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Reactions of Chlorine and Some of Its Oxygen Derivatives with Phenol

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REACTIONS OF CHLORINE AND SOME OF ITS
OXYGEN DERIVATIVES WITH PHENOL

by

Lizhuo Zhang

A Thesis
Submitted to the
Faculty of The Graduate College
in partial fulfillment of the
requirements for the
Degree of Master of Arts
Department of Chemistry

Western Michigan University
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Lizhuo Zhang

REACTIONS OF CHLORINE AND SOME OF ITS OXYGEN DERIVATIVES WITH PHENOL

Lizhuo Zhang, M.A.

Western Michigan University, 1996

Chlorine is widely used in industry. It is also the most commonly used disinfectant in water treatment plants. Since the amount of chlorine used is increasing each year, environmental and health concerns arise due to its reactivity with various of organic compounds. Many chlorinated organic compounds are toxic and as a result other non-chlorinating compounds, such as chlorine dioxide, might be potential substitutes in the future, especially in water treatment plants.

Previous studies have indicated that chlorinated organic compounds are not formed when chlorine dioxide is used as a disinfectant. Furthermore no reaction occurs between chlorite and phenol in the absence of activated carbon. A careful investigation of the reactions of chlorine, chlorine dioxide and chlorite with phenol was made in this study. UV/VIS absorption spectrometry, Gas Chromatography/Mass Spectroscopy and High Performance Liquid Chromatography were extensively used in this study for separation and identification purposes.

Results show that fewer chlorinated phenolic compounds are formed when phenol is treated with chlorine dioxide relative to chlorine. Also UV/VIS and HPLC results indicate that chlorite does react with phenol in the absence of activated carbon.

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INTRODUCTION

Background

Chlorine has been widely used in industry since the early 1930's. The annual consumption of chlorine in the world is 37.4 million metric tons. Approximately 11 million tons, worth \$72 billion, were used in the United States in 1990. About 25% of the chlorine was used to make PVC plastic, while the pulp and paper industry was the second largest user, consuming about 14% of the total. Chlorine is also the most commonly used disinfectant in the water treatment plants consuming approximately 5% of the annual chlorine production. Chlorine is so active that it can react with a variety of organic compounds. It is estimated that there are more than 15,000 synthetically-produced chlorinated compounds that are used in industry and more than 2,000 naturally-occurring chlorinated compounds found (1). Unfortunately, chlorine-based pollutants have side effects on both human and animal subjects such as memory problems, stunted growth and cancer (2). An eventual ban of the most troublesome chlorine-based chemicals has already been proposed (3). Therefore, alternatives are expected to be found and used in industry, and especially in the water treatment plants in the future.

Chlorine dioxide is one of the prospective alternatives. It is used as a bleach in the paper industry. In some European countries, it is often used as a source of disinfectant to protect drinking water distribution systems from microbiological

recontamination and fouling. The first known use of chlorine dioxide as a water treatment process in the United States occurred at Niagara Falls, New York in 1944 (4). Chlorine dioxide is preferred in the water treatment process because it does not lead to the formation of trihalomethanes (THM), which are carcinogens. The taste of water is also greatly improved (5). Chlorine dioxide has higher disinfection efficiency than chlorine, especially against viruses (6). Its disinfection efficiency is independent of pH and also the presence of ammonia (7). However, there are limitations on the use of chlorine dioxide because it is reduced to chlorite, which is considered to be a hemotoxin (8). Studies have shown that chlorite is a potent chemical species for causing signs of red blood cell oxidative stress in experimental animals (10, 11). Consequently typical dosages for drinking water treatment are in the range of 0.04-0.4 mg/l range (4). At such low concentrations, the lifetime of aqueous chlorine dioxide is highly dependent on the quality of water (9). Therefore, chlorine dioxide is generally applied when the raw water quality is comparably good and often applied following a preoxidation stage.

Phenol and its derivatives are abundant in nature. The main natural source of phenol is from the decomposition of humic substances, such as plant materials. Man-made sources are from the coal, gas and petroleum industrial wastes. The determination of the phenolic content in drinking water and river water samples has been carried out for decades by using distillation, extraction, titration and various other analytical methods. However, instrumental methods are now the most extensively used due to their simplicity, sensitivity and selectivity (12).

Objective

Previous investigations have been done on the reactions between chlorine dioxide with organic compounds, such as humic materials, amines and amino acids, olefines, hydrocarbons, alcohols, carbonyl compounds and carboxylic acids (13). Even though some researchers have investigated the kinetics of some reactions between chlorine dioxide and phenolic compounds (9), there still has been no thorough comparison of the specific reaction products from chlorine and chlorine dioxide with phenol. Therefore, the purpose of this study was to compare chlorine and chlorine dioxide as water treatment disinfectants based upon the reaction products with phenol. An understanding of what reaction products are formed under certain conditions might be valuable in selecting chlorine or chlorine dioxide as a disinfectant.

While it is known that chlorite is a reduction product of chlorine dioxide, there has been little work done on the interaction of chlorite with phenol under normal conditions (neutral pH, absence of activated carbon, etc.). The effect of activated carbon on phenolic compounds and chlorite have been reported (14, 15). It is difficult to detect the interaction between chlorite and phenol since the acid disproportionation of chlorite produces chlorine dioxide. Phenol, chlorite and chlorine dioxide exhibit overlapping spectra in the ultraviolet region, thus making it difficult to follow the progress of the reaction. Therefore, another goal of this study is to investigate the interaction between chlorite and phenol and confirming that the reaction occurs as well as determining the reaction products.

Proposed Methodology

A great many procedures and methods have been developed for both qualitative and quantitative analysis of phenols. Among these are spectroscopic techniques (16), paper electrophoresis, thin-layer chromatography, TLC (17), gas chromatography, GC (18), gas chromatography-mass spectrometry, GC/MS (19), and high-performance liquid chromatography HPLC (20, 21). Several analysis strategies have been developed ranging from simple to more complicated procedures involving preconcentration and derivatization reactions prior to chromatographic analysis.

In this work, GC/MS was chosen for the analyses for phenolic compounds and reaction products from reactions with chlorine and chlorine dioxide. A GC/MS system with an electron impact source and a quadrupole mass filter was employed for most analyses of organic species. While all reactions were carried out in aqueous solution, organic reaction products were extracted using methylene chloride prior to injection into the GC/MS. The extraction efficiency for phenol was determined to be approximately 95% for two successive extractions with equal volumes of methylene chloride.

Low concentrations and low volatility products result from the phenol-chlorite reaction. Preconcentration using HPLC followed by derivatization with pentafluorobenzyl bromide were used as preliminary steps prior to analysis by GC/MS.

The analysis of chlorine, chlorine dioxide, and chlorite ion could be carried out using UV absorption spectrophotometry since they all exhibit an ultraviolet spectrum. Chlorine exhibits two pH dependent bands, one at 233-236 nm ($\epsilon \approx 78$) and another one

in the range from 315-325 nm ($\epsilon \approx 1.6$). Chlorine dioxide and chlorite ion exhibit bands at 358 nm ($\epsilon \approx 1090$) and at 262 nm ($\epsilon \approx 160$) respectively. Direct absorbance measurements for these compounds are adequate for moderately low concentrations but often are inadequate at trace levels due to the relatively low molar absorptivities. Furthermore the bands of these compounds tend to strongly overlap with one another as well as with the spectra of phenol and many of its derivatives. A more sensitive method for the determination of chlorine, chlorine dioxide, and chlorite has been proposed by Howell et.al. (22) which is an indirect differential method employing the tris-1,10-phenanthroline iron (II) complex which absorbs in the visible region ($\lambda = 510$ nm) and exhibits effective molar absorptivities of 22,200, 55,500, and 44,400 L•mole⁻¹•cm⁻¹ for chlorine, chlorine dioxide, and chlorite ion respectively. Mixtures of chlorine and chlorine dioxide can also be accommodated using this procedure by pretreating the sample with malonic acid which reacts to remove chlorine (23). The analysis of mixtures of chlorite and chlorine are of no consequence since these two compounds are incompatible and react to form chlorine dioxide and chloride ion. The analysis of mixtures of chlorine dioxide and chlorite ion are particularly difficult and cannot be made by this procedure.

In carrying out any reactions or analyses of chlorine, chlorine dioxide, and chlorite ion, it must be kept in mind that each species undergoes disproportionation reactions depending on the solution pH. For example chlorine solutions tend to disproportionate to hypochlorite and chloride at moderately high pH and thus to uniquely study chlorine reactions, low pH conditions (pH < 4) must be maintained. Chlorine dioxide solutions

also tend to disproportionate at high pH ultimately yielding chlorate and chloride ions. Consequently chlorine dioxide solutions must be kept at relatively low pH ($\text{pH} < 6$). Chlorite on the other hand undergoes acid disproportionation at low pH producing chlorine dioxide and chlorine. The chlorine produced will further react with any unreacted chlorite ion to produce more chlorine dioxide and chloride ion. Consequently reaction conditions for studying and analyzing chlorite ions must be such as to maintain the pH at moderately high values ($\text{pH} \geq 7$).

REACTION OF CHLORINE WITH PHENOL

Chlorinated water which contains phenol causes bad taste and odor arising from chlorinated organic compounds. In order to study the effects of chlorine and chlorine dioxide on phenol, initially a careful investigation of the reaction products of the chlorine-phenol reaction was carried out. It is well recognized that aqueous chlorine can undergo a disproportionation reaction according to the following equation:



In order to minimize the effect from hypochlorite, the aqueous solutions should be kept at low pH in order to favor the reverse reaction. Two possible reaction types are exhibited by chlorine since it is a strong oxidizing agent as well as being a good chlorinating agent.

Apparatus

Gas chromatograph/Mass spectrometry (GC/MS): A Hewlett-Packard model 5890 gas chromatograph with a mass selective detector was used to identify the reaction products. The injector was set in the splitless mode and the injector temperature was set up at 210°C. The chromatography was done using a HP-5 (Hewlett-Packard 25m•0.2mm•0.33µm, crosslinked 5% Ph-Me silicone) capillary column. The column temperature was programmed from 40°C to 170°C at 15.0°C/min, ramped to 175°C at

0.2°C/min, and ramped to 290°C at 15.0°C/min. The parameters for the quadrupole mass spectrometer included electron impact (EI) ionization mode, transfer line temperature of 280°C, m/z range of 50.0 to 500.0, helium pressure 30 psi, head pressure 5 psi, and detector temperature of 225°C.

UV/VIS Spectrometer: Cary-14 (Olis modified) spectrometer was used with 1.1 nm effective bandwidth.

Reagents

1. Phosphate Buffer Solution, 0.05 molar (pH = 1.55): Mix 1.656 g sodium phosphate monobasic (Mallinckrodt Chemical Works, analytical purity) and 2.585 mL phosphoric acid (J.T. Baker Chemical Co., 95% purity) and dilute to 1 liter.

2. Chlorine Aqueous Stock Solution: The chlorine gas from the tank (AGA, 99.5% purity) is vigorously bubbled into ice cold 0.05 molar phosphate buffer for about 10 minutes. This solution is kept in an amber bottle and refrigerated at 0°C.

