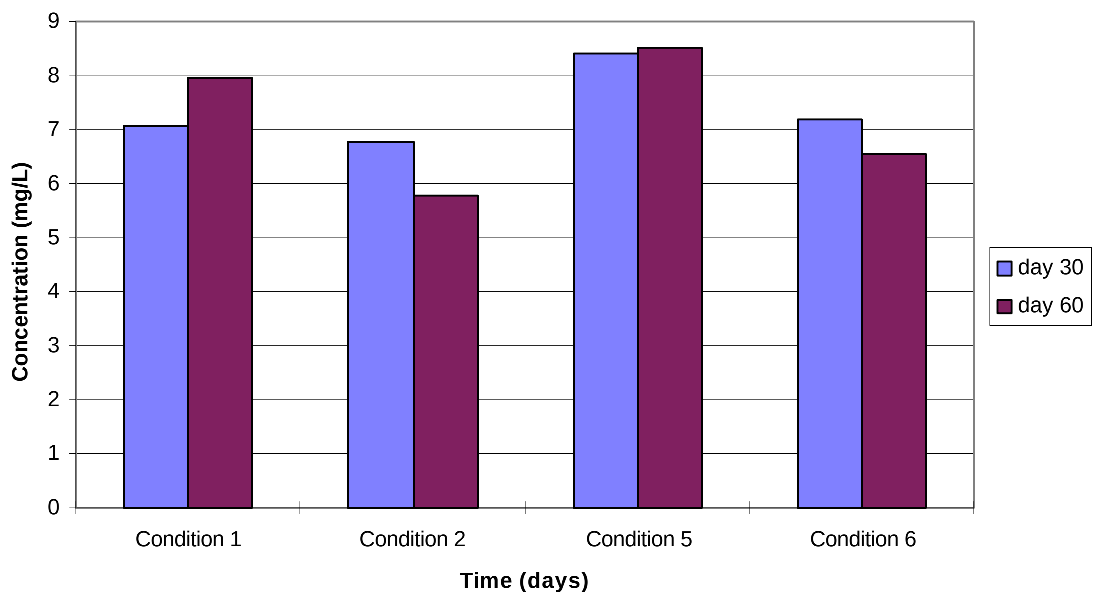


**Figure 23: Total Iodine/Iodide ($I_2$, HOI, and $I^-$) Measurements for Formaldehyde Conditions 1,2,5, and 6**

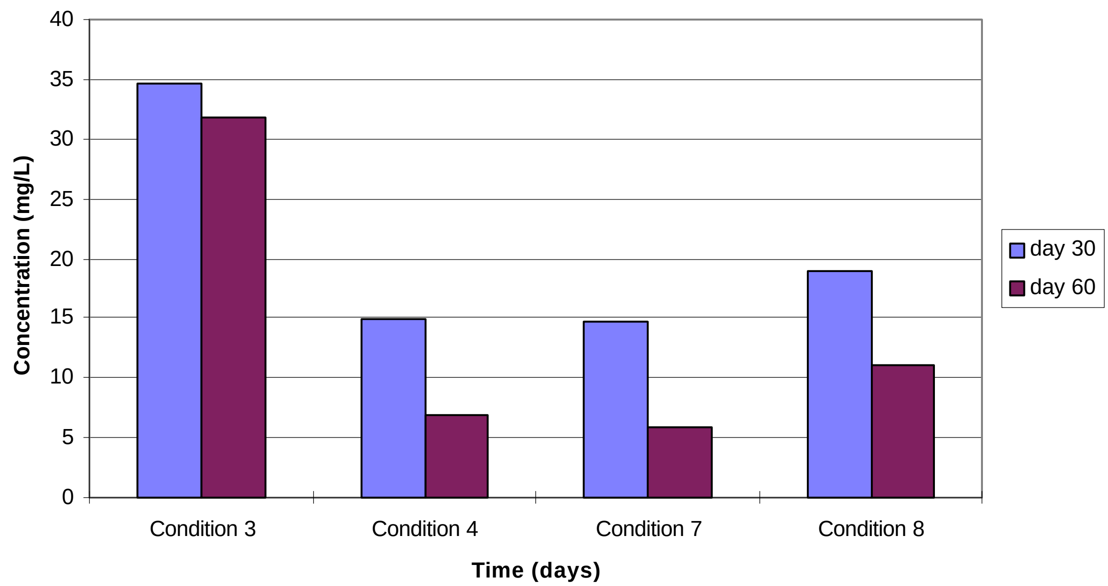


**Figure 24: Iodine ($I_2$ and HOI) Measurements for Formaldehyde Conditions 3,4,7, and 8**

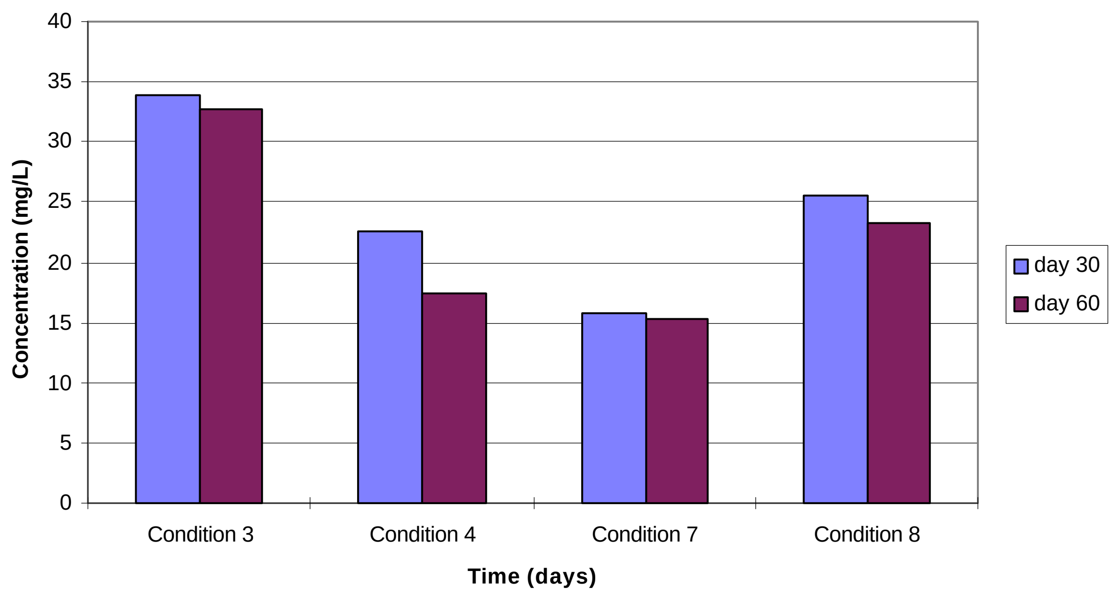


**Figure 25: Total Iodine/Iodide ($I_2$, HOI, and $I^-$) Measurements for Formaldehyde Conditions 3,4,7, and 8**

*1-PROPANOL*

Iodinated disinfection by-products were not detected in any of the 1-propanol experiments after 29 days of reaction. Figure 26 and 27 present plots of the concentration of 1-propanol versus time. Regression analysis (Table 7) indicated that the concentration of 1-propanol significantly decreased in condition 2 and significantly increased in condition 6. Note from Figures 28 and 30 that by day 60, only reactions under condition 6 had an iodine concentration less than 3 mg/L. Although statistical analysis was not performed on the data due to the low number of data, large decreases in the total I did not appear to have occurred. The largest decrease was in condition 4 from 40.65 mg/L to 36.77 mg/L.

