

**CHEMICAL IDENTIFICATION AND FLAVOR PROFILE ANALYSIS OF  
IODINATED PHENOLS PRODUCED FROM DISINFECTION  
OF SPACECRAFT DRINKING WATER**

By

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## **ABSTRACT**

The National Aeronautics and Space Administration (NASA) is considering the use of iodine for disinfection of recycled wastewater and potable water in the International Space Station. Like chlorine and other halogen compounds, iodine can form disinfection by-products (DBPs) in the presence of organic compounds. Recycled wastewater sources proposed for reuse in the space station include laundry, urine, and humidity condensate. These contain large concentrations of iodine-demanding compounds, including phenol (Barkely *et al.*, 1992). Therefore, the potential formation for iodine disinfection by-products (IDBPs) is of concern.

Based on the characteristics of the International Space Station recycled wastewater sources and potable water treatment system, a series of experiments was designed to evaluate the formation of IDBPs under different experimental conditions. Studies were conducted by reacting various concentrations of iodine with phenol at pH 5.5 and 8.0. Iodine residuals for NASA potable water standards are targeted to be in 1-4 mg/L range; increased amounts of iodine (greater than four mg/L) may be used if breakdown in water purification system occurs. Iodine concentrations of 10 and 50 mg/L and phenol concentrations of 5 and 50 mg/L were used. These concentrations were chosen to ensure detection of organic by-products without need for experimental manipulations such as extraction. Also, iodine may be added early in the recycle water treatment process prior to the removal of organic compounds by cation and anion

exchange or granular activated carbon sorption. Reactions were monitored for up to 32 days for formation of IDBPs. All reactions were maintained at 20<sup>0</sup> C in dark. High Performance Liquid Chromatography (HPLC) and Gas Chromatography/Mass Spectrometry (GC/MS) were used for identification and quantitative analysis of phenolic compounds. Spectrophotometry was used to monitor the iodine concentrations. Flavor Profile Analysis (FPA) method was used to evaluate the odor characteristics of the phenolic compounds.

Reactions of iodine with phenol resulted in the formation of the following by-products: 2-iodophenol, 4-iodophenol, diiodophenols, and 2,4,6-triiodophenol. Most reaction conditions studied resulted in the formation of all or some of the specified iodophenols. The initial mass ratio of iodine to phenol was the major determining factor in the concentrations and types of by-products formed. The IDBPs were formed within one hour after initiation of the reactions. Extended reaction times did not lead to significant increases in concentrations of IDBPs. Under most reaction conditions, mono-substituted phenols were detected at significantly higher concentrations than di-substituted phenolic compound; triiodophenol was the major by-product when the I<sub>2</sub>:phenol mass ratio was 10:1. The greatest numbers of IDBPs were formed when reaction solutions consisted of a 1:1 ratio of iodine to phenol. FPA panel indicated the odor threshold concentrations for phenol, 2-iodophenol, and 4-iodophenol were 5 mg/L, less than 1 µg/L, and 0.5 mg/L respectively. The most common odor descriptions for all these compounds were “chemical”, “phenolic”, and “medicinal”.

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## CHAPTER 1. INTRODUCTION

### BACKGROUND

Historically, the use of iodine in public drinking water supplies has been limited to emergency treatment and disinfection. While chlorine is the most widely used disinfectant for water supplies on earth, the National Aeronautics and Space Administrations (NASA) is considering the use of iodine as a water disinfectant. The International Space Station potable water will be produced from recycled wastewater. Iodine will be used for disinfection of wastewater and potable water sources.

In order to remain in space for extended orbit missions, NASA has been developing methods for water reclamation and recovery. Water will be needed for human consumption, personal hygiene, food and beverage reconstitution. Since the 1960's, NASA has generated water from H<sub>2</sub> and O<sub>2</sub> fuel cells during short-term space missions. Iodine has been used for disinfection of the water generated in the fuel cells (Sauer *et al.*, 1991). The use of iodine as a disinfectant in combination with the water reclamation and wastewater reuse system has led to concerns about potential health effects associated with the formation of iodine disinfection by-products (IDBPs). In the space water recycle system large amounts of iodine must be added to maintain an approximately 4 mg/L residual of oxidized iodine to kill bacteria and viruses (Dodd, 1997, Sauer *et al.*, 1991). As such, reactions yielding potentially harmful IDBPs could occur.

Previous research performed by NASA scientists revealed the presence of phenolic compounds in the Space Station cabin humidity condensate, a source considered for the production of potable water. Phenol was among the compounds found in the raw humidity condensate in concentrations ranging from 35 to 146 µg/L (Sauer *et al.*, 1993). The presence of even trace amounts of phenolic compounds in the raw humidity condensate presents a problem since phenol can react with iodine (Barkley *et al.*, 1992,

Sauer *et al.*, 1993, Symon & Muckle, 1990). Other organic compounds present in recycled water include: alcohols, organic acids, formaldehyde, and acetone (Straub II *et al.*, 1995). The reactivities of these compounds with iodine to form IDBPs have also been studied. Dodd (1997) evaluated iodination by-products in separate reactions of iodine with methanol, ethanol, 1-propanol, 2-propanol, 1-methoxy-2-propanol, acetone, and formaldehyde. Acetone was the only compound identified as an IDBP precursor.

Although NASA scientists have conducted a variety of studies designed to characterize the recycled water and identify associated disinfection by-products, studies on the IDBP compounds identification and health effects are limited. Furthermore, design and development of water quality monitoring procedures and instrumentation for use in the Space Station are issues of concern for NASA.

## **OBJECTIVES**

The objectives of this research were to:

1. Identify the iodine DBPs associated with iodination of phenol.
2. Evaluate the formation of iodine-phenol DBPs under various experimental conditions relevant to the NASA Space Station water treatment system.
3. Evaluate the potential use of Flavor Profile Analysis (FPA) for monitoring space station drinking water quality with respect to iodine DBPs.
4. Identify the conditions under which the formation of IDBPs associated with phenol can be minimized.

## CHAPTER 2. LITERATURE REVIEW

### IODINE CHEMISTRY AND DISINFECTION PROPERTIES

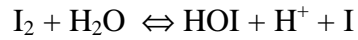
Iodine, a nonmetallic element with an atomic weight of 126.92 amu is the heaviest of the halogen group. It is the only halogen that is solid at room temperature, and it can sublime (change spontaneously into the vapor state without first passing through a liquid phase). Various forms of iodine are used as catalysts in the chemical industry, antiseptic agents, medicinal (treatment of goiter), and industrial and household disinfectants (White, 1992).

The iodine use in drinking water treatment has been recognized for a long time. However, due to its high cost, limited availability, and physical and chemical characteristics, the iodine use as a drinking water disinfectant has not generated sufficient interest to replace chlorine. Iodine use has been limited to emergency water treatment under circumstances where chlorinating or more complex water treatment is not practical. The first known use of iodine in water treatment was during World War I, where iodine was used as an alternative water disinfectant for the United States troops (White 1992, Chang, 1966).

The following components are considered in the reaction of elemental iodine with water (Chang, 1958, White, 1992).

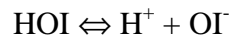
Elemental Iodine	$I_2$
Hypoiodous acid	HOI
tri-iodide ion	$I_3^-$
Iodate ion	$IO_3^-$

Reactions include hydrolysis of  $I_2$  to form hypoiodous acid and dissociation of hypoiodous acid at various pH levels to form hypoiodite ion:



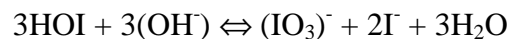
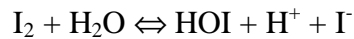
$$K_h = \frac{[\text{HOI}][\text{H}^+][\text{I}^-]}{[\text{I}_2]} = 3 \times 10^{-13} \text{ at } 25^\circ \text{C}$$

Hypoiodous acid dissociation with variation in pH results in the formation of hypoiodite ion:



$$\frac{[\text{H}^+][\text{OI}^-]}{[\text{HOI}]} = K_a = 4.5 \times 10^{-13}$$

Both elemental iodine and hypoiodous ion exhibit effective germicidal properties. The formation of hypoiodite ion ( $\text{OI}^-$ ) is insignificant at drinking water pH values. Other ions potentially formed in insignificant amounts include tri-iodine ion ( $\text{I}_3^-$ ) and iodate ion ( $\text{IO}_3^-$ ). These ions have shown ineffective germicidal properties (Black *et al.*, 1968). The formation of iodate ion in the presence of elemental iodine proceeds as follows:



Based on the reaction kinetics, the formation of iodate ion is not likely to interfere with the disinfecting efficiency of iodine until the pH levels rise above 8.0. Among the aqueous iodine species, the elemental iodine  $\text{I}_2$  and hypoiodous acid  $\text{HOI}$  are the most powerful disinfecting agents. The disinfecting abilities of  $\text{I}_2$  and  $\text{HOI}$  are variable in response to different organisms. For example,  $\text{I}_2$  has been reported to be more effective

in destruction of *E. histolytica* cyst than HOI (Chang, 1966), while, HOI is a more powerful than  $I_2$  in destroying viruses (Clark *et al.*, 1962, Sobsey *et al.*, 1991).

The knowledge on the chemistry associated with iodine disinfection of water is limited. However, it has been reported that iodine treatment of some surface waters has resulted in formation of high concentrations of iodomethanes (Luther *et al.*, 1991). Trihalomethane formation in disinfected surface waters has been reported to be 70% less with iodine than chlorine. There has also been evidence that iodine reaction with phenol may lead to the formation of iodobenzoquinones and benzoquinones (Thorstenson *et al.*, 1987, Rav-Acha, C.H., 1984).

## **HALOGENATION OF PHENOLIC COMPOUNDS**

It is well known that chlorine disinfection of water supplies containing organic compounds produces chlorine-containing by-products, however less is known about the chemistry associated with iodine disinfection of water. Generally, reaction of iodine in organic containing water is similar to chlorine reactions. However, among the four halogens fluorine, chlorine, bromine, and iodine, iodine is the least reactive element (Black *et al.*, 1965, Kinman *et al.*, 1970). Like chlorine and bromine, iodine forms iodoform in the presence of alkanes (Koski *et al.*, 1966). Both chlorine and iodine react in similar ways with phenol to make phenolic disinfection by-products which are odorous in nature (Lee, 1967).

The kinetics of reactions between chlorine and phenolic compounds has been described by Lee (1967). The results of this study showed that chlorination of phenol proceeds by initial substitution of chlorine on 2 and 4 positions of the aromatic ring. Phenol chlorination reaction proceeds with further substitutions on the aromatic ring resulting in the formation diiodophenols, triiodophenols and leading to the formation of non-phenolic oxidation products. This reaction has been described as a second-order rate

kinetic expression where reaction rate is proportional to the product of concentrations of aqueous chlorine and phenolic compound. Phenol chlorination reaction was shown to be highly pH dependent and the maximum reaction rate is expected to occur at neutral or slightly basic pH level.

According to a study conducted to evaluate the formation of IDBPs in a recycle wastewater system (Barkley *et al.*, 1992) iodine was shown to react with phenol to form DBPs similar to that of chlorination reactions, however, the chlorination reaction resulted in the formation of more by-products. While iodination of phenol resulted in the formation of four by-products, phenol chlorination reactions led to the formation of nine by-products. This is expected, as iodine is less reactive than chlorine.

## **DRINKING WATER REGULATIONS**

The Safe Drinking Water Act amendments direct the United States Environmental Protection Agency (USEPA) to establish Maximum Contaminated Level Goals (MCLG) for 83 specific contaminants and to develop a list of contaminants every three years to be considered for regulation. The Maximum Contaminant Levels (MCL) for each regulated compound are set as close to MCLGs as possible to prevent potential health hazards. Currently, the USEPA regulates disinfectants and disinfection by-products in drinking water (“Environmental Pollution control Alternatives: Drinking Water Treatment for small communities”, EPA/625/5-90/025.). The current MCL for total trihalomethanes in drinking water supplies is at 0.1 mg/L. These include chloroform, bromoform as well as other halogenated, volatile organic compounds. A secondary MCL has been established by the USEPA. A threshold odor number (TON) of three is the current MCL for odor in drinking water supplies (CFR 40, 1997).



NASA has established drinking water standards specific for the International Space Station water purification system. Generally, the MCL standards are similar to those established by the USEPA for drinking water supplies on earth (Table 1, Dodd, 1997, Sauer *et al.*, 1991). However, due to the different treatment conditions experienced under microgravity, the potable water standards for International Space Station water may be adjusted accordingly.

Table 1. Specific EPA and Space Station Water Quality Standards

Water 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

## **SPACECRAFT WATER RECLAMATION SYSTEM**

Before astronauts can remain in space for extended orbit missions, a water reclamation and recycle system must be developed for the US space program. During current and previous space flights, NASA has been generating water for personal hygiene, food, and beverage preparation through fuel cell operations. An estimated 42,000 kg of water would be required for a 90-day orbit mission. This amount is above the shuttle's payload ascent capacity, as such, the development of a water reclamation and recycle system is needed (Symons and Muckle, 1990).

The characteristics of the recycled water for NASA in the proposed water reclamation system are presented in the following sections. In addition, potentials for the formation of IDBPs associated with the disinfection of the recycled water are discussed.

### **Characterization of Spacecraft Recycled Wastewater**

On the International Space Station, water will be available for treatment from several sources. These include urine, shower water, wash water, and humidity condensate from the cabin (National Academy Press, Washington D.C. 1992). According to a study by Traweck *et al.*, (1991) a proposed water reclamation and recovery system for the Space Station consists of two systems, one for drinking water and one for hygiene water. The drinking water will be produced from the cabin humidity condensate, which originate from respiration, perspiration, and equipment emissions sources. The potable-water loop will remove contaminants from the condensate. The hygiene loop reclaims water for non-potable use. This treatment system consists of an ultrafiltration/reverse osmosis unit and a series of multifiltration beds. The urine water reclamation will be achieved by initial treatment with oxone and sulfuric acid, followed by distillation and multifiltration to further remove contaminants. The product water will

be disinfected by a microbial check valve (MCV) unit consisting of iodine-containing resins. Iodine is being considered as a disinfectant for both potable and recycled wastewater sources.

Many data have been generated on the characterization of the potable and recycled wastewater sources for the International Space Station (Straub II *et al.*, 1995, Traweek *et al.*, 1991). The major chemical constituents of the humidity condensate (principal source for potable water production) have been reported to consist of the following classes of compounds: alcohols, amides, amines, carboxylic acids, ethers, esters, ketones, phenols, and thiourea. The efficiency of the Space Shuttle water purification and treatment system has been evaluated to determine its effectiveness in removal of the organic compounds and other inorganic components.

A study performed by Sauer *et al.*, (1995) showed that the shuttle multifiltration unit (Shuttle Condensate Adsorptive Device) effectively reduced the concentration of organic carbon by 72 percent, and organic acids and total semivolatile organics were reduced by 88 percent. The concentrations of anions, cations, and metals were reduced to part-per-billion levels. However, small molecular weight organics, including one to three carbon alcohols, formaldehyde and propylene glycol were reduced less effectively. Methanol levels were not reduced very effectively.

### **Toxicological Aspects of Iodine Disinfection Products**

Because of the potentials for breakthrough and ineffective removal of the organics in the space water purification and reuse system, the formation of disinfection by-products is of concern. Identification of iodinated DBPs is important because of unknown toxicological properties. The toxicological data associated with the use of iodine as a water disinfectant is very limited. The effects of prolonged use of iodinated water supplies were studied by Black *et al.*, (1965) who showed that iodine doses up to

1.0 ppm did not produce any objectionable color, taste, or odor in the water. There was also no evidence of adverse health effects on the studied population. Iodine (I<sub>2</sub>) is the chemical form that is used to disinfect drinking water. Because of its extreme corrosivity, I<sub>2</sub> has acute toxicological effects that are not characteristics of other forms of iodine (i.e. iodide and iodate). A known chronic effect of I<sub>2</sub> is a change in thyroid gland function, which is related to the total iodine intake (Bull, 1987, Freund, *et al.*, 1966, Thomas *et al.*, 1969). Thomas *et al.*, (1969) showed that thyroid function in human subjects was depressed by consumption of water containing 1 mg/L of I<sub>2</sub>.

Toxicological properties of iodinated organic disinfection by-products have not been studied: however, widely-studied chlorination organic products have been shown to produce carcinogenic products, including trihalomethanes, chlorinated acids, halogenated acids and ketones (Jolley *et al.*, 1985, Bull, 1986). Iodine DBPs are thought to be absorbed through gastrointestinal tract, and many can be absorbed through skin and mucous membranes and enter the blood stream or cells (Bull, 1987, Thorstenson *et al.*, 1987, National Academy Press, 1980).

### **Iodine Disinfection By-Products of Selected Organic Compounds**

Chlorine disinfection of waters containing organic compounds leads to the formation of well known potentially hazardous by-products that are regulated by the U.S. Environmental Protection Agency (USEPA) (Recknow and Singer, 1990). Only limited information is available on the iodination disinfection by-products in water treatment application on earth, however, iodine involvement in the formation of iodoform in natural waters has been reported (Luther *et al.*, 1991).

Several studies have been conducted by NASA and other researchers to evaluate the formation of IDBPs associated with the use of I<sub>2</sub> in the production of potable water

for space missions (Barkley *et al.*, 1993, Dodd, 1997). Barkley *et al.*, (1993) studied reactions of iodine with several organic compounds found in the space shuttle humidity condensate. This study showed that the reactions of I<sub>2</sub> with aqueous solutions of acetic acid and dextran produced iodinated alkyl compounds, including iodoform, diiodomethane, and iodoethane. Iodine reactions with phenol were similar to chlorination reactions. Reactions of phenol with iodine resulted in the formation of mono- and diiodophenols as reported by this study.

Dodd (1997) studied the reactions of iodine with several organic compounds found in the wastewater sources considered for recycling and reclamation by NASA. The results of this study showed that among the organic compounds studied (methanol, ethanol, 1-propanol, 2-propanol, 2-methoxy-2propanol, acetone, formaldehyde), acetone was the only one that produced quantifiable levels of by-products. The DBPs associated with iodination of acetone were iodoform and iodoacetone.

The influence of I<sub>2</sub> on the treatment of spacecraft humidity condensate for drinking water production was studied by Symons and Muckle (1990). They showed that several compounds in the shuttle humidity condensate reacted with iodine to form total organic iodine compounds (TOI) in concentrations ranging from 3.0 to 3.5 mg/L of TOI. Phenol, ethanol, acetaldehyde and sodium formate, were among the organic compounds that were reactive with I<sub>2</sub>. The investigators also found that the space shuttle humidity condensate contained small, highly soluble organic compounds, such as alcohols and organic acids, that passed through the water purification system.

## **FLAVOR PROFILE ANALYSIS**

The importance of the organoleptic properties (particularly taste and odor) of drinking water supplies is recognized by consumers worldwide. The taste-and-odor characteristics of potable water affect the palatability as well as the quality of potable

water. For this reason, the U.S. EPA has established an odor standard for drinking water supplies. This corresponds to a threshold odor number (TON) of three as the secondary maximum contaminated level (MCL) (Water Works Regulations, 1995). The TON is approximately equal to the number of times a sample can be diluted with odor-free water and still result in barely detectable odor (Suffet, 1995).

Numerous studies have been conducted to characterize various taste and odors typically formed in water supplies (Dietrich *et al.*, 1995, Brady *et al.*, 1988, Suffet *et al.*, 1995). These studies have led to the development of the drinking water taste-and-odor wheel. The wheel describes the major taste-and-odor categories and associated chemicals, (if known), for each taste and odor category (AWWA Research Foundation, Suffet *et al.*, 1995). The Flavor Profile Analysis (FPA) is a sensory method, which utilizes the taste-and-odor wheel to characterize and quantify taste-and-odor properties in a water sample (Suffet *et al.*, 1986; Standard Methods, 1994). The FPA method involves a group of trained panelists who provide taste-and-odor descriptions of a water sample and specify odor-intensity levels. The odor intensity ranges from minimum of 1 to a maximum level of 12, and the reported intensity level is the average of values assigned by individual FPA panel members. Typically, an average intensity value is computed when at least 50% of the panelists agree on similar odor descriptors. The Weber-Fechner Plot model can be used to determine an odor threshold level. The odor threshold concentration (OTC) corresponds to the compound concentration that results in an average intensity level of 2 when the average intensity data are plotted against the log concentrations of the compound in the water sample (Suffet *et al.*, 1991, Krasner, 1988).

The organoleptic properties of iodine have been described as follows: at disinfection concentrations (0.1-ppm residual) it imparts a crystalline yellow hue, is described as less odorous than chlorine, and has a slight metallic odor. The taste threshold of iodine in water is approximately 0.2 mg/L (Sauer *et al.*, 1987, Black *et al.*, 1970, Chang SL, 1958). Iodine and IDBPs impart distinct medicinal odors (Bruchet *et al.*, 1989, Dodd, 1997). Likewise, phenol chlorination by-products have medicinal odors

(Burttschell *et al.*, 1959, Lee 1967). The OTC level for iodoform, boromoform, and chloroform have been reported at 0.3 µg/L, 5.0 µg/L and 100 µg/L, respectively (Bruchet *et al.*, 1989).

## **CHAPTER 3. METHODS AND MATERIALS**

In this section, specific experimental procedures and methods used in identifications and quantification of the iodine and phenolic reaction components are presented. The preparations of phenolic compounds for FPA and odor characterization are discussed along with methods of data analysis.

### **GLASSWARE**

Prior to use in testing, all glassware was washed with standard dishwashing detergent, rinsed several times with tap water, rinsed with chromic acid, and rinsed at least five times with distilled-deionized water. All glassware used for FPA was dried at 110 °C oven prior to use.

### **REAGENTS**

Distilled, deionized water was used for the preparation of all reagents and carrying out the experimental reactions were conducted using laboratory distilled-deionized water. This water was produced by a Milli-Q (Millipore Corporation, Nerwalk, CT) reagent-water deionization system, which consists of anion, cation, and granular activated carbon (GAC) columns to purify water. The characteristics of this reagent water are similar to the finished water expected to be produced by NASA's water purification system prior to final iodination.