3. Starch Solution, 1% w/v: 1.0 g starch (J. T. Baker Chemical Co., ACS grade) in 100 ml distilled water. Boil for 5 minutes and keep the clear supernatant liquid after it is cooled to room temperature.

4. Sodium Thiosulfate Solution, 2.5 millimolar: 0.3981 g $\text{Na}_2\text{S}_2\text{O}_3$ anhydrous (J. T. Baker Chemical Co., ACS grade) with about 1.0 g NaOH in 1.00 L volumetric flask. Cool boiled distilled water is used for the preparation. Leave for overnight before use.

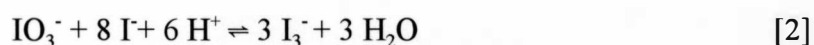
5. Potassium Iodate, 0.428 millimolar: Dissolve 0.0458 g KIO_3 (Spectrum, 99.4-

100.4% purity) with 10 ml concentrated HCl in 500-mL volumetric flask and dilute to volume.

6. Potassium Iodide (Mallinckrodt, USP grade).
7. Phenol (Matheson Coleman & Bell, ACS grade).
8. Methylene Chloride (Fisher Chemical, HPLC Grade).

Procedures

Standardization of Sodium Thiosulfate Solution: 15 ml 0.428 millimolar KIO_3 was mixed with excess KI (app. 1 g) and then was titrated with $\text{Na}_2\text{S}_2\text{O}_3$ until the solution became light yellow. Several drops of starch solution were added and a dark purple color appeared. Continue titration until the solution became colorless.



Standardization of Chlorine Solution: 25 ml Cl_2 stock solution was diluted with ice cold 0.1 molar sulfuric acid into 250 ml volumetric flask. Excess KI was dissolved in approximately 10 mL distilled water in Erlenmeyer flask and then 2.00 ml of diluted Cl_2 was added. This solution was titrated with standardized sodium thiosulfate solution in the same way as described in equation [3].



Calibration of Chlorine: The titrimetric method described above is tedious and time consuming. Aqueous chlorine exhibits two pH dependent absorbance maxima in the ultraviolet region (315-325 nm and 233-236 nm). At pH 1.20 (0.1 molar sulfuric acid), chlorine solutions exhibit an absorption maximum at 319 nm (Figure 1). A series of standard chlorine solutions were prepared as follows: Use previously calibrated class A (0°C) transfer pipets to deliver 2.00, 6.00, 10.00, 15.00 and 25.00 mL of the previously standardized chlorine stock solution to 25 mL volumetric flasks. Dilute to the mark with ice-cold 0.1 molar sulfuric acid solution. The solutions were subsequently measured at 319 nm vs. a 0.1 molar sulfuric acid reference. A 2.000-cm silica cell with a cap was used for the measurements to reduce the volatility loss of chlorine. The effective bandwidth was controlled at 1.1 nm. Thus, a calibration plot of the aqueous chlorine solutions was obtained in the range between 0.68 and 8.5 millimolar. The linear regression coefficient is 0.997, the slope is $73.7 \text{ (cm}\cdot\text{mol/l)}^{-1}$ and the intercept is -0.0326.

Reaction Mixtures: After the chlorine concentration was determined from its calibration plot, aliquots were mixed with phenol at different molar ratios. A pH 1.55 buffer solution is used in order to minimize chlorine disproportionation. The mixtures were kept in amber bottles at 0°C for 24 hours.

Extraction and Sample Preparation: Aqueous reaction mixtures were mixed with methylene chloride at volume ratio 8:1 (aqueous : organic) in separatory funnels. The organic phase was transferred into a Kaderuda-Danish (K-D) apparatus. Two extractions

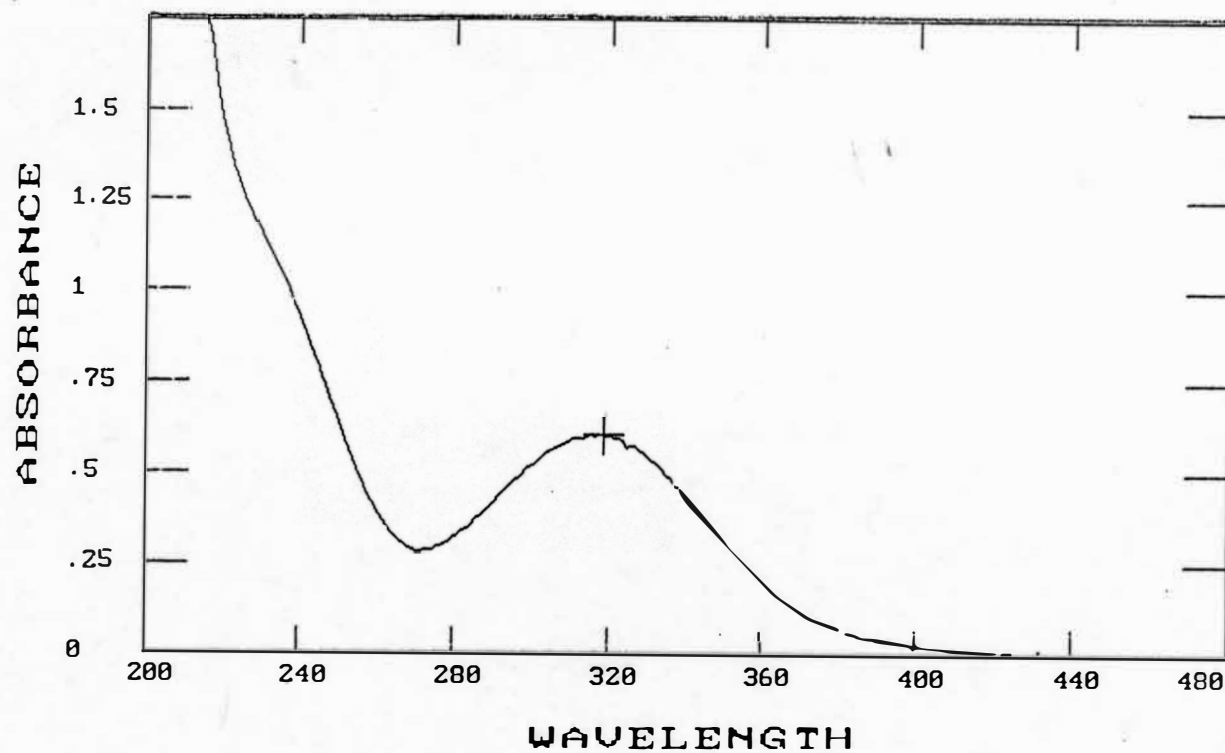


Figure 1. Spectrum of Aqueous Chlorine Solution (8.5 Millimolar Cl_2 in 0.1 Molar H_2SO_4).

were used in order to quantitatively extract the organic compounds. A steam bath was used to concentrate the methylene chloride extracts. Then a gentle stream of nitrogen gas was blown into the Mills tube to reduce the solvent to approximately 1 mL. This concentrated sample was injected into GC/MS for identification.

Results

Table 1 shows the major reaction products of chlorine with phenol that are identified by GC/MS using the Probability-Based Matching (PBM) algorithm.

Table 1

Reaction Products of Chlorine With Phenol at Different Phenol to Chlorine Molar Ratios (0.05 Molar Phosphate Buffer, pH = 1.55, at 0°C)

1:1	1:5	1:10
2,5-Cyclohexadiene-1,4-dione, 2,6-dichloro- (+++)	2,5-Cyclohexadiene-1,4-dione, 2,6-dichloro- (+++)	2,5-Cyclohexadiene-1,4-dione, 2,6-dichloro- (+++)
Phenol, 2,4,6-trichloro (++)	2,5-Cyclohexadiene-1,4-dione, 2-chloro- (+)	Ethane, 1,1,2,2-tetrachloro- (++)
Phenol, 2-chloro- (+)	Methane, trichloro- (+)	Methane, trichloro- (+)
Phenol, 3-chloro- (+)		2,5-Cyclohexadiene-1,4-dione, 2-chloro- (+)
Phenol, 2,6-dichloro- (+)		
2,5-Cyclohexadiene-1,4-dione, 2-chloro- (+)		

+++ : major product, >15% of total peak area (solvent peak included)

++ : minor product, 5-15% of total peak area (solvent peak included)

+ : trace, < 5% of total peak area (solvent peak included)

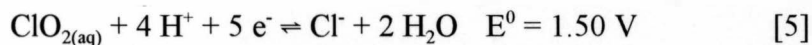
Chlorine can undergo either oxidation or substitution reactions. At low chlorine to phenol ratios, substitution seems to be a prevalent reaction although the principle species is a chlorinated oxidation product. At high chlorine to phenol ratios, a greater number of oxidation products are observed even though they tend to be chlorinated. The results from Table 1 tend to match what is predicted by theory (24). At low chlorine to phenol molar ratios, chlorinated phenols are observed, such as mono- and dichlorophenols. 2,5-Cyclohexadiene-1,4-dione is an oxidation product, even though it is chlorinated and is observed as a chlorinated form, 2-chloro-2,5-cyclohexadiene-1,4-dione. As we can see from the table, when the chlorine to phenol molar ratio is increased (5:1, 10:1), chlorinated oxidation products are the main products. Simple chlorination becomes less prevalent. However, higher levels of chlorination are also observed, such as trichloromethane and tetrachloroethane. Thus, not surprisingly there are many chlorinated organic compounds produced with chlorine treatment. These chlorinated organic compounds are often the source of bad odor and taste in drinking water, as well as being potential toxins and carcinogens.

One problem encountered in this part of the study was to differentiate 3-chlorophenol and 4-chlorophenol. Both have the same molecular weight, similar boiling points (3-chlorophenol, b.p. 214°C; 4-chlorophenol, b.p. 220°C) and consequently are not separated by GC. Mass spectrometry is also unable to differentiate these two compounds. There are two approaches to solve this problem. One is to use HPLC with gradient elution (25). The other method is to use GC/FTIR since 3-Chlorophenol and 4-

chlorophenol have different dipole moments, they can be differentiated by FTIR. This unpublished method has been developed by Howell and Brown (26). Since no serious effort was made to discriminate between these two isomers, neither of the preceding techniques were employed. Future work should consider employing these techniques.

REACTION OF CHLORINE DIOXIDE WITH PHENOL

Chlorine dioxide is a well recognized bleach in paper industries because of its high oxidizing efficiency on lignin and coupled organic matter without damaging cellulose or simple carbohydrates (27). It is commonly used in milling industries to remove carotenoid pigments from flour effectively while no degradation of vitamins occurs (28). Chlorine dioxide is a stronger oxidizing agent than chlorine due to its higher oxidation potential (29, 30).

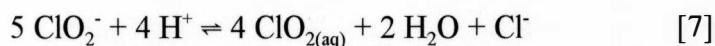


Chlorine dioxide is also used as a disinfectant in the water treatment plants (4). It is for this reason the reaction of chlorine dioxide with phenol was carefully examined.

