# An Exploration of the Gas Phase Reactions of Chlorine Dioxide and Malodorous Compounds of Putrefaction Using FT-IR Instrumentation

*Anna M. Love and Ngee Sing Chong*

*Deans' Distinguished Essay Award recipient*

## Abstract

*Chlorine dioxide has been used to replace traditional water treatments, deactivate Anthracis bacillus, and remediate various molds and bacteria. This study aims to analyze the products of the gas phase reaction between chlorine dioxide and malodorous compounds produced during putrefaction. The study focuses on the reactions between chlorine dioxide and three specific chemicals: cadaverine (amine), 2-hexanone (ketone), and cyclohexyl mercaptan (thiol). The analysis of the gas phase reaction products is carried out using a Varian 7000 Fourier Transform infrared spectrometer (FTIR) with a 2.4 m gas cell. The measurement of most reaction by-products requires spectral resolution of 0.5 cm$^{-1}$ because the spectra of most gas phase standards are available for spectral resolutions of 0.5 cm$^{-1}$ or 0.25 cm$^{-1}$ only. The reaction between cadaverine and chlorine dioxide resulted in the rapid formation of ammonia gas. The GC-MS analysis of the reaction between chlorine dioxide and cadaverine showed the presence of the following nitrogenous compounds: cyanogen chloride; chloromethane; dichloromethane; chloroform; dichloro-acetonitrile; and hexachloroacetone. The reaction by-products of cyclohexyl mercaptan were identified as sulfur dioxide, methanesulfonyl chloride, cyclohexene, 1-chlorocyclohexene, cyclohexanone, and 2-chlorocyclohexanone. Detected byproducts of the reaction between the Tenax sorbent material and chlorine dioxide include acetophenone; 2-chlorophenol; benzyl chloride; chlorobenzene, benzeneacetaldehyde; phenylethyne; and benzene. Increasing concentrations of carbon dioxide and other reaction products were mirrored by decreased concentrations of chlorine dioxide and the malodorous chemicals.*

## Introduction

Mammal putrefaction has many noxious products, including mercaptans, amines, and carbonyl compounds. In the past a 15% lead acetate solution has been used to convert odorous compounds in coffins into salts, which, in turn, must also be removed via glass wool (*1*). Chlorine dioxide is a safer, more practical method for neutralizing these compounds.

Chlorine dioxide is also "more powerful, easier to use, and more environmentally friendly than equivalent chlorine treatments" (*6*). Although chlorine dioxide treatments are not as cost efficient as chlorination, they do not produce the same harmful byproducts as chlorine when reacting with organic compounds, and as a result many water treatment plants for highly populated areas have replaced traditional chlorination with a chlorine dioxide treatment (*7*). In addition to the treatment of water, the Environmental Protection Agency acknowledged liquid chlorine dioxide as a safe and effective treatment for: bleaching textiles, washing fruits and vegetables, bleaching paper and pulp, disinfecting meat and poultry in 1967, and in 1988, chlorine dioxide in the gas phase was registered as a sterilant for manufacturing laboratory equipment, environmental surfaces, tools, and clean rooms (*8*). There are, of course, many more cited applications for chlorine dioxide.

In 1998, Hisashi Inomura and Yoshinao Makino applied for a patent for a method of generation for chlorine dioxide gas for sterilization, citing coffin disinfection as a possible application (*4*). The following year another Japanese patent application was filed for chlorine dioxide products to be used for disinfecting the dead (*2).* The products include a spray solution and an injectable solution of chlorine dioxide, which are used to disinfect and deodorize bodies before placement in coffins (*2).* While these patents are on file, little to no other information is available on the gas phase reaction between chlorine dioxide and the compounds associated with decomposing cadavers.

Cemeteries, livestock farms, and disaster areas often encounter challenges with cadavers, especially the noxious gases released during decomposition. In an effort to characterize several types of reactions between chlorine dioxide and volatile organic compounds released during mammalian decay, model compounds with three distinct functional groups were chosen for the study: cadaverine (a biogenic amine), 2-hexanone (a ketone), and cyclohexyl mercaptapan (a thiol).

The relationship between cadaverine and chlorine dioxide gas is especially significant because liquid chlorine dioxide is currently an accepted treatment of the volatile sulfuric compounds that cause bad breath, which is also caused, in part, by cadaverine (*3*)(*6*). Also, cold-smoked fish are undergoing scrutiny by the Food and Drug Administration because of the hazardous biogenic amines that are still present after processing; cadaverine is among these biogenic amines (*9*). As mentioned previously, the EPA considers chlorine dioxide an effective treatment of meat and poultry; therefore, it also has the potential to reduce concentrations of cadaverine and other biogenic amines in cold-smoked fish (*8*).

The analysis of the gas phase reaction between chlorine dioxide and these compounds associated with putrefaction explores the various reaction byproducts and their respective concentrations. This project seeks to determine the efficacy of chlorine dioxide as a disinfectant and deodorizer of malodorous compounds released during decomposition.

## Materials and Methods

### *Chlorine Dioxide Production*

Z Series Research – Fast Release Chlorine Dioxide requires mixing equal amounts of Part A and Part B chemical precursors to generate chlorine dioxide gas (ICA TriNova; Newnan, GA). For these trials, approximately 2 g, unless noted otherwise, of Part A and Part B were mixed in a 500 mL Büchner flask, which was sealed with a rubber stopper while the sidearm of the flask had a short piece of hose that was pinched shut with a clamp.

As the ClO2 gas was generating, a silicon-lined 6-L gas stainless steel canister was prepared by evacuation to -30 in Hg followed by the injection of 5 μL of the malodorous compound with a gas-tight syringe into the canister. Then, after approximately 60 minutes of generation, the chlorine dioxide gas was introduced to the 6-L gas canister. Nitrogen gas was immediately used to pressurize the canister to 30 psi, and samples were taken successively for 40 minutes. The samples were collected with a 2.4 m gas cell, which was evacuated to -30 in Hg between each sample and was filled with the gaseous reaction mixture to a pressure of 0 psig to minimize the transfer of gas between the gas cell and the ambient air.

This reaction involves a second procedure, which is similar to the aforementioned method with the exception of the resolution, the quantities of the starting materials, and a glass tube with a Teflon seal in lieu of the 6-L gas canister. For this reaction, 3 μL of cadaverine and 4 g of Part A and Part B of the chlorine dioxide precursor materials are used. Also, the chlorine dioxide gas production occurs over a 3-week period in a 6-L gas canister, after which it is introduced to the glass tube with Teflon seal containing 3 μL of cadaverine.

### Instrumentation

A Varian 7000 Fourier transform infrared spectrometer (FT-IR) was used to analyze the samples in the 2.4 m gas cell. A 4 $cm^{-1}$ spectral resolution allows the sample spectra to be acquired at a shorter time interval and hence a greater frequency relative a higher resolution at 0.5 $cm^{-1}$ so that, while the spectral features are not as well defined or sharp in peak shape, the time series gives a more accurate depiction of the reactions' chronological phases and can better identify any transient intermediate products. Each sample spectrum is processed using 25 co-added scans with an open aperture. When the cadaverine was analyzed, the FT-IR's resolution setting was0.5 $cm^{-1}$ in order to facilitate the measurement of ammonia gas evolved. Both methods have a sensitivity setting of 1 on the FT-IR.