The chemicals and reagents used in various parts of this study included those listed below. Phenol (CAS# 108-95-2), 2-iodophenol (CAS# 533-58-4), 4-iodophenol (CAS# 540-38-5), were purchased from Aldrich Chemical Company. Iodine was



purchased from Fisher Scientific. The leuco crystal violet compound, 4,4,4-methylidynetris (N, N-dimethylaniline), and potassium peroxymonosulfate ( $\text{KHSO}_5$ ) were purchased from Eastman.

## **EXPERIMENTAL DESIGN**

Aboard the International Space Station humidity condensate will be a source of potable water. It will be collected from the atmosphere and treated along with water from hygiene uses and urine. The water treatment purification system will consist of a series of anion and cation exchange resins, and activated carbon beds. Low-molecular-weight polar organics will be oxidized by a catalytic oxidation unit. The disinfection process will be controlled by the Microbial Check Value (MCV), which consists of a column of iodinated anion exchange resin. The MCV releases  $\text{I}_2$  which will disinfect the water both in the MCV and in the distribution system. The MCV provides antimicrobial contact and an iodine residual of 1 to 4 mg/L for destruction of microbial contaminants (Sauer *et al.*, 1992). However, at times amounts of  $\text{I}_2$  greater than 4 mg/L may be necessary when iodinated water supplies are stored for extended periods or when potential breakdowns in the water purification system occur during space flights (Dodd, 1997), so the iodine concentrations used for this study were 10 mg/L and 50 mg/L of iodine ( $\text{I}_2$ ) as the low and high concentrations of disinfectant.

Phenol is among the organic compounds found in the spacecraft humidity condensate (Sauer *et al.*, 1993) and was chosen for this study because it reacts with iodine (Barkley, *et al.*, 1993). The presence of even trace amounts of phenol in the humidity condensate is a concern because it may form phenolic IDBPs when iodinated and pose potential health risks.

Experiments were conducted with high (50 mg/L) and low (10 mg/L) concentrations of phenol reacted with iodine to determine how various experimental

conditions and phenol concentration affected the reactions. The phenol concentrations were set at high level to ensure detection of organic compounds without need for experimental manipulations (such as extractions) and potential loss of volatile by-products.

Since iodination reactions were found to be pH dependent (Symons and Muckle, 1990), experiments were conducted under both acidic (pH 5.5) and basic (pH 8) conditions. The target pH level for the produced drinking water from space station water purification system has been reported to be in the range of 6 to 8.5 (Sauer *et al.*, 1991). A series of experiments was conducted in order to evaluate the formation of IDBPs under eight different experimental conditions (Table 2).

Table 2. Experimental Conditions

Experimental Condition *	Iodine Concentration <sup>(1)</sup>		Phenol Concentration <sup>(2)</sup>		I <sub>2</sub> : Phenol		pH <sup>(3)</sup>
	mg/L	moles/L	mg/L	moles/L	Mass Ratio	Molar Ratio	
1	10	0.04	5	0.05	2: 1	1:1.25	5.5
2	10	0.04	5	0.05	2: 1	1:1.25	8.0
3	50	0.20	5	0.05	10: 1	4:1	5.5
4	50	0.20	5	0.05	10: 1	4:1	8.0
5	10	0.04	50	0.50	0.2: 1	1:12.5	5.5
6	10	0.04	50	0.50	0.2: 1	1:12.5	8.0
7	50	0.20	50	0.50	1: 1	1:2.5	5.5
8	50	0.20	50	0.50	1: 1	1:2.5	8.0

\* The experimental conditions were selected based on NASA Space Station water specific use and treatment conditions. All experiments were conducted at 20 °C.

- (1) Iodine residuals for NASA potable water standards are targeted to be in 1-4 mg/L range. Increased amount of iodine (4 mg/L or greater) may be used if break down in water purification occurs. 10 and 50 mg/L of I<sub>2</sub> were chosen as high and low concentrations.
- (2) 5 and 50 mg/L were selected as high and low levels to ensure detection of organic compound without need for experimental manipulations such as extractions. Also, iodine may be added early in the recycle water treatment process, prior to the removal of organic compounds by cation or anion exchange or GAC sorption.
- (3) pH of 5.5 was chosen to simulate the acidic condition similar to distilled deionized water, the expected finished water of the Space Station. pH of 8 was selected to evaluate any base catalyzed reactions.

High performance Liquid Chromatography (HPLC) was the primary method used for separating and quantifying the phenolic compounds. Gas Chromatography/ Mass Spectrometry (GC/MS) was used to identify unknown compounds that were unavailable

as commercially pure, manufactured products. A spectrophotometric method was used to quantify the iodine concentrations.

## **EXPERIMENTAL PROCEDURE**

### **Preparation of Reaction Vials**

The experiments were conducted by preparing reaction mixtures of iodine and phenol under the specified experimental conditions (Table 2). Reactions were allowed to proceed for 32 days. Prior to initiation of the experiments, stock solutions of each reactant (iodine and phenol) were prepared. These consisted of 100 mg/L aqueous solutions of each individual reactant. The iodine stock solutions were made by continuous stirring of 100 mg of solid I<sub>2</sub> (99.9 percent) in a liter of reagent water for a minimum of five hours until complete dissolution was achieved. For each of the experimental conditions, reaction mixtures were prepared by combining sufficient volumes of iodine and phenol in the reaction vessel to achieve the desired concentrations of each reactant. The pH of the reaction mixture was typically below 5 units but was pH adjusted to the designed level by sodium hydroxide addition. All reactions were performed headspace-free in 40 mL, amber glass vials with Teflon septa and screw caps. Reaction vessels were stored in the dark.

Odor threshold concentrations of selected phenolic IDBPs were determined if the pure commercial products were available. The experimental methods used for determinations of phenol and iodine and the FPA method are discussed in the proceeding sections.

## Phenols Analysis

The separation and quantification of phenol and corresponding iodinated phenols was achieved by a HPLC method. Quantification procedure consisted of HPLC analysis of various concentrations of known standards ranging from 0.5 to 100 mg/L of each phenolic compound. Standard curves were developed for phenol, 2-iodophenol, and 4-iodophenol. Identities of these compounds were verified by determining the retention times of the pure compounds (available for phenol, 2-, and 4- iodophenol) on the HPLC.

A Hewlett-Packard (H-P) Liquid Chromatograph with UV diode array detector was used for separation and quantification of the phenolic compounds. The instrument operating conditions are presented in Table 3. Concentrations below 0.5 mg/L were not measured.

Table 3. High Performance Liquid Chromatography Instrument Settings

INSTRUMENT PARAMETER	SETTING
<u>Eluents:</u>	
1% Acetic acid in mili-Q deionized water	50%
1% acetic acid in HPLC grade methanol	50%
Detector	Diode Array, Ultra Violet
Wavelength response factor	254 nm
Sample size	10 $\mu$ L, autosampler
Column	150 mm, I.D. 4.6mm, Econosphere C <sub>18</sub> 5U

The quantification of di-substituted phenols (2,4- and 2,6-diiodophenols) could not be achieved due to the lack of commercially available pure compounds. However, these were identified by GC/MS methods. A H-P 5890 series II GC and H-P 5970 MS detector operated in full scanning and selected ion monitoring modes were used to identify the potential presence of diiodophenols and triiodophenol in selected reaction mixtures. The instrument operating conditions are presented in Table 4.

The mass spectra for the iodinated phenolic compounds were found in the WILEY-NBS mass spectral database. Retention times were determined for those compounds for which pure compounds were available; these included phenol, 2-iodophenol, 4-iodophenol, 2, 4,6-triiodophenol. The molecular ion and major m/z (mass/charge) values for these compounds are presented in Table 5.

Table 4. Gas Chromatography-Mass Spectrometry Instrument Settings

INSTRUMENT PARAMETER	SETTING
Instrument Calibration	Autotune
Source pressure	Approx. $4 \times 10^{-4}$ torr
Initial Temperature	80 °C
Final temperature	300 °C
Rate	20 °C/min
Purge off time	3 min
Run time	16 min
Final time	2 min
Ion scan range	50 to 500 amu
Sample size	Approx. 3.0 $\mu$ L; split injection
Column	H-P Ultra II capillary column

Table 5. Mass Spectral Information for the Monitored Iodinated Phenols

COMPOUND	RETENTION TIME ( Minutes)	MOLECULAR ION MASS (amu)	MAJOR m/z VALUES
Phenol	5.09	94	65, 94
2-iodophenol	7.30	220	65, 127, 220
4-iodophenol	9.65	220	65, 94, 127,220
Diiodophenol	11.52	346	346
Triiodophenol	13.47	472	472

### Iodine Analysis

The iodine concentrations in the controls and experimental reactions were determined by the leuco crystal violet (LCV) method as described in the *Standard Methods for the Examination of Water and Wastewater* 19th edition (1994), section 4500-I B. Iodine concentrations were determined by direct oxidation of the colorless Leuco Crystal Violet compound 4, 4, 4, methylidynetris (N, N-dimethylalinine) to its highly colored dye form, crystal violet. The concentration of iodine was subsequently determined by measuring the absorbance of the color in a Beckman DU6 spectrophotometer at a wavelength of 592 nm. Iodine concentrations were quantified using a standard curve developed on known concentrations of iodine standards ranging from 0.1 to 6.0 mg/L. Reaction solutions were diluted with reagent water to reduce iodine concentrations to between 0.1-6.0 mg/L. Likewise, the total iodine (iodine/iodide) was determined using the LCV method (standard methods 4500-I B). The total iodine concentration was determined by selective oxidation of iodide to iodine using potassium peroxymonosulfate,  $\text{KHSO}_5$  (oxone) and subsequent reaction with the LCV and

development of crystal violet dye. Color intensities were determined by measuring absorbance at 592 nm in a spectrophotometer. Total iodine concentrations were determined by constructing a standard curve on known concentrations of iodide (KI) standards. The minimum concentration that could be detected was 0.1 mg/L

### **Organoleptic Evaluation**

The organoleptic evaluations of the phenolic compounds were performed in accordance to the Flavor Profile Analysis (FPA) method described in the *Standard Methods for Examination Water and of Wastewater*, 19th edition, (section 2170, 1994 ), and the procedure outlined in the American Water Works Association (AWWA) handbook entitled *Flavor Profile Analysis: Screening and Training of Panelists* (1992). FPA was performed on phenol, 2-iodophenol, and 4-iodophenol as these compound were likely to produce the most odor and were available as pure compounds.

The FPA panel consisted of seven graduate students and faculty members from the Charles E. Via Department of civil Engineering at Virginia Tech. The FPA panel was trained by Dr. Diana Rashash (Rashash Consulting, Jacksonville, NC) over a two-day period. During this time, participating panelists were screened by the intensity ranking, odor recognition exercises, and "triangle tests" to evaluate their abilities in recognizing various intensities and types of odors in selected odorous compounds. These included, iodoform ("medicinal"), geosmin ("earthy"), MIB ("musty"), and 2t, 6c-nonadienal ("cucumber"). Subsequent panel meetings were held regularly with at least five panelists present at each session; meetings were held in an odor-free room. Four to six samples were presented to the FPA panel at each session. Samples of a 200 mL volume were stored in 500-mL stoppered flasks, cleaned by rinsing with Mili-Q reagent water and oven drying. Samples were heated to 45 °C in a water bath. At least one of the samples unknown to the panelists was a blank consisting of only Mili-Q reagent water. In



addition, a known sample labeled as "Odor-free" (OF) was provided to the panelists to allow for odor comparison and calibration of senses between the samples. At least one sample of a known odorous compound was also included with the unknown samples at each session to monitor the panelists odor recognition abilities. No experimental samples were tasted, as this required monitoring the microbiological quality of the water.

### **Data Analysis**

The analytical data for concentrations of phenolic compounds and total iodine/iodide concentrations were plotted against the reaction times. Flavor profile analysis data were evaluated in accordance to the methods or modification thereof described in the Standard Method 2170 (Standard Methods, 19<sup>th</sup> ed. 1994). Average intensity values for each of the phenolic compounds were obtained when majority (50% or greater) of panelists agreed on the odor description. When the panelists responses included odor intensity of less than two, an intensity value of one was used in calculation of average intensity. "Odor-free" responses that did not agree with the majority of panelists were not included in the calculation of average intensity when it was previously known that the panel member was anosmic to the odor of the compound being evaluated. Weber-Fechner plots on the FPA data were constructed for each compound to determine the odor threshold concentration. The odor threshold concentration corresponded to the concentration of compound, which resulted in an average odor intensity of two, when the average intensity data were plotted against log concentration of the compound.

## CHAPTER 4. RESULTS

### IODINE DETERMINATIONS

As discussed in the previous chapter, iodine and total iodine/iodide concentrations were monitored in conjunction with the phenolic compounds to evaluate changes in iodine residuals during the reaction period. Iodine and total iodine/iodide concentrations were measured at 24-hours and 32 days reaction times. Concentrations of iodine species in iodine controls and iodine-phenol reaction mixtures were also monitored. The results of these analyses are discussed in the following sections.

#### Iodine Controls

Iodine control solutions for each acidic (pH 5.5) and basic (pH 8) condition were analyzed to determine the concentrations of iodine ( $I_2$  and HOI) and total iodine/iodide ( $I_2$ , HOI, I) species. Iodine concentrations declined more rapidly in the basic solutions and most of the decline occurred in the first 24 hours. Iodine ( $I_2$ ) declined 17 percent during the first 24 hours and 64 percent over the entire 32-day period in the pH 5.5 controls. In pH 8 controls,  $I_2$  declined to a much greater extent (91% in 24 hr., 99.96% in 32 days). In both pH 5.5 and pH 8 controls, the pH levels did not vary more than 0.4 units. The total iodine/iodide concentrations remained stable by the initial 24-hr reading time, however, a decline in total iodine/iodide levels was observed after 32 days.

As a quality assurance measure, selected concentrations of iodine and iodide check standards were included with each analytical run to ensure acceptable method performance. The results of the iodine and total iodine/iodide analyses on the controls

and check standards are presented in Table 6. Standard curves for iodine and iodide are included in Appendix 1.

Table 6. Iodine and Total Iodine/Iodide Concentrations in Controls

Initial conditions		Measured concentrations (mg/L)					
Iodine concentration (mg/L)	pH	1 day			32 days		
		Iodine	Total I <sub>2</sub> / I <sup>-</sup>	pH	Iodine	Total I <sub>2</sub> / I <sup>-</sup>	pH
10	5.5	8.3	10.9	5.7	4.6	7.5	5.9
10	8.0	0.9	10.6	8.2	0.04	6.5	8.3
50	5.5	48.0	50.9	5.7	22.0	30.6	5.9
50	8.0	24.2	50.3	8.1	8.4	32.4	8.2
Check Standards (mg/L)							
2.5	-	2.6	2.6	-	2.5	2.6	-
6.0	-	5.9	5.8	-	5.9	5.7	-

A graphical representation of the total iodine/iodide concentrations in the control samples after reaction time of 1 day and 32 days is presented in Figure 1.

### **Iodine-Phenol Reactions**

Concentrations are reported in mg/L and iodine-phenol ratios are reported as mass: mass ratios throughout the results and discussions. Phenol iodination of phenol

reactions were performed twice, but a more complete set of iodine/iodide measurements was made during only one of the experimental sets. The more complete data set is presented here; the other set of data is in Appendix 2.

The concentrations of iodine and total iodine/iodide were measured after 24 hours and 32 days reaction times to confirm the presence of iodine in the reaction mixtures and to determine the reactive amounts of the iodine species present in solution. The results of these iodine and total iodine/iodide quantitative analyses reaction are summarized in Table 7.

Conditions: 1,3,5,7 were at pH 5.5  
Conditions: 2,4,6,8 were at pH 8.0

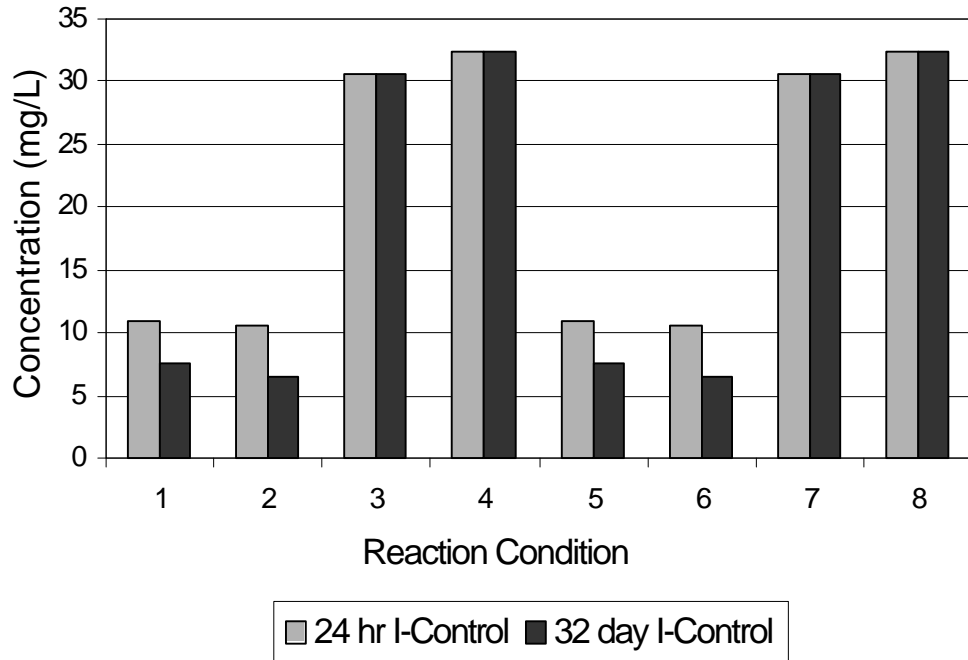


Figure 1. Total Iodine/Iodide Concentrations in Controls

Conditions: 1,3,5,7 were at pH 5.5  
Conditions: 2,4,6,8 were at pH 8.0

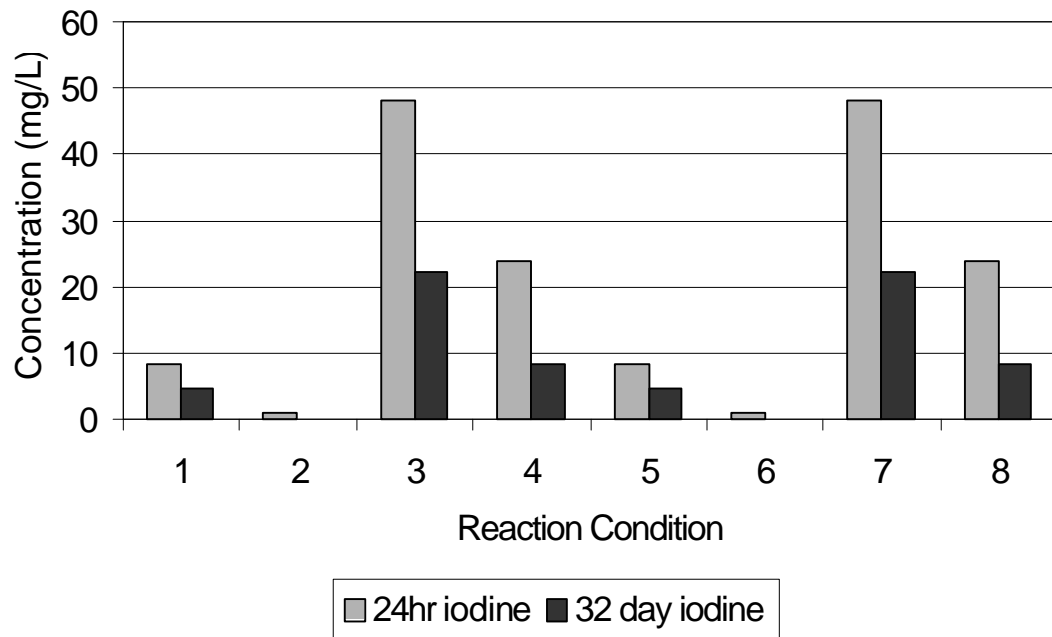


Figure 2. Iodine ( $I_2$  and HOI) Concentrations in Controls

Table 7. Iodine and Total Iodine/Iodide Concentrations in Experimental Reactions

Initial Conditions				Measured Concentrations (mg/L)					
				1 Day			32 Days		
Condi- tion	pH	Reactants		Iodine <sup>1</sup>	Total I <sub>2</sub> /I <sup>-</sup>	pH	Iodine	Total I <sub>2</sub> /I <sup>-</sup>	pH
		I <sub>2</sub>	Phenol						
1	5.5	10	5	ND*	3.3	5.5	ND	1.1	5.6
2	8.0	10	5	ND	4.0	8.0	ND	2.3	7.9
3	5.5	50	5	4.5	36.9	5.5	2.9	26.6	5.6
4	8.0	50	5	0.8	34.7	8.0	0.2	19.2	7.8
5	5.5	10	50	ND	1.2	5.5	ND	0.8	5.6
6	8.0	10	50	ND	0.8	8.0	ND	0.3	7.9
7	5.5	50	50	0.1	15.3	5.5	ND	4.9	5.8
8	8.0	50	50	ND	12.8	8.0	ND	10.0	8.0
Check Standards (mg/L)									
2.5		-	2.6	2.6	-	2.5	2.6	-	
6.0		-	5.9	5.8	-	5.9	5.7	-	

(1) Iodine concentrations include I<sub>2</sub> and HOI :

(2) Total Iodine/Iodide concentrations include I<sub>2</sub>, HOI, I<sup>-</sup>

\* ND = Not Detectable at minimum detection limit of 0.1 mg/L

These data show a substantial decline in both iodine and total iodine/iodide levels in each phenol reaction mixture after 24-hours. Further decline in total iodine/iodide levels was observed after 32 days of reaction time. As predicted, greater decrease in total iodine concentrations was observed in reaction mixtures with higher concentrations of phenol in solution and lower iodine: phenol ratios. For each experimental condition, pH levels

were measured after 1 day and 32 days. The pH levels did not vary more than 0.3 units (Table 7). The initial decrease in total iodine concentrations, measured at 24-hours showed 98 percent to 26 percent reduction in total iodine/iodide levels under all experimental conditions studied. No reduction in total iodine/iodide was observed in the control samples after 24 hour. Likewise, the iodine concentrations, measured at 24-hours showed were substantially reduced. As depicted in Table 7, the iodine concentrations at 24-hours were reduced to nondetectable levels ( $< 0.1$  mg/L) under most experimental conditions. Detectable iodine concentrations were measured in reaction conditions 3, 4, and 7; these reactions showed 91 percent to 98 percent reduction in iodine concentrations. After 24 hours, iodine concentrations in control samples ranged from 0.9 to 8.3 in 10 mg/L controls, and from 24.2 to 48 mg/L in the 50 mg/L controls. The lowest iodine levels (0.9 and 24.2 mg/L) in the controls were measured at high pH (8.0) level. This is expected as iodide species are the dominant forms at higher pH levels (White, 1992). As predicted, a greater decrease in iodine concentrations was observed at at lower, initial iodine: phenol ratios. This is likely due to the presence of phenol in solution and reaction of iodine with phenol to form iodophenols. The phenolic iodine is not measured by the LCV method. A graphical presentation of iodine concentrations in controls, measured after 24-hours and 32-days contact times is provided in Figure 2.