Table 7: Regression Data for 1-Propanol Concentrations vs. Time

| Experimental Conditions | | | | Regression Statistics for 1-Propanol | | |
|---|---|---|---|---|---|---|
| Condition | pH | $I_2$ mg/L | 1-propanol mg/L | Slope | Std. error | P value |
| 1 | 5.5 | 10 | 5 | -0.025 | 0.019 | 0.2609 |
| 2 | 8.0 | 10 | 5 | -0.034 | 0.013 | 0.0436 |
| 3 | 5.5 | 50 | 5 | 0.024 | 0.014 | 0.1484 |
| 4 | 8.0 | 50 | 5 | 0.018 | 0.017 | 0.3242 |
| 5 | 5.5 | 10 | 50 | 0.031 | 0.142 | 0.8483 |
| 6 | 8.0 | 10 | 50 | 0.329 | 0.095 | 0.0258 |
| 7 | 5.5 | 50 | 50 | 0.120 | 0.119 | 0.3508 |
| 8 | 8.0 | 50 | 50 | 0.031 | 0.048 | 0.5404 |

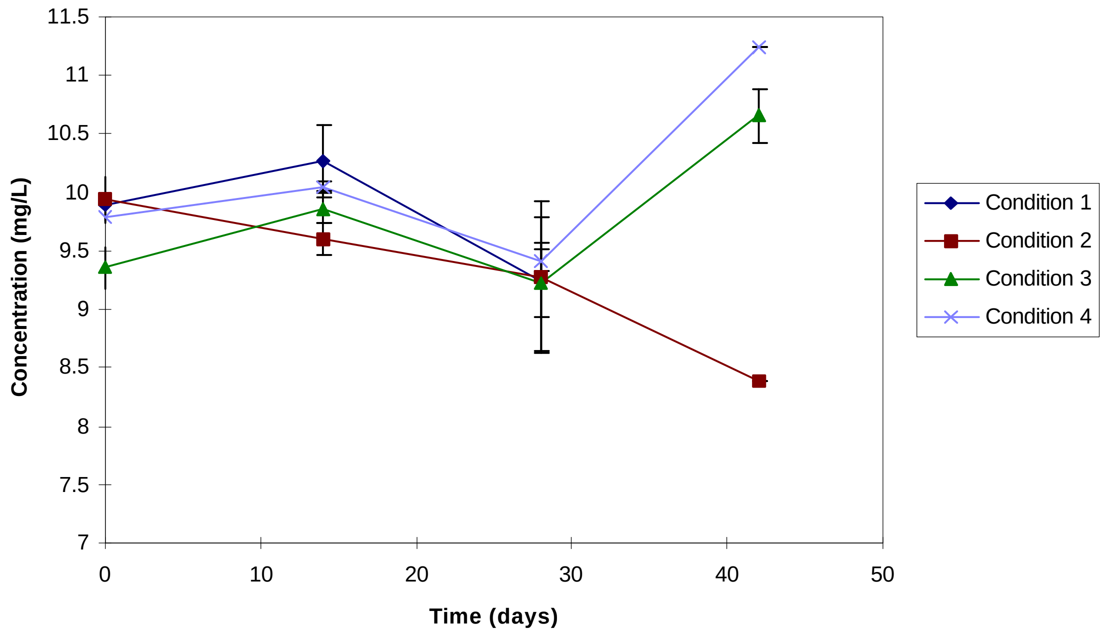


**Figure 26: 1-Propanol Measurements for Conditions 1-4**

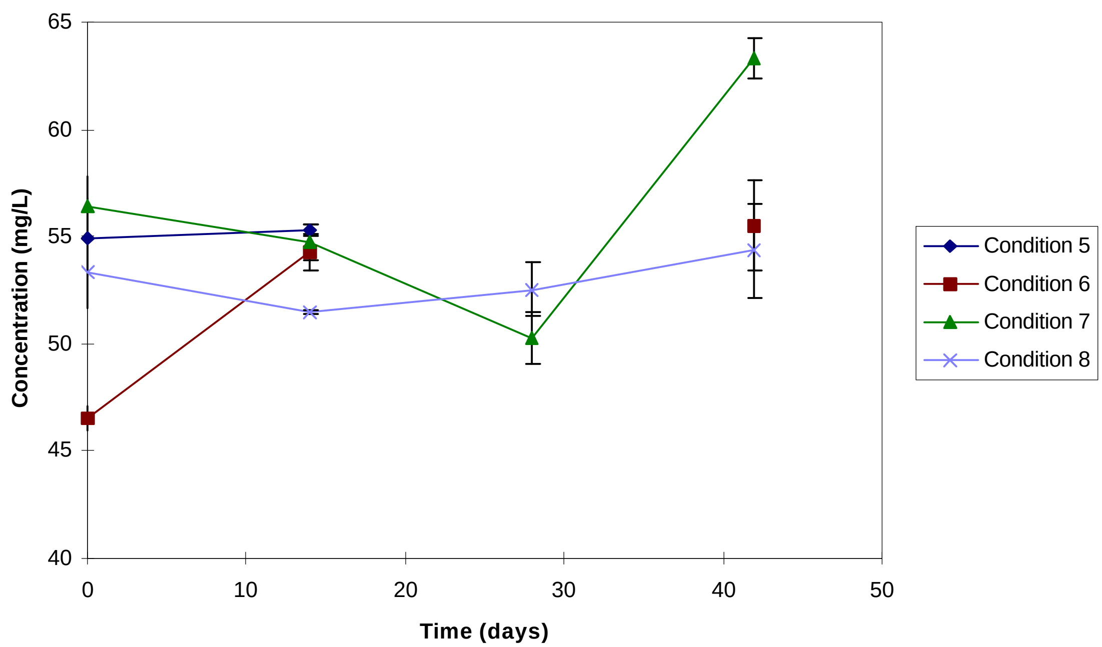


**Figure 27: 1-Propanol Measurements for Conditions 5-8**

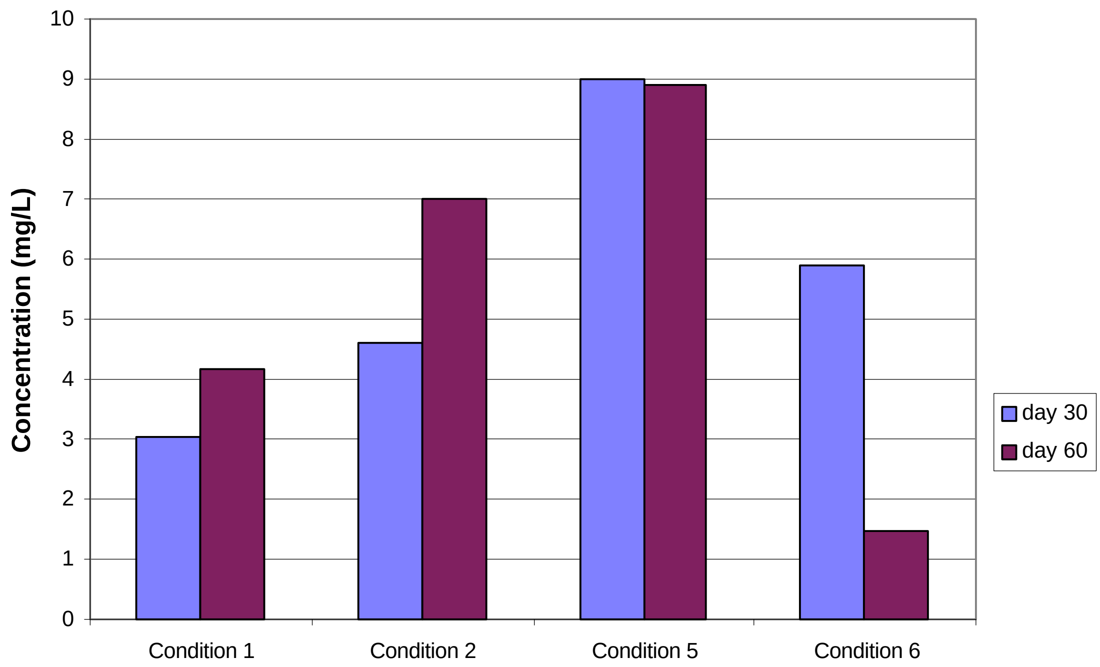


**Figure 28: Iodine ($I_2$ and HOI) Measurements for 1-propanol conditions 1,2,5, and 6**

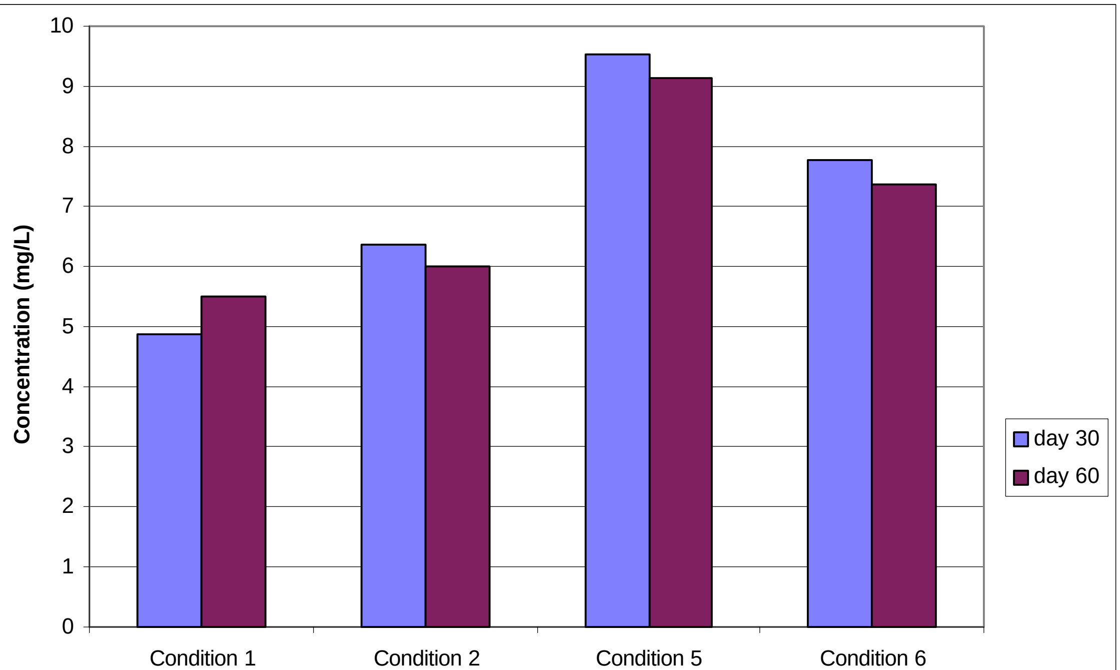


**Figure 29: Total Iodine/Iodide ($I_2$, HOI, $I^-$) Measurements for 1-Propanol Conditions 1,2,5, and 6**

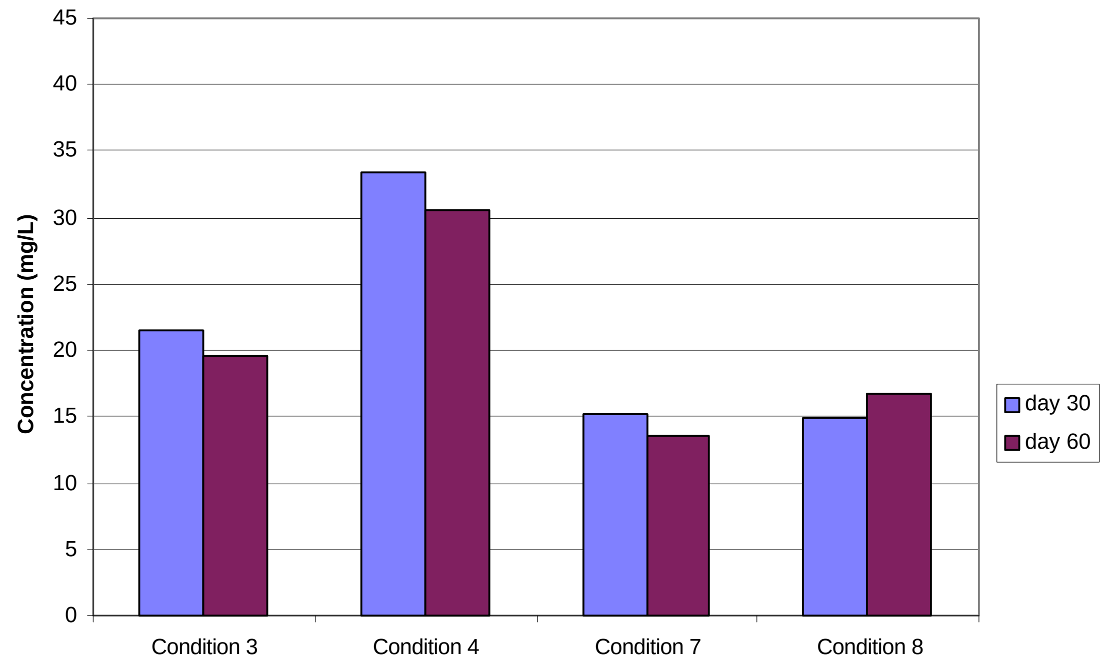


**Figure 30: Iodine ($I_2$ and HOI) Measurements for 1-Propanol Conditions 3,4,7, and 8**

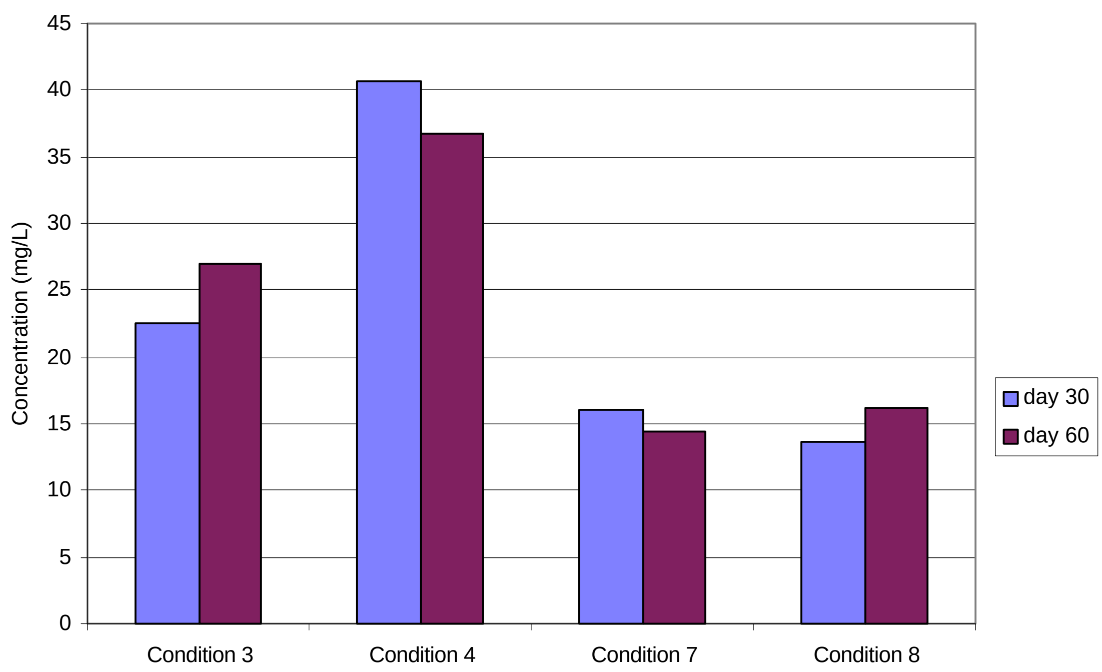


**Figure 31: Total Iodine/Iodide ($I_2$, HOI, and $I^-$) Measurements for 1-Propanol Conditions 3,4,7, and 8**

*1-METHOXY-2-PROPANOL*