## Results

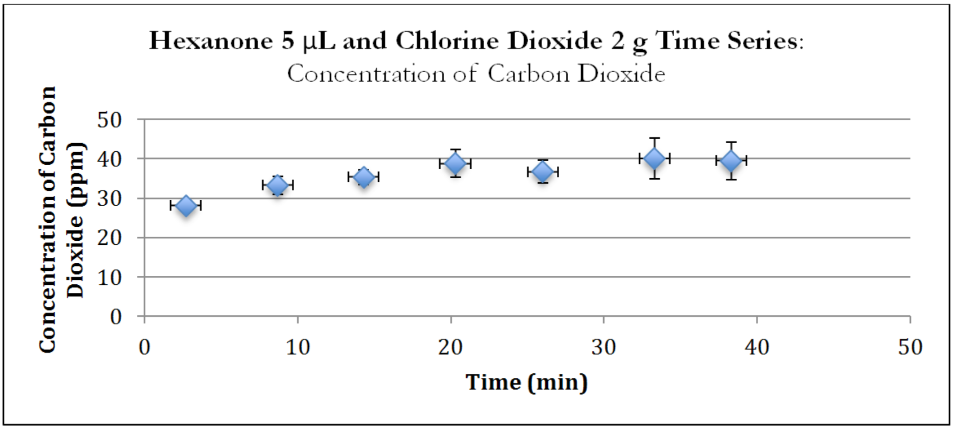

**Figure 1.1: Concentration of Carbon Dioxide Graph in 2-Hexanone and Chlorine Dioxide Reactions**

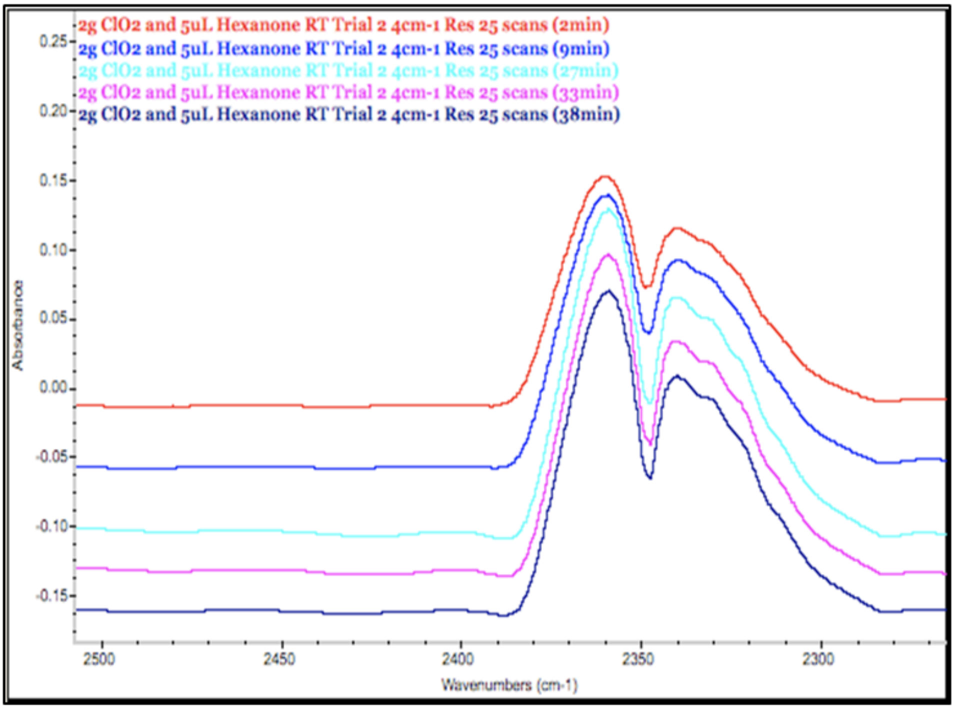

**Figure 1.2: FTIR Spectrum; Region of C-O Asymmetric Stretch Indicative of Carbon Dioxide Concentration in 2-Hexanone and Chlorine Dioxide Reaction, Trial 1**