The measured concentrations of iodine and total iodine/iodide levels in each experimental condition along with other reaction components were plotted against the reaction times to monitor the decrease in total iodine levels and the corresponding increase in formation of reaction by-products. The graphical representations of these data are presented in Figures 4 to 11.



## **IODINE-PHENOL DISINFECTION BY-PRODUCTS**

As discussed in the previous chapter iodine-phenol reactions were conducted under eight different experimental conditions. The formation of iodine disinfection by-products (IDBPs) were evaluated under acidic (pH 5.5) and basic (pH 8.0) conditions and various concentrations of reactants. The reaction components were identified and measured by HPLC and GC/MC methods. Phenol proved to be readily reactive in presence of iodine. Various IDBPs were formed within one hour of reactions initiation. The ratio of phenol to iodine was important in the degree of reactivity and product formation. The greatest numbers of IDBPs were formed when 1:1 ratios of iodine to phenol were reacted. No significant differences were observed in quantities of IDBPs formed under acidic conditions relative to the basic conditions. The results of each experiment are discussed in proceeding sections.

### **High Performance Liquid Chromatography Analyses**

Control solutions of phenol were included with each experimental condition to monitor the stability of phenol over the reaction period. The results of the HPLC analyses on the controls samples (consisting of 5 and 50 mg/L concentrations of phenol at pH 5.5 and 8.0) showed that the concentrations of phenol remained relatively stable over the 32 days reaction period. Graphical representation on the stability of phenol in control samples is presented in Figure 3. As an additional quality assurance measure check standards consisting phenol and iodinated phenols were included with each analytical run. A summary of HPLC quantitative data on phenol controls, check standards, and iodinated phenolic by-products are included in Tables 8 and 9. Graphical representation of the reaction progress under each experimental condition are depicted in Figures 4 to 11.

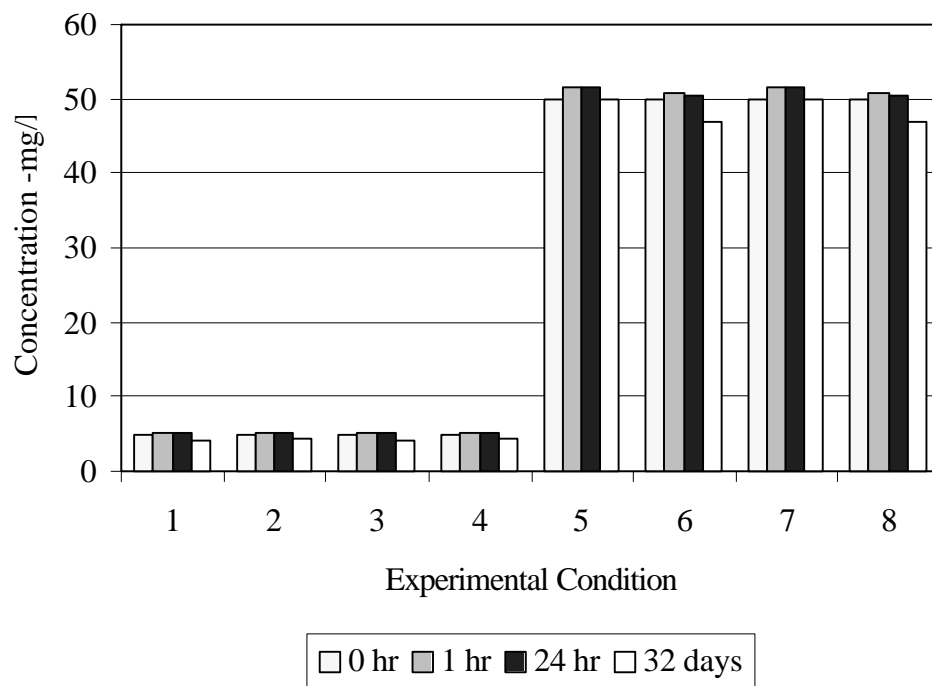


Figure 3. Stability of Phenol in Control Samples

Table 8. Relative Abundance of Iodinated Phenols as Detected By HPLC Method

Experimental Condition	HPLC Chromatogram Integration Data-Peak Areas												
	Reaction Components and By-Products												
	Phenol				2-iodophenol			4-iodophenol			Diiodophenols		
	Initial	1 hr.	1 day	32 days	1 hr.	1 day	32 days	1 hr.	1 day	32 days	1 hr.	1 day	32 days
1	16.4	9.3	9.7	7.0	20.1	18.8	20.1	0.5	0.6	0.4	5.1	7.7	6.0
2	16.6	8.8	9.5	9.6	21.4	20	22.7	0.7	0.7	1.7	5.2	6.9	5.0
3	16.4	0.4	0.2	0.2	0.9	0.2	0.2	ND	0.1	ND	ND	ND	ND
4	16.6	0.3	0.2	0.4	0.7	0.1	0.1	ND	0.1	ND	ND	ND	ND
5	188	174	171	176	38.4	34.3	44.1	ND	ND	ND	ND	ND	ND
6	176	174	173	177	37.9	36.7	35.9	ND	ND	ND	ND	ND	ND
7	188	131	141	135	153	152	149	14.3	13.0	16.0	16.0	22.1	21.0
8	176	135	131	131	152	154	150	12.6	16.0	16.0	22.0	18.0	19.0

(1) Reported values for Phenol at initial reaction time correspond to phenol controls for each experimental condition.

ND = No HPLC peaks were detected for the indicated compound.

Table 9. Summary of HPLC Quantitative Data on Iodine-Phenol Disinfection By-Products

Experimental Condition	Concentration mg/L								
	Phenol			2-iodophenol			4-iodophenol		
	1 hr.	1 day	32 days	1 hr.	1 day	32 days	1 hr.	1 day	32 days
1	2.3	2.5	1.7	4.2	4.0	4.2	ND	ND	ND
2	2.2	2.4	1.8	4.5	4.2	4.7	ND	ND	ND
3	ND*	ND	ND	ND	ND	ND	ND	ND	ND
4	ND	ND	ND	ND	ND	ND	ND	ND	ND
5	46.3	45.3	46.7	7.6	6.9	8.7	ND	ND	ND
6	46.3	46.0	46.9	7.5	7.3	7.2	ND	ND	ND
7	34.7	37.5	35.9	29.1	28.9	28.4	4.2	4.5	5.2
8	35.7	34.7	35.0	28.8	29.1	28.4	4.8	5.3	5.6
Check standards <sup>(1)</sup>									
5 mg/L	5.3	5.3	4.7	5.0	4.9	5.0	4.9	4.8	4.8
50 mg/L	50.0	49.8	48.3	49.3	49.2	49.1	50.3	50.2	49.5
Controls									
5 mg/L pH 5.5	5.2	5.2	4.2	-	-	-	-	-	-
5 mg/L pH 8.0	5.1	5.2	4.3	-	-	-	-	-	-
50 mg/L pH 5.5	51.5	51.5	50.0	-	-	-	-	-	-
50 mg/L pH 8.0	50.6	50.4	46.8	-	-	-	-	-	-

\* ND = Not detectable at Minimum Detection Limit of 0.5 mg/L.

(1) Check standard were included in each analytical run to ensure acceptable method performance

Reaction Condition 1  
5 mg/L Phenol, 10 mg/L Iodine, pH=5.5; Iodine:Phenol Ratio=2:1  
Iodine was not measured at 1 hour.

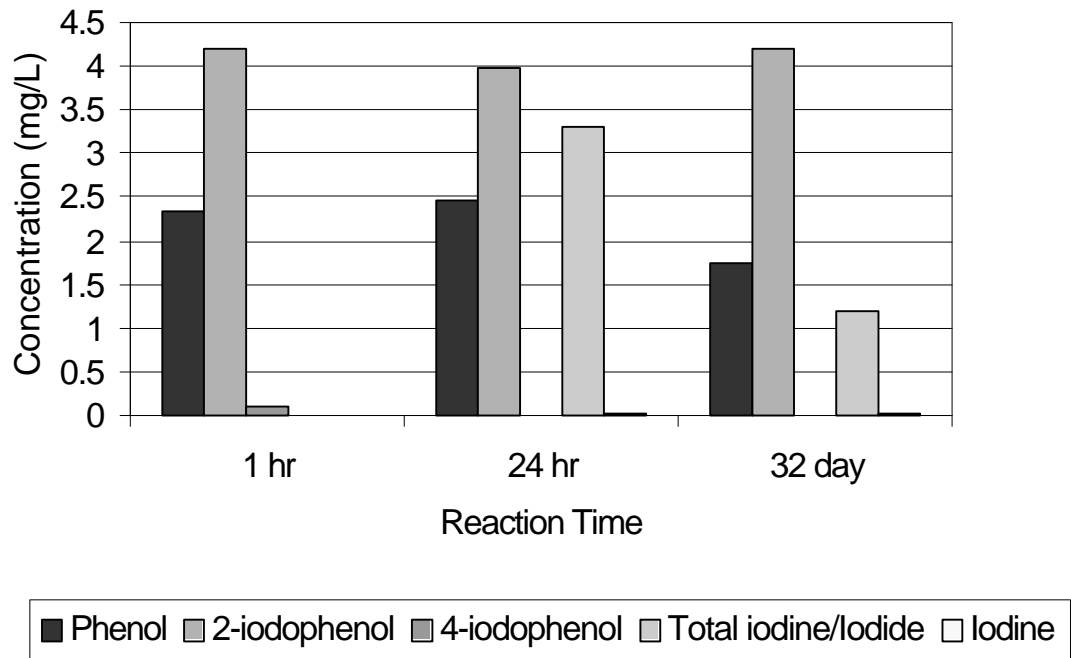


Figure 4. Reaction Results in Experimental Condition 1

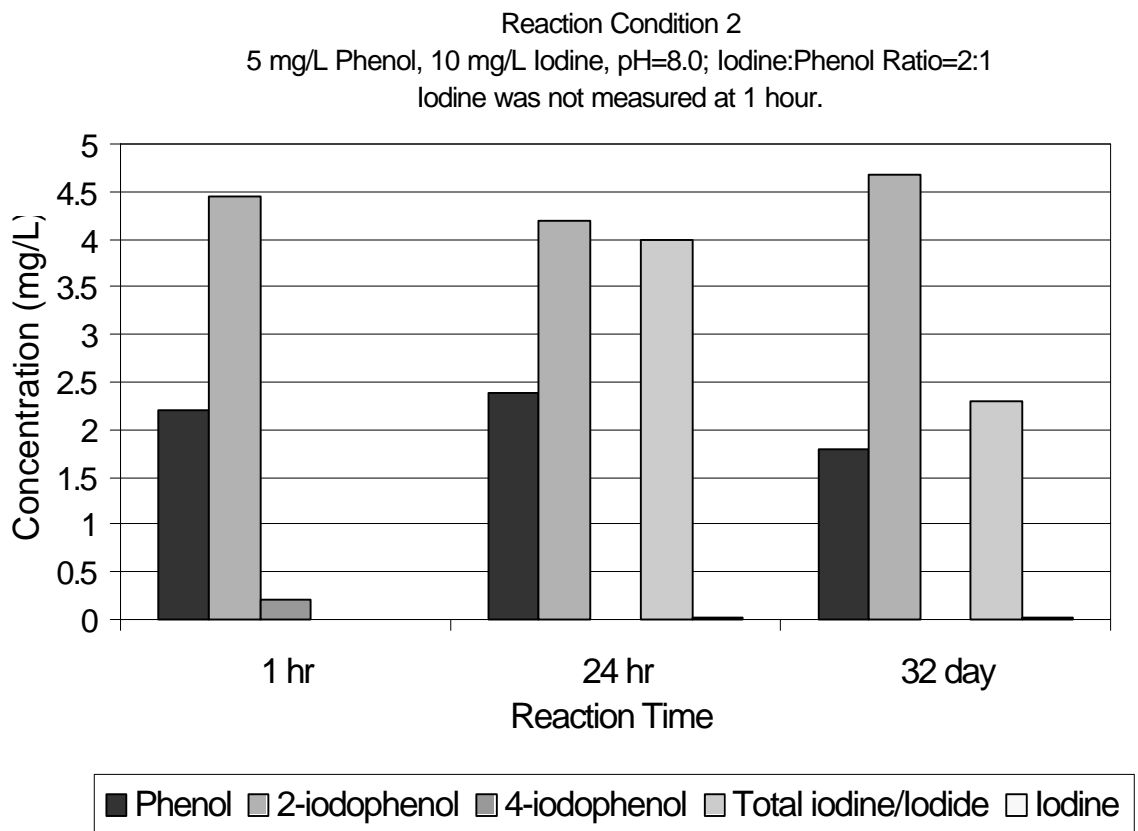


Figure 5. Reaction Results in Experimental Condition 2

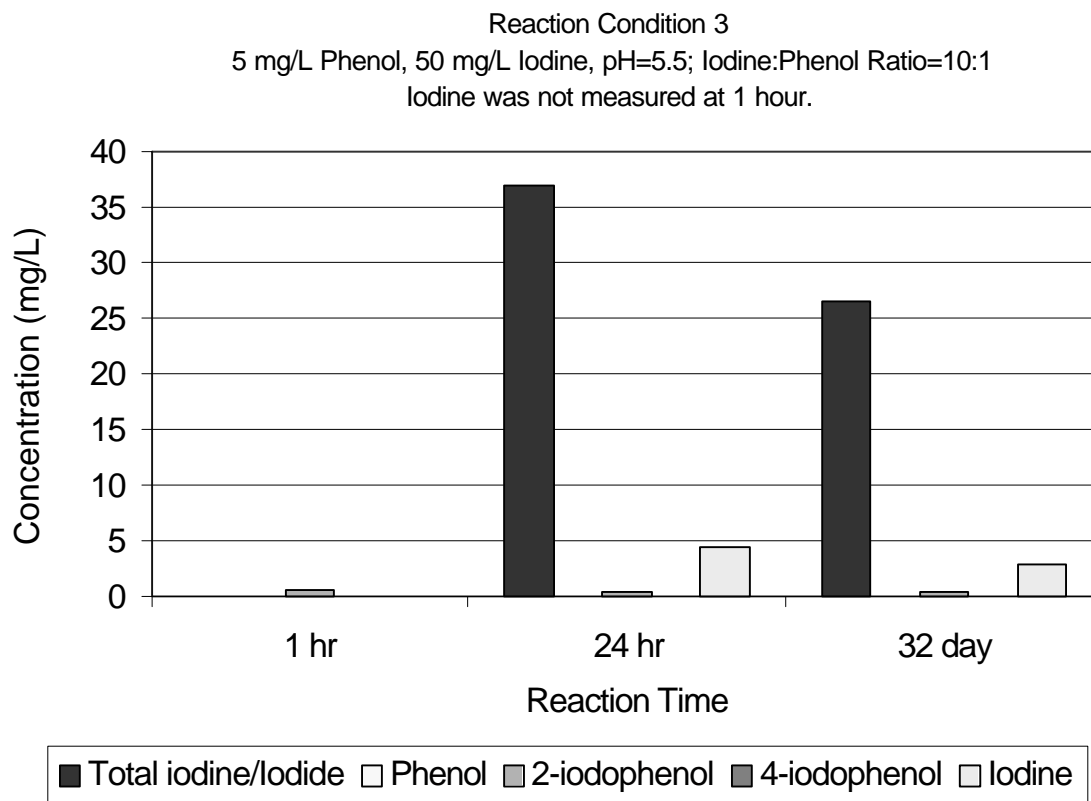


Figure 6. Reaction Results in Experimental Condition 3

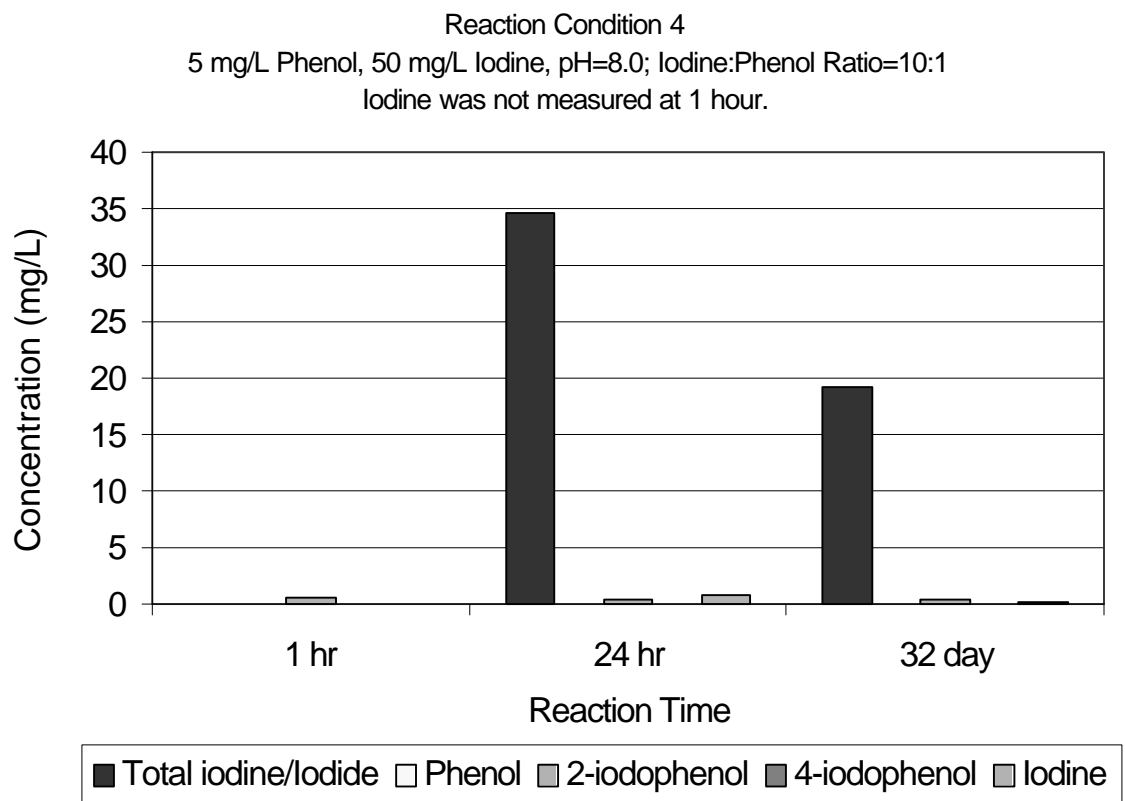


Figure 7. Reaction Results in Experimental Condition 4



Reaction Condition 5  
50mg/L Phenol, 10 mg/L Iodine, pH=5.5; Iodine:Phenol Ratio=0.2:1  
Iodine was not measured at 1 hour.

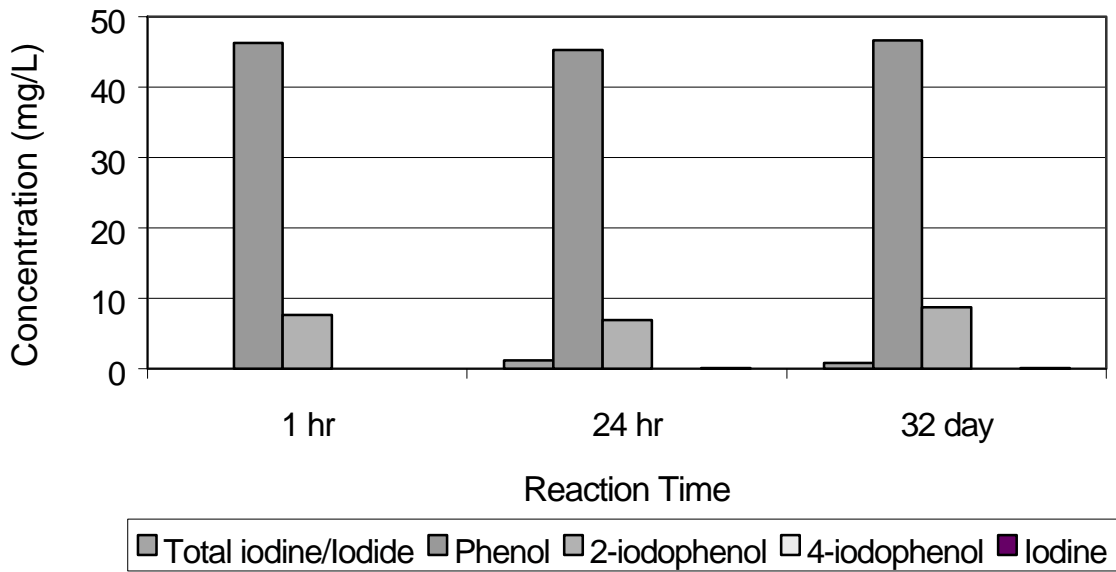


Figure 8. Reaction Results in Experimental Condition 5

Reaction Condition 6  
 50mg/L Phenol, 10 mg/L Iodine, pH=8.0; Iodine:Phenol Ratio=0.2:1  
 Iodine was not measured at 1 hour.

