Collection of gas phase chlorine using bonded silica sorbents

Bhaskar Tadepalli
University of Nevada, Las Vegas

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Collection of Gas Phase Chlorine using Bonded Silica Sorbents

by

Bhaskar Tadepalli

A thesis submitted in partial fulfillment
of the requirements for the degree of

Master of Science
in
Chemistry

University of Nevada, Las Vegas

August, 1995
The thesis of Bhaskar Tadepalli for the degree of Master of Science in Chemistry is approved.

Chairperson, Brian J. Johnson, Ph.D

Examine Committee Member, David W. Emerson, Ph.D

Examine Committee Member, Vernon F. Hodge, Ph.D

Graduate Faculty Representative, Malwane M. Ananda, Ph.D

Interim Graduate Dean, Cheryl L. Bowles, Ed.D.

University of Nevada, Las Vegas

August, 1995
ABSTRACT

Sulfonamide functionalities bound to silica substrates have been investigated for collection of gas phase chlorine. Sorbents were prepared by bonding aminopropyl groups to a substrate (silica gel or filters) and then reacting with alkyl or aryl substituted sulfonyl chloride to produce the corresponding surface bound sulfonamide. Silica gel surfaces were investigated for collection efficiency using synthetic laboratory gas mixtures. After satisfactory collection efficiencies were demonstrated, sampling and analytical procedures were developed for analysis of air in the vicinity of a swimming pool. This method shows promise for applications in industrial settings and in atmospheric studies of the geochemical chlorine cycle.
ACKNOWLEDGMENTS

At the outset, I would like to thank Dr. Brian J. Johnson for the help he has extended to me during the course of my graduate program. But for his constant encouragement and guidance, completion of this thesis would have been beyond my capability. I would also like to thank Dr. David W Emerson for his time and help. Special thanks to Dr. Ananda Malwane of Mathematics department and swimming team coach Ms. Vaune Koulubek.

I dedicate this humble effort to my family.
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Chapter 1

Introduction

1.1 Chlorine and its atmospheric interactions

1.1.1 Properties and industrial sources

Chlorine is defined as liquid or gaseous molecular chlorine. It is greenish yellow in color and molecular weight is 70.906. Exposure to chlorine leads to irritation in the eyes and the nasal and bronchial tract. It is therefore classified as a health hazard. Chlorine finds many commercial and industrial uses due to its bleaching and disinfection properties. A list of the chemical and physical properties is given in table 1.1; and a list of occupations affected by chlorine exposure is given in table 1.2. It occurs naturally in salt, NaCl, sylvite KCl, and carnallite KMgCl₃·6H₂O. Salt being an important constituent of sea water, it naturally occurs in marine aerosols, swimming pools, chlor-alkali industries and commercial laundromats.
Chemical and physical properties of chlorine

<table>
<thead>
<tr>
<th>Property</th>
<th>Measured Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Critical Temperature</td>
<td>144°C</td>
</tr>
<tr>
<td>Critical Pressure</td>
<td>78.64 kg/sqcm</td>
</tr>
<tr>
<td>Latent heat of vaporization</td>
<td>68.8 cal</td>
</tr>
<tr>
<td>Density of gas at 0°C</td>
<td>3.214 g/L</td>
</tr>
<tr>
<td>Density of Liquid</td>
<td>1468 g/L</td>
</tr>
<tr>
<td>Boiling Point</td>
<td>-34°C</td>
</tr>
<tr>
<td>Solubility in water at 20°C</td>
<td>7.30 g/L</td>
</tr>
<tr>
<td>Specific Gravity of Liquid at 20°C</td>
<td>1.41 g/mL</td>
</tr>
<tr>
<td>Specific Gravity of Gas at 20°C</td>
<td>2.49 g/L</td>
</tr>
</tbody>
</table>

Table 1.1: Chemical and physical properties of chlorine [22]

1.1.2 Sources of active chlorine in the clean troposphere

Sodium chloride present in marine aerosols is volatized by sulfuric and nitric acid. The following equations describe the volatization process [2]:

\[
NaCl(s) + HNO_3(g) \rightarrow NaNO_3(s) + HCl(g) \tag{1.1}
\]

\[
2NaCl(s) + H_2SO_4(l) \rightarrow Na_2SO_4(s) + 2HCl(g) \tag{1.2}
\]

Several researchers have measured Cl and Na ratio in aerosols the declining ratios as one moves inland from marine sources has traditionally been attributed to the reactions in equations 1.1 and 1.2. However more recent measurements of NO_3^- and SO_4^{2-} in the Atlantic ocean (sea water) have suggested that these reactions are insufficient to explain the loss of chlorine.

The presence of alternative mechanisms or reactions involving chlorine was explored by Finlayson-Pitts [13] in 1983 leading to the following hypothesized equations for volati-
Workers with exposure to Chlorine

<table>
<thead>
<tr>
<th>Alkali salt makers</th>
<th>Submarine workers</th>
</tr>
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<tbody>
<tr>
<td>Dye makers</td>
<td>Iodine makers</td>
</tr>
<tr>
<td>Carpet makers</td>
<td>Chemical Synthesizers</td>
</tr>
<tr>
<td>Insecticide makers</td>
<td>Gold Extractors</td>
</tr>
<tr>
<td>Laundry workers</td>
<td>Paper Bleachers</td>
</tr>
<tr>
<td>Silver Extractors</td>
<td>Refrigerant makers</td>
</tr>
<tr>
<td>Vinyl Chloride makers</td>
<td>Tetraethyl lead makers</td>
</tr>
<tr>
<td>Water treaters</td>
<td>Swimming pool maintenance workers</td>
</tr>
<tr>
<td>Fluorocarbon makers</td>
<td>Benzene Hexachloride makers</td>
</tr>
</tbody>
</table>

Table 1.2: Workers with exposure to chlorine [22]

Active chlorine is defined as chlorine atoms which are generated via photolysis of Cl₂, HOCl, NOCl, and NO₂Cl. In 1989 research by Finlayson-Pitts et al. [14] explored the possibilities of other avenues of active chlorine generation through the following equations:

\[
2NO_2(g) + NaCl(s) \rightarrow NOCl(g) + NaNO_3(s) \tag{1.3}
\]

\[
N_2O_5(g) + NaCl(s) \rightarrow ClNO_2 + NaNO_3(s) \tag{1.5}
\]

Preliminary measurements appear to confirm the presence of active chlorine in the background marine troposphere [19], although accuracy of the methodology needs to be improved, as does the ability to resolve different active chlorine species.
1.2 Reaction of active chlorine with sulfonamides

1.2.1 Introduction

Sulfonamides [4] are characterized by the readiness with which they form derivatives when treated with hypochlorous acid. Amidic hydrogen is replaced by halogen. This property can be used for collecting chlorine in aqueous as well as gaseous media. Sulfochloramides also display greater stability when compared to other chloramides. They can be safely heated above their melting points. On application of a direct flame sulfonamides form tetrachloramides. Tetrachloramides tend to explode violently.

All sulfonamides generally participate in reactions in which the amidic hydrogen is replaced by halogen. The following figure explains the reaction.

2) Sulfondichloramides can react with alcohols under laboratory conditions:

\[
C_6H_5SO_2NCl_2 + 2C_2H_5OH \rightarrow C_6H_5SO_2NH_2 + 2C_2H_5OC\text{I}
\]

Ethyl hypochlorite is formed which then decomposes to hydrogen chloride and acetaldehyde

3) Sulfondichloramides can also react with hydroxides

\[
C_6H_5SO_2NCl_2 + 2KOH \rightarrow C_6H_5SO_2KNC\text{I} + KOCl + H_2O
\]
Salts of the sulfonmonochloramides are formed along with water of crystallization.