Iodinated disinfection by-products were not detected in any of the 1-methoxy-2-propanol experiments after 23 days of reaction. Figures 32 and 33 present plots of the concentration of 1-methoxy-2-propanol versus time. Regression analysis (Table 8) indicated that the concentration 1-methoxy-2-propanol significantly decreased in condition 7 and significantly increased in condition 1. Only one set of measurements were made of iodine for the 1-methoxy-2-propanol experiments. Figures 34-37 compare the initial concentration of iodine with the concentration measured on the 13th day. Note from Figures 34 and 36 that all of the conditions had concentrations of iodine above 5 mg/L.

Table 8: Regression Data for 1-Methoxy-2-Propanol Concentrations vs. Time

| Experimental Design | | | | Reg. Statistics for 1-methoxy-2-propanol | | |
|---|---|---|---|---|---|---|
| Condition | pH | $I_2$ mg/L | 1-methoxy-2-propanol mg/L | Slope mg/L/day | Std. error | P value |
| 1 | 5.5 | 10 | 5 | 0.208 | 0.004 | 0.0128 |
| 2 | 8.0 | 10 | 5 | 0.125 | 0.075 | 0.1940 |
| 3 | 5.5 | 50 | 5 | -0.097 | 0.092 | 0.3530 |
| 4 | 8.0 | 50 | 5 | -0.154 | 0.135 | 0.3354 |
| 5 | 5.5 | 10 | 50 | 1.402 | 1.271 | 0.3506 |
| 6 | 8.0 | 10 | 50 | -0.110 | 1.371 | 0.9398 |
| 7 | 5.5 | 50 | 50 | -2.047 | 0.298 | 0.0063 |
| 8 | 8.0 | 50 | 50 | -2.818 | 1.036 | 0.0529 |

