A high-performance liquid chromatography system with Fenton's reagent for detection of gas-phase hydrogen peroxide

Jun Liu
University of Nevada, Las Vegas

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UMI®
A HIGH PERFORMANCE LIQUID CHROMATOGRAPHY SYSTEM
WITH FENTON'S REAGENT FOR DETECTION OF
GAS-PHASE HYDROGEN PEROXIDE

by

Jun Liu
Bachelor of Science
East China University of Science and Technology
1993

A thesis submitted in partial fulfillment
of the requirements for the

Master of Science Degree
Department of Chemistry
College of Science

Graduate College
University of Nevada, Las Vegas
May 2000
The Thesis prepared by

Jun Liu

Entitled

A High Performance Liquid Chromatography System

with Fenton's Reagent for Detection of Gas-Phase Hydrogen Peroxide

is approved in partial fulfillment of the requirements for the degree of

Master of Science

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Graduate College Faculty Representative
ABSTRACT

A High Performance Liquid Chromatography System with Fenton’s Reagent for Detection of Gas-Phase Hydrogen Peroxide

by

Jun Liu

Dr. Spencer M. Steinberg, Examination Committee Chair
Professor of Chemistry
University of Nevada, Las Vegas

A simple quantitative HPLC method for analysis of gas-phase hydrogen peroxide (H₂O₂) has been developed. This method relies on conversion of sodium salicylate to dihydroxybenzoic acid, sodium salts by using Fenton’s reagent (a mixture of H₂O₂ and ferrous iron) under the proper conditions. Hydroxyl radicals generated from Fenton’s reagent will react with sodium salicylate and generate 2,3-, 2,4-, and 2,5-dihydroxybenzoic acid (sodium salts), which can be quantitatively determined by HPLC-UV at wavelength 310 nm. The cryogenic sampling system was chosen to collect gas-phase H₂O₂. The detection limit for this method is 0.03 ppm. The seasonal variation of H₂O₂ in Las Vegas was observed, and the correlations between the concentrations of O₃, CO, NOₓ and that of H₂O₂ were studied.
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ACKNOWLEDGEMENTS

I would like to thank my advisor and committee chair Dr. Spencer M. Steinberg, and my co-advisor Dr. Brian J. Johnson for their constant instruction, guidance and great help during this research.

I am grateful to my other committee members Dr. Vernon F. Hodge and Dr. Jacimaria R. Batista for their valuable suggestions and encouragement. I would thank Dr. Sapochak for lending me the dewar. I give my sincere thanks to Mr. Dennis L. Stevens for his great help in my TA job, and for his kindness to answer my so many questions. I also thank the Department of Chemistry, University of Nevada, Las Vegas for supporting me to study and get the degree.

I would like to especially thank my dear father and mother, whose greatest love supported my study and research. I thank my twin sister Jian, who gives me the invaluable help and encouragement in my study and life. I also thank my younger brother Qin, who sacrificed much for me. Without my family’s love and encouragement, it would be impossible for me to get the master’s degree in chemistry.
CHAPTER 1

INTRODUCTION

1.1. Applications of H$_2$O$_2$ in Industry

Hydrogen peroxide, H$_2$O$_2$, is colorless syrupy liquid. Its melting point is -0.4°C, its boiling point is 150°C, and its density is 1.45 g/ml. H$_2$O$_2$ is often used in an aqueous solution. The pure liquid is stable but aqueous solutions are unstable. H$_2$O$_2$ can act as a powerful oxidizing agent (E$_0$, acid solution +1.77 volts) when converted to H$_2$O (2 H$^-$ + 2 e + H$_2$O$_2$ $\rightarrow$ 2 H$_2$O), and as a reducing agent (E$_0$ +0.68 volts) when converted to O$_2$ (H$_2$O$_2$ $\rightarrow$ 2 H$^-$ + 2 e + O$_2$). H$_2$O$_2$ product is used in the following: chemicals (33%), pollution control (19%), textiles (17%), paper (13%). Free H$_2$O$_2$ is used as a rocket propellant.

Hydrogen peroxide can be used to oxidize various inorganic and organic pollutants. Table 1-1 (modified from Venkatadri and Peters, 1993) shows some of the numerous applications of H$_2$O$_2$ for removal of inorganic pollutants. These activities include prevention of sulfides odors from wastewater collection and treatment units, removal of sulfites, hypochlorites, nitrites, cyanides, and chlorine. Also a number of organic contaminants can be removed in wastewaters, including formaldehyde, phenols, and fat, oil, grease, and suspended solids. H$_2$O$_2$ treatment can reduce the toxicity and

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Examples of these organics are: nitrobenzene, cresols, aniline, monochlorophenols, dichlorophenols, and trichlorophenol (Eckenfelder, 1992).

Table 1-1: Application of $\text{H}_2\text{O}_2$ in Industries

(Modified from Venkatadri and Peters, 1993)

<table>
<thead>
<tr>
<th>Application</th>
<th>Problems Addressed by Reaction with $\text{H}_2\text{O}_2$</th>
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<tr>
<td>Odor and Corrosion Control</td>
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<td>Oxygen Supply</td>
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<td>Removal of Sulfite ($\text{SO}_3^{2-}$)</td>
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<td>Removal of Hypochlorite ($\text{OCl}$)</td>
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<td>Removal of Formaldehyde ($\text{CH}_2\text{O}$)</td>
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<tr>
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</tr>
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<td>Removal of Sulfides ($\text{S}^{2-}$)</td>
<td>Toxicity, oxygen demand, odors</td>
</tr>
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<td>Removal of Sulfur Dioxide ($\text{SO}_2$)</td>
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<td>Removal of Nitrogen Oxides ($\text{NO}_x$)</td>
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$\text{H}_2\text{O}_2$ can also be used in the bleaching of pulp and paper, and in organic syntheses, and by the surface treatment industry, for cleaning, decorating, protecting, and etching metals.
H₂O₂ is also very useful in biological treatment facilities and in the bioremediation of contaminated sites, because it can supply oxygen to microorganisms by disassociation into O₂ and H₂O. When used as a disinfecting agent, it can control undesirable biofilm growth (Huling, et al., 1991).

1.2. Environmental Effects of H₂O₂

1.2.1. Atmospheric Photochemistry of H₂O₂

Photochemical processes significantly affect the formation of H₂O₂. In general, it has been observed that the atmospheric concentration of H₂O₂ is highest during heavy photochemical smog episodes. The seasonal variation of gaseous H₂O₂ was studied in southern California (Sakugawa and Kaplan, 1989), over the central United States (Boatman, et al., 1989) and at the top of Whitetop Mountain, VA (Olszyna, et al., 1988). These results showed that the concentration of H₂O₂ is highest in the summer. A clear diurnal variation of gaseous H₂O₂ concentrations was observed by Sakugawa and Kaplan (1989) and Possanzini et al. (1988). It showed that H₂O₂ level was low in the early morning and increased in the afternoon with the maximum peak occurring at 2-5 p.m. H₂O₂ concentration significantly decreased at night. The same diurnal variation, which attributed to the photochemical formation of H₂O₂ was also obtained by Downs et al. (1989) and Das et al. (1983). Regional variation of gaseous H₂O₂ was studied too, and the results showed that H₂O₂ may be higher in rural areas than those in pollutant-impacted urban areas (Sakugawa and Kaplan, 1989), and higher in the inland sites than sites near the coast (Sakugawa and Kaplan, 1990).
Hydrogen peroxide plays an important role in photochemical reactions. It is expected to be a mechanistically significant species in atmospheric photochemistry as a chain terminator and as an index of hydroperoxyl radical (HO$_2$) concentrations.

\[
\text{HO}_2^* + \text{HO}_2^* \longrightarrow \text{H}_2\text{O}_2 + \text{O}_2 \quad (1)
\]

\[
\text{H}_2\text{O}_2 + \text{hv} \longrightarrow 2\text{OH}^* \quad (2)
\]

\[
\text{H}_2\text{O}_2 + \text{OH}^* \longrightarrow \text{H}_2\text{O} + \text{HO}_2^* \quad (3)
\]

Sakugawa et al. (1990a) showed that HO$_2^*$ radicals are formed by photochemical reactions which involve volatile organic compounds (VOC), nitrogen oxide (NO$_x$) and carbon monoxide (CO), which are major air pollutants in urban and rural atmospheres. Modeling studies demonstrated that high concentrations of VOC and CO would favor the formation of H$_2$O$_2$, whereas high concentrations of NO$_x$ would inhibit the formation of H$_2$O$_2$. Meteorological conditions, such as solar radiation, air temperature, and high water vapor concentration, are primary factors that determine the atmospheric formation and content of gaseous H$_2$O$_2$.

Thus, knowledge of the concentration of H$_2$O$_2$ in both polluted ambient atmospheres and in simulated atmospheric system is of great interest. The quantitative determination of H$_2$O$_2$ in the environment has vital implications for atmospheric chemistry and the investigation of photochemical smog.

1.2.2. An Important Role in the Acid Precipitation

A number of models (Hov, 1983; Calvert and Stockwell, 1983) have demonstrated that H$_2$O$_2$ is a major oxidant for sulfur dioxide (SO$_2$) which leads to the formation of sulfate in the atmosphere. The oxidation of dissolved sulfur dioxide (SO$_2$) to sulfuric acid (H$_2$SO$_4$) by H$_2$O$_2$ is the peroxidic reaction, which is of great environmental
concern, and has been demonstrated in numerous experiments (Rodhe et al., 1981; Kunen et al., 1983; Kelly et al., 1985). Hydrogen peroxide is highly soluble and the oxidation of \( \text{SO}_2 \) to \( \text{H}_2\text{SO}_4 \) by \( \text{H}_2\text{O}_2 \) is relatively fast in acidic solution, whereas the oxidation of \( \text{SO}_2 \) by \( \text{O}_3 \) and the catalytic oxidation of \( \text{SO}_2 \) by \( \text{O}_3 \) in the presence of \( \text{Fe} \) and \( \text{Mn} \) is very slow at lower \( \text{pH} \) (\( \text{pH} < 5 \)) (Nair and Peters, 1989; Tsai et al., 1990). Thus, hydrogen peroxide plays an important role in the formation of acidic rain, fog, and cloud waters. During the 1980s, acid rain became a worldwide concern. Therefore, the role that \( \text{H}_2\text{O}_2 \) plays and the degree that it is involved in the formation of acid rain is significant. In cloud environments, it was found that there is an inverse relationship between the concentrations of \( \text{H}_2\text{O}_2 \) and \( \text{SO}_2 \) (Kelly et al., 1985; Heikes et al., 1987; Mohnen and Kadlec, 1989). There is a nonlinear relationship between the \( \text{SO}_2 \) emission and the wet deposition of sulfate, which suggests that a limiting factor in the acidification of precipitation is often the amount of \( \text{H}_2\text{O}_2 \) available in the cloud-precipitation system.

Although, the important role that \( \text{H}_2\text{O}_2 \) plays in the oxidation of \( \text{SO}_2 \) is well established, the role it plays in the atmospheric oxidation of \( \text{NO}_x \) compounds to \( \text{HNO}_3 \) is in dispute. Hartkamp and Bachhausen (1987) thought there was a strong indication for the oxidation of \( \text{NO}_x \) by \( \text{H}_2\text{O}_2 \) to \( \text{HNO}_3 \) in acidic precipitation. On the contrary, Tanner and Kelly (1989) declared this idea a misconception. \( \text{H}_2\text{O}_2 \) appears to play no significant role in this oxidation.

