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Development of aqueous scrubber to oxidize and absorb nitric oxide

Wanna Lolertpiphop
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ABSTRACT

The use of sodium chlorite (NaClO_2) and alkaline aqueous cumene hydroperoxide (CHP) as oxidizing agents to promote the absorption of nitric oxide from flue gases was investigated in a semi-continuous bubbling scrubber. The efficiency of the scrubbing solutions to remove nitric oxide was evaluated as a function of operating conditions such as pH, concentration of the oxidants, residence time, temperature, flue gas compositions.

Under acid conditions, sodium chlorite can stoichiometrically react and absorb 99.5% NO and 80% SO_2 in the same scrubber with 0.672 M NaClO_2 in buffered solution at pH 6, and 0.3 M NaOH. During the reaction, nitric oxide was oxidized to nitrates and nitrites and sulfur dioxide to sulfates. Consequently, sodium chlorite can be used to control NO as well as SO_2 . However, the parasitic effect of SO_2 in consuming the reactant results in a relatively high operating cost. On the other hand, organic cumene hydroperoxide scrubbing solution has been found to operate under high alkalinity to control nitric oxide. The hydroperoxide used in this study was less expensive than sodium chlorite system and commercially available. The removal of 92% nitric oxide was achieved at 94 °C, 1.531 min residence time (scrubber contains 1.49 dm^3 solution and flue gas is bubbled at 0.94 dm^3/min), with 0.12 M cumene hydroperoxide and 0.1 M potassium hydroxide. The major products obtained from the NO oxidation by alkaline cumene hydroperoxide are NO_2^- and NO_3^- and cumyl alcohol. Other products such as acetophenone and α -methyl styrene are observed as a result of the decomposition of the reactant and intermediates.

**DEVELOPMENT OF AQUEOUS SCRUBBER TO
OXIDIZE AND ABSORB NITRIC OXIDE**

by
Wanna Lolertpiphop

**A Thesis
Submitted to the Faculty of
New Jersey Institute of Technology
In Partial Fulfillment of the requirements for the Degree of
Master of Science in Chemical Engineering**

**Department of Chemical Engineering,
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APPROVAL PAGE

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OXIDIZE AND ABSORB NITRIC OXIDE**

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for their love, encouragement, and unceasing support

TABLE OF CONTENTS

Chapter		Page
1	INTRODUCTION	1
	1.1 NO _x Formation and Sources	1
	1.2 Effect of Nitrogen Oxides Emission	4
	1.3 NO _x Control Technology	6
	1.3.1 Combustion Modifications	6
	1.3.2 Flue Gas Treatment Techniques	8
2	LITRATURE REVIEW	11
	2.1 NO Absorption into Solution Accompanied by Oxidation Reaction ...	11
3	EXPERIMENTAL	19
	3.1 Chemicals	19
	3.2 Experimental Setup and Procedure	21
	3.2.1 Experimental Setup	21
	3.2.2 Experimental Procedure	24
	3.3 Flue Gas Analysis	25
	3.4 Determination of Cumene Hydroperoxide by Iodometric Titration	27
	3.5 Scrubbing Solution Analysis	28
	3.5.1 Sample Preparation	28
	3.5.2 Ion Chromatography Analysis	28
	3.5.3 Gas Chromatography-Fourier Transform Infrared Spectrometer Analysis	32

TABLE OF CONTENTS
(Continued)

Chapter	Page
4 RESULTS AND DISCUSSIONS	41
4.1 NO Absorption into Sodium Chlorite Solutions	41
4.1.1 Effect of pH on the Absorption of NO and SO ₂ into NaClO ₂ Solutions	41
4.1.2 Effect of NaClO ₂ and NaOH Concentrations on NO and SO ₂ Absorption in Buffer Solution pH 6.3	46
4.1.3 Material Balance for the Oxidation and Absorption of NO and SO ₂ by NaClO ₂	49
4.2 NO Absorption into Alkaline Aqueous Cumene Hydroperoxide Solutions	52
4.2.1 Effect of Cumene Hydroperoxide and KOH Concentrations on NO Removal	52
4.2.2 Effect of Residence Time on NO Removal	56
4.2.3 Effect of Temperature on NO Removal	58
4.2.4 Effect of Base Compounds on NO Removal	61
4.2.5 Products Analysis and Material Balance	63
5 CONCLUSIONS	71
6 RECOMMENDATIONS	73
7 REFERENCES	74

LIST OF TABLES

Table	Page
1.1 Sources of Nitrogen Oxides	1
3.1 Physical and Chemical Data of Sodium Chlorite	19
3.2 Physical and Chemical Data of Cumene Hydroperoxide	20
3.3 GC and FTIR Data for Model Organic Compounds	33
4.1 Capability of NaClO ₂ on the Absorption of NO and SO ₂ under Various Scrubbing Media	44
4.2 Effect of the Concentrations of NaClO ₂ on the Absorption of NO and SO ₂	47
4.3 Mass Balance for NO and SO ₂ Oxidation by NaClO ₂	50
4.4 Material Balance for NO and SO ₂ Oxidation by NaClO ₂	50
4.5 Effect of KOH Concentrations on the Solubility and Stability of CHP	53
4.6 Thermal Stability of Cumene Hydroperoxide at 90°C	54
4.7 Nitrogen Balance for NO Oxidation by Alkaline Aqueous CHP Solution	64
4.8 Carbon Balance for NO Oxidation by Alkaline Aqueous CHP Solution ...	64

LIST OF FIGURES

Figure	Page
3.1 Schematic Diagram Showing the Setup for Gas Scrubbing System	23
3.2 Calibration of Standard Sodium Nitrite Solution	29
3.3 Calibration of Standard Sodium Nitrate Solution	30
3.4 Calibration of Standard Sodium Sulfate Solution	30
3.5 Typical IC Chromatogram of Standard Solutions from Conductivity Detector	31
3.6 Typical IC Chromatogram of Standard Solutions from UV Detector	31
3.7 GC Calibration of Standard Acetophenone Solution at 16.755 min	33
3.8 GC Calibration of Standard Cumyl Alcohol Solution at 20.19 min	34
3.9 GC Calibration of Standard alpha Methyl Styrene Solution at 10.64 min ..	34
3.10 GC Calibration of Standard Isobutyl Nitrate Solution at 6.21 min	35
3.11 GC Calibration of Standard tert-Butyl Nitrite Solution at 2.4 min	35
3.12 FTIR Spectrum of Standard Acetophenone	36
3.13 FTIR Spectrum of Standard Cumyl Alcohol	37
3.14 FTIR Spectrum of Standard alpha Methyl Styrene	38
3.15 FTIR Spectrum of Standard tert-Butyl Nitrite	39
3.16 FTIR Spectrum of Standard Isobutyl Nitrate	40
4.1 Relationship between the Conversion of NO and pH Change as a Function of Time in NaClO ₂ Solution	41
4.2 Absorption of SO ₂ in NaClO ₂ Solution	43
4.3 %Absorption of NO and SO ₂ in 0.0128 M NaClO ₂ at pH 6.2	45

LIST OF FIGURES
(Continued)

Figure	Page
4.4 Effect of NaOH Concentrations on the Absorption of NO and SO ₂ in NaClO ₂	48
4.5 IC Chromatogram of the Spent Scrubbing Solution of Sodium Chlorite ...	51
4.6 Effect of CHP and Alkali Concentrations on NO Removal	55
4.7 Effect of Residence Time on NO Removal	57
4.8 Effect of Temperature on NO Removal	59
4.9 Relationship between Conversion of NO and Concentration Change of CHP at 94°C	60
4.10 Effect of Base Compounds on NO Removal	62
4.11 IC Chromatogram from Conductivity Detector of Spent Scrubbing Solution	65
4.12 IC Chromatogram from UV Detector of Spent Scrubbing Solution	65
4.13 FTIR Spectrum of Cumyl Alcohol in the Spent Scrubbing Solution	66
4.14 FTIR Spectrum of Acetophenone in the Spent Scrubbing Solution	67
4.15 FTIR Spectrum of α -Methyl Styrene in the Spent Scrubbing Solution	68

CHAPTER 1

INTRODUCTION

The nitrogen oxides, or NO_x , consist principally of nitric oxide (NO) and nitrogen dioxide (NO_2). The compositions of NO_x change with time due to the ease of their transformation from one to the other in the presence of oxygen in the air. They are the major contributors to ground-level ozone. Other known oxides of nitrogen include nitrous oxide (N_2O), nitrogen sesquioxide (N_2O_3), nitrogen tetroxide (N_2O_4), and nitrogen pentoxides (N_2O_5), but only N_2O is present in the atmosphere in appreciable concentration because of its stability. Oxides of nitrogen are generally found in effluents from stationary fuel combustion and from transportation vehicles. In the industrialized countries, about 45% of the total nitrogen oxide emissions originate from transport systems, approximately 35% from power plants and remainder from industrial installations and other activities (Blanco, *et al.*, 1996). Also, significant quantities of NO_x are formed from the oxidation of nitrogen compounds found in fuels, or in wastes being incinerated.

1.1 NO_x Formation and Sources

Nitrogen oxides are emitted from a variety of sources. Table 1.1 (Singh, 1987) shows that about 70-90% atmospheric NO_x emissions are from anthropogenic sources, which are contributed by fossil fuel combustion and biomass burning. The other 10 to 30% NO_x emissions are the result of natural sources consisting of lightning, microbial activity in soil, and diffusion from the stratosphere.

Table 1.1 Sources of Nitrogen Oxides (Singh, 1987)

Source	Nature of Source	Emissions (10^{12} g(N)/yr)	
		US.	Global
Fossil fuel combustion	A	6.0	21
Biomass burning	A	0.1	12
Lightning	N	0.3	8
Biogenic production	N	0.3	8
From stratosphere	N	0.03	0.5
Total		6.8	50

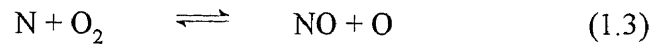
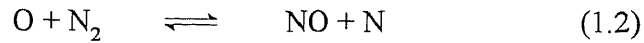
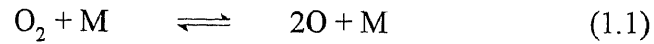
A-anthropogenic; N-natural

Global numbers are probably uncertain to 50%

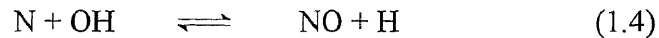
Fossil Fuel Combustion

In general, NO_x is formed by three mechanisms during the combustion process. The first, and least significant, is prompt NO_x which is created from the reaction of combustion products with atmospheric nitrogen (N_2) very close to the flame front. Generally, the formation of prompt NO_x does not occur at particularly high temperatures. The second mechanism of NO_x production is due to the combustion of nitrogen contained in the fuel or waste itself. The most significant source of NO_x is due to the interaction at high temperature of atmospheric nitrogen with the available oxygen. These three types are called, respectively, prompt NO_x , fuel NO_x and thermal NO_x . Factors that influence production of fuel NO_x include distribution of combustion air, refuse nitrogen content, and total excess air rates. Thermal NO_x formation increases with temperatures higher than 1600°F , oxygen availability, heat release rate, and flue gas residence time at high temperatures. During high temperature combustion processes, once atomic oxygen has

been generated in the system, this initiates the Zeldovich Chain Reaction (1946), which leads to the formation of NO as follows, where M is a third body:



The second reaction is the rate-limiting step for NO production and highly temperature sensitive because it has relative high activation energy, due to the need to break the strong N₂ bond. The formation of NO depends on N₂ to the first power and on O₂ to the one-half power (MacKinnon, 1974). When oxygen concentrations are low (fuel rich zones) and the rate of reaction 1.3 is slow, NO may also be formed via the following reaction (Shaw, 1974):



Lightning and Microbial Production

Nitric oxide is created naturally via two major sources: atmospheric lightning creating high local temperatures that promote the atmospheric oxygen and nitrogen reactions and microbial production. It has been estimated that lightning account for 1/3 of all natural NO_x production, and microbes in soil generate the other 2/3 (Bolin and Cook, 1983).

The temperature of a column air, which is exposed to atmospheric lightning is a function of the energy deposited by that lightning. For a typical energy deposition of 10 J/m, the column of air immediately surrounding the charge is heated to the temperatures on the order of 30,000 K. At temperatures above 2,300 K, NO is in thermodynamic

equilibrium with N_2 and O_2 . However, as the temperature drops below 2,000 K, the NO “freezes out” as a stable compound. The total global production of NO due to atmospheric lightning is a product of two terms; 1) the production NO per energy input of lightning (J) or the NO per lightning flash and 2) the total energy deposited by lightning or the lightning flash frequency (Levine, *et al.*, 1984).

Regarding biogenic production, laboratory experimental results have indicated that soil microorganisms produce appreciable amounts of NO. Levine, *et al.*, (1984) were able to quantify the amount of NO exhaled from the soil. A series of experiments were performed by using two common bacteria, *Nitrosomonas Europea* (a nitrifier) and *Alcaligenes Faecalis* (a denitrifier) to prove that nitrification was an aerobic process in which ammonium cations are oxidized to inorganic nitrite and nitrate ions. NO and N_2O are direct and indirect intermediates of this pathway.

1.2 Effects of Nitrogen Oxides Emission

NO_x contributes to acid rain and is a precursor to the formation of photochemical oxidants. It can also pose a health hazard at high ambient levels.

Acid Deposition

Acid deposition has been implicated in damage to aquatic ecosystems, forests, structural materials, visibility and health. NO_2 in the atmosphere is hydrolyzed to form nitric acid (HNO_3) which estimated to cause 30% to 40% of acid precipitation. The amount of acid deposition is thought to be nearly linearly related to emissions of sulfur dioxide (SO_2) and NO_x , though the complex reactions between various atmospheric compounds and the

influence of meteorology suggest that this linearity is only valid on large geographic and temporal scales. This nearly linear relationship between emissions and deposition implies that a sensible policy option for the control of acid rain is the control of emissions of SO_2 and NO_x , and this is the approach taken in Title IV of the Clean Air Act Amendments of 1990 (CAAA) (Molburg, 1993).

Formation of Photochemical Oxidants

One of the concerns with NO_x is its role in the formation of photochemical oxidants, such as ozone, which have an adverse effect on human health, vegetation, and materials exposed to the environment. This problem is more prevalent in urban areas, where increased emissions of nitrogen compounds and volatile organic compounds (VOCs) react in the atmosphere to form ozone. These chemical reactions depend on sunlight and temperature.

NO_x are formed during high temperature combustion processes. Most of the NO_x emitted into the atmosphere are in form of NO , which subsequently oxidizes slowly to NO_2 in the atmosphere. NO_2 emissions are generally less than 10%. Once in the atmosphere, NO takes part in chemical reactions which can lead to the formation of NO_2 and ozone (O_3), nitric acid (HNO_3), hydrogen peroxide (H_2O_2), and peroxyacetyl nitrate (PAN). Volatile organic compounds (VOC), primarily non-methane hydrocarbons (NMOC), also play an important role in the reactions leading to ozone formation. Thus, the rate of conversion of NO to NO_2 and subsequently to ozone is dependent upon the VOC/NO_x ratio. It has been found that the limiting reactant is NO_x because there are many natural sources of VOC.

Health Effects

In term of human health, NO is a relatively nonirritating gas and is therefore believed to pose no health threat at ambient levels. However, NO can be oxidized to NO₂, which is a lung irritant and can produce pulmonary edema at very high concentrations. Healthy humans show increases in airway resistance after 1-15 minutes of exposure to NO₂ concentrations ranging from 1.6 to 2.5 ppm. Short- and long-term exposure to high concentrations of NO₂ can enhance susceptibility to respiratory infections.

1.3 NO_x Control Technology

There are several control technologies available which reduce NO_x emissions from industrial boilers and heaters. The strategies involve combustion modification and flue gas treatment.

1.3.1 Combustion Modifications

Low NO_x burners can reduce NO_x emissions 40% to 60% and are commercially available. They maintain conditions unfavorable to NO_x formation. They restrict the air and fuel mixing in the combustion zone nearest the burners which reduces the amount of nitrogen that is oxidized and minimizes NO_x formation in early stages of combustion. They are designed to create a longer, cooler flame so that the air and combustion gases thoroughly mix in the latter part of the flame. The formation of NO_x from nitrogen in the combustion air is controlled by limiting temperatures to less than 2700° F. They can be installed on many pulverized-coal-fired boilers, but they cannot be adapted to cyclone-fired boilers (Katzberger, *et al.*, 1988).

Reburning can potentially reduce NO_x emissions by 60%. Reburning diverts 10% to 20% of the heat input to create a second zone that is oxygen-deficient and encourages reduction of NO and NO_2 to N_2 (Rhoads, *et al.*, 1990). The reburning fuel can be natural gas, synthetic gas, oil, or pulverized coal, but NO_x emissions are lowest with natural gas. The most likely application will be for retrofitting coal firing or cyclone boilers (Katzberger, *et al.*, 1988).

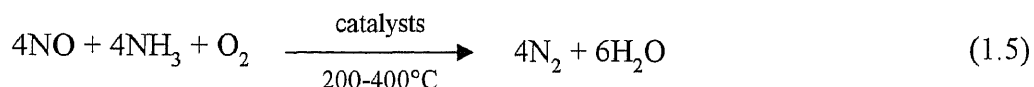
Flue gas recirculation systems involve recycling of flue gases, which typically contain combustion products and lower oxygen concentrations, from the boiler exit back into the furnace. This lowers NO_x formation by slightly diluting the flame oxygen concentrations and limiting the flame temperature. This strategy is used primarily to lower thermal NO_x , but when circulated to the primary air zone, it can improve the staging of the combustion process and reduce fuel NO_x as well (Marjorie, 1989).

Off-stoichiometric combustion (OSC) (often called staged combustion) combusts the fuel in two or more steps. The initial or primary flame zone is fuel-rich, and the secondary (and following) zones are fuel-lean. Without retrofitting with specially designed burners, OSC can be accomplished (a) by firing some of the burners (usually the lower row) fuel-rich and the rest fuel-lean, or (b) by taking some of the burners out of service and allowing them to admit only air to the furnace, or (c) by firing all of the burners fuel-rich and admitting the remaining air over the top of flame zone (overfire air) (Cooper and Alley, 1994).

Water injection (or steam injection) can be an effective means of reducing flame temperatures, thus reducing thermal NO_x . Water injection has been shown to be very effective for gas turbines, with NO_x reductions of about 80% for a water injection rate of 2% of the combustion air. The energy penalty for a gas turbine is about 1% of its rate output, but for a utility boiler, it can be as high as 10% (Crawford, *et al.*, 1977).

1.3.2 Flue Gas Treatment Techniques

Selective catalytic reduction (SCR) processes use a catalyst bed and anhydrous ammonia (NH_3) as the reducing agent for removal of as much as 85% NO_x emissions from industrial effluents that contain elevated concentrations of oxygen. The catalytic reduction of NO_x with ammonia occurs at temperature between 200-400°C. Most commercial catalysts are comprised of vanadium and tungsten oxides supported or mixed with titanium oxide as the principal component (Blanco, *et al.*, 1996).



Selective noncatalytic reduction (SNCR) involves injections of ammonia or urea solution into high-temperature regions of furnace and boiler, but not in the presence of a catalyst. At $\text{NH}_3:\text{NO}_x$ molar ratios of 1:1 to 2:1, about 40-60% NO_x reduction can be achieved. Two major SNCR systems are commercially available: the Exxon Thermal De NO_x ammonia injection system and the Fuel Tech NO_xOUT urea injection system. The Thermal De NO_x uses the NO_x /ammonia reaction to convert NO to molecular nitrogen. The Electric Power Research Institute originally developed the NO_xOUT

process of using urea to convert nitrogen oxides to nitrogen and water. This process of urea injection was further developed and patented by Fuel Tech, Inc. The third system is the Emcotek Two Stage DeNO_x urea/methanol injection system. In this process, the primary function of methanol is to reduce ammonia slip and air preheater deposits (Rhoads, *et al.*, 1990).

Adsorption A number of adsorbents such as silica gel, alumina, charcoal, and commercial zeolites have been used for removal of oxides of nitrogen. Most studies showed that commercial zeolites are the best sorbents in terms of capacity in acidic media. Zeolite ability to adsorb water and nitrogen oxides simultaneously is particularly beneficial in treating nitric acid plant tail gas. The advantage is that, during the regeneration process, the previously adsorbed nitrogen oxides are recovered in the form of diluted nitric acid and recycled to several points of the nitric acid process. However, the nitric acid recovery credit might be insignificant when compared with the cost of molecular sieves required (Michalek, 1976).

Wet scrubbing or wet absorption processes usually remove SO_x as well as NO_x. A number of inorganic scrubbing solutions have shown high capacity for NO₂ absorption, but NO is absorbed with difficulty. Due to the low solubility of NO, the removal of NO in wet scrubbers can be enhanced by oxidizing NO further to NO₂, HNO₂, and HNO₃ (the acid gases are much more soluble in water than NO).

In this thesis, a semi-continuous bubbling scrubber was utilized to determine the feasibility of sodium chlorite and alkaline aqueous cumene hydroperoxide (CHP) as

oxidizing agents to promote the absorption of nitric oxides (NO_x) from flue gases. The efficiency of the scrubbing solutions to remove nitric oxides was evaluated as a function of operating conditions such as pH, temperature, and residence time. The process stoichiometry and complete products analysis were also determined to obtain information on NO conversion in the proposed scrubbing system.

CHAPTER 2

LITERATURE REVIEW

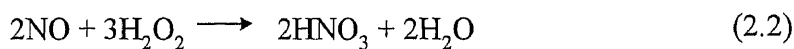
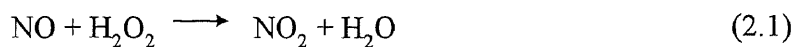
Due to the growing importance of nitrogen oxides removal from flue and off gases, it would be desirable to find a suitable absorption process as an alternative to the conventional selective catalytic reduction of NO_x by ammonia, which is expensive because of catalyst costs, uncertain lifetime, especially in high dust operation, and the problems related to ammonia breakthrough. In the removal process of NO by wet scrubbing, the low solubility of NO in absorbents results in scrubbing difficulties. Therefore, chemical enhancement is required to oxidize NO to other N-containing compounds (NO_2 , HNO_2 , and HNO_3) that are much more soluble than NO. One technique for chemical enhancement involves the gas-phase oxidation of NO to soluble acid gases by strong oxidizers prior to the absorption into the liquid phase. Another technique is the oxidation of NO in the liquid phase as soon as it is absorbed into the solution containing strong oxidizers.