1.3 Immobilization of Sulfonamide Functions

Emerson et al. [6] have carried out extensive research in the area of immobilizing the sulfonamides on materials such as polystyrene resins. Immobilized sulfonamides were very useful for stripping aqueous chlorine and found applications in disinfection of water. Resins were made by reacting sulfochlorinated, macroporous styrene divinylbenzene copolymer with a strength greater than 15% DVB in the presence of an excess of α, ω alkanediamines. Amberlyst-15™ (Rohm and Haas Chemicals) was used as a cation-exchange resin. After the resin was sulfochlorinated it was treated at 0°C with alkanamine or alkanediamine. Similarly this process can also be used with Dowex™ 50-X-8 (Dow Chemical Company).

1.4 Immobilized Sulfonamides for Collection of Gas-Phase Chlorine.

Emerson et al [8] [9] [10][11] have thoroughly studied the reactions of various species with the sulfonamide and N-alkyl sulfonamide resins (named Haloscrubs). For example bromine is quantitatively collected as well as chlorine [8], and simple reductants such as hydrazine quantitatively regenerate the parent sulfonamide or N-alkylsulfonamide resin from its chlorinated derivative.

\[
\text{SO}_2\text{N}^+\text{Cl}^- + \frac{1}{2} \text{N}_2\text{H}_4 \rightarrow \text{SO}_2\text{N}^+\text{H}^- + \frac{1}{2} \text{N}_2
\]

Figure 1.2: Reduction of chlorinated sulfonamides with hydrazine
Furthermore the haloscrubs appear to be very selective towards reaction with active bromine and chlorine. The only other reacting species identified was HNO$_2$, which produces a diazo product easily distinguished from the halogenated derivatives.

While designed for use in aqueous systems, the chemistry appeared suitable for application to gas-phase collection of chlorine (and bromine). Johnson et al [16] had developed an aminopropyl material for collection of atmospheric acids, and further reaction to create sulfonamide functions appeared feasible. A study to investigate the development and application of such surfaces was undertaken.

1.4.1 Proposed work

After a complete study of the relevant references [8] [9] [10] [11] [16], it was decided to use filters as a substrate to collect gaseous chlorine. The above mentioned references deal with the collection of chlorine in an aqueous media and the collection of formic acid and acetic acid in a gaseous media using aminopropyl filters. Accordingly it was decided to begin the project by preparing aminopropyl filters and treating with methanesulfonyl chloride and 1,8-diazobicyclo [5.4.0] undecene (DBU). Experiments would then be carried out both in gaseous media and aqueous media. Based on the results obtained on sampling in both modes, evaluation and modification steps (if necessary) would be undertaken. Characterization studies would be done in lab testing. If quantifiable collection efficiencies were obtained the method would be tested in analytical applications, such as swimming pools, chlor alkali industries, etc.
Chapter 2

Analytical methods for chlorine

There are primarily three types of techniques for measurement of chlorine. They are the electrolytic method, (2) colorimetric methods, (3) titrimetric method.

2.1 Electrolytic method for Chlorine

This method [3] utilizes the oxidizing properties of chlorine. An air sample containing chlorine is passed through an electrolytic solution containing bromide ions. The bromide ions are then oxidized by the chlorine. The oxidation causes a change in the output current of the cell. The change in current is calibrated in terms of ppm of chlorine. A variation of this technique is used along with a pyrolysis/microcoulometric cell. Electrolytic techniques generally are more suited for industrial type settings where the gas concentration may vary from 0-50 ppm.
2.2 Colorimetric techniques for chlorine

2.2.1 Methyl orange and o-tolidine methods

These techniques involve colorimetric reagents such as methyl orange or o-tolidine [20] [17]. In the case of methyl orange a 10mL solution of methyl orange is placed in an impinger with a glass fritter. Samples containing chlorine are bubbled through the impinger at 1 to 2 L per minute. Sampling time is 15 minutes. The methyl orange procedure is suited for a range of 5 to 10 μg of Cl₂ per 10 mL of sampling solution. The measuring range varies from 0.5 to 1 ppm of Chlorine.

The estimatable decolorization of methyl orange 4[N[(4-dimethylamino)phenylazo]benzene-sulfonate) is a basis for colorimetric estimation of chlorine. It depends on the fact that at 505 nm, at a pH of methyl orange shows a decrease in absorbance on exposure to chlorine. One of the reactions is [20]

\[
\text{Na}_2\text{S}_2\text{O}_3 + \text{N}^\bullet \text{N}^\bullet \text{N}^\bullet \text{N}^\bullet + \text{X}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 + \text{OH}^- + \text{X}^- + \text{N}_2 + \text{NaX}
\]

Figure 2.1: Mechanism 1 for the reaction of methyl orange and chlorine

The methyl orange method has several limitations such as interference from chlorides. The presence of other halogens in the air sample may give a reading of total halogen instead of chlorine. It also shows temperature and pH dependence. There also could be lower values obtained due to the halogenation of reaction products. Similarly, orthotolidine can be used for colorimetric determination. It has several limitations such as color...
interferences from manganese, nitrite, and monochloramine. It is possible to reduce the limitations with stabilizers. It is also a health hazard as it is a carcinogen.

2.2.2 N,N-Diethylphenylenediamine Method for Chlorine:

DPD is N,N-Diethyl-phenylenediamine indicator solution. The solution is prepared by dissolving 1 g of DPD oxalate or 1.1 g of DPD sulfate 1-L of water. About 200 mg of disodium ethylene diamine tetraacetic acid are also added to the solution along with 3 mL of sulfuric acid. The solution is stored in dark amber bottles. It is always discarded when there is discoloration due to oxidation. It usually turns pink on discoloration and will interfere with absorbance results.

Other reagents required for analysis:

Phosphate buffer solution was made up by adding 24 g Na$_2$HPO$_4$ and 46 g KH$_2$PO$_4$ (anhydrous). These amounts are added to 100 mL distilled water containing 800 mg of EDTA. This solution is further diluted to 1000 mL, with the addition of 20 mg of HgCl$_2$ to prevent any development of bacterial mold.

Ferrous Ammonium Sulfate Solution was made up by dissolving 1.106 g of
Fe(NH₄)₂(SO₄)₂·6H₂O 3 mL of sulfuric acid diluted to 1 L with fresh distilled water. The other regents used were EDTA and potassium iodide crystals. The method can be used in two ways: colorimetrically or titrimetrically. The FAS reagent is used for the titrimetric method only. Because of its versatility and sensitivity this method was eventually the one selected for this study.

2.3 Ion Chromatograph method

This method uses silver filters to collect Cl₂ and Br₂ forming the corresponding silver halide [3]. The halide ion is released by complexing the silver ion with aqueous thiosulfate thus liberating the halide. The halide (chloride in this case) is measured by ion chromatography.

Working Ranges

The working range for this method is from 0.007 ppm Cl⁻ to around 0.5 ppm Cl⁻. There could be interferences from hydrogen sulfide and hydrogen chloride, and collection efficiency is dependent on ambient humidity.

2.4 Titrimetric Methods:

2.4.1 Technique used in DPD method titration

Add about 5 mL each of phosphate buffer, EDTA, DPD, and a pinch of potassium iodide crystals. Add 100 mL of sample. Let the solution develop its full potential for color which is usually dark pink. It is then titrated against ferrous ammonium sulfate solution. The end point is a colorless solution. The upper limit for this technique is 5 mg of chlorine per liter. It can be extended by diluting all the reagents to a lower concentration prior to titration.
Limitations of the DPD technique

1. Higher pH causes dissolved oxygen to give color.

2. Higher temperature causes color fading.

3. Interference by metals such as copper can reduce the color stability of DPD. This can be limited to certain extent by chelating agents such as EDTA.

4. Success of the method depends upon clean glassware.

2.4.2 Titration of commercial bleach with sodium thiosulfate and potassium iodide

Mechanism

The oxidizing power of sodium hypochlorite is determined by titrating it with an excess solution of potassium iodide in a solution of acetic acid. The iodide is oxidized to iodine. A solution of sodium thiosulfate is standardized against a primary standard such as potassium iodate. Starch solution is used as a indicator as it gives a characteristic blue color on reacting with iodine.