1.2.3. Harmful Effect on Plants

It is well known that \( \text{H}_2\text{O}_2 \) has harmful effects on plant cells (Kaiser, 1979; Robinson et al., 1980; Tanaka et al., 1982, 1985). Hydrogen peroxide and organic
hydroperoxide are potent plant phytotoxins because they are fairly soluble in lipids, e.g., in the waxes of leaves. Lipids usually prevent aqueous phase components from entering the leaf structure, thus. \( \text{H}_2\text{O}_2 \) may play a contributory role in damaging vegetation. It is already clearly indicated by microscopic studies that dissolved \( \text{H}_2\text{O}_2 \) in acidic solution can cause morphological damage to Norway spruce (Masuch et al., 1986). Some researchers suggested that \( \text{H}_2\text{O}_2 \) may be one of the major reasons for recent declining of forests in North America and central Europe (McLaughlin, 1985; Möller, 1988, 1989), and the damaging of forest trees in the mountains surrounding Los Angeles. Therefore, research on atmospheric \( \text{H}_2\text{O}_2 \) has important ramifications to the study of anthropogenic effects on the environment.

### 1.3. Formation of Gas-Phase \( \text{H}_2\text{O}_2 \)

In nature, the coupling reaction of two hydroperoxyl radicals is thought to be the main mechanism to produce atmospheric \( \text{H}_2\text{O}_2 \):

\[
\text{HO}_2^\cdot + \text{HO}_2^\cdot \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \quad (1)
\]

Hydroperoxyl radicals can be produced by several sources. During the daytime, the major source is the photolysis of formaldehyde (Bufalini et al., 1972):

\[
\text{HCHO} + \text{hv} \rightarrow \text{H}^\cdot + \text{HCO}^\cdot \quad (4)
\]

\[
\text{H}^\cdot + \text{O}_2 \rightarrow \text{HO}_2^\cdot \quad (5)
\]

\[
\text{HCO}^\cdot + \text{O}_2 \rightarrow \text{HO}_2^\cdot + \text{CO} \quad (6)
\]

During the night time, the main source is the reaction of formaldehyde with \( \text{NO}_x \) (Cantrell et al., 1985):

\[
\text{NO}_3^\cdot + \text{HCHO} \rightarrow \text{HNO}_3 + \text{HCO}^\cdot \quad (7)
\]
HCO $^\cdot$ + O$_2$ $\rightarrow$ HO$_2$ $^\cdot$ + CO \hspace{1cm} (6)

Or the reaction of R-CH$_3$ with NO$_2$:

\[
\begin{align*}
R\cdot CH_3 + NO_2 $^\cdot$ &\rightarrow R\cdot CH_2 $^\cdot$ + HNO$_3$ \hspace{1cm} (8) \\
R\cdot CH_2 $^\cdot$ + O$_2$ &\rightarrow R\cdot CH_2O$^\cdot$ \hspace{1cm} (9) \\
R\cdot CH_2O$^\cdot$ + NO &\rightarrow R\cdot CH_2O $^\cdot$ + NO$_2$ \hspace{1cm} (10) \\
R\cdot CH_2O $^\cdot$ + O$_2$ &\rightarrow R\cdot CHO + HO$_2$ $^\cdot$ \hspace{1cm} (11)
\end{align*}
\]

There is a strong correlation of gas phase H$_2$O$_2$ with O$_3$ (Olszyna et al., 1988), because the photolysis of O$_3$ can generate electronically excited O (\textsuperscript{1}D). The O atoms can then react with water vapor to form hydroxyl radicals (HO$^\cdot$). hydroxyl radicals are the major oxidants, which can then react with carbon-containing molecules, such as CO, CH$_4$, C$_2$H$_4$, HCHO, etc., to produce HO$_2$ $^\cdot$:

\[
\begin{align*}
O_3 + hv &\rightarrow O (\textsuperscript{1}D) + O_2 \hspace{1cm} (12) \\
O (\textsuperscript{1}D) + H_2O &\rightarrow 2 HO^\cdot \hspace{1cm} (13) \\
HO^\cdot + CO &\rightarrow H^\cdot + CO_2 \hspace{1cm} (14) \\
H^\cdot + O_2 &\rightarrow HO_2^\cdot \hspace{1cm} (5) \\
HO_2^\cdot + HO_2^\cdot &\rightarrow H_2O_2 + O_2 \hspace{1cm} (1)
\end{align*}
\]

The peroxyacetyl radicals, released from the thermal decomposition of peroxyacetyl nitrate (PAN), can react as follows to produce HO$_2$ $^\cdot$ and HCHO:

\[
\begin{align*}
CH_3CO-OONO_2 &\leftrightarrow CH_3CO-OO^\cdot + NO_2 \hspace{1cm} (15) \\
CH_3CO-OO^\cdot + NO &\rightarrow CH_3CO-O^\cdot + NO_2 \hspace{1cm} (16) \\
CH_3CO-O^\cdot &\rightarrow CH_3^\cdot + CO_2 \hspace{1cm} (17) \\
CH_3^\cdot + O_2 &\rightarrow CH_3O_2^\cdot \hspace{1cm} (18) \\
CH_3O_2^\cdot + NO &\rightarrow CH_3O^\cdot + NO_2 \hspace{1cm} (19)
\end{align*}
\]

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\[
\text{CH}_3\text{O}^* + \text{O}_2 \rightarrow \text{HCHO} + \text{HO}_2^* \quad (20)
\]

In addition, the HO\textsubscript{2}^* radical will be produced by the temperature-dependent decomposition of peroxynitric acid HO\textsubscript{2}NO\textsubscript{2}.

The photooxidation of isoprene can generate HO\textsubscript{2}^* according to the mechanism proposed by Gu \textit{et al.} (1985).

\[
\text{CH}_3\text{I} \quad \text{H}_2\text{C} = \text{CCH} = \text{CH}_2 \quad \cdot \text{OH} \quad \text{O}_2 \quad \rightarrow \text{HOCH}_2\text{CCH} = \text{CH}_2
\quad \text{(21)}
\]

\[
\text{HOCH}_2^* \quad \text{CH}_3\text{I} \quad \text{H}_2\text{C} = \text{CCH} = \text{CH}_2 \quad \rightarrow \text{HOCH}_2\text{CCH} = \text{CH}_2 \quad \text{O}^* \quad \text{NO}_2 \quad \text{(90\%)} \quad \text{(22)}
\]

\[
\text{HOCH}_2^* \quad \text{CH}_3\text{I} \quad \text{H}_2\text{C} = \text{CCH} = \text{CH}_2 \quad \rightarrow \text{HOCH}_2\text{CCH} = \text{CH}_2 \quad \text{O}^* \quad \text{NO}_2 \quad \text{(10\%)}
\quad \text{(23)}
\]

The reactions above involve the production of HO\textsubscript{2}^*, which undergo self-coupling to form H\textsubscript{2}O\textsubscript{2}. However, there exists a route that could form H\textsubscript{2}O\textsubscript{2} without HO\textsubscript{2}^* radical as an intermediate (Simonaitis \textit{et al.}, 1991). This route involves the reaction of ozone with natural alkenes. This reaction may be a significant source of atmospheric H\textsubscript{2}O\textsubscript{2}, especially in forest and natural rural areas. The following mechanism of ozonolysis of ethene has been proposed by Horie, \textit{et al.} (1994):

\[
\text{C}_2\text{H}_4 + \text{O}_3 \quad \rightarrow \text{[primary ozonide]} \quad \rightarrow \text{HCHO} + \cdot \text{CH}_2\text{OO}^* \quad (24)
\]

\[
\cdot \text{CH}_2\text{OO}^* + \text{M} \quad \rightarrow \text{(collisional stabilization)} \quad \rightarrow \cdot \text{CH}_2\text{OO}^* + \text{M} \quad (25)
\]
Any alkene with terminal double bonds, which includes isoprene and some of the terpenes such as α-pinene, β-pinene, d-limonene, and sabinene, may be ozonolyzed in the presence of water vapor to form H$_2$O$_2$ and organic hydroperoxides, such as HOCH$_2$OOH, and CH$_3$OOH (Simonaitis et al., 1991; Horie, et al., 1994).

It has also been demonstrated that meteorological parameters such as solar radiation, temperature, and water vapor concentration favor the formation of gaseous H$_2$O$_2$ (Kleinman, 1986; Dodge, 1989; Sakugawa et al., 1990b).

The main formation pathways for H$_2$O$_2$ are summarized in Figure 1-1.

![Figure 1-1: The Reaction Pathways Yielding Gas-Phase H$_2$O$_2$](Modified from Gunz and Hoffmann, 1990)
1.4. Decomposition of Atmospheric H$_2$O$_2$

In the gas phase, two major destruction pathways for atmospheric H$_2$O$_2$ are thought to be the reaction with OH radical and the photolysis of H$_2$O$_2$.

\[
\begin{align*}
H_2O_2 + OH^* & \rightarrow H_2O + HO_2^* \quad (27) \\
H_2O_2 \overset{hv}{\rightarrow} 2 OH^* & \quad (28)
\end{align*}
\]

However, the atmospheric chemistry of H$_2$O$_2$ is also strongly influenced by heterogeneous reactions mediated by Henry's Law, which has a great effect on the decomposing or wet scavenging of gaseous H$_2$O$_2$. The Henry’s law is expressed as:

\[[H_2O_2]_{aq} = K_H * P \quad (Lind and Kok. 1986),\]

where $P$ is the partial pressure of H$_2$O$_2$ in the gas phase, and $K_H$ is the Henry’s Law constant. The Henry's Law constant, $K_H$ can be expressed as:

\[K_H \cdot [M * atm^{-1}] = e^{(A + T^2 - B)} \quad (Staffelbach and Kok, 1993),\]

where $T$ is in degrees Kelvin, $A = -\Delta H / R$, $B = -\Delta S / R$, $\Delta H$ is standard heat of solution, here the value is 55.0 KJ/mol, and R is the gas constant. Because of the high Henry's law constant of H$_2$O$_2$ (Lind and Kok, 1986; Staffelbach and Kok, 1993), gas-phase H$_2$O$_2$ is easily absorbed into water droplets and rapidly equilibrated with aqueous-phase. It was already observed that gas-phase H$_2$O$_2$ decrease significantly during the formation of clouds and rainfall (Tavares and Klockow, 1987 and Mohnen, 1989). Aqueous-phase H$_2$O$_2$ can react with S (IV) in cloud and rain droplets, thus, consuming the atmospheric H$_2$O$_2$.

\[
\begin{align*}
HSO_3^- + H_2O_2 (aq) + H^+ & \rightarrow SO_4^{2-} + 2 H^+ + H_2O \quad (29) \\
SO_2 + \overset{M}{H_2O_2} & \rightarrow H_2SO_4 \quad (30)
\end{align*}
\]

It was observed that high NO$_x$ concentrations would inhibit the formation of H$_2$O$_2$ in the atmosphere (Sakugawa, et al., 1990b; Tsai, et al., 1991). The possible reactions are:

\[
H_2O_2 + NO_3^- \rightarrow HO_2^- + HNO_3 \quad (31)
\]
\[(1 + \alpha) \text{H}_2\text{O}_2 + 2\text{NO}_2 \rightarrow 2\text{HNO}_3 + \alpha\text{H}_2\text{O} + \alpha/2 \text{O}_2 \] (32)

The \text{H}_2\text{O}_2 will also be decomposed by ferric or ferrous ion in dilute acid solution:

\[
\text{H}_2\text{O}_2 + \text{Fe}^{3+} \rightarrow \text{Fe}^{2+} + \text{H}^+ + \text{HO}_2^* \] (33)

\[
\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{HO}^- + \text{HO} \cdot \] (34)

\[
\text{HO} \cdot + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2^* \] (35)

\[
\text{HO}_2^* + \text{Fe}^{3+} \rightarrow \text{O}_2 + \text{Fe}^{2+} + \text{H}^+ \] (36)

\[
\text{HO}_2^* + \text{Fe}^{2+} \rightarrow \text{HO}_2^- + \text{Fe}^{3+} \] (37)

1.5. The History of Measurement of Atmospheric \text{H}_2\text{O}_2

Schöne (1874), a Russian scientist, was the first person to study atmospheric hydrogen peroxide. He used a colorimetric method to measure the concentration of \text{H}_2\text{O}_2 in rain- and snow- water and found the range was from 1 to 30 \(\mu\text{M}\). During the 1970s, Buffalini et al. (1972) and Kok et al. (1978a), using either colorimetry or chemiluminescence method, first measured the concentration of gas phase \text{H}_2\text{O}_2 in Los Angeles. Since the late 1970s, a large number of modeling and field has been performed which showed that \text{H}_2\text{O}_2 plays an important role in the formation of acidic precipitation (Penkett et al., 1979; Möller, 1980; Jacob, 1986; Tsai et al., 1990; Walcek et al., 1990).