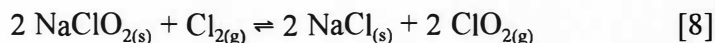
Apparatus

Generation of Chlorine Dioxide: There are numerous methods to generate chlorine dioxide (31). Some of the reactions that are used both in laboratory and industrial scales are as follows:

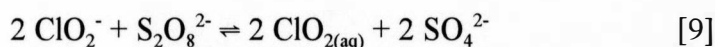
acidification of chlorite



oxidation of chlorite by chlorine



oxidation of chlorite by persulfate



There are other methods to generate chlorine dioxide (31), but like those listed above they often tend to produce impurities either from the original reaction agents or from the secondary reactions or both. An electrochemical method was used to generate chlorine dioxide free of contaminants and is as follows:

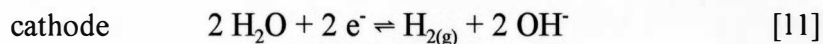
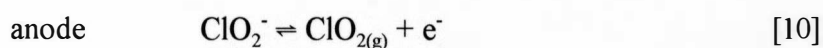


Figure 2 shows the generation apparatus used to produce chlorine dioxide solutions. The procedure is described by Howell (22). Instead of using 0.09 - 0.1 molar sulfuric acid to absorb chlorine dioxide, 0.1 molar (pH 6.00) ice-cold phosphate buffer solution was used to absorb the chlorine dioxide.

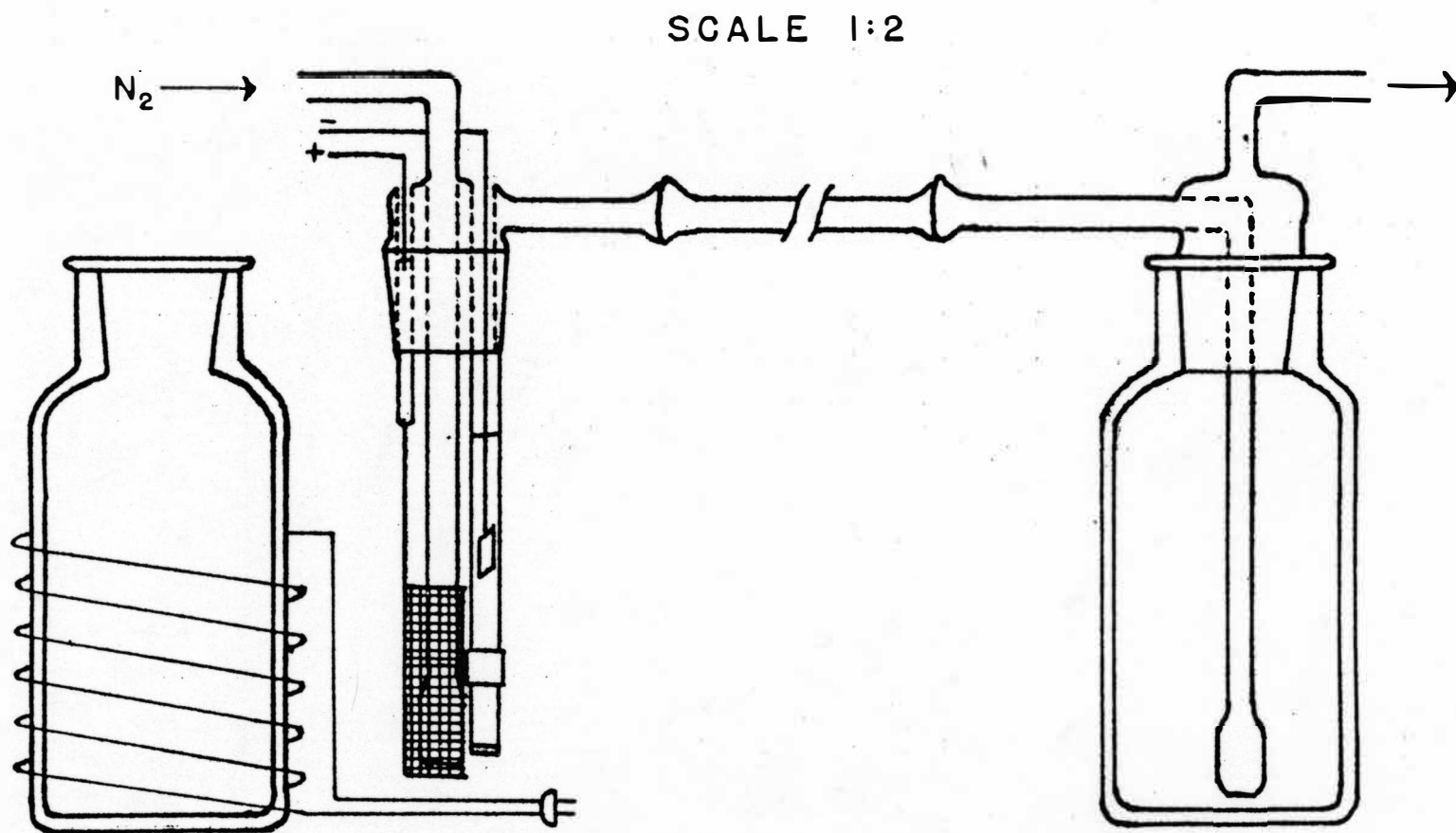
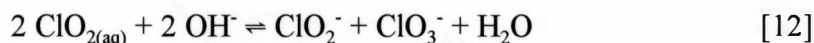


Figure 2. Chlorine Dioxide Generation Apparatus.

Chlorine dioxide also readily disproportionates at high pH forming chlorite and chlorate:



This reaction is complete at pH higher than 11. Chlorine dioxide is stable at low pH. Therefore aqueous chlorine dioxide solutions are kept at neutral pH.

GC/MS: Used for the identification of the reaction products purpose with the parameters remaining the same as mentioned earlier in chlorine reaction section.

UV/VIS Spectrometer: Cary-14 (Olis modified) spectrometer was used with a 1.1 nm effective bandwidth.

Reagents

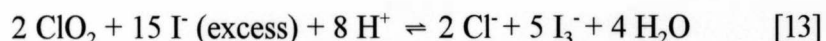
1. Sodium Chlorite Solution, 0.15 molar: Approximately 4.78 g NaClO_2 (Olin Chemicals, analytical grade purity) was dissolved in 350 ml distilled water.

2. Phosphate Buffer Solution, 0.1 molar (pH 6.00) (32): 6.804 g KH_2PO_4 (Fisher Scientific Company, 99.3% purity) was dissolved and diluted to 500 mL. 0.2 g NaOH was dissolved and diluted to 50 mL. 400 mL of KH_2PO_4 solution was then mixed with 44.8 mL of the NaOH solution.

3. Reagents and solution preparation for 1% w/v starch solution, sodium thiosulfate solution, potassium iodate and potassium iodide were the same as described in the earlier section dealing with Reaction of Chlorine with Phenol.

Procedures

Standardization of Chlorine Dioxide Stock Solution: The procedures are the same as described earlier for the standardization chlorine.



Calibration of Chlorine Dioxide: A series of standard chlorine dioxide solutions were prepared from the previously standardized chlorine dioxide stock solution. Chlorine dioxide shows a maximum absorbance at 359 nm ($\epsilon = 1240$), shown in Figure 3. All the spectra measurements were performed at 359 nm using 1.000-cm silica cell with a cap to prevent volatilization. A linear calibration plot for chlorine dioxide was obtained from 0.07 to 0.89 millimolar with a slope of $1241 \text{ (cm}\cdot\text{mol/l)}^{-1}$ and a intercept of -0.003. The linear regression coefficient is 0.9996.

Reaction Mixtures: Chlorine dioxide concentrations were determined from the calibration plot. Then certain amounts of chlorine dioxide are mixed with phenol at different molar ratios. The mixtures were kept in amber bottles with the temperature controlled at 0°, 25° and 30°C for 24 hours.

Extraction and Sample Preparation: The procedure used here is the same as described for the reaction of chlorine and phenol.

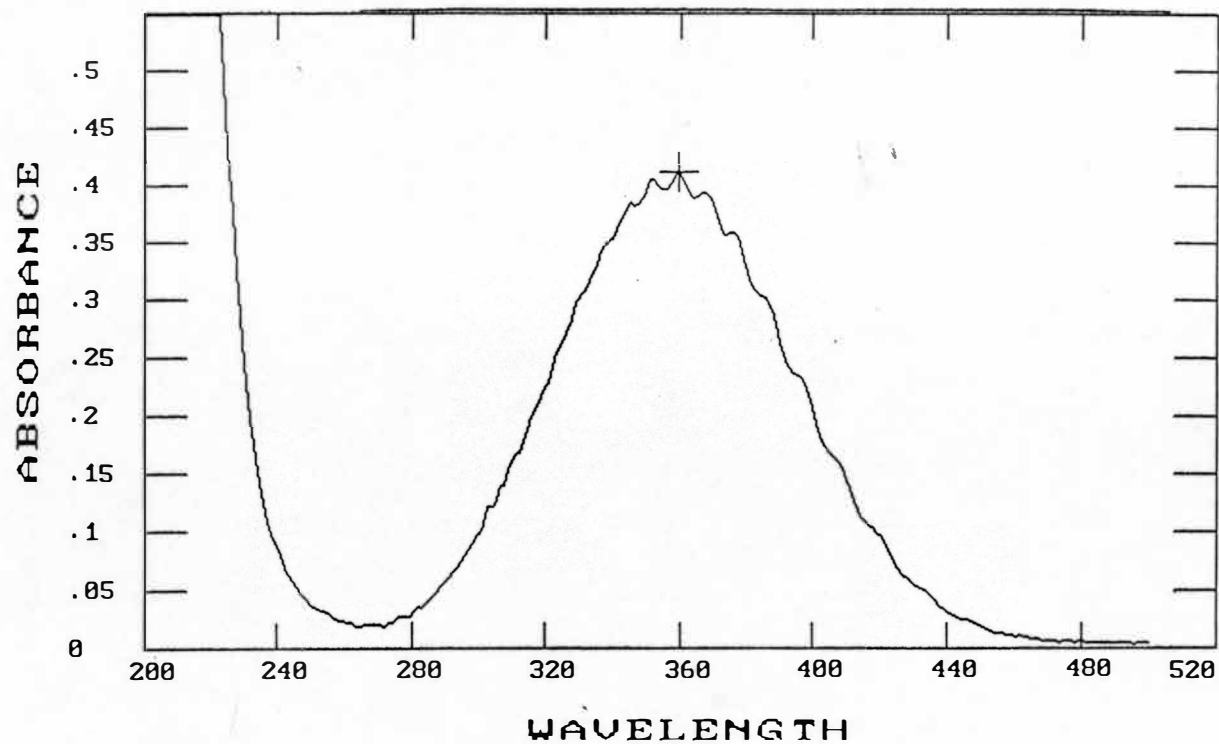


Figure 3. Spectrum of Aqueous Chlorine Dioxide (0.4 Millimolar ClO_2 in 0.1 Molar H_2SO_4).

Results

Table 2 lists the major reaction products from the reaction of chlorine dioxide with phenol at different molar ratios at 0°C and pH 6.00. They were observed and identified by GC/MS. The percentages shown above are based on the fraction of total peak areas observed on GC/MS.