The equations for standardization of sodium thiosulfate are

\[ IO_3^- + 8I^- + 6H^+ \rightarrow 3I_3^- + 3H_2O \]  \( (2.1) \)

\[ I^- + 2S_2O_3^{2-} \rightarrow 3I^- + S_4O_6^{2-} \]  \( (2.2) \)

The equation for the determination of the sample will be
2.4.3 Analysis of hypochlorite in commercial bleach by iodometric Titration

Sodium hypochlorite is allowed to react with an excess of iodide in an acetic acid solution. The iodine produced is then allowed to react with a standardized sodium thiosulfate solution using starch as an indicator. The advantage of this method for chlorine analysis is its high accuracy, since KIO₃ for standardization can be obtained in its primary form. Its main disadvantage is its lack of sensitivity. In this project the method was used to standardize the chlorine solutions.

\[ \text{ClO}^- + 3\text{I}^- + 2\text{H}^+ \rightarrow \text{Cl}^- + 3\text{H}_2\text{O} \]  (2.3)
Chapter 3

Experimental Procedures

3.1 Introduction

In this chapter analytical and substrate preparation methods are discussed. There are two types of procedures, standards and techniques specially developed for this project. Standard procedures were based on previous work. Explanation of the techniques specially developed for this project will be discussed in detail in chapter 4.

3.2 Preparation of Aminopropyl Filters

This method is used to prepare aminopropyl coated filters. Aminopropyl filters are an intermediate step in the preparation of sulfonamido filters. The equipment and the reagents necessary for preparation of aminopropyl filters are as follows.

1. Dry (distilled) toluene 30mL.

2. Aminopropyltriethoxysilane or aminopropyltrimethoxysilane.
3. Glass stirring rods.

4. 25 quartz filters with diameter of 3.7 cm.

5. 1 mL propylamine dissolved in 100 mL ultra pure water.

6. Vacuum source and tubing.


1. Using forceps make sure all the filters are placed on the Teflon surface of the desiccator.

   The desiccator should be placed in a fume hood.

2. A 5% solution of aminopropyltrimethoxysilane is made by adding 1.5 mL of the solution to 30 mL of toluene. The addition and subsequent mixing should be done in a fume hood.

3. Using a micropipet carefully add 750 μL of the solution to each filter. Precautions should be taken so as not to apply the solution at a particular spot but throughout the filter as much as possible.

4. After sealing the desiccator it is placed under vacuum so as to completely evaporate the toluene.

5. Release the vacuum upon doing so carefully add 0.75 mL of propylamine solution to the filters.

6. The filters are then dried in oven at 80 C. Care must be taken so as not to over dry them.

7. The dried filters are then stored in Petri dishes.

   A batch of filters usually contain around 25 filters. If 0.75 mL of aminopropyltrimethoxysilane is added to each filter it corresponds to 0.75 x 0.05, which is equal to
0.0375 g. The formula weight of aminopropyltrimethoxysilane is 179.1. In terms of number of moles per filter we get $2.09 \times 10^{-4}$. For 25 filters it would be $5.23 \times 10^{-3}$. The formula weight of methanesulfonyl chloride being 114.45 the total amount required will be $114.45 \times 5.23 \times 10^{-3}$ which is equal to 0.6 g. Similarly for DBU formula weight = 152, the requirements would be 0.8 g.

**Preparation of Methane sulfonamido propyl filters**

The reagents used for this method are methanesulfonylchloride, DBU and methylene chloride.

1. Dissolve 0.4 ml of methanesulfonylchloride (density=1.48 g/cm$^3$) and 0.8 ml of DBU in approximately 50 mL of methylene chloride.

2. Add filters to the solution. Let them react for at least one hour in a sealed container, preferably a container made up of polyvinyl chloride.

3. Completely dry the filters under vacuum. Make sure the filters are dry.

**3.2.1 Preparation of Propyl Sulfonamido Silica Gel**

The reagents used for this method are aminopropyltrimethoxysilane, toluene silica gel, methanesulfonylchloride and DBU.

1. Dissolve 1.5 g of aminopropyltrimethoxy silane in 100 mL of dry toluene in a 400 mL beaker.

2. Mix the solution while heating up to 80° C over a magnetic stirrer hot plate.

3. Upon complete mixing add 50 g of silica gel to the solution.
4. Continue heating and stirring for 30 minutes.

5. Treat the silica gel with methanesulfonylchloride and DBU. This is to convert the aminopropyl group to methanesulfonamidopropyl group.

3.2.2 Use of sulfonamido silica gel cartridges for air sampling

This experimental set up was used to sample airborne chlorine at the Buchanan Natatorium at UNLV. Direct measurement tubes usually tubes used for collecting organics from air were completely stripped of activated carbon. They were packed with treated silica gel. Prior to sampling the flow rate of each individual tube was determined in the laboratory.

![Diagram of a tube with silica gel layers](image)

Figure 3.1: Tubes used for measuring chlorine in UNLV pools.
3.3 Standardization of bleach by titration with Sodium Thiosulfate

Reagents necessary for titration

Reagents such as potassium iodate, potassium iodide, sodium carbonate, glacial acetic acid, 6M hydrochloric acid, dilute sulfuric acid, and starch solution were assembled. Reagents such as 0.01M potassium iodate were prepared in the lab itself. The steps for preparing the standard are,

1. Measure about 1.5 g of potassium iodate and heat to about 120° C for about 2 hrs. Cool the potassium iodate in a desiccator for about 30-40 minutes. Accurately weigh about 1 to 1.4g of potassium iodate. Upon weighing dissolve the measure amount in a 200-mL beaker. Transfer the solution to a 500-mL volumetric flask with rinsing. Fill to the mark. The molarity of the solution is then determined.

2. For sodium thiosulfate around 1.2-L of distilled water are boiled for around 5-10 minutes to expel the carbon dioxide. Sodium thiosulfate solutions are prone to mold formation and the presence of carbon dioxide as well as mold can alter the molarity of the solution. Boiling ensures the molarity will remain constant for a longer period of time. Rinsing the vessel to be used for making the thiosulfate solution with dichromate ensures complete sterilization. However, care should be taken as dichromate solution is a highly toxic agent. After carefully weighing about 25g of sodium thiosulfate crystals they are transferred to the 1-L bottle. It is then filled with the freshly cooled and boiled distilled water. A small amount of sodium carbonate is then added to the solution to keep the solution slightly neutral or alkaline. The solution is stored in a
Standardization of the Sodium Thiosulfate solution

Thoroughly rinse a buret with sodium thiosulfate solution. Fill it to the nearest 0.02mL with sodium thiosulfate solution. To a clean Erlenmeyer flask add about 50mL of potassium iodate and about 2g of potassium iodide. Thoroughly mix the the solution and add about 5mL of dilute sulfuric acid. This solution is then titrated immediately with the thiosulfate solution. In the presence of an acid medium iodate solution is immediately oxidized to iodine which is volatile, hence the quickness necessary for titration. Titrate until a pale yellow color is noticed. At this time add about 2-3mL of the starch solution. The solution turns blue. Titrate until all the blue color disappears. If the method is done right it takes an additional 0.5mL of the thiosulfate solution to completely remove all the blue color. This procedure was repeated until a set of consistent readings were obtained.

Estimation of hypochlorite in an unknown sample

1. Take a thoroughly cleaned weighing bottle. Add about 12mL of distilled water. Weigh the bottle along with the water.

2. Thoroughly clean the weighing bottle. Dry it completely. Obtain the weight of the empty bottle.

3. Transfer the contents of the weighing bottle to a 250 mL volumetric flask about 100mL water, using a funnel make sure all the contents of the flask are transferred.

4. Dilute the flask to the mark.

5. Take three 50mL aliquots of the sample.
6. Transfer the aliquots to 250 mL flasks containing 50mL water.

7. Ensure that the sample is completely rinsed.

8. Fill a buret to the mark with 0.1M sodium thiosulfate solution.

9. Add about 10mL of glacial acetic acid and 2g of potassium iodide to the hypochlorite sample.

10. Immediately titrate the sample the contents in the Erlenmeyer flask.

11. Add sodium thiosulfate solution until the color is pale yellow. At this time the addition of 2-3mL of starch turns the color blue. Continue the titration until it becomes colorless.