In the late 1980s, several scientists studied the atmospheric \text{H}_2\text{O}_2 concentrations in southern California at Long Beach, downtown Los Angeles, Claremont, and Rubidoux (Downs, et al., 1989; Sakugawa and Kaplan, 1989b), in eastern U.S. (Heikes et al., 1987; Van Valin et al., 1987) and in other areas or countries, such as: in the central US (Boatman et al., 1989), at Mauna Loa on the island of Hawaii (Heikes, 1989), in southern England (Dolland et al., 1989), in Bahia, Brazil (Jacob et al., 1990), at Trombay in
Bombay, India (Das. et al., 1983), and in Norway (Masuch et al., 1986). The concentration of H₂O₂ was measured under a variety of conditions and seasons: from tropical (Jacob et al., 1990) to polar (De Serves, 1994); from desert (Farmer and Dawson, 1982; Sakugawa and Kaplan, 1989) to heavily forested (Lee et al., 1993); from remote mountaintop (Heikes, 1992; Olszyna et al., 1988) or rural area (Sakugawa et al., 1990c) to urban (Mackay et al., 1990); and from winter (Van Valin et al., 1987; Heikes et al., 1988; Barth et al., 1989) to summer (Olszyna et al., 1988; Sakugawa and Kaplan, 1989; Fels and Junkermann 1994).

H₂O₂ has been extensively measured in the gas phase, in the atmospheric aqueous phase, and in cloud-, rain-, and fogwater as well as in snow and ice. The typical concentration range of H₂O₂ is 0.1-2 ppbv (parts per billion by volume) in the gas phase and 10⁻⁷ - 10⁻⁴ M in rain- and cloudwater. In the eastern U.S.A., the concentration of H₂O₂ vapor has ranged from 30 pptv (parts per trillion by volume) to 4 ppbv. In Los Angeles and its vicinity, observed concentrations of gaseous H₂O₂ are 0.02-4.9 ppbv. While in other regions of the United States and in other countries, concentrations of gaseous H₂O₂ are in the range of 0.01-7.0 ppbv (Das, et al., 1983).

1.6. Current Analytical Methods for Determination of Atmospheric H₂O₂

There are many reliable methods for the measurement of atmospheric H₂O₂. Most of them are included as follows:

(1) Classical methods: H₂O₂ is reacted with titanium oxalate (Wagner and Ruck, 1984) or cobaltous bicarbonate to form a colored complex (Bufalini et al., 1972; Masschelein et al., 1977;).
(2) Iodometric titration methods (Kieber and Helz, 1986): H₂O₂ oxidizes iodide to iodine at pH 4 in the presence of molybdate catalyst. The I₂ produced reacts with excess phenylarsine oxide, and the remaining phenylarsine oxide is then titrated to an amperometric end point with a standardized iodine titrant.

(3) Peroxidase-catalyzed reactions lead to formation of a dye (Mottola et al., 1970; Vlasova et al., 1987), or a fluorescent compound, or destruction of a fluorescent compound (Zepp et al., 1988).

(4) Chemiluminescence methods: Chemical reaction of certain chemicals with H₂O₂ can generate electronically excited products, which emit ultraviolet, visible or near-infrared radiation, the radiation is sensitively detected with a photomultiplier tube. The typical chemicals used to react with H₂O₂ are: luminol (5-amino-2,3-dihydro-1,4-phthalazinedione) (Kok et al., 1978b; Kleindienst et al., 1988), and bis(2,4,6-trichlorophenyl)-oxalate (TCPO). Some other methods include: peroxyoxalate chemiluminescence (Beltz et al., 1987), cryogenic trapping with peroxylate chemiluminescence detection (Jacob et al., 1986), a novel luminol-H₂O₂-KIO₄ chemiluminescence system (Zhou et al., 1999), and an immobilized fluorophores TCPO chemiluminescence method (Gübitz et al., 1985), etc.

(5) Tunable diode laser absorption spectroscopy TDLAS (Slemr et al., 1986; Kleindienst et al., 1988).

(6) Amperometric detection with Pt electrode (Keuken et al., 1987).

(7) Fiber-optic sensor (Abdel-Latif and Guilbault, 1988). This method used cetyltrimethylammonium bromide (CTAB) as a surfactant which increases the

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chemiluminescence intensity from the reaction of bis(2,4,6-trichlorophenyl) oxalate (TCPO) with \( \text{H}_2\text{O}_2 \) in the presence of perylene with incorporation of fiber optics.

(8) Enzyme analytical techniques.

Various enzyme analytical methods were already studied. Some examples are shown as follows: the enzyme-catalyzed oxidation of \( \text{N,N-diethyl-p-phenyldiamine (DPD)} \) (Bader et al., 1988), the enzyme-catalyzed dimerization of \( \text{p-hydroxyphenyl acetic acid} \) with continuous flow concurrent extraction (Lazrus et al., 1985). The same enzyme analytical technique was used with diffusion collection of the \( \text{H}_2\text{O}_2 \) (Hwang and Dasgupta, 1985; Dasgupta and Hwang, 1985). A dual-enzyme fluorescence method using both peroxidase and catalase to differentiate \( \text{H}_2\text{O}_2 \) and organic hydroperoxides (Lazrus et al., 1986). An enzyme fluorescence method using \( \text{MnO}_2 \) to differentiate \( \text{H}_2\text{O}_2 \) and organic hydroperoxides (Hwang and Dasgupta, 1986). The enzyme analytical technique with nitric oxide pretitration of the ozone and subsequent collection of the \( \text{H}_2\text{O}_2 \) with an impinger (Tanner et al., 1986), etc.

(9) A nonenzymatic fluorescence method using Fenton's reagent and benzoic acid (Lee et al., 1990; Lee et al., 1994). This method was based on the hydroxylation of benzoic acid by Fenton reagent to form the fluorescent product, hydroxybenzoic acid.

(10) Spectrophotometric determination with \( \text{N-ethyl-N-(sulfopropyl)aniline sodium salt} \) (Madsen and Kromis, 1984); and the ozo-peroxopyridine-2,6-dicarboxylatovanadate (V) chelate (Hartkamp and Bachhausen, 1987).

The above methods are not an exhaustive review of \( \text{H}_2\text{O}_2 \) methods but are meant to illustrate the various sampling system and analysis conditions, which have been used.
to determine atmospheric H$_2$O$_2$. There have been significant differences in the gaseous H$_2$O$_2$ values determined by various methodologies. Thus, experimental artifacts are an ongoing challenge.

1.7. Organic Hydroperoxides

Organic peroxides have been identified in present in air and precipitation (Hellpointer and Gab, 1989; Hewitt and Kok, 1991). Organic peroxides possibly have some effects on the results of this study, so it is important to discuss the formation and properties of several organic peroxides, which potentially interfere with H$_2$O$_2$ measurements.

Like hydrogen peroxide, organic peroxides can oxidize dissolved sulfur dioxide (SO$_2$) to sulfuric acid (H$_2$SO$_4$) (Lind et al., 1987; Zhou and Lee, 1992), and may also be phytotoxic. Organic peroxides have been shown to be present inside leaves of plants exposed to O$_3$ (Hewitt et al., 1990). Organic peroxides play an important role in the atmospheric chemistry as a sink and temporary reservoir of HO$_2$ and RO$_2$ radicals.

Several atmospheric organic peroxides have been measured in air and precipitation samples (Kleinman, 1986; Lee, et al., 1995; Fels and Junkermann, 1994). Of these, the most frequently detected hydroperoxides are methyl hydroperoxide CH$_3$OOH (MHP) and hydroxymethyl hydroperoxide HOCH$_2$OOH (HMHP). These two compounds make up more than 90% of total organic hydroperoxides (ROOH). In ambient air samples, HMHP and MHP are the most concentrated organic hydroperoxides measured. In precipitation, the concentration of HMHP constitutes about 10% - 40% of the concentration of H$_2$O$_2$ (Fels and Junkermann, 1994).
Organic hydroperoxides were thought to be formed via peroxo radical recombination (Simonaitis, et al., 1991):

\[
RO_2^\cdot + HO_2^\cdot \rightarrow ROOH + O_2
\] (38)

Recently, many experiments have showed that an additional pathway for peroxide production is the ozonolysis of alkenes (Gib et al., 1985; Simonaitis, et al., 1991; Horie, et al., 1994). The reaction of water with a Criegee biradical formed by ozonolysis of ethene leads to the formation of HMHP (Horie, et al., 1994):

\[
\text{C}_2\text{H}_4 + \text{O}_3 \rightarrow \text{[primary ozonide]} \rightarrow \text{HCHO} + \cdot\text{CH}_2\text{OO}\cdot \] (24)

\[
\cdot\text{CH}_2\text{OO}\cdot + \text{M} \rightarrow \text{(collisional stabilization)} \rightarrow \cdot\text{CH}_2\text{OO}\cdot + \text{M} \] (25)

\[
\cdot\text{CH}_2\text{OO}\cdot + \text{H}_2\text{O} \rightarrow \text{HOCH}_2\text{OOH} \] (39)

Another possible mechanisms is (Atkinson, 1990; Lightfoot et al., 1992):

\[
\text{HOCH}_2\text{OO}^\cdot + \text{HO}_2^\cdot + \text{M} \rightarrow \text{HOCH}_2\text{OOH} + \text{O}_2
\] (40)

A possible pathway for the formation of HOCH_2OO^\cdot radical is (Su et al., 1979 a, b):

\[
\text{HO}_2^\cdot + \text{HCHO} \rightarrow \text{HOCH}_2\text{OO}^\cdot
\] (41)

The major pathway for the formation of MHP is the recombination of HO_2^\cdot radical with CH_3O_2 radical produced during the photochemical oxidation of the homogeneously distributed CH_4 (Logan et al., 1981; Atkinson and Lloyd, 1984; Lurmann and Lloyd, 1986):

\[
\text{CH}_3\text{OO}^\cdot + \text{HO}_2^\cdot \rightarrow \text{CH}_3\text{OOH} + \text{O}_2
\] (42)

HMHP can be formed only in the presence of water vapor (wet condition: [H_2O]_0 = 2 \times 10^4 \text{ ppm}), while MHP can be formed under both wet and dry ([H_2O]_0 = 0.5 \text{ ppm}) conditions, and it is the only organic peroxide that is found under dry conditions (Horie, et al., 1994).
The seasonal variation of HMHP/MHP ratio was studied (Fels and Junkermann 1994), and it was shown that HMHP was the dominant organic peroxide in the early summer whereas MHP dominated in late summer. This trend may reflect the seasonal changes in biogenic alkene emissions, which suggests that the alkenes may be mostly of biogenic origin.