2.1 NO Absorption into Solution Accompanied by Oxidation Reaction

In the absorption of NO into a solution, it is important to select a highly active reactant because of the low reactivity of the oxidation of NO to NO_2 . Various types of oxidizing agents show promise of reacting with NO in solutions, including processes that use hydrogen peroxide, potassium permanganate, sodium chlorite, peroxyacids, organic peroxides, etc.

Hydrogen Peroxide

Shaw (1976) conducted an experimental study of the oxidation of NO to NO₂ by using large excess quantities of H₂O₂ in order to obtain a high conversion of NO. Takahashi et al. (1979) also conducted gas phase oxidation of NO in H₂O₂ at a ratio of 1:1.3 NO to H₂O₂ and at temperature greater than 400°C. The extent of NO oxidation was reported more than 95%. Baveja, *et al.*, (1979) and Robinson (1993) studied the reaction kinetics of liquid phase oxidation of NO in H₂O₂ solution. The reaction includes the following steps:



The rate of reaction was found to be the first order in both reactants. The absorption of NO is accompanied by a fast pseudo-first order reaction. The rate of reaction was found to be $8.42 \times 10^2 \text{ m}^3/\text{kgmol}\cdot\text{s}$ with an activation energy of 57.3 kJ/kgmol at 30°C.

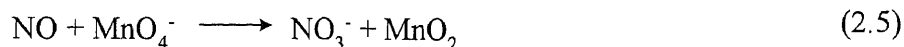
Potassium Permanganate/Sodium Hydroxide

Sada, *et al.*, (1977) conducted experiments of NO absorption into KMnO₄/NaOH solutions and obtained the result that the reaction is first-order with respect to NO concentration in the gas phase and KMnO₄ concentration in the liquid phase. As reported by Uchida, Kobayashi, and Kageyama (1983), their basic chemical equations for NO absorption in aqueous KMnO₄/NaOH are presented by:

At high pH:



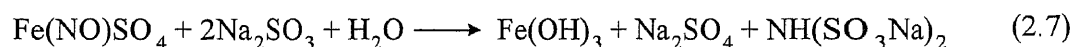
At low or neutral pH:



In the solution of low pH, KMnO_4 is reduced to MnO_2 , which floats on the surface of the solution and reduces the absorption rate, and is therefore not practical. But when NO is absorbed into strong alkali solution, the production of MnO_2 is prohibited and the absorption rate does not decrease.

Sodium Sulfite/Ferric Sulfate

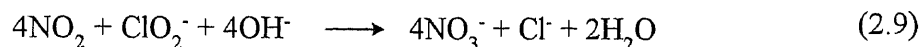
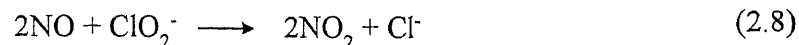
Uchida, *et al.*, (1983) reported that the NO absorption into $\text{Na}_2\text{SO}_3/\text{FeSO}_4$ solution involves the following reactions,



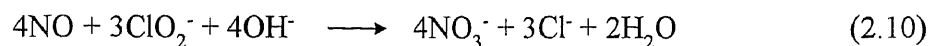
The absorption rate increases with Na_2SO_3 concentration and reaches the maximum at a concentration of about $1 \times 10^{-4} \text{ gmol/cm}^3$. When the Na_2SO_3 concentration is too high, $\text{Fe}(\text{OH})_2$ precipitates due to the higher pH of the solution and the absorption rate decreases.

Sodium Chlorite

The absorption of NO in aqueous mixed solutions of NaClO_2 and NaOH was performed by Sada, *et al.*, (1978, 1979). The reaction between NO and ClO_2^- in an alkaline solution is considered to be



The overall reaction reduces to

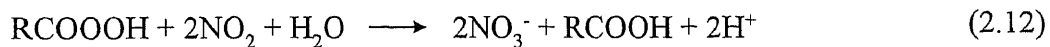
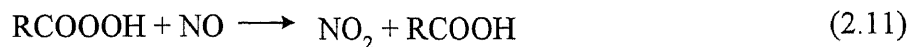


The reaction was found to be the parallel reactions involving oxidation and hydrolysis and to be second order with respect to NO_2 . In addition, the overall reaction was found to be second order in NO and first order in NaClO_2 in the range of NaClO_2 concentration greater than 1.0 M.

Yang (1990) also reported that high concentrations of NaOH inhibit the absorption of NO in NaClO_2 . The upper limit for NaOH concentration necessary to completely absorb NO in NaClO_2 solution depends on the concentration of NaClO_2 . The upper limit of NaOH in 0.08 M NaClO_2 solution is 0.1 M.

Peracid Solution

Peracids, which are formed by a reaction of hydrogen peroxide and some compounds containing a carboxylic acid group, have found to be effective in NO removal (Littlejohn, *et al.*, 1990). These compounds can rapidly oxidize NO to its respective oxyanions. The reactions involving the oxidation of NO by peracids are presented below:



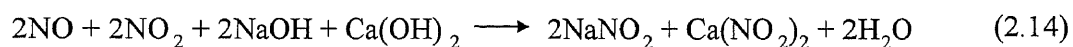
High temperature scrubber operation was found to be advantageous for NO removal. However, a negative aspect of the high temperature operation is the increased decomposition rate of the peracid.

Soda Lime

Soda lime was found to be effective in absorbing NO₂ from NO₂-containing gas, but NO was absorbed minimally when NO₂ was not present as NO is less water soluble (Ishibe, *et al.*, 1996). Where NO coexists with NO₂, however, NO is absorbed with equimolecular amounts of NO₂. The chemical neutralization reaction of NO₂ with soda lime is as follow:

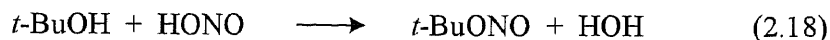
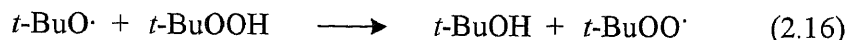
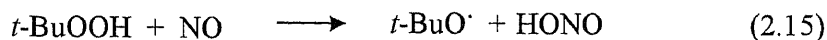


If NO is also present, the following additional reaction may also occur:

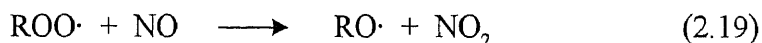


Organic Hydroperoxide

Shelton and Kopczewski (1967) reported the reaction of t-butyl hydroperoxide in benzene solution with nitric oxide to form t-butyl nitrite and t-butyl nitrate as reaction products. The reaction sequence involves a free-radical reaction sequence (equations 2.15-2.18) induced by concentrated nitric oxide.



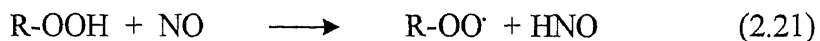
The yields of alkyl nitrates formed in the NO-air photooxidations of n-alkanes were observed by Darnall, *et al.*, (1976) and Atkinson, *et al.*, (1984). The significant path for the smaller alkoxy radicals (<C₄), formed in the reaction of OH radicals with the alkanes, such as methylperoxy radical is oxidation of NO to NO₂ and formation of alkoxy radicals:



However, for large (≥C₄) alkoxy radicals the reaction with NO to form alkyl nitrates is attributed to the formation via equation 6.

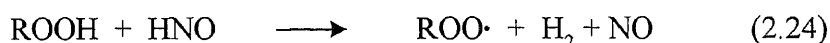


Carlsson, *et al.*, (1987 and 1988) reported that the NO reaction with hydroperoxides, generated from oxidized polyolefins and in concentrated solutions model of hydroperoxides, give only nitrates as the dominant products, with only traces (< 5%) of nitrite. At low concentration of hydroperoxides, equimolar quantities of nitrate and nitrite mixtures were obtained. Rather than the initially NO attack on the O-O bridge in the hydroperoxides proposed by Shelton and Kopczewski (1967), Carlsson, *et al.*, proposed that at high hydroperoxide levels, the hydrogen is abstracted by NO via the following reactions:

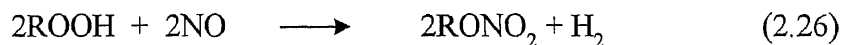


The detection of pale yellow-green gas after NO reaction with oxidized polyolefins is consistent with the formation of HNO.

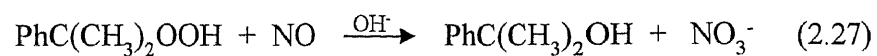
Perlmutter, *et al.*, (1993) and Huihong Ao (1992) investigated the selective removal of NO from gas streams using 3,6-dimethyl-3-octyl hydroperoxide, p-menthanyl hydroperoxide, pinanyl hydroperoxide, and cumene hydroperoxide in solutions of n-hexadecane. The influence of parameters such as temperature, gas flow rate (residence time), and concentration of hydroperoxide compounds on the efficiency of NO removal was evaluated. The highest rates of removal were obtained at the highest temperature, concentrations, and residence times. All of the hydroperoxides were effective in oxidizing NO, but overall cumene hydroperoxide was found to be the most efficient. The NO reacted with the hydroperoxides to produce alkyl nitrates, which are easily hydrolyzed with ammonium hydroxide to ammonium nitrate and alcohol. The reactions each of the hydroperoxides undergo as they react with NO can be found on the following reactions:



The overall reaction is as follow:



The removal of NO in n-hexadecane solution of cumene hydroperoxide (CHP) was studied in more detailed by Chen (1993). The NO removal ability of cumene hydroperoxide was found to be 70% at 0.5 M CHP concentration, 100°C, and 80 seconds residence time. The half-life of cumene hydroperoxide was found to be 467 hours at 100°C. The organic nitrates, produced from the NO oxidation, were then hydrolyzed to inorganic nitrate (NO_3^-) and nitrite (NO_2^-) ions via alkaline hydrolysis.



CHAPTER 3

EXPERIMENTAL

3.1 Chemicals

Sodium Chlorite

Commercial sodium chlorite containing approximately 80% NaClO₂, 18% Na₂CO₃, and 2% Na₂SO₄ was used as oxidizing agent for NO removal in an inorganic aqueous scrubbing system. Textone, which is a commercial name of sodium chlorite, was purchased from Pfaltz & Bauer, Inc., Waterburg, CT. The physical and chemical properties of sodium chlorite are listed in Table 3.1.

Table 3.1 Physical and Chemical Data of Sodium Chlorite

Physical description	White crystals and hygroscopicity
Molecular formula	NaClO ₂
Molecular weight	90.44 g/mol
Melting point	190°C
Solubility in water at 20°C	Soluble

Cumene Hydroperoxide

Commercial cumene hydroperoxide (CHP) or Luperox CU90 was obtained 88% pure from Elf Atochem North America, Inc., Philadelphia, PA and used without further purification. The impurities in CHP consist of 4.8% cumene, 6% cumyl alcohol, and 1.2% acetophenone. The physical and chemical properties of CHP are listed in Table 3.2.

Table 3.2 Physical and Chemical Data of Cumene Hydroperoxide

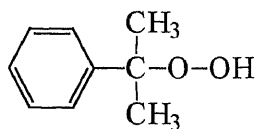
Physical description	Clear, colorless to pale yellow liquid; sharp aromatic odor
Cost	\$1.25/lb
Molecular weight	152.21 g/mole
Density	1.03 g/mL at 25°C
Boiling point	127°C (decomposes)
%Volatile by volume	100
pH	~ 4
Solubility in water	< 0.1mg/mL at 20°C

Alkaline Aqueous Solutions

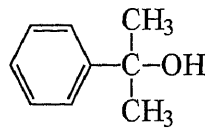
Potassium hydroxide, calcium oxide, and commercial sodium hydroxide, obtained from Aldrich Chemical Co., and Pfaltz & Bauer, Inc., were used as alkali for preparing an aqueous solution of cumene hydroperoxide.

Standard Reagents Used for Ion Chromatography (IC) and Gas Chromatography-Fourier Transform Infrared Spectroscopy (GC-FTIR)

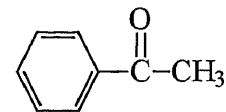
Sodium sulfate, sodium nitrate, sodium nitrite, and sodium chloride were used as standards for IC analysis to determine the inorganic product concentrations in the scrubbing solutions. Acetophenone (99%), α -methyl styrene (99%), cumyl alcohol (97%), isobutyl nitrate (99%), and t-butyl nitrite (96%) were used as GC-FTIR standards to quantify and qualify the distribution of organic products in the scrubbing solutions. These chemicals were purchased from Aldrich Chemical Co. The structure of these compounds including cumene hydroperoxide are shown below:



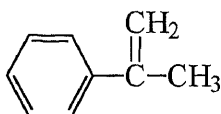
Cumene Hydroperoxide



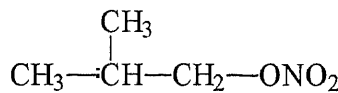
Cumyl Alcohol



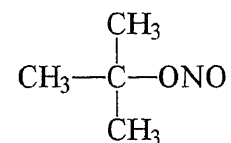
Acetophenone



alpha-Methyl Styrene



Isobutyl Nitrate



Tert-butyl Nitrite

Reagents for Iodometry

Sodium iodide, isopropanol, glacial acetic acid, and sodium thiosulfate were used in iodometric titration (Mair and Graupner, 1964) to determine the concentrations of cumene hydroperoxide. These chemicals were purchased from Aldrich Chemical Co.

Gases

The sulfur dioxide (SO₂) and nitric oxide (NO) balance in nitrogen were purchased from Matheson Gas Co. and used directly from the cylinder. The NO cylinder contained a small quantity of NO₂ (less than 13 ppm). Different concentrations of NO and SO₂ were obtained by mixing with pure nitrogen through mass flow controllers.

3.2 Experimental Setup and Procedure

3.2.1 Experimental Setup

A schematic diagram of the experimental equipment is shown in Figure 3.1. Two bubble column scrubbers consisted of 5.1-cm diameter by 61-cm long ACE Pyrex glass column

with Teflon cap on both ends. One of the scrubbers was used as a main scrubber while another was used as a reference scrubber. A polyethylene diffuser was inserted into the bottom of the glass column. The flue gas was introduced into the scrubbing solution through the diffuser. Stainless steel tubing connected to the source of hot water was inserted at the bottom of the main scrubber and was used as a medium to provide heat to the scrubbing solution. The liquid temperature was regulated by a controlled-temperature bath having provision for water circulation within the stainless steel tubing at a constant temperature. A thermocouple probe was inserted at the main scrubber to monitor the temperature. To avoid condensation of the moisture and organic vapor in the exhaust tubing and analytical systems, two condensers immersed in the ice were used as cold traps. The gas to be absorbed was supplied from cylinders of N₂-balanced NO or SO₂ and was diluted with nitrogen from the other in a gas mixer to desired concentrations. Each component gas was delivered through ¼ inch polyethylene tubing to mass flow meter in order to control the flow rate and fed to the scrubber. The effluent gas was carried through ¼ inch polypropylene tubing to NO_x or SO_x analyzers and vented into the building exhaust system.

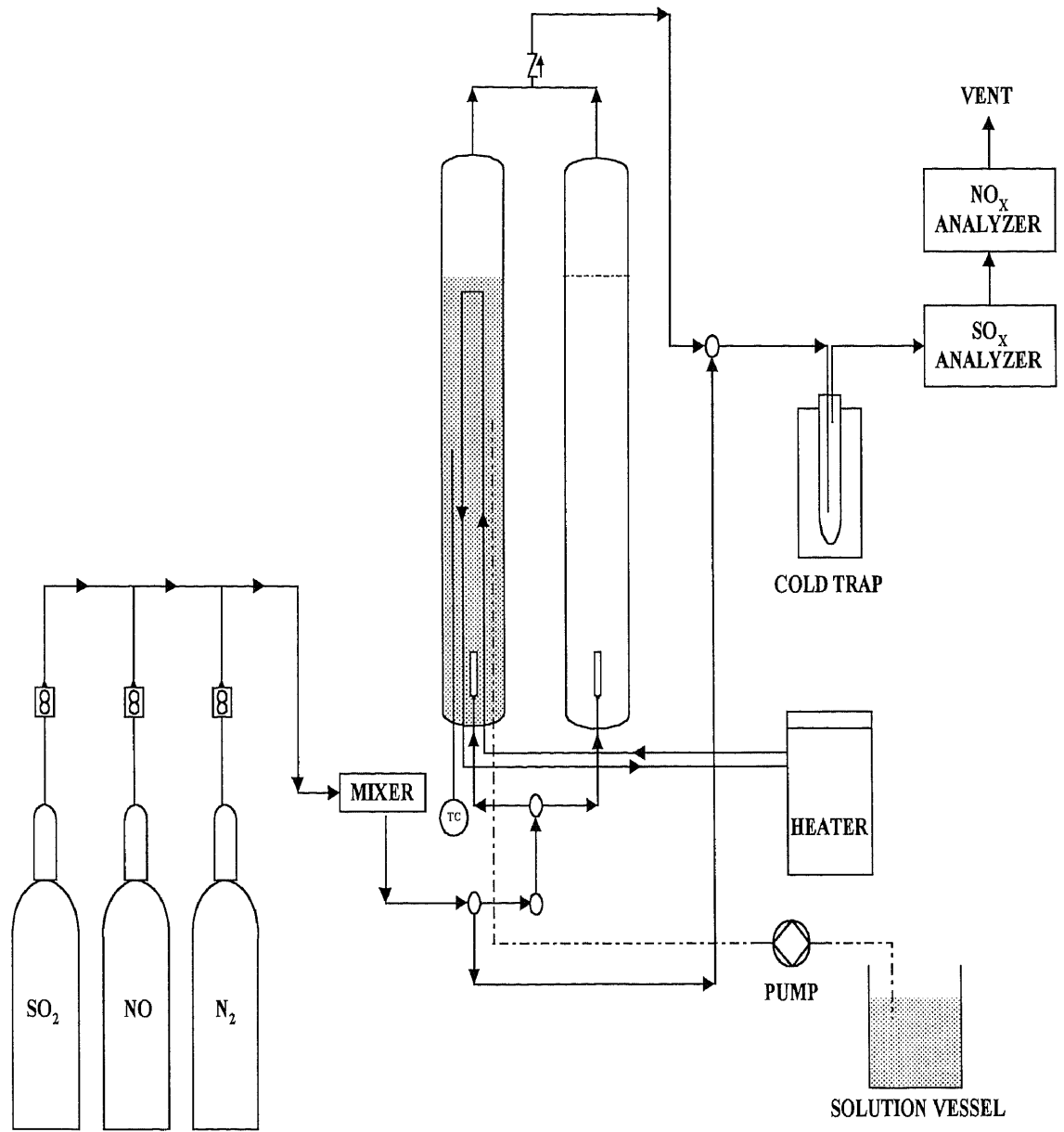


Figure 3.1 Schematic Diagram Showing the Setup for Gas Scrubbing System

3.2.2 Experimental Procedure

In this study, two different types of oxidizing agents were used to absorb NO: (a) inorganic: an aqueous solution of sodium chlorite (NaClO_2); (b) organic: an alkaline aqueous solution of cumene hydroperoxide (CHP).

Absorption of NO into NaClO_2 Solutions

A premixed 1.25 dm^3 NaClO_2 solution of known concentration and pH was pumped to the main scrubber while the reference scrubber was filled with water. An inlet gas mixture with the desired flow rate, which controlled accurately by the mass flow meter, and concentrations of NO and SO_2 , was analyzed by bypassing the reactor to the Thermoelectron NO_x or Rosemount Model 890 UV SO_x analyzers. It then passed through a diffuser at the bottom of the reference scrubber in order to determine the concentrations of the incoming gases. The gas mixture with known concentration was switched by a three-way valve to the main scrubber containing the NaClO_2 solution. All inorganic experiments were conducted at ambient temperature. The effluent gas flowed through a cold trap to NO_x and SO_2 analyzers and vented into a hood. Small samples of the scrubbing solution were collected to measure pH change and for analysis by ion chromatography.

Absorption of NO into Alkaline Aqueous Cumene Hydroperoxide Solution

A known volume of 88% purity of CHP was dissolved with a specified concentration of alkaline solutions of sodium hydroxide or potassium hydroxide in a volumetric flask and transferred to a separatory funnel after stirring. After settling in the separatory funnel, the

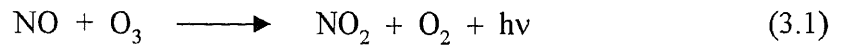
solution was appeared to form a two-phase system between aqueous phase at the top and organic phase at the bottom due to a precipitation of hydroperoxide salts. The aqueous phase was separated from the separatory funnel and determined the pH and concentration of CHP by iodometry. A known concentration and pH of the alkaline aqueous CHP was fed to the main scrubber and heated to a desired temperature by circulating hot water through a stainless steel heat exchanger. A type K thermocouple was used to monitor the temperature of the solution. The CHP concentration was also determined by iodometric titration after heating to experimental conditions. A N₂ stream was swept to the main scrubber for 15-20 min prior to NO admission to completely remove residual O₂. The inlet flue gas compositions and flow rate were set and passed through the reference column to determine the concentrations. When the scrubbing liquid temperature achieved the desired temperature, the flue gases were switched by a three-way valve to the main scrubber. The effluent gas flowed through a cold trap before analysis with NO_x or SO_x analyzers. Approximately 2 cm³ reaction volume was collected periodically to measure the pH change and analyze the concentration change of CHP and reaction products by iodometry, ion chromatography (IC), and Fourier transform infrared spectrometer (FTIR).

3.3 Flue Gas Analysis

During scrubbing, concentration change of NO, NO₂, and SO₂ in the gas phase was analyzed by Thermoelectron chemiluminescent model 10 AR and Rosemount model 890 UV SO₂ analyzer. All instruments were always calibrated with known concentrations of NO and SO₂ in N₂ before and after each experiment.