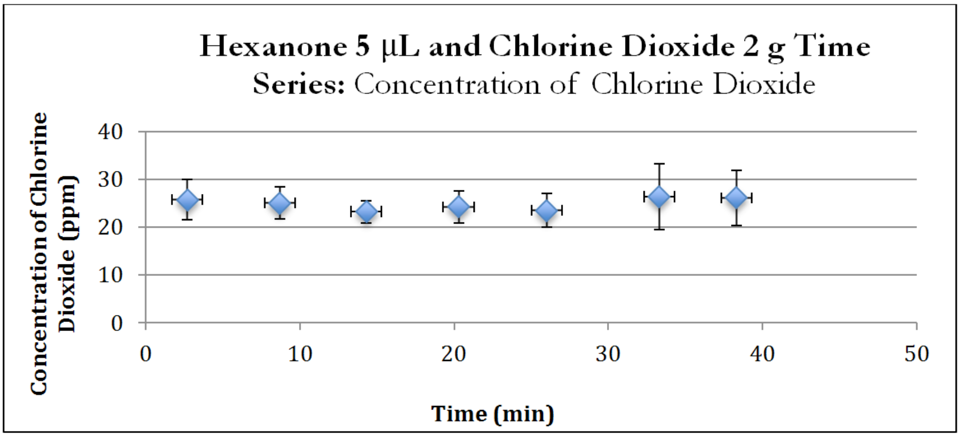

**Figure 2.1: Concentration of Chlorine Dioxide Graph in 2-Hexanone and Chlorine Dioxide Reactions**

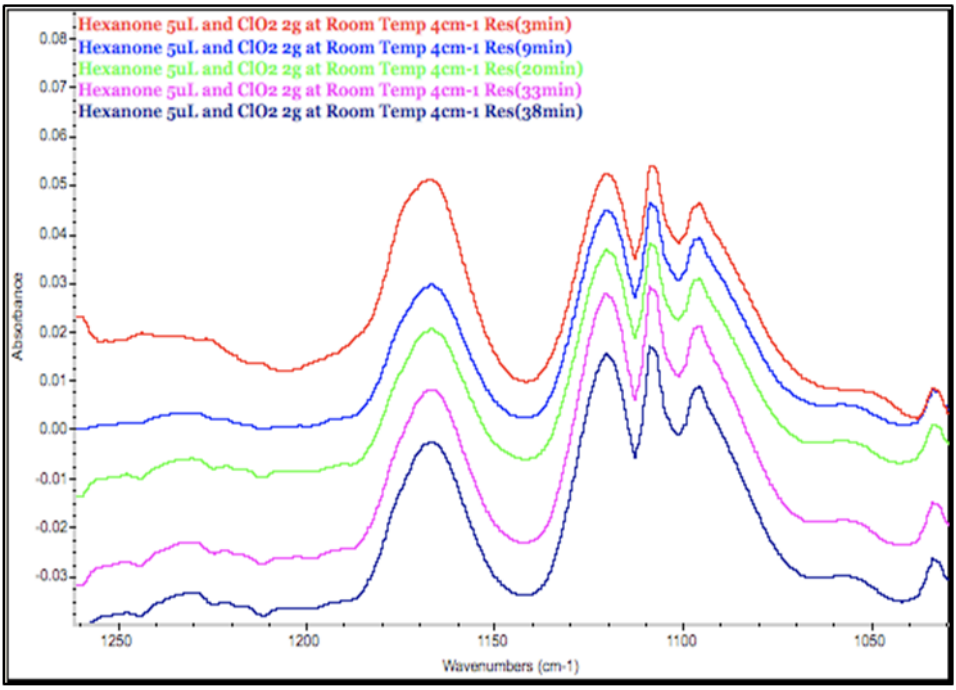

**Figure 2.2: FTIR Spectrum; Region of Cl-O Asymmetric Bending Indicative of Chlorine Dioxide Concentration in 2-Hexanone and Chlorine Dioxide Reaction, Trial 1**

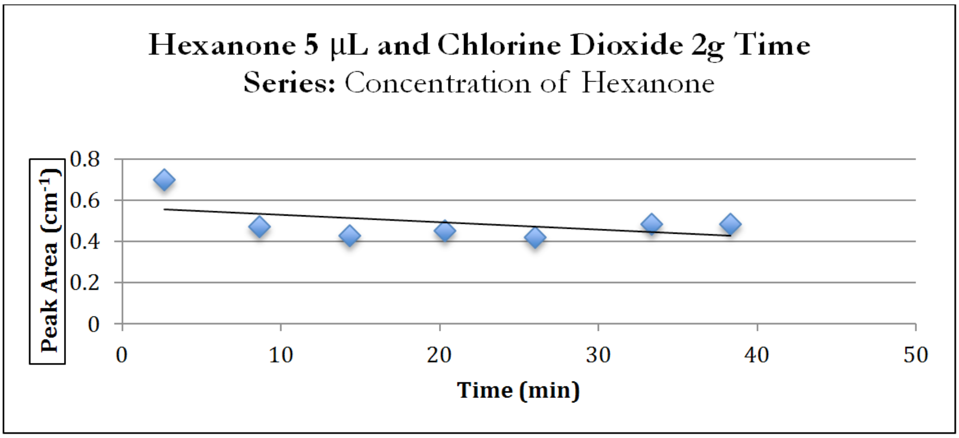

**Figure 3.1: Variation of Hexanone Concentrations as a Function of Time in Reactions of 2-Hexanone and Chlorine Dioxide**

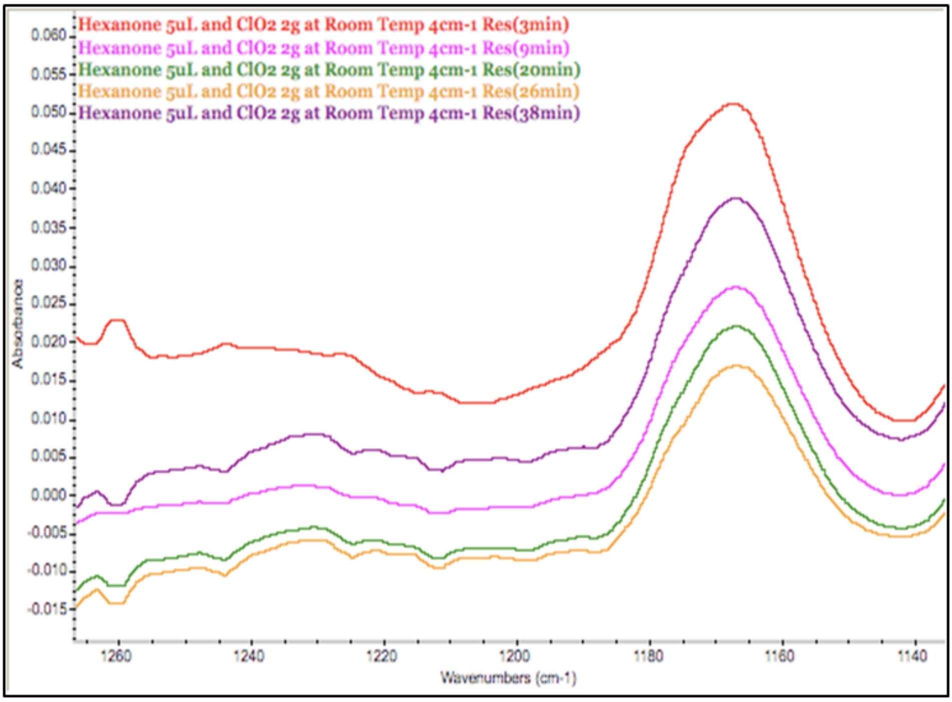

**Figure 3.2: FTIR Spectrum of the Fingerprint Region Featuring 2-Hexanone Concentrations in 2-Hexanone and Chlorine Dioxide Reaction (Trial 1)**