Organic peroxide can be analyzed by fluorescence detection, or amperometric detection, techniques that are used for H$_2$O$_2$ (Keuken et al., 1987). Organic peroxides and H$_2$O$_2$ are kinetically distinguished by different rates of decomposition by catalase (Lazrus et al., 1985), by MnO$_2$ (Dasgupta and Hwang, 1985; Hwang and Dasgupta, 1986) or differences in the peroxidase-catalyzed rate of the substrate oxidation (Frew et al., 1983). Recently, a HPLC technique (isocratic, reversed phase conditions), combined with fluorescence detection of the $p$-hydroxyphenylacetic acid (POPHA) dimer, was used to separate and quantitate the organic hydroperoxides and H$_2$O$_2$ (Kok et al., 1995; Lee et al., 1995). Kok et al (1995) used a HPLC-fluorescence technique for the separation and quantification of hydrogen peroxide and 10 organic hydroperoxides that have the potential to be found in the atmosphere. Lee et al (1995) used a continuous-flow glass scrubbing coil to collect gas-phase hydroperoxide samples, which were then analyzed by this technique.

Henry’s law constants: \( K_H \) \([\text{M atm}^{-1}] = e^{(A - B \cdot T)}\) for aqueous solutions of MHP, peroxyacetic acid, \(\text{H}_2\text{O}_2\), and HMHP were measured (Lind and Kok, 1986; Staffelbach and Kok, 1993), and the reported values were:

\[
\begin{align*}
K_H &= e^{(5607 \cdot T - 13.41)} \text{ for MHP} \\
K_H &= e^{(6171 \cdot T - 14.55)} \text{ for peroxyacetic acid} \\
K_H &= e^{(6621 \cdot T - 11.00)} \text{ for } \text{H}_2\text{O}_2 \\
K_H &= e^{(10240 \cdot T - 20.03)} \text{ for HMHP} \\
K_H &= e^{(7514 \cdot T - 13.63)} \text{ for } \text{H}_2\text{O}_2
\end{align*}
\]

\(K_H\) for MHP and peroxyacetic acid are about 2-3 orders of magnitude lower than the value for \(\text{H}_2\text{O}_2\). Compared with \(\text{H}_2\text{O}_2\), they have low water solubility, and they are not significant contributors to S (IV) oxidation, which leads to the acidification of the atmospheric aqueous phase. In contrast, the high solubility of HMHP and \(\text{H}_2\text{O}_2\) make these compounds major contributors to S (IV) oxidation. \(K_H\) for HMHP is even higher than \(\text{H}_2\text{O}_2\), thus indicating that HMHP could be the major peroxide in the liquid phase at low pH. The importance of HMHP should be considered in cloud and rain samples.

HMHP can be formed only in the presence of water vapor, and the humidity in Las Vegas is very low. Therefore, the concentration of HMHP in gas phase, especially during the summer in Las Vegas, can be assumed to be very low.
1.8. Outline of This Research

1.8.1. Theory

In this study, a high performance liquid chromatography (HPLC) with Fenton's reagent method was used to determine the concentration of peroxides in aqueous extracts of gas-phase samples. Based on the strong oxidant properties of Fenton's reagent (hydrogen peroxide with ferrous iron), sodium salicylate can be oxidized to dihydroxybenzoic acids, which can be separated and detected by HPLC-UV. The amount of dihydroxybenzoic acids produced should be directly proportional to the original amount of \( \text{H}_2\text{O}_2 \) present in the sample. Therefore, there should be a linear relationship between the peak area of the dihydroxybenzoic acids and the concentration of atmospheric \( \text{H}_2\text{O}_2 \).

1.8.2. Introduction to Fenton's Reagent

Fenton's reagent is a mixture of hydrogen peroxide and ferrous iron (\( \text{Fe}^{2+} \)). More than 100 years ago, it was first reported by H. J. H. Fenton (1894) that ferrous ion strongly promotes the oxidation of malic acid by hydrogen peroxide. Since this discovery, the oxidation of compounds with Fenton's reagent has been a subject of profound interest. The possible stoichiometry of Fenton's reagent has been studied (Walling, 1975; Ito, et al., 1992) with the primary reaction being:

\[
\text{Fe}^{2+} + \text{H}_2\text{O}_2 \xrightarrow{\text{Fe}^{2+}, \text{H}_2\text{O}_2} \text{Fe}^{3+} + \text{OH}^- + \text{HO}^* \quad (34)
\]

Other competing reactions also occur in Fenton's systems, including: reactions of \( \text{OH}^- \) with \( \text{Fe}^{2+} \) and \( \text{H}_2\text{O}_2 \), and the cycling of \( \text{Fe}^{3+} \) to \( \text{Fe}^{2+} \):

\[
\text{HO}^* + \text{Fe}^{2+} \xrightarrow{} \text{Fe}^{3+} + \text{OH}^- \quad (43)
\]

\[
\text{HO}^* + \text{H}_2\text{O}_2 \xrightarrow{} \text{H}_2\text{O} + \text{HO}_2^* \quad (35)
\]
Hydroxyl radical generated from reaction (34) is a very strong oxidant, even stronger than hydrogen peroxide, and is capable of oxidizing many compounds. Because of this property, Fenton’s reagent is very useful for the treatment of hazardous pollutants and organic contaminants in environmental applications. Several instances of the use of Fenton’s reagent in wastewater treatment and in soil decontamination technology have been reported (Venkatadri and Peters, 1993). The mechanism of enhanced desorption of sorbed chloroaliphatic compounds by Fenton-like reactions was also studied (Watts, et al., 1999).

Many studies have already demonstrated the oxidation by Fenton’s reagent of the following compounds: benzene (Steinberg and Walker, 1995), phenol (Sudoh, et al. 1986), chlorophenols (Barbeni. et al, 1987), 2,4-dichlorophenol and dinitro-o-cresol (Bowers. et al. 1989), hydroxymethanesulfonic acid (Martin, et al. 1989), formaldehyde (Murphy, et al. 1989), PAHs (Kelley, et al. 1990), chlorobenzene (Sedlak and Andren, 1991a), PCBs (Sedlak and Andren, 1991b), nitrophenols and nitrobenzene (Lipczynska-Kochany, 1991), and chlorinated aliphatic compounds (Watts et al., 1999) etc.

Sodium salicylate can be oxidized by hydroxyl radical, produced from Fenton’s reagent, to 2,3-, 2,4- and 2,5 - dihydroxybenzoic acid (DHBA) (Jen et al., 1998).

\[
\text{HO}_2^* + \text{Fe}^{3+} \rightarrow \text{O}_2 + \text{Fe}^{2+} + \text{H}^+ \quad (36)
\]

\[
\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH}^- + \text{HO}^* \quad (34)
\]
The dihydroxybenzoic acids can be separated by HPLC and analyzed by UV detector at a wavelength of 310 nm. The optimum pH range for oxidation of organics by Fenton's reagent is in the acidic range of 2 to 4. In this study, the pH value of the reaction solution was about 3.

1.8.3. Selecting An Appropriate Sampling System

Gaseous $\text{H}_2\text{O}_2$ has been collected by aqueous stripping from the air using impingers (Bufalini, et al., 1972; Kok, et al., 1978a, b; Das, et al., 1983; Daum, et al., 1984), diffusion scrubbers (Tanner et al., 1986; Dasgupta, et al., 1990), scrubbing coils (Kok et al., 1978b; Lazrus et al., 1986; Lee et al., 1990; Heikes, 1992), or cryogenic traps (Sakugawa and Kaplan, 1987; Hellpointner and Gab, 1989; Jacob et al., 1990; Hewitt and Kok, 1991; Fels and Junkermann, 1994). In this study, two different sampling systems, impinger bubbling sampling and cryogenic sampling, were compared.
Cryogenic sampling was eventually selected and used to collect gaseous H₂O₂ in the Las Vegas ambient air.

1.8.4. The Goal of This Research

In this research, the feasibility of HPLC analysis using this Fenton's reagent method was investigated. Gas-phase H₂O₂ samples from Las Vegas were collected and analyzed. The effects of meteorological conditions on the concentration of H₂O₂ and the correlation between the concentrations of gas-phase H₂O₂ and CO, NO, NO₂ and O₃ were also studied.
CHAPTER 2

EXPERIMENTAL

2.1. Chemicals

All reagent solutions were prepared using purified deionized water, which was produced using a Barnstead Nanopure deionization system (Barnstead Thermolyne Corporation, Dubuque, IA, USA).

Hydrogen peroxide standard solutions were prepared by dilution of a 30% stock \( \text{H}_2\text{O}_2 \) solution. The concentration of the standard was calibrated by titration with potassium permanganate. A stock Fe (II) solution (0.1 M) was prepared by dissolving an appropriate amount of \( \text{FeSO}_4\cdot7\text{H}_2\text{O} \) in 0.1 M \( \text{H}_2\text{SO}_4 \). Sodium salicylate (\( \text{NaC}_7\text{H}_5\text{O}_3 \)) was obtained from Mallinckrodt Inc. and the stock solution (1.08 g/l) was prepared by dissolving 0.2700 g sodium salicylate in water and then diluting to 250 ml. Standards of 2,3-, 2,5-dihydroxybenzoic acid (DHBA) were purchased from Aldrich Chemical Co. Inc. The 2,4-dihydroxybenzoic acid was obtained from Eastman Organic Chemicals. The HPLC buffer was 10% methanol, 10% Acetonitrile, 0.03M acetic acid, 0.03M citric acid (J. T. Baker Chemical Co., Phillipsburg, N. J.) and water.
2.2. UV Absorption Measurements

To determine the optimum wavelength for UV detection, the spectra of the three standards, 2,3-, 2,4-, 2,5-DHBA, were recorded using a UV-visible spectrophotometer over the range 200 to 500 nm. It was observed that all three compounds have significant absorbance at 310 nm. (See Figure 2-1). Although the absorption intensities of all three compounds were higher below 250 nm, these wavelengths were deemed unsatisfactory because of spectral interference.

![UV Absorption Spectra](image)

**Figure 2-1: UV Absorption Spectra**
2.3. HPLC Instrumentation

The high performance liquid chromatography system contained the following major components: one HPLC pump (Eldex Laboratories Inc.), a Spectroflow 757 UV VIS detector (Kratos Analytical Instruments), and an IBM 286 computer with “Peak Simple” software (SRI). An injection loop of 20 μl volume was used. The guard column was 30 μm pellicular C-18 silica, and the analytical column was an Econosphere C-18 silica reversed phase column with a 5 μm particle size, column length of 250 mm, and I. D. of 4.6 mm (Allteck Associates, Inc.).