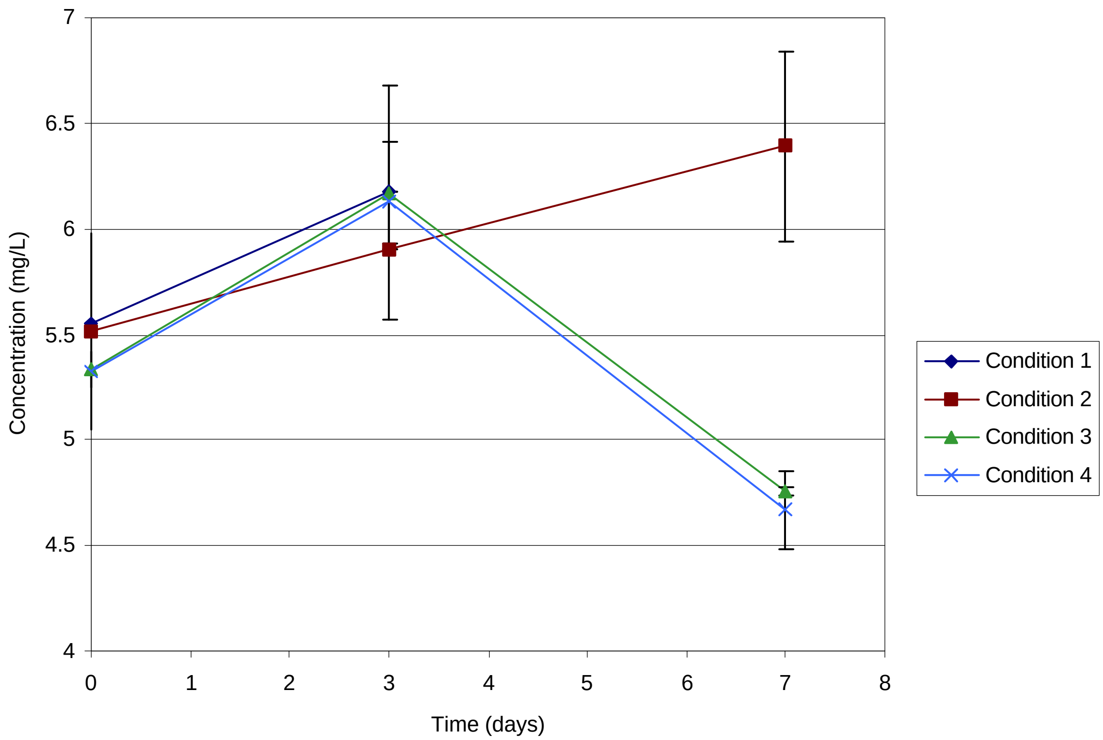


**Figure 32: 1-Methoxy-2-Propanol Measurements for Conditions 1-4**

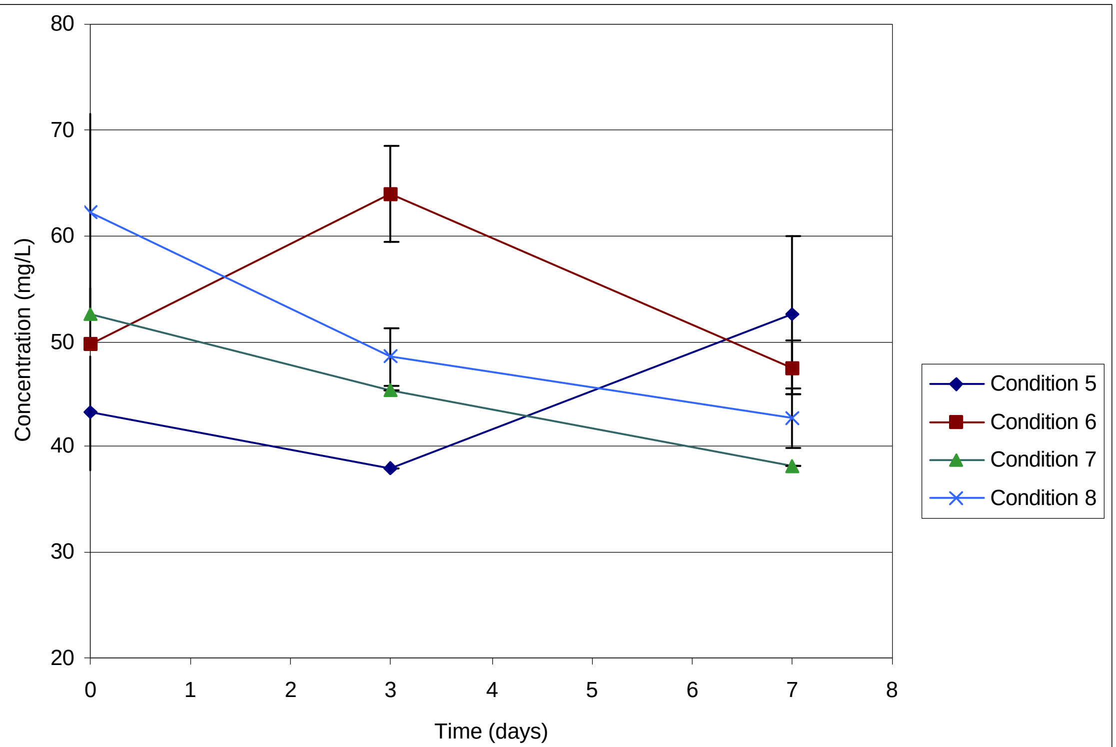


**Figure 33: 1-Methoxy-2-Propanol Measurements for Conditions 5-8**

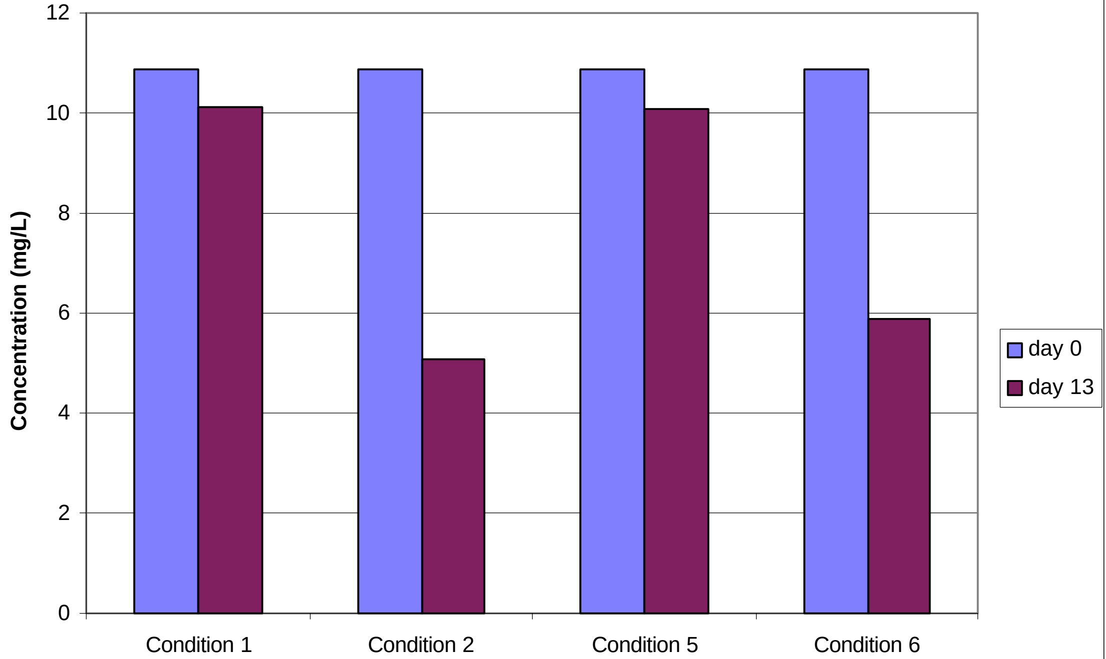


**Figure 34: Iodine ($I_2$ and HOI) Measurements for 1-Methoxy-2-Propanol Conditions 1,2,5, and 6**

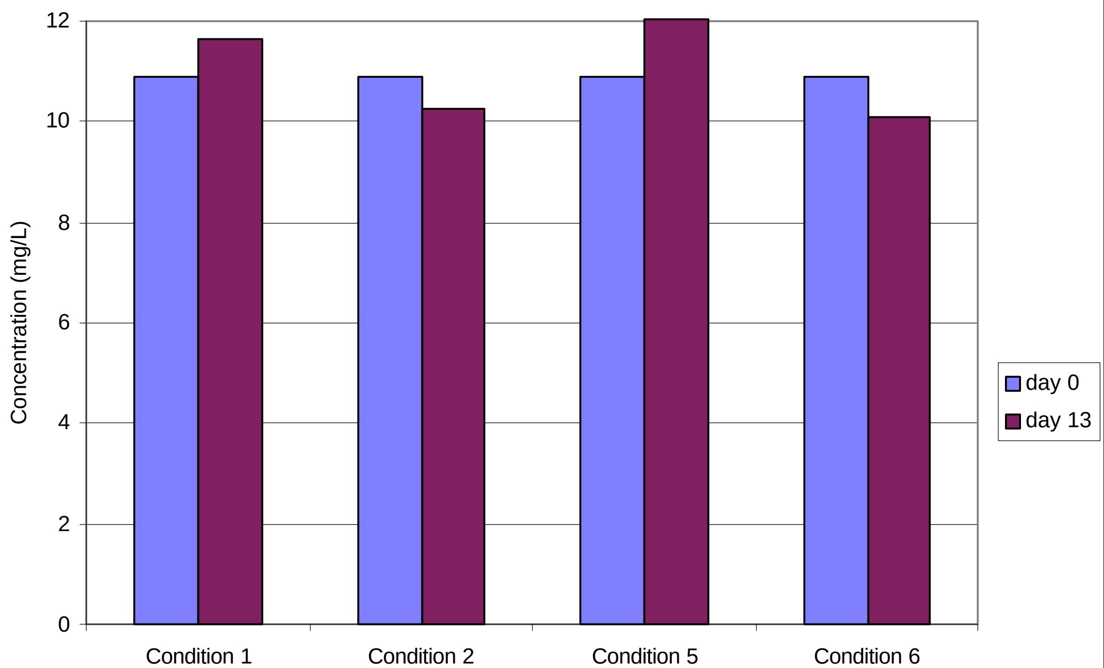


**Figure 35: Total Iodine/Iodide ($I_2$, HOI, and $I^-$) Measurements for 1-Methoxy-2-Propanol Conditions 1,2,5, and 6**

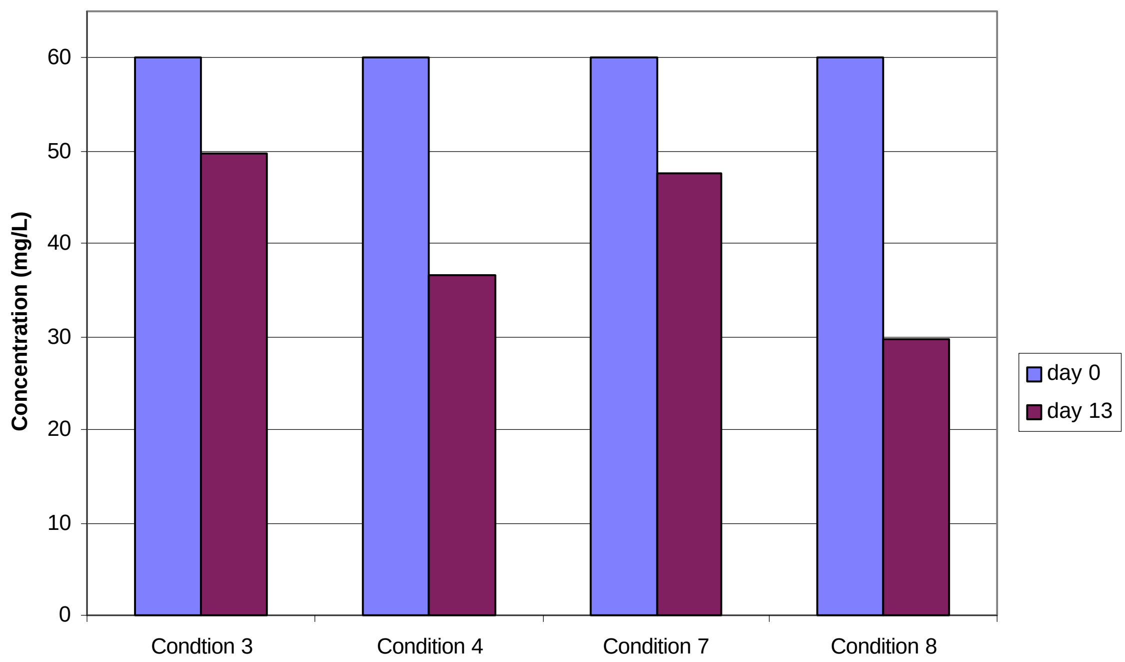


**Figure 36: Iodine ($I_2$ and HOI) Measurements for 1-Methoxy-2-Propanol Conditions 3,4,7, and 8**

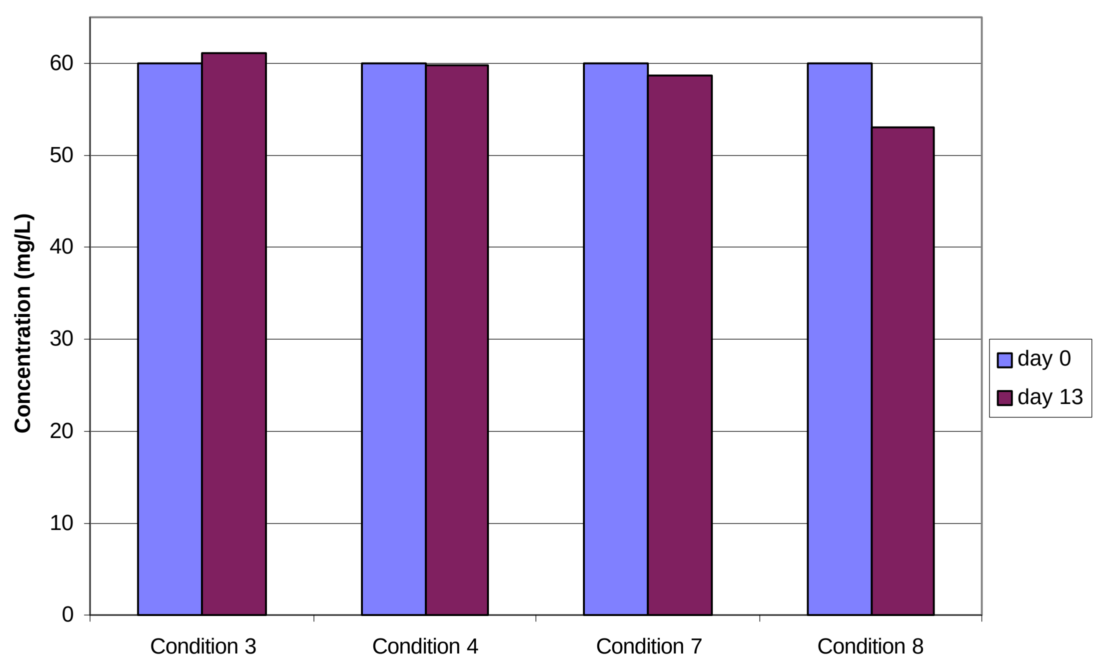


**Figure 37: Total Iodine/Iodide ($I_2$, HOI, and $I^-$) Measurements for 1-Methoxy-2-Propanol Conditions 3,4,7, and 8**

*METHANOL AND ETHANOL*

Iodinated disinfection by-products were not detected in any of the methanol or ethanol experiments after 54 days of reaction. Figures 38 and 39 present the initial concentration of methanol and the concentration after 10 days. Figures 40 and 41 present the initial concentration of ethanol and the concentration after 10 days. Statistical analysis was not performed due to the low number of data.

*PHENOL*

Selected experiments were performed with phenol (Mirlohi, 1997). Preliminary tests conducted under condition 8 (50 mg/L phenol, pH 8, 50 mg/L iodine) indicated that iodine and phenol reacted to produce 2-iodophenol. The quantity of 2-iodophenol produced was readily detectable by SIM GC/MS and liquid chromatography with UV-Vis detector. Phenol itself has a "chemical, phenolic" odor and an OTC of about 4 mg/L. The iodophenols have "chemical, medicinal" odors somewhat like iodoform. The OTC for 2-iodophenol is about 5 μg/L, and for 4-iodophenol the OTC is greater than 20 μg/L. Although the data are limited, it appears that phenol definitely reacts with iodine to produce odorous IDBP. More research in this area is warranted.