Chemiluminescent NO/NO_x Analysis

The chemiluminescent reaction of NO and O₃ provides the analysis signal for this technique. Specifically,



To measure NO concentrations, the gas sample to be analyzed is blended with O₃ in a reaction chamber. The O₃ is generated in situ by a high voltage arc ozone generator. The resulting chemiluminescent is monitored through an optical filter by a high sensitivity photomultiplier positioned at one end of the chamber. The filter/photomultiplier combination responds to light in a narrow wavelength band unique to reaction (1). The output from the photomultiplier is linearly proportional to the NO concentration.

Basically, chemiluminescent analysis is only sensitive to NO. To measure NO_x concentrations, NO plus NO₂, the sample gas flow is diverted through a high temperature NO₂ to NO converter. A temperature controller is used to maintain the proper temperature for NO₂ thermal conversion to NO which is 670 °C. The chemiluminescent response in the reaction chamber to the converter effluent is linearly proportional to the NO_x concentration entering the converter.

Ultraviolet SO₂ Analysis

The Rosemount model 890 UV analyzer is designed to determine continuously the concentration of SO₂ in the gaseous mixture. This instrument is capable of measurement in the 50-5,000 ppm range. The ultraviolet source emits a pulsed beam of energy. This energy is split by a beam splitter, each beam being directed to pairs of detectors before

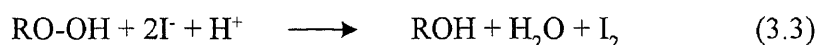
and after the sample cell. Four detectors are used in this system, two before the sample cell, sample before [S_b] and reference before [R_b], and two after, sample after [S_a] and reference after [R_a]. S_b and S_a receive energy in the 265-310 nm wavelength region, R_b and R_a in the 310-355 range. These four detectors measure SO_2 concentration and correct for NO_2 interference and UV lamp fluctuations. The difference between detector determinations is the SO_2 concentration, following this equation:

$$SO_2 = [f(R_b) - S_b] - [f(R_a) - S_a] \quad (3.2)$$

where f is the attenuation factor for the reference signal, adjusted to compensate for NO_2 interference.

3.4 Determination of Cumene Hydroperoxide by Iodometric Titration

The method of Mair and Graupner (1964) was used for quantitative analysis of organic hydroperoxide. The iodide ion reacts stoichiometrically with hydroperoxides in acidic solution, producing iodine, which can be titrated with thiosulfate. The reaction can be illustrated as follow:



Forty- cm^3 of isopropanol reagent grade, 2 cm^3 of glacial acetic acid, and 5 cm^3 of sample were combined in a 250 cm^3 round-bottom flask and heated to reflux. Then 10 cm^3 of NaI-IPA reagent (contained 2 g of NaI) was added into the solution and refluxed another 5-10 minutes, 5 cm^3 of distilled water was added. After refluxing, the solution was titrated while it was hot with standard 0.1 M sodium thiosulfate to a brown-to-colorless end point. Blank titration was done on the isopropanol, glacial acetic acid, and NaI-IPA combined mixture.

3.5 Scrubbing Solution Analysis

3.5.1 Sample Preparation

All samples collected from the scrubbing solutions of NO-CHP system were prepared before further analysis with IC and GC-FTIR. The samples were extracted in a separatory funnel by shaking with anhydrous ethyl ether as organic solvent to separate the inorganic and organic layers. After equilibration the two layers were allowed to separate completely, and the organic layer at the bottom was removed. The aqueous layer retained in the separatory funnel was extracted with fresh ethyl ether two more times to remove additional organic components. The aqueous phase, obtained after the extraction, was purged with N₂ to remove organic residue and then analyzed with IC. On the other hand, the organic phase was dried by passing it through a glass funnel containing anhydrous sodium sulfate. The dried extract was collected in a 10 cm³ concentrator tube. The extract was concentrated by changing the solvent to hexane, which has higher boiling point than ethyl ether. The level of liquid in the concentrator tube was adjusted to 10 cm³ with hexane. The concentrator tube was placed in a warm water bath and the solvent volume evaporated to about 0.1 cm³ using a gentle stream of dry nitrogen. The concentration of the extract was repeated at least two times. The extract obtained was analyzed for the organic products from the reaction using GC-FTIR.

3.5.2 Ion Chromatography Analysis

A Waters ion chromatograph, equipped with sample injector, UV-Visible detector, and conductivity detector, was used to detect the inorganic sulfate, nitrate, and nitrite ions in the aqueous solutions. In this system, the sample injector was pumped by an eluent of

1.2-mM Na_2CO_3 and 1.2-mM NaHCO_3 through the ion exchange column of 4.6 x 75-mm IC-Pak Anion HR. and was detected by conductivity and UV-Visible detectors. The wavelength of UV-Visible detector was set at 214-nm for detection of NO_2^- and NO_3^- . The calibrations of standard sodium nitrite (NO_2^-), sodium nitrate (NO_3^-), and sodium sulfate (SO_4^{2-}) solutions are shown in Figure 3.2, 3.3, and 3.4 respectively. Retention times obtained for NO_2^- , NO_3^- , and SO_4^{2-} ions were 6.783, 10.567, and 15.833 min respectively. The chromatogram of these ions is shown in Figure 3.5 and 3.6.

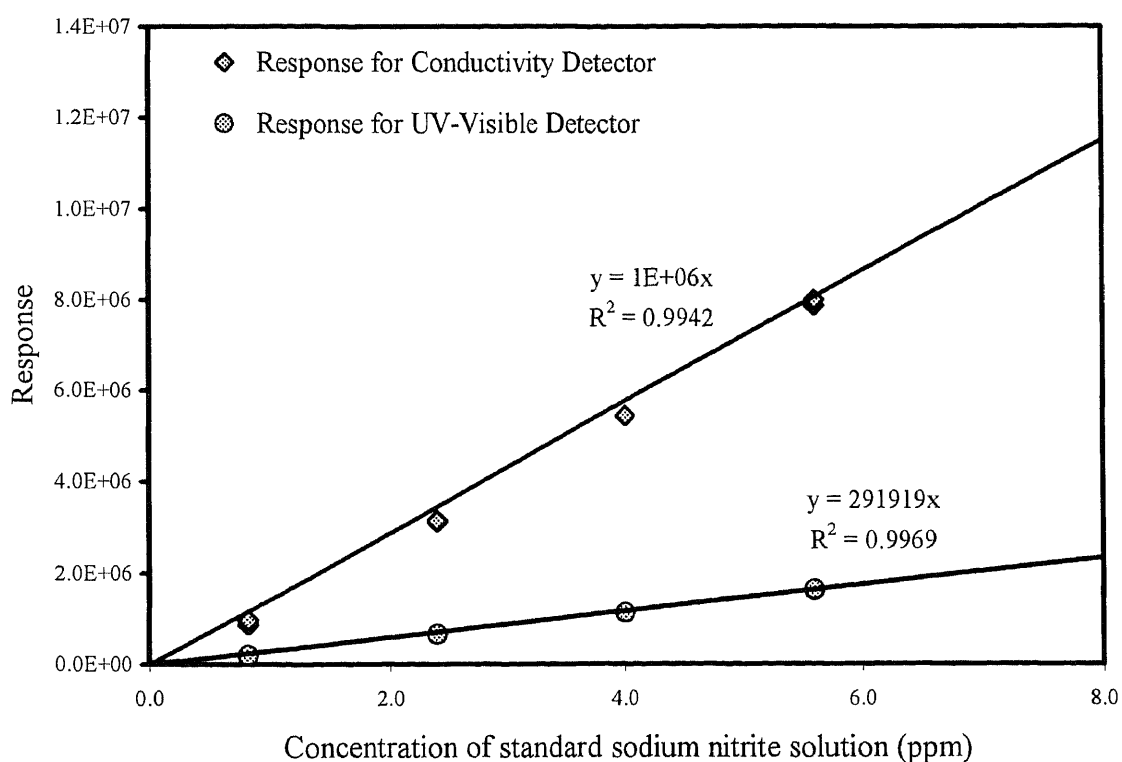


Figure 3.2 Calibration of Standard Sodium Nitrite

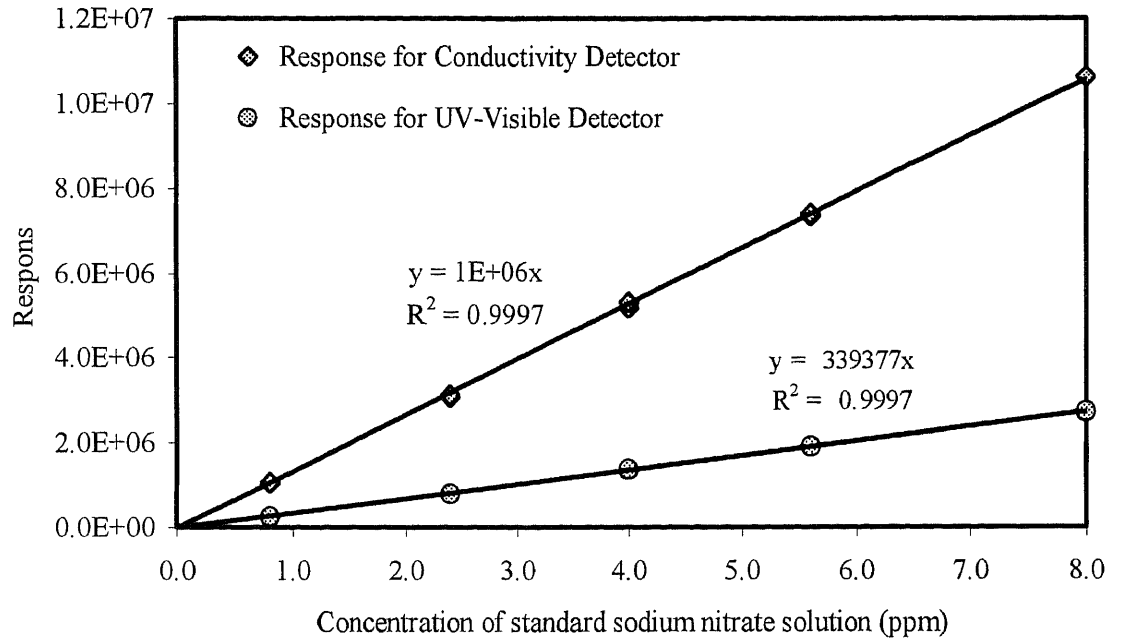


Figure 3.3 Calibration of Standard Sodium Nitrate

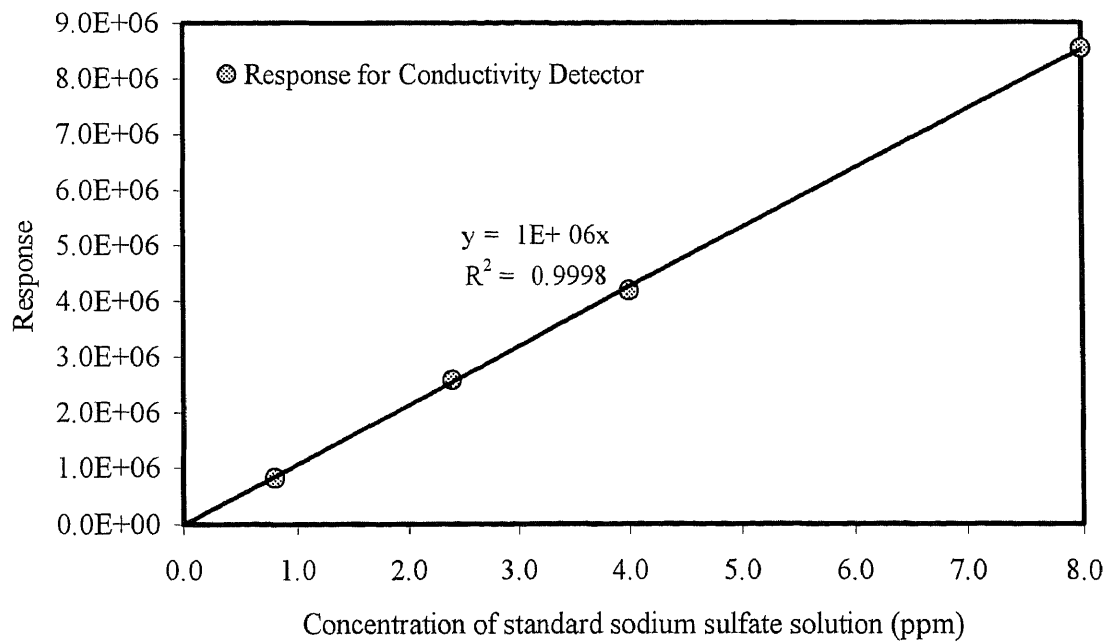


Figure 3.4 Calibration of Standard Sodium Sulfate Solution

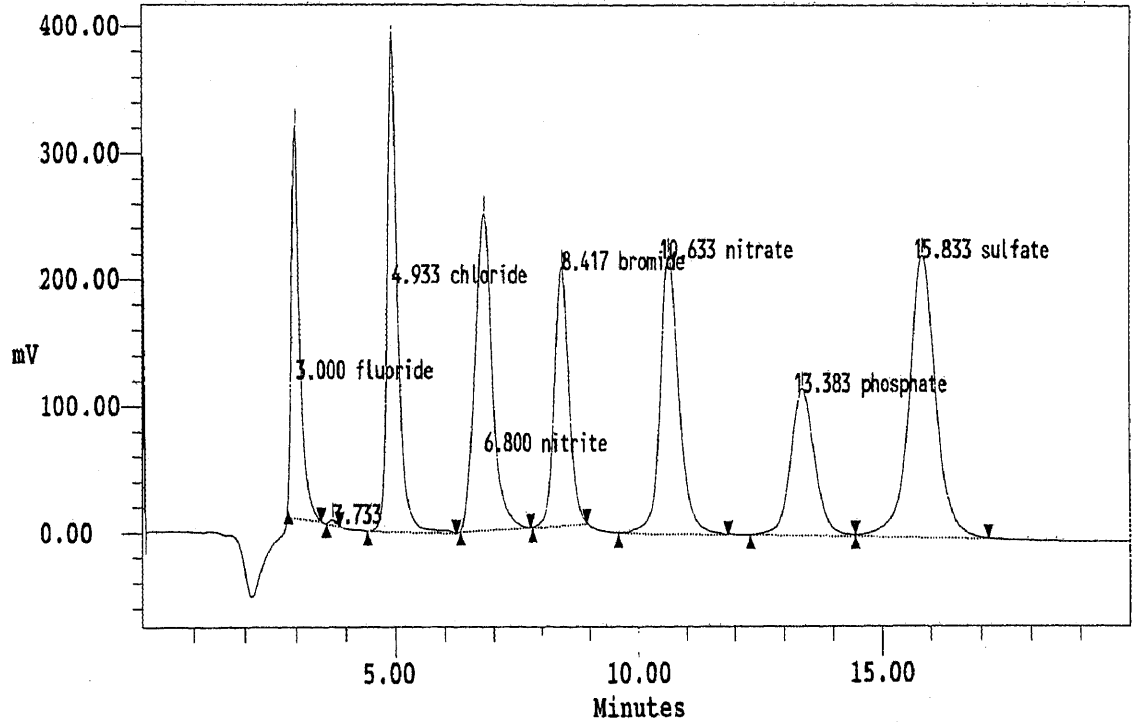


Figure 3.5 Typical IC Chromatogram of Standard Solutions from Conductivity Detector

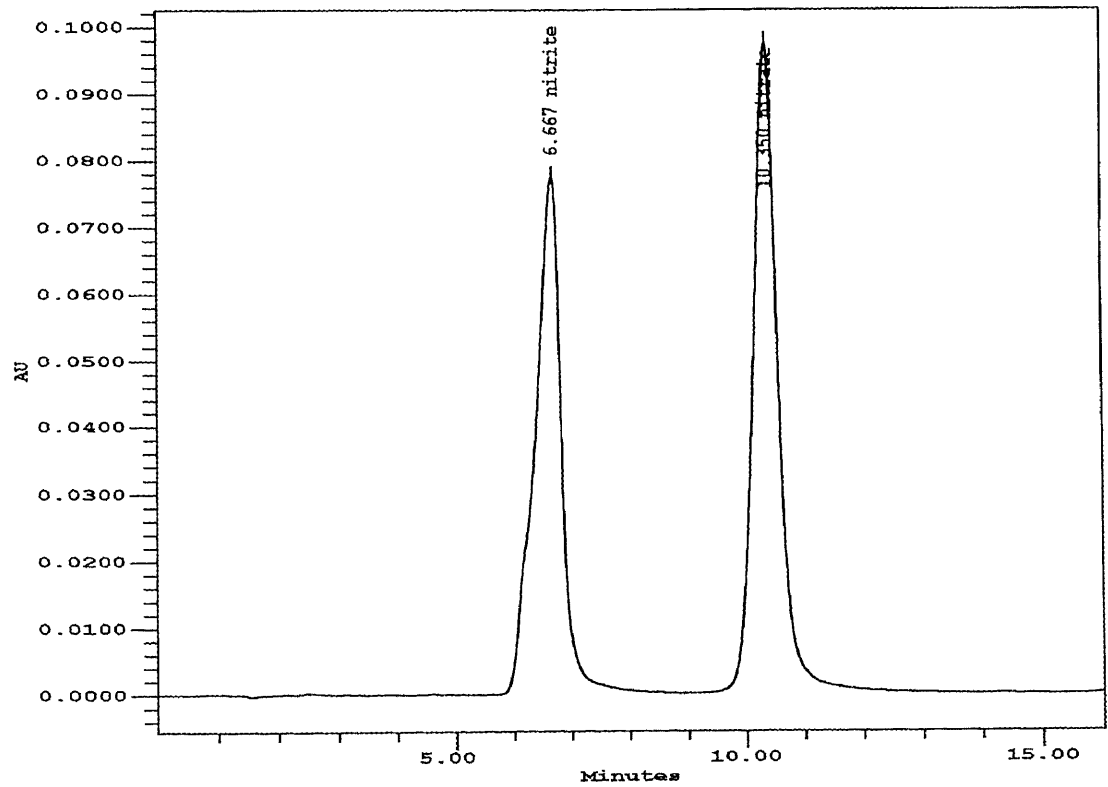


Figure 3.6 Typical IC Chromatogram of Standard Solutions from UV Detector

3.5.3 Gas Chromatography-Fourier Transform Infrared Spectrometer Analysis

A gas chromatograph with flame ionization detector (FID) (model 5398 Hewlett Packard) equipped with Bio-Rad Fourier transform infrared spectrometer (FTIR) was used for qualitative and quantitative analysis of all organic products including organic nitrate, nitrite, acetophenone, α -methyl styrene, and cumyl alcohol in the scrubbing solutions. The precolumn and column used for gas chromatograph (GC) were 0.53-mm ID x 5-m Hydroguard and 0.32-mm ID x 30.0-m, 0.5- μ m thickness DB-Wax, respectively. Organic samples were injected into the GC-FID and the effluent passed through the FTIR light pipe, which is connected between the GC column and FTIR. The following is an overview of the experimental conditions for GC-FTIR analysis used for calibration of standard organic compounds and organic compounds in the scrubbing solutions:

Oven temperature:	35°C
Injection temperature:	210°C
Detector temperature:	250°C
Temperature program (splitless mode):	
Oven temperature	35°C hold 2 min
	150°C at 10°C/min hold 1 min
	160°C at 1°C/min hold 0 min
	205°C at 10°C/min hold 5 min
Pressure program (psi):	Initial (psi) 20 hold 0.3 min
	to 10 at 99 psi/min hold 12 min
	to 6 at 99 psi/min hold 15 min
Inlet purge A:	on
Purge A off:	0.5 min
Purge A on:	1.0 min

The GC calibrations and FTIR spectra of standard acetophenone, cumyl alcohol, α -methyl styrene, isobutyl nitrate, and *t*-butyl nitrite are shown in Figure 3.7-3.16. The retention time and the absorbance of all organic standards are summarized in Table 3.3.