Table 2

Reaction Products of Chlorine Dioxide With Phenol at Different Phenol to ClO₂ Molar Ratios (0.1 Molar Phosphate Buffer, pH = 6.00, at 0°C)

1:1	1:5	1:10
2,5-Cyclohexadiene-1,4- dione (+++)	2,5-Cyclohexadiene-1,4- dione (++)	2,5-Cyclohexadiene-1,4- dione (++)
Phenol, 2-chloro- (++)	Cyclohexanone, 2-chloro- (+)	2-Cyclohexen-1-one (+)
Phenol, 2,4,6- trichloro- (+)		Cyclohexanone, 2-chloro- (+)
Phenol, 3-chloro- (+)		
Phenol, 2,6-dichloro- (+)		
Phenol, 2,4-dichloro- (+)		
2,5-Cyclohexadiene-1,4- dione, 2-chloro- (+)		

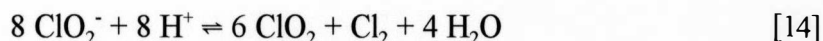
+++ : major product, >15% of total peak area (solvent peak included)

++ : minor product, 5-15% of total peak area (solvent peak included)

+ : trace, < 5% of total peak area (solvent peak included)

Surprisingly that there are a number of different kinds of chlorinated phenols

observed when phenol is treated with chlorine dioxide. This is contrary to the common belief that there are no chlorinated organic compounds produced with chlorine dioxide (33, 34, 35, 36). This phenomenon is much more obvious when the chlorine dioxide to phenol molar ratio is low. At chlorine dioxide to phenol molar ratios of 1:1, monochlorophenols, dichlorophenols and even trichlorophenols are observed. However, they are all not in large amounts. The main source of chlorine likely comes from the disproportionation of chlorite, the initial reduction product of chlorine dioxide, forming chlorine and chlorine dioxide.



The free chlorine produced can react further with organic species and thus chlorination may occur.



This conclusion is supported by the fact that higher ClO_2 : phenol ratios resulted in less chlorinated products due to the greater production of chlorite and its subsequent reaction with chlorine. Figure 4 shows a proposed reaction scheme of chlorine dioxide with phenol (13). Mechanistically the first step is that phenol dissociates into phenolate ion. The rate determining step is the transferring of an electron to chlorine dioxide from the phenolate ion. According to Wayon and coworkers (37), the overall reaction rate is $2-4 \times 10^4 \text{ (M}\cdot\text{s)}^{-1}$ at 25 °C pH 7.00, producing 2,5-cyclohexadiene-1,4-dione. This reaction product was observed as a principle reaction product shown in Table 2. As the chlorine

dioxide concentration is increased, the main reaction products are oxidized compounds rather than chlorinated compounds.

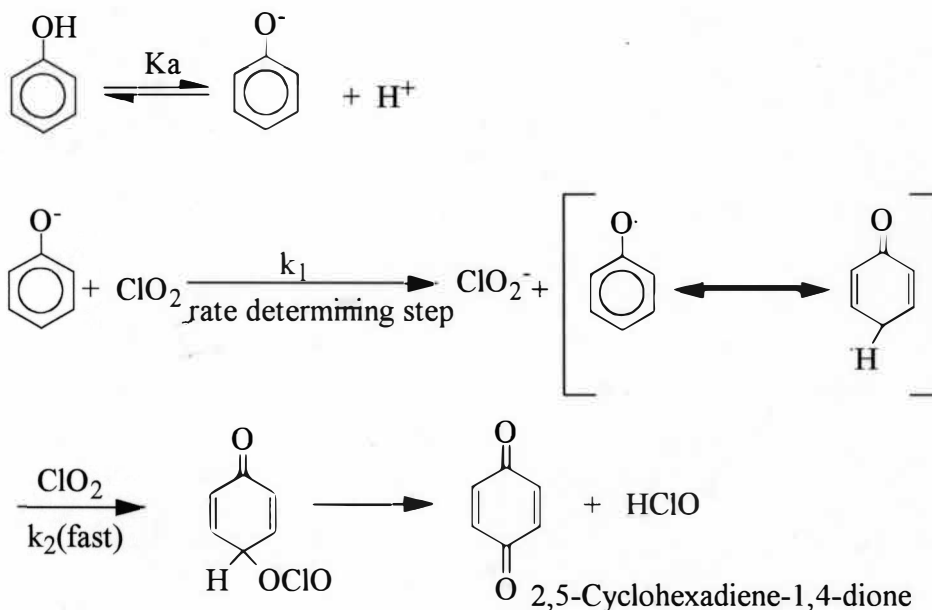


Figure 4. Proposed Reaction Pathway for Chlorine Dioxide and Phenol.

The temperature effect was also studied for the reaction of chlorine dioxide with phenol. Tables 3 and 4 show the reaction products from chlorine dioxide with phenol at 25° and 30°C respectively.

Examination of the data in Table 2, 3 and 4 does not clearly reveal an obvious effect by temperature upon the chlorine dioxide-phenol reaction. It might be anticipated that at higher temperatures, chlorine dioxide could undergo decomposition yielding a chlorine species which might subsequently chlorinate the phenolic substances.

Table 3

Reaction Products of Chlorine Dioxide With Phenol at Different Phenol to ClO_2
Molar Ratios (0.1 Molar Phosphate Buffer, pH = 6.00, at 25°C)

1:1	1:5	1:10
2,5-Cyclohexadiene-1,4-dione (+++)	2,5-Cyclohexadiene-1,4-dione (++)	2,5-Cyclohexadiene-1,4-dione (++)
Phenol, 2-chloro- (+)	Cyclohexanone, 2-chloro- (+)	2-Cyclohexen-1-one (+)
Phenol, 2,6-dichloro- (+)	2-Cyclohexen-1-one (+)	
Phenol, 2,4,6-trichloro-(+)		
Phenol, 3-chloro- (+)		
Phenol, 2,4-dichloro- (+)		
2,5-Cyclohexadiene-1,4-dione, 2-chloro- (+)		

+++ : major product, >15% of total peak area (solvent peak included)

++ : minor product, 5-15% of total peak area (solvent peak included)

+ : trace, < 5% of total peak area (solvent peak included)

Table 4

Reaction Products of Chlorine Dioxide With Phenol at Different Phenol to ClO_2
Molar Ratios (0.1 Molar Phosphate Buffer, pH = 6.00, at 30°C)

1:1	1:5	1:10
2,5-Cyclohexadiene-1,4-dione (++)	2,5-Cyclohexadiene-1,4-dione (++)	Ethane, 1,1,2,2-tetrachloro- (++)
Phenol, 2-chloro- (+)	Cyclohexanone, 2-chloro- (+)	2,5-Cyclohexadiene-1,4-dione (+)
Phenol, 2,6-dichloro- (+)		Cyclohexanone, 2-chloro- (+)

Table 4 --- Continued

1:1	1:5	1:10
Phenol, 2,4,6-trichloro-(+)		2,5-Cyclohexadiene-1,4-dione, 2,6-dichloro(+)
Phenol, 3-chloro- (+)		2,5-Cyclohexadiene-1,4-dione, 2-dichloro-(+)
Phenol, 2,4-dichloro-(+)		

+++ : major product, >15% of total peak area (solvent peak included)

++ : minor product, 5-15% of total peak area (solvent peak included)

+ : trace, < 5% of total peak area (solvent peak included)

Conclusion

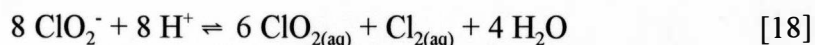
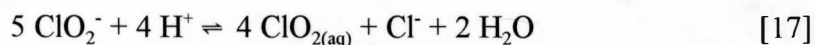
By comparing the reaction of phenol with chlorine dioxide and with chlorine, it is obvious that the quantity of chlorinated products is greatly reduced when phenol is treated with chlorine dioxide rather than chlorine. Even though other studies show that no chlorination occurs when phenol is treated with chlorine dioxide (33, 34, 35, 36), chlorinated organic products were observed in this study. Only the total amount is much smaller, which improves the water quality. Therefore, we can conclude that chlorine dioxide is a better disinfectant compared to chlorine based upon the quantity of the chlorinated compounds. Unfortunately chlorine dioxide is still not a perfect disinfectant simply because it still chlorinates to some degree as well as producing toxic chlorite ion.

REACTION OF CHLORITE ION WITH PHENOL

It is known that chlorite results from the reduction of chlorine dioxide. This ion is toxic to animals and humans and can cause hemolytic stress at concentrations as low as 50 ppm (8). A search of the literature reveals no thorough studies of the interaction of chlorite with phenol. One study, however, indicates that there is no reaction between chlorite and phenol in the absence of activated carbon (14). It was initially felt that this lack of reaction with phenol might be the basis for an analytical procedure which would differentiate chlorite ion from chlorine dioxide.

Photometric Method

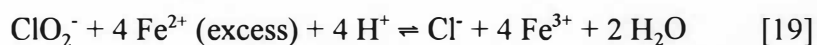
Chlorite ion absorbs in the ultraviolet region exhibiting a maximum absorbance at 260 nm with a molar absorptivity between 50 and 800 L•mole⁻¹•cm⁻¹ depending on the pH of the solution. Chlorite ion is not stable under acidic conditions since it disproportionates according to the following equations:



Thus the reaction conditions for chlorite and phenol must be studied at pH \geq 5.00.

Phenol also exhibits absorption in the ultraviolet region between 200 and 300 nm.

There are two major maxima with one at 210 nm ($\epsilon = 6200$) and the other at 270 nm, ($\epsilon = 1450$). Due to the strong overlap of the chlorite and phenol bands and the small molar absorptivity of chlorite, it is very difficult to determine whether chlorite ion reacts with phenol by monitoring the ultraviolet region. An indirect method to determine chlorite ion was developed using iron(II) and 1,10-phenanthroline (o-phen).



The unreacted iron(II) complexes with 1,10-phenanthroline, which gives an orange color. This complex has a molar absorptivity of $11,000 \text{ L}\cdot\text{mole}^{-1}\cdot\text{cm}^{-1}$ at 510 nm. Since each chlorite ion reacts with four iron(II) ions, the chlorite ion has an effective molar absorptivity of $44,400 \text{ L}\cdot\text{mole}^{-1}\cdot\text{cm}^{-1}$ at 510 nm. Thus iron(II) can be used as a sensitive probe to monitor the chlorite ion concentrations. A preliminary investigation indicated that phenol, oxidation products of phenol, chlorite, and $\text{Fe}(\text{phen})_3^{3+}$ do not exhibit a significant absorbance at 510 nm. However it was noted that a weak complex between iron(II) and phenol seems to exist but does not exhibit an absorbance at 510 nm. Thus in an effort to confirm that a reaction between chlorite and phenol occurs, four solutions as described in Table 5 were prepared and their absorbances measured at 510 nm using 1.00 cm cells.