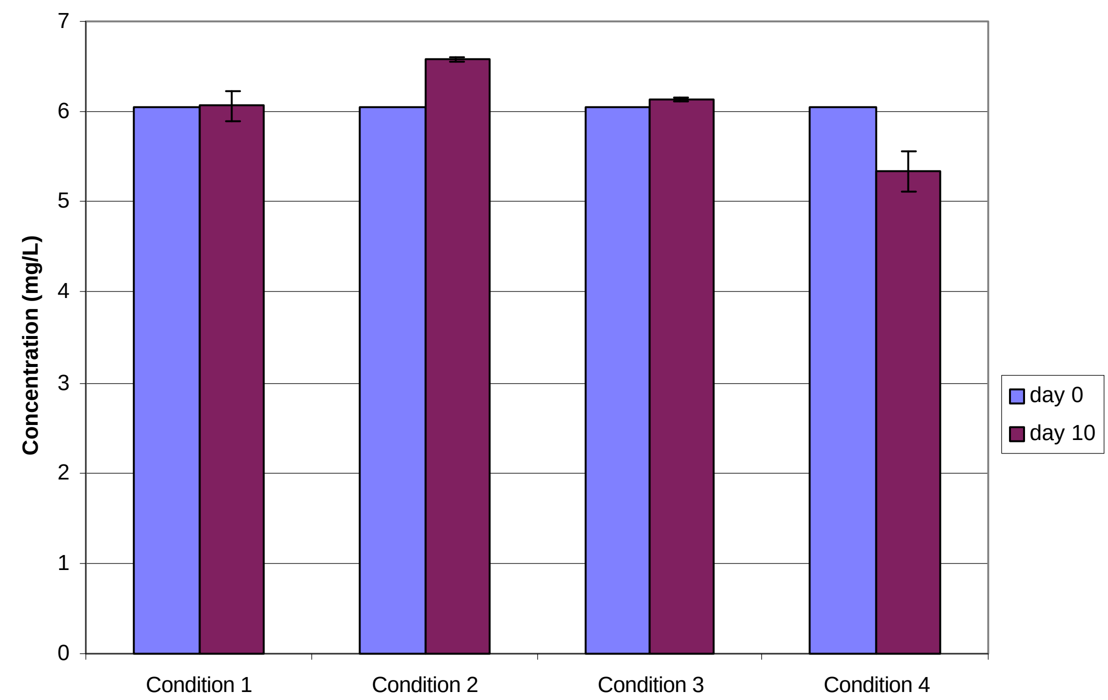


**Figure 38: Methanol Measurements for Conditions 1-4**

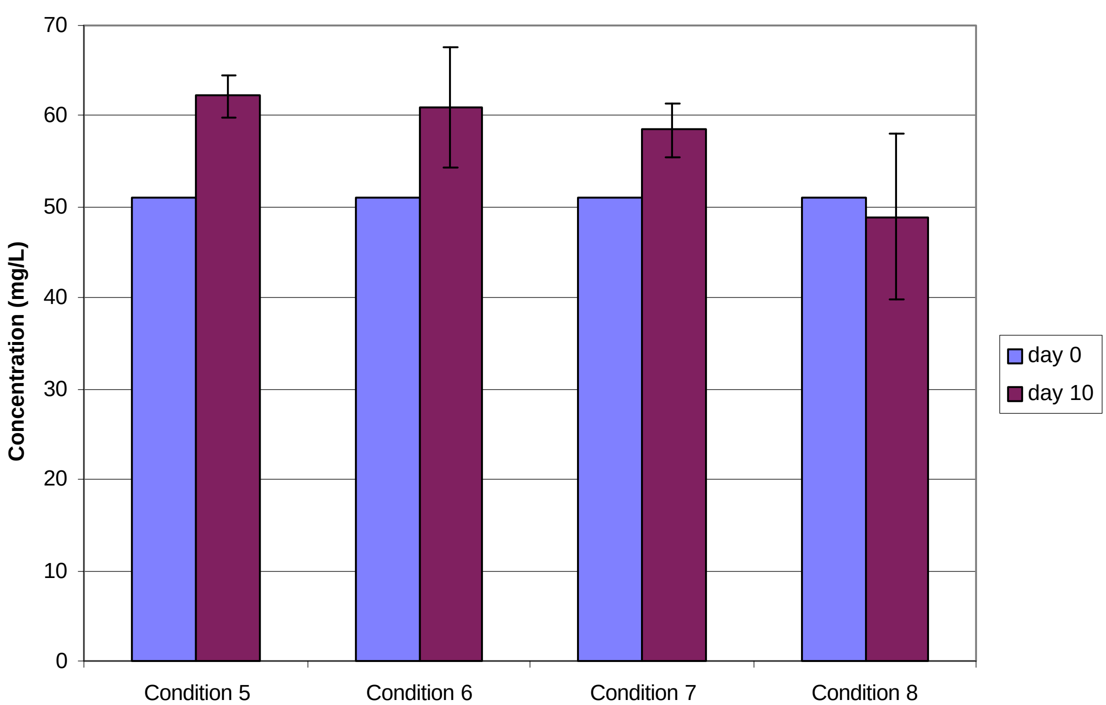


**Figure 39: Methanol Measurements for Conditions 5-8**

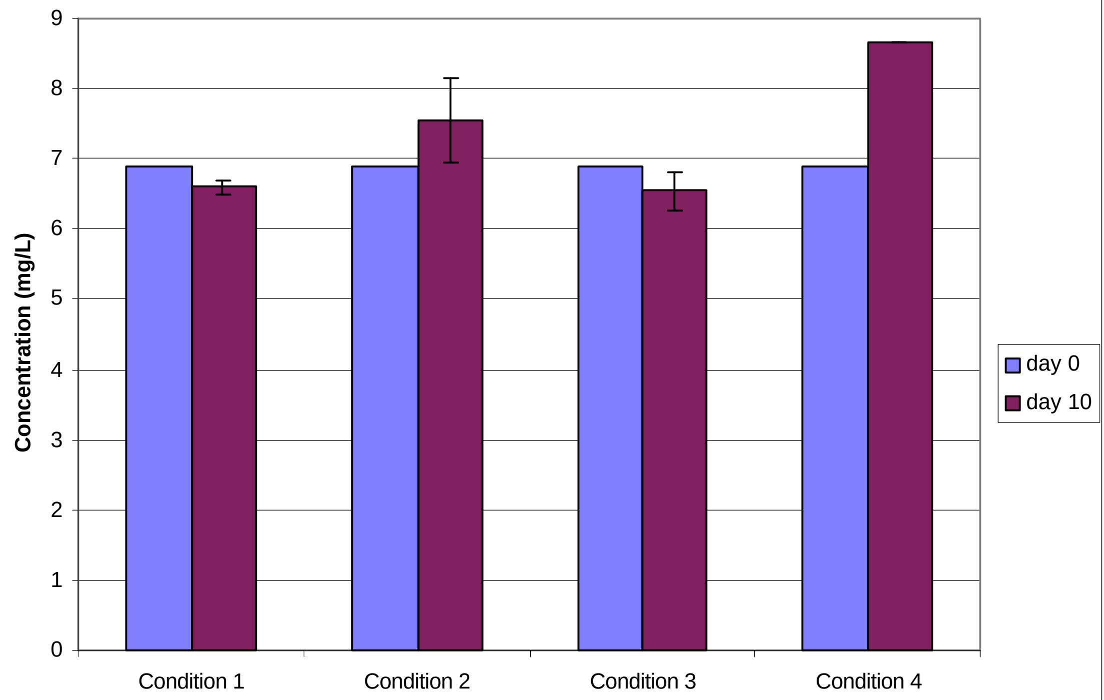


**Figure 40: Ethanol Measurements for Conditions 1-4**

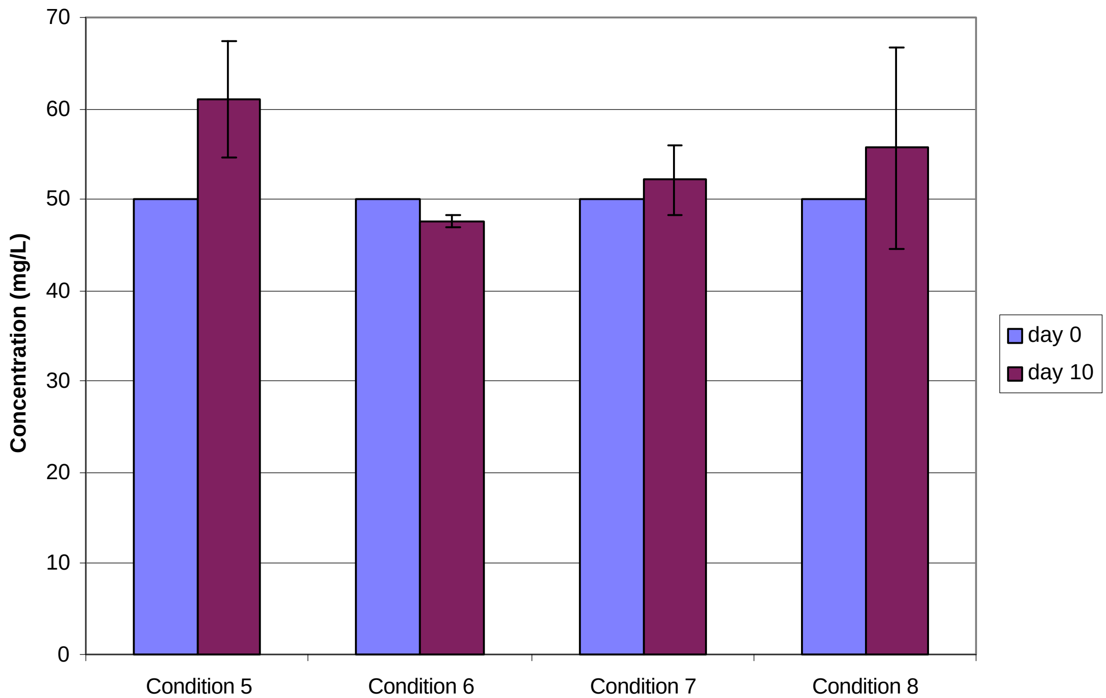


**Figure 41: Ethanol Measurements for Conditions 5-8**

ORGANOLEPTIC EVALUATION

The FPA panel primarily evaluated iodine and iodoform. Iodine was evaluated in order to compare the odor descriptors of iodine with the odor descriptors of IDBPs expected to be produced. Iodoform and iodoacetone were the only IDBPs determined to be produced. Iodoacetone could not be purchased commercially, thus, it was not evaluated by the panel. Acetone was also evaluated by the panel, but not enough data were collected to produce a Weber-Fechner plot for acetone. Acetone concentrations of 50 mg/L were assigned an average intensity of 3 with common descriptors of sweet and chemical.