2.4. HPLC Analysis

2.4.1. Calibration Standards

A series of H2O2 standards of 0.09 ppm, 0.18 ppm, 0.30 ppm, 0.60 ppm, and 1.50 ppm were prepared as follows: a 300 ppm standard H2O2 was prepared freshly by diluting stock standard 30 % H2O2, which was calibrated by KMnO4 titration. The 6.0 ppm standard H2O2 was made by diluting the above 300 ppm standard H2O2. The H2O2 standards from 0.09 ppm to 1.5 ppm were prepared by serial dilution of the 6.0 ppm stock standard in 5 ml volumetric flasks. An excess amount of sodium salicylate and ferrous solution were added to ensure that the hydroxyl radical trapping was quantitative (Jen, et al., 1998). In this research, 200 μl (1.08 g/l) sodium salicylate (about 43 ppm), and 50 μl 0.1 M Fe2⁺ (about 55 ppm) were used.
2.4.2. Sampling Apparatus

Gas-phase samples were collected from the atmosphere by a cryogenic sampling method. The portable sampler consisted of a large impinger and a battery operated rechargeable sampling pump. The impinger was put in a large deep dewar flask, which was filled with the liquid nitrogen (the cooling agent). The apparatus was covered with aluminum foil to protect the impinger from sunshine, and then connected to the pump (Model 224-PCXR7, SKC Inc.). The sampling flow rate was 2.5 l/min for more than 2 hours. The air sampler was located on the roof of the Chemistry building on the University of Nevada, Las Vegas campus (see Figure 2-2).

Figure 2-2: Sampling System

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After sampling, the trap contents were allowed to melt at room temperature. The reagents (200 µl sodium salicylate (1 g/l) and 50 µl Fe²⁺ (0.1 M FeSO₄·7H₂O / 0.1 M H₂SO₄)) were then added to the sample.

The reaction solution was then injected into the HPLC-UV system for analysis (see Figure 2-3), or refrigerated for later analysis.

Figure 2-3: Schematic Diagram of HPLC-UV System
The injection volume for all measurements was 20 μl. and the UV detection wavelength was 310nm. Isocratic elution can separate 2,5-DHBA from 2,3- and 2,4-DHBA, but 2,3-DHBA can not be separated from 2,4-DHBA (see Figure 2-4). The flow rate of the mobile phase was 1.0 ml/min.

Calibration standards were analyzed before the samples. A calibration curve was obtained from the relationship of $H_2O_2$ concentration vs. peak area (See Figure 2-5). From the calibration curve, the concentration of $H_2O_2$ in the sample was obtained. The $H_2O_2$ concentrations in the air by volume were then calculated by using the ideal gas law equation (Equation 47 in the section 2.4.3).
Figure 2-4: HPLC Chromatograms of the Reaction Products of Standard $\text{H}_2\text{O}_2$ solutions with Sodium Salicylate under Fenton conditions

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2.4.3. Calculation of the concentration of gas-phase $\text{H}_2\text{O}_2$ in the atmosphere

$$X(\mu \text{g} \cdot \text{ml}) \times 10^{-6} \text{ g} \cdot \mu \text{g} \times V(\text{ml}) \times \frac{R \times T}{34 \text{ g} \cdot \text{mol}} \times \frac{1}{P} \times \frac{1}{760} \times \frac{1}{\text{FR (l/min) \times ST (min)}} \times 10^3 \text{ ppb}$$

$$= \text{ppbv (parts per billion by volume)} \quad (47)$$

$X$: $\text{H}_2\text{O}_2$ measured in aqueous solution (ppm or mg/l)

$V$: Volume of aqueous solution used to collect the sample (ml)

$\text{FR}$: Flow rate of sampling (l/min)

$\text{ST}$: Sampling Time (min)

$R$: The gas constant, its value is 0.0821 atm*l/K*mol

$T$: Temperature of atmosphere (K)

$P$: Pressure of atmosphere (mmHg)
3.1. OH Radical Trapping Methods

Two analytical methods with Fenton's reagent were studied. Initially, Fenton's reagent was used to oxidize methanol (CH$_3$OH) to formaldehyde (HCHO), which then reacts with 2,4-dinitrophenylhydrazine (DHBA) to form the 2,4-dinitrophenylhydrazone, which can be separated (gradient mobile phase), and detected by HPLC using a UV absorption 360 nm. The reactions are:

\[
\begin{align*}
&\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH}^- + \text{HO}^+ \quad (34) \\
&\text{HO}^+ + \text{CH}_3\text{OH} \rightarrow \cdot\text{CH}_2\text{OH} + \text{H}_2\text{O} \quad (48) \\
&\cdot\text{CH}_2\text{OH} + \text{O}_2 \rightarrow \text{CH}_2\text{O} + \text{HO}_2^- \quad (49) \\
&\text{HCHO} + \text{NH-NH}_2 \rightarrow \text{NH-N=CH}_2 - \text{H}_2\text{O} \quad (50)
\end{align*}
\]

The first method worked well with laboratory analysis of standards, but the sensitivity was too low for determination of H$_2$O$_2$ at the levels expected in the atmosphere. Therefore, a second analytical method was developed. Fenton's reagent was...
used to oxidize salicylic acid. The oxidation products can be separated by HPLC with isocratic elution and detected by UV absorption 310 nm.

\[
\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH}^- + \text{HO}^* \quad (34)
\]

The second method has a significantly better detection limit than the first method, approximately one order of magnitude. The method also produced measurable response in analysis of air sample extracts as well as for the standards.

3.2. The Products Generated from the Reaction

The reaction of hydroxyl radical with sodium salicylate results in addition of a hydroxyl function to the aromatic ring to form 2,3-, 2,4- and 2,5- dihydroxybenzoic acids (DHBA) (Jen, et al., 1998). These products were identified by comparing the retention
time of standards (2.3-DHBA, 2.4-DHBA, 2.5-DHBA and 2.6-DHBA) with the reaction products. 2.6-DHBA was not produced in the experiment, and 2.3- and 2.4-DHBA cannot be separated under these conditions (see Figure 2-4).

3.3. Detection Limit and Linear Range

The detection limit is defined as the analyte concentration that produces a peak height equal to 3 times the standard deviation of the background noise. Blank samples (six) were injected, and the standard deviation of the background noise was calculated according to the following equation:

$$\sigma_{n-1} = \sqrt{\frac{\sum(x_n - \bar{x})^2}{(n-1)}}$$

The detection limit is defined as $3\sigma_{n-1}$. In this study, the detection limit was determined as 0.03 ppm (see Table 3-1). The response was linear from 0.09 ppm to 1.5 ppm H$_2$O$_2$ with correlation coefficient ($R^2$) of 0.995 after subtraction of the blanks (see Figure 3-1). From 0.09 ppm to 6.0 ppm, the correlation coefficient ($R^2$) was lower (see Figure 3-2). Therefore, the calibration range was limited to the range of 0.09 ppm to 1.5 ppm for routine analysis.

<table>
<thead>
<tr>
<th></th>
<th>BK1</th>
<th>BK2</th>
<th>BK3</th>
<th>BK4</th>
<th>BK5</th>
<th>BK6</th>
<th>Avg.</th>
<th>$\sigma_{n-1}$</th>
<th>$3\sigma_{n-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak Area</td>
<td>2.19</td>
<td>2.53</td>
<td>2.62</td>
<td>2.55</td>
<td>1.47</td>
<td>2.05</td>
<td>2.235</td>
<td>0.437</td>
<td>1.31</td>
</tr>
</tbody>
</table>

Peak area value was converted to ppm using response factor for the calculation.
BK: blank solution. DL: detection limit.
Calibration Curve of 2,3-2,4-DHBA

\[ y = 15.044x - 2.9367 \]

\[ R^2 = 0.9948 \]

Figure 3-1: Linearity of calibration curve at low concentration of \( \text{H}_2\text{O}_2 \)

(Obtained on October 18, 1999)

Calibration Curve of 2,3-2,4-DHBA

\[ y = 10.151x + 5.9809 \]

\[ R^2 = 0.9768 \]

Figure 3-2: Linearity at high concentration of \( \text{H}_2\text{O}_2 \)

(Obtained on October 18, 1999)
3.4. Comparison of Two Sampling Systems

3.4.1. Impinger Bubbling Sampling

Initially, in this research, the air impinge bubbling system was used to collect gas-phase $\text{H}_2\text{O}_2$. Hydrogen peroxide was trapped from the atmosphere by pulling the air sample through a reagent-filled (ferrous sulfate and sodium salicylate solution) impinger. Sampling solution consisted of 100 $\mu\text{l} \text{Fe}^{3+} (0.1\text{M}/0.1\text{M} \text{H}_2\text{SO}_4)$, and about 2 ml sodium salicylate solution (0.006M), with air sampled at a flow rate of about 1.0 l/min. The sampler was put on the roof of chemistry building for 5-24 hours. Because it is a simple and low costly method, trapping gas phase $\text{H}_2\text{O}_2$ in impingers is the most widely employed collection method used in many studies (Baufalini, et al., 1972; Kok, et al., 1978a, b; Das, et al., 1983; Daum, et al., 1984). However, the liquid medium may produce favorable conditions for dissolution of other interfering compounds, such as $\text{SO}_2$ (Heikes, et al., 1982). Also, peroxides are preferentially produced by ozonation of aqueous phase organic compounds having aromatic and olefinic ($\text{C}=$C) bond (Sakugawa and Kaplan, 1987). In this study, one of the reagents used was sodium salicylate, an aromatic compound, which might theoretically produce artifact $\text{H}_2\text{O}_2$ and organic peroxides.

To check the efficiency of the impinger, a second impinger was connected to the first one, and hydrogen peroxide in both impingers was analyzed by HPLC. The $\text{H}_2\text{O}_2$ concentration in the second was found almost equal to or larger than that in the first impinger (see Table 3-2). Different sampling flow rate and sampling time were tried, and the results were the same. This result agreed with what Sakugawa and Kaplan (1987) observed in their comparison of the cold trap method with the impinger bubbling method.
The reaction of water with O2 and O3, which would involve the O2 ·, HO2 ·, HO2 ·, HO · radicals (Zika and Saltzman, 1982; Heikes, 1984), and the reaction of O3 with organic compounds, especially aromatic and unsaturated compounds, may result in the generation of artifact H2O2 and organic peroxide in the impingers. The surface catalytic effect of glass is thought to be another mechanism for generation of H2O2 in impingers. As Sakugawa and Kaplan (1987) discussed, the high amount of peroxides in the second impinger is unlikely due to the escape of H2O2 collected in the first impinger. hence, it may be the transfer of organic compounds and/or their subsequent ozonation in the second impinger that produces peroxides. In this research, since the second impinger contained an aromatic compound, its reaction with O3 could be the major reason for peroxide artifacts.

Table 3-2: The Efficiency of the Impinger Bubbling Sampling (Flow Rate: 1 l/min)

<table>
<thead>
<tr>
<th>Date of sampling</th>
<th>Peak area (from the first impinger)</th>
<th>Peak area (from the second impinger)</th>
</tr>
</thead>
<tbody>
<tr>
<td>May 13</td>
<td>6.12</td>
<td>4.06</td>
</tr>
<tr>
<td></td>
<td>4.94</td>
<td>5.45</td>
</tr>
<tr>
<td></td>
<td>4.20</td>
<td>8.06</td>
</tr>
<tr>
<td>May 14</td>
<td>3.66</td>
<td>4.86</td>
</tr>
<tr>
<td>May 21</td>
<td>1.79</td>
<td>2.64</td>
</tr>
</tbody>
</table>

3.4.2. Cryogenic Sampling

Cryogenic sampling techniques have been applied to avoid unfavorable reactions occurring in the liquid phase. Cryogenic sampling also can improve detection limits of
trace analytes (Campos and Kok, 1996). Different cooling agents can decrease the sampling to different trap temperatures. The following table (see Table 3-3) shows the various temperatures of different cooling agents (Staffelbach et al., 1995).

