A STUDY OF CARBONYL FORMATION WITHIN AN INNOVATIVE INDOOR AIR POLLUTION ABATEMENT SYSTEM

by

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(ABSTRACT)

Testing was conducted on the pre-prototype unit of an innovative indoor air pollution abatement system which used catalytic ozonation as a mechanism for oxidation and removal of organic contaminants. The system was evaluated for carbonyl production when the system was challenged with chemicals used to simulate polluted indoor air. Carbonyl compounds, which are potentially toxic partial oxidation products, were monitored using EPA Method IP-6A. The objectives of the study were to qualitatively and quantitatively determine if carbonyls were formed in the airstream when the system was operated, and if so, to determine what factors affected the concentrations of these compounds.

Trials were conducted using benzene and 2-butanol as challenge chemicals. A variety of test conditions were used to determine factors affecting carbonyl concentrations, including temperature, presence of challenge chemicals, sample location, relative humidity, presence of ozone in the airstream, and two interaction variables. No carbonyls were detected in the airstream within the air cleaning system when benzene was used as the challenge chemical. When 2-butanol was used, four carbonyls were detected at various stages of the system,

under varying conditions. The carbonyls detected during these trials were formaldehyde, acetaldehyde, acetone, and butanone. Statistical analyses of the data indicated that the pre-prototype unit of the air cleaning system caused increased levels of acetaldehyde and butanone, and possibly formaldehyde, in the airstream when challenged with 2-butanol. Acetone concentrations in the system were affected only by humidity conditions.

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CHAPTER 1. INTRODUCTION

Awareness of the magnitude and potential seriousness of indoor air quality problems in commercial buildings has increased significantly since the mid-1970's. In response to what is potentially a significant health threat, a wide array of possible solutions are being researched and investigated for their usefulness in combating indoor air pollution and other indoor air quality problems. Air cleaning systems that use a variety of mechanisms and configurations are used to treat indoor air. Current indoor air-cleaning systems suffer a variety of drawbacks, including, but not limited to, filter disposal and regeneration costs, selectivity problems, ineffectiveness at low pollutant concentrations, and high maintenance costs.

A novel air cleaning technology has been developed which uses ozone-accelerated catalysis to oxidize organic contaminants to carbon dioxide and water, and to reduce levels of microbiological aerosols. The system uses an activated carbon catalyst to remove all ozone from the airstream prior to reintroducing it to the occupied space. Preliminary evaluations of this technology suggest that a significant percentage of volatile organic compounds in the airstream are destroyed per pass through the system. It is hoped that this technology will provide a safe, effective, and efficient solution to indoor air quality problems.

As part of the evaluation of the ozone accelerated catalysis system, a complete safety evaluation of the system was necessary. One safety concern was that partial oxidation products could be introduced to the indoor environment if the catalysis system did not completely oxidize organic chemicals initially present in the airstream. There is potential for these partial oxidation products to be more toxic than the original compounds. Therefore, as part of the safety evaluation, it was necessary to determine if the system produced partial oxidation products when operated under conditions simulating actual operating conditions.

Due to the fact that the technology was new, the potential for partial oxidation product formation had not been thoroughly investigated. More studies investigating the mechanisms or kinetics of ozone accelerated catalysis needed to be conducted. Tests were conducted to determine if the process produced carbonyls as partial oxidation products using a pre-prototype unit. In this study, the air cleaning unit was challenged with simulated pollutants and air samples were collected at several stages of the process and analyzed for carbonyls. The objectives of the study were to:

1. Determine if carbonyls were produced in the airstream when the air cleaning system was challenged with benzene or 2-butanol as simulated pollutants.
2. If carbonyls were detected in the air, then qualitatively identify and quantify the carbonyl compounds.

3. If carbonyls were detected in the system during the operations of the air cleaning system, determine which operational factors affected the production of these chemicals.