Table 3.3 GC and FTIR Data For Model Organic Compounds

Model Compound	GC Retention Time (min)	FTIR Wavenumber Used (cm ⁻¹)
Acetophenone	16.76	1707and 1260
Cumyl alcohol	20.19	3637and 2980
α -Methyl styrene	10.64	3080and 894
Isobutyl nitrate	6.21	1657and 1282
Tert-butyl nitrite	4.24	1651and 747

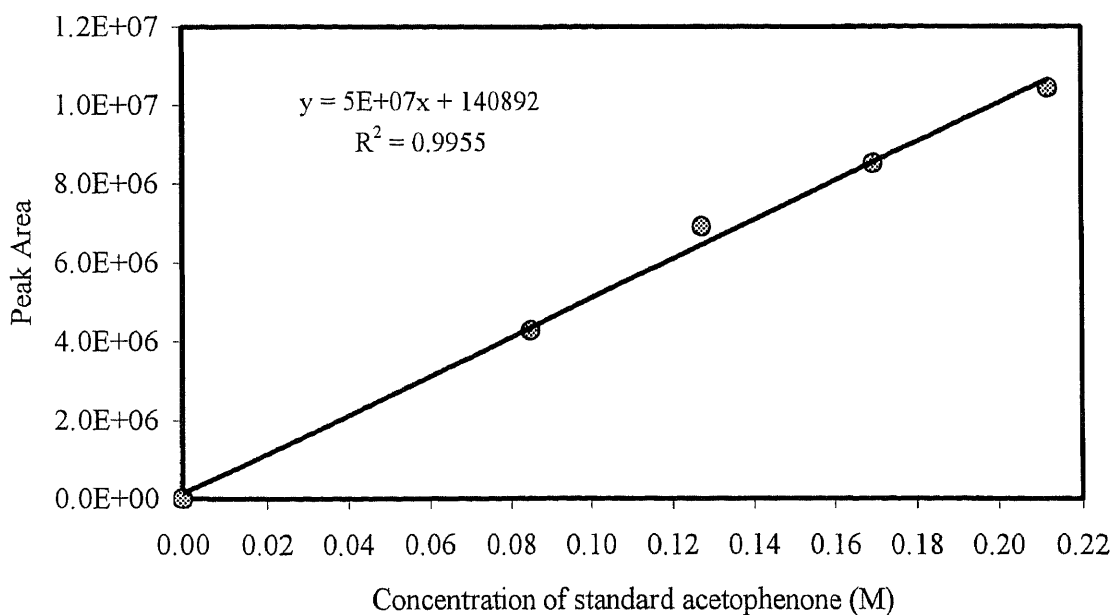


Figure 3.7 GC Calibration of Standard Acetophenone Solution at 16.76 min

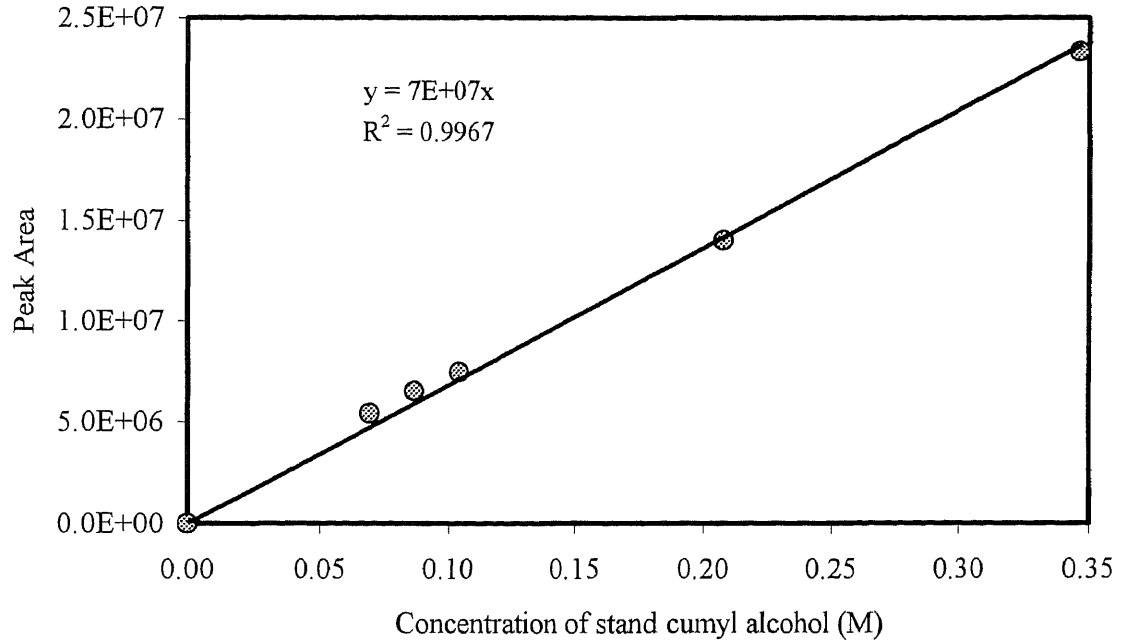


Figure 3.8 GC Calibration of Standard Cumyl Alcohol Solution at 20.19 min

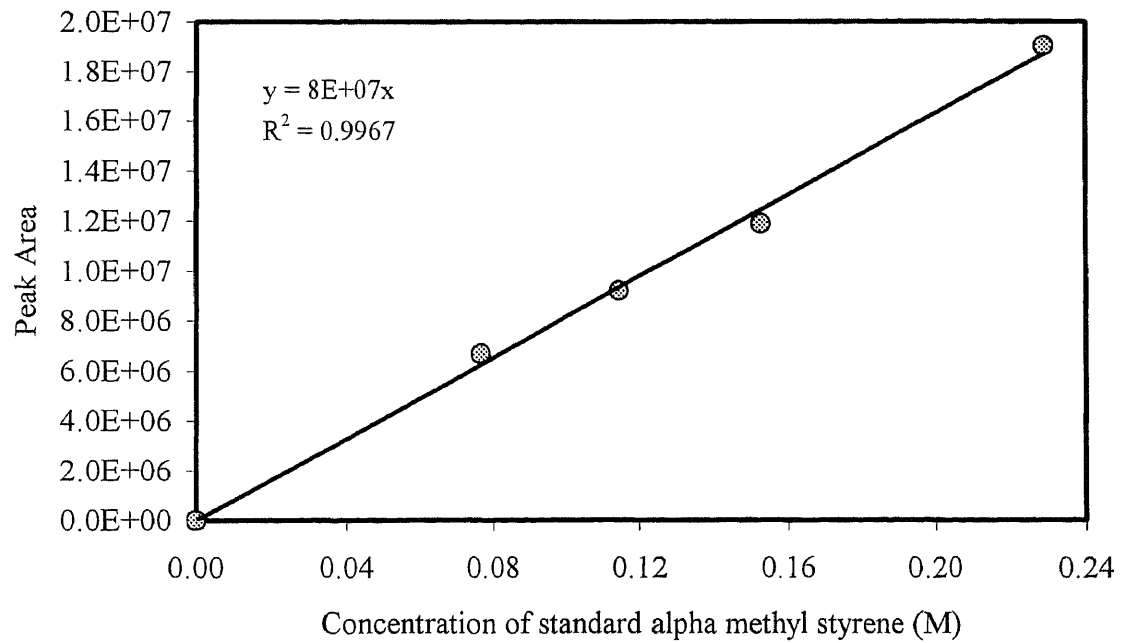


Figure 3.9 GC Calibration of Standard Alpha Methyl Styrene Solution at 10.64 min

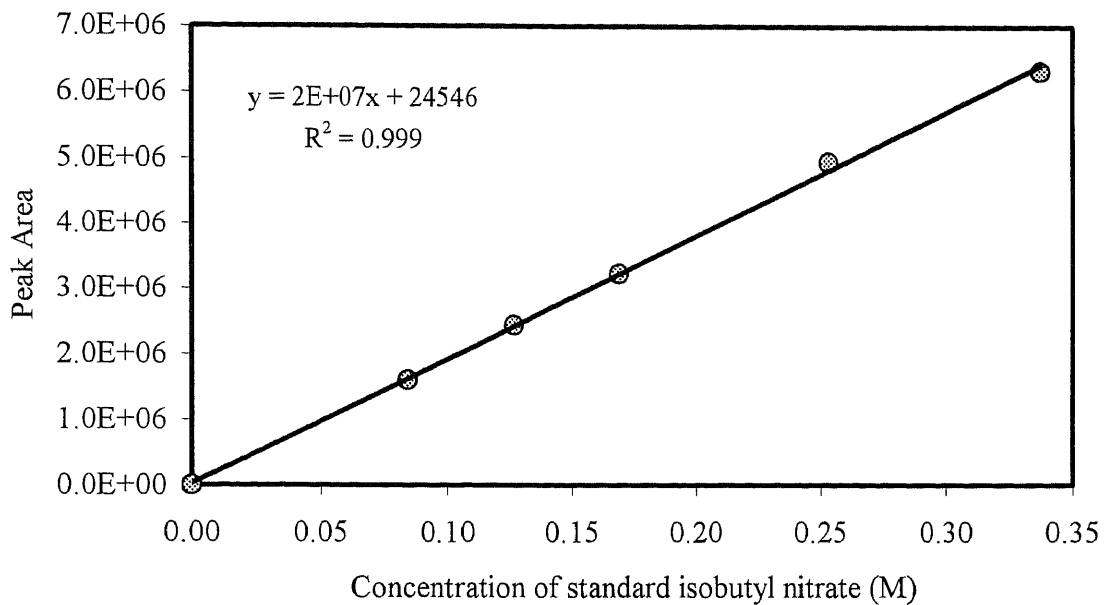


Figure 3.10 GC Calibration of Standard Isobutyl Nitrate Solution at 6.211 min

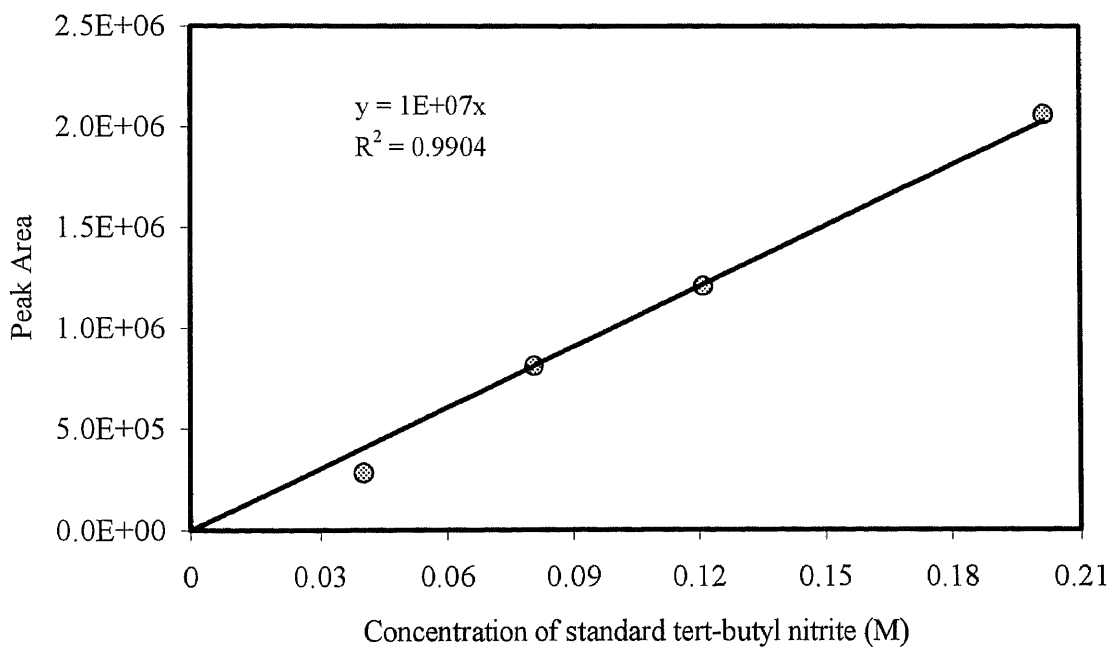


Figure 3.11 GC Calibration of Standard Tert-Butyl Nitrite Solution at 2.4 min

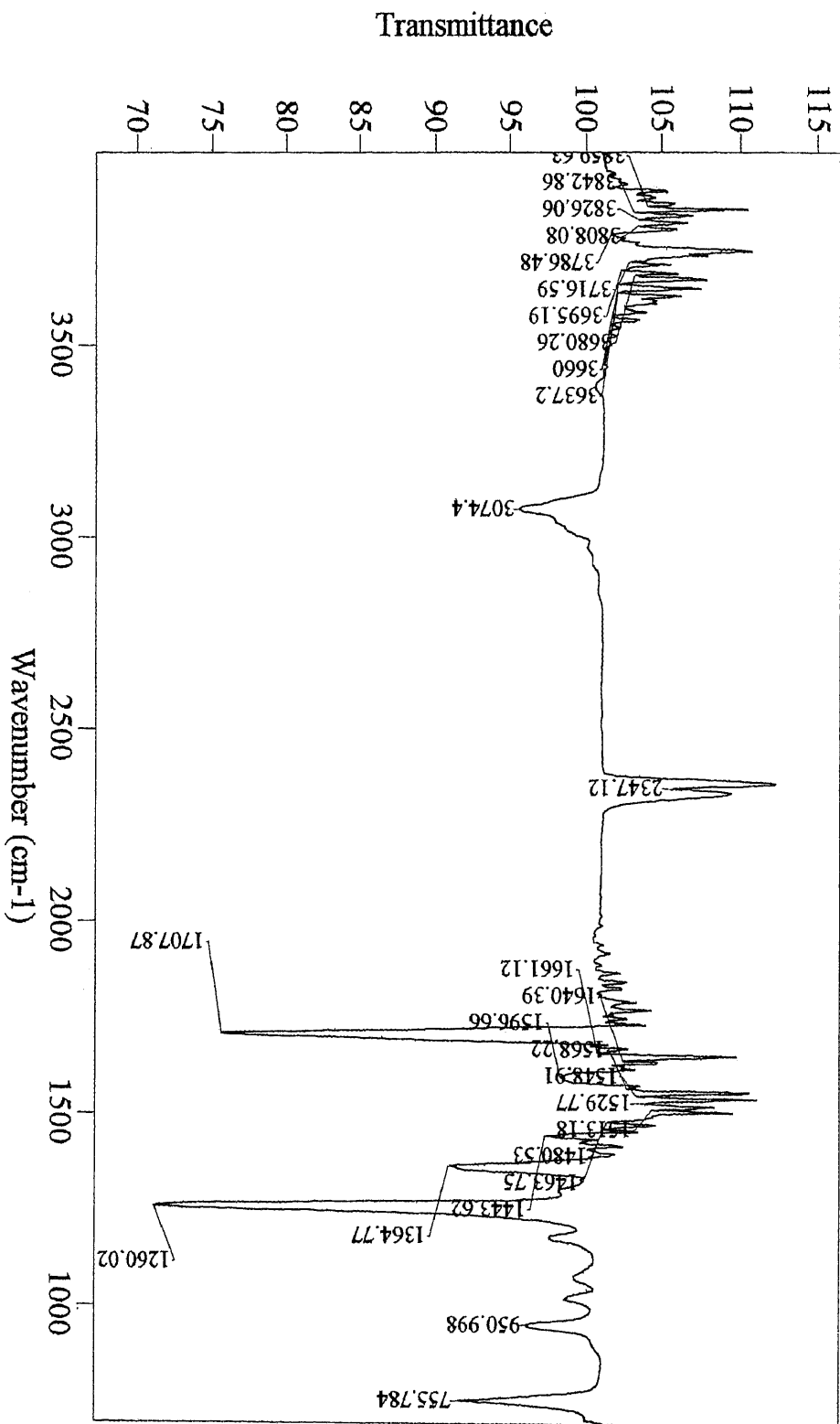


Figure 3.12 FTIR Spectrum of Standard Acetophenone

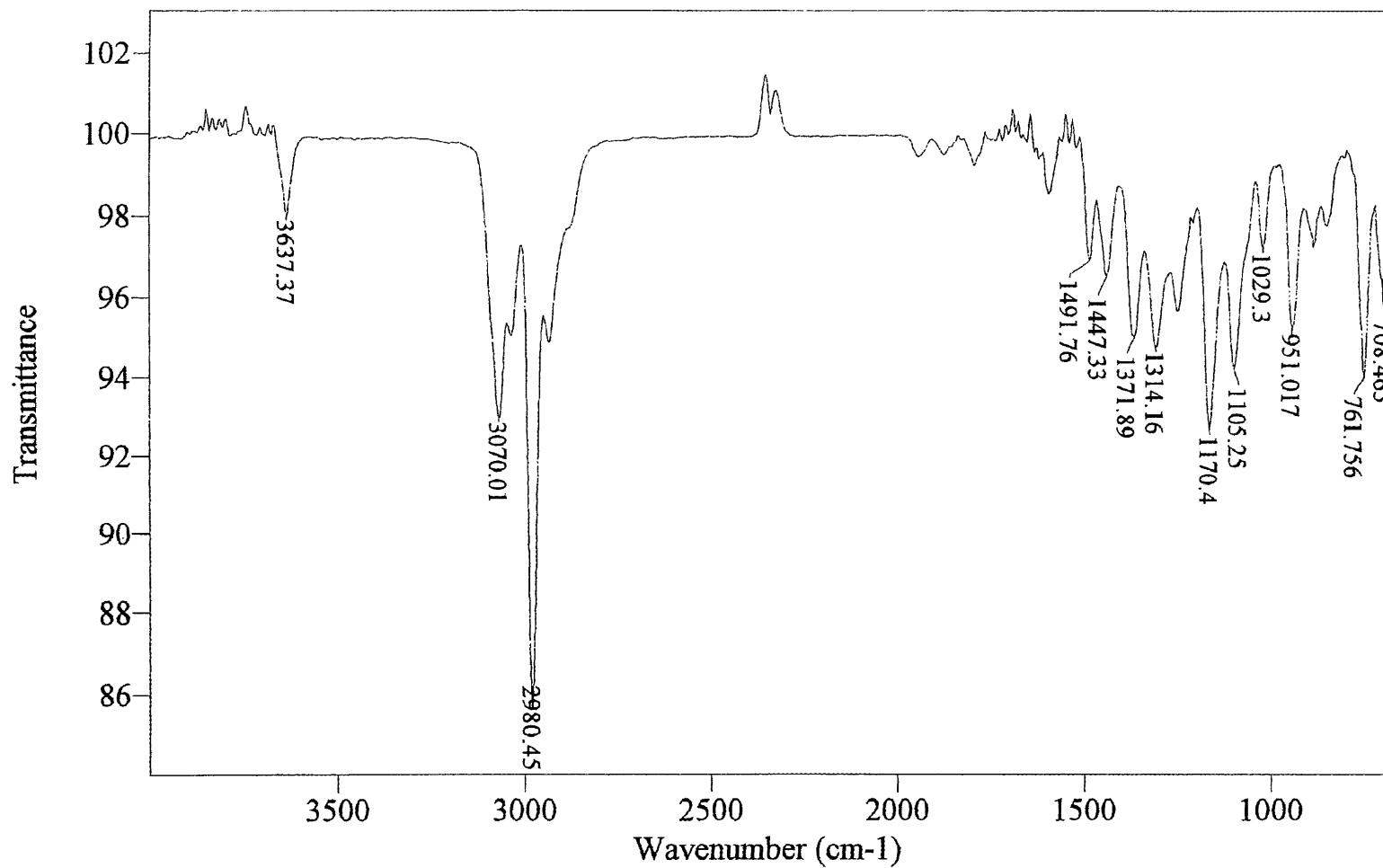


Figure 3.13 FTIR Spectrum of Standard Cumyl Alcohol

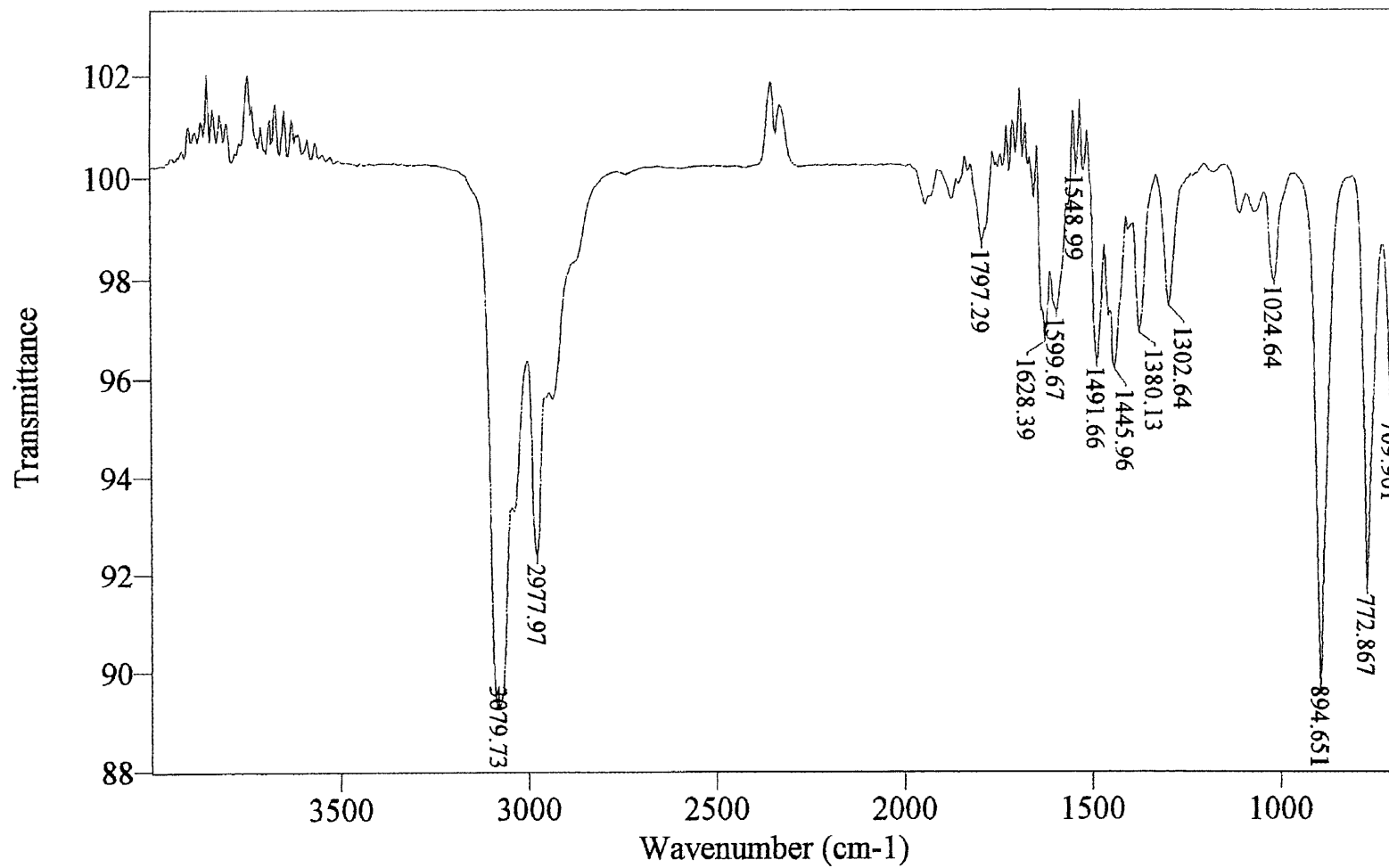


Figure 3.14 FTIR Spectrum of Standard Alpha Methyl Styrene

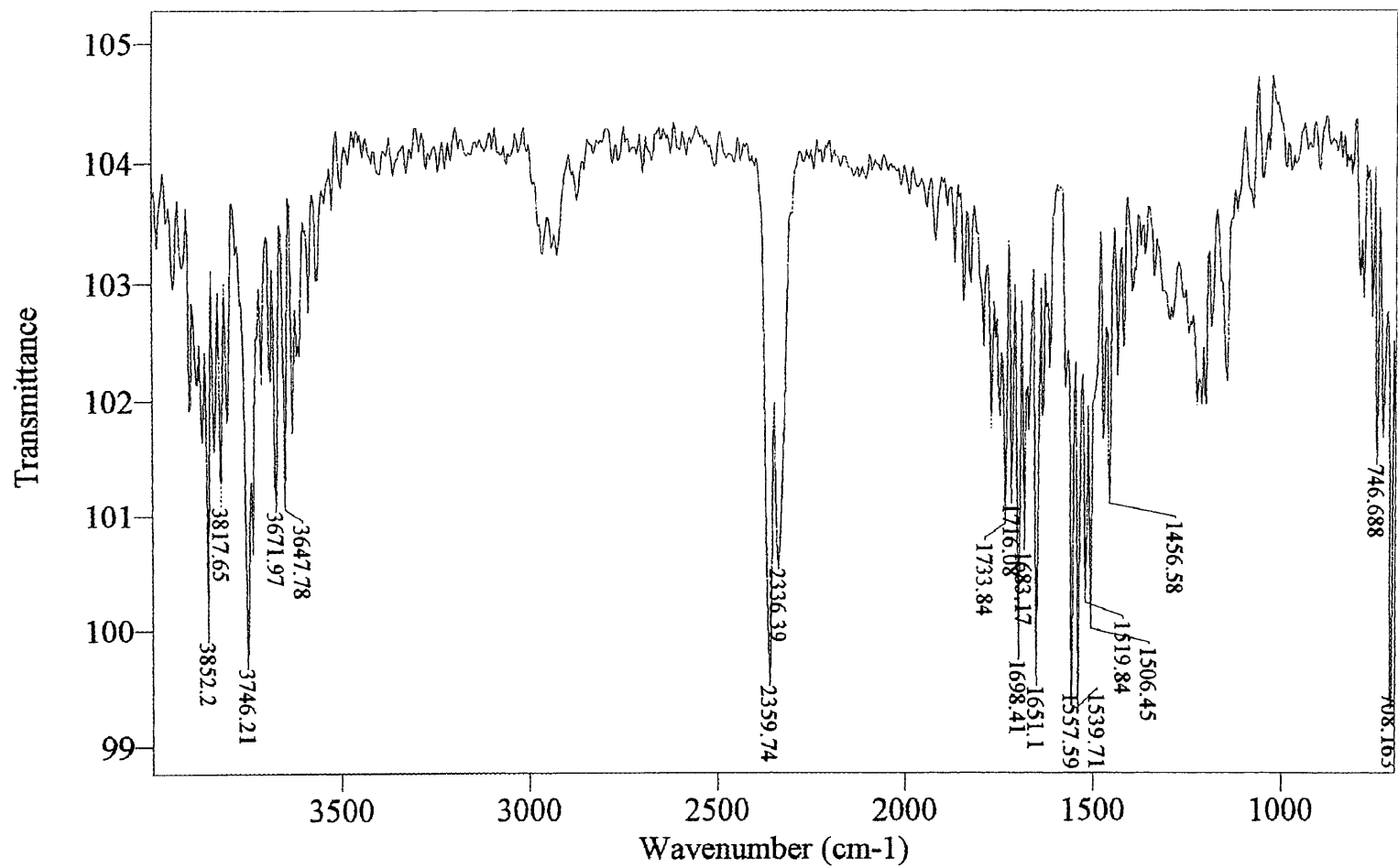


Figure 3.15 FTIR Spectrum of Standard Tert-Butyl Nitrite

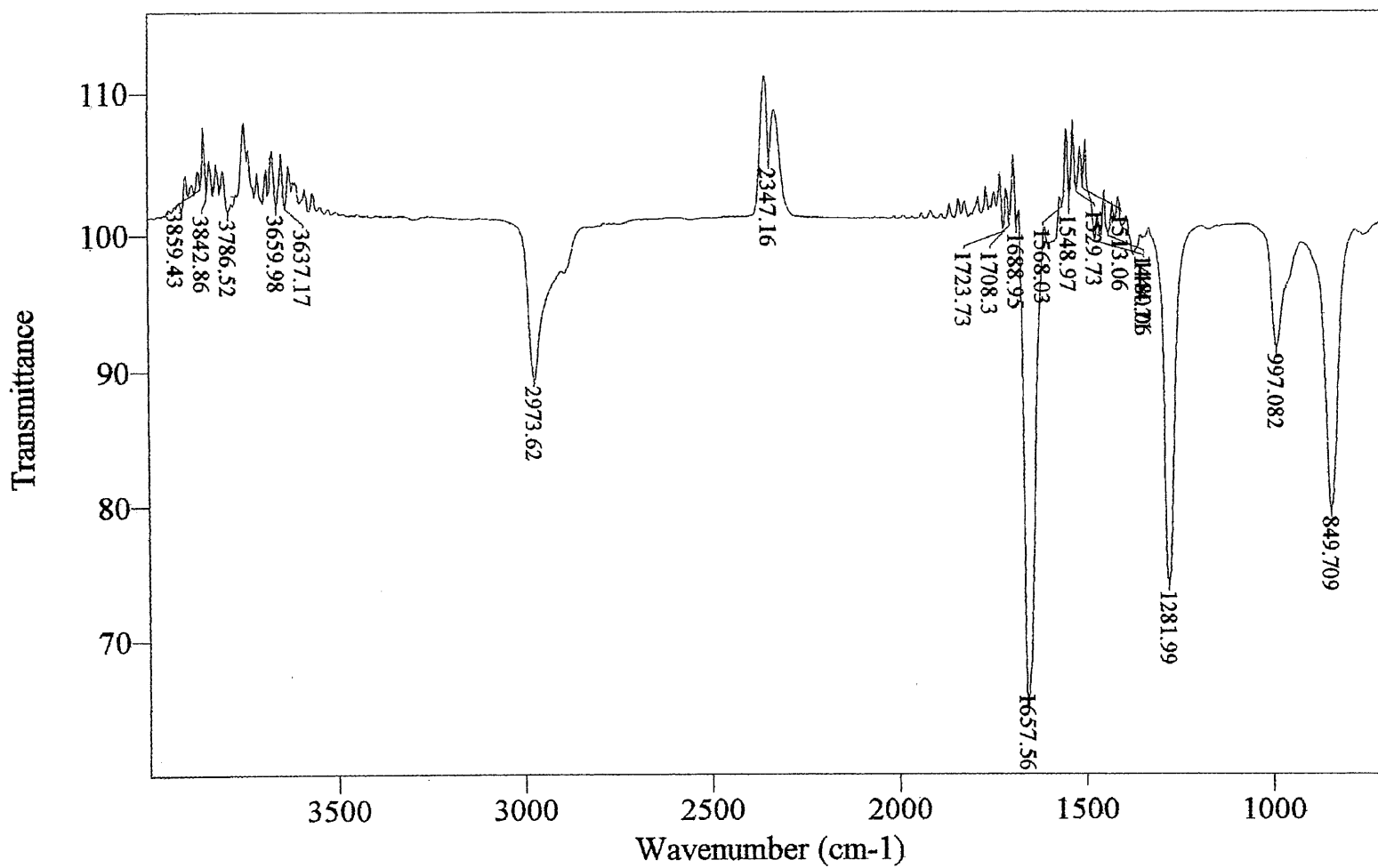


Figure 3.16 FTIR Spectrum of Standard Isobutyl Nitrate

CHAPTER 4

RESULTS AND DISCUSSION

Aqueous scrubbing solutions of sodium chlorite (NaClO_2) and alkaline aqueous cumene hydroperoxide (CHP) solutions were tested as oxidizing agents to oxidize and absorb NO. Experiments were performed in a semi-continuous bubbling scrubber under simulated flue gas compositions to study the effect of each parameter on the oxidation and absorption of NO. The experiments were performed at different pH's, concentrations of scrubbing solutions, gas flow rates (residence time), temperatures, and alkaline compounds.

4.1 NO Absorption into Sodium Chlorite Solutions

The previous work by Yang (1990) has shown that NO can be quantitatively absorbed in aqueous media provided a strong oxidizing agent of sodium chlorite (NaClO_2). This study has taken advantage of Yang's findings to develop a system which is capable of controlling both criteria pollutants, NO and SO_2 .

4.1.1 Effect of pH on the Absorption of NO and SO_2 into NaClO_2 Solutions

A number of experiments were performed in the 5.1 cm bubble scrubber to evaluate the effect of pH on the ability of sodium chlorite to oxidize and absorb NO and SO_2 simultaneously in aqueous scrubbing. Due to the impurities of 18% Na_2CO_3 and 2% Na_2SO_4 in sodium chlorite (NaClO_2), an aqueous scrubbing solution has an initial pH of 9.3. In separate absorption experiments of NO and SO_2 in 0.0128 M NaClO_2 , 97%

removal of NO was obtained at pH between 9 to 4.5 and 99% removal of SO₂ was obtained at pH between 9 to 6. The relationship between NO oxidation and pH as a function of a reaction time is shown in Figure 4.1. The experiments for the absorption of NO were performed with a flue gas composition of 1750 ppm NO balance N₂ and 3 dm³/min of gas flow rate. For the absorption of SO₂, the experiment was conducted using 5184 ppm SO₂, balance N₂, with 1.25 dm³/min of gas flow rate and the result are shown in Figure 4.2. In both cases, the volume of liquid in the bubble column was 1.25 dm³.

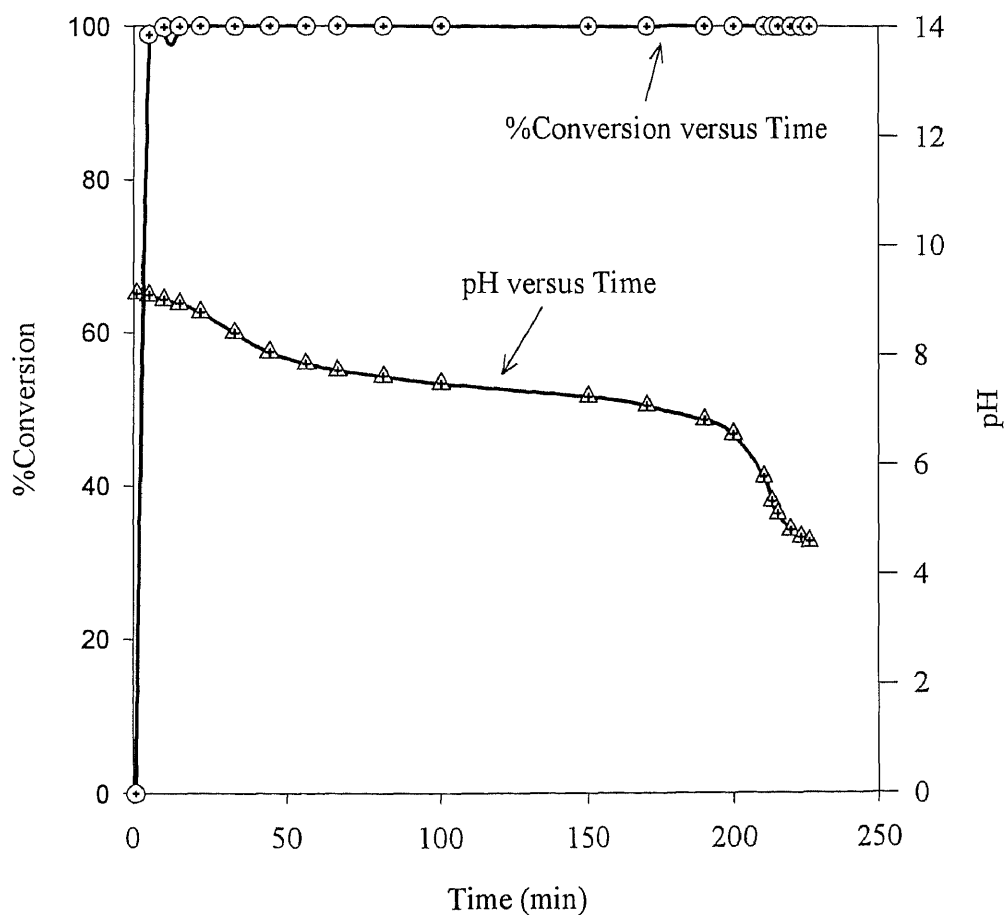


Figure 4.1 Relationship between the Conversion of NO and pH Change as a Function of Time in NaClO₂ Solution

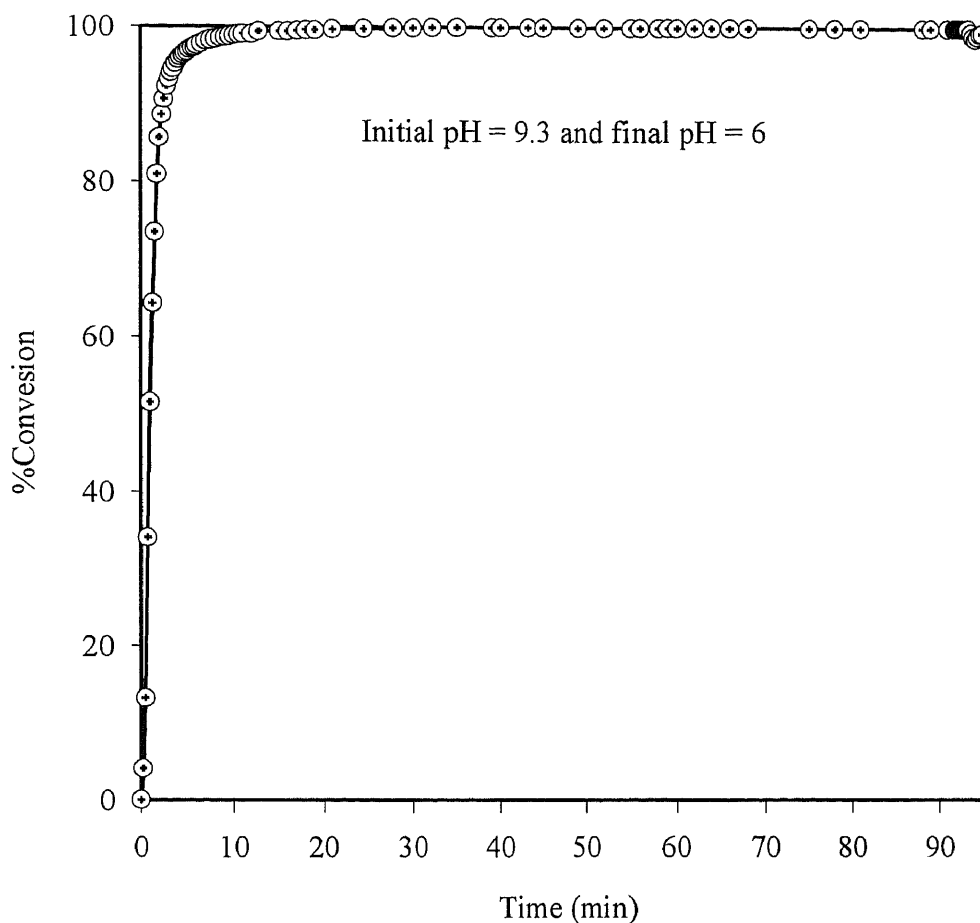


Figure 4.2 Absorption of SO_2 in NaClO_2 Solution