3.3.1 Establishment of Capacity of Sulfonamido Silica Gel in Aqueous Media

1. Weigh exactly 1 g of treated silica gel into a beaker.

2. Add about 25 mL of water, 200 \( \mu \)L of bleach, 200 \( \mu \)L of 6M HCl to the silica gel.

3. Stir the solution and filter it with a Buchner funnel. Measure the volume of the rinsate. Titrate 10 mL portions with FAS method to measure the residual chlorine.

3.3.2 Determination of chlorine collected on propyl sulfonamide silica gel

The following technique was developed, to analyze chlorine collected on sulfonamide-derivatized gel. It is essentially a modification of a previously published method.

1. 5 mL of bleach was diluted to 1000 mL, i.e. a dilution ratio of \( \frac{1}{200} \).
2. Four separate beakers 5 mL volumetric flasks were taken. 0.1 g of derivatized silica gel was added to each of the flask.

3. To the first flask 10 μL of the bleach was added, to the second 20 μL, to the third 30 μL, to the fourth 40 μL.

4. One mL of phosphate buffer and EDTA solution and 2 or 3 large potassium iodide crystals were added to the sample followed by heating for a few minutes to increase the rate of reaction.

5. The solution was cooled completely followed by addition of 1 ml of DPD reagent and diluted to volume.

6. On developing a color, the solutions were transferred to test tubes and absorbances was noted on spectrophotometer with absorbance set at at 550 nm.

7. A plot of absorbance versus ppm of chlorine was obtained.

8. This technique did not however give stability of color. It was changed by adding phosphate buffer, EDTA, potassium iodide crystals to the sample followed by heating for a few minutes to allow better interaction between the silica gel and potassium iodide crystals.

3.4 FAS titration method

3.4.1 Reagents required for titration

The reagents required are phosphate buffer solution, DPD solution used as an indicator, ferrous ammonium sulphate (FAS) solution used as a titrant, EDTA solution and potassium
iodide crystals. The titration is carried out as follows,

1. To a 250 mL Erlenmeyer pipet a known volume of sample. Add about 5 mL of the buffer, EDTA, and a pinch of potassium iodide. Add 5 mL DPD to this solution. A sharp red colored solution is obtained.

2. Dilute the total volume in the flask to about 100 mL if less than 100 mL of sample was pipetted.

3. Titrate the contents of the flask with FAS solution in the burette. The solution is titrated from a sharp red colored solution to a colorless end point. For a 100 mL sample, 1 mL of FAS titrant = 1.00 $\frac{mL}{FAS}$ of Cl as Cl₂.

3.5 Other procedures:

3.5.1 Preparation of samples for NMR analysis.

Some characterization experiments were undertaken to investigate whether model sulfonamide compounds were attached irreversibly (i.e., in their alkyl position. The experiment is discussed more thoroughly in section 4.3. Some of the steps were,

1. A proton NMR spectrum of the starting model compound

(1, 3-bis[methanesulfonamido]propane; synthesized by Dr. David Emerson was obtained on the Varian XL-300 NMR in UNLV Chemistry Dept. [25]. Conditions: a 5% solution in deuterochloroform vs. TMS reference, 300MHZ.

2. A sample of the compound reacted with excess chlorine for 15-20 minutes to form the chlorosulfonamide, then reduced back to the sulfonamide with excess NaHSO₃.
3. The NMR spectrum was run on the “recycled” sulfonamide compound, using the same conditions as in step 1.
Chapter 4

Results and Discussions

4.1 Development of Sulfonamido Preparation Procedures

Based on the previous work of Johnson et al, [16] who developed aminpropyl filters to collect atmospheric acids and the work of Emerson et al, [6] on sulfonamides it was decided to proceed combining both these areas of research towards preparation of sulfonamido surfaces. Accordingly, two surfaces were developed for evaluation, filters and silica gel.

4.1.1 Filters

Aminopropyl filters were prepared according to the procedure discussed in section 3.2.1. Gran plot titrations with standardized hydrochloric acid were used to establish the acid capacity [16]. A least squares plot of $\frac{V_a}{H^+}$ versus $V_a$ where $V_a$ is the volume of acid yields a slope of $\frac{1}{K_a}$ and an intercept of $\frac{V_0}{K_a}$. A typical analysis, as shown in Figure 4.1, yielded a $K_a$ of $8.1 \times 10^{-5}$ and an acid capacity of 0.366 millimoles due to amino groups.
Figure 4.1: Gran Plot to determine amino-functionalized filters. Titration was conducted in 50ml of 0.1 M NaCl (for constant ionic strength) using 0.0313 M HCl
Based on the capacity of the filters, a method for creating sulfonamide groups was devised whereby a stoichiometric excess of a sulfonyl chloride (toluene and methanesulfonyl chlorides were used) and were added in toluene solvent in the presence of an aprotic base, 1,8-diazobicyclo[5.4.0]undec-7-ene (DBU); Figure 4.2. Note that the DBU drives the reaction by reacting with the acid product HCl. The characterization of these filters is described in section 4.2.2. Due to an inability to obtain high collection efficiencies reproducibly and because of analytical considerations, new implementations of the chemistry (i.e., new substrates) were considered. Silica gel was selected as a candidate because of the ability to transfer the filter chemistry to a more convenient granular form.

Figure 4.2: Conversion of immobilized amino groups to sulfonamide groups

4.2 Silica Gel

Preparation of the sulfonamido-functionalized silica gel utilized the same reagents and chemistry as the filters with slightly different experimental implementation. The preparation steps were conducted in a reaction vessel to evenly coat the substrate; to remove solvent after the reaction was complete, a rotary evaporation step was employed. There was no necessity of intermediate handling with forceps or other instruments as in the case of fil-
ters which is a further advantage to this substrate and preparation method. After reacting
the gel with aminopropyltrimethoxysilane, a 0.1 g portion of the amino-functionalized gel
was titrated with hydrochloric acid to obtain its acid capacity. Utilizing this information
the sulfonamido derivative was then synthesized by adding a 20% stoichiometric excess of
methanesulfonyl chloride in the presence of DBU (section 3.2.1). The characterization of
this surface is described in section 4.2.3.

4.2.1 Characterization of Sulfonamido surfaces

4.2.2 Filters

Emerson et al [6] carried out previous work on the application of Haloscrubs (i.e., sulfonamido-
functionalized polystyrene resins) as aqueous chlorine scavengers. It was decided to begin
characterization studies by conducting experiments in aqueous media to establish aqueous
chlorine uptake. Aqueous investigations were then followed by gas phase studies.

Aqueous testing

Objective: To determine the amount of chlorine uptake and affinity for chlorine in the
aqueous phase. An aqueous chlorine solution was prepared by adjusting the pH of com-
mercial aqueous bleach to pH 4 by adding hydrochloric acid, then diluting with distilled
water. The filters were then introduced into an aliquot of chlorine solution. After approx-
imately 10 minutes the filters were then removed from the chlorine solution. The filters
were washed with distilled water and were analyzed by titrating with FAS solution with
DPD as an indicator. The results of a typical experiment are presented in Table 4.1. (note:
a negligible amount of chlorine was collected on blank quartz filters using this method.)
Table 4.1: Aqueous sampling

<table>
<thead>
<tr>
<th>Filter Number</th>
<th>Amount of Chlorine collected by the filter</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>130 μg</td>
</tr>
<tr>
<td>2</td>
<td>220 μg</td>
</tr>
<tr>
<td>3</td>
<td>230 μg</td>
</tr>
</tbody>
</table>

Two major effects were noted, as can be seen from the data in Table 4.1. Capacities were much lower than expected based on moles of amino groups present at the start of the reaction, and the quantitative results were variable. There are several identifiable reasons or possible reasons for these occurrences:

1. Reactions of chlorine with the surface may be subject to kinetic effects in aqueous solutions (particularly in this experiment); therefore the full chlorine capacity of the filters may not be realized in this experiment.