CHAPTER 2. LITERATURE REVIEW

2.1 HISTORICAL ASPECT OF INDOOR AIR POLLUTION

The energy conservation programs triggered by the energy crisis of 1973 were focused largely on buildings and building systems, which consume between 20-50% of the energy used in the United States (National Research Council, 1982). To a large degree, energy use was curtailed by designing buildings better insulated to maximize heating and cooling efficiency, and by minimizing the use of outdoor air for ventilation. This situation, combined with an increasing number of indoor air contaminant sources such as synthetic building materials, has resulted in a sharp increase in complaints related to indoor air quality since the mid-1970s (Wallingford and Carpenter, 1986; Molhave, 1986). Woods (1991a) suggests that 20-30% of the buildings in developed countries may have indoor environment conditions that could lead to adverse health or comfort effects.

The nature of these indoor air quality complaints generally involve a variety of symptoms including headaches, mucous membrane irritation, eye irritation, fatigue, dizziness and nausea. When these symptoms persist in 20% or more of the building occupants, when the causes of the symptoms are not obvious, and when relief is usually obtained upon leaving the building, the building is considered to manifest Sick Building Syndrome (SBS) (Woods, 1991a). A smaller percentage of complaints involve symptoms of SBS combined with symptoms of frank illness, a condition classified as Building Related Illness.

Various studies have documented the existence of a wide variety of volatile organic compounds (VOCs) in indoor air. While the causes of SBS remain unknown, the tendency for many VOCs to produce symptoms at low concentrations characteristic of SBS make them a prime suspect (Molhave, 1982; 1986). Several studies have been conducted which have identified VOCs as major contributors to indoor air quality problems in commercial buildings (Woods et al., 1987; National Research Council, 1982; Wallingford and Carpenter, 1986; Robertson, 1988). The fact that several VOCs found in indoor air are known or suspected human carcinogens has also served to focus attention on them as a significant factor in indoor air quality problems (Wallace, 1991).

2.2 VOLATILE ORGANIC COMPOUNDS IN INDOOR AIR

2.2.1 Characteristics and Concentrations

Volatile organic compounds are found in all indoor environments. A number of studies done since the late 1970's have identified more than 350 organic compounds in indoor air at concentrations greater than 1 part per billion (ppb) (Sterling, 1985). These VOCs include aromatic hydrocarbons, aliphatic hydrocarbons, halogenated hydrocarbons, alcohols, esters, aldehydes, and ketones. Typical concentrations for these VOCs are less than 1 part per million (ppm) (Wallace, 1991). The number of VOCs commonly found indoors is around fifty and includes several compounds such as benzene, vinyl chloride, and formaldehyde, all of which may cause serious health effects (Wallace, 1991).

Although the indoor concentrations of VOCs are almost always far below standards set for industrial occupational settings, average indoor levels of many compounds exceed outdoor levels (Wallace, 1991; Sterling, 1985). Average indoor concentrations of specific VOCs have been found to be as much as ten times higher than average outdoor levels. Peak concentrations of VOCs over a 12 hour period are often 100 to 1000 times higher than outdoor levels (Wallace, 1991). These high indoor VOC concentrations imply that the pollutants are generated within the building (National Research Council, 1981).

2.2.2 Sources

The sources of VOCs in indoor air are many and varied. Studies have identified building materials and consumer products, such as particle board, carpets, insulation, wall paper, room fresheners and caulks as major sources of airborne organic contaminants (Molhave, 1982; Miksch et al, 1982; Wallace et al., 1987; Tichenor and Mason, 1988; Wallace, 1991). The study by Molhave (1982) of 42 building materials including carpeting, paints, and caulks, found a total of 52 VOCs emitted, with each material emitting an average of 22 compounds. Other sources include, but are not restricted to, human bio-effluents, cleaning solvents, office machines, tobacco smoke, paint, and contaminated outside air. Research also indicates that materials such as upholstery and carpets which have absorbed organic compounds can, under certain circumstances, also act as sources by re-emitting chemicals previously adsorbed (Wallace, 1991).