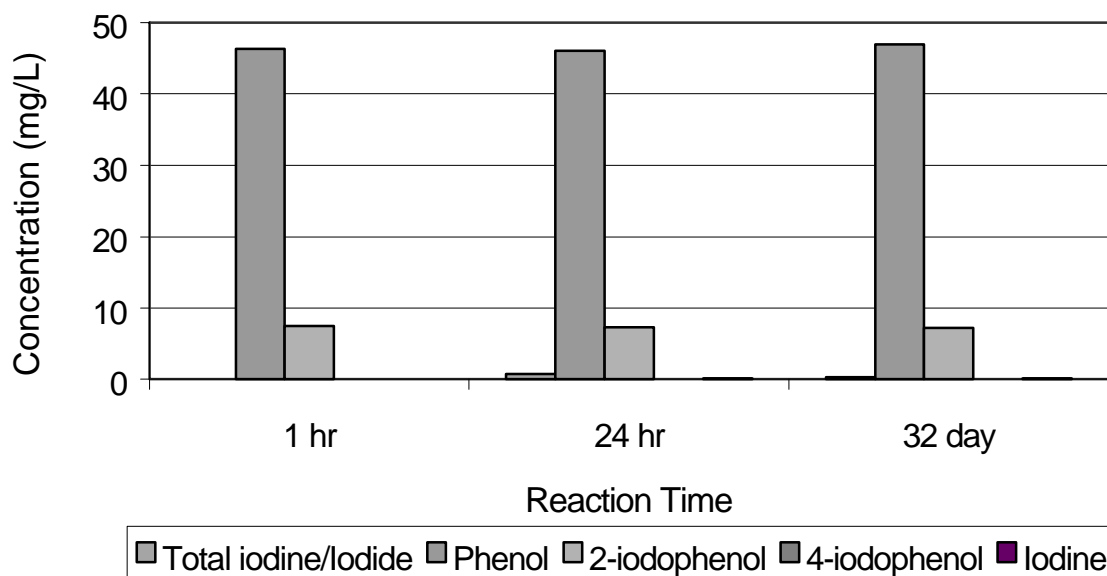


Figure 9. Reaction Results in Experimental Conditions 6

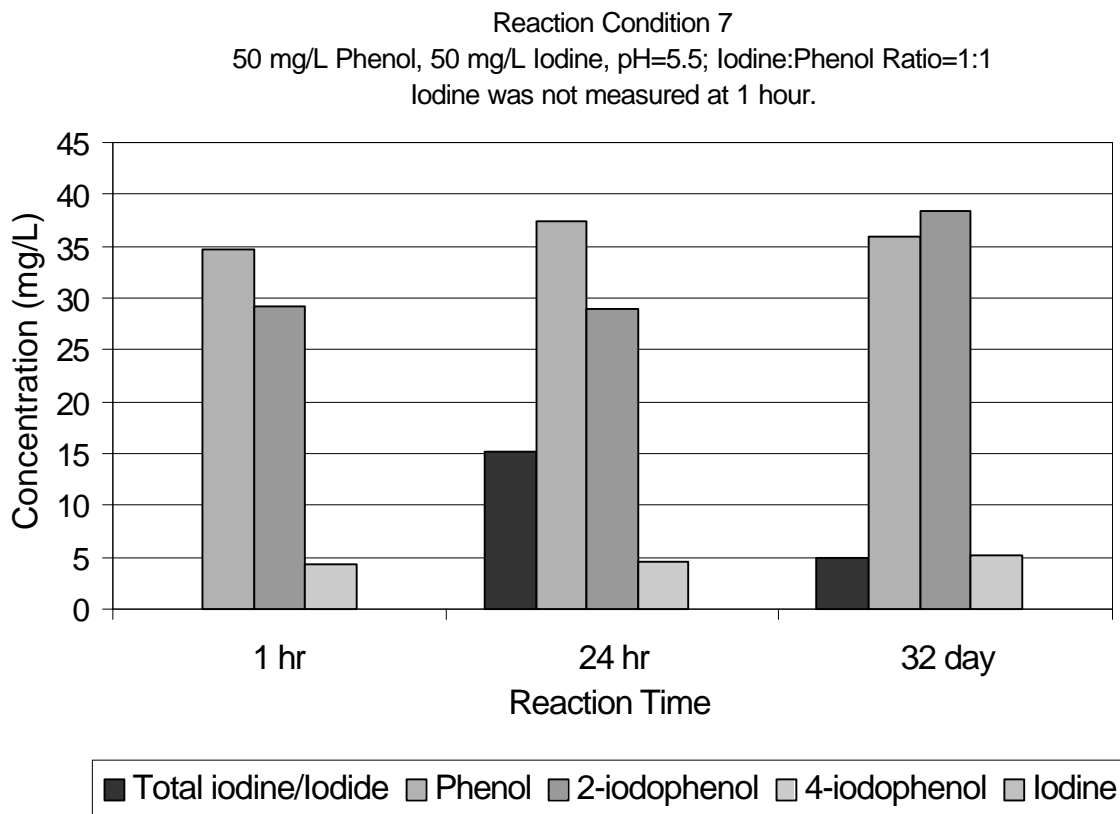


Figure 10. Reaction Results in Experimental Condition 7

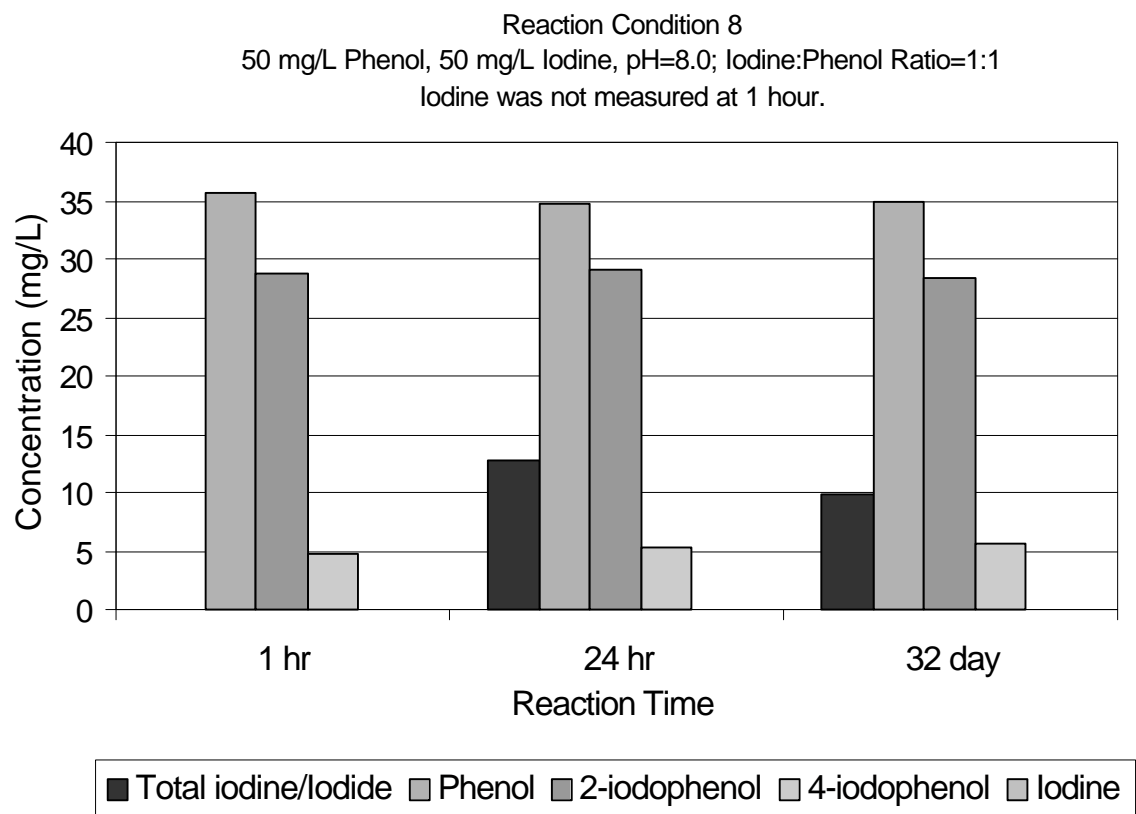


Figure 11. Reaction Results in Experimental Condition 8

The major mono-iodo disinfection by-product associated with iodination of phenol was 2-iodophenol. This compound was detected in all experimental conditions in mg/L concentrations ranging from 11 percent to 85 percent of the initial phenol reactant concentration. For reaction conditions 3 and 4, 2,4,6-triiodophenol was the major IDBP. All iodine-phenol reactions resulted in formation of two or more detectable by-products. Iodine disinfection by-products were detected by HPLC method after one hour of reaction time. With extended reaction times, slight increases or decreases in the one hour IDBP concentrations were observed. The initial ratio of iodine to phenol concentrations in reaction mixture determined the quantity and number of by-products formed under each condition.

Reactions conducted with initial 1:2 ratio of phenol to iodine (conditions 1 and 2, I<sub>2</sub>: phenol molar ratio 1: 1.25) resulted in the formation of 2-iodophenol and 4-iodophenol in reaction mixtures in the initial one-hour reaction monitoring time. 2-iodophenol, at 4.2 mg/L concentration, was the most significant by-product; 4-iodophenol was formed (0.1 mg/L) below the established minimum standard of 0.5 mg/L. In addition to the mono-substituted phenols, a third reaction by-product was detected by HPLC method. This compound was tentatively identified as diiodophenol on the basis of its retention time (compound separated on the chromatogram at a later retention time than mono-iodophenols), phenolic UV-Spectrum (254 nm), and mass spectrum (see below). Due to the unavailability of the pure compound, diiodophenol concentrations could not be quantified. However, review of the HPLC peak integration data (Table 8) shows the relative amounts of diiodophenol detected in each experimental condition. Based on these data, measurable amounts of diiodophenol were present in reaction conditions 1, 2, 7, and 8; the integration data on diiodophenol are comparable to those of mono iodinated phenols. The HPLC chromatograms for these experiments, generated at one-hour reaction time are presented in Figures 12 and 13. There were no significant changes in reaction components at later reaction times compared to the initial one-hour reaction monitoring data.

Reaction mixtures consisting of 1:10 ratio of phenol to iodine (conditions 3 and 4, I<sub>2</sub>: phenol molar ratio 4:1) resulted in rapid iodination of phenol. At one-hour reaction monitoring time, phenol concentration was reduced to non-detectable levels. But, the formation of mono- or di- IDBPs could not be easily detected by HPLC. However, later extraction and analysis by GC/MS revealed the presence of diiodophenol (2,4 or 2,6-isomers) and triiodophenol (2,4,6-triiodophenol) in the reaction mixtures. Also, a substantial amount of a white precipitate occurred under these conditions. This precipitate was identified as 2,4,6-triiodophenol by GC/MS analysis. The HPLC chromatograms for these experiments are presented in Figure 14 and 15.

Reaction mixtures consisting of 0.2:1 (conditions 5 and 6, I<sub>2</sub>: phenol molar ratio 1:2.5) ratio of phenol to iodine resulted in the formation of 2-iodophenol at the initial one-hour reaction monitoring time. The concentration of 2-iodophenol in the reaction mixture remained stable throughout the 32 days reaction-monitoring period. No other IDBPs were detected under these conditions as indicated by the HPLC method. The HPLC chromatograms generated at one-hour reaction time for reaction conditions 5 and 6 are presented in Figures 16 and 17.

Reaction mixtures with initial 1:1 ratio of iodine to phenol (conditions 7 and 8, I<sub>2</sub>: phenol molar ratio 1: 2.5) resulted in the formation of highest number of IDBPs. The compounds that were detected by the HPLC method included phenol, 2-iodophenol, 4-iodophenol, and diiodophenol (Figures 18 and 19). The presence of the mono and di-iodinated phenols was detected in the reaction mixtures after one hour of reaction time. Only slight changes in the concentrations of IDBPs were detected over the 32 days reaction monitoring period. Qualitative analysis of the reaction mixture by GC/MS revealed the presence of triiodophenol in addition to the diiodophenol in the reaction mixtures (see below).

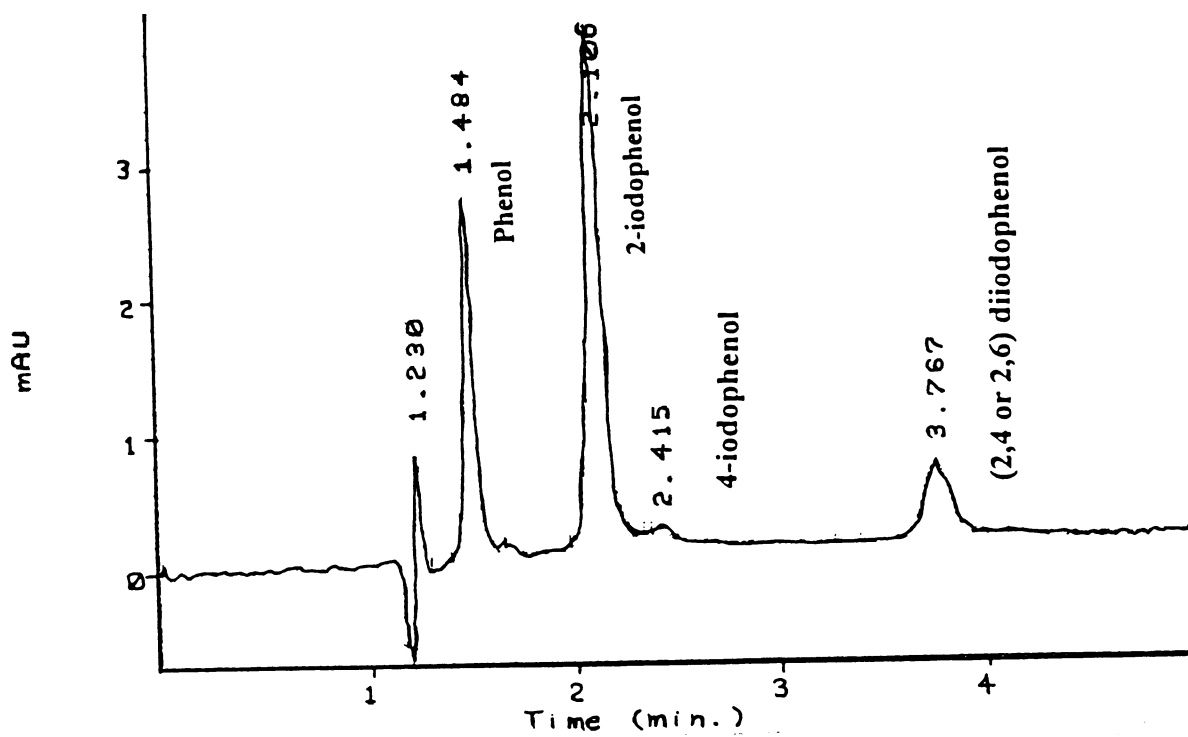


Figure 12. HPLC Chromatogram for Experimental Condition 1  
One hour reaction time

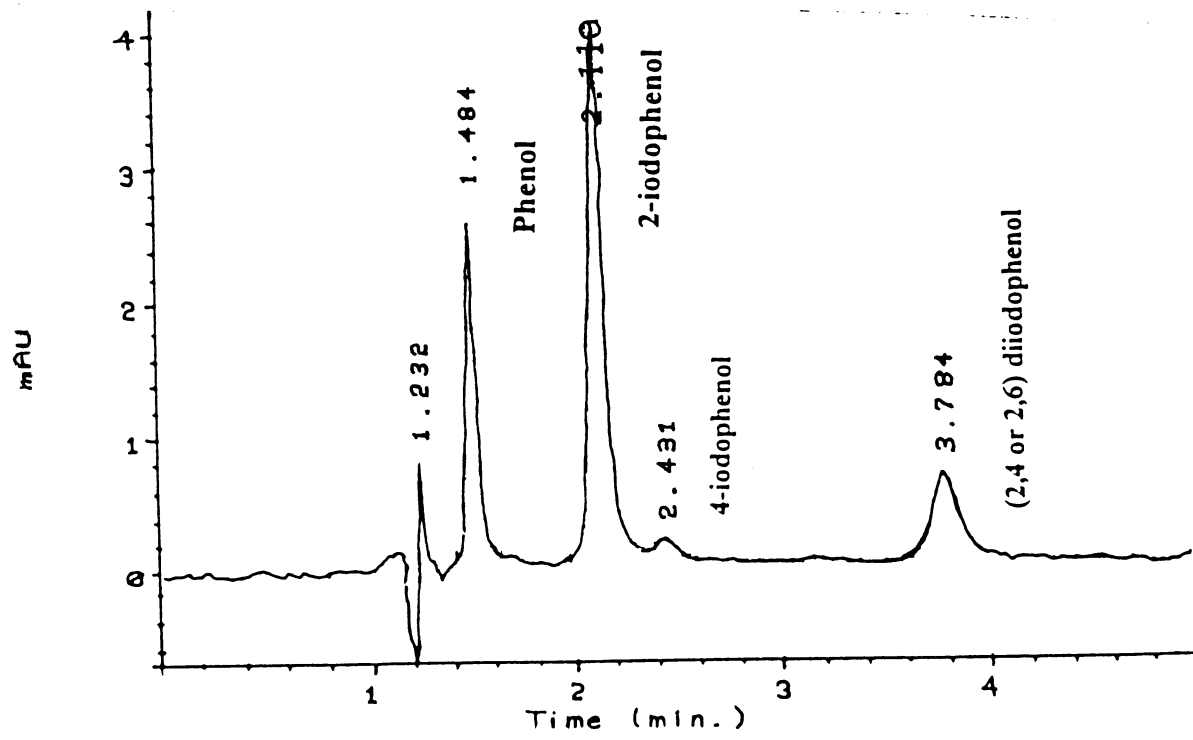


Figure 13. HPLC Chromatogram for Experimental Condition 2  
One hour reaction time



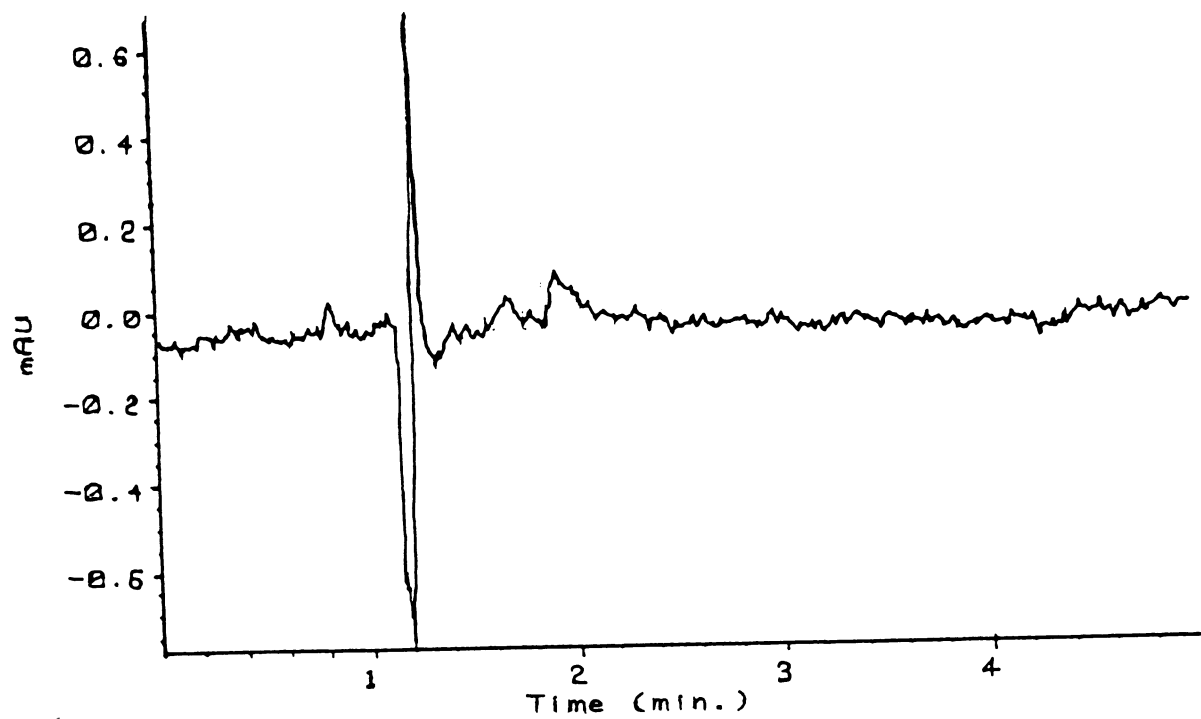


Figure 14. HPLC Chromatogram for Experimental for Experimental Condition 3  
One hour reaction time

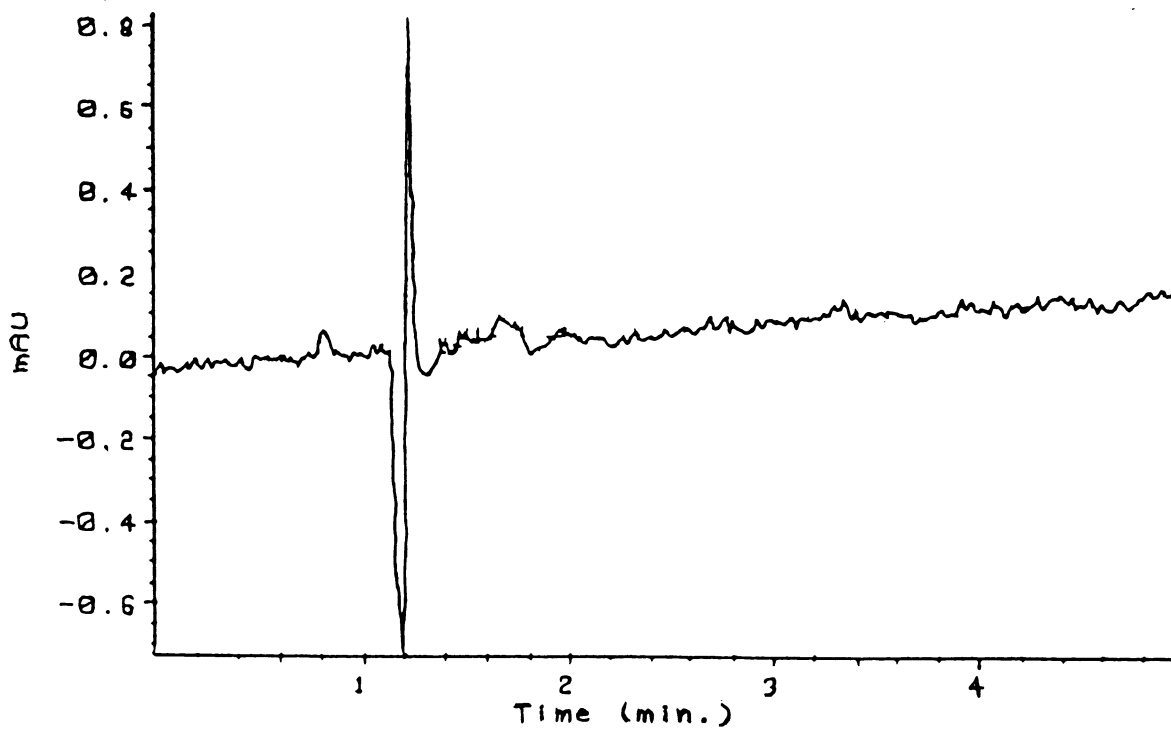


Figure 15. HPLC Chromatogram for Experimental Condition 4  
One hour reaction time