2. The analytical methodology was later shown to have a negative bias (section 4.3).

3. Both the aminopropyl filters and the Haloscrubs are known to be subject to steric hindrance effects under some conditions [6] [17], access to some of the sulfonamido groups may be blocked on these filters, again leading to diminished capacity.

4. The active sulfonamido groups appear to be inhomogenously distributed on the filter surface. Experimental evidence for this occurrence was obtained by treating chlorinated filters with aqueous KI solution and noting the colored I\(_2^-\) was very localized on the filters.

In summary, the filters did demonstrate an affinity for aqueous chlorine in preliminary experiments, but their collection properties did not appear to be optimum. The filters
were next tested for their ability to collect airborne chlorine.

**Passive air sampling**

Objective: To measure the uptake of chlorine in gaseous media in a passive state. It was known that the filters could collect chlorine from aqueous solution, but it was not known if the filters could collect gas-phase chlorine, and whether a wetted surface was necessary for chlorine collection. To investigate these concerns, a plexiglass chamber dimensions of $(0.76 \, \text{m} \times 0.61 \, \text{m} \times 0.61 \, \text{m})$ was specially constructed. Care was taken to make the chamber air tight. Mixtures of chlorine gas were prepared by dilution, i.e. adding pure chlorine gas from a lecture bottle via a syringe. The concentrations varied from 2-3ppm. Inside the chamber were sulfonamido filters both of the wetted and unwetted kind, with both glycerol and water used as wetting agents. The conclusions of the study were that the filter uptake was variable and that wetting the filters did not appear to affect uptake (Table 4.2).

<table>
<thead>
<tr>
<th>Filter Number</th>
<th>Experiment</th>
<th>Results Obtained</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>24 hr passive sampling</td>
<td>27.5 ( \mu \text{g} )</td>
</tr>
<tr>
<td>2</td>
<td>24 hr passive sampling wetted</td>
<td>45 ( \mu \text{g} )</td>
</tr>
<tr>
<td>3</td>
<td>24 hr passive sampling unwetted</td>
<td>40 ( \mu \text{g} )</td>
</tr>
</tbody>
</table>

Table 4.2: Typical result of a passive sampling experiment

**Active sampling**

Objective: To establish the capacity of filters when exposed to a flowing stream of air spiked with chlorine gas. Varying amounts of chlorine gas (usually about 100 \( \mu \text{g} \)) were added to flowing air stream via syringe to two sulfonamide filters connected in sequence
to a vacuum pump (Figure 4.3). After collection, the filters were analyzed using the FAS titration method. Although chlorine was collected and was usually concentrated on the first filter to some extent, breakthrough to the second filter was always observed, indicating low collection efficiency.

Figure 4.3: Setup for measuring collection efficiency for chlorine in air.

The collection experiments with the filters, though preliminary in nature, demonstrated that the sulfonamide surfaces collect chlorine, but that changes would be necessary if a sorbent surface with adequate collection efficiency for chlorine were desired. Some effort in changing filter preparation techniques was undertaken without notable success. Therefore efforts were focussed on developing sulfonamido-derivatized silica gel.

4.2.3 Silica gel experiments

Aqueous sampling

The objective of the silica gel aqueous sampling experiments of silica gel was to measure the amount of chlorine uptake by the gel in an aqueous medium. A standard chlorine solution (actually, HOCl) was prepared by diluting 5 ml of bleach to 1000 ml, and adding 5 ml of 6 molar hydrochloric acid to adjust the pH of the solution to 4. The bleach was titrated with
FAS (section 3.4) to establish the chlorine content, which was 98 ppm as Cl₂. Two different types of experiments each involving a weighed amount of silica gel, were carried out. In the first experiment about 0.1 g (weighed accurately) of silica was introduced into a beaker containing 10.00 ml bleach solution. After letting the gel react for 10 minutes the gel was filtered out. The solution was then titrated by the FAS method (section 3.4). In the second experiment, after letting the gel react with the aqueous chlorine the solution was titrated without filtering (i.e., the gel was still in the container). Since the chlorinated sulfonamido group retains the oxidizing power of the chlorine, the second experiment should yield the same amount of chlorine as the initial chlorine solution before gel addition in the absence of any analytical bias caused by the presence of the gel. Results for a typical experiment are shown in Table 4.3. It is clear from the data that the gel does remove chlorine from the solution; however some of the chlorine collected on the gel is “lost”. Subsequent experiments showed that a negative interference by the FAS method and the related DPD method is responsible for this discrepancy (Section 4.3).

<table>
<thead>
<tr>
<th>Aqueous Phase Experiments</th>
<th>Results obtained</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experiment</td>
<td>results obtained</td>
</tr>
<tr>
<td>Initial bleach</td>
<td>980 µg</td>
</tr>
<tr>
<td>Silica gel filtered</td>
<td>470 µg</td>
</tr>
<tr>
<td>Silica Gel not filtered</td>
<td>580 µg</td>
</tr>
</tbody>
</table>

Table 4.3: Typical result for a chlorine capacity experiment

**Passive sampling**

Passive sampling experiments were not performed since granular materials are less amenable to this format of sampling than filters. This feature is a disadvantage of a granular substrate versus a filter substrate.
Active sampling

Air sampling of silica gel was done in a similar manner to that of filters. About 0.1 g of silica gel was packed into two separate compartments of a glass tube. Each compartment was separated by glass wool. Figure 4.4 illustrates the design of the glass tubes. The appropriate amount of silica gel was determined from aqueous DPD titrations used to establish the chlorine capacity of the functionalized silica gel. These measurements indicated a capacity of 5 mg \( \frac{\text{Cl}_2}{g} \) of gel, so 0.1 g of gel has a capacity of 500 \( \mu \text{g} \) of \( \text{Cl}_2 \). Flow rates of approximately 50 ml per minute were used in the initial characterization studies. Chlorine was added to the ambient air stream entering the tube via a syringe, i.e., in a manner similar to the filter experiments. The sampling time varied from 1 to 10 minutes. In active sampling, no breakthrough from the first plug of the silica gel to the second plug was noticed. All the silica gel samples were analyzed by the DPD spectrophotometric method (section 3.3.3). The amount of chlorine collected was repeatable and quantifiable.

In another set of experiments, two gas samples containing the same amount of chlorine were subjected to two separate treatments: one was introduced into the air stream of a silica gel cartridge and the other was directly bubbled into aqueous potassium iodide. Both the samples were then analyzed by the DPD method. It was observed that the silica gel consistently lowered the chlorine assay. As noted above this effect was also observed in the aqueous experiments (section 4.2.3). Some attempts at addressing this problem were undertaken and are discussed in the next section.
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Figure 4.4: Cartridges used for collecting chlorine in active air sampling experiments.

4.3 Analysis

Three possibilities for the discrepancy in the chlorine assay described in section 4.2 were hypothesized:

1. The colored DPD complex is adsorbed by silica gel.

2. Chlorine can attack the alkyl hydrogen in the sulfonamido silica gel.

3. Active iodine generated for the DPD colorimetric reaction interacts with the gel.

The first possibility was easily tested and dismissed. Chlorine DPD standards were prepared according to standard procedure and the absorbance was measured. Silica gel was added, and the absorbance was checked again. The absorbance did not change significantly.

To test the possibility of chlorine attacking alkyl hydrogen (i.e., hypothesis number 2) a NMR study of model compound 1,3-bis(methanesulfonamido)propane (Figure 4.5) (synthesized by Dr.David Emerson) UNLV Department of Chemistry was performed [26].
About 1 gram of the compound was chlorinated and an NMR was run on the sample. Sodium sulfite was then used to strip the chlorine in the chlorinated sample, an NMR was run again. There was no evidence of alkyl hydrogen being chlorinated (Figures 4.6, 4.7 and 4.8).