2.2.3 Health Effects

The health effects of chronic exposure to low levels of VOCs are not well understood. While many of the compounds commonly found in indoor air, including formaldehyde, are known or suspected to be either membrane irritants or central nervous system depressants, the effects of low level exposure to most VOCs have not been fully evaluated (Sterling, 1985; National Research Council, 1982; Molhave, 1982). Molhave describes the most frequent effects of low level exposure to VOCs as irritation of the mucous membranes of the eyes, mouth, and nose, skin, and airways. The effects appear to be the result of surface reactions and are reversible (Molhave, 1990). It is also theorized that odor caused by VOCs may act as stressors and cause adverse health effects (Sterling, 1985). The possible synergistic effects of the large mixtures of compounds found have not been evaluated adequately.

Research done by Molhave (1986, 1990) on the effects of a mix of common indoor air pollutants on human test subjects, suggest that total VOC levels at or above 3 mg/m^3 will result in occupant dissatisfaction with indoor air quality and irritation of mucous membranes. Furthermore, Molhave (1990) suggested that at VOC levels between 0.2 and 3 mg/m^3 irritation and odor discomfort may occur if other contributing factors, such as high temperatures or low humidity, are present; levels above 25 mg/m^3 may be toxic. Studies of the health effects of exposure to low levels of formaldehyde, a common indoor pollutant, have shown that significant irritation of mucous membranes occurs at levels below 3 ppm and that this irritation increases with the concentration (Sterling, 1985). Kjaergaard et al. (1987) documented increased levels of mucous membrane irritation in subjects when they were exposed to n-decane concentrations as low as 1 ppm. Field studies have not always supported this connection between VOC levels and irritation, however, and much more research is necessary to fully understand the impact VOCs in indoor air have on human health (Woods, 1991b).

2.3 CONTROL STRATEGIES

The most widely used methods for control of chemical contamination of indoor air include source control strategies, ventilation strategies, and air cleaning technologies (McNall, 1986).

Control of chemical pollutant sources is the most effective strategy for improving indoor air quality (Indoor Air Bulletin, 1991; EPA, 1990). Source control methods focus on isolating contaminant sources from buildings to alleviate indoor air pollution problems. Specific examples of source control methods include restricting smoking indoors and avoiding, removing, or isolating building materials and furnishings known to emit high levels of VOCs (Godish, 1989).

Another source control approach, known as "bake-out", is the practice of maintaining a new building at elevated temperatures and normal or increased ventilation rates for a period of time prior to occupancy. The principle behind this method is that the increased temperature will increase the vapor pressure of residual solvents and, given time, deplete them (Godish, 1989). Significant decreases in indoor VOC levels after bake-out have been documented (Godish, 1989). A study by Bayer (1991) did not find evidence supporting the effectiveness of bake-outs as a source reduction strategy. Bayer concluded that the high temperatures actually released chemicals into the air that would not be volatilized at all at normal room temperatures.

Source control of VOCs is often not practical. Many sources of VOCs, such as the building occupants, activities in the building, and contaminated outside air cannot be reduced or eliminated (Wallace, 1991; Rodberg et al., 1991). In some situations it is difficult or impossible to identify sources of contamination. Under these circumstances other strategies for control of indoor VOC levels must be adopted.

Dilution ventilation is defined as "the dilution of contaminated air with uncontaminated air for the purpose of health hazard or nuisance control" (ACGIH, 1984). The American Society of Heating, Ventilation, and Air Conditioning Engineers (ASHRAE) has published guidelines for achieving acceptable indoor air quality via two alternative methods for ventilation design. These methods are known as the Ventilation Rate Procedure (VRP) and the Indoor Air Quality Procedure (AQP) (ASHRAE, 1989).