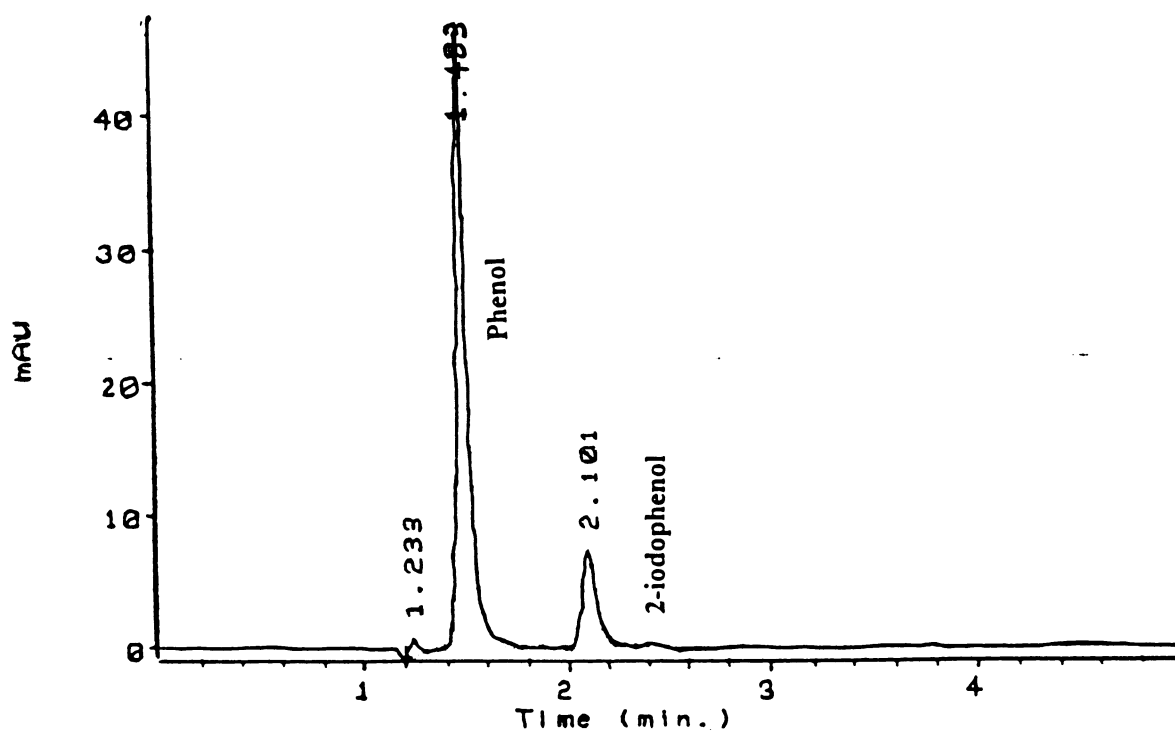


Figure 16. HPLC Chromatogram for Experimental Condition 5  
One hour reaction time

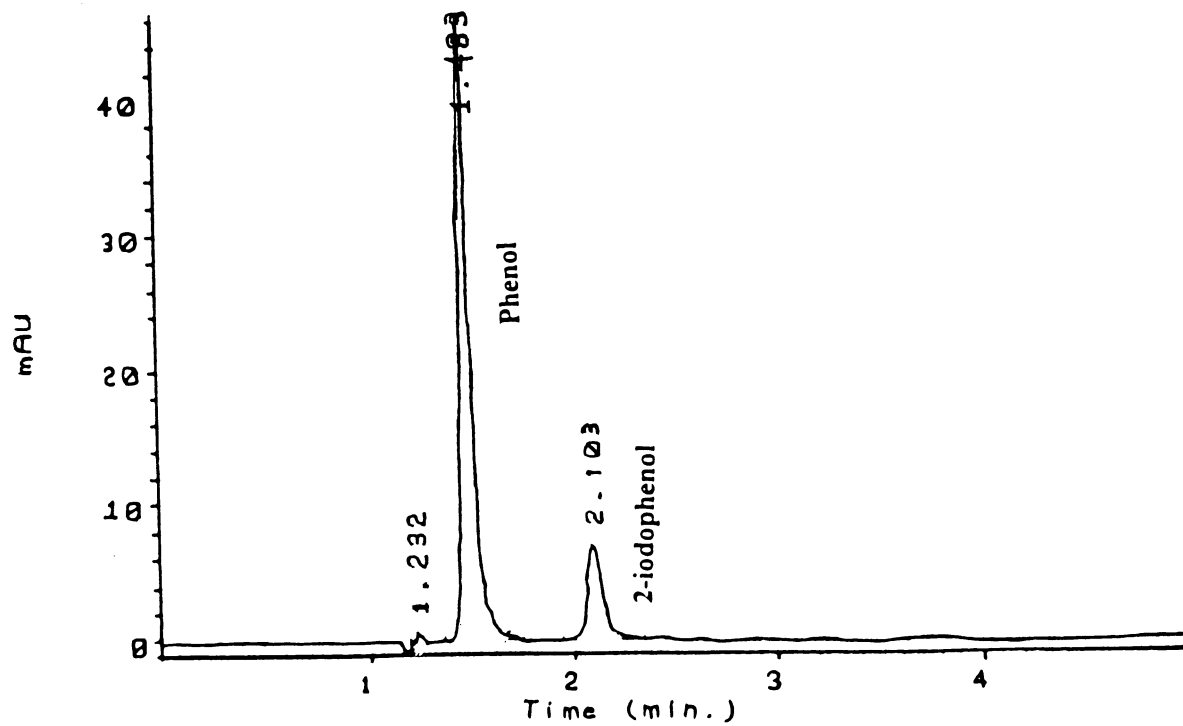


Figure 17. HPLC Chromatogram for Experimental Condition 6  
One hour reaction time

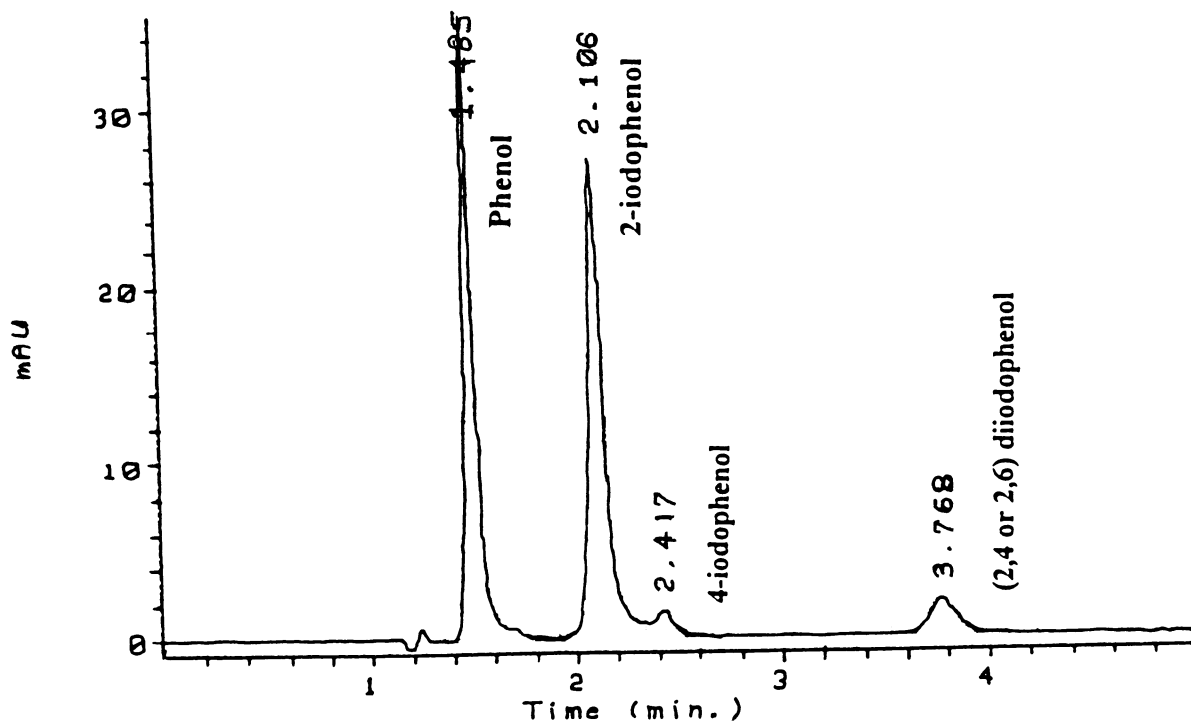


Figure 18. HPLC Chromatogram for Experimental Condition 7  
One hour reaction time

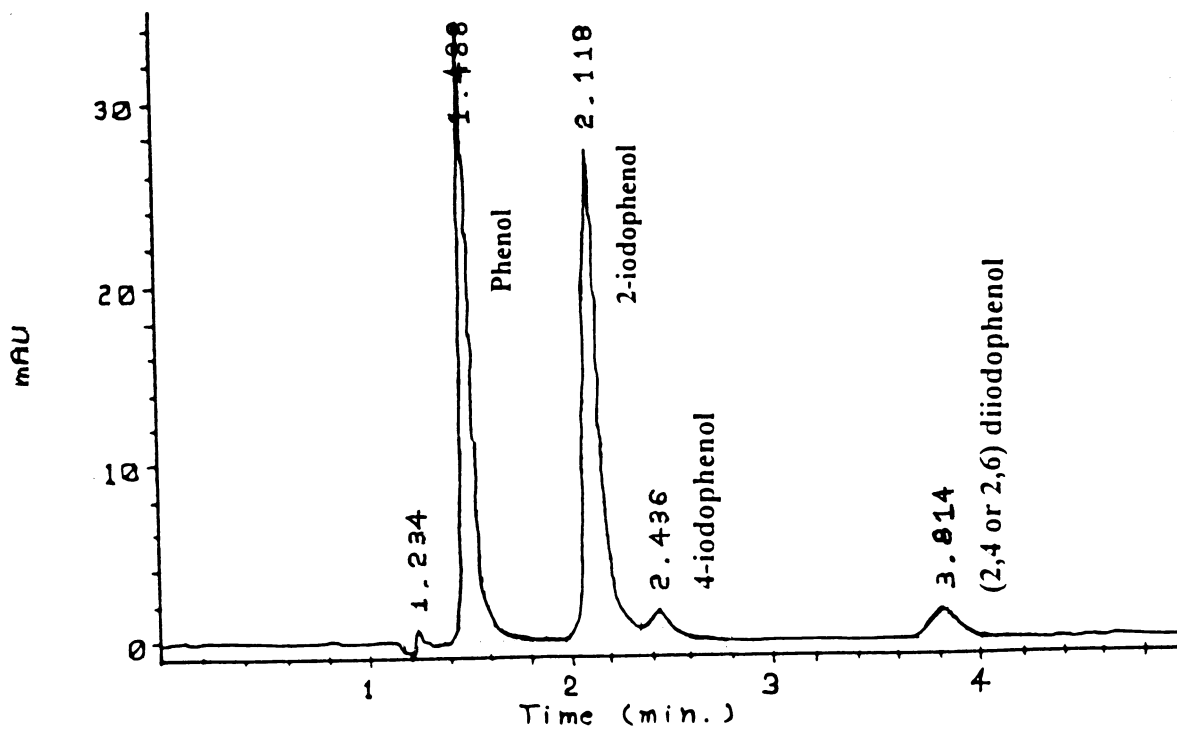


Figure 19. HPLC Chromatogram for Experimental Condition 8  
One hour reaction time

## Gas Chromatography/Mass Spectrometry Evaluations

In an effort to identify reaction components detected by the HPLC method, a series of GC/MS analyses were performed on selected experimental reactions. These included experimental conditions 2 and 7, which consisted of 2:1 and 1:1 ratio of phenol to iodine as reactants. As discussed in the previous section, these reactions resulted in the formation of the highest number of IDBPs. In experimental conditions 2 and 7, two iodinated, phenolic by-products that were conclusively identified by the HPLC included 2-iodo and 4-iodophenols. However, a third reaction by-product also appeared on the HPLC chromatograms (Figures 13 and 18). This compound was tentatively identified as diiodophenol on the basis of its retention time (compound separated on the chromatogram at a later retention time than mono-iodophenols), phenolic UV-Spectrum (254 nm). Although, the formation of triiodophenol was hypothetically expected, the unknown compound detected on the HPLC chromatogram was not believed to be triiodophenol, since analyses of a standard solution of the pure 2, 4, 6-triiodophenol showed that the detection of this compound could not be achieved under the HPLC operating conditions (Table 3) utilized during this study. The 2,4,6-triiodophenol was shown to be insoluble in the matrix (Mili-Q deionized water) used.

A series of GC/MS analyses were performed on methylene chloride extracted samples of reaction conditions 2 and 7. The results of these analyses further confirmed the presence of diiodophenols in these reaction mixtures as indicated by the GC/MS chromatograms and characteristic mass spectra for these compounds (Figures 20 to 22). Furthermore, the presence of 2,4,6-triiodophenol in these reaction mixtures was verified by a matching retention time to that of the known pure compound and the characteristic mass spectrum for 2,4,6-triiodophenol. The GC/MS chromatogram and mass spectrum for mono, di, and triiodophenols are presented in Figures 20 to 25.

Observations made during the experimental studies showed that a white, solid precipitate was formed in those reaction mixtures where a 10:1 ratio of iodine to phenol

was reacted. Dissolution of the white precipitate in methylene chloride and subsequent analysis by GC/MS showed the presence of triiodophenol in these samples. Figure 26 shows the mass spectrum and the corresponding chromatogram on the dissolved solid precipitate from experimental condition 4, verifying the presence of 2,4,6-triiodophenol in the sample.