The Weber-Fechner plot for iodine (Figure 42) has an $r^2$ value of 0.9124. The odor threshold concentration (the concentration at which the average intensity value is 2) for this Flavor Profile panel determined for this plot was approximately 600 µg/L. Common descriptors for iodine used by this panel included iodine, medicinal, chemical, acrid, pungent, and Brazilian hospital (Brazilian hospital was used by a panel member from Brazil).

The Weber-Fechner plot for iodoform (Figure 42) has an $r^2$ of 0.7053. The odor threshold concentration for this panel determined from this plot is approximately 1.5 µg/L. Common descriptors used by this panel to describe iodoform include iodine-like, sweet, chemical, and solvent.

Three of the panel members were able to detect concentrations of iodoform as small as 4 µg/L in the presence of 4000 µg/L of iodine, but because iodine and iodoform have such similar odors, concentrations could not be determined. In addition, descriptors that this panel used for acetone were similar to those used for iodoform: sweet, chemical, and medicinal.

Selected data for the FPA sessions are presented in Table 9. Iodine was easily detected at 4 mg/L and described as “iodine”. Iodoform at 4 µg/L was described as both “iodine-like” and “iodoform”. The mixture of iodine and iodoform was described by a mixture of descriptors. Panelist 1, 2 and 5 detected a mixture of iodine and iodoform odors, while panelist 3 and 4 detected only iodine odors. Panelist 1, 2, and 5 did not directly identify iodoform.

Table 9: Selected FPA data

| Panelist | 4 mg/L iodine (descriptor – intensity) | 4 µg/L iodoform (descriptor – intensity) | 4mg/L iodine and 4µg/L iodoform (descriptor – intensity) |
|---|---|---|---|
| 1 | Iodine – 4 | Medicinal / iodoform – 6 | Medicinal / iodine – 4<br>Sweet – 2 |
| 2 | Iodine – 6 | Iodine like – 4 | Fruity / pungent – 6 |
| 3* | Iodine – 4 | Odor free * | Iodine – 2 |
| 4 | Iodine – 2 | Iodoform – 6 | Iodine – 4 |
| 5 | (no data) | Sweet/ iodoform - 2 | Iodine / sweet – 4 |

* Panelist 3 is anosmic to iodoform

One liter samples of acetone and iodine under conditions 2, 5, and 8 were allowed to react for 35 days. 200 mL aliquots were presented to the FPA panel for evaluation, while the remaining 800 mL were liquid-liquid extract and evaluated by SIM GC/MS for IDBPs. Table 10 presents the FPA data. The IDBP evaluation of the samples found iodoform in only condition 8, although the FPA descriptors of solutions at conditions 2 and 5 suggest that iodoform was present.

Table 10: Selected FPA Data

| | Acetone / Iodine Reactions | | |
|---|---|---|---|
| Panelist | Condition 2 | Condition 5 | Condition 8 |
| 1 | Medicinal (not iodine) – 8<br>Sweet / musty – 3 | Medicinal – 6 | Iodine – 6<br>Acrid / medicinal – 8 |
| 2 | Iodine – 6<br>Sweet – 2 | Iodine – 4 | Sweet / slightly citrus – 6 |
| 3 | Iodine – 2<br>Acetic acid – 2 | Iodine – 4<br>Chlorine – 2 | Iodine – 4<br>Something – 6 |
| 4 | Sweet / iodoform – 6 | Iodine / disinfectant – 6 | Sweet / pungent – 8 |
| 5 | Iodine – 2<br>Candy sweet – 4 | Iodine – 2<br>Tangy / sweet – 4 | Iodine / chemical – 8 |
| 6 | Iodine – 6 | Iodine – 2<br>Sweet - 2 | Medicinal (not iodine) - 4 |

Footnote: Condition 2 (pH 8, 5 mg/L acetone, 10 mg/L iodine; no iodoform detected by SIM GC/MS)
Condition 5 (pH 5.5, 50 mg/L acetone, 10 mg/L iodine; no iodoform detected by SIM GC/MS)
Condition 8 (pH 8, 50 mg/L acetone, 50mg/L iodine; 4 mg/L iodoform detected by SIM GC/MS)

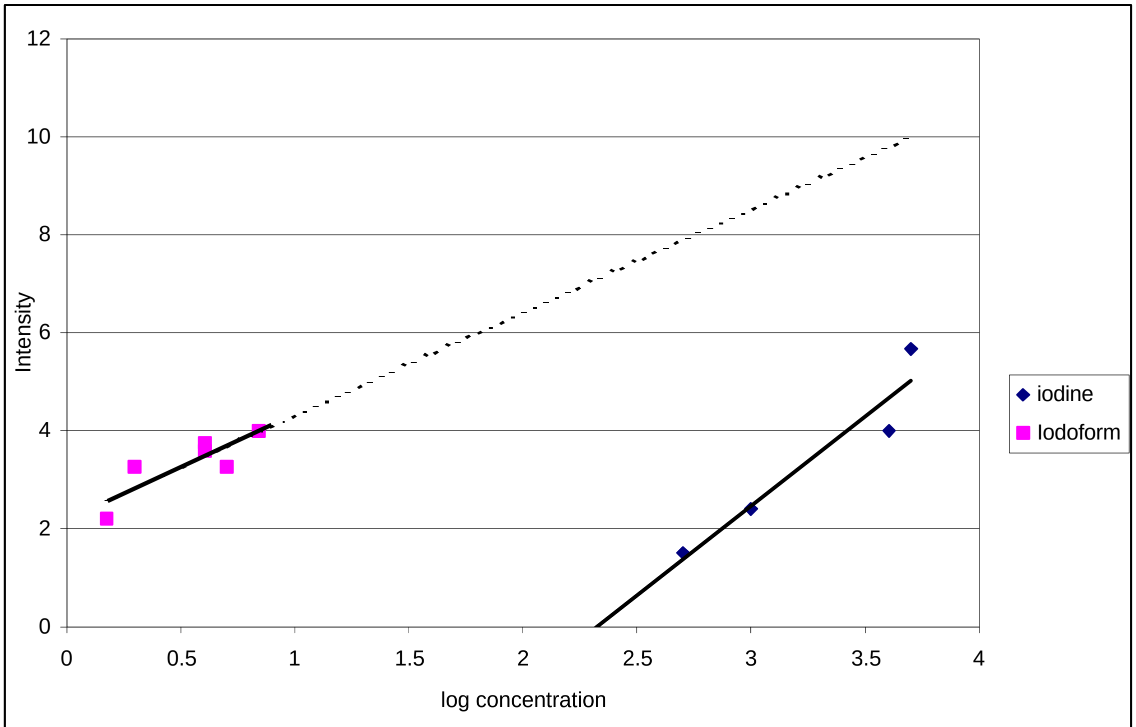


**Figure 42: Weber-Fechner plots for Iodine and Iodoform**

# CHAPTER V: DISCUSSION

## CHEMICAL ANALYSIS

Acetone was the only organic of the seven studied that was shown to produce iodinated disinfection by-products when mixed with iodine. This was expected as ketones can be readily halogenated in the $\alpha$-position by molecular iodine (March, 1977). This explains the formation of iodoform from the reaction of acetone and iodine. Aldehydes with $\alpha$-hydrogens follow the same reaction as ketones. Formaldehyde does not have an alpha-hydrogen. Halogenation of the aldehydic hydrogen was possible, but monoiodoformaldehyde was not detected. Reactions between formaldehyde and iodine were not detected and were not expected.

According to March (1977), possible reactions of primary, secondary, and tertiary alcohols with iodine may form alkyl halides, alkenes, or trihalomethanes. Because halogen acids were not promoted in these experiments, the alcohols (methanol, ethanol, 1-propanol, isopropanol, and 1-methoxy-2-propanol) would not be expected to form alkyl halides. The dehydration of alcohols by iodine to form alkenes would not have been detected by the SIM-GC/MS method used and was not of primary importance. If the alcohols were oxidized by the iodine, then iodoform would probably have been produced. Because iodoform was not detected, the oxidation of alcohol by iodine may not have occurred or the amount produced was below detection limits.

The study by Symons and Muckle (1990) identified acetone, acetaldehyde, and ethanol as organic compounds that reacted with iodine at a pH equal to or greater than seven. Their research measured total organic iodide (TOI); it did not specifically measure iodinated disinfection by-products. The results from Symons and Muckle (1990) are similar to the results found in this paper in that acetone was found to react with iodine to form IDBPs. The results of this research indicated that although acetone produced more iodoform at a higher pH, iodoform was also produced at a pH less than seven. Acetaldehyde was not studied in this research, but formaldehyde was not found to react with iodine. Acetaldehyde would be expected to be more reactive than formaldehyde due to the presence of alpha-hydrogens. Ethanol was not found to form iodoacetic acid or any of the iodoalkanes that were monitored in this study. Disinfection by-products may have formed below the detection limit or the reaction in the Symons and Muckle (1990) study may be a reaction that did not form an IDBP, such as the dehydration of ethanol to form an alkene.