Figure 4.5: Model compound used for running NMR experiments.
Figure 4.6: NMR of the model compound
Figure 4.7: Comparison of NMRs of the model compound before and after chlorination and dechlorination.

Work performed subsequent to this project [15] suggests that HOCl bids strongly to alkyl-derivitized silica, but it is released very slowly.

For this project, an empirical correction for the negative interference was discovered by adding constant amount of gel to all chlorine standards and samples, thereby reducing color intensity uniformly for all samples.
Figure 4.8: NMR of the N-Chlorosulfonamide
Since 0.1 g portions of gel were used for collection this weighed amount of gel was also added to the standards. The unsampled sulfonamido gel was added to volumetric flasks, and varying amounts of chlorine were added by micropipetting standardized chlorine (HOCl) solution into the flasks. The phosphate buffer, and EDTA solutions were then added, followed by a few crystals of KI the DPD color reagent,(section 3.3.3), and distilled water to volume. Addition of the gel visually diminishes the intensity of the red color produced for a given amount of chlorine. However with the gel present, a linear relationship between chlorine concentration and absorbance at 550 nm is consistently observed. Figure 4.9 and Table 4.4 display results for a typical calibration curve, and Appendix A contains the raw data for several more calibration curves.

Figure 4.6 (a) NMR spectrum of a 1,3-bis(methanesulfonamido)propane chlorination and dechlorination.

The equation for the calibration curve shown in Figure 4.9 is $y = 0.067x + 0.0235$ with $r^2 = 0.99$; raw data is given in Table 4.4.

<table>
<thead>
<tr>
<th>Concentration (µg)</th>
<th>Absorbance</th>
<th>blank</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.44</td>
<td>0.075</td>
<td>0.01</td>
</tr>
<tr>
<td>0.88</td>
<td>0.12</td>
<td></td>
</tr>
<tr>
<td>1.31</td>
<td>0.165</td>
<td></td>
</tr>
<tr>
<td>1.75</td>
<td>0.25</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.4: Data Set for air sampling at UNLV pool
Figure 4.9: Calibration curve for chlorine by DPD spectrophotometric method
4.4 Measurements of Chlorine in Air

To test the method in a "real world" application, measurements of gas phase chlorine were conducted at the UNLV swimming pool facility. Flow rates of the packed silica tubes were obtained by connecting one end to an air pump and the other end (of the air pump) to a soap bubble flow meter. Uniform flow rates were obtained for all the tubes packed with silica gel (section 4.4.1). The silica gel tubes were then used for air sampling in the UNLV swimming pool facility. Sampling times were from 120 minutes to 125 minutes. The silica gel tubes were then analyzed by the DPD method and the absorbance was recorded. The concentrations were calculated from the calibration curve.

4.4.1 Airborne Concentration of Chlorine (HOC1) in UNLV swimming pool

Cartridges packed with treated silica gel were used for sampling for chlorine in air above the swimming pool. After sampling both segments of silica in the tubes were analyzed by the modified DPD method. Absorbances were recorded for the first portion and the second portion. The second portion consistently gave about blank level absorbance readings. This indicated that there was no breakthrough.

<table>
<thead>
<tr>
<th>Tube No</th>
<th>Absorbance in First portion</th>
<th>Absorbance in Second portion</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.115</td>
<td>0.02</td>
</tr>
<tr>
<td>2</td>
<td>0.12</td>
<td>0.015</td>
</tr>
<tr>
<td>3</td>
<td>0.095</td>
<td>0.03</td>
</tr>
</tbody>
</table>

Table 4.5: Swimming pool measurements set 1

Using the calibration curve data, concentrations were determined for the samples.
A new calibration curve was created for each sampling date. A summary of the aqueous extract concentration and flow rates are given in Table 4.6.

### Sample Calculation of Air concentration above UNLV swimming pool

<table>
<thead>
<tr>
<th>Tube Number</th>
<th>Absorbance</th>
<th>Concentration $\mu g/mL$</th>
<th>Flow Rate $m^3/sec$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.115</td>
<td>0.81</td>
<td>$7.41 \times 10^{-7}$</td>
</tr>
<tr>
<td>2</td>
<td>0.12</td>
<td>0.85</td>
<td>$6.81 \times 10^{-7}$</td>
</tr>
<tr>
<td>3</td>
<td>0.095</td>
<td>0.65</td>
<td>$5.17 \times 10^{-7}$</td>
</tr>
<tr>
<td>4</td>
<td>0.10</td>
<td>0.68</td>
<td>$7.94 \times 10^{-7}$</td>
</tr>
<tr>
<td>5</td>
<td>0.11</td>
<td>0.75</td>
<td>$8.06 \times 10^{-7}$</td>
</tr>
<tr>
<td>6</td>
<td>0.125</td>
<td>0.85</td>
<td>$7.46 \times 10^{-7}$</td>
</tr>
<tr>
<td>7</td>
<td>0.115</td>
<td>0.78</td>
<td>$7.81 \times 10^{-7}$</td>
</tr>
<tr>
<td>8</td>
<td>0.10</td>
<td>0.51</td>
<td>$7.69 \times 10^{-7}$</td>
</tr>
<tr>
<td>9</td>
<td>0.11</td>
<td>0.57</td>
<td>$7.81 \times 10^{-7}$</td>
</tr>
<tr>
<td>10</td>
<td>0.11</td>
<td>0.59</td>
<td>$7.94 \times 10^{-7}$</td>
</tr>
<tr>
<td>11</td>
<td>0.12</td>
<td>0.63</td>
<td>$7.58 \times 10^{-7}$</td>
</tr>
</tbody>
</table>

Table 4.6: Data Set for air sampling at UNLV pool

To convert the extract concentrations to air concentrations, the following equation was used:

$$
\frac{([\text{aqueousconc.}] \times 5 \text{mL})/70.906 \times R \times T/P}{[(\text{flowrate}) \times (time)]}
$$

(4.1)

In this equation the chlorine measured in the aqueous extract is multiplied by the volume of the volumetric flask. This gives the total $\mu g$ of chlorine in the sample in terms of $\mu g$ per mL. This is divided by the molecular weight of chlorine to convert it to $\mu$ moles. Using the ideal gas law the $\mu$ moles are converted into $\mu$ liters (an average pressure of 0.93 atm and temperature of 25°C were used). The resultant quantity is divided by flowrate.
\times \text{time} \text{ which gives a unit of } m^3. \text{ The final quantity is the ppb volume ratio.}

<table>
<thead>
<tr>
<th>Tube Number</th>
<th>Date</th>
<th>Air Conc in ppbv.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1-4-95</td>
<td>270</td>
</tr>
<tr>
<td>2</td>
<td>1-4-95</td>
<td>305</td>
</tr>
<tr>
<td>3</td>
<td>1-4-95</td>
<td>310</td>
</tr>
<tr>
<td>4</td>
<td>1-18-95</td>
<td>188</td>
</tr>
<tr>
<td>5</td>
<td>1-18-95</td>
<td>240</td>
</tr>
<tr>
<td>6</td>
<td>1-18-95</td>
<td>290</td>
</tr>
<tr>
<td>7</td>
<td>1-18-95</td>
<td>260</td>
</tr>
<tr>
<td>8</td>
<td>1-25-95</td>
<td>170</td>
</tr>
<tr>
<td>9</td>
<td>1-25-95</td>
<td>190</td>
</tr>
<tr>
<td>10</td>
<td>1-25-95</td>
<td>190</td>
</tr>
<tr>
<td>11</td>
<td>1-25-95</td>
<td>210</td>
</tr>
<tr>
<td>Mean Air Conc.</td>
<td></td>
<td>240</td>
</tr>
<tr>
<td>Std. Dev.</td>
<td></td>
<td>51</td>
</tr>
</tbody>
</table>

Table 4.7: Data Set for air sampling at UNLV pool
Chapter 5

Conclusions

In this chapter the chlorine (HOCI) concentration data obtained in the study are compared to the calculated thermodynamic equilibrium value and to previously reported measured values. A summary of findings and a list of possible future research directions are given.