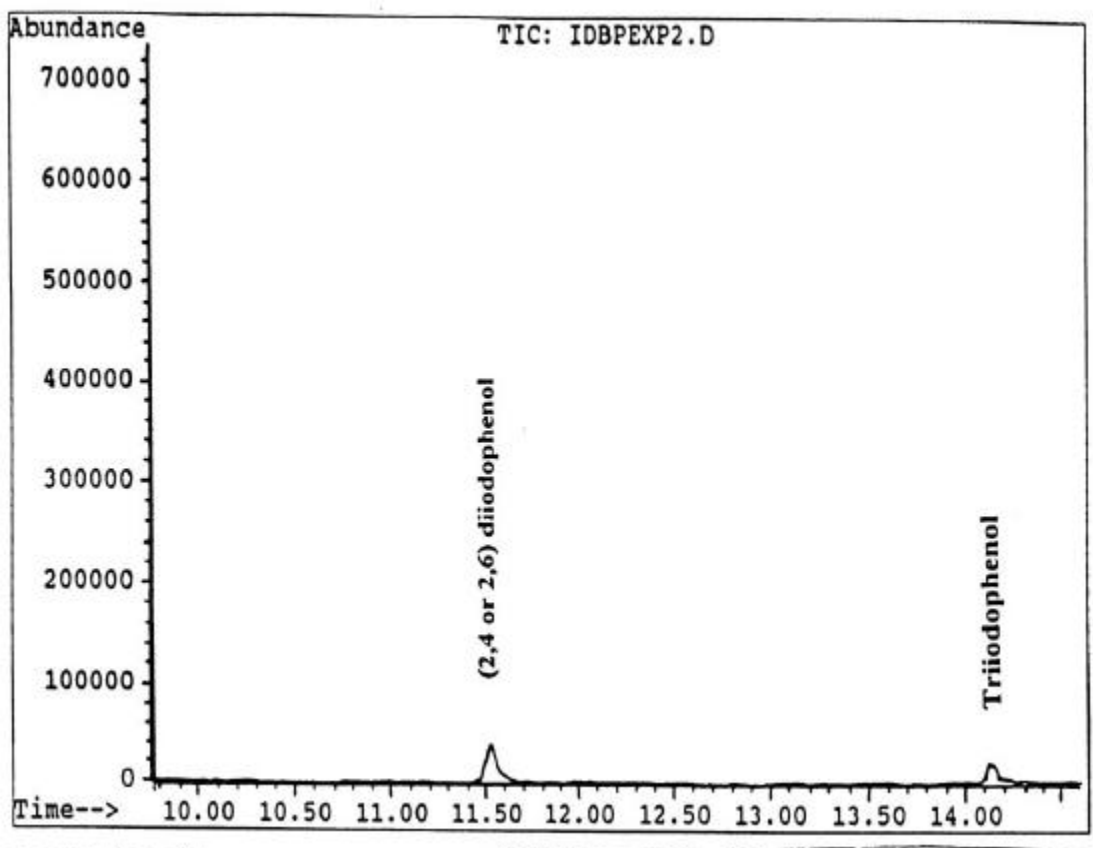


Figure 20. GC/MS Chromatogram for Condition 2

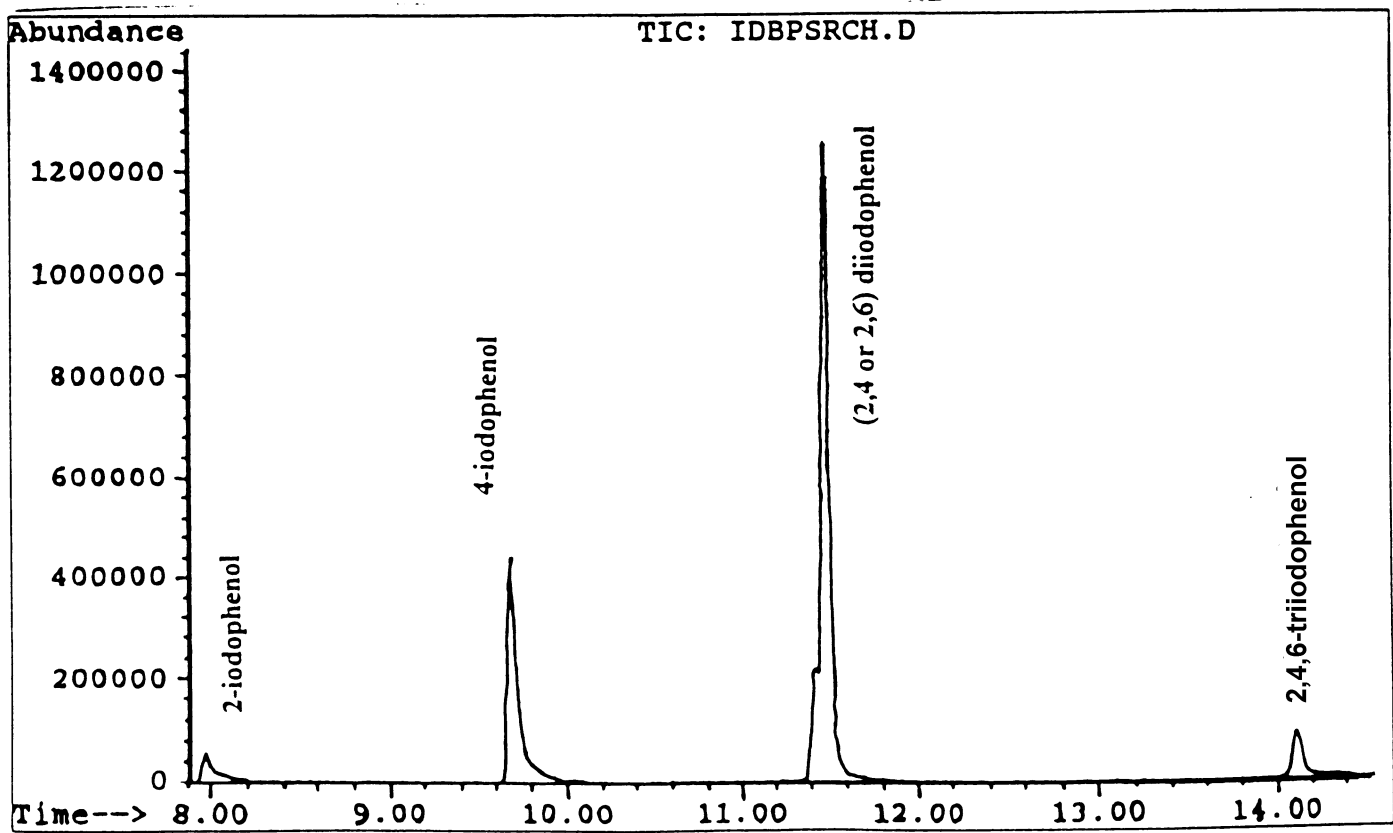


Figure 21. GC/MS Chromatogram for Condition 7

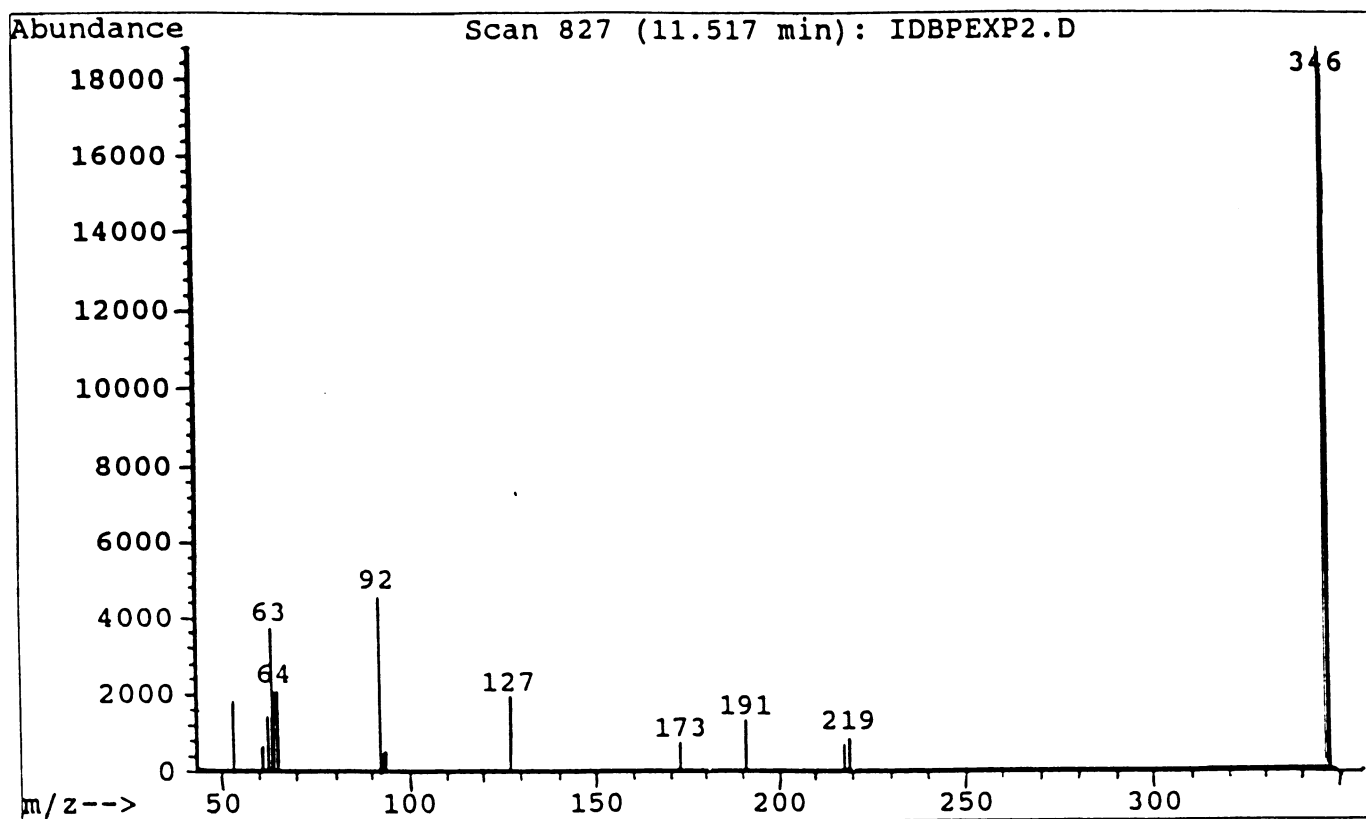


Figure 22. Mass Spectrum for Diiodophenol, MW 346 amu

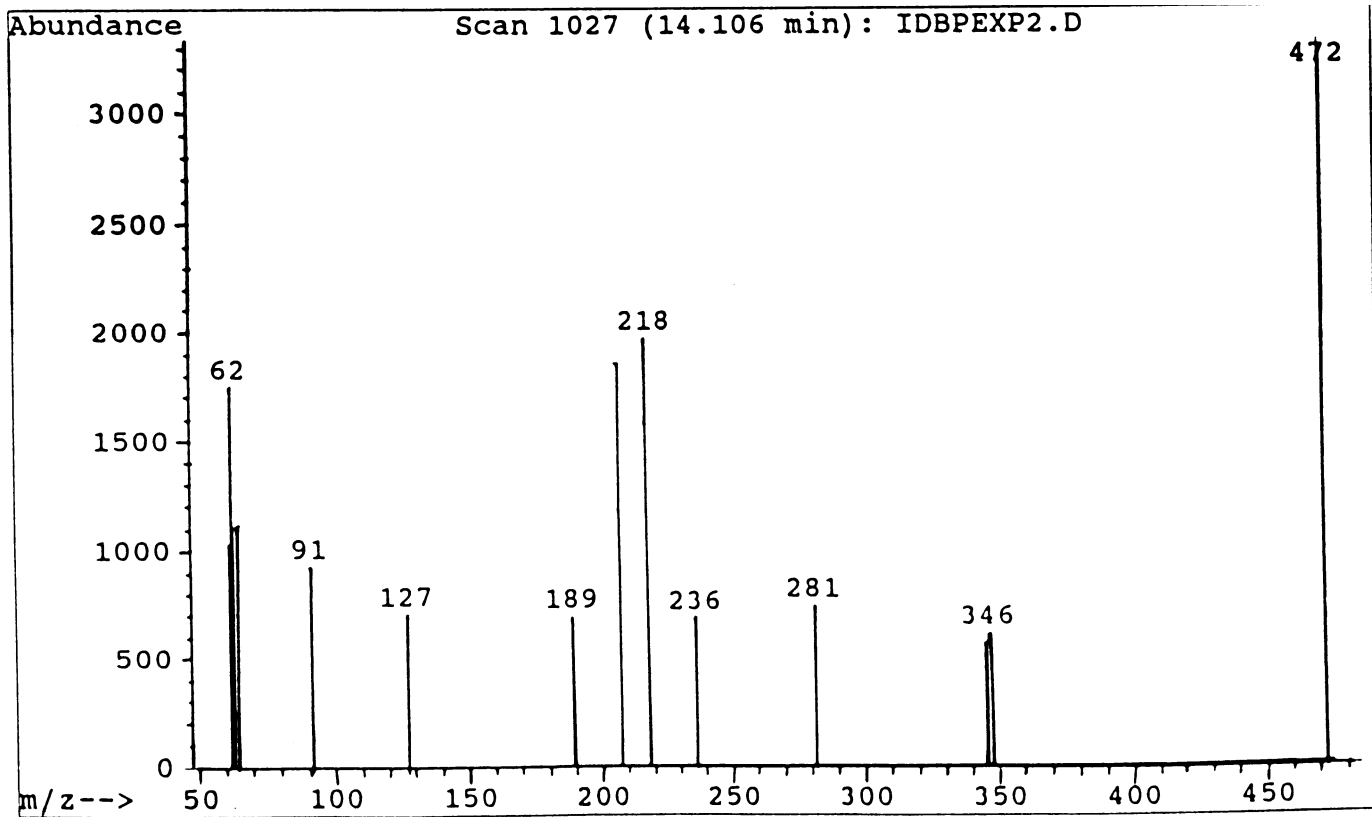


Figure 23. Mass Spectrum for 2,4,6-Triiodophenol, MW 472 amu

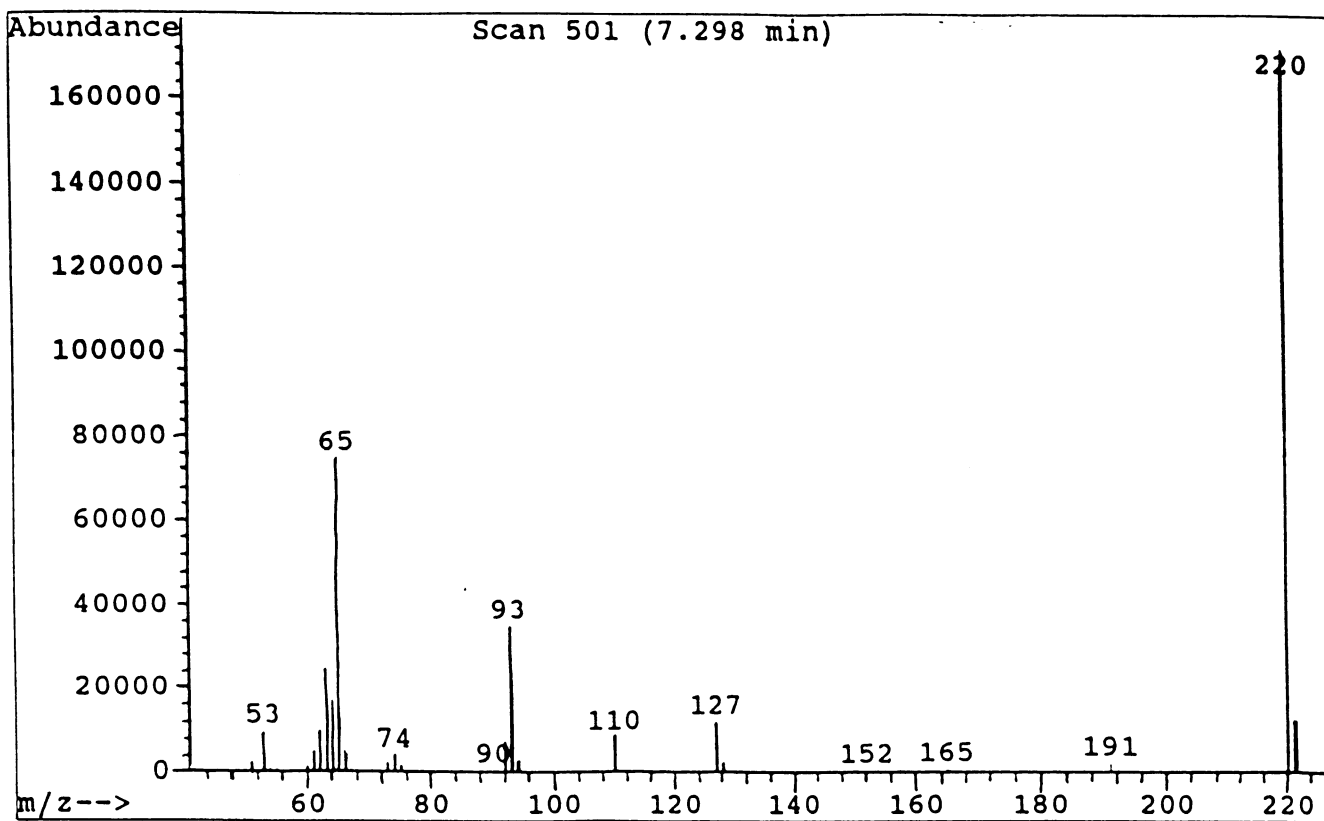


Figure 24. Mass Spectrum for 2-Iodophenol, MW 220 amu

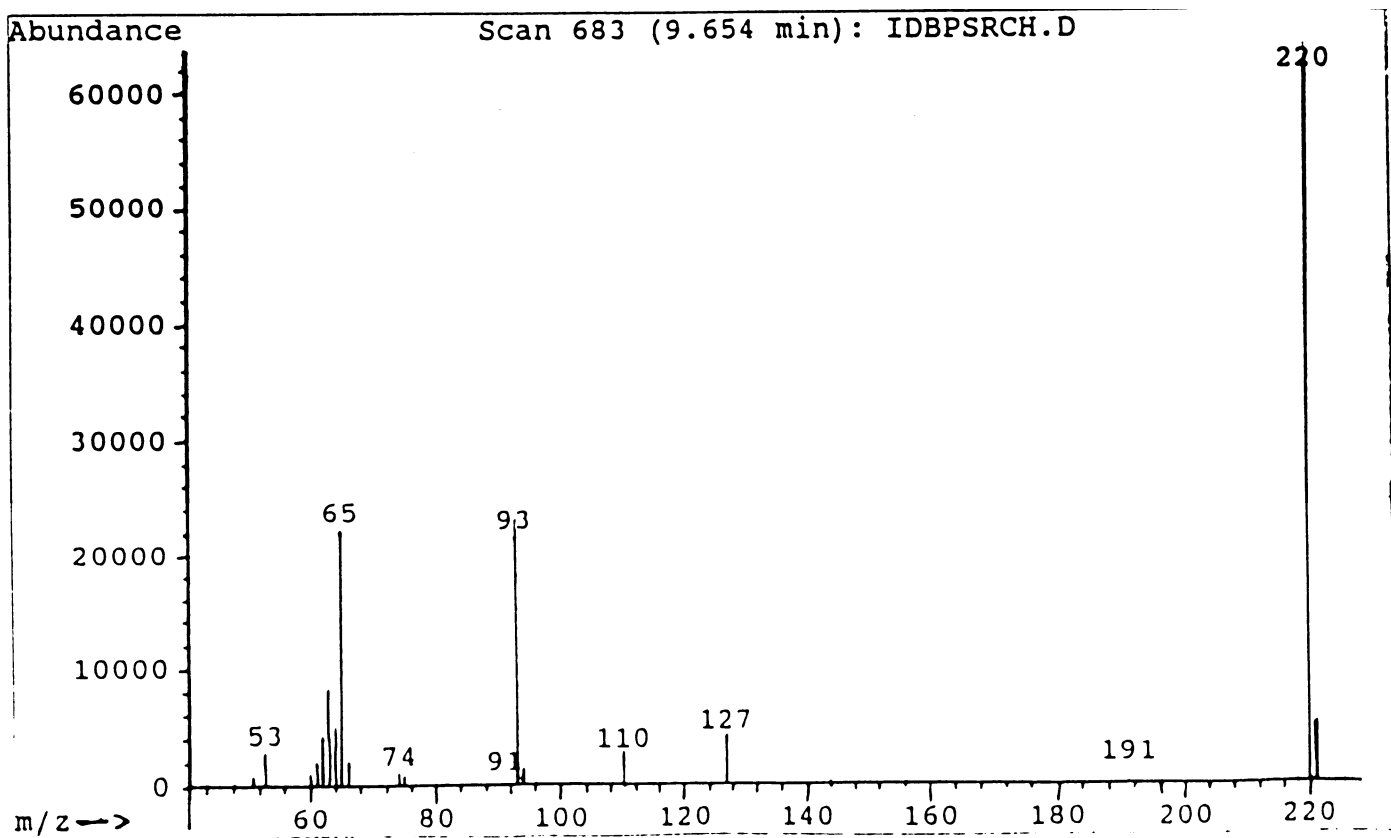


Figure 25. Mass Spectrum for 4-Iodophenol, MW 220 amu

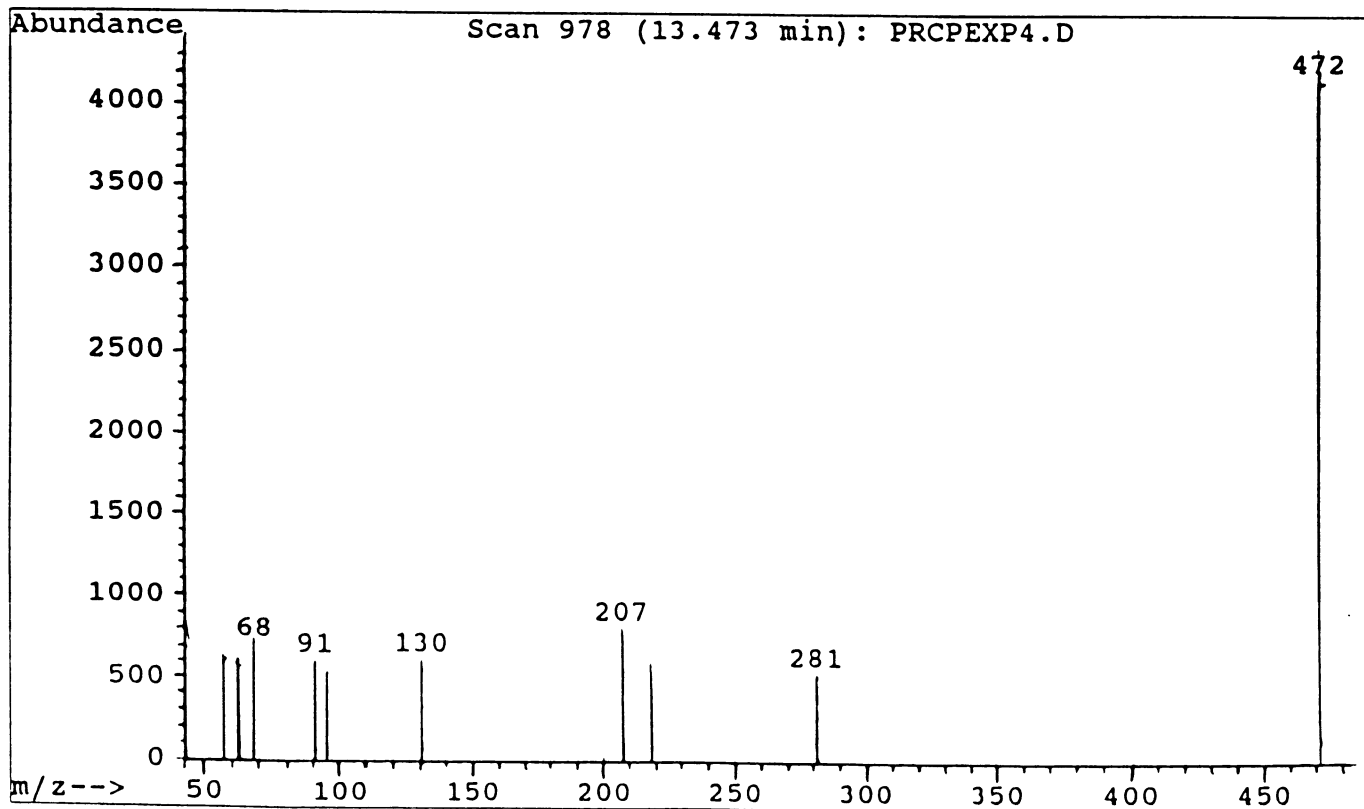
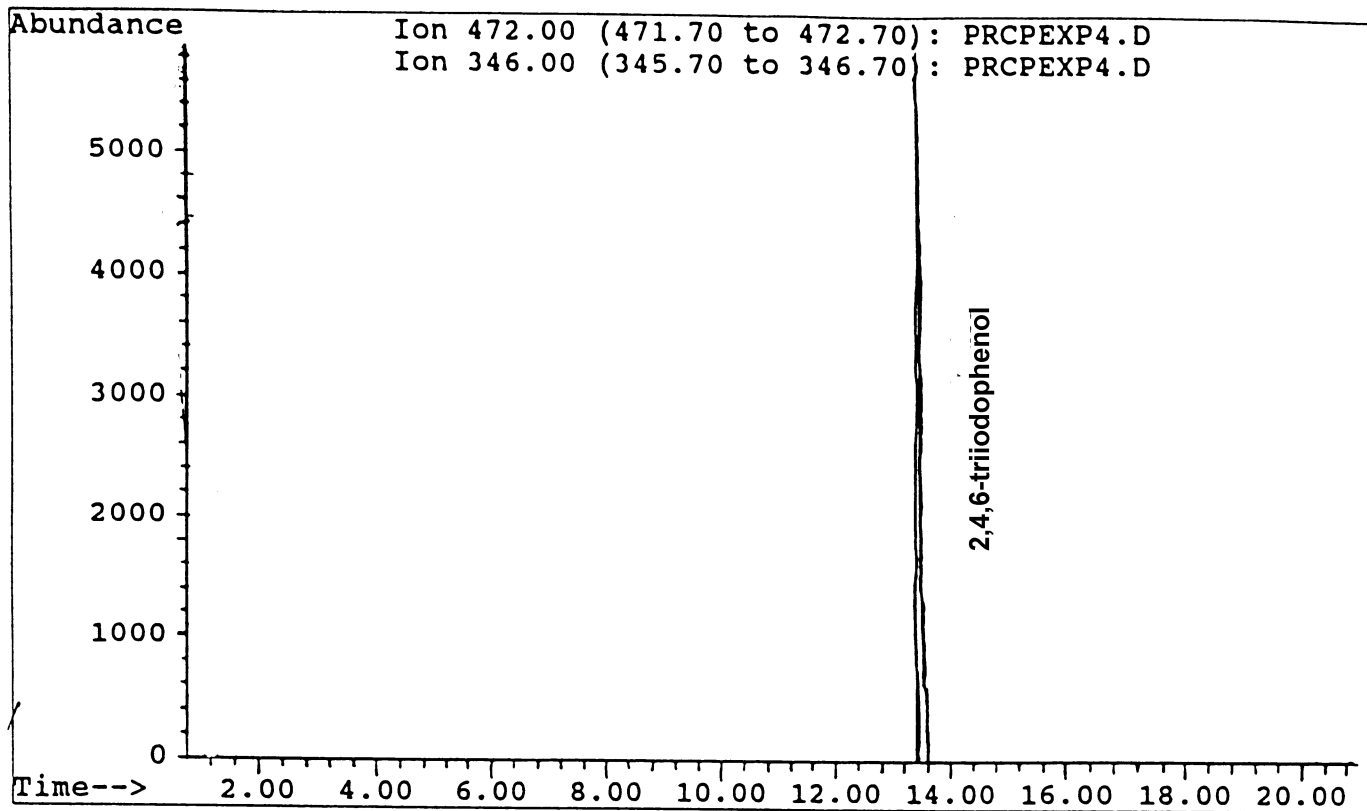


Figure 26. Mass Spectrum for 2,4,6-triiodophenol-Condition 4

A summary of the number and type types of IDBPs formed under the different ratios of I<sub>2</sub>: phenol is provided in Table 10.

Table 10. Types of IDBPs Formed under the different ratios of iodine to phenol

Initial I <sub>2</sub> : phenol mass ratio	Number of IDBPs detected by HPLC at 1 hr, 1 day, and 32 days
2:1	2-iodophenol <sup>1</sup> , 4-iodophenol <sup>2</sup> diiodophenol <sup>3</sup> , 2,4,6-triiodophenol <sup>4</sup>
10:1	diiodophenol , 2,4,6-triiodophenol
0.2:1	2-iodophenol
1:1	2-iodophenol , 4-iodophenol diiodophenol, 2,4,6-triiodophenol

- 1) 2-iodophenol was detected by HPLC and quantitated by comparing to 2-iodophenol standards
- 2) 4-iodophenol was detected by HPLC and quantitated by comparing to 2-iodophenol standards
- 3) diiodophenols were detected by HPLC and their identity confirmed by GC/MS. Two isomers were detected by could not be identified because pure standards are not commercially available
- 4) 2,4,6-triiodophenol was detected either visually by presence of white precipitate and/or by GC/MS

The minimum detection limit utilized in the analytical determination of the phenolic compounds by HPLC method was approximately at 0.5 mg/L. This was the lowest standard analyzed and detected for each compound which was commercially available in pure form. The standard curves developed for quantitative analysis of each compound are included in Appendix 1.



## ORGNOLEPTIC EVALUATION

FPA results on the odor analysis of the phenol and mono-iodophenols are summarized in Tables 11 to 13. Weber-Fechner Plots for each of the phenolic compounds are depicted in Figures 27 to 29.