The result (Figure 4.1 and 4.2) indicates that NO and SO_2 are absorbed because they are oxidized by NaClO_2 to nitrate and sulfate ions, which cause a decrease in pH. A second set of experiments was conducted in the bubble column to determine the ability of NaClO_2 to simultaneously oxidize NO and SO_2 and absorb in the aqueous medium at controlled pH at 6.3 by using sodium and potassium phosphate buffer solution (Na_2HPO_4 and KH_2PO_4). Experiments were performed using flue gas compositions of 1000 ppm

NO and 491 ppm SO₂. The gas mixture was bubbled into the reservoir containing 1.25 dm³ of 0.0053 M NaClO₂ solutions at a flow rate of 5 dm³/min. Various solutions were tested such as deionized water (10 MΩ-cm), 0.001 M NaOH, 1 g and 50 g sodium and potassium phosphate buffer solutions. The experimental results are summarized in Table 4.1.

Table 4.1 Capability of NaClO₂ on the Absorption of NO and SO₂ under Various Scrubbing Media

Scrubbing Medium Containing 0.0053 M NaClO ₂	%NO Removal	%SO ₂ Removal	Initial pH	Final pH
Deionized Water (10 MΩ-cm)	74	100	9.3	2.3
0.001 M NaOH Solution	69	100	10.8	2.3
1 g Buffered Solution	72	100	6.2	2.2
10 g Buffered Solution	87	100	6.3	5.3

The experiment results summarized in Table 4.1 clearly indicates that when pH was kept between 6.3 and 5.3 by using enough buffer in the solution, both NO and SO₂ were absorbed more efficiently than unbuffered solutions. In the unbuffered scrubbing solutions, pH of the solutions drops to 2.2 because of the formation of nitrate and sulfate ions in the liquid during scrubbing. In addition, a color change was observed in the scrubbing solution without pH control. The solution color changed from colorless to greenish yellow, and then gradually became colorless again before NO breakthrough. The greenish yellow color is believed due to a formation of ClO₂ intermediate, which was identified by Yang (1990). The formation of nitrate and sulfate ions causes pH to drop, and increase the equilibrium concentration of ClO₂ [Yang 1990].

In order to oxidize and absorb both NO and SO₂ more effectively, another set of experiment was carried out at higher concentration of NaClO₂ and used larger quantities of buffer to keep pH of the scrubbing solution at 6.2. This experiment was conducted at the following conditions:

Flue gas composition: 1200 ppm NO + 4994 ppm SO₂ balance N₂

Gas flow rate: 3.09 dm³/min

Scrubbing solution: 0.0128 M NaClO₂ in 50g Na₂HPO₄ and KH₂PO₄ buffer pH 6.2

Scrubbing solution volume: 1.25 dm³

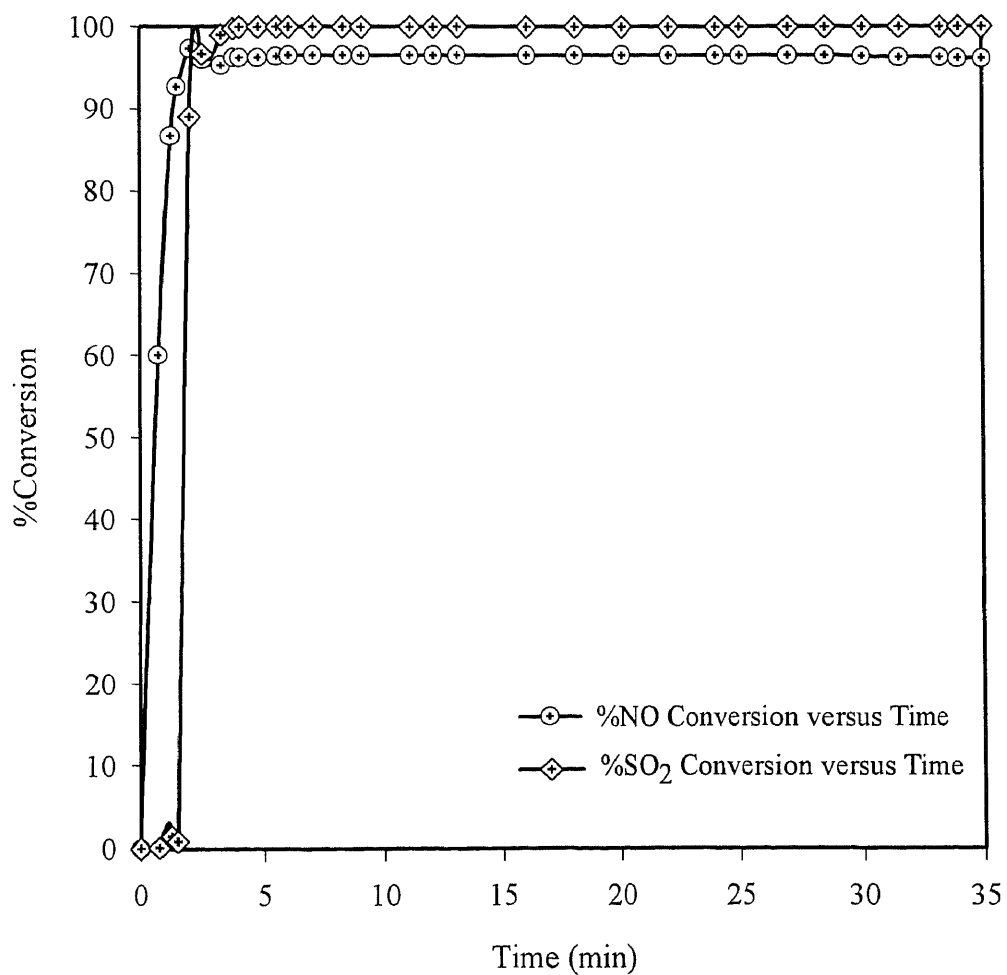


Figure 4.3 % Absorption of NO and SO₂ in 0.0128 M NaClO₂ at pH 6.2

Figure 4.3 shows that the effectiveness of NO and SO₂ absorption was improved by a well buffered scrubbing solution at pH 6.2. From the result of this experiment, SO₂ was fully absorbed and 97.5% absorption of NO was obtained. In addition, no color change was observed throughout the experiment.

4.1.2 Effect of NaClO₂ and NaOH Concentrations on NO and SO₂ Absorption in Buffer Solution pH 6.3

In order to study the concentration effect of NaClO₂ on simultaneously NO and SO₂ removal, a series of experiments were conducted with different concentrations of NaClO₂ in 50 g sodium and potassium phosphates (Na₂HPO₄ and KH₂PO₄) buffer solution with an initial pH 6.3. Experiments were conducted at the following conditions:

Flue gas compositions: 1200 ppm NO + 5000 ppm SO₂ balance N₂

Gas flow rate: 3 dm³/min

Scrubbing solutions:

- 0.00533 M NaClO₂ in 50 g sodium and potassium phosphate buffer solution with an initial pH 6.3
- 0.0128 M NaClO₂ in 50 g sodium and potassium phosphate buffer solution with an initial pH 6.3
- 0.5 M NaClO₂ in 50 g sodium and potassium phosphate buffer solution with an initial pH 6.3

The results of these experiments are tabulated in Table 4.2. The result indicates that an increase in the concentration of NaClO₂ in the buffer solution at pH 6.3 improved the

efficiency of NO absorption. But, on the other hand, the absorption of SO₂ decreased at high concentration of NaClO₂ because the scrubbing solutions became more acidic.