Table 3-3: Various Cryogenic Temperatures

<table>
<thead>
<tr>
<th>Cooling Agents</th>
<th>Temperatures</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry ice-acetone</td>
<td>-60°C - -70°C</td>
</tr>
<tr>
<td>Dry ice and ethanol mixture</td>
<td>-78.6°C</td>
</tr>
<tr>
<td>Liquid argon</td>
<td>-185.7°C</td>
</tr>
<tr>
<td>Liquid nitrogen and ethanol mixture</td>
<td>-117.3°C</td>
</tr>
<tr>
<td>Liquid nitrogen</td>
<td>-196°C</td>
</tr>
</tbody>
</table>

Various cryogenic trap temperatures were used in a variety of analytical methods: -45 °C (Jacob, et al., 1986); -60 °C - -70 °C (Sakugawa and Kaplan, 1987); -70 °C (Hellpointer and Gab, 1989); -80 °C (Staffelbach et al., 1995); -78 °C - -186 °C (Staffelbach et al., 1995); -85 °C and -196 °C (Campos and Kok, 1996).

In this research, liquid nitrogen was used as the cooling agent. Its temperature is -196 °C, the lowest among all the coolants, so it should have the highest collection efficiency.
3.5. The Effect of O₂ on the Products

Under the conditions of the Fenton’s reagent (Fe²⁺ and H₂O₂), oxygen may oxidize the key intermediate, thus it may affect the concentration of the final products. To test the effect of oxygen, nitrogen gas was used to purge the reaction solution for about 30 minutes to remove the oxygen, then the results were compared with those without purging N₂. No significant difference was observed (see Figure 3-3 and Table A-1). Therefore, all future experiments were done without removing oxygen.

![Figure 3-3: The Peak Area of 0.6 ppm and 1.2 ppm H₂O₂ obtained from removing or without removing O₂](image-url)
3.6. The Effect of Henry’s Law Constant on the Gas-Phase H₂O₂

Henry’s law is expressed as:

\[ [\text{H}_2\text{O}_2]_{\text{aq}} = K_{\text{H}} \times P \]  

(Lind and Kok, 1986)

\[ [\text{H}_2\text{O}_2]_{\text{aq}} \] is the molar concentration of hydrogen peroxide in a solution which is in equilibrium with the gas phase. \( P \) is the partial pressure of H₂O₂. The proportionality constant \( K_{\text{H}} \), also known as the Henry’s law constant, is a function of pressure, temperature and the chemical composition of the system. Because the effects of pressure on the condensed phase are small, the pressure dependence of \( K_{\text{H}} \) can usually be neglected. In both phases the species has to exist in the same chemical form, otherwise an “effective Henry’s Law constant” has to be considered. The temperature dependence of the Henry’s Law constant can be expressed as:

\[ K_{\text{H}} \left[ \text{M atm}^{-1} \right] = e^{(A \cdot T + B)} \]  

(Staffelbach and Kok, 1993)

\( A = -\Delta H / R \); \( B = -\Delta S / R \); \( \Delta H \): standard heat of solution, here the value is 55.0 KJ/mol;

\( R \): the gas constant; \( T \) is in degrees Kelvin.

Table 3-4: The Parameters for Henry’s Law Constant

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>( K_{\text{H}} \times 10^5 \left[\text{Matm}^{-1}\right] ) at 22 °C</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.920</td>
<td>15.44</td>
<td>0.89</td>
<td>Hwang and Dasgupta, 1985</td>
</tr>
<tr>
<td>6.621</td>
<td>11.00</td>
<td>0.92</td>
<td>Lind and Kok, 1986</td>
</tr>
<tr>
<td>7.514</td>
<td>13.63</td>
<td>1.37</td>
<td>Staffelbach and Kok, 1993*</td>
</tr>
</tbody>
</table>

The parameters for Henry’s law constant for H₂O₂ were measured respectively

* Values were obtained at a pH of 2.1 to 2.4, others at neutral pH.

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From the above data, it showed that $K_{H}$ is lower at higher pH, which is contrary to the expectation, because at higher pH, $H_2O_2$ is more ionized, which would enhance the $H_2O_2$ solubility in water. From the equation: $K_{H} = \frac{[H_2O_2]_{aq}}{P_g}$, $K_{H}$ should be higher. The reason of this contradiction maybe result from the different methods used to measure the $K_{H}$.

Due to the high Henry's Law constant of $H_2O_2$, even low concentrations of gas phase (< 2 ppb) would lead to significant partition into the aqueous phase. For example if $K_{H}$ is $1 \times 10^5$ Matm$^{-1}$, a gas phase concentration of 1 ppb would produce at equilibrium a liquid-phase concentration of $1 \times 10^{-4}$ M. Tavares and Klockow (1987) and Mohnen and Kadlec (1989) observed that there is a significant decrease of gas phase $H_2O_2$ during the formation of clouds and rainfall.

The concentrations of gas phase $H_2O_2$ on different days were measured (see Table A-2). The first group of samples was collected on August 19, 23, 24, 25, 26, 27 (1999) respectively and analyzed on August 27. Figure 3-4 illustrates the observed relationship between relative humidity and the concentration of $H_2O_2$. We can see that the relative humidity on August 19 was the highest among those 6 days: Relative humidity was 31% (cloudy). The concentration of gaseous $H_2O_2$ was lowest: 0.82 ppbv. The dates of August 24 and 27 were sunny, the temperatures were higher, the relative humidities were lower, and the concentrations of gas phase $H_2O_2$ were highest: 2.40 ppbv and 2.28 ppbv, respectively. The second group of samples was collected on September 8, 9, 10, 15, 16, and 17 (1999), and analyzed on September 17. Except for the sample peaks for Sept. 15 and 16 which were overlapped by interference (the relative humidities on these two days were 26% and 34% respectively, and the concentrations of $H_2O_2$ in the air were

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apparently below the detection limit). The concentration of H$_2$O$_2$ on September 17 was lowest: 0.81 ± 0.17 ppbv. The relative humidity was highest on that day and that was mostly cloudy too (see Figure 3-5). These observations agreed with our expectations that the concentrations of gas-phase H$_2$O$_2$ were lower when the relative humidities were higher, and it also support the observations of Mohnen and Kadlec (1989) that the concentration of gas phase H$_2$O$_2$ decreases during the formation of clouds and rainfall.

![Effect of Humidity in Aug.](image)

Figure 3-4: Concentration of Gas-Phase H$_2$O$_2$ vs. Rel. Humidity in August (1999)
3.7. Seasonal Variation of H$_2$O$_2$ Concentration

Concentrations of gas phase H$_2$O$_2$ in Las Vegas were measured from June to December (1999). Their ranges were from 0.012 ppbv to 2.74 ppbv. The data obtained (see Table A-2) showed that the concentration of H$_2$O$_2$ varied with the different seasons (see Figure 3-6). It was higher in summer (the highest was 2.74 on July 19, 1999) and lower in winter (the lowest was 0.012 ppbv on December 1, 1999). These results strongly suggest that photochemical effects play a very important role in the formation of H$_2$O$_2$. 

Figure 3-5: Concentration of Gas-Phase H$_2$O$_2$ vs. Rel. Humidity in Sept. (1999)
Figure 3-6: Seasonal Variation of Gaseous $\text{H}_2\text{O}_2$ in Las Vegas

3.8. Relationships Between $\text{H}_2\text{O}_2$ and NO$_x$, CO and O$_3$

It is expected that the concentrations of important atmospheric species, such as CO, O$_3$, NO, may bear some relation to the concentration of gaseous $\text{H}_2\text{O}_2$. Therefore the correlations between $\text{H}_2\text{O}_2$ and the individual compounds were determined.

3.8.1. Negative Correlation Between $\text{H}_2\text{O}_2$ and NO$_x$

The average of every month's concentrations of $\text{H}_2\text{O}_2$, which were measured on the campus of University of Nevada, Las Vegas (UNLV) and that of NO$_x$ (equals the amount of NO and NO$_2$), which were provided by Clark County Health District and
measured hourly at the E. Sahara Station (4001 Sahara Ave.) were calculated. There exists a negative correlation between concentrations of H$_2$O$_2$ and that of NO$_x$. The correlation coefficient of determination ($R^2$) value was 0.5676 for the linear regression between H$_2$O$_2$ and NO$_x$ (see Figure 3-7 and Table A-4), and the t-test result showed that there is a > 95% probability for the existence of this negative correlation (see Table A-5). The concentrations of NO and NO$_2$ were lower in summer and higher in winter (see Figure 3-8 and Table A-3), which is opposite to the general trend for H$_2$O$_2$. From Table 3-5, an interesting result showed that in November, the concentrations of NO and NO$_2$ were much higher (about 2-10 times) than the other days, while the concentration of H$_2$O$_2$ during this time could not be detected. In December, three continuous days' samples were measured; during the second day, the concentration of H$_2$O$_2$ was not detected, but the concentration of NO$_x$ on this day was 4 times that of the first day, and 6 times that of the third day.

This result was consistent with the studies on several mechanisms for photochemical smog (Lurmann and Lloyd, 1986), which implied that the high level of oxides of nitrogen (NO$_x$) would inhibit the formation of H$_2$O$_2$. Because NO is easily oxidized to NO$_2$, when [NO] $>>$ [HO$_2$·], HO$_2$· will preferentially react with NO to form NO$_2$, rather than with another HO$_2$· molecule to form H$_2$O$_2$. 

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Figure 3-7: Plot of Mean H₂O₂ vs NOₓ Concentrations
(June, 1999 – December, 1999)

\[ y = -0.0096x - 0.0285 \]

\[ R^2 = 0.5676 \]

Conc. of H₂O₂ (ppb)

Figure 3-8: Seasonal Variation of NOₓ and H₂O₂ in Las Vegas
(Compared with the seasonal variation of H₂O₂ in Las Vegas)
Table 3-5: Comparison of the Concentrations of $\text{H}_2\text{O}_2$ with NO, NO$_2$, and NO$_r$

<table>
<thead>
<tr>
<th>Date (1999)</th>
<th>NO (ppm)</th>
<th>NO$_2$(ppm)</th>
<th>NO$_r$ (ppm)</th>
<th>$\text{H}_2\text{O}_2$ (ppbv)</th>
</tr>
</thead>
<tbody>
<tr>
<td>23-Aug</td>
<td>0.007</td>
<td>0.019</td>
<td>0.026</td>
<td>1.49</td>
</tr>
<tr>
<td>24-Aug</td>
<td>0.005</td>
<td>0.010</td>
<td>0.015</td>
<td>2.40</td>
</tr>
<tr>
<td>25-Aug</td>
<td>0.005</td>
<td>0.008</td>
<td>0.013</td>
<td>1.43</td>
</tr>
<tr>
<td>26-Aug</td>
<td>0.004</td>
<td>0.006</td>
<td>0.010</td>
<td>1.05</td>
</tr>
<tr>
<td>27-Aug</td>
<td>0.005</td>
<td>0.015</td>
<td>0.020</td>
<td>2.27</td>
</tr>
<tr>
<td>9-Nov</td>
<td>0.007</td>
<td>0.017</td>
<td>0.024</td>
<td>ND</td>
</tr>
<tr>
<td>10-Nov</td>
<td>0.024</td>
<td>0.031</td>
<td>0.055</td>
<td>ND</td>
</tr>
<tr>
<td>12-Nov</td>
<td>0.077</td>
<td>0.052</td>
<td>0.129</td>
<td>ND</td>
</tr>
<tr>
<td>16-Nov</td>
<td>0.030</td>
<td>0.030</td>
<td>0.060</td>
<td>ND</td>
</tr>
<tr>
<td>18-Nov</td>
<td>0.013</td>
<td>0.015</td>
<td>0.028</td>
<td>ND</td>
</tr>
<tr>
<td>29-Nov</td>
<td>0.110</td>
<td>0.061</td>
<td>0.171</td>
<td>ND</td>
</tr>
<tr>
<td>30-Nov</td>
<td>0.177</td>
<td>0.068</td>
<td>0.245</td>
<td>ND</td>
</tr>
<tr>
<td>1-Dec</td>
<td>0.006</td>
<td>0.012</td>
<td>0.018</td>
<td>0.012</td>
</tr>
<tr>
<td>2-Dec</td>
<td>0.052</td>
<td>0.026</td>
<td>0.078</td>
<td>ND</td>
</tr>
<tr>
<td>3-Dec</td>
<td>0.006</td>
<td>0.006</td>
<td>0.012</td>
<td>0.021</td>
</tr>
</tbody>
</table>