Reaction conditions 2, 5, and 8 which produced iodoform from acetone did not have a common factor. Condition 2 was pH 8 with 10 mg/L iodine and 5 mg/L acetone; condition 5 was pH 5.5 with 10 mg/L iodine and 50 mg/L acetone; and condition was pH 8 with 50 mg/L iodine and 50 mg/L acetone. Conditions 8 and 2 consistently produced more iodoform than condition 5, which follows the expectation that more iodoform would be produced by the haloform reaction at a basic pH. Condition 8 produced more iodoform than condition 2, possibly due to the fact that the iodine concentration in condition 2 was below 3 mg/L by the twelfth day. Although condition 8 produced an average of 5.36 mg/L of iodoform, neither the acetone or the iodine concentration could be measured to have significantly decreased.

Clearly, the interactions of iodine and acetone to produce iodinated disinfection by-products are reaction condition dependent. When pure iodine and acetone were mixed in the presence of a small amount of water, iodoacetone was a major product and iodoform could not be detected. In dilute aqueous solution containing mg/L quantities of iodine and acetone, μg/L to mg/L quantities of iodoform were produced and accumulated over time; μg/L amounts of iodoacetone sometimes formed as an intermediate, but this intermediate disappeared over time. The latter situation is more amenable to the conditions expected for potable water on the Space Station. Thus, small amounts of iodoacetone could be present in potable water soon after iodine is added, but after several days the iodoacetone is likely not to be present and larger amounts of iodoform should occur. Iodoacetic acid was not detected under any reaction condition.

Iodinated disinfection by-products were not detected in any other set of experiments, but decreases in organic concentration and iodine concentration were noted. The increase in the concentration of formaldehyde in condition 4 may be attributed to the loss of internal standard, but no other condition had such a clear explanation. Table 11 presents conditions that had significant changes in organic concentration or iodine concentrations below 3 mg/L.

Table 11: Experimental conditions with significant changes in organic compound and iodine concentrations.

| | **Experimental Condition** | | |
|---|---|---|---|
| Organic Compound | Decreased Organic Compound Concentration | Increased Organic Compound Concentration | Measured $I_2$ Concentration below 3 mg/L |
| Acetone | none | none | 2 |
| Isopropyl Alcohol | 2, 3, 6 | none | 1, 2 |
| Formaldehyde | 1 | none | 2, 6 |
| 1-Propanol | 2 | 6 | 6 |
| 1-Methoxy-2-Propanol | 7 | 1 | none |

Acetone, isopropyl alcohol, and formaldehyde each had the iodine concentration decrease below 3 mg/L in condition 2. The same was true for condition 6 in formaldehyde and 1-propanol. All condition 2 (pH 8, initially iodine 10 mg/L, organic 5 mg/L) and 6 (pH 8, initially iodine 10 mg/L, organic 50 mg/L) experiments tended to start with low concentrations of $I_2$ even if the total iodine/iodide concentration was approximately 10 mg/L. This was expected as basic pH values cause the conversion of iodine to iodide. The reason for the significant decreases in organic concentrations under some conditions is not clear. Experimental errors may possibly be a factor, but the fact that conditions 1, 2, and 6 appear multiple times in Table 11 may warrant closer inspection.

## ORGANOLEPTIC EVALUATION

The $r^2$ values for the Weber-Fechner plot of iodine and iodoform showed a good correlation between the intensities assigned by the panel and the concentrations in the samples. The descriptors used by this panel for both iodine and iodoform were in agreement with descriptors commonly used by other panels for these substances (Bruchet *et al*., 1989; Mallevialle and Suffet, 1987). The odor threshold concentration for iodoform, 1.5 μg/L, was also similar to that found in the literature (Bruchet *et al*., 1989).

Even with the good correlation of both plots and the low odor threshold concentrations, complications occur when flavor profile analysis is applied to the monitoring of iodinated by-products. Iodoform, one of NASA's most commonly found iodinated disinfection by-products, should be accurately monitored on the Space Station. As shown in the results, the descriptors used for iodoform are similar to the descriptors used for both iodine and acetone, precursors of iodoform. Therefore, as was seen with this panel, iodoform in the presence of iodine and/or acetone was difficult to evaluate by flavor profile analysis at the concentrations applied in this research.

# CHAPTER VI: CONCLUSIONS

Of the seven organic compounds studied; acetone, formaldehyde, 1-propanol, isopropanol, 1-methoxy-2-propanol, methanol, and ethanol; acetone was the only compound to definitively produce measurable amounts of iodinated disinfection by-products within the up to 2 month reaction times applied in this research. Acetone reacted with iodine to produce both iodoacetone and iodoform. Based on the principles of organic chemical reactions, acetone and other aldehydes and ketones possessing $\alpha$-hydrogens were predicted to participate in halogenation reactions. The base-catalyzed haloform reaction was predicted to result in iodoform formation from acetone. Alcohols, ethers, and formaldehyde were not expected to substantially participate in halogenation reactions.

Iodoform was produced from reactions of acetone and iodine at both pH 5.5 and 8, with more iodoform produced at pH 8. Iodoform is a trihalomethane; as a class, THMs are regulated in drinking water under the USEPA's Safe Drinking Water Act. Iodoform, at μg/L concentrations, was detectable after 2 days of reaction time. The concentration increased until 8.64 mg/L iodoform was measured after 35 days of reaction under the following initial conditions: pH 8, 50 mg/L of acetone, and 50 mg/L iodine. Iodoacetone, an intermediate in the production of iodoform, also formed and was detected after a reaction time of a few days but not detectable after several weeks. Iodoacetone is a haloketone; under the 1996 Information Collection Rule, the USEPA requires water utilities to monitor for this class of halogenated disinfection by-products. Although NASA expects potable spacecraft water to be about pH 5 and contain μg/L concentrations of precursor organic compounds and 1-4 mg/L iodine, the possible formation of iodinated disinfection by-products is still a concern.

Flavor profile analysis was applied to monitor iodine and iodinated disinfection by-products in simulated spacecraft water. The odor threshold concentration for iodine was about 600 μg/L and the iodine odor was described as “medicinal, chemical, iodine, acrid”. The odor threshold concentration for iodoform was about 1.5 μg/L and its odor was described as “medicinal, chemical, iodine-like, sweet”. This research indicated that although μg/L concentrations of iodoform could be detected by FPA, mixtures of mg/L concentrations of iodine with μg/L concentrations of iodoform were too complicated to reliably differentiate the iodine and iodoform odors. At higher μg/L iodoform concentrations in the presence of low mg/L iodine, the odor of iodoform may be strong enough to be differentiated from iodine. This situation was not tested due to a desire to avoid placing the FPA panel at risk.

# CHAPTER VII: RECOMMENDATION

At present, NASA's potable water quality program monitors for an extensive list of organic compounds in spacecraft water. With respect to formation of IDBPs, this program should continue to monitor for acetone and iodoform and also should consider monitoring for iodoacetone. The measurement of iodoacetone will be hampered by the lack of a commercially available pure standard.

NASA should stay informed on changes in USEPA drinking water regulation for halogenated disinfection by-products, particularly those portions of the Safe Drinking Water Act pertaining to trihalomethanes and haloketones.

A reasonable approach to minimizing halogenated organic disinfection by-products is to minimize the conditions that result in their formation. These reaction conditions include: concentration of precursor organic compound, concentration of disinfectant, reaction time, temperature, and pH. NASA should continue its efforts to purify water by removing the precursor organic compounds prior to the addition of iodine. In the treatment scheme, the preferred point for iodine addition should be after the concentrations of precursor organic compounds have been minimized.

Further investigation of the production of iodinated disinfection by-products from organic compounds other than those studied this research should be considered. The health effect of the known iodinated disinfection by-products should continue to be assessed.

NASA may want to train astronauts to evaluate iodine and iodinated organic compound odors as a supplemental means to assess water quality aboard spacecraft. FPA is readily applicable to monitoring mg/L concentrations of iodine in water and could complement spectrophotometric methods that are in current use. Although low µg/L concentrations of iodinated disinfection by-products (e.g., 1.5 μg/L iodoform and 5 μg/L 2-iodophenol) are detectable by FPA, detection and identification of these low ug/L concentrations is hampered in the presence of mg/L quantities of iodine. Nonetheless, organoleptic detection could possibly be used to detect higher concentrations of iodinated disinfection by-products even in the presence of mg/L concentrations of iodine. An instrument, the AROMA SCAN®, has been developed to simulate the human sense of smell. This instrument could be evaluated for its ability to monitor for the presence of selected organic compounds with distinct odors such as iodoform.

## CHAPTER VIII: REFERENCES

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