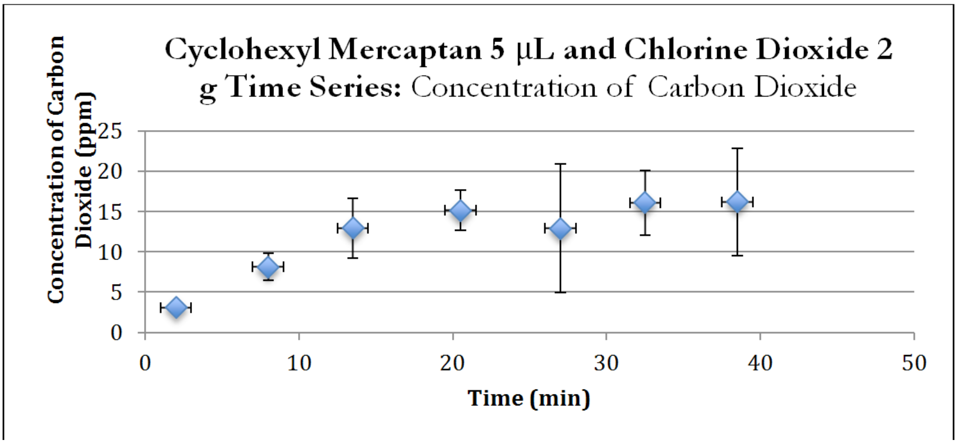

**Figure 4.1: Concentrations of Carbon Dioxide Produced in the Reactions of Cyclohexyl Mercaptan and Chlorine Dioxide**

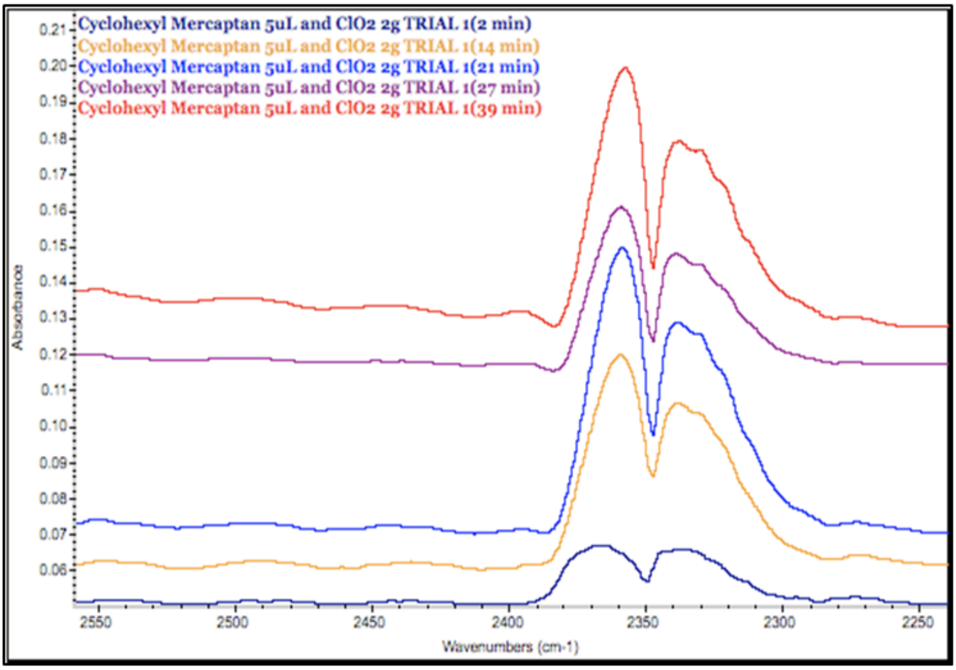

**Figure 4.2: FTIR Spectral Region of C-O Asymmetric Stretch of Varying Carbon Dioxide Concentrations Resulting from the Reaction between Cyclohexyl Mercaptan and Chlorine Dioxide (Trial 1)**

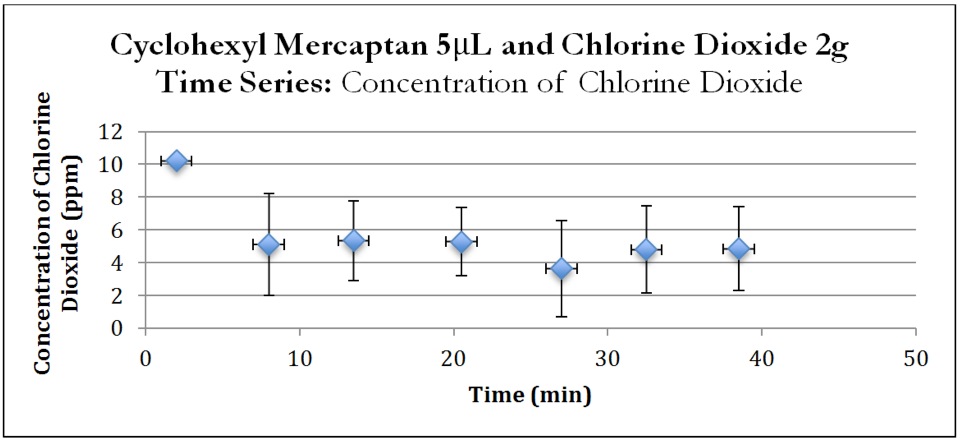

Figure 5.1: Time-Dependent Concentrations of Chlorine Dioxide in Reactions between Cyclohexyl Mercaptan and Chlorine Dioxide

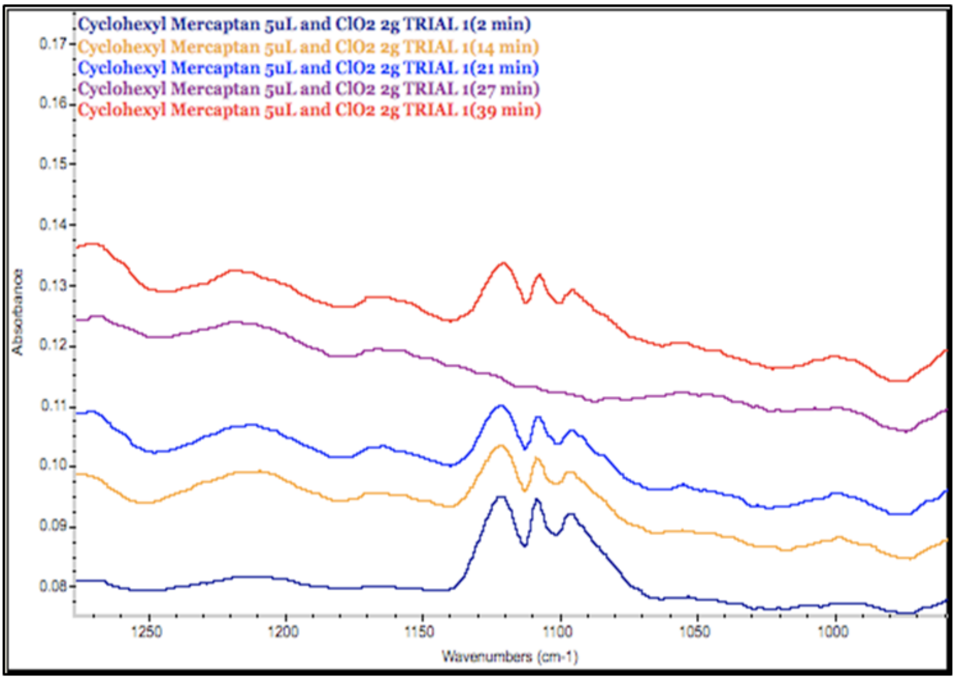

Figure 5.2: FTIR Spectrum; Region of Cl-O Asymmetric Bending Indicative of Chlorine Dioxide Concentration in 2-Hexanone and Chlorine Dioxide Reaction, Trial 1