3.8.2. Correlation Between $\text{H}_2\text{O}_2$ and CO

Many modeling studies have showed that high concentrations of carbon monoxide (CO) favor the formation of gaseous $\text{H}_2\text{O}_2$ (e.g., Sakugawa, et al., 1990a). However, the positive correlation between $\text{H}_2\text{O}_2$ and CO, which was provided by Clark County Health District and measured hourly at the Flamingo East Air Monitoring Station (584 E. Flamingo Road), was not observed in this study (see Figure 3-9 and Table A-3). Since CO is a primary pollutant, produced mainly from mobile emitters, its concentration variations may not be reflective of photochemical activity. Thus a strong correlation between $\text{H}_2\text{O}_2$ and CO is not necessarily expected in the atmosphere.
3.8.3. Positive Correlation Between H$_2$O$_2$ and O$_3$

The average of every month's concentrations of H$_2$O$_2$ and that of O$_3$, which was provided by Clark County Health District and measured hourly at the City Center Station (559 N. 7th St.), were calculated. A strong positive correlation between gas phase concentration of H$_2$O$_2$ and that of O$_3$ was observed in this study. The correlation coefficient was 0.7935 for the linear regression between H$_2$O$_2$ and O$_3$ (see Figure 3-10 and Table A-4), and the t-test result showed that there is a > 95% probability for the existence of this positive correlation (see Table A-5). This correlation was consistent with the observations of Olszyna et al., (1988). He explained that the electronically excited O (\textsuperscript{1}D) generated by the photolysis of O$_3$, can react with water vapor to form hydroxyl radicals HO\textsuperscript{*} (the major oxidants), which can react with the carbon-containing molecules.
such as CO, CH₄, C₃H₄, HCHO, etc. to produce HO₂⁺ and then H₂O₂. Horie, et al. (1994) also concluded that O₃ can react with natural alkene to form H₂O₂. Therefore, O₃ favor the formation of gaseous H₂O₂.

Figure 3-10: Plot of Mean H₂O₂ vs and O₃ Concentrations
(June, 1999 – December, 1999)
CHAPTER 4

CONCLUSIONS AND FUTURE WORK

4.1. Conclusion

This research represents the study of gas-phase H₂O₂ in Las Vegas air. The concentration of H₂O₂ in the atmosphere in Las Vegas is about from 0.012 ppbv (December) to 2.74 ppbv (July) in Las Vegas ambient air (see Table A-2).

So far three major advances have been made: (1) A new analytical method for the detection of gaseous hydrogen peroxide by HPLC-UV was developed. (2) A sampling system (cryogenic method) was established. (3) The seasonal variation of H₂O₂ was studied, and the result was consistent with other areas, such as Los Angeles: low in winter and high in summer. The correlation between H₂O₂ and other pollutants: CO, O₃ and NOₓ were studied. A negative correlation between H₂O₂ and NOₓ, and a positive correlation between H₂O₂ and O₃ were observed. However, there was no established correlation between H₂O₂ and CO. Finally, a negative correlation between H₂O₂ concentration and atmospheric humidity was observed. The observed correlations are consistent with expectations, but should be subject to verification in future studies.
4.2. Future Work

Future work will focus on the correlation of $\text{H}_2\text{O}_2$ and CO, the effect of Henry's law constant on the concentration of $\text{H}_2\text{O}_2$, and the relationship between the concentration of $\text{H}_2\text{O}_2$ and the weather (temperature, relative humidity, wind direction, etc).

As to the sampling system, the different coolants used in the cryogenic sampling, such as: (dry ice-acetone, etc) should be tested in order to check the sampling efficiency and their effects on the results. Potential interferences during sampling, such as $\text{O}_3$ (potential positive interference), and $\text{S}$ (IV) (potential negative interference) should be further studied. The amount of organic peroxide compounds present in the hydrogen peroxide sample extracts should be identified and quantitated.
### Table A-1: The Effect of removing O₂ on the Peak Area

<table>
<thead>
<tr>
<th></th>
<th>Concentration of H₂O₂</th>
<th>Peak Area</th>
<th>(Total)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Purge with N₂</td>
<td>0.6 ppm</td>
<td>2.5-DHBA: 5.01</td>
<td>32.25</td>
</tr>
<tr>
<td>(35 min)</td>
<td></td>
<td>2.3+2,4-DHBA: 27.24</td>
<td></td>
</tr>
<tr>
<td>Without purge</td>
<td>0.6 ppm</td>
<td>2.5-DHBA: 8.88</td>
<td>38.51</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.3+2,4-DHBA: 29.63</td>
<td></td>
</tr>
<tr>
<td>Purge with N₂</td>
<td>1.2 ppm</td>
<td>2.5-DHBA: 13.71</td>
<td>68.17</td>
</tr>
<tr>
<td>(60 min)</td>
<td></td>
<td>2.3+2,4-DHBA: 54.46</td>
<td></td>
</tr>
<tr>
<td>Without purge</td>
<td>1.2 ppm</td>
<td>2.5-DHBA: 12.69</td>
<td>64.32</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.3+2,4-DHBA: 51.63</td>
<td></td>
</tr>
<tr>
<td>Collecting Time</td>
<td>Temp (C)</td>
<td>Cond.</td>
<td>Humid.</td>
</tr>
<tr>
<td>-----------------------</td>
<td>----------</td>
<td>-------</td>
<td>--------</td>
</tr>
<tr>
<td>6/3, 10:00 - 15:00</td>
<td>20</td>
<td>P/Cloud</td>
<td>0.29</td>
</tr>
<tr>
<td>6/15, 10:00 - 15:00</td>
<td>36</td>
<td>Sunny</td>
<td>0.13</td>
</tr>
<tr>
<td>7/1, 11:40 - 14:10</td>
<td>43</td>
<td>Sunny</td>
<td>0.08</td>
</tr>
<tr>
<td>7/2, 12:45 - 16:00</td>
<td>41</td>
<td>Sunny</td>
<td>0.13</td>
</tr>
<tr>
<td>7/16, 16:00 - 17:00</td>
<td>35</td>
<td>Sunny</td>
<td>0.18</td>
</tr>
<tr>
<td>7/19, 11:45 - 14:00</td>
<td>35</td>
<td>Sunny</td>
<td>0.20</td>
</tr>
<tr>
<td>7/21, 12:00 - 14:50</td>
<td>36</td>
<td>Sunny</td>
<td>0.16</td>
</tr>
<tr>
<td>7/22, 11:30 - 14:30</td>
<td>37</td>
<td>Sunny</td>
<td>0.18</td>
</tr>
<tr>
<td>7/23, 11:15 - 14:55</td>
<td>38</td>
<td>Sunny</td>
<td>0.16</td>
</tr>
<tr>
<td>7/19, 12:40 - 14:45</td>
<td>33</td>
<td>Cloud</td>
<td>0.31</td>
</tr>
<tr>
<td>7/23, 12:15 - 14:15</td>
<td>35</td>
<td>Cloud</td>
<td>0.25</td>
</tr>
<tr>
<td>7/24, 11:15 - 13:35</td>
<td>35</td>
<td>Sunny</td>
<td>0.25</td>
</tr>
<tr>
<td>7/25, 11:45 - 14:35</td>
<td>37</td>
<td>Sunny</td>
<td>0.21</td>
</tr>
<tr>
<td>7/26, 11:45 - 14:25</td>
<td>38</td>
<td>Sunny</td>
<td>0.22</td>
</tr>
<tr>
<td>7/27, 11:15 - 14:30</td>
<td>38</td>
<td>Sunny</td>
<td>0.20</td>
</tr>
<tr>
<td>8/8, 11:45 - 14:00</td>
<td>36</td>
<td>Sunny</td>
<td>0.16</td>
</tr>
<tr>
<td>8/9, 11:15 - 13:30</td>
<td>35</td>
<td>Sunny</td>
<td>0.22</td>
</tr>
<tr>
<td>8/10, 11:48 - 14:45</td>
<td>35</td>
<td>Sunny</td>
<td>0.21</td>
</tr>
<tr>
<td>8/15, 12:15 - 14:45</td>
<td>31</td>
<td>Sunny</td>
<td>0.26</td>
</tr>
<tr>
<td>8/16, 11:15 - 13:35</td>
<td>32</td>
<td>Sunny</td>
<td>0.34</td>
</tr>
<tr>
<td>8/17, 11:40 - 14:10</td>
<td>32</td>
<td>Sunny</td>
<td>0.30</td>
</tr>
<tr>
<td>9/11, 13:30 - 16:00</td>
<td>33</td>
<td>Sunny</td>
<td>0.17</td>
</tr>
<tr>
<td>9/12, 13:30 - 15:25</td>
<td>32</td>
<td>Sunny</td>
<td>0.16</td>
</tr>
<tr>
<td>9/13, 13:00 - 14:40</td>
<td>32</td>
<td>Sunny</td>
<td>0.17</td>
</tr>
<tr>
<td>9/15, 12:15 - 14:40</td>
<td>30</td>
<td>Sunny</td>
<td>0.14</td>
</tr>
<tr>
<td>9/18, 11:35 - 16:00</td>
<td>23</td>
<td>Sunny</td>
<td>0.13</td>
</tr>
<tr>
<td>9/25, 13:00 - 18:18</td>
<td>29</td>
<td>Sunny</td>
<td>0.26</td>
</tr>
<tr>
<td>9/27, 13:30 - 17:40</td>
<td>27</td>
<td>Sunny</td>
<td>0.30</td>
</tr>
<tr>
<td>9/28, 11:00 - 16:00</td>
<td>26</td>
<td>Sunny</td>
<td>0.30</td>
</tr>
<tr>
<td>9/29, 10:30 - 14:55</td>
<td>20</td>
<td>Sunny</td>
<td>0.16</td>
</tr>
<tr>
<td>10/9, 11:15 - 17:20</td>
<td>20</td>
<td>Sunny</td>
<td>0.30</td>
</tr>
<tr>
<td>10/10, 10:45 - 16:50</td>
<td>21</td>
<td>Sunny</td>
<td>0.30</td>
</tr>
<tr>
<td>11/12, 10:40 - 13:30</td>
<td>23</td>
<td>Sunny</td>
<td>0.18</td>
</tr>
<tr>
<td>11/16, 10:00 - 16:00</td>
<td>24</td>
<td>Sunny</td>
<td>0.28</td>
</tr>
<tr>
<td>11/18, 9:00 - 16:00</td>
<td>17</td>
<td>Sunny</td>
<td>0.20</td>
</tr>
<tr>
<td>11/29, 10:45 - 16:15</td>
<td>20</td>
<td>P/Cloud</td>
<td>0.22</td>
</tr>
<tr>
<td>11/30, 9:00 - 15:50</td>
<td>17</td>
<td>P/Cloud</td>
<td>0.25</td>
</tr>
<tr>
<td>12/1, 11:00 - 16:00</td>
<td>16</td>
<td>Sunny</td>
<td>0.18</td>
</tr>
<tr>
<td>12/2, 8:30 - 16:00</td>
<td>13</td>
<td>Sunny</td>
<td>0.22</td>
</tr>
<tr>
<td>12/3, 10:00 - 14:00</td>
<td>11</td>
<td>Sunny</td>
<td>0.39</td>
</tr>
</tbody>
</table>