Solution 1 is a control representing the maximum absorbance which could result from iron(II). Solution 2 is another control representing the minimum absorbance that would be observed from the excess iron(II) remaining after complete reaction with

Table 5

Solution Composition of Chlorite-Phenol Reaction Study

Solution No.	mL 0.12 millimolar ClO_2^-	g $\text{C}_6\text{H}_5\text{OH}$	mL 0.90 millimolar Fe^{2+}	mL 2.4% w/v acetate buffer	ml 0.1% w/v o-phen
1 (control 1)	0.00	0	5.00 [1]	5.00 [2]	4.00 [3]
2 (control 2)	5.00 [1]	0	5.00 [2]	5.00 [3]	4.00 [4]
3 (blank)	0.00	1.0 [1]	5.00 [2]	5.00 [3]	4.00 [4]
4 (sample)	5.00 [1]	1.0 [2]	5.00 [3]	5.00 [4]	4.00 [5]

[] indicates the order of addition

chlorite ion. The absorbance of this solution is what one would expect assuming no reaction between chlorite and phenol occurs. Solution 3 is simply a blank and would give the same absorbance as solution 1 except for the existence of the weak complex between iron(II) and phenol. Of course solution 4 is a sample containing both chlorite ion and phenol which is being test to determine if a significant reaction occurs.

Apparatus

UV/VIS Spectrometer: Cary-14 (Olis modified) spectrometer was used with a 0.8 nm effective bandwidth.

Reagents

1. 0.12 millimolar Sodium Chlorite: Dissolve 0.0011 g NaClO_2 (Olin Chemicals, analytical purity) in 100 mL distilled water.
2. Phenol (Matheson Coleman & Bell).
3. 0.90 millimolar Iron(II) Ammonium Sulfate: Dissolve 353 mg $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ (Matheson Coleman & Bell, ACS grade) in 300 to 400 mL distilled water; add approximately 1.5 mL concentrated sulfuric acid and dilute to 1 liter.
4. 0.1% w/v 1,10-Phenanthroline Solution: Dissolve 1.0 g of 1,10-phenanthroline monohydrate (G. Frederick Smith Chemical Company, ACS grade) in 300 mL of distilled water, heating and/or using ultrasonic bath if necessary to help dissolution and dilute to one liter.

5. 0.6 molar Sulfuric Acid Solution: Dilute 33.3 mL concentrated sulfuric acid (Hi-Pure Chemicals, Inc., ACS grade) to one liter with distilled water.

6. 2.4% w/v Saturated Sodium Acetate Solution: Add 1200 g anhydrous sodium acetate (J.T. Baker Chemical Co., 100.3% pure) to 500 mL distilled water, dilute to one liter and mix thoroughly to insure saturation.

Procedures

The sample solution was prepared when 5.00 mL of 0.12 millimolar chlorite solution was mixed with excess (ca. 1 g) of phenol in a 25-mL volumetric flask. This mixture was kept under dark for about 1 hour. It was observed that the reaction of phenol with chlorite was fast and was found to be complete within 2 hours. Consequently reaction studies for the chlorite-phenol reaction were concluded after about 1 hour. Then 5.00 mL of 0.90 millimolar iron(II) solution was added and 5 minutes are allowed for complete reaction. 5.00 mL of saturated sodium acetate solution was then added, followed by 4.00 mL of 0.1% 1,10-phenanthroline. This solution was mixed thoroughly and then diluted to the mark. Solution 2 (control 2) was made in the same way but no phenol was added while for the third solution (blank), no chlorite was used. The solution 1 (control 1) was prepared in the same way, except that only 5.00 mL of 0.90 millimolar iron(II) was mixed with 4.00 mL of 1,10-phenanthroline and 5.00 mL acetate buffer. Each mixture was prepared and measured in quadruplicate.

Results

From Table 6, it is seen that absorptivity from standard 2 is lower than standard 1, as is expected. Standard 3 has almost the same absorptivity as standard 1 but a little bit lower because phenol weakly complexes with iron(II) also. The absorbance of the sample was between standard 2 and standard 3. Clearly this indicates that chlorite does react with phenol.

The μmoles of Fe^{2+} and ClO_2^- shown in Table 6 were computed from the absorbance values and using $11,100 \text{ L}\cdot\text{mole}^{-1}\cdot\text{cm}^{-1}$ as the molar absorptivity for the iron complex, a cell path of 1.000 cm, and the reaction ratio of $\text{Fe}^{2+}:\text{ClO}_2^-$ as 4:1 (see equation [19]). The data in the table clearly show that approximately 52% of the chlorite has reacted with the phenol in one hour under the given reaction conditions. While it is significant to note that chlorite ion does react with phenol, more interesting is the question of what are the reaction products of this reaction.

High-Performance Liquid Chromatography Method

High Performance Liquid Chromatography (HPLC) is one of the most widely used analytical separation techniques due to its sensitivity, adaptability and especially its ability to separate nonvolatile and thermally sensitive species. It was used in this study to determine and isolate the products from the chlorite-phenol reaction. The composition of mobile phase was studied and the optimum conditions were found to be as follows:

Table 6

Confirmation of Reaction Between Chlorite and Phenol

Solution No.	Absorbance 510 nm	Mean Absorbance	Standard Deviation	$\mu\text{moles Fe}^{2+}$ measured	$\mu\text{moles ClO}_2^-$ reacted
1 control 1	1.9254, 1.9116, 1.9188, 1.9194	1.9188	0.0056	4.32	---
2 control 2	0.8833, 0.8925, 0.8847, 0.8888	0.8873	0.0042	2.00	0.58
3 blank	1.8416, 1.8521, 1.8330, 1.8758	1.8506	0.0019	4.17	0.00
4 sample	1.2732, 1.3322, 1.3098, 1.3413	1.3141	0.0303	2.96	0.30

Apparatus

1. Varian 5020 high performance liquid chromatograph: A 30 cm • 4 mm Micropak MCH-10 reverse-phase column (a C₁₈ hydrocarbon monolayer covalently bonded to 10 µm microparticulate silica as the stationary phase) was used. Injection loops are 10 µL and 100 µL for separation and collection purposes. The column temperature was set up at 30°C. The mobile phase was composed of 60% water and 40% acetonitrile. The flow rate was 1.8 mL/min. The maximum pressure on the column was 250 atm and the minimum was 10 atm. This HPLC is coupled with a UV detector. And the wavelength was set up at 210 nm.

2. Teflon Millipore Filter (Millipore Corporation): pore size 0.45 µM.

Reagents

1. Sodium Chlorite (Olin Chemicals).
2. Phenol (Matheson Coleman & Bell).
3. Iron(II) Ammonium Sulfate (Matheson Coleman & Bell).
4. Acetonitrile, HPLC grade (EM Science).
5. 3 molar Sulfuric Acid and Milli-Q Water.

Procedures

Sodium chlorite was mixed with excess phenol and allowed to react for approximately 1 to 2 hours in darkness. Then excess iron(II) (relative to the chlorite ion)

was added to the mixture in order to remove unreacted chlorite. Chlorite is an oxidizing agent which could possibly oxidize and damage the HPLC column. Thus, some of the iron(II) was oxidized by chlorite and form iron(III). Several drops of 3 molar sulfuric acid were then added to prevent iron(II) and (III) from forming hydroxide precipitates. This solution was then filtered with a 0.45 μm millipore filter and injected into the HPLC system. The detector responses for standards of iron(II), iron(III) and phenol were obtained for the comparison with the reaction mixture's response.

Results

Figure 5 shows a HPLC spectra of chlorite and phenol mixture. Table 7 lists the absorbance maxima that were observed by the HPLC detector.

Table 7

Retention Times for Standards and Reaction Products From Chlorite and Phenol

$t_R(\text{Iron(II)}) \text{ min}$	$t_R(\text{Iron (III)}) \text{ min}$	$t_R(\text{Phenol}) \text{ min}$	$t_R(\text{Mixture}) \text{ min}$
			0.78
0.94 ($\pm 5\%$)	0.93($\pm 5\%$)		0.91
			1.01
			1.82
			2.15
		2.77	2.76
			4.32
			4.78

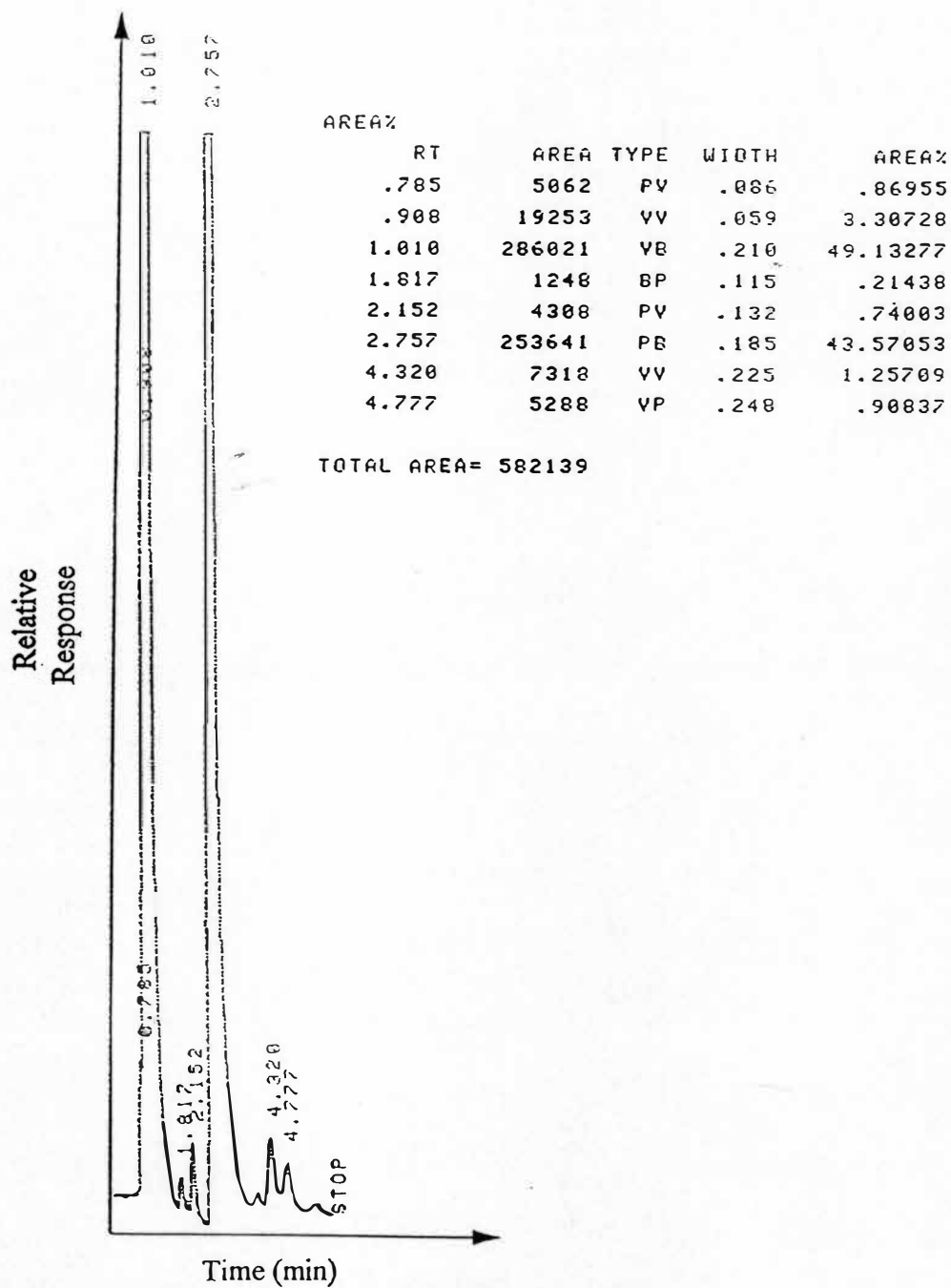


Figure 5. High-Performance Liquid Chromatogram of a Chlorite and Phenol Mixture (0.3 g/L Phenol with Excess ClO_2^- and Fe^{2+}).