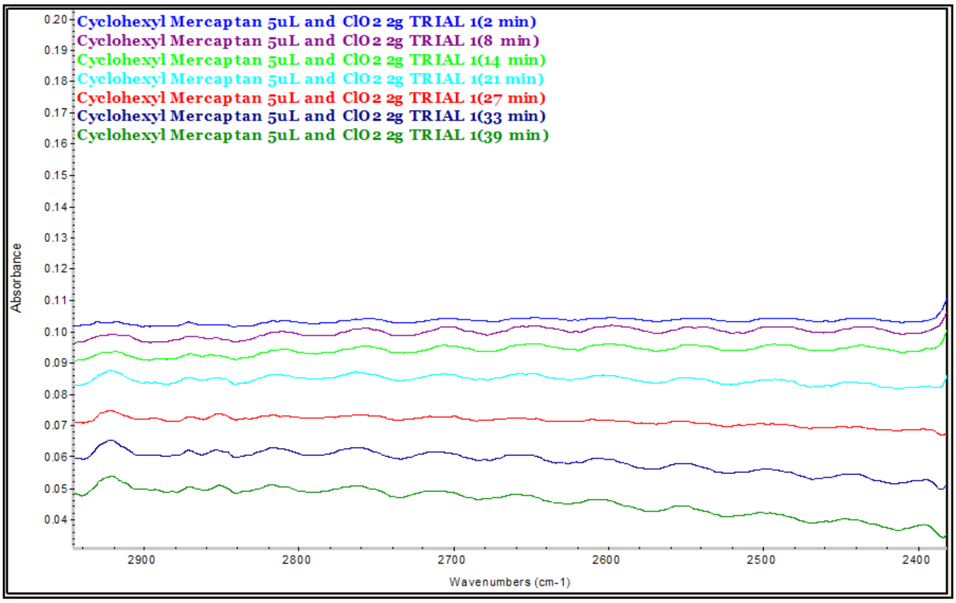

**Figure 6.1: FTIR Spectrum; Region of S-H Stretch, Absence of Peak Indicates Depletion of Cyclohexyl Mercaptan Concentrations**

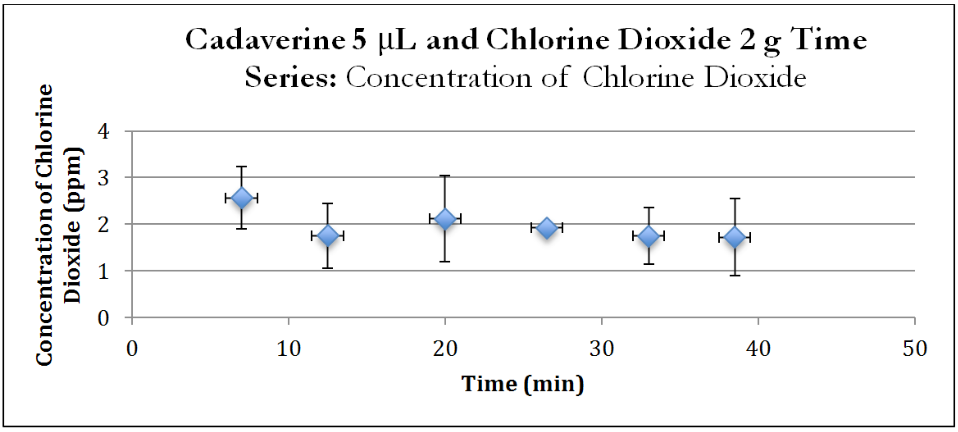

Figure 7.1: Concentration of Chlorine Dioxide Graph in Cadaverine and Chlorine Dioxide Reactions at 4 cm-1 Resolution

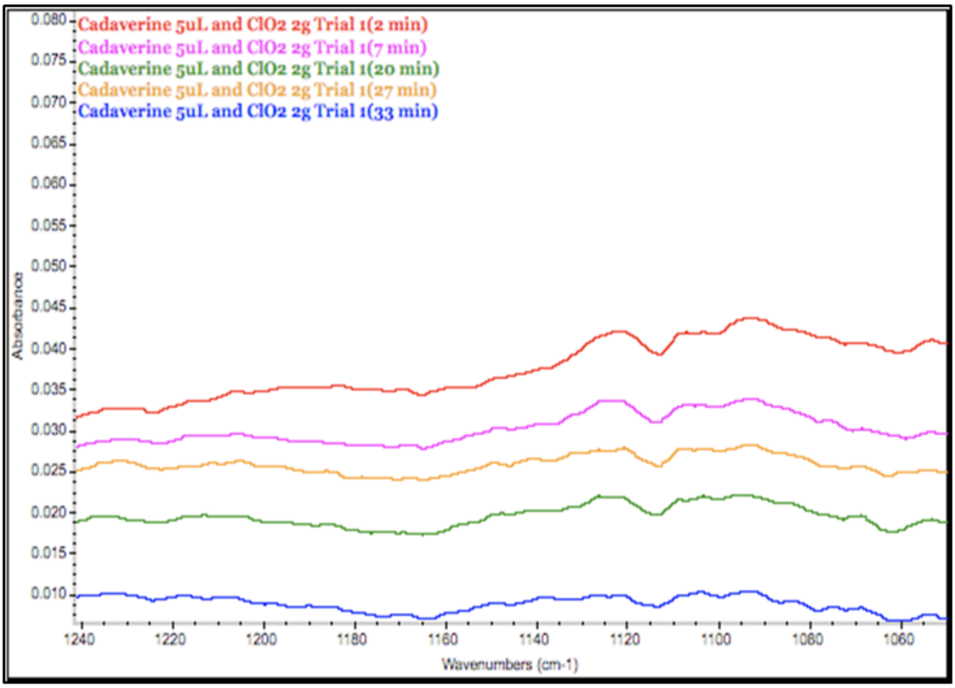

Figure 7.2: FTIR Spectrum; Region of Cl-O Asymmetric Bending Indicative of Chlorine Dioxide Concentration in Cadaverine and Chlorine Dioxide Reaction, Trial 1 at 4 cm-1 Resolution

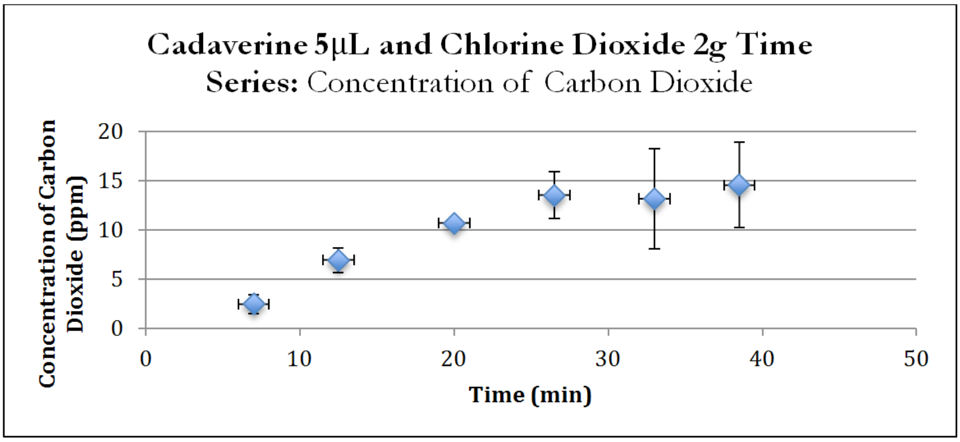

**Figure 8.1: Concentration of Chlorine Dioxide Graph in Cadaverine and Chlorine Dioxide Reactions at 4 cm-1 Resolution**