5.1 Calculated thermodynamic HOCI(g) concentrations

Chlorine undergoes a number of reaction with aqueous species. The primary equilibrium involving chlorine species and water are:

\[ \text{Cl}_2(g) = \text{Cl}_2(aq) \quad K_H = 0.062 \quad (5.1) \]

\[ \text{Cl}_2(g) + \text{H}_2\text{O} = \text{HCl}(aq) + \text{HOCl}(aq) \quad (5.2) \]

\[ K_{eq} = \frac{[\text{H}^+][\text{Cl}^-][\text{HOCl}]}{p\text{Cl}_2} \]
\[ K_{eq} = 4.2 \times 10^{-4} \]

\[ HOCl(aq) \rightleftharpoons H^+ + OCl^- (aq) \quad (5.3) \]

\[ K_a = \frac{[H^+][OCl^-]}{HOCl} \]
\[ K_a = 3.0 \times 10^{-8} \]

\[ HOCl(g) \rightleftharpoons HOCl(aq) \quad (5.4) \]

\[ K_H = 260 \quad \text{(from Appendix B and references)} \]

Swimming pools typically have a pH in the range of 7.0 to 8.0; at these pH's the \( Cl_2 \) is negligible, even considering an elevated aqueous chloride concentration (Appendix A and eq.5.2). The pH, chloride and active chlorine concentration in pool water were measured and are given in the tables below. Using these data and eqns 5.3 and 5.4 the equilibrium concentration of HOCl above the pool can be calculated.

From eq 5.3 and table 5.1

\[ \frac{OCl^-}{HOCl} = \frac{K_a}{K_H} = \frac{3.0 \times 10^{-8}}{10^{-7.5}} = A \]

the pH has been assumed as 7.5 substituting the values we get \( A = 0.95 \)

From eq 5.4 and table 5.3

\[ [HOCl] = \frac{C_{eq}}{A} = 2.88 \times 10^{-5} = B \]

From eqns 5.4 and 5.3

air concentration of HOCl = \( \frac{B \times 10^6}{260} = C = 111 \text{ ppb} \)

This is for 25°C; if the pool temperatures are higher than 25°C which is normally the case it would increase this number. When the effect of temperature is considered there
Table 5.1: Typical values for chlorides in UNLV pool

<table>
<thead>
<tr>
<th>Chlorides in the UNLV pool</th>
<th>PPM Chloride in the pool</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>310</td>
</tr>
<tr>
<td></td>
<td>310</td>
</tr>
<tr>
<td></td>
<td>297</td>
</tr>
</tbody>
</table>

Table 5.2: Data on titration of pool water using FAS method

is reasonable agreement with the measured value of 240 ± 51 ppb. Differences could be due to a number of factors, including day to day variability in pH, chlorine concentration, temperature and the concentration of chloride in the water.

5.1.1 Conclusions:

Going back to the progress of this project, initial work was done with treated filters. The result was difficulty in quantification of the chlorine collected on the filters. It was then decided to use silica gel as a substrate. Experiments were carried out in the aqueous phase and gas phase. Initial lab scale aqueous phase and gas phase experiments gave encouraging results. The next step was packing the silica gel into tubes for outdoor sampling. At the same time modifications were also carried out in analytical method. The DPD method was suitably modified. The modified method has given consistent results as evidenced from calibration curves and linear curve fitting of data points obtained from outdoor sampling. In summation the following points explain the advantages of this method.
1. Good sensitivity and limit of detection (L.O.D.) of approx. 0.5 µg Cl₂.

2. Method is amenable to gaseous measurements.

3. The samples can be concentrated into smaller volumes in a flask. Quick measurement of chlorine concentration can be done.

4. This method has many future possibilities such as altering the substrate to e.g., poly-tetrafluoroethylene.

5. The method is selective to chlorine only. Many analytical methods convert the chlorine to chloride, which means that chloride from the environment can constitute a major contaminant.
Bibliography


Appendix A

<table>
<thead>
<tr>
<th>Tube Number</th>
<th>Unknown Absorbance</th>
<th>Concentration $\mu g/mL$</th>
<th>Flow Rate $m^3/sec.$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.115</td>
<td>0.80</td>
<td>$7.41 \times 10^{-7}$</td>
</tr>
<tr>
<td>2</td>
<td>0.12</td>
<td>0.84</td>
<td>$6.81 \times 10^{-7}$</td>
</tr>
<tr>
<td>3</td>
<td>0.095</td>
<td>0.65</td>
<td>$5.17 \times 10^{-7}$</td>
</tr>
<tr>
<td>4</td>
<td>0.10</td>
<td>0.68</td>
<td>$7.94 \times 10^{-7}$</td>
</tr>
<tr>
<td>5</td>
<td>0.11</td>
<td>0.74</td>
<td>$8.06 \times 10^{-7}$</td>
</tr>
<tr>
<td>6</td>
<td>0.125</td>
<td>0.85</td>
<td>$7.46 \times 10^{-7}$</td>
</tr>
<tr>
<td>7</td>
<td>0.115</td>
<td>0.77</td>
<td>$7.81 \times 10^{-7}$</td>
</tr>
<tr>
<td>8</td>
<td>0.10</td>
<td>0.50</td>
<td>$7.69 \times 10^{-7}$</td>
</tr>
<tr>
<td>9</td>
<td>0.11</td>
<td>0.57</td>
<td>$7.81 \times 10^{-7}$</td>
</tr>
<tr>
<td>10</td>
<td>0.1125</td>
<td>0.59</td>
<td>$7.94 \times 10^{-7}$</td>
</tr>
<tr>
<td>11</td>
<td>0.12</td>
<td>0.63</td>
<td>$7.58 \times 10^{-7}$</td>
</tr>
</tbody>
</table>

Table A.1: Data Set for air sampling at UNLV pool
### Data set of air sampling results

<table>
<thead>
<tr>
<th>Tube Number</th>
<th>Time in sec</th>
<th>Air Conc in ppb</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7500</td>
<td>270</td>
</tr>
<tr>
<td>2</td>
<td>7500</td>
<td>305</td>
</tr>
<tr>
<td>3</td>
<td>7500</td>
<td>310</td>
</tr>
<tr>
<td>4</td>
<td>8400</td>
<td>190</td>
</tr>
<tr>
<td>5</td>
<td>7200</td>
<td>240</td>
</tr>
<tr>
<td>6</td>
<td>7320</td>
<td>290</td>
</tr>
<tr>
<td>7</td>
<td>7200</td>
<td>260</td>
</tr>
<tr>
<td>8</td>
<td>7200</td>
<td>170</td>
</tr>
<tr>
<td>9</td>
<td>7200</td>
<td>190</td>
</tr>
<tr>
<td>10</td>
<td>7200</td>
<td>190</td>
</tr>
<tr>
<td>11</td>
<td>7200</td>
<td>210</td>
</tr>
</tbody>
</table>

Table A.2: Data Set for air sampling at UNLV pool

### Concentration data set of air sampling results set 1

<table>
<thead>
<tr>
<th>Concentration</th>
<th>µl of 200:1</th>
<th>Absorbance</th>
<th>blank</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.44</td>
<td>10</td>
<td>0.075</td>
<td>0.01</td>
</tr>
<tr>
<td>0.88</td>
<td>20</td>
<td>0.165</td>
<td></td>
</tr>
<tr>
<td>1.31</td>
<td>30</td>
<td>0.25</td>
<td></td>
</tr>
<tr>
<td>1.75</td>
<td>40</td>
<td>0.25</td>
<td></td>
</tr>
</tbody>
</table>