A comparison of the retention times of the reaction mixture with those of the standards of iron(II), iron(III) and phenol reveals that new products have been formed. The retention time of 0.79 is the solvent peak while the values of 0.91 and 1.01 minutes match the retention times of iron(II) and (III). The retention time of 2.76 minutes matches the phenol retention time. At least four product peaks are observed. Another three minor peaks were observed but deemed to be too small to list. Thus chromatographic analysis further confirms the fact that chlorite does react with phenol.

Product Isolation and Identification

Initial attempts of injecting the reaction products of the chlorite-phenol reaction into the GC/MS yielded no chromatographic peaks. It was felt that this was due to low concentrations of the products and that these products were likely to be relatively non-volatile. Consequently multiple injections of the reaction mixture were made on the HPLC using a 100 μ L injection loop. The fractions were collected as they eluted off and the eluates were then combined and prepared for derivatization in order to increase their volatility in preparation for GC/MS analysis. Due to the presumed polar nature of the products and considering that they might be phenols, alcohols, ketones, or carboxylic acids, pentafluorobenzyl bromide was chosen as the derivatizing agent.

Apparatus

Vacuum distillation was used to concentrate the sample fractions obtained from

HPLC which consisted primarily of water and acetonitrile, the mobile phase composition. Since water and acetonitrile have relatively high boiling points (water, 100°C; acetonitrile, 82°C), vacuum distillation was applied.

Reagents

1. Pentafluorobenzyl Bromide (Sigma Chemical Co., catalog # P3534).
2. Methylene Chloride (Fisher Scientific, HPLC grade).
3. Sodium Hydroxide: 50% v/v.

Procedures

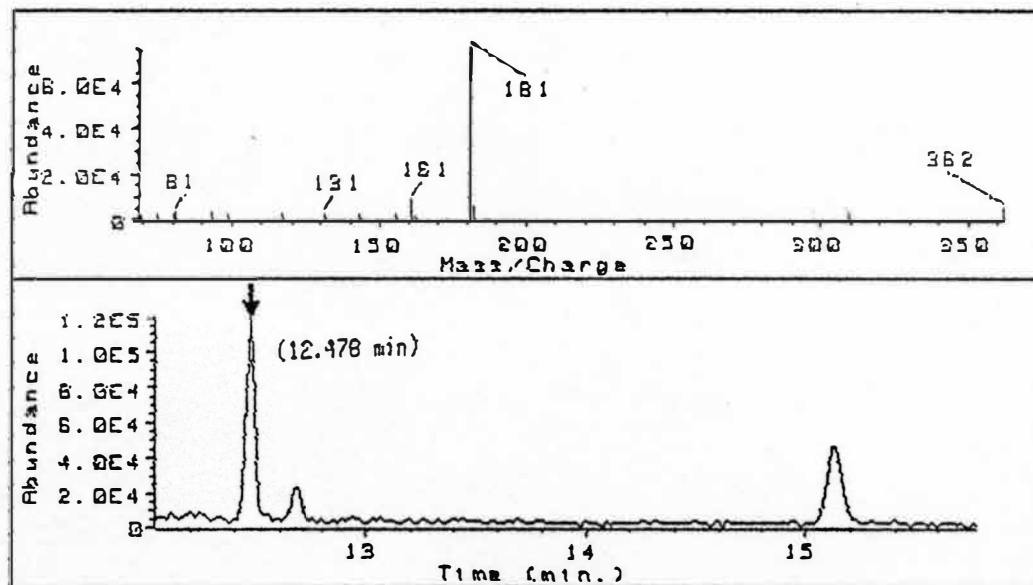
After the eluates of twenty-five injections were concentrated under vacuum distillation at 45°C, 50% sodium hydroxide solution was added to the samples to raise the pH to 10-12. Since the volume of the samples were so small after distillation, only several milliliters of methylene chloride were necessary for the extraction. A syringe was used to transfer the organic phase into a 10-mL vial with a screwed cap. Approximately 0.1-0.2 g pentafluorobenzyl bromide was added to the vial and shaking for about 5 minutes was required. This liquid was then injected into GC/MS for analysis.

Results

Figure 6 through 14 show the mass spectrum of each unknown peak from two different fractions, A (2.1-2.6 min) and B (4.4-4.8 min), collected from HPLC. Peak 2

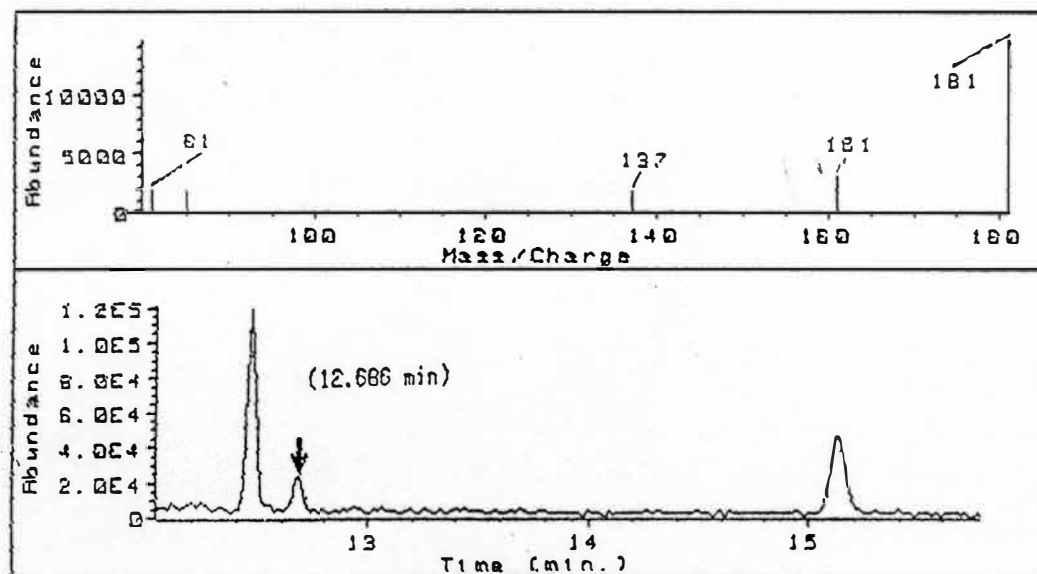
and 3 of fraction A (Figure 7, 8 respectively) show similar mass spectra. The fragment of $m/z = 181$ might be $C_7F_5H_2^+$, the pentafluorobenzyl ion. Peak 1 of fraction A shows an m/z fragment of 362 (Figure 6), which is consistent with the $C_{14}F_{10}H_4^+$. Since these three peaks were not observed in the blank, pentafluorobenzyl bormide in methylene chloride, they might possibly be from reaction products of chlorite and phenol. Peaks 1 and 5 of fraction B (Figure 9, 13 respectively) have not been identified at this time. The fragment m/z 361 in peak 2 of fraction B (Figure 10) could be $(C_6F_5)CH_2-C^+H(C_6F_5)$ although this has not been confirmed. Peak 3 and 4 of fraction B (Figure 11, 12 respectively) show very similar mass spectra. The fragment of m/z 308 does match the molecular weight of $C_{13}F_5H_6OCl$, which is the pentafluorobenzyl bromide complex with monochlorophenol. The relative abundance ratio of 3 for $m/z = 308$ to $m/z = 309$ is consistent with a species having only one chlorine atom. Since peaks 3 and 4 have different retention times, they might be isomers of monochlorophenol. Standard 3-chlorophenol was observed with a retention time of 20.926 minute after being derivatized with pentafluorobenzyl bromide (Figure 14). However, the data was insufficient to make the identification of the monochlorophenol isomers possible.

Unfortunately at this time none of these peaks from reaction products of chlorite and phenol have been positively identified and confirmed. Further investigation is necessary by using other analytical techniques, such as IR, NMR and possibly LC/MS. Other derivatization reagents other than pentafluorobenzyl bormide should also be considered.



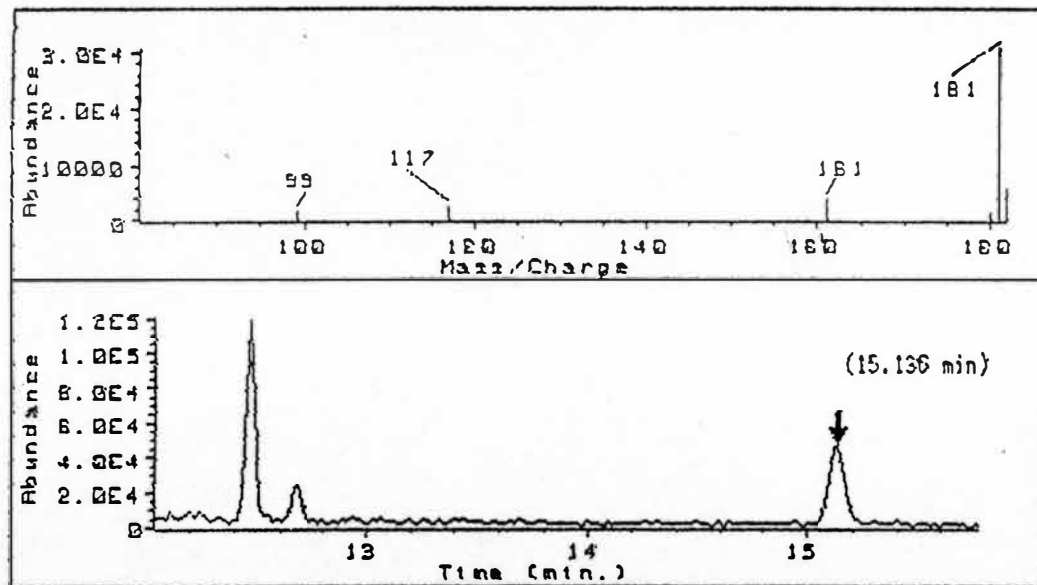
m/z	abund.	m/z	abund.	m/z	abund.	m/z	abund.
69.05	2576	93.10	2973	143.00	2032	181.00	75304
75.05	1722	99.10	2061	155.00	1953	182.00	6012
80.05	1925	116.95	1839	161.05	8177	362.05	5026
81.05	2998	131.05	2108	162.05	1626		

Figure 6. Mass Spectra of Chlorite-Phenol Mixture (Fraction A, Peak 1).