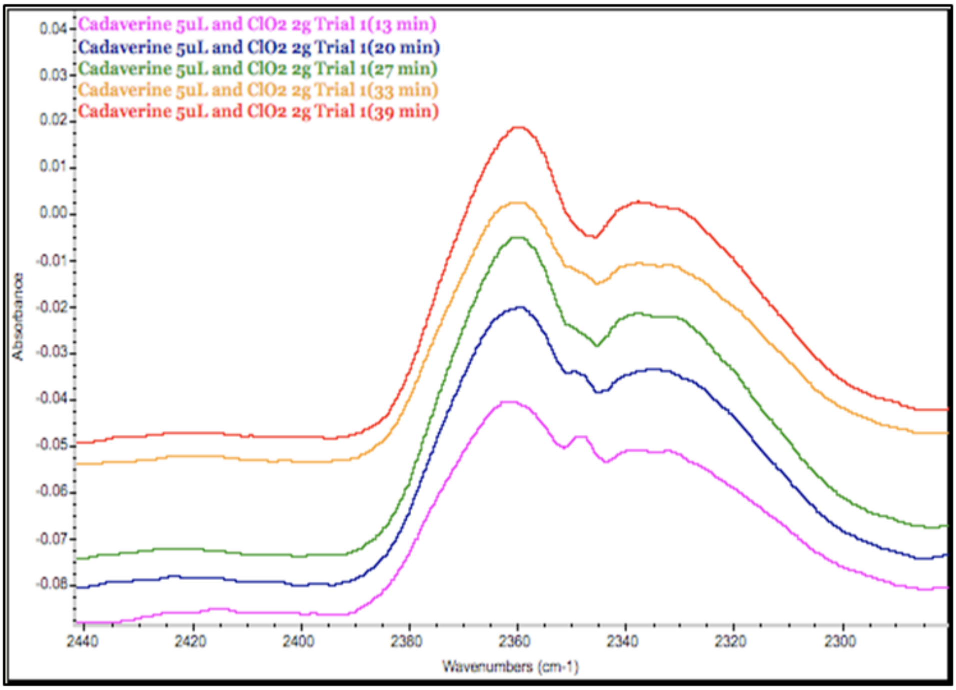

**Figure 8.2: FTIR Spectrum; Region of C-O Asymmetric Stretch Indicative of Carbon Dioxide Concentration in Cadaverine and Chlorine Dioxide Reaction, Trial 1 at 4 cm-1 Resolution**

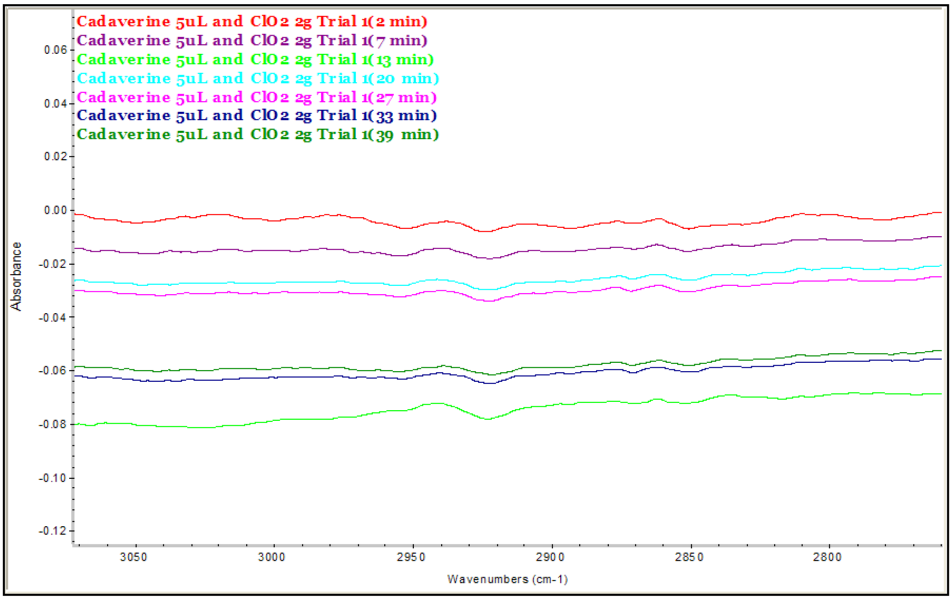

**Figure 9.1: FTIR Spectrum; 2800-3000 cm-1 Region of Cadaverine Presentation**

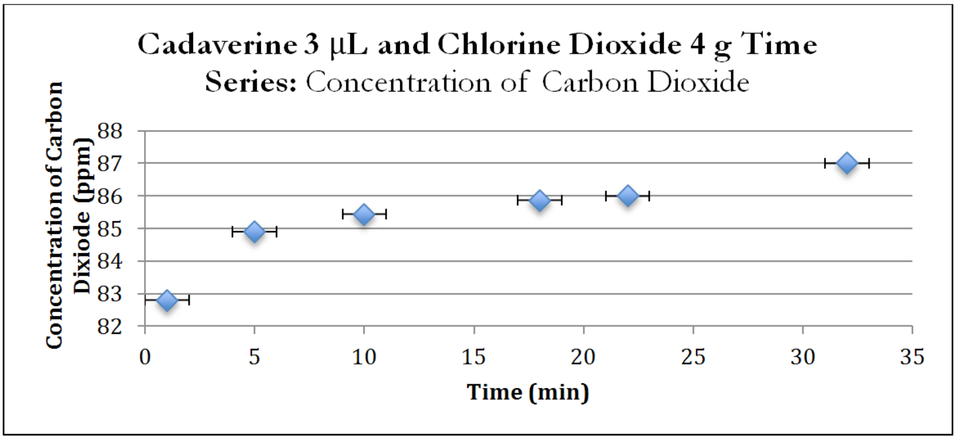

**Figure 10.1: Concentration of Chlorine Dioxide Graph in Cadaverine and Chlorine Dioxide Reactions at 0.5 cm-1 Resolution**