Table 4.2 Effect of the Concentrations of NaClO₂ on the Absorption of NO and SO₂

Concentration of NaClO ₂ (M)	%NO Conversion	%SO ₂ Conversion
0.00533	87.0	100.0
0.01280	96.3	100.0
0.50000	99.8	70.8

To improve the efficiency of the absorption of SO₂, another set of experiment was performed by introducing sodium hydroxide into the scrubbing solution under the following conditions:

Flue gas compositions: 1500 ppm NO and 5184 ppm SO₂

Gas flow rate: 4 dm³/min

Scrubbing solutions: 0.672 M NaClO₂ in buffer solution pH 6.85 and 0.1 M NaOH

0.672 M NaClO₂ in buffer solution pH 6.85 and 0.3 M NaOH

The scrubbing solutions with 0.1 and 0.3 M NaOH have an initial pH of 6.85 and 7.15, respectively. The scrubbing solution volume used was 0.5 dm³.

According to the result shown in Figure 4.4, higher conversion of SO₂ can be achieved at higher concentrations of NaOH in the scrubbing solution while NO can be absorbed effectively in both conditions.

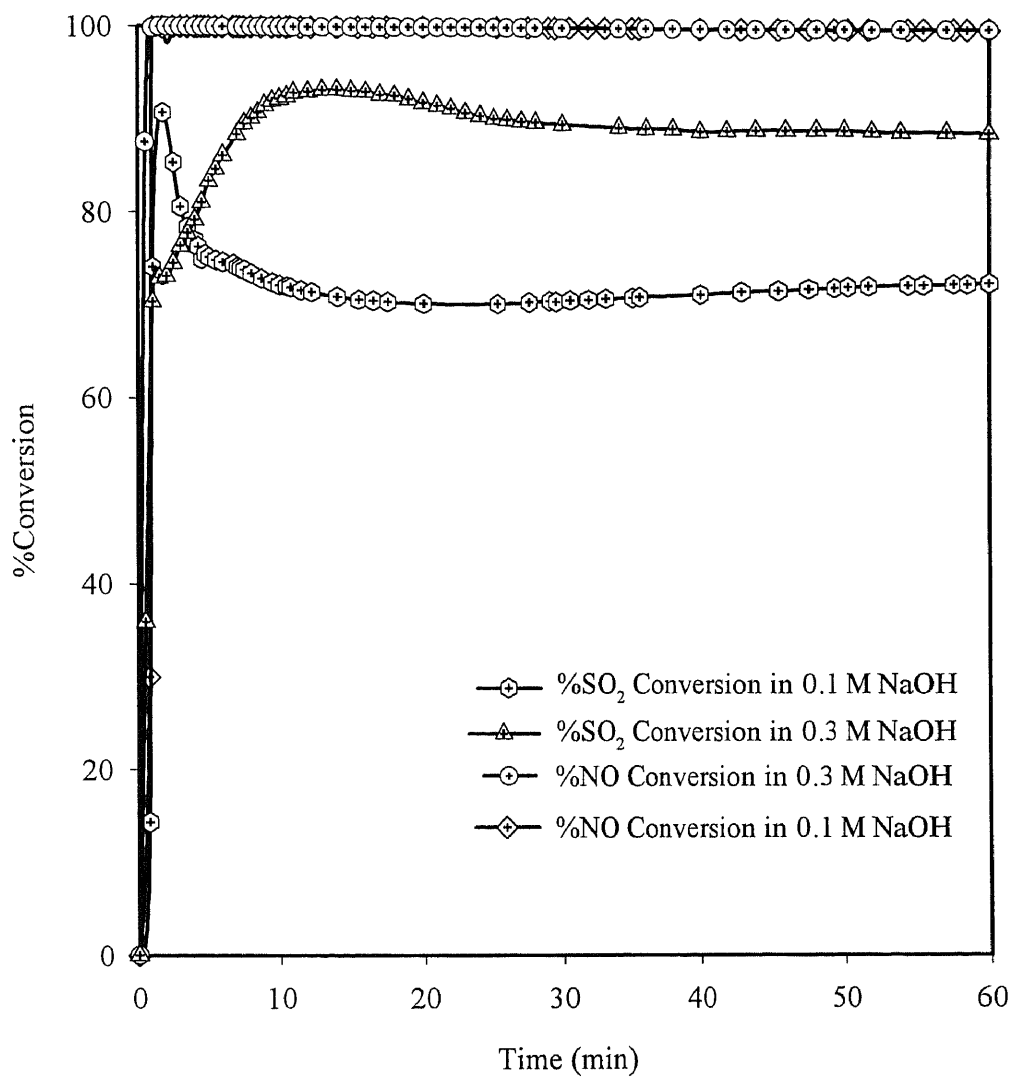


Figure 4.4 Effect of NaOH Concentrations on the Absorption of NO and SO_2 in $NaClO_2$

4.1.3 Material balance for the Oxidation and Absorption of NO and SO₂ by NaClO₂

To analyze and determine the inorganic products of the scrubbing solutions quantitatively, a liquid sample from the scrubbing solution was taken after NO breakthrough and analyzed by using ion chromatography (IC) while the NO_x and SO_x analyzers were used to determine unreacted NO and SO₂. Standard solutions of sodium nitrate (NaNO₃), sodium nitrite (NaNO₂), and sodium sulfate (Na₂SO₄), and sodium chloride (NaCl) were used for the calibration. The experiment that was performed to determine the material balance was conducted under the following conditions:

Flue gas compositions: 1450 ppm NO and 2677.5 ppm SO₂ balance N₂

Gas flow rate: 2 dm³/min

Concentration of NaClO₂: 0.016 M

Liquid volume: 1.25 dm³

The nitrogen, sulfur, and chloride throughout the experiment can be calculated from the gas flow rate, breakthrough time, and concentration change of these compounds. The nitrogen, sulfur, and chloride balances are defined as follow:

$$(N_g)_{in} = (N_g)_{out} + (N_l)_{out} \quad (4.1)$$

$$(S_g)_{in} = (S_g)_{out} + (S_l)_{out} \quad (4.2)$$

$$(ClO_2^-)_{in} = (Cl)_{out} \quad (4.3)$$

Where, (N_g)_{in} and (S_g)_{in} are total moles of NO and SO₂ that were bubbled through the scrubbing solution, (N_g)_{out} and (S_g)_{out} are total moles of NO and SO₂ that left in the effluent gas, (ClO₂⁻)_{in} are moles of chlorite initially present in the scrubbing solution, and (N_l)_{out}, (S_l)_{out}, and (Cl)_{out} are the moles of nitrate, nitrite, sulfate, and chloride

compounds in the spent scrubbing solution. The result for the material balance is shown in Tables 4.3 and 4.4.

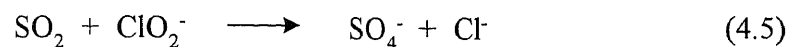
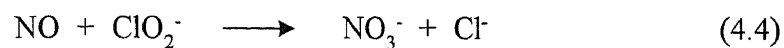
Table 4.3 Mass Balance for NO and SO₂ Oxidation by NaClO₂

Phase	Compounds	Feed to the Scrubber (moles)	Effluent from the Scrubber (moles)
<i>Gas</i>	NO	0.01216	-
<i>Gas</i>	SO ₂	0.00636	-
<i>Gas</i>	NO ₂	-	0.00044
<i>Liquid</i>	NO ₂ ⁻	-	0.00089
<i>Liquid</i>	NO ₃ ⁻	-	0.01127
<i>Liquid</i>	SO ₄ ²⁻	0.00032	0.00946
<i>Liquid</i>	ClO ₂ ⁻	0.02	-
<i>Liquid</i>	Cl ⁻	-	0.02077

Table 4.4 Material Balance for NO and SO₂ Oxidation by NaClO₂

Material Balance	Percent (%)
Nitrogen	103.62
Sulfur	141.62
Chlorine	103.85
Oxygen	112.32

The result tabulated in Table 4.3 indicates that out of 0.01216 moles NO oxidized, 0.00044 moles of NO₂ were discharged in the gas and 0.00089 moles of NO₂⁻ and 0.01127 moles of NO₃⁻ in the scrubbing solution. Thus, 0.01216 moles entered the system and 0.0126 moles left the system for slight excess (3.6%) in the effluent. All of SO₂ was oxidized to SO₄²⁻ in the scrubbing solution.



From the balance, more sulfate ion in the solution was obtained than it was input as SO_2 . This result indicates that the feed gas mixing process, which depends on mass flow meter, was not working properly. Based on the material balance considerations, it appears that the actual amount of SO_2 that was fed to the bubbler was 0.00914 moles rather than 0.00636 moles. In addition, the scrubbing agent of NaClO_2 was completely converted to chloride. The chromatogram, obtained from the product analysis of the scrubbing solution, is shown in Figure 4.5.

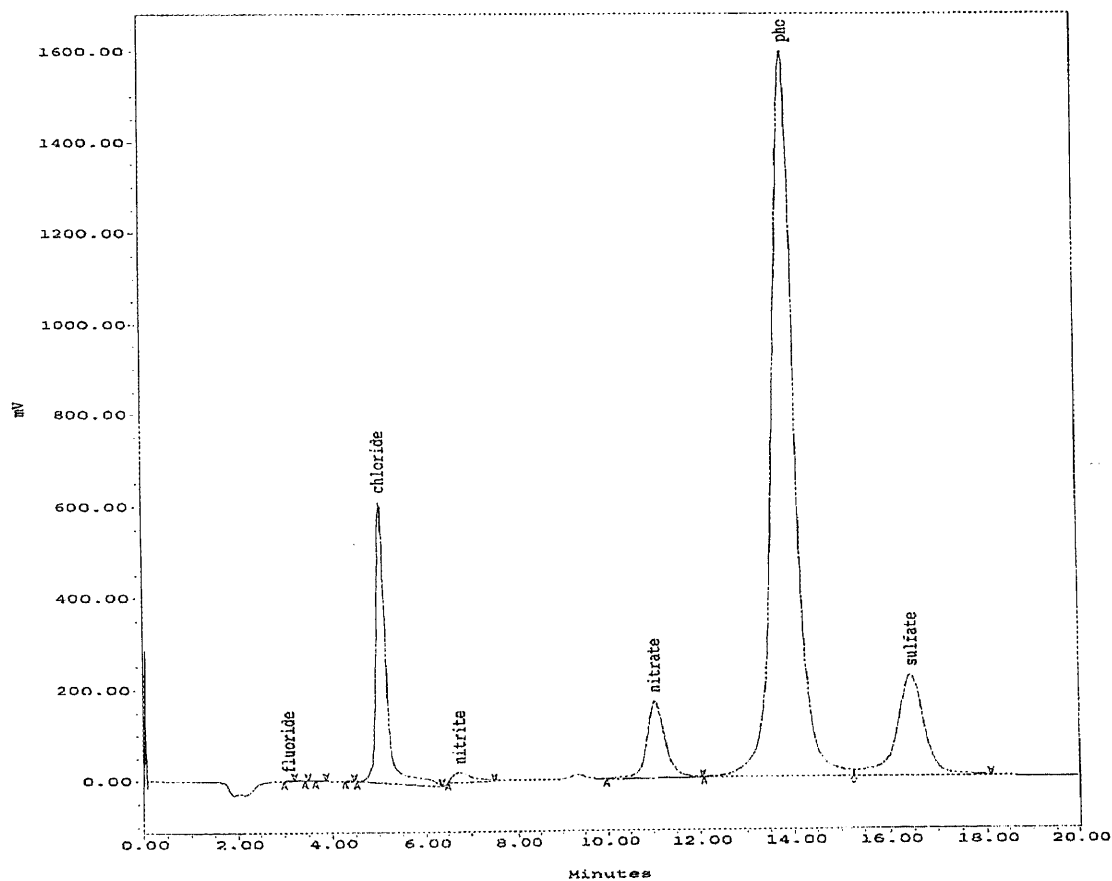


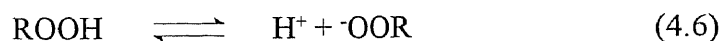
Figure 4.5 IC Chromatogram of the Spent Scrubbing Solution of Sodium Chlorite

4.2 NO Absorption into Alkaline Aqueous Cumene Hydroperoxide Solutions

The alkaline aqueous cumene hydroperoxide (CHP), which shows promise of being less expensive than the inorganic scrubbing solution of NaClO_2 , was developed to study the feasibility of this compound as an oxidizing agent to promote the absorption of NO. A number of alkaline aqueous scrubbing solutions of CHP were evaluated in a semi-continuous bubble column to obtain the optimum conditions for NO removal. The effect of operating parameters such as concentrations of base and CHP, temperature, gas residence time, and alkaline compounds was investigated.

4.2.1 Effect of Cumene Hydroperoxide and KOH Concentrations on NO Removal

As opposed to NaClO_2 inorganic scrubbing solution which operated under acidic conditions, the organic CHP is being developed to operate under alkaline conditions in order to improve the likelihood of absorbing SO_2 without consuming the oxidant. Hydroperoxides are stronger acids than alcohols and form salts in aqueous alkaline solution such as sodium hydroxide and potassium hydroxide. The acid strength, pK_a (27°C), of CHP in aqueous solution determined from the dissociation constants in the presence of a strong base is 12.6 (Davies 1961 and Swern 1971). As a result, CHP is sufficiently acidic that it can be dissolved in alkaline aqueous solutions.



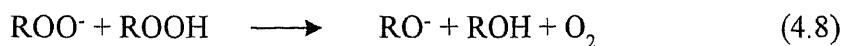
In order to study the solubility and stability of CHP in alkaline solutions and feasibility of alkaline aqueous CHP in NO removal, various concentrations of potassium hydroxide (KOH) were used to prepare the potassium salt of CHP. Equal amounts of 50.4-cm^3 CHP, which had a concentration of approximately 0.3 M, were dissolved in 0.75, 0.1, 0.08,

0.05, and 0.02 M KOH. After mixing two compounds, a homogeneous solution was obtained in 0.75 M KOH while the solutions prepared from lower concentrations of KOH formed a two-phase system. The majority of the solutions remained clear, but a small layer of precipitate formed at the bottom of the solution after settling in a separatory funnel. The precipitate was removed and the concentration of CHP in the alkaline aqueous solutions was analyzed by iodometry. The results are summarized in Table 4.5.

Table 4.5 Effect of KOH Concentrations on the Solubility and Stability of CHP

Initial CHP Concentration (M)	KOH Concentration (M)	CHP Concentration in the Light Phase (M)	pH
0.3	0.75	0.29830	13.17
0.3	0.10	0.13152	12.33
0.3	0.08	0.11899	12.20
0.3	0.05	0.10960	12.00
0.3	0.02	0.08768	11.56

The decrease in the concentration of CHP in the light aqueous phase can be explained by postulating that a deficiency of alkali results in the elimination of oxygen and formation of the corresponding alcohol. In addition, some CHP was also found in the precipitate that analyzed by iodometry. Equations 4.7 and 4.8 show the decomposition of CHP as predicted by Tobolsky and Mesrobian (1954). However, the decomposition is slow in the presence of concentrated and excess alkali.



In addition, thermal decomposition of CHP also involved the generation of free radicals from O-O bond scission (equation 4.9) postulated by Swern (1971). The thermal stability of the alkaline aqueous CHP solutions when heated to a temperature of 90°C for 2 hours was determined. The concentrations of CHP after heating to the desired temperature were tabulated in Table 4.6.

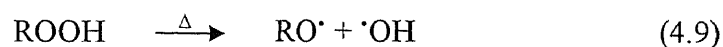


Table 4.6 Thermal Stability of Cumene Hydroperoxide at 90°C

KOH Concentration (M)	CHP Concentration at Room Temperature (M)	CHP Concentration after Heating to 90°C (M)
0.10	0.13152	0.11586
0.08	0.11899	0.11273
0.05	0.10960	0.10647
0.02	0.08768	0.08450

The experiments on the ability of alkaline aqueous CHP solutions to absorb NO were performed using 900 cm³ of aqueous scrubbing (light phase) solutions obtained from the above results (Table 4.5) except for the 0.75 M KOH solution. The scrubbing solutions were heated to a temperature of 90°C. The experiments were performed with flue gas containing 1050 ppm NO and the balance is N₂ at a flow rate of 1 dm³/min. The experimental results are summarized in Figure 4.6.

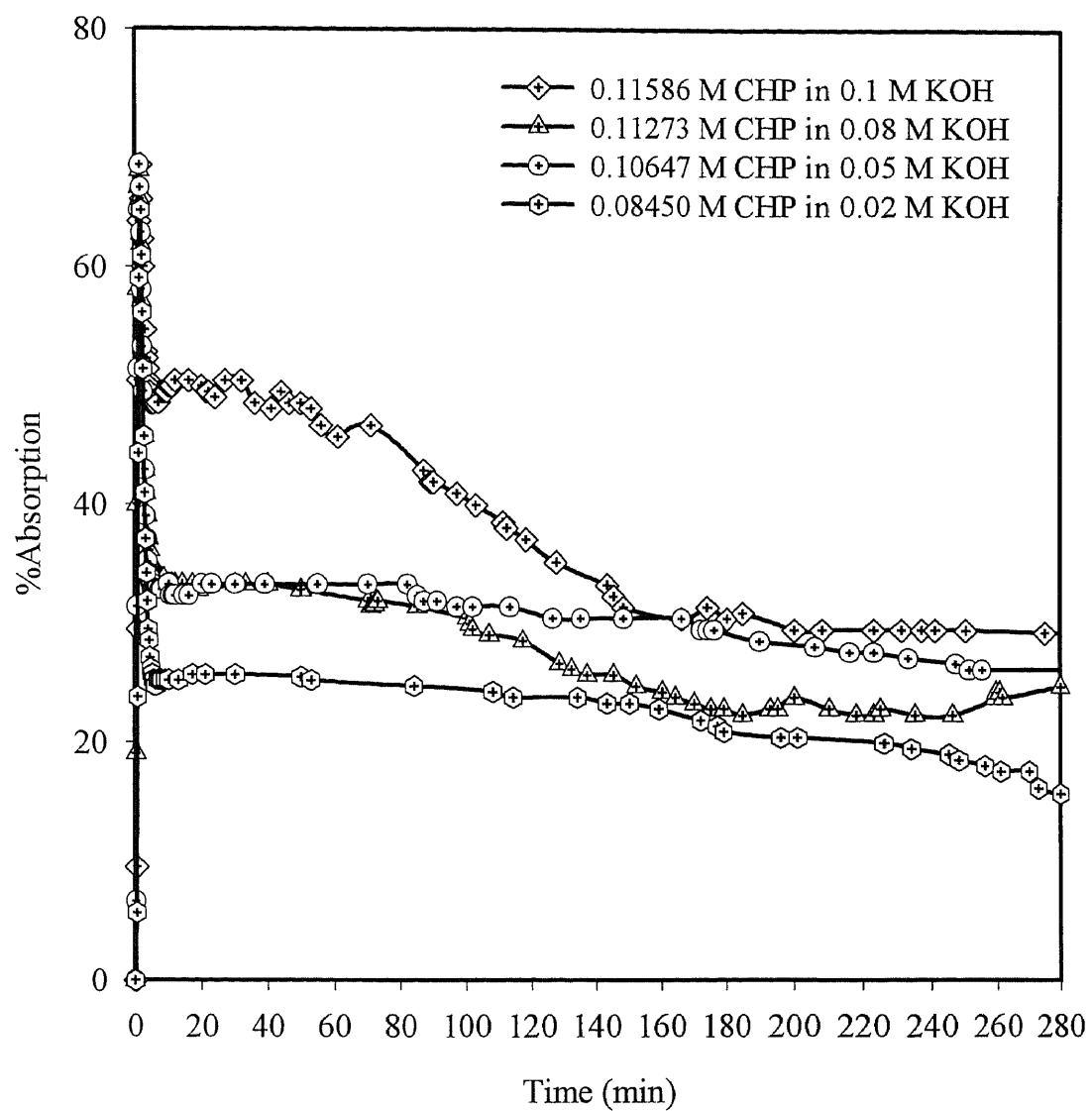


Figure 4.6 Effect of CHP and Alkali Concentrations on NO Removal

The result (Figure 4.6) indicates that better NO removal was obtained at higher concentrations of alkali and CHP due to the greater stability of CHP salt when a full equivalent of alkali was used (Tobolsky and Mesrobian, 1954 and Kharasch *et al.*, 1952). An increase in conversion in the first 2 minutes (Figure 4.6) is due to the dilution effect of gas left in the headspace of the column and tubing. Therefore, the reading of NO from NO_x analyzer was less than the actual concentrations of NO that was fed to the reactor.

4.2.2 Effect of Residence Time on NO Removal

A number of experiments were carried out to test the oxidation of NO in 1.2 M CHP and 0.1 M KOH (pH 12.4) as a function of gas residence time (flow rates). These experiments were performed with 1025 ppm NO balance N₂ and the temperature of the scrubbing solutions were kept at 90°C. The gas residence time used in these experiments were 0.63, 0.95, and 1.53 minutes.

The results shown in Figure 4.7 indicate that higher residence time or lower gas flow rates improve the oxidation of NO. The % conversions of NO obtained at the residence time of 0.63, 0.95, and 1.53 minutes were 15, 27, and 48% respectively.