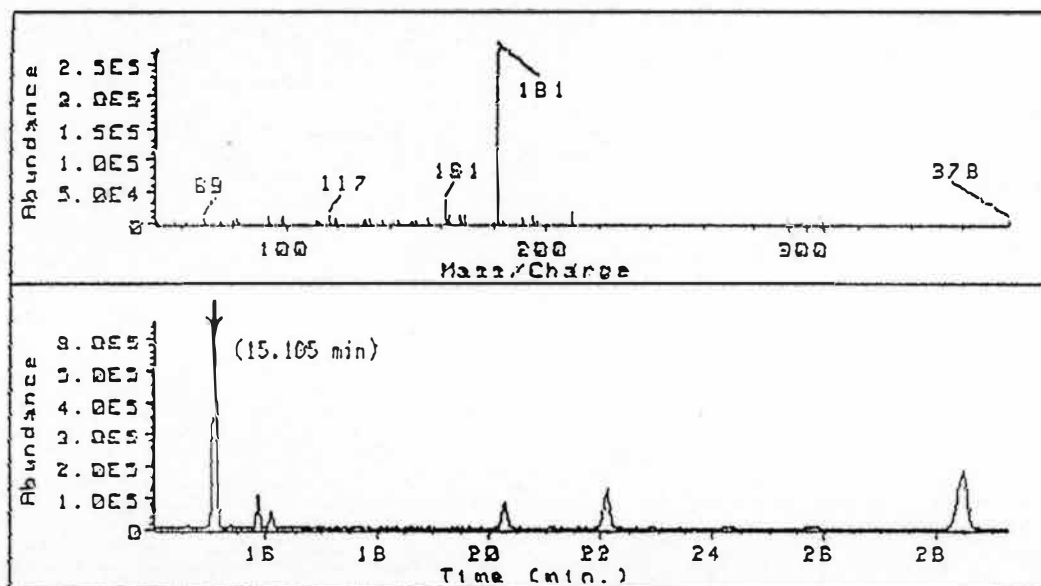
m/z	abund.	m/z	abund.	m/z	abund.	m/z	abund.
80.05	1486	85.00	1557	160.95	2964	181.00	14595
81.05	1839	137.00	1626				

Figure 7. Mass Spectra of Chlorite-Phenol Mixture (Fraction A, Peak 2).



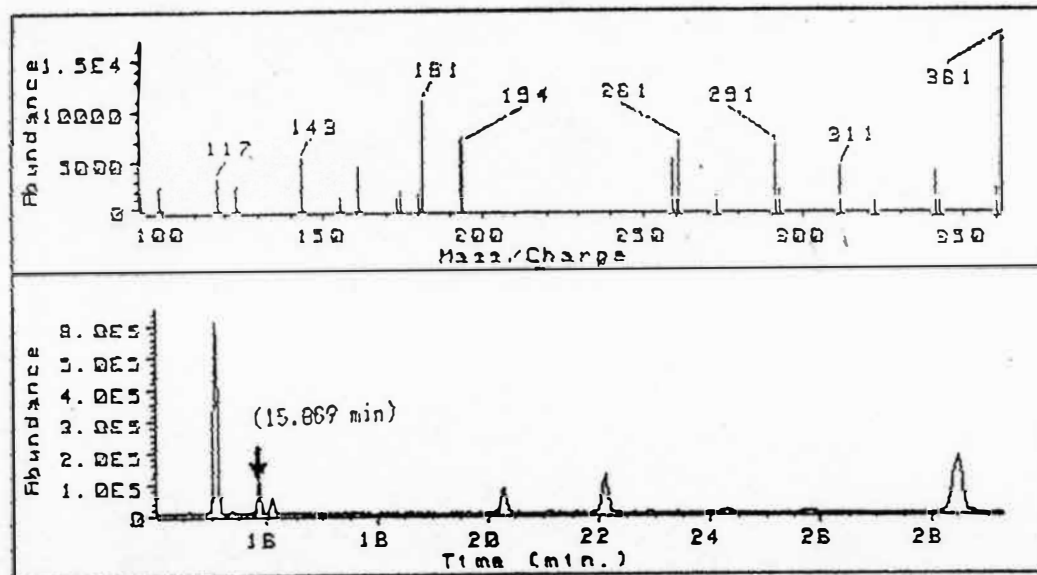
m/z	abund.	m/z	abund.	m/z	abund.	m/z	abund.
81.05	1631	116.95	2361	180.10	1260	182.00	5400
99.10	1562	161.05	3778	181.00	30592		

Figure 8. Mass Spectra of Chlorite-Phenol Mixture (Fraction A, Peak 3).



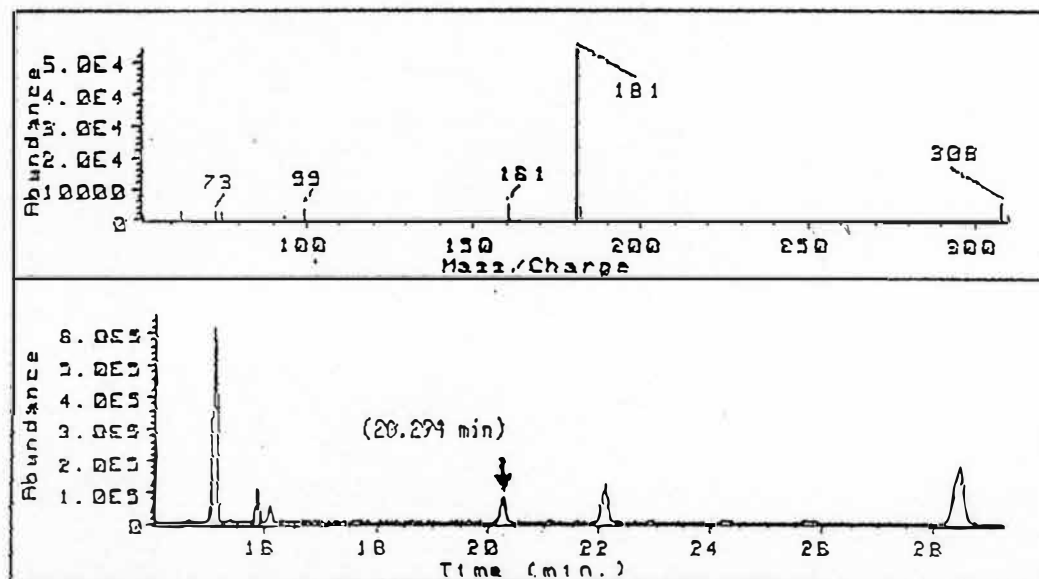
m/z	abund.	m/z	abund.	m/z	abund.	m/z	abund.	m/z	abund.
51.10	3515	98.00	4257	137.00	3242	167.95	5326	82.05	1271
57.10	2132	99.00	11830	141.00	1589	169.05	12631	93.00	10124
61.05	1517	111.05	2948	143.00	5785	179.05	1309	131.05	8000
62.05	2540	112.05	5505	148.00	2328	181.00	275712	132.00	7348
69.05	8245	112.95	1834	149.00	2672	182.00	64000	166.95	10291
74.05	2435	117.05	12124	150.10	5195	183.00	3554	378.00	4462
75.05	5505	118.05	1792	155.00	7449	191.00	7699		
79.05	2672	119.05	8829	161.05	32120	195.00	12224		
80.05	3100	129.15	1114	162.05	6062	197.00	3188		
81.05	7699	130.05	3315	163.05	10207	209.95	18448		

Figure 9. Mass Spectra of Chlorite-Phenol Mixture (Fraction B, Peak 1).



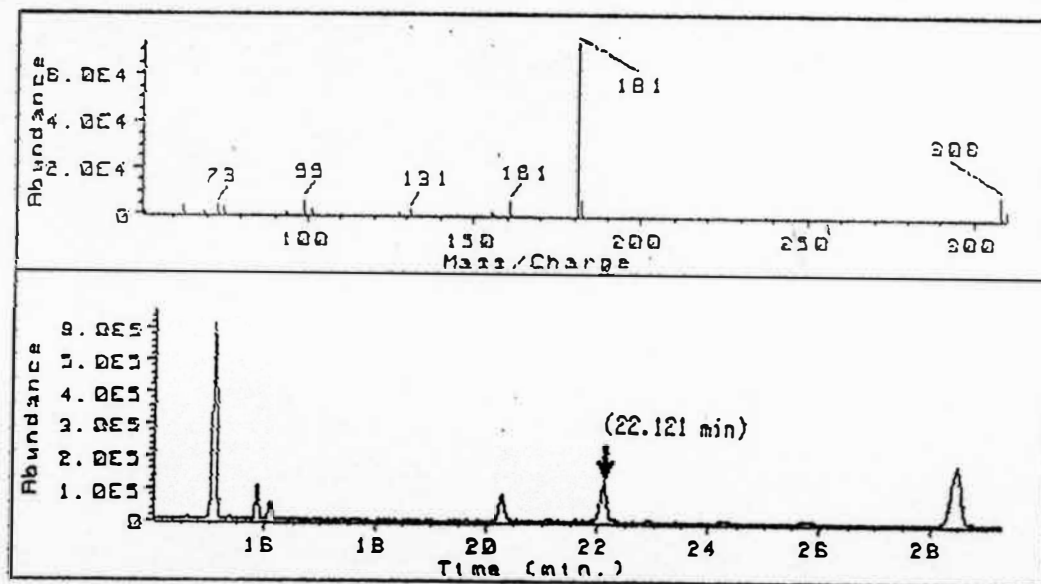
m/z	abund.	m/z	abund.	m/z	abund.	m/z	abund.
93.00	1969	173.05	1181	259.95	1363	322.05	1217
99.10	2442	174.05	1898	260.85	6785	341.00	3939
117.05	3233	180.00	1603	273.05	1500	342.10	1571
123.05	2555	181.00	10810	291.00	6493	360.05	2206
143.00	5267	193.00	7169	292.10	2151	361.05	16952
155.10	1290	194.00	6352	311.05	4305	362.05	2882
161.05	4210	258.85	5054				

Figure 10. Mass Spectra of Chlorite-Phenol Mixture (Fraction B, Peak 2).



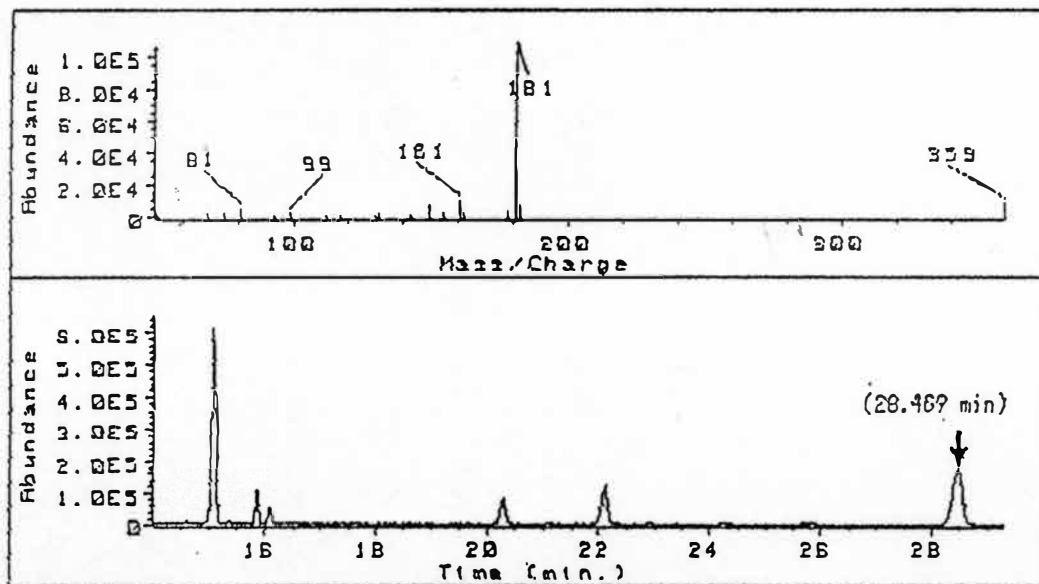
m/z	abund.	m/z	abund.	m/z	abund.	m/z	abund.
51.10	1829	75.05	2562	161.05	4889	307.95	5535
63.05	2620	93.10	1140	181.00	53656	309.95	1698
73.05	2657	99.10	3634	182.00	4152		

Figure 11. Mass Spectra of Chlorite-Phenol Mixture (Fraction B, Peak 3).