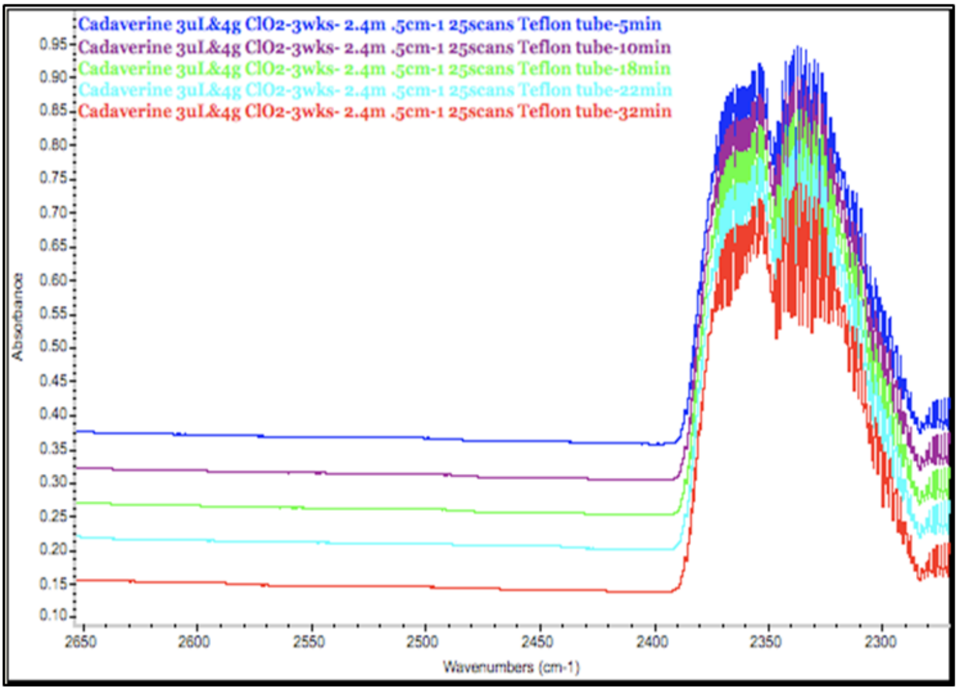

**Figure 10.2: FTIR Spectrum; Region of C-O Asymmetric Stretch Indicative of Carbon Dioxide Concentration in Cadaverine and Chlorine Dioxide Reaction, Teflon tube trial at 0.5 cm-1 Resolution**

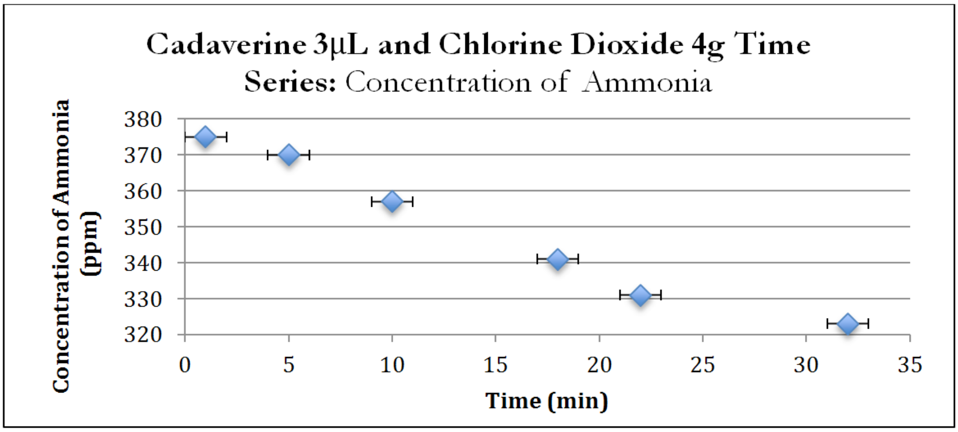

**Figure 11.1: Concentration of Ammonia Graph in Cadaverine and Chlorine Dioxide Reactions at 0.5 cm-1 Resolution**

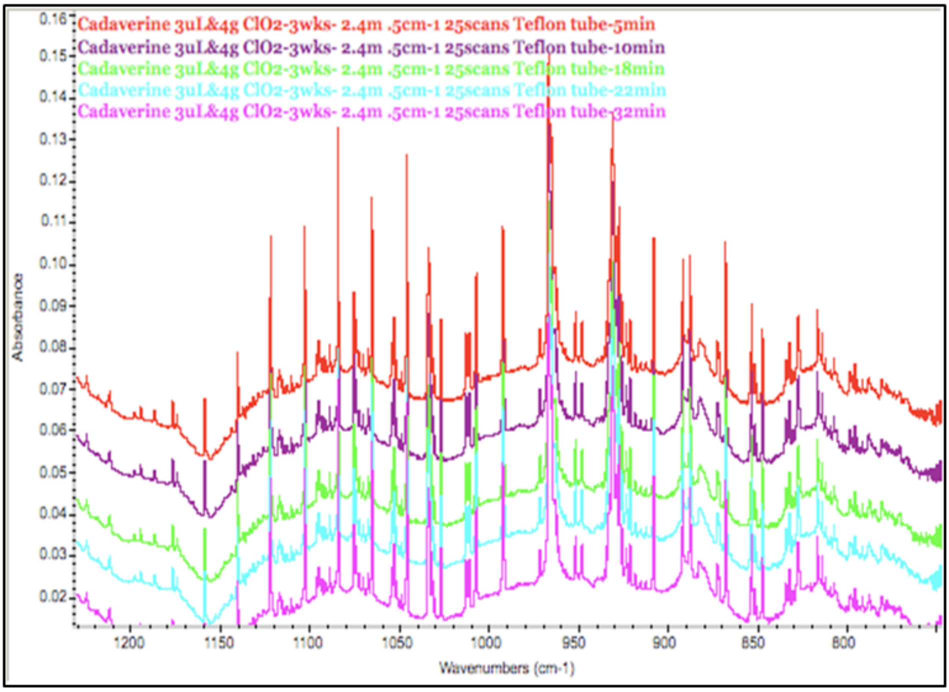

**Figure 11.2: FTIR Spectrum; Region of Asymmetric Deformation for N-H Bonds Indicative of Ammonia Concentration in Cadaverine and Chlorine Dioxide Reaction, Teflon tube trial at 0.5 cm-1 Resolution**

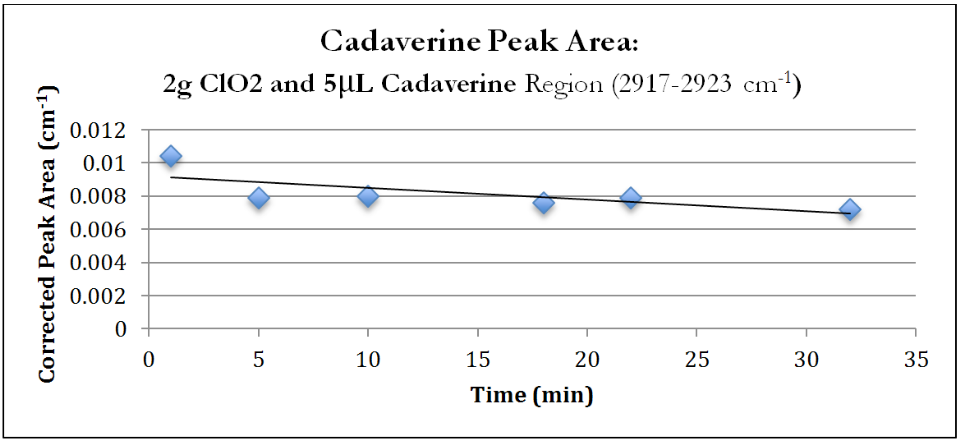

**Figure 12.1: Graph of Cadaverine Peak Area in the Reaction Between Chlorine Dioxide and Cadaverine at 0.5 cm-1 Resolution**