Table A.3: Data Set for air sampling at UNLV pool

### Concentration data set of air sampling results set 2 Jan 18 1995

<table>
<thead>
<tr>
<th>Concentration</th>
<th>µl of 200:1</th>
<th>Absorbance</th>
<th>blank</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.44</td>
<td>10</td>
<td>0.065</td>
<td>0.02</td>
</tr>
<tr>
<td>0.88</td>
<td>20</td>
<td>0.135</td>
<td></td>
</tr>
<tr>
<td>1.31</td>
<td>30</td>
<td>0.18</td>
<td></td>
</tr>
<tr>
<td>1.75</td>
<td>40</td>
<td>0.25</td>
<td></td>
</tr>
</tbody>
</table>

Table A.4: Data Set for air sampling at UNLV pool
### Concentration data set of air sampling results set 3 Jan 25 1995

<table>
<thead>
<tr>
<th>Concentration</th>
<th>µl of 200:1</th>
<th>Absorbance</th>
<th>Blank</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.44</td>
<td>10</td>
<td>0.085</td>
<td>0.03</td>
</tr>
<tr>
<td>0.88</td>
<td>20</td>
<td>0.165</td>
<td></td>
</tr>
<tr>
<td>1.31</td>
<td>30</td>
<td>0.23</td>
<td></td>
</tr>
<tr>
<td>1.75</td>
<td>40</td>
<td>0.30</td>
<td></td>
</tr>
</tbody>
</table>

Table A.5: Data Set for air sampling at UNLV pool

### Data set for establishing molarity of bleach

<table>
<thead>
<tr>
<th>Mls start</th>
<th>Mls stop</th>
<th>Volume</th>
<th>Molarity</th>
<th>Molarity of 200:1 bleach</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.73</td>
<td>23.23</td>
<td>2.4</td>
<td>0.6177</td>
<td>0.00308</td>
</tr>
</tbody>
</table>

Table A.6: Titration data for standardizing bleach

### Chlorides in the UNLV pool

<table>
<thead>
<tr>
<th>PPM Chloride</th>
<th>Calibration Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1ppm</td>
<td>75</td>
</tr>
<tr>
<td>2ppm</td>
<td>156</td>
</tr>
<tr>
<td>4ppm</td>
<td>346</td>
</tr>
<tr>
<td>6ppm</td>
<td>493</td>
</tr>
</tbody>
</table>

Table A.7: Calibration values of chlorides in pool water by IC

### Chlorides in the UNLV pool

<table>
<thead>
<tr>
<th>PPM Chloride in the pool</th>
</tr>
</thead>
<tbody>
<tr>
<td>310</td>
</tr>
<tr>
<td>310</td>
</tr>
<tr>
<td>297</td>
</tr>
</tbody>
</table>

Table A.8: Chloride concentrations in pool water by IC
### Concentration data set of air sampling results set 2 Jan 18 1995

<table>
<thead>
<tr>
<th>Concentration</th>
<th>μl of 200:1</th>
<th>Absorbance</th>
<th>blank</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.44</td>
<td>10</td>
<td>0.065</td>
<td>0.02</td>
</tr>
<tr>
<td>0.88</td>
<td>20</td>
<td>0.135</td>
<td></td>
</tr>
<tr>
<td>1.31</td>
<td>30</td>
<td>0.18</td>
<td></td>
</tr>
<tr>
<td>1.75</td>
<td>40</td>
<td>0.25</td>
<td></td>
</tr>
</tbody>
</table>

Table A.9: Data Set for air sampling at UNLV pool

### Concentration data set of air sampling results set 3 Jan 25 1995

<table>
<thead>
<tr>
<th>Concentration</th>
<th>μl of 200:1</th>
<th>Absorbance</th>
<th>blank</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.44</td>
<td>10</td>
<td>0.085</td>
<td>0.03</td>
</tr>
<tr>
<td>0.88</td>
<td>20</td>
<td>0.165</td>
<td></td>
</tr>
<tr>
<td>1.31</td>
<td>30</td>
<td>0.23</td>
<td></td>
</tr>
<tr>
<td>1.75</td>
<td>40</td>
<td>0.30</td>
<td></td>
</tr>
</tbody>
</table>

Table A.10: Data Set for air sampling at UNLV pool
Appendix B

B.1 Calculation of Henry’s Law constant for HOCl

The formation of HOCl(aq) can be represented as a sum of three thermodynamic equations from [1]. These equations are given as

\[ \frac{1}{2}Cl_2(g) + H_2O \rightarrow HClO(aq) + H^+(aq) + e^- \]  \hspace{1cm} (B.1)

where

\[ E^0 = -1.630 \text{v} \quad \text{and} \quad \Delta G^0 = -nF E = +157 \ \frac{KJ}{mole} \]

\[ \frac{1}{2}O_2(aq) + 2H^+(aq) + 2e^- \rightarrow H_2O \]  \hspace{1cm} (B.2)

where

\[ E^0 = 1.2291 \times \Delta G^0 = -nF E = -237.0 \ \frac{KJ}{mole} \]

\[ \frac{1}{2}H_2(g) \rightarrow H^+ + e^- \ E^0 = 0 \ \text{therefore} \ \Delta G^0 = 0 \]  \hspace{1cm} (B.3)
cancelling all like quantities we get equation 4 represented below,

\[
\frac{1}{2} \text{Cl}_2(g) + \frac{1}{2} \text{O}_2(g) + \frac{1}{2} \text{H}_2(g) \rightarrow \text{HClO(aq)}
\]  
(B.4)

since equation 4 was arrived at by adding equations 1-4 and cancelling like terms the \( \Delta \text{fGo} \) for \( \text{HOCl(aq)} \) will be equal to \(-237.2 + 157\) which equals \(-79.9 \text{ KJ/mole}\). This compares well to another literature value for the \( \Delta G^\circ \) of formation for \( \text{HOCl(aq)} \) of \(-79.6 \text{ KJ/mole}\).

From literature survey the \( \Delta \text{fGo} \) for \( \text{HOCl(g)} \) is \(-66.1 \text{ KJ/mole}\). While for \( \text{HOCl(aq)} \) we obtained a similar value = \(-79.9 \text{ KJ/mole}\). Therefore for the entire reaction the difference in free energy will be \(-79.9 - (-66.1) = 13.8 \text{ KJ/mole}\).

From the equation \( \Delta \text{Go} = -RT \ln K_H \), the Henry’s Law constant \( K_H \) can be calculated. Transposing the equation,

\[
K_H = \exp \left( \frac{13800}{(8.316)(298.15)} \right)
\]  
(B.5)

The value of \( K_H \) is 263 moles/L-atm, which can be used to calculate the concentrations of \( \text{HOCl} \) gas in equilibrium with aqueous media containing \( \text{HOCl} \), such as swimming pools.
Appendix C

C.1 Sources of chemicals and supplies

Note: All chemicals reagent grade unless otherwise specified.

1. 3 Aminopropyltrimethoxysilane- Huls petrarch, Bristol PA

2. Sodium Chloride- VWR, Los Angeles, CA

3. Chlorine cylinders- Matheson, Los Angeles,

4. 1,8 diazobicyclo [5.4.0] undecene- Aldrich, Milwaukee, WI

5. N,N -Diethyl-phenylenediamine- VWR, Los Angeles, CA

6. EDTA- Mallinckrodt, Paris, KY

7. Ferrous ammonium sulfate- VWR, Los Angeles, CA

8. Glass cartridges- SKC, Eightyfour, PA

9. Glacial acetic acid- Spectrum, Gardena, CA

10. HCl- Fischer, Fairlawn, NJ

11. Methane sulfonyl chloride- Aldrich, Milwaukee, WI

12. Methylene Chloride- Baxter, Muskegon, MI
15. Potassium Iodide- Mallinckrodt, Paris, KY
16. Propylamine- MCB, Cincinatti, OH
17. Quartz filters- Pallflex, Putnam, CN
18. Silica gel 600-mesh grade- Aldrich, Milwaukee, WI
19. Sodium sulfite- Fischer, Fairlawn, NJ
20. Sodium thiosulfate- VWR, Los Angeles, CA
21. Toluene- Aldrich, Milwaukee, WI
22. Toluene sulfonyl chloride- Aldrich, Milwaukee, WI.