Table 11. Summary of FPA Data on Phenol

Concentration (mg/L)	FPA Intensity	Odor Descriptor
3.75	1.3	Sweet, Chemical, Solvent, Phenolic
4.00	1.4	
7.50	2.4	
10.0	3.67	
15.0	6.17	

Table 12. Summary of FPA Data on 2-iodophenol

Concentration ( $\mu\text{g/L}$ )	FPA Intensity	Odor Descriptors
0.5	1.7	Medicinal, Stale, Phenol, Sweet, Iodophenol, Acidic, Pungent, Chemical
2	4.3	
5	4.4	
10	4.5	
15	4.5	
25	4.3	
50	4.8	
100	6.0	

Table 13. Summary of FPA Data on 4-iodophenol

Concentration (mg/L)	FPA Intensity	Odor Descriptors
0.03	-	Odor free
0.5	-	
1	1.5	Iodophenol, Medicinal, Stale, Phenol, Burnt rubber
3	5.17	
5	4.75	

As depicted by the FPA data and the Weber-Fechner (WF) plot, of the three phenolic compounds, 2-iodophenol has the strongest organoleptic properties. The odor threshold concentration (the concentration at which the average odor intensity is 2) for phenol was calculated to be at 5 mg/L concentration. The coefficient of correlation ( $r^2$ ) calculated from the WF plot is 0.905 for phenol (Figure 27). The most common odor descriptors used by the panelists to describe phenol were "chemical" and "phenolic".

The WF plot for 2-iodophenol (Figure 27) shows a  $r^2$  value of 0.7495. Based on the WF plot the odor threshold level for this compound was calculated to be approximately at 0.2  $\mu\text{g/L}$ . However, as indicated by the FPA intensity data in Table 12, the odor intensity levels detected by the panelists did not appear to be directly proportional to the concentration of the compound. The odor intensity levels perceived by the panelists increased by only 0.4 units when the concentrations of compound was increased from 5 to 50  $\mu\text{g/L}$ . However, a 1.2 unit increase in intensity level was achieved when a 100  $\mu\text{g/L}$  concentration of 2-iodophenol was evaluated. These data suggest that 2-iodophenol has strong odor characteristic, which can be approximately detected in concentrations ranging from 1-2  $\mu\text{g/L}$ , however, the intensity levels are not easily

distinguished with increase in concentrations. The FPA results on 2-iodophenol indicates that this compound does not follow the W-F model (Theimer, 1982) typically used for data exhibiting a dose-dependant response. Therefore, based on the FPA data evaluations, the true odor threshold level for 2-iodophenol occurs below 1  $\mu\text{g/L}$  concentration. The most common odor descriptors used by the panelists to describe this compound were “medicinal, iodophenol, acidic, and chemical”.

The W-F plot for 4-iodophenol (Figure 29) shows a  $r^2$  value of 0.9161 (correlation coefficient was calculated excluding the lowest data point), as shown on the graph. An odor threshold level of 1 mg/L was determined for this compound. The most common odor descriptors used by the panelists to describe this compound included “iodophenol” and “medicinal”.

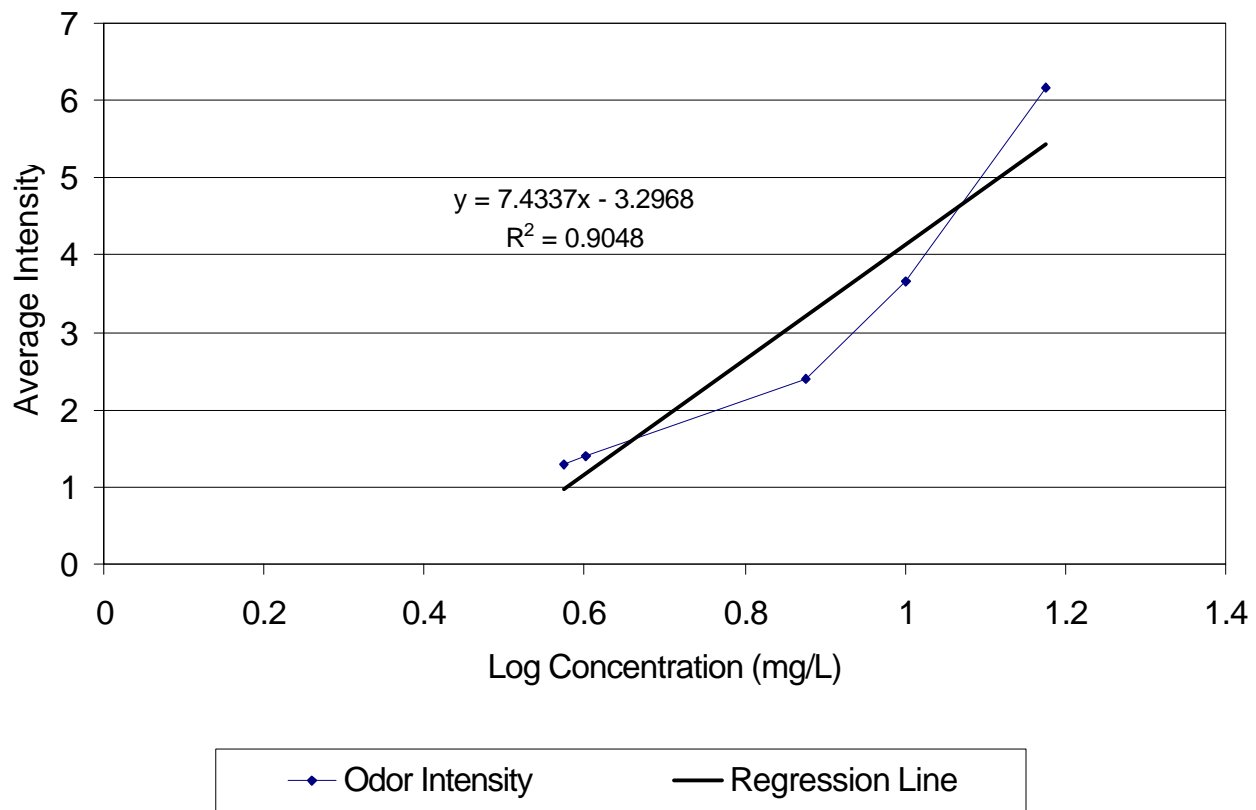


Figure 27. Weber-Fechner Plot for Phenol

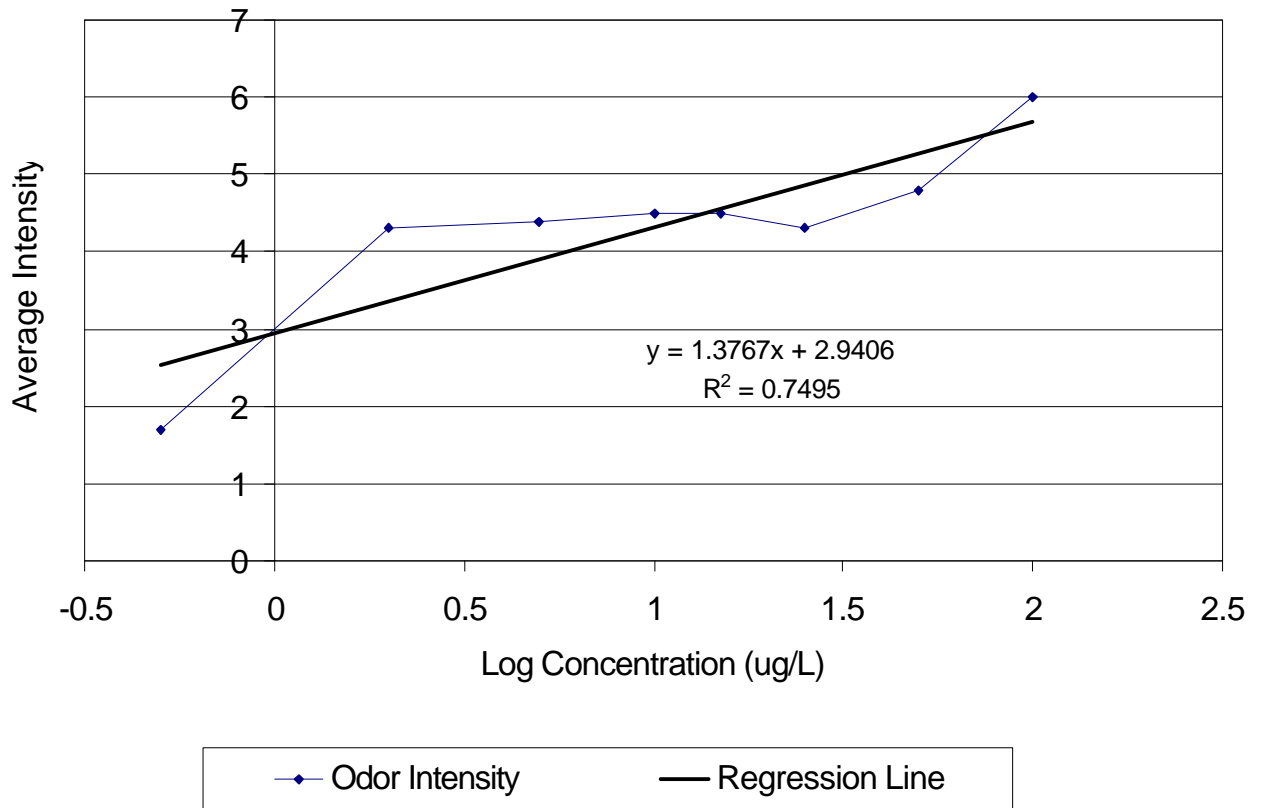


Figure 28. Weber-Fechner Plot for 2-iodophenol

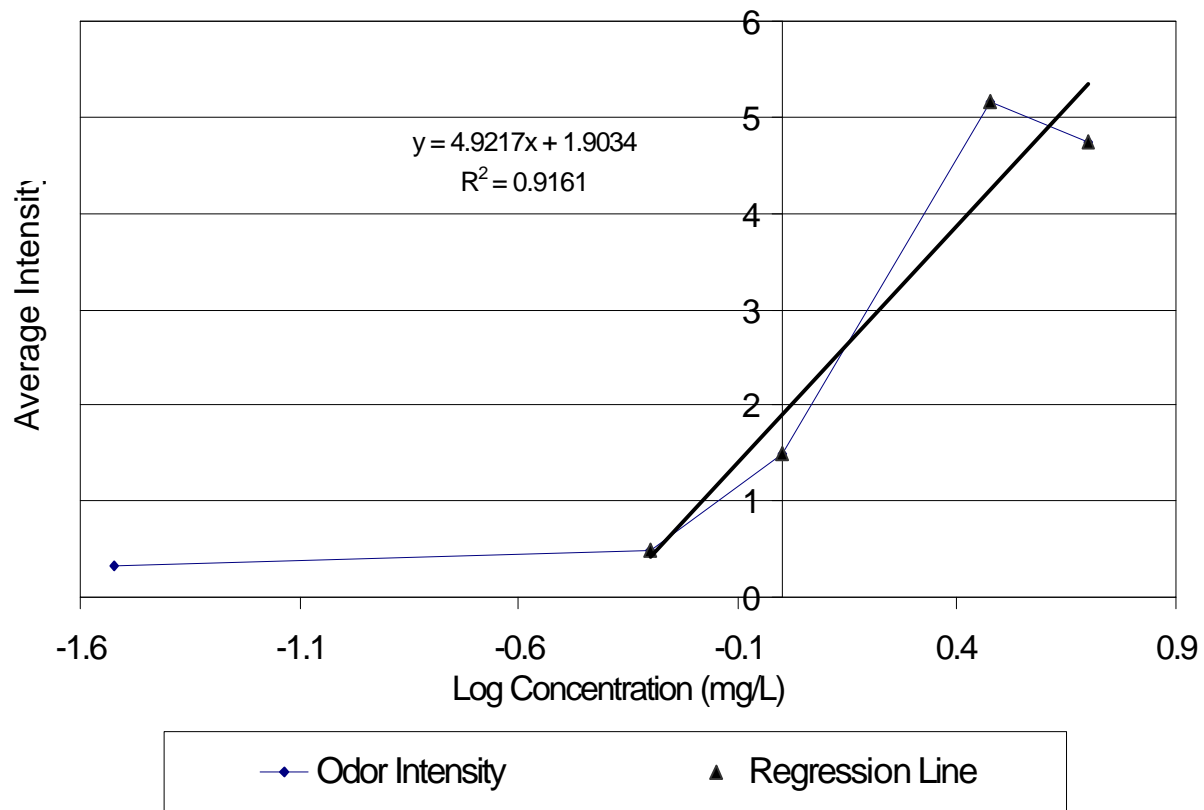


Figure 29. Weber-Fechner Plot for 4-iodophenol

## CHAPTER 5. DISCUSSION

### CHEMICAL ANALYSIS

Phenol proved to be readily reactive in the presence of iodine under all experimental conditions studied during this research. However, the degree of reactivity and number of IDBPs formed varied under different experimental conditions. In the presence of excess iodine (conditions 3 and 4, 10:1 I<sub>2</sub>: phenol ratio) the reaction appeared to proceed to near completion by conversion of all the initial phenol reactant concentrations into higher substituted iodinated phenols; the major IDBP identified as 2,4,6-triiodophenol by GC/MS. Under all experimental conditions, reaction by-products were formed within one hour of reaction initiation times. Comparable results were obtained with reactions conducted under acidic or basic conditions. However, it is expected that the reaction rate may be more rapid under basic conditions. This is likely to occur due to the presence of iodine in its more reactive form (HOI) in a basic solution (pH 8). At pH 8, 88% of iodine in solution is present in HOI form, compared to only 1% at pH 5 (White, 1992).

Based on the results of this study, iodination reaction of phenol is similar to that of chlorination reaction previously reported (Burttschell *et al.*, 1959). The reaction likely proceeds first with mono-substitution of 2 and 4 positions of the aromatic ring. Additional steps include the formation of 2, 4- and 2, 6-diiodophenol isomers. The diiodophenols are further iodinated to form 2, 4, 6-triiodophenol.

The study by Barkley *et al.*, (1993) showed that aqueous solutions of iodine and phenol at neutral pH yielded iodine-substituted phenols at noticeable concentrations after seven days reaction time. The phenolic compounds that were identified in this study included 2-iodo, 4-iodophenols, and diiodophenol isomers. According to another study conducted by Barkely *et al.*, (1992) comparative chlorination of phenol resulted in

formation of nine organic by-products compared to four reaction products in iodination reactions. This is expected, as iodine is less reactive than chlorine (March, 1997).

The number of IDBPs identified during this study ranged from one to five depending on the initial ratio of reactants in solution. The highest number of IDBPs (4 to 5) were formed when the initial ratios of reactants in solution consisted of 1:2 and 1:1 weight ratios of phenol to iodine. Under reaction conditions 5 and 6 where initial 5:1 weight ratios of phenol to iodine were reacted, 2-iodophenol was the only readily detectable by-product as indicated by HPLC analyses. This result can be expected based on the understanding of kinetics of phenol chlorination reactions (Lee, 1967). The initial product of phenol halogenation reaction includes mono-substituted phenols. In the case of iodination reactions, these include 2-iodo and 4-iodophenols. Further iodine substitutions on the aromatic ring occur from reaction of monoiodophenols with available iodine in solution. However, competing reactions occur in solution as both initial phenol reactant and iodine substituted phenols react with the free iodine in solution. It is speculated that under reaction condition 5 and 6 where phenol reactant concentration exceeds the iodine concentration by a factor of 5, phenol as a reactant more successfully competes with the iodinated by-products (2-iodophenol) in reacting with free iodine in solution; therefore, the primary by-product under conditions 5 and 6 (excess concentration of phenol with respect to iodine as a reactant) appear to be 2-iodophenol. Nevertheless, 4-iodophenol or higher substituted phenolic compounds may have been also formed in trace amounts, not detectable under the experimental conditions.

Table 14 provides a summary of relative amounts of reactants (phenol and iodine) remaining in solution after each reaction time and under each experimental condition. A review of these data shows that the phenol concentration remains relatively stable over the 1 hour to 32 day reaction period. However, a reduction in total iodine/iodide levels was observed between the 24-hour and 32 days reaction times. The iodine concentrations at 24-hours were reduced to non-detectable levels ( $< 0.1$  mg/L) under most experimental conditions. Detectable iodine concentrations were measured in reaction conditions 3, 4,



and 7; these reactions showed 91 percent to 98 percent reduction in iodine concentrations. At 24 hour reading, iodine concentrations in control samples ranged from 0.9 to 8.3 in 10 mg/L controls, and from 24.2 to 48 mg/L in 50 mg/L controls. In the controls, the lowest iodine levels (0.9 and 24.2 mg/L) were measured at high pH (8.0) level. This is expected as iodide species are the dominant forms at higher pH levels (White, 1992). As predicted, greater decrease in iodine concentrations was measured in reaction conditions with a lower, initial I<sub>2</sub>: phenol ratios. This is likely due to the presence of phenol in solution and reaction of iodine with phenol and incorporation of iodine (I) into phenol. The reduction in iodine levels will be associated with the formation of higher iodine substituted phenolic compounds in solution. However, based on the quantitative data on experimental controls a 25 to 39 percent reduction in total iodine/iodide is expected in the absence of any phenolic reaction, for the conversion of I<sub>2</sub> to I<sup>-</sup> because of spontaneous decay. Likewise, 0 to 16 percent reduction in phenol concentrations was observed in phenol experimental controls. Nevertheless, reduction in phenol and total iodine/iodide levels in reaction mixture coincided with the formation of reaction by-products.

Table 14. Iodine/Phenol Reaction Progress Summary

Experimental Condition (mass ratio) I <sub>2</sub> : phenol	Initial Reactant Conc. (mg/L)		% Mass Reactant Remaining in Solution after the Reaction					
	Phenol	Iodine	Phenol			Iodine		
			1 hr.	24 hrs.	32 days	1 hr.	24 hrs.	32 days
1 (2:1)	5	10	47%	49%	35%		33%	11%
2 (2:1)	5	10	44%	48%	36%		40%	23%
3 (10:1)	5	50	ND	ND	ND		74%	53%
4 (10:1)	5	50	ND	ND	ND		69%	38%
5 (0.2:1)	50	10	93%	91%	94%		12%	8%
6 (0.2:1)	50	10	93%	92%	94%		8%	3%
7 (1:1)	50	50	69%	75%	72%		31%	9%
8 (1:1)	50	50	71%	69%	70%		26%	20%
Iodine controls (mg/L)								
10 pH=5.5		10					109%	75%
10 pH=8.0		10					106%	65%
50 pH=5.5		50					102%	61%
50 pH=8.0		50					100%	65%
Phenol controls (mg/L)								
5 pH=5.5	5		104%	104%	84%			
5 pH=8.0	5		102%	104%	84%			
50 pH=5.5	50		103%	103%	100%			
50 pH=8.0	50		101%	100%	94%			

Observations made during experimental studies suggested that under experimental condition 3 and 4 where excess iodine was present in solution relative to phenol (4:1 molar ratio), the major IDBP was 2,4,6-triiodophenol, this was evident by the formation of a white precipitate in 2 reaction mixtures under conditions 3 and 4. The white precipitate was shown to consist of 2,4,6-triiodophenol by GC/MS analysis.

## **ORGANOLEPTIC EVALUATION**

The FPA data on phenol and mono-substituted phenols suggest that 2-iodophenol has the strongest organoleptic properties. 2-iodophenol was detected by the panelists at  $\mu\text{g/L}$  concentrations, in contrast to 4-iodophenol and phenol, which were detected at  $\text{mg/L}$  concentrations. The odor characteristics of the iodinated phenols are comparable to those of chlorinated phenols as studied by Burttschell *et al.*, (1959) and Lee (1967). According to these studies a 2-chlorophenol, 2, 4, dichlorophenol, and 2, 6-dichlorophenol are the compounds with the strongest organoleptic properties. The odor threshold concentration for 2-chlorophenol was determined to be at 2 to 3  $\text{mg/L}$ . These studies also demonstrated the importance of chlorine-to-phenol ratio in the formation of chlorine disinfection by-products, which in turn determines the odor characteristics of the water.

The Weber-Fechner plot on phenol showed a good correlation ( $r^2=0.91$ ) between the phenol concentrations and the odor intensity levels identified by the panelists. Odor descriptors used by the panelists remained unchanged with different concentrations of phenol. The "chemical" and "phenolic" descriptors used by this panel have been previously reported (Bruchet *et al*, 1989). Although the Weber-Fechner Plots on mono-iodophenols did not form an ideal correlation plot, the data provide a good representation of the odor characteristics of the compounds. Clearly, 2-iodophenol was the more odorous of the two moniodophenols. The Weber-Fechner Plot pattern on 2-iodophenol

shows that the odor intensity levels did not change significantly with an increase in concentration ranging from 2 to 50  $\mu\text{g/L}$ . However, characteristic odors were detected at 0.5  $\mu\text{g/L}$  concentration. The odor threshold level occurred between 0.5 to 1  $\mu\text{g/L}$ . This value is comparable with that of 2-chlorophenol reported by Burttschell *et al.*, (1959). The most common odor descriptors used by the panelists were "medicinal", "chemical", and "iodophenol". The FPA data suggested that the odor characteristic of iodophenol was recognized by the panelists, however, in the presence of iodine or phenol the odor characteristic specific of iodophenols may not be distinguishable.

## CHAPTER 6. SUMMARY AND CONCLUSIONS

The results of this study showed that phenol is readily reactive in the presence of iodine at both acidic and basic pH values. The formation of several IDBPs is expected from the iodination of phenol in dilute aqueous solutions. Phenol is among the organic precursor compounds present in wastewater for recycling on the Space Station. Phenol may react with iodine during initial iodination of the wastewater prior to recycling. Phenol may even pass through the treatment system associated with the NASA potable water treatment system.

One of the major problems associated with disinfection of drinking water supplies containing organic compounds is the potential for the formation of DBPs. In the case of phenol, additional problems may be associated with the increase in iodophenolic tastes and odors in the treated water.

Conclusions concerning the flavor profile analysis and generation of disinfection by-products associated with iodination of phenol in spacecraft drinking water are as follows:

- ◆ The iodination reaction of phenol could be similar to that of chlorination reactions previously reported in the literature. The halogenation reaction proceeds first with mono substitution of 2 and 4 positions on the aromatic ring. Additional substitutions on the aromatic ring will likely occur following the formation of mono substituted phenols. Iodination reactions of phenol occur rapidly (within one hour) and the associated IDBPs remain stable, at least, up to 32 days.
- ◆ Iodination of phenol leads to formation of highly odorous disinfection by-products. Particularly, 2-iodophenol is the most odorous by-product associated with these reactions. Due to their strong organoleptic properties, odor evaluations of

iodophenols and other IDBPs may provide a useful supplementary tool in assessment of water quality aboard the Space Station.