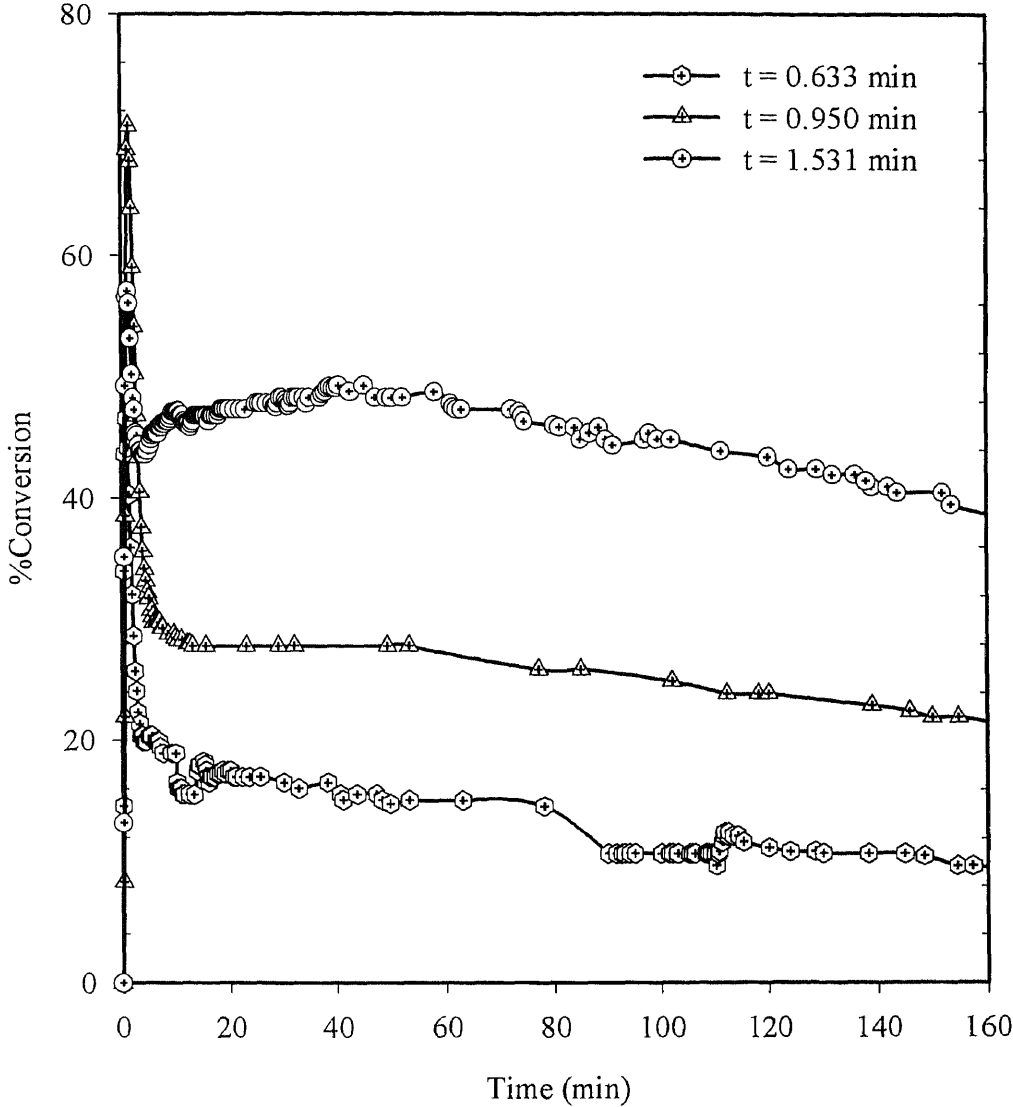


Figure 4.7 Effect of Residence Time on NO Removal

4.2.3 Effect of Temperature on NO Removal

Experiments were conducted to determine the effect of temperature on NO oxidation under operating conditions of 0.12 M CHP, 0.1 M KOH (pH 12.4), and 1.53-min residence time. The volume of the scrubbing solutions was kept at 1.439 dm³ with the gas flow rate of 0.94 dm³/min. The flue gas compositions used were 1030 ppm NO balance N₂. The different temperatures were evaluated over the range of 80 to 94°C.

The experimental conversion-time curves at different operating temperatures are shown in Figure 4.8. From the experimental results it was found that the high conversion of NO up to 90% could be obtained when operating at elevated temperature (94°C) and residence time (1.53 min). An increase in operating temperatures from 90 to 94°C significantly increased the conversion of NO from 50 to 92% while only 28% conversion of NO was obtained at temperature of 80°C. A drop in NO conversion in first 60-min was observed when operated at 94°C and then the conversion started increasing again. This phenomenon can be explained by postulating that as the reaction of CHP (A) and NO (B) proceeded, products (C) that was being formed may affect the oxidation of NO at a certain time when CHP (A) and products (C) were in equilibrium. The concentration changes of CHP-conversion-time curves at 94°C are plotted in Figure 4.9.

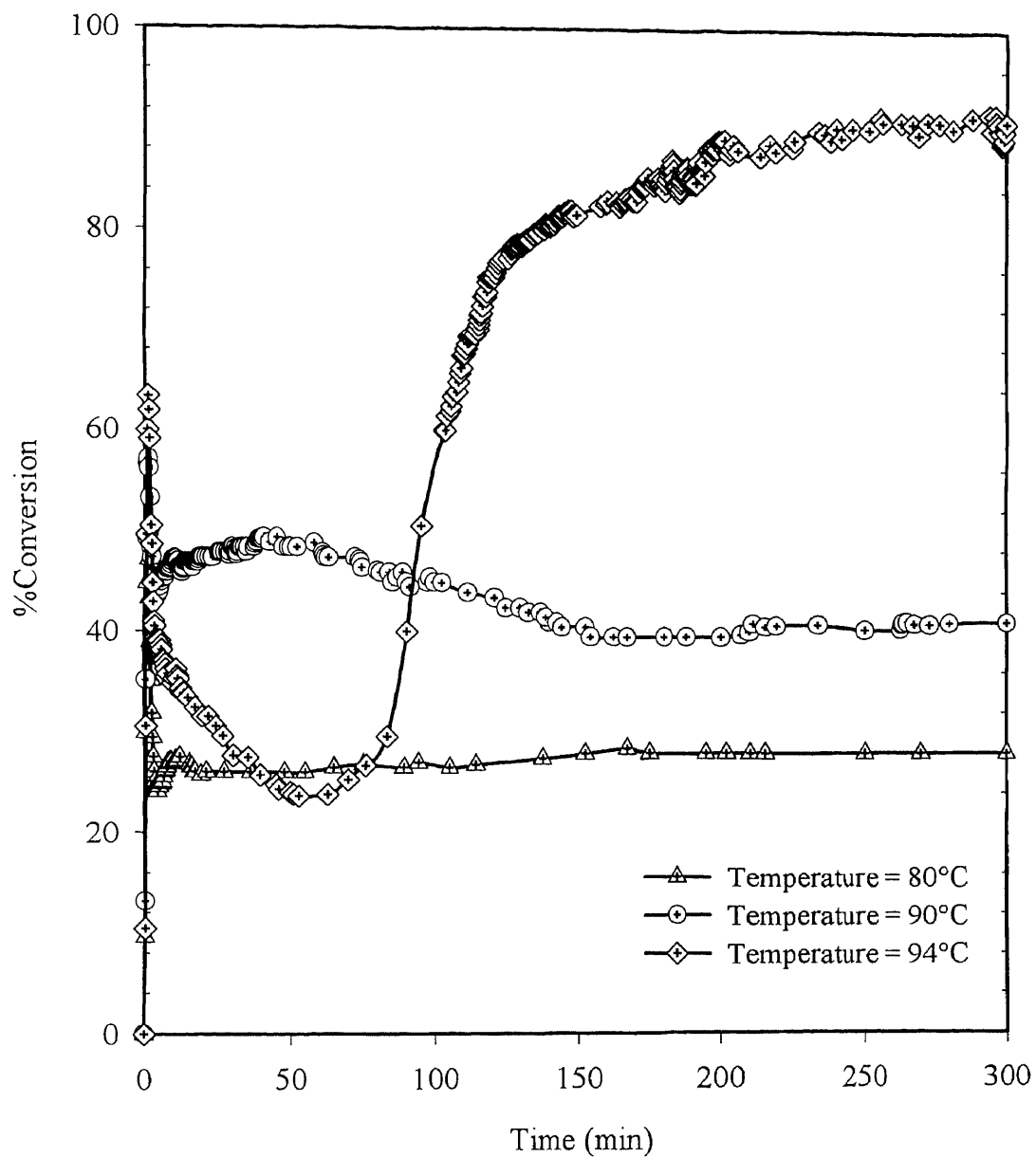


Figure 4.8 Effect of Temperature on NO Removal

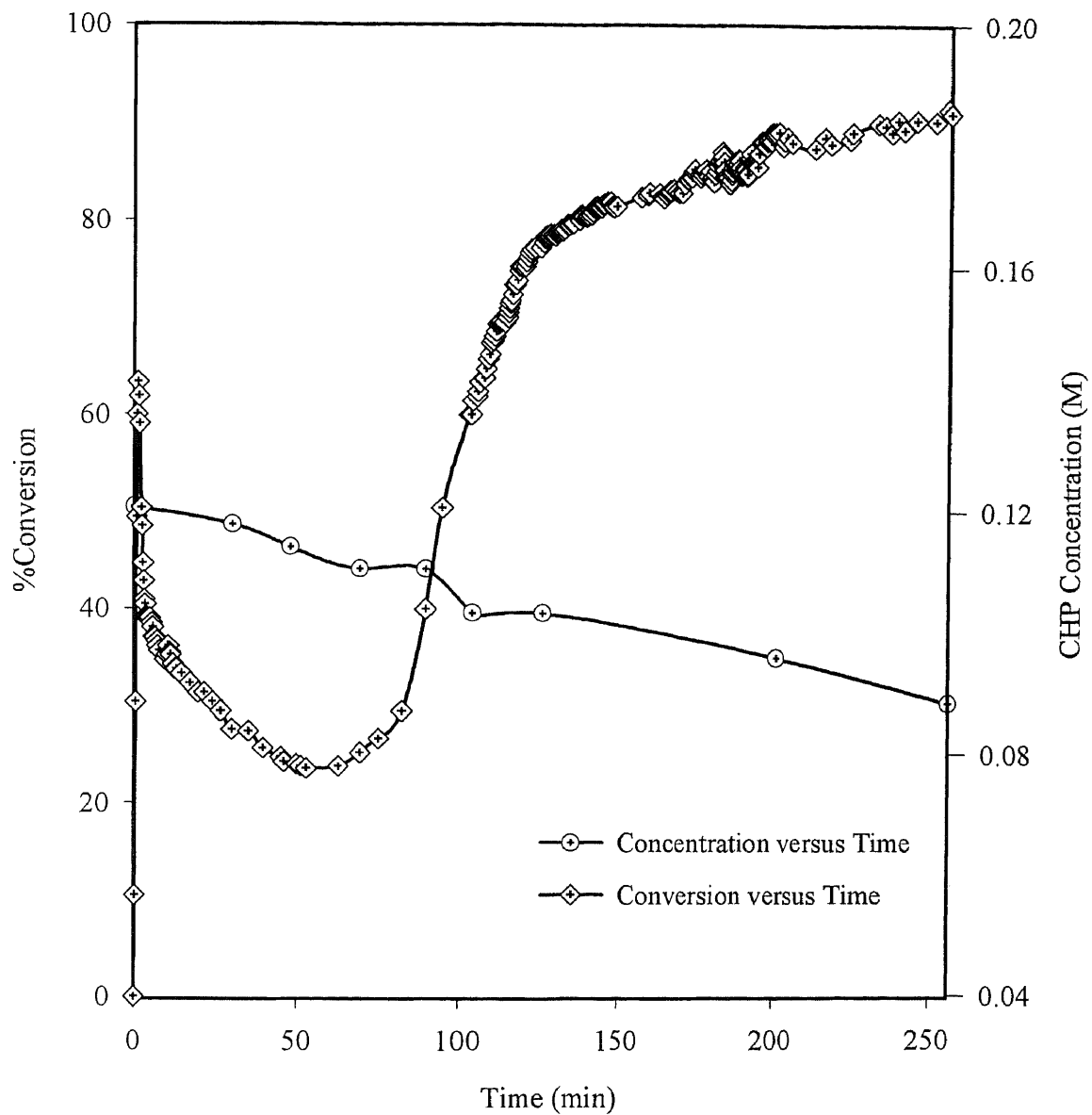


Figure 4.9 Relationship between Conversion of NO and Concentration Change of CHP at 94°C

4.2.4 Effect of Base Compounds on NO Removal

To study the effect of alkali on NO removal, different alkali, KOH, NaOH, and CaO, were used as a medium to prepare aqueous solutions of CHP. The CHP salts of potassium and sodium were prepared in the same manner as was described previously whereas the salt of calcium was used without removing the precipitates. The alkali concentrations of KOH, NaOH, and CaO used in the experiments were 0.1 M. CHP concentrations used were 0.125M. The experiments were performed at 94°C and 1.531 min residence time with 1040 ppm NO balance N₂ in the alkaline solutions of KOH and NaOH, whereas the temperature of the solution with CaO was set at 90°C.

The experimental results for KOH and NaOH are shown in Figure 4.10. It was found that 92% conversion of NO was obtained in both alkali but the faster NO oxidation rate was obtained in the presence of KOH. This can be reasonably explained by the assumption that NaOH is dissolved much more slowly than KOH because of the smaller cation radius of sodium compounds (Lyavinets, *et al.*, 1993). On the other hand, less than 13% conversion of NO was obtained for the CHP salt prepared using calcium oxide.

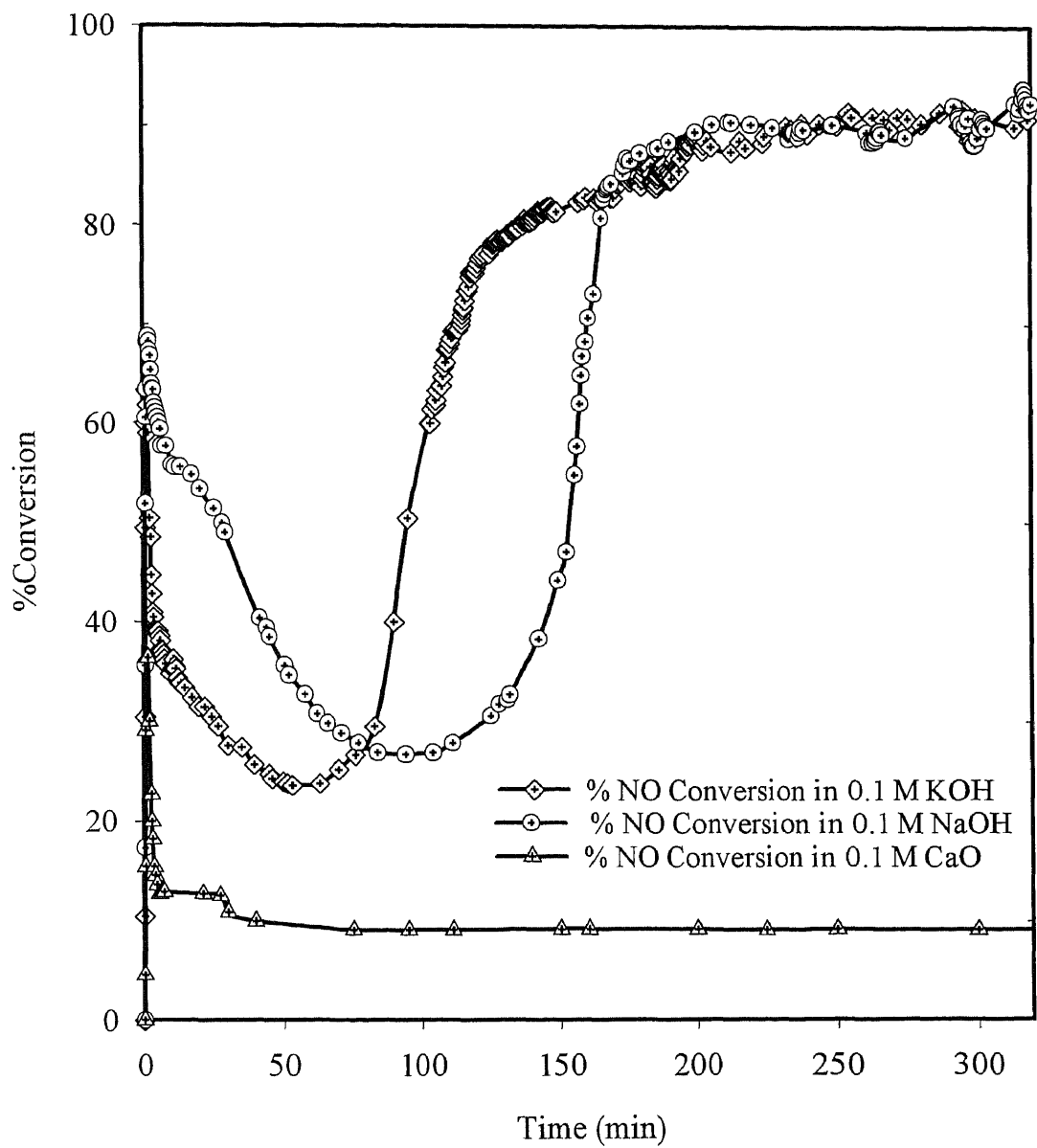


Figure 4.10 Effect of Base Compounds on NO Removal

4.2.5 Products Analysis and Material Balance

All reactants and products from the reaction were determined qualitatively and quantitatively to complete the material balance that accounts for nitrogen and carbon balances. The nitrogen balance will equate nitrogen from the NO input with nitrates and nitrites in the scrubbing solution. The organic reactant and products including CHP, cumyl alcohol, α -methyl styrene, acetophenone, organic nitrates and nitrites were determined to obtain the carbon balances.

Ion chromatography (IC) was employed to analyze all inorganic nitrates and nitrites quantitatively and qualitatively in the spent scrubbing solution while the NO_x analyzer was used to determine unreacted NO. The IC calibrations and chromatograms of nitrate and nitrite solution are shown in Figures 3.2 to 3.5. To analyze all organic products, iodometric titration was used to quantitatively analyze unreacted CHP in the spent solution, whereas GC-FTIR was used to analyze all possible organic products mentioned above. The gas chromatograph (GC) was equipped with FTIR via the transfer line and FTIR light pipe so the analysis could be made at the same time. The gas chromatograph was used to quantitatively determine the concentration of the organic products based on calibrations of all standard solutions (as shown in Figures 3.6 to 3.10). FTIR was useful for product identification by comparing the products' spectra to the spectra derived from the standard solutions (as shown in Figures 3.11 to 3.15).

The material balance was performed at the optimum scrubbing conditions determined from the above results. The following conditions were used in this experiment:

Flue gas compositions: 1050 ppm NO balance N₂

Scrubbing solution: 0.12 M CHP in 0.1 M KOH (pH 12.4)

Gas flow rate: 0.94 dm³/min (0.52 dm³/min NO and 0.42 dm³/min N₂)

Liquid volume: 1.439 dm³

Temperature: 94°C

The results of nitrogen balance and carbon balance are tabulated in Tables 4.7 and 4.8. The IC chromatograms and FTIR spectra of the products in the spent scrubbing solution are shown in Figures 4.11 to 4.15. The concentrations of reaction products were measured and calculated at the reaction time of 350 min corresponding to NO breakthrough.