The Ventilation Rate Procedure prescribes the rate at which clean outdoor air must be supplied to various indoor spaces in order to provide acceptable indoor air quality. Recommended ventilation rates (cubic feet per minute per person, cfm/person) for residential, commercial, institutional, vehicular, and industrial spaces are provided, with a minimum of 15 cfm/person. This procedure also prescribes outdoor air quality acceptable for ventilation, outdoor air treatment if necessary, and criteria for reducing outdoor air quantities when recirculated air is treated with an air cleaning system (ASHRAE, 1989). In most circumstances if the recommended ventilation rate is utilized, the quality of indoor air will be acceptable.

The VRP assumes that ventilation effectiveness is high. Ventilation effectiveness is defined as the percent of the outdoor air delivered to the space which reaches the occupied space. Under some circumstances ventilation effectiveness must be increased to produce acceptable indoor quality. This can be accomplished by creating plug flow conditions (local exhaust), actively mixing the air in the space, or changing factors such as the location of supply and return air vents and performance of supply air diffusers (ASHRAE, 1989).

Most of the ventilation rates prescribed in the VRP were established based upon the assumption that the contamination in the space is in proportion to the number of persons in the space. For this reason, when unusual indoor contaminants or sources are present or anticipated, the rates prescribed in the VRP may not be sufficient to provide acceptable indoor air quality. Under these circumstances, if source control is ineffective, ASHRAE recommends using the Indoor Air Quality Procedure (ASHRAE, 1989).

The Indoor Air Quality Procedure provides control of indoor air quality by establishing concentration limits for pollutants of concern. Concentration limits for 9 pollutants found in indoor air have been set based on National Primary Ambient-Air Quality Standards, federal regulations, and ASHRAE recommendations. These pollutants include carbon dioxide, ozone, lead, carbon monoxide, sulfur dioxide, nitrogen dioxide, chlordane (an insecticide), particles, and radon gas. The acceptability of the air quality is evaluated using both quantitative measurements and subjective methods described in the procedure. Ventilation and recirculation rates are then based upon the results of the evaluation.

Often circumstances exist which restrict the use of outdoor air for dilution ventilation. Examples include poor outdoor air quality, economic considerations and design constraints (Rodberg et al. 1991). Under these conditions both design procedures allow a combination of recirculated and outdoor air to be used to dilute contaminants to acceptable levels. Recirculated air must be cleaned prior to being reintroduced to the occupied space with an air cleaning system capable of removing the pollutants of concern. If outdoor air ventilation rates are reduced below the rates required by the VRP, the Indoor Air Quality Procedure must be used to evaluate the resulting indoor air quality (ASHRAE, 1989).

2.4 CURRENT TECHNOLOGY USED TO REMOVE GASEOUS CONTAMINANTS FROM INDOOR AIR

In buildings where outdoor air dilution and source control are not feasible or effective solutions to chemical contamination of indoor air, air cleaning technology can be used effectively. A variety of applicable air cleaning technologies are available, utilizing physical adsorption, absorption, chemisorption and catalysis as contaminant removal mechanisms.

2.4.1 Physical Adsorption

The most common methods for removing VOCs from indoor air utilize the chemical/physical phenomenon known as adsorption (Viner et al., 1991). Physical adsorption occurs when molecules of gases, vapors, or liquids become bound to the surface of a solid by residual physical forces known as van der Waal's forces

(Godish, 1989). No chemical reaction occurs but heat is liberated as a result of adsorption.

The ability of a sorbent to adsorb gas molecules is finite and is generally related to the surface area of the sorbent. Once all or most of the sorption sites on a sorbent are occupied by sorbate molecules, the sorbent is said to be saturated and will no longer be effective as a contaminant removal mechanism. Adsorbed molecules can be re-emitted to the airstream under certain circumstances. A molecule with a strong affinity for the adsorbent can displace previously adsorbed molecules with a weaker attraction for the adsorbent. Polar sorbents will adsorb water vapor, possibly displacing previously adsorbed molecules (Godish, 1989).