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Table A-3: Average Concentration of CO, NO, NO₂ and O₃ in Las Vegas Ambient Air (ppm). (06/1999-12/1999)

<table>
<thead>
<tr>
<th>Collecting Time</th>
<th>CO (ppm)</th>
<th>NO (ppm)</th>
<th>NO₂ (ppm)</th>
<th>O₃ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 3, 10:00 - 15:00</td>
<td>0.44</td>
<td>0.005</td>
<td>0.007</td>
<td>0.032</td>
</tr>
<tr>
<td>6 15, 10:00 - 15:00</td>
<td>0.53</td>
<td>0.005</td>
<td>0.015</td>
<td>0.044</td>
</tr>
<tr>
<td>7 1, 11:00 - 14:00</td>
<td>0.70</td>
<td>0.003</td>
<td>0.009</td>
<td>0.055</td>
</tr>
<tr>
<td>7 2, 12:00 - 16:00</td>
<td>0.42</td>
<td>0.004</td>
<td>0.009</td>
<td>0.033</td>
</tr>
<tr>
<td>7 16, 16:00 - 17:00</td>
<td>0.55</td>
<td>0.005</td>
<td>0.010</td>
<td>0.034</td>
</tr>
<tr>
<td>7 19, 11:00 - 14:00</td>
<td>0.42</td>
<td>0.005</td>
<td>0.005</td>
<td>0.035</td>
</tr>
<tr>
<td>7 21, 12:00 - 15:50</td>
<td>0.52</td>
<td>0.005</td>
<td>0.008</td>
<td>0.031</td>
</tr>
<tr>
<td>7 22, 11:00 - 15:00</td>
<td>0.42</td>
<td>0.006</td>
<td>0.014</td>
<td>0.043</td>
</tr>
<tr>
<td>7 23, 11:00 - 15:00</td>
<td>0.32</td>
<td>0.004</td>
<td>0.008</td>
<td>0.031</td>
</tr>
<tr>
<td>7 19, 12:00 - 15:00</td>
<td>-0.09</td>
<td>0.007</td>
<td>0.014</td>
<td>0.052</td>
</tr>
<tr>
<td>8 23, 12:00 - 14:00</td>
<td>0.24</td>
<td>0.007</td>
<td>0.019</td>
<td>0.009</td>
</tr>
<tr>
<td>8 24, 11:00 - 14:00</td>
<td>-0.03</td>
<td>0.005</td>
<td>0.010</td>
<td>0.058</td>
</tr>
<tr>
<td>8 25, 11:00 - 15:00</td>
<td>0.05</td>
<td>0.005</td>
<td>0.008</td>
<td>0.058</td>
</tr>
<tr>
<td>8 26, 11:00 - 15:00</td>
<td>0.04</td>
<td>0.004</td>
<td>0.006</td>
<td>0.059</td>
</tr>
<tr>
<td>8 27, 11:00 - 15:00</td>
<td>0.30</td>
<td>0.005</td>
<td>0.015</td>
<td>0.054</td>
</tr>
<tr>
<td>9 8, 11:00 - 14:00</td>
<td>0.43</td>
<td>0.007</td>
<td>0.016</td>
<td>0.054</td>
</tr>
<tr>
<td>9 9, 11:00 - 14:00</td>
<td>0.76</td>
<td>0.005</td>
<td>0.005</td>
<td>0.039</td>
</tr>
<tr>
<td>9 10, 11:00 - 15:00</td>
<td>0.45</td>
<td>0.005</td>
<td>0.010</td>
<td>0.046</td>
</tr>
<tr>
<td>9 15, 12:00 - 15:00</td>
<td>0.32</td>
<td>0.005</td>
<td>0.004</td>
<td>0.054</td>
</tr>
<tr>
<td>9 16, 11:00 - 14:00</td>
<td>0.40</td>
<td>0.005</td>
<td>0.007</td>
<td>0.047</td>
</tr>
<tr>
<td>9 17, 11:00 - 14:00</td>
<td>0.05</td>
<td>0.005</td>
<td>0.004</td>
<td>0.043</td>
</tr>
<tr>
<td>10/11, 13:00 - 16:00</td>
<td>0.39</td>
<td>0.001</td>
<td>0.011</td>
<td>0.042</td>
</tr>
<tr>
<td>10 12, 13:00 - 16:00</td>
<td>0.43</td>
<td>0.002</td>
<td>0.017</td>
<td>0.040</td>
</tr>
<tr>
<td>10 13, 13:00 - 15:00</td>
<td>0.34</td>
<td>0.004</td>
<td>0.025</td>
<td>ND</td>
</tr>
<tr>
<td>10 15, 12:00 - 15:00</td>
<td>0.35</td>
<td>0.004</td>
<td>0.020</td>
<td>0.045</td>
</tr>
<tr>
<td>10 18, 11:00 - 16:00</td>
<td>0.83</td>
<td>0.010</td>
<td>0.023</td>
<td>0.018</td>
</tr>
<tr>
<td>10 25, 13:00 - 18:00</td>
<td>1.80</td>
<td>0.005</td>
<td>0.051</td>
<td>0.034</td>
</tr>
<tr>
<td>10 27, 13:00 - 18:00</td>
<td>0.40</td>
<td>0.004</td>
<td>0.023</td>
<td>0.032</td>
</tr>
<tr>
<td>10 28, 11:00 - 16:00</td>
<td>0.24</td>
<td>0.002</td>
<td>0.011</td>
<td>0.019</td>
</tr>
<tr>
<td>10 29, 10:00 - 15:00</td>
<td>0.17</td>
<td>0.007</td>
<td>0.009</td>
<td>0.042</td>
</tr>
<tr>
<td>11 9, 11:00 - 18:00</td>
<td>ND</td>
<td>0.007</td>
<td>0.017</td>
<td>0.028</td>
</tr>
<tr>
<td>11 10, 10:00 - 17:00</td>
<td>1.16</td>
<td>0.024</td>
<td>0.031</td>
<td>0.009</td>
</tr>
<tr>
<td>11 12, 10:00 - 14:00</td>
<td>0.75</td>
<td>0.077</td>
<td>0.052</td>
<td>0.015</td>
</tr>
<tr>
<td>11 16, 10:00 - 16:00</td>
<td>0.62</td>
<td>0.030</td>
<td>0.030</td>
<td>0.016</td>
</tr>
<tr>
<td>11/18, 9:00 - 16:00</td>
<td>0.06</td>
<td>0.013</td>
<td>0.015</td>
<td>0.031</td>
</tr>
<tr>
<td>11/29, 10:00 - 16:00</td>
<td>1.14</td>
<td>0.110</td>
<td>0.061</td>
<td>0.013</td>
</tr>
<tr>
<td>11/30, 9:00 - 16:00</td>
<td>2.11</td>
<td>0.177</td>
<td>0.068</td>
<td>0.001</td>
</tr>
<tr>
<td>12/1, 11:00 - 16:00</td>
<td>0.24</td>
<td>0.006</td>
<td>0.012</td>
<td>0.035</td>
</tr>
<tr>
<td>12/2, 8:00 - 16:00</td>
<td>1.13</td>
<td>0.052</td>
<td>0.026</td>
<td>0.018</td>
</tr>
<tr>
<td>12/3, 10:00 - 14:00</td>
<td>0.25</td>
<td>0.006</td>
<td>0.006</td>
<td>0.032</td>
</tr>
</tbody>
</table>

Note: The above average concentrations were provided by Clack County Health District.

CO was measured at Flamingo Station (584 E. Flamingo Rd.).

NO and NO₂ were measured at E. Sahara (4001 Sahara Ave.).

O₃ was measured at City Center (559 N. 7th St.).
Table A-4: Average Concentration of \( \text{H}_2\text{O}_2 \), CO, NO\(_x\), and \( \text{O}_3 \) in Las Vegas of Every month (from June to December)

<table>
<thead>
<tr>
<th>Month</th>
<th>( \text{H}_2\text{O}_2 )</th>
<th>NO(_x)</th>
<th>CO (FL)</th>
<th>O(_3) (CC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>0.36</td>
<td>0.016</td>
<td>0.049</td>
<td>0.038</td>
</tr>
<tr>
<td>7</td>
<td>1.40</td>
<td>0.014</td>
<td>0.044</td>
<td>0.039</td>
</tr>
<tr>
<td>8</td>
<td>1.58</td>
<td>0.018</td>
<td>0.051</td>
<td>0.048</td>
</tr>
<tr>
<td>9</td>
<td>1.43</td>
<td>0.013</td>
<td>0.04</td>
<td>0.047</td>
</tr>
<tr>
<td>10</td>
<td>0.34</td>
<td>0.025</td>
<td>0.055</td>
<td>0.034</td>
</tr>
<tr>
<td>12</td>
<td>0.017</td>
<td>0.036</td>
<td>0.054</td>
<td>0.028</td>
</tr>
<tr>
<td>11</td>
<td>0.00</td>
<td>0.102</td>
<td>0.097</td>
<td>0.019</td>
</tr>
</tbody>
</table>

CO was measured at Flamingo Station (584 E. Flamingo Rd.).

NO\(_x\) were measured at E. Sahara (4001 Sahara Ave.).

\( \text{O}_3 \) was measured at City Center (559 N. 7\(^{th}\) St.).

Table A-5: Probability of Correlation Coefficient Between \( \text{H}_2\text{O}_2 \)

<table>
<thead>
<tr>
<th>Related Compounds</th>
<th>n</th>
<th>( f (=n-2) )</th>
<th>( r )</th>
<th>( r^2 )</th>
<th>( t )</th>
<th>p</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO(_x)</td>
<td>6</td>
<td>4</td>
<td>0.75339</td>
<td>0.5676</td>
<td>2.29143</td>
<td>&gt; 95%</td>
</tr>
<tr>
<td>( \text{O}_3 )</td>
<td>6</td>
<td>4</td>
<td>0.89079</td>
<td>0.7935</td>
<td>3.92053</td>
<td>&gt; 95%</td>
</tr>
</tbody>
</table>

The calculation of t-test is shown as following (Graham, 1993):

\[
t_{\text{test}} = \frac{r \cdot \sqrt{n - 2}}{\sqrt{1 - r^2}}
\]

\( r^2 \): correlation coefficient; \( f (=n-2) \): degrees of freedom; p: probability or confidence level.
REFERENCES


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Walling, C., Fenton’s reagent revisited. Accounts of chemical research, 8, 125-131, (1975).


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VITA

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Master of Science, Chemistry, 2000
University of Nevada, Las Vegas, U.S.A.

Thesis Title:
A High Performance Liquid Chromatography System with Fenton’s Reagent
For Detection of Gas-Phase Hydrogen Peroxide.

Thesis Examination Committee:
Chairperson, Dr. Spencer M. Steinberg, Ph.D.
Co-advisor, Dr. Brain J. Johnson, Ph.D.
Committee Member, Dr. Vernon F. Hodge, Ph.D.
Graduate Faculty Representative, Dr. Jacimaria R. Batista, Ph.D.