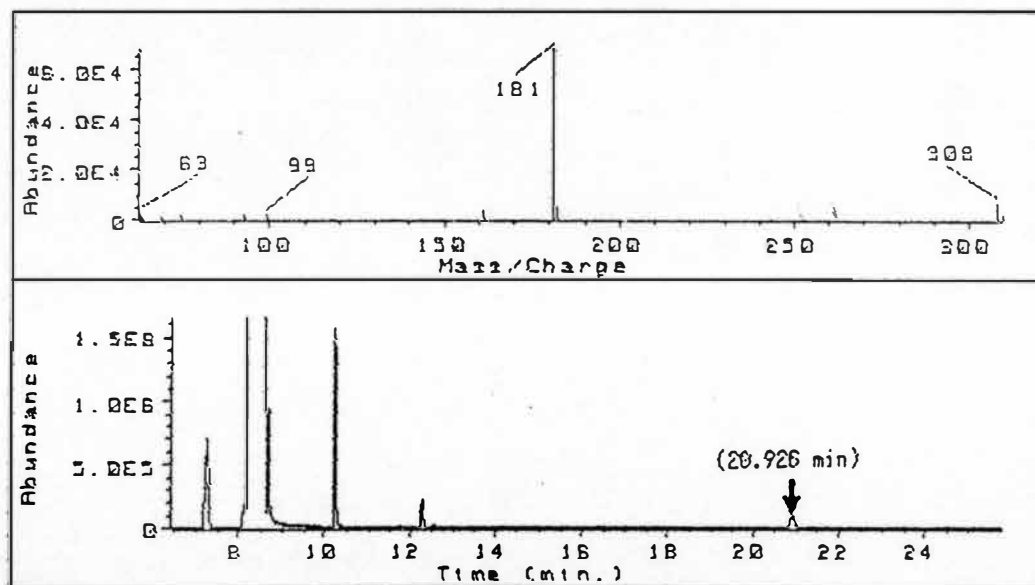
m/z	abund.	m/z	abund.	m/z	abund.	m/z	abund.
51.10	1448	75.05	3188	127.05	1399	181.00	73488
63.05	3399	93.00	1347	131.05	2061	182.00	6214
69.15	1424	99.00	5195	155.10	1635	308.05	8685
73.05	3664	101.10	1909	160.95	5385	309.95	2899

Figure 12. Mass Spectra of Chlorite-Phenol Mixture (Fraction B, Peak 4).



m/z	abund.	m/z	abund.	m/z	abund.	m/z	abund.
51.00	1379	99.10	3197	143.10	2381	178.05	3874
69.05	2672	111.95	2067	150.10	8497	181.00	106544
75.15	2470	117.05	1249	155.00	2672	182.00	8428
81.05	5817	130.15	1199	161.05	10519	359.05	8829
93.10	2157	131.05	2891	162.05	3015		

Figure 13. Mass Spectra of Chlorite-Phenol Mixture (Fraction B, Peak 5).



m/z	abund.	m/z	abund.	m/z	abund.	m/z	abund.
63.00	2442	74.95	1958	161.00	3604	308.00	6387
64.00	1483	93.00	1777	180.95	68304	309.90	2212
69.05	1324	99.00	2175	181.95	5520		

Figure 14. Mass Spectra of Standard 3-Chlorophenol After Being Derivatized With Pentafluorobenzyl Bromide.

RECOMMENDATIONS

This study has substantiated some earlier work in the literature regarding the reactions of chlorine and chlorine dioxide with phenol. It has also shown that contrary to other studies chlorite does react with phenol even in the absence of activated charcoal. Further work is needed in each of these areas in order to study a wider range of reaction conditions such as pH, concentration, and temperature. Quantitative determination of reaction products as well as kinetic studies could provide much needed information to permit establishing reaction mechanisms. Of particular interest is the lack of a good method for differentiating chlorine dioxide and chlorite ion in mixtures. Methodology permitting this analysis could contribute a great deal toward following reactions of these species. The identification of the reaction products of the chlorite-phenol reaction remain unclear. Further analysis of the data collected here along with the collection of more data using different derivatizing agents and with a greater degree of preconcentration is suggested.

REFERENCES

1. Krasean, Bill, "Kalamazoo Gazette", July 11, 1994
2. Dolara, P., Ricci, V., Burrini, D. and Griffini, D., Environ. Contam. Toxicol., 27: 1, 1981.
3. Tyson, Rae, "A green week for congress", USA Today, February 2, 1994
4. White, G.C., Handbook of Chlorination, Van Nostrand Reinhold, New York, N.Y., pp. 744, 1976.
5. Colclough, C.A., Johnson, J.D., Christman, R.F. and Millington, D.S., "Organic reaction products of ClO_2 and natural aquatic fulvic acid", water chlorination: Environmental Impact and Health Effects, 4: 219-299, 1983
6. Longley, K.E., Moore, B.E. and Sorber, C.W., "Comparison of chlorine and ClO_2 disinfectants", J. Wat. Pollut. Control Fed., 52: 2098, 1980
7. Benarde, M.A., Israel, B.M., Olivieri, H.P. and Davidson, B., "Efficiency of ClO_2 as a bactericide", Appl. Microbiol., 13: 776, 1965
8. Condie, Lyman W., "Toxicological effects associated with drinking water disinfectants and their by-products", The Toxicology --- Water Chlorination, chapter 21, 281-292
9. Hoigne J. and Bader H., "Kinetik typischer reaktion von chlordinoxid mit Wasserinhaltsstoffen", Vom Wasser, 59: 253-267, 1982
10. Couri, D. and Abedl-Rahman, M.S. "Effect of chlorine dioxide and metabolites on glutathione dependent systems in rat, mouse and chicken blood", J. Environ. Pathol. Toxicol., 3: 451-60, 1979
11. Moore, G.S. and Calabrese, E.J., "The effects of chlorine dioxide and sodium chlorite on Erythrocytes of A/J and C57L/J Mice", J. Environ. Pathol. Toxicol., 4: 513-24, 1980
12. Tesarova, E. and Pacakova, A.V., "Gas and high-performance liquid chromatography of phenols", Chromatographia, 17: 269-284, 1983

13. Rav-Acha, Ch., "The reaction of chlorine dioxide with aquatic organic materials and their health effects", Water Research, 18: No. 11, pp. 1329-1341, 1984
14. Vel Keitner, N.K., De Laat, J., Dore, M., Suty, H. and Pouillot, M., "Inorganic and organic byproducts of the reactions between chlorite, activated carbon, and phenolic compounds", Environ. Sci. Technol., 28: 222-230, 1994
15. Voudrias, Evangelos A., Larson, Richard A. and Snoeyink, Vernon L., "Effects of activated carbon on the reactions of free chlorine with phenols", Environ. Sci. Technol., 19: No. 5, 1985
16. Norwitz, G., and Keliher, P.N., "Spectrophotometric determination of phenol by the 4-aminoantipyrine method after steam distillation in a semimicro Kjeldahl apparatus in the presence of a large amount of sodium chloride", Anal. Chim. Acta., 144: 273-276, 1982
17. Perez, M., Barrios, C., Saelzer, R., Vega, M., and Villegas, R., "Determination of pentachlorophenol by high performance thin layer chromatography", J. High Resol. Chromatogr., 12: 419-421, 1989
18. Chriswell, C.D., Chang, R.C., and Fritz, J.S., "Chromatographic determination of phenols in water", Anal. Chem., 47: 1325-29, 1975
19. O.H. Masi and W.M. Gulick, "An optimized gas chromatographic determination of priority pollutant phenols", J. High Resol. Chromatogr., 10: 647-49, 1987
20. S.F.Y. Li and H.K. Lee, "Retention prediction of substituted phenols in reversed-phase HPLC", Chromatographia, 25: 515-19, 1988
21. O. Busto, J.C. Olucha and F. Borrull, "Determination of phenolic compounds in water by HPLC by linear gradient. An optimised method", Chromatographia, 32: 423-28, 1991
22. Howell, J.A., "Spectrophotometric study of some oxy halogen species in aqueous solution", pp. 44 -48, doctor of philosophy dissertation, Wayne State University, 1964
23. Ying-Chien Chu, "Analysis of mixtures of chlorine, chlorine dioxide and chlorite", Master thesis, Western Michigan University, pp. 24-31, September, 1979
24. Allinger, Cava, DeJongh, et al., "Organic Chemistry", 2nd Ed., Worth Publishers, Inc., pp. 591, 1976

25. Baiocchi, C., Roggero, M.A., Giacosa, D. and Marengo, E., "HPLC separation and determination of complex mixtures of phenolic compounds on different stationary phases. An efficient general screening method for the presence of phenols in water", Journal of Chromatographic Science, 33: pp. 338-346, 1995
26. Howell, J.A. and Brown, personal communication
27. Salnis, K.Yu., Trudy Leningrad. Teknol. Inst., im V. M. Molotova, 1958, 5: 113-121; Chem. Abstracts, 56: 26121
28. Wright, R.S., "History and development of chemical flour bleaching and aging", pp.3, Wallace & Tiernan Inc., Belleville, N.J.
29. Latimer, W.M., "Oxidation potentials", pp. 51-69, Prentice Hall, Inc., Englewood Cliffs, N.J.,-1961
30. Moeller, T., "Inorganic chemistry", pp. 432, John Wiley & Sons, Inc., New York, 1958
31. Masschelein, W.J., "Chemistry and environmental impact of oxychlorine compounds --- chlorine dioxide", pp. 10, Ann Arbor Science Publishers Inc., 1979
32. "Properties of standard aqueous buffer solutions at 25°C", CRC Handbook of Chemistry & Physics, 55th edition, D-112, 1974-1975
33. Lykins, B.W., Goodrich, J.A. and Hoff, J.C. Aqua, 39: 376-386, 1990
34. Lykins, B.W. and Griesse, M.H., J. A. Water Works Assoc., 78: 88-93, 1986
35. Mario, Fabris, "The disinfection in surface water drinking treatment in the near future", Water Nagoya, 31S-07-A14, pp. 225-233, 1989
36. Synon, J.F., MacMahon, J.D. and Vicent, G.P., J. New Engl. Water Works Assoc., 58: 264-269, 1944; Chem. Abstracts, 39: 5695
37. Wayon, J.E., Rosenblatt, D.H., and Burrows, E.P., "Oxidation of phenol and hydroquinone by ClO_2 ", Envir. Sci. Technol., 16: 396-402, 1982