Table 4.7 Nitrogen Balance for NO Oxidation by Alkaline Aqueous CHP Solution

Phase	Compounds	Initial Concentrations (mole)	Final Concentrations (mole)
<i>Gas</i>	NO	8.53×10^{-3} (1050 ppm)	7.71×10^{-4} (95 ppm)
<i>Liquid</i>	Inorganic NO ₃ ⁻	-	2.44×10^{-3}
<i>Liquid</i>	Inorganic NO ₂ ⁻	-	5.31×10^{-3}
	Total	8.53×10^{-3}	8.52×10^{-3}

Table 4.8 Carbon Balance for NO Oxidation by Alkaline Aqueous CHP Solution

	Compounds	Initial Concentrations (mole)	Final Concentrations (mole)
Reactant	Cumene Hydroperoxide	0.1784	0.09583
Product	Acetophenone	-	0.05032
Product	Cumyl Alcohol	-	0.01915
Product	α-Methyl Styrene	-	0.00605
	<i>Total</i>	0.1784	0.17135

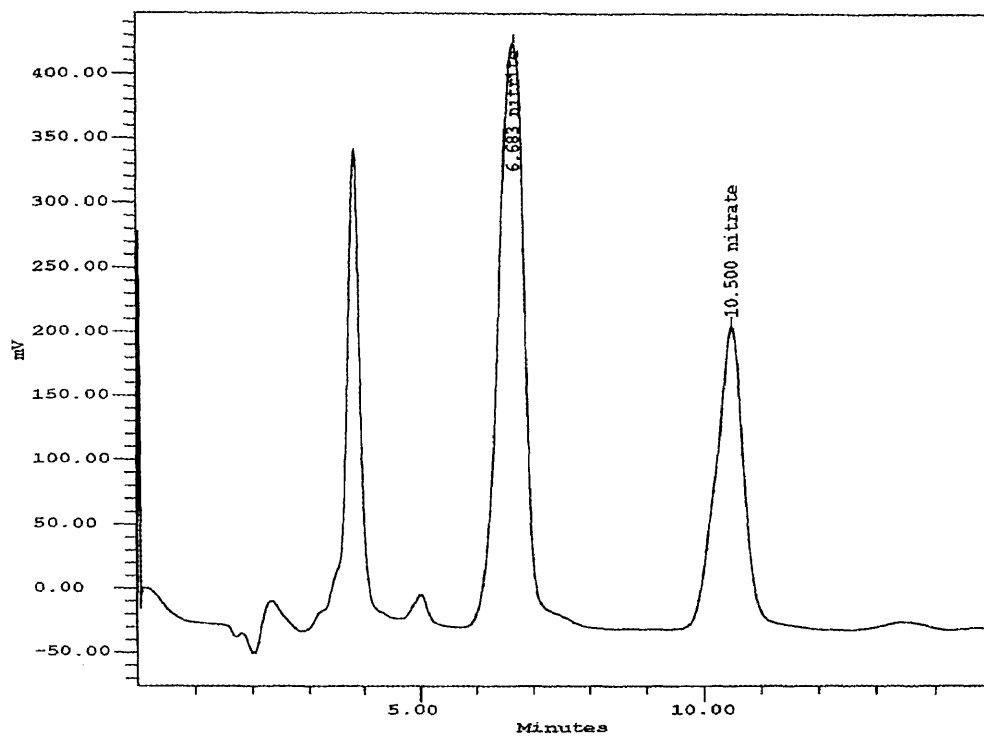


Figure 4.11 IC Chromatogram from Conductivity Detector of Spent Scrubbing Solution

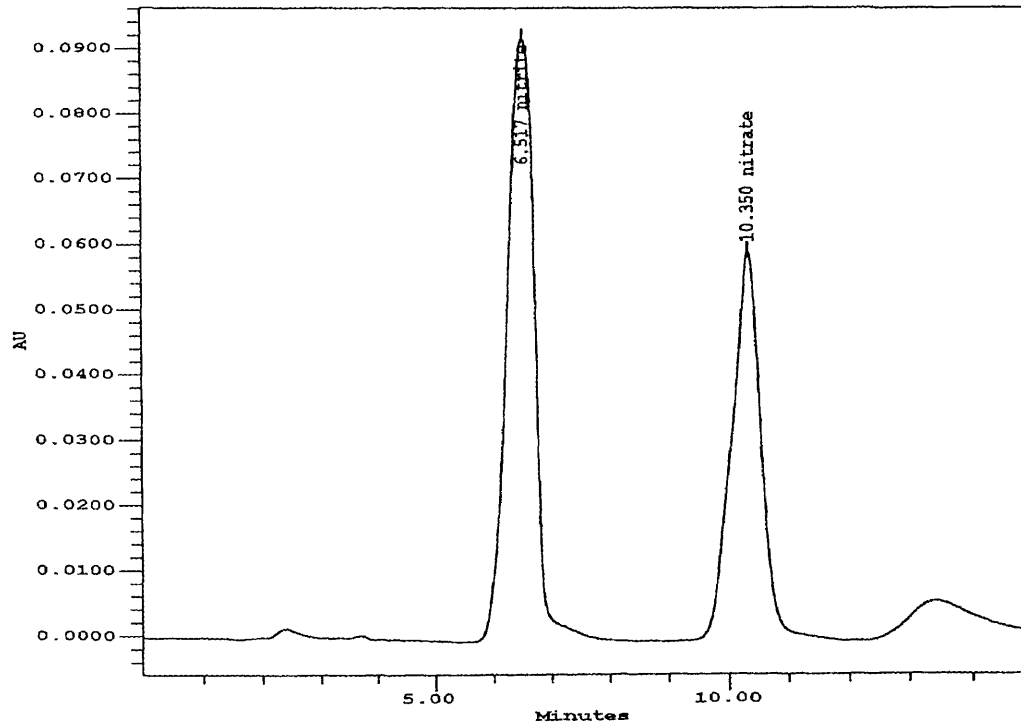


Figure 4.12 IC Chromatogram from UV Detector of Spent Scrubbing Solution

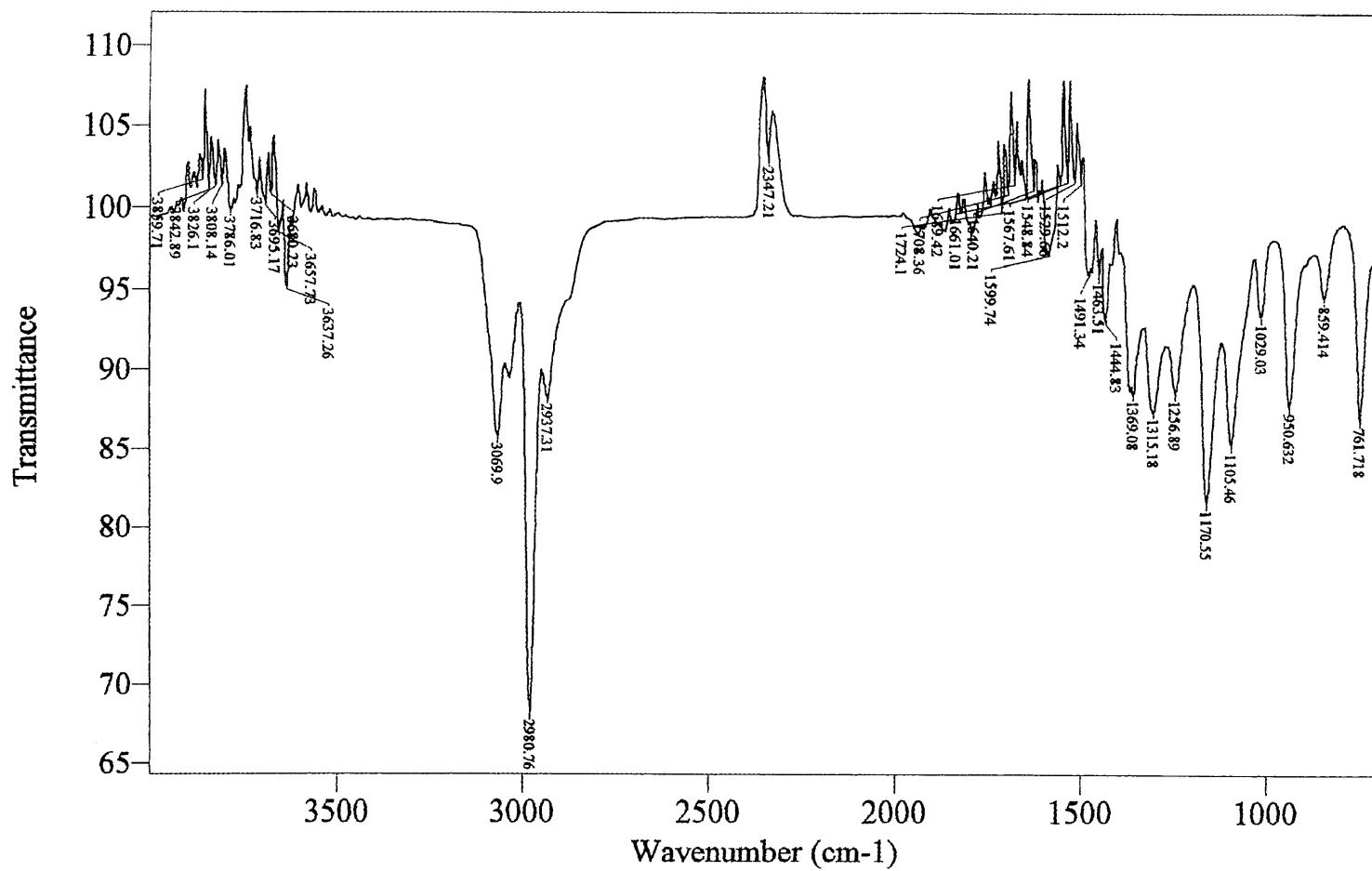


Figure 4.13 FTIR Spectrum of Cumyl Alcohol in the Spent Scrubbing Solution

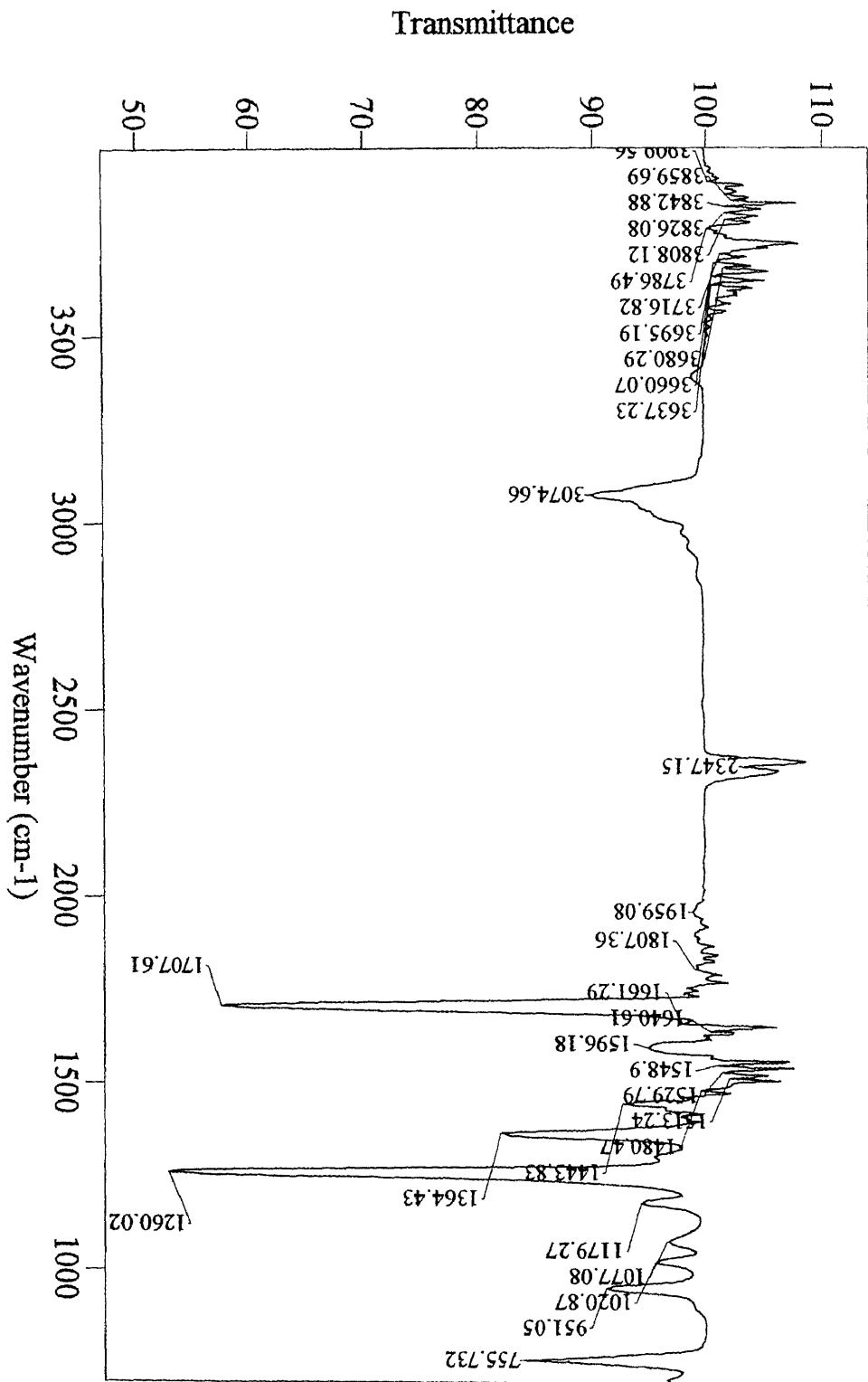


Figure 4.14 FTIR Spectrum of Acetophenone in the Spent Scrubbing Solution

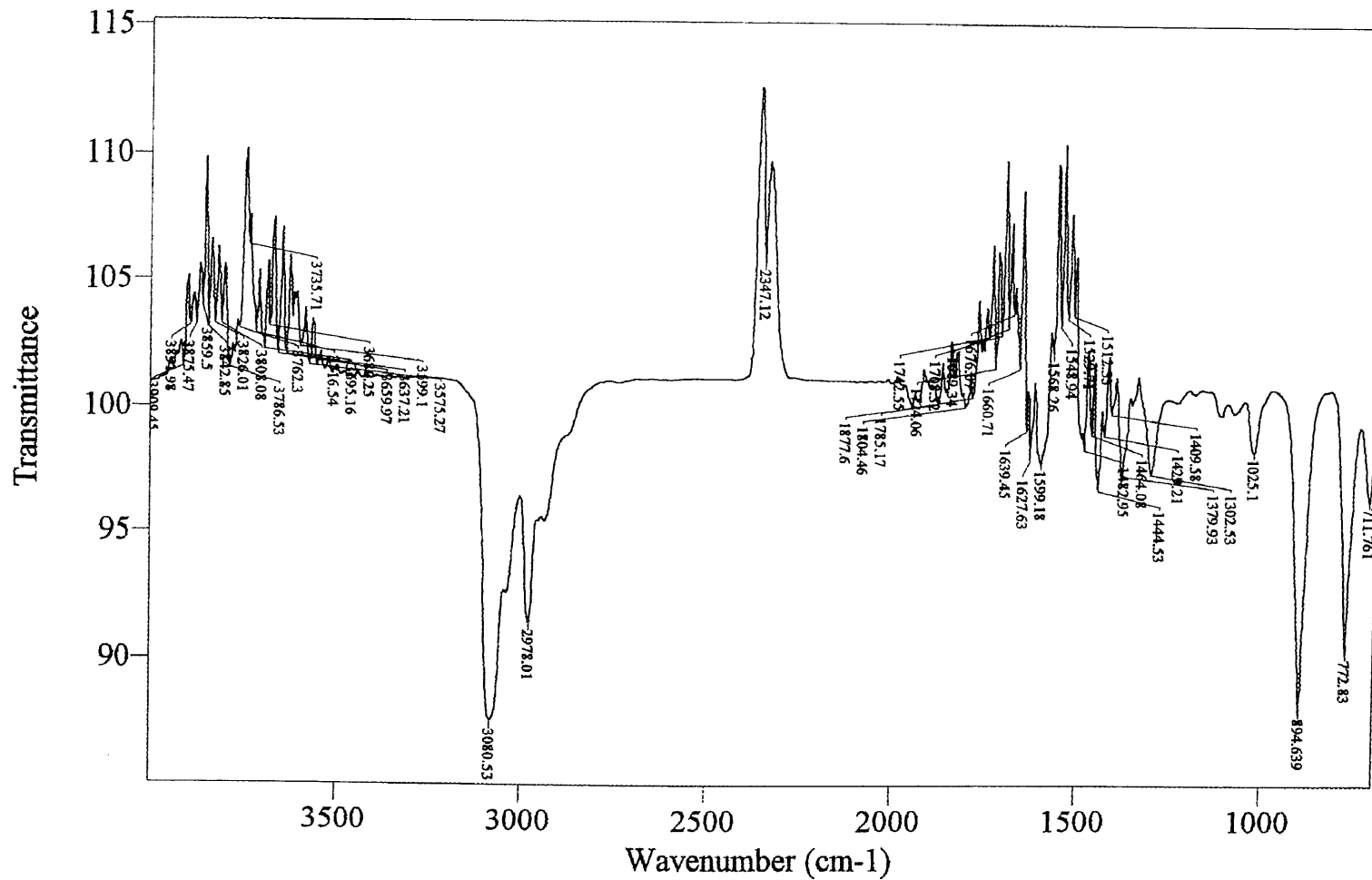
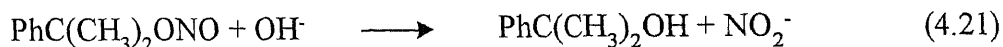
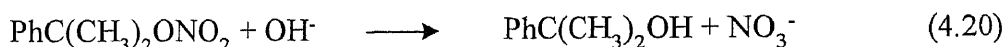
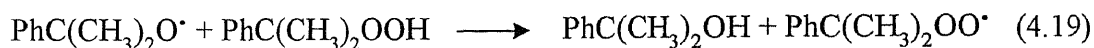
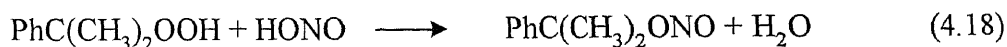
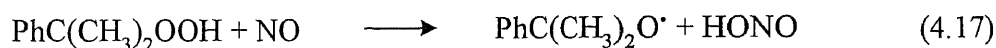
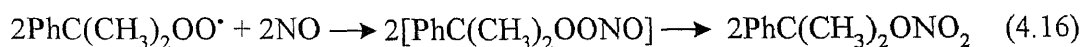
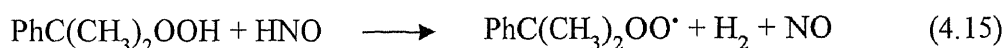
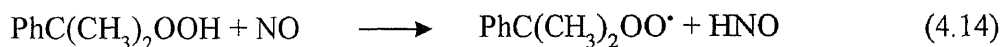
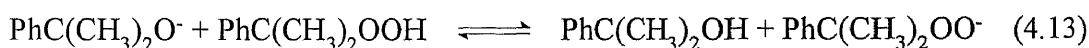
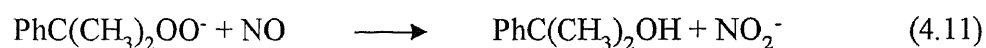
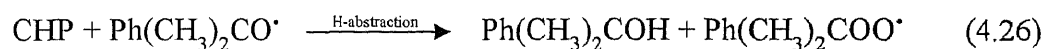
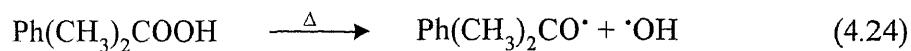
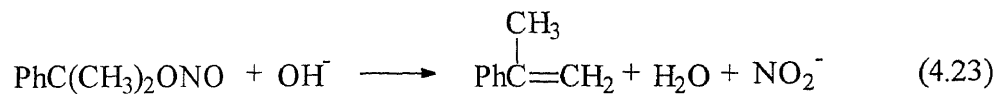
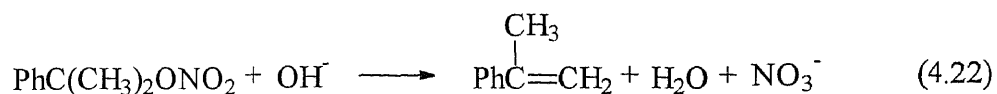


Figure 4.15 FTIR Spectrum of α -Methyl Styrene in the Spent Scrubbing Solution

According to the experimental results obtained from nitrogen and carbon balances and product identifications from IC and GC-FTIR, it was found that NO was oxidized to mostly NO_2^- which accounted for 69% of all nitrogen compounds found in the spent solution. About 31% yields of NO_3^- were also found in the spent solution. In addition, no organic nitrates and nitrites were observed in the detection of the absorption of these compounds in FTIR spectra. The organic compounds formed during the scrubbing are cumyl alcohol, acetophenone, and α -methyl styrene. These results can be explained by the following series of reactions:





The product formations can be explained as follows:

1. Reaction with NO could occur via dissociated ROO^- (Equations 4.11, 4.12, and 4.13) and/or undissociated ROOH (Equations 4.14 to 4.19) depending on the equilibrium constant, K_{eq} for Equation 4.10 and the relative rates of Equations 4.11-4.19.
2. Formation of NO_3^- and NO_2^- could occur via Equations 4.11, 4.12, 4.20-4.23.
3. Formation of cumyl alcohol, $\text{PhC}(\text{CH}_3)_2\text{OH}$ could occur via Equations 4.13, 4.19-4.21, 4.26.
4. Formation of α -methyl styrene, $\text{PhC}(\text{CH}_3)=\text{CH}_2$ could occur via Equations 4.22 and 4.23.
5. Formation of acetophenone, PhCOCH_3 could occur via Equations 4.24 and 4.25.

The formation of both NO_2^- and NO_3^- is consistent with both the NO-induced O-O cleavage of ROOH postulated by Shelton and Kopczewski (1967) (Equation 4.17) and NO-induced O-H cleavage of ROOH claimed by Carlsson, et al., (1987) (Equation 4.14). However, the relative importance of these two mechanisms, or for that matter any other one, must await results of further study of this complex reaction.

CHAPTER 5

CONCLUSIONS

A series of experiments were performed in order to evaluate the feasibility of aqueous scrubbing systems of sodium chlorite and alkaline cumene hydroperoxide to oxidize and absorb NO under the simulated flue gas compositions. The inorganic scrubbing solution sodium chlorite is capable of quantitative reaction with NO and SO₂ to stoichiometrically produce nitrates and sulfates in the well-buffered solution at pH 6. An increase in the concentrations of sodium chlorite in the buffer solution improved the efficiency of NO absorption while the absorption of SO₂ decreased because at high concentration of NaClO₂ the scrubbing solutions became more acidic. Up to 99.5% NO and 80% SO₂ are absorbed in the same scrubber at 0.672 M NaClO₂ in the buffer solution and 0.3 M NaOH. However, this scrubbing system has major drawbacks due to the toxicity of the chlorine containing compounds and the parasitic effect of SO₂ in consuming the reactant that results in a relatively high operating cost.

Alkaline aqueous cumene hydroperoxide scrubber shows promise of being relatively inexpensive. The use of aqueous cumene hydroperoxide scrubbing solution eliminates the need for an organic solvent inventory. A 92% removal of 1050 ppm NO balance N₂ was obtained at 94 °C, 1.531-min residence time, with 0.12 M cumene hydroperoxide and 0.1 M potassium hydroxide (pH 12.4). Rate of NO removal increases with residence time (low flow rate), temperature, and enough alkali. Both cumene hydroperoxide salts of sodium and potassium are effective in NO oxidation but the faster

rate of the oxidation was obtained with the use of potassium. Less than 13% conversion of NO was obtained in the cumene hydroperoxide salt prepared from calcium oxide.

The major products obtained from the oxidation of NO by alkaline cumene hydroperoxide are NO_2^- , NO_3^- and cumyl alcohol. Other products such as acetophenone and α -methyl styrene are also observed as a result from the decompositions of the reactant and intermediates. About 99.9% of nitrogen balance and 96% carbon balance were obtained in this scrubbing system.

CHAPTER 6

RECOMMENDATIONS

It is recommended that the study on the effectiveness of alkaline aqueous cumene hydroperoxide for NO oxidation be continued in the following areas:

- Study the effect of other operating conditions such as flue gas temperature and flue gas compositions of NO, O₂, CO₂, NO₂, and SO₂ in the same scrubber
- Determine the reaction mechanism between NO and cumene hydroperoxide
- Explain the broad minimum of NO conversion at 94°C before it started to increase and determine the reaction intermediates
- Improve the oxidation of NO in alkaline solution of CaO
- Determine kinetics parameters and overall mass transfer coefficients for scale-up
- Evaluate packed, spray, and ejector Venturi scrubbers for this system
- Compare the performance of cumene hydroperoxide to the other common hydroperoxide such as t-butyl hydroperoxide which is being currently investigated. Tertiary butyl hydroperoxide has lower molecular weight than cumene hydroperoxide that it will be more expensive on an equivalent mass basis but t-butyl hydroperoxide has advantageous effect on the solubility in low concentration of alkaline solution (lower pH) because it does not contain an aromatic ring.

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