- ◆ Iodophenols have much lower OTC values than phenol; the OTC values for iodophenols are comparable to those of chlorophenolic compounds. The iodophenolic odors were most commonly described as “medicinal”.
- ◆ Iodine which will be present at 1-4 mg/L concentrations in potable spacecraft water will likely mask or interfere with the use of odor analysis to detect iodophenols as both iodine and iodophenols have medicinal odors.
- ◆ The formation of disinfection by-products associated with phenol can be significantly minimized by reduction in concentration of phenol in NASA water purification system prior to iodination. In addition, increased iodine residuals relative to concentration of phenol present in the system can minimize the formation of phenolic IDBPs in drinking water. However, higher iodine residuals will likely effect the organoleptic properties of the drinking water.
- ◆ The major determining factor in the formation of IDBPs associated with phenol, is the initial ratio of iodine to phenol present in the water. This determines the numbers and quantities of IDBPs formed in solution. Higher I<sub>2</sub>:phenol ratios result in lower residual phenol concentrations and more highly substituted iodophenols. Lower I<sub>2</sub>:phenol ratios result in higher concentrations of monoiodophenols and lower amounts of di- and tri- substituted phenols compared to higher I<sub>2</sub>: phenol ratios.
- ◆ The pH level for the produced water from the spacecraft water purification system is expected to be in the range of 6 to 8.5; at this pH range iodination of phenol should

occur. Phenol iodination reactions occur rapidly (nearly complete within one hour) at both pH 5.5 and pH 8 levels and the reactions are pH independent.

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## **APPENDIX 1: STANDARD CURVES**

### HPLC Standard Curve for Phenol

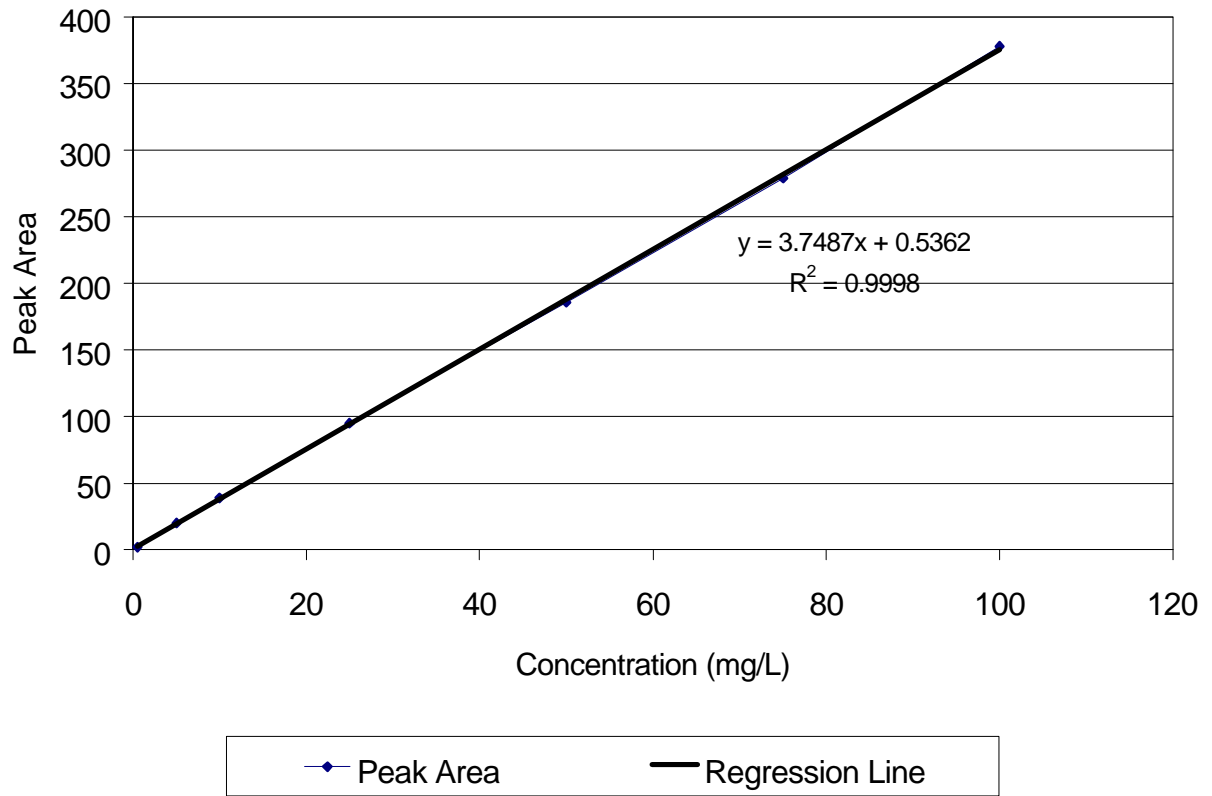


Figure 1.1



HPLC Standard Curve for 2-iodophenol

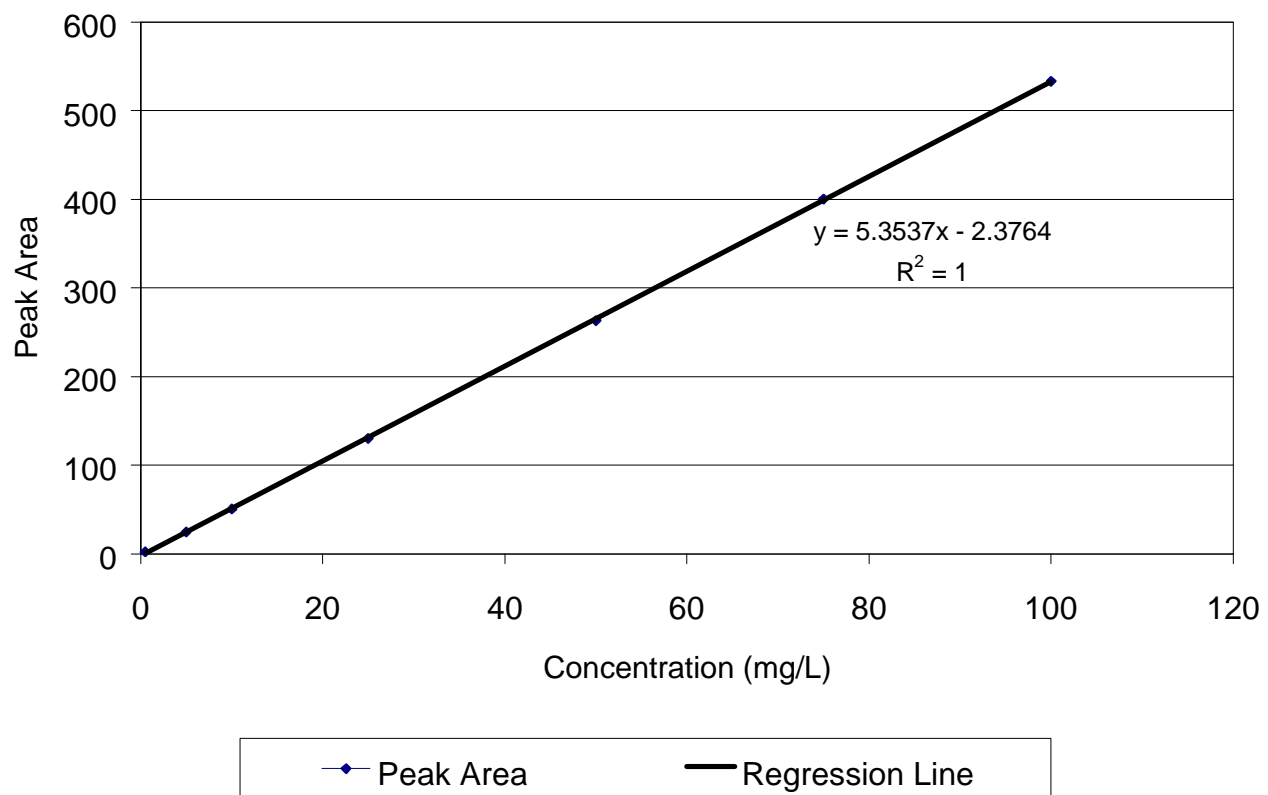


Figure 1.2

HPLC Standard Curve for 4-iodophenol

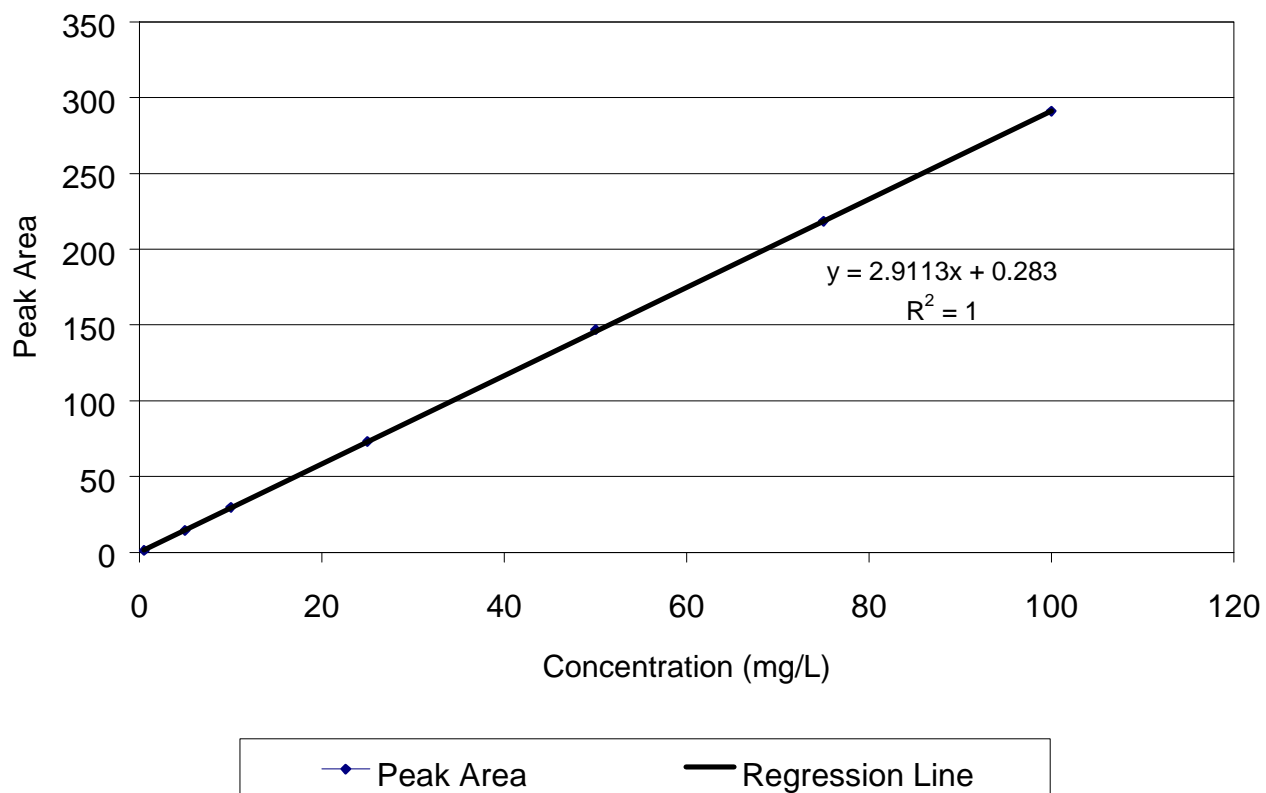


Figure 1.3

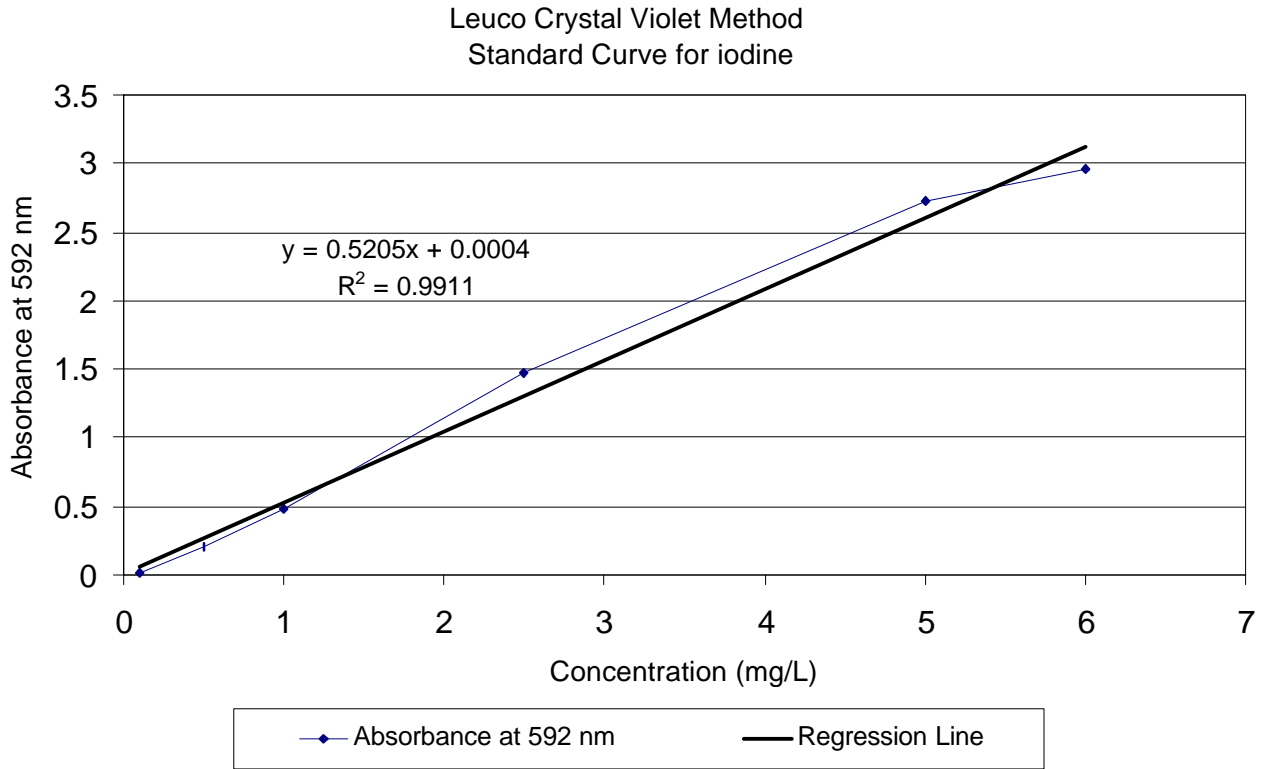


Figure 1.4

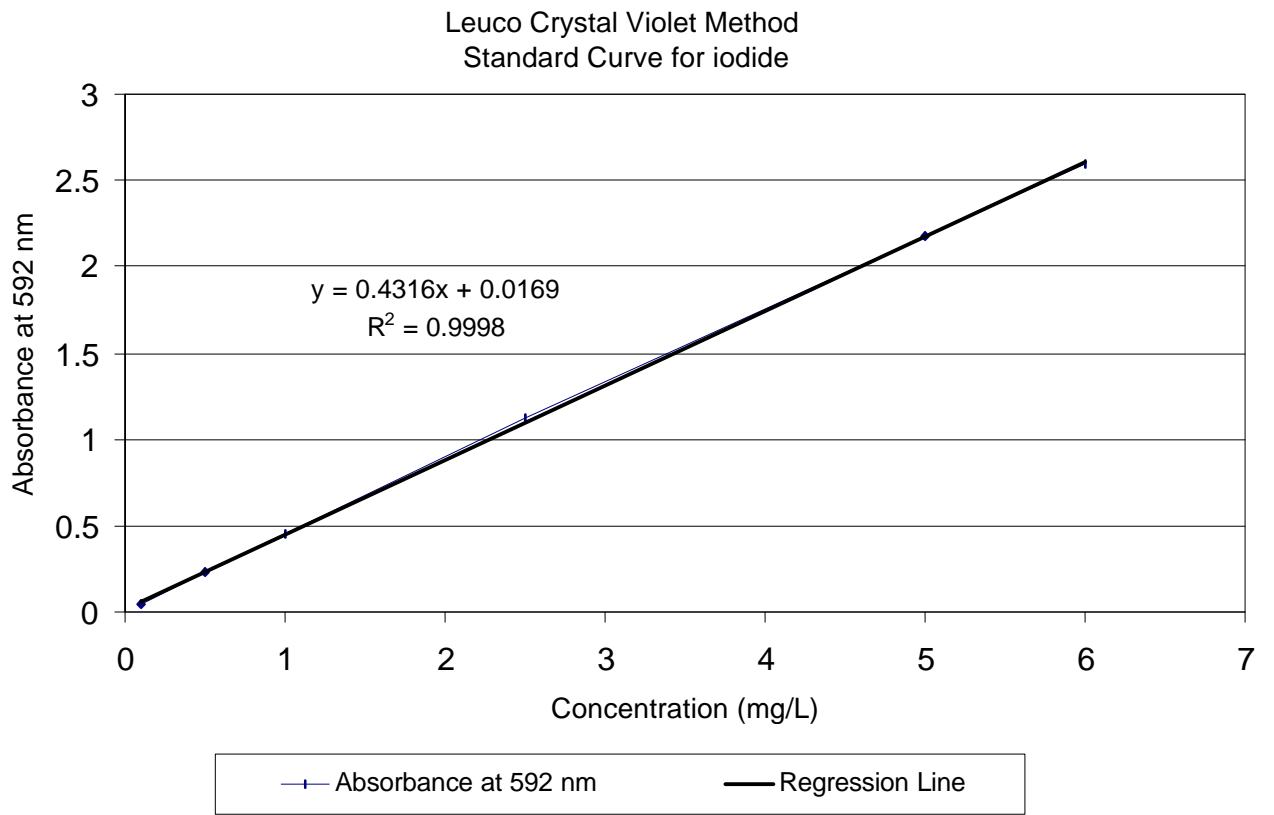


Figure 1.5

**APPENDIX 2: Data for Iodine, Total Iodine/Iodide, Phenol, and MonoIodophenol  
Concentrations for Series 2 Experiments for Iodination of Phenol at Acid and Basic  
pH Values**

Figure 2.1 Iodine and Total Iodine/Iodide Concentrations in Reactions  
for Experiment series 2 for Iodination of Phenol

Initial Conditions				Measured Concentrations (mg/L)					
Condi- tion	pH	Reactants		Iodine <sup>1</sup>	Total I <sub>2</sub> /I <sup>-</sup>	1 Day		32 Days	
		I <sub>2</sub>	Phenol			pH	Iodine	Total I <sub>2</sub> /I <sup>-</sup>	pH
1	5.5	10	5	-	-	-	ND**	0.9	-
2	8.0	10	5	-	-	-	ND	1.9	-
3	5.5	50	5	-	-	-	2.4	25.2	-
4	8.0	50	5	-	-	-	ND	18.6	-
5	5.5	10	50	-	-	-	ND	0.4	-
6	8.0	10	50	-	-	-	ND	0.6	-
7	5.5	50	50	-	-	-	ND	5.4	-
8	8.0	50	50	-	-	-	ND	10.6	-
Check Standards (mg/L)									
2.5		-*	-	-	-	-	2.6	2.4	-
6.0		-	-	-	-	-	5.8	5.6	-

(1) Iodine concentrations include I<sub>2</sub> and HOI :

(2) Total Iodine/Iodide concentrations include I<sub>2</sub>, HOI, I<sup>-</sup>

\* No measurements were taken

\*\* ND = Not Detectable at minimum detection limit of 0.1 mg/L

Figure 2.2 HPLC Quantitative Data on Iodine-Phenol Disinfection By-Products for series 2 Experiments

Experimental Condition	Concentration mg/L											
	Phenol				2-iodophenol				4-iodophenol			
	1 hr.	1 day	10 days	30 days	1 hr.	1 day	10 days	30 days	1 hr.	1 day	10 days	30 days
1	2.4	2.4	2.2	2.0	4.5	4.1	3.9	3.6	ND	ND	ND	ND
2	2.2	2.4	2.3	2.2	3.8	3.7	3.6	3.6	ND	ND	ND	ND
3	ND*	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
4	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
5	49.1	45.0	45.0	44.9	7.5	7.5	6.4	5.5	ND	ND	ND	ND
6	49.6	45.1	45.2	45.4	7.2	7.3	7.4	7.4	ND	ND	ND	ND
7	36.8	36.5	36.4	35.1	27.4	27.9	28.0	28.7	4.5	4.4	5.0	5.2
8	37.1	36.8	36.5	36.1	27.9	28.4	28.5	28.8	4.6	5.4	5.4	5.6
Check standards <sup>(1)</sup>												
5 mg/L	5.0	5.5	4.7	4.9	5.1	4.3	4.7	5.1	4.9	4.8	5.4	5.1
50 mg/L	50.1	51.2	50.7	49.0	49.8	49.9	50.1	50.8	51.2	52.6	51.1	50.5
Controls												
5 mg/L pH 5.5	5.1	5.1	4.9	4.8	-	-	-	-	-	-	-	-
5 mg/L pH 8.0	5.0	5.1	4.9	4.7	-	-	-	-	-	-	-	-
50 mg/L pH 5.5	52.5	52.2	50.8	50.1	-	-	-	-	-	-	-	-
50 mg/L pH 8.0	52.6	52.1	49.8	47.9	-	-	-	-	-	-	-	-

\* ND = Not detectable at Minimum Detection Limit of 0.5 mg/L.

(1) Check standard were included in each analytical run to ensure acceptable method performance

## VITA

The author was born in March of 1968 in Tehran, Iran. She completed her high school education in the United States and received her B.S. degree in Biology from Radford University, Radford, Virginia, in 1992. She continued a professional career in environmental and biological field while completing her M.S. degree in Environmental Sciences and Engineering at Virginia Tech. Her research interests and areas of expertise include: drinking water quality including chemical, microbiological, and organoleptic properties and wastewater toxicity assessment including biological monitoring and toxicity reduction evaluations.