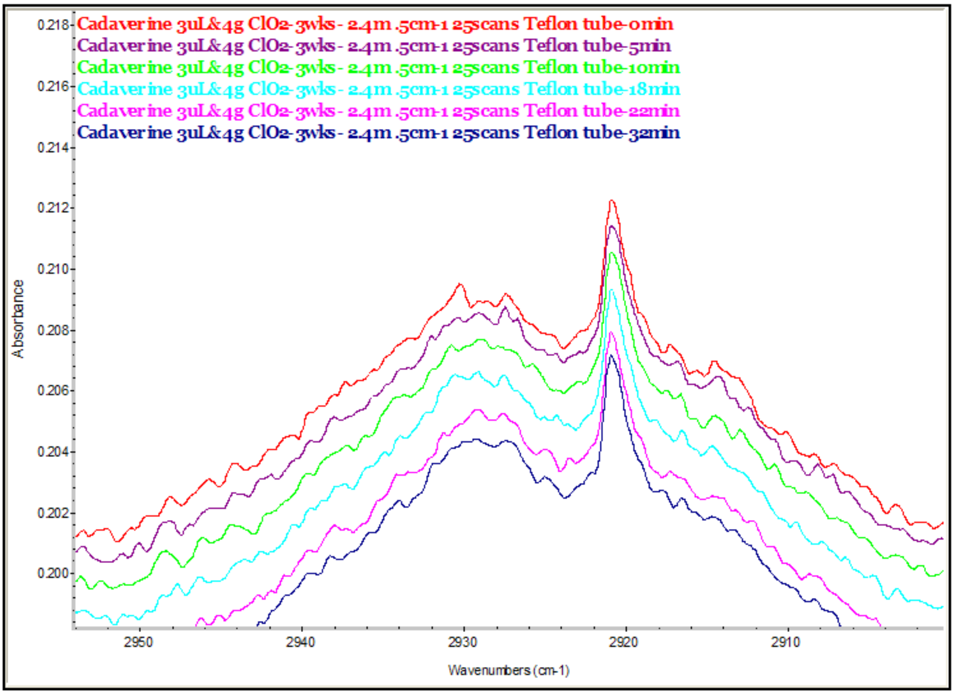

**Figure 12.2: FTIR Spectrum, Cadaverine Peak Area Time Series for the Reaction Between Chlorine Dioxide and Cadaverine at 0.5 cm-1 Resolution**

## Conclusions

The experimental trials all exhibited the same trend: the concentrations of carbon dioxide and intermediate organic products of the malodorous precursors increased as a function of time, while the concentrations of the gaseous chlorine dioxide and the malodorous compounds decreased or were undetectable in the spectra. Overall, the results suggest that chlorine dioxide successfully diminished the concentrations of the malodorous compounds in question.

A preliminary study on chlorine dioxide gas generation and concentrations as a function of time was complete prior to this study. The study consisted of several time series to indicate the concentrations of chlorine dioxide gas as generation and degeneration occurred. The gas reached peak concentrations at around 20 minutes and began to degenerate after that time. When 2g of each precursor were allowed to react, the concentration of chlorine dioxide was 749 ppm at the 20-minute interval. As suspected, when 5g of each precursor were allowed to react, the concentration was higher at the 20-minute interval at 923 ppm.

Of the three studies on the model compounds, the trials involving 2-hexanone produced the most dramatic results. The reaction between 2-hexanone and chlorine dioxide presented very high concentrations of chlorine dioxide (*Fig 2.1*) and carbon dioxide (*Fig 1.1)*, while the peak area of 2-hexanone diminished significantly (*Fig 3.1*). During the reaction between 2-hexanone and chlorine dioxide, the peaks representing 2-hexanone were visible in the fingerprint region spectra (*Fig 3.2*).

In the analysis of the reactions involving cadaverine and cyclohexyl mercaptan, the chlorine dioxide concentrations were lower than expected. In this instance, the reaction was occurring very quickly producing large quantities of carbon dioxide and even larger quantities of hydrocarbons while simultaneously depleting the concentrations of chlorine dioxide and malodorous chemicals. The reactions occurred, to a large extent, in these experiments before the first sample of the time series could be processed, which was approximately 2 minutes after the introduction of the chlorine dioxide to the malodorous compounds.

The results of the cyclohexyl mercaptan time series presented no peaks at the 2550 $cm^{-1}$ wavenumber, which is where the S-H stretch of a mercaptan would be visible (*Fig 6.1*). The diminished peaks were another signifier that the reaction occurred very quickly before the first sample was processed by the FTIR. During the characterization of this reaction, the chlorine dioxide concentrations decreased by approximately 50%, while the carbon dioxide concentration increased almost 400% (*Fig 5.1 and 4.1*).

The studies on cadaverine were done at 0.5 $cm^{-1}$ and 4 $cm^{-1}$ spectral resolutions. Prior to completing the study of the reaction between chlorine dioxide and cadaverine, a sample of cadaverine was processed with a Golden Gate ATR to create a reference spectrum; this spectrum presented two strong peaks between 2800 $cm^{-1}$ and 2950 $cm^{-1}$ wavenumbers. In the 0.5 $cm^{-1}$ resolution study, these peaks were very small, and they continued to diminish as a function of time (*Fig 12.1*). In contrast, the study at 4 $cm^{-1}$ had no detectable peaks in that region (*Fig 9.1*). The reaction characterized with a higher resolution displayed concentrations of ammonia that decreased as a function of time (*Fig 11.2)*. Because the ammonia peaks overlapped the chlorine dioxide peaks in this reaction, the concentrations of chlorine dioxide could not be calculated. However, the reaction analyzed at 4 $cm^{-1}$ showed a decrease in chlorine dioxide concentrations (*Fig 7.1)*. Overall, the cadaverine was no longer detectable or had significantly diminished concentrations, which supports the efficacy of the chlorine dioxide.

While all of the studies presented consistent results, further analysis of the reactions should be carried out using gas chromatography mass spectrometry to positively identify the intermediate organic byproducts of the reactions. A preliminary GC-MS study was carried out on the reactions between cadaverine and chlorine dioxide and cyclohexyl mercaptan and chlorine dioxide using a pre-concentrator. However, the Tenax sorbent material in the pre-concentrator reacted with the chlorine dioxide contaminating the reaction and muddling the results. Some of the contaminated products were acetophenone; 2-chlorophenol; benzyl chloride; chlorobenzene; benzeneacetaldehyde; phenylethyne; and benzene. In spite of the contamination, the cadaverine reaction showed the presence of several nitrogenous compounds: cyanogen chloride; chloromethane; dichloromethane; chloroform; dichloro-acetonitrile; and hexachloroacetone. In the cyclohexyl mercaptan study, sulfur dioxide; methanesulfonyl chloride; cyclohexene; 1-chlorocyclohexene; cyclohexanone; and 2-chlorocycloheanone were present. A glass bead trap may be used to substitute the Tenax sorbent material to prevent contamination of the reactions.

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