Physical adsorption occurs on many surfaces, but only a few have adsorptive characteristics strong enough for use in air cleaning applications (Godish, 1989). These materials, including activated carbon, silica gel, zeolites and clays, typically have high surface area to volume ratios and contain large numbers of microscopic pores (Ludwig and Turner, 1991). Activated carbon is the most commonly used sorbent for indoor air cleaning applications (Godish, 1989).

Activated carbons have varying physical qualities that affect their performance as adsorbents and serve to characterize them (Godish, 1989). These characteristics include, hardness, size, adsorption capacity, retentivity, residence time and service life. Retentivity is a measure of how well an activated carbon retains pollutants when dry, clean air is passed over it.

The hardness and size of activated carbons differ due to variations in raw materials and production processes. Hardness helps to maintain structural integrity which in turn prevents the development of voids in filter that reduce contaminant removal efficiency. Small, tightly packed carbon granules are desirable because they reduce the distances that pollutant molecules must travel to adsorbent surfaces (Godish, 1989). Hardness is also important because the formation of extremely small particles, or fines, tend to increase the pressure drop across the unit.

Adsorption capacity is the unit weight of contaminant collected per unit weight of adsorbent. This quality is affected by sorbent surface area, pore volume, pollutant properties such as polarity, and environmental conditions such as temperature and humidity.

The service life of an activated carbon filter refers to the amount of time required for the filter to become saturated and allow significant levels of contaminants to penetrate. This variable, known as breakthrough, can be calculated using formulas, but in practice is very difficult to predict accurately (Godish, 1989).

Air cleaning systems based on adsorption are available in a variety of designs (Godish, 1989). Filter beds are generally thin and can be found in different configurations for use as part of an HVAC system, in self contained systems, or in residential air cleaners. The removal efficiency of air cleaners is proportional to the product of contaminant removal rate and residence time in the system (Holbrook, 1991). The use of thin bed filters in indoor air quality applications is necessary to minimize the pressure drop across the cleaning device (Godish, 1989). This factor makes residence time a critical factor in the performance of these systems.

The effectiveness of activated carbon filters as indoor air cleaners is a point of debate (Indoor Air Quality Update, 1991). Air cleaning efficiency at VOC levels commonly found indoors has not been extensively investigated but at least one study suggests that carbon filters are not effective at these levels due to extremely short filter lives of a matter of minutes (ASHRAE, 1991; Viner et al., 1991). There is also concern that many low molecular weight compounds, such as ammonia and formaldehyde, cannot be adsorbed by activated carbon (Daisey and Hodgsen, 1989; Indoor Air Quality Update, 1991; Wadden and Scheff, 1983). Other concerns focus on disposal or regeneration cost of used filters. Regeneration of filters used in indoor air cleaning devices is often not practical. As a result disposal and replacement costs can be a significant concern.

2.4.2 Absorption

In absorption processes gaseous pollutants are dissolved in an absorbing liquid (ASHRAE, 1991). These gases will absorb in liquids when the partial pressure of the pollutant airstream is greater than its corresponding solution vapor pressure. Factors affecting this process are complex and include physical properties of the pollutants and absorbent, geometry of the gas/liquid contact system and the temperature and velocity of the airstream.

Process technologies employing this mechanism are known as scrubbers, and are most often used in industrial applications such as the removal of pollutants from stack gases. Absorption systems are also used in spacecraft and submarines to reduce carbon dioxide (CO_2) and carbon monoxide (CO) , freeing oxygen to be returned to the occupied space (ASHRAE, 1991; Carhart and Thompson, 1975).

Absorption technology is generally not considered for indoor air cleaning applications for several reasons (AHSRAE, 1991; Turk, 1983). Treated air is often saturated with vapor from the absorbent resulting in the introduction of an additional pollutant to the occupied space. In addition, space and power requirements are often too large for these systems to be cost a cost effective air cleaning alternative.

2.4.3 Chemisorption

The process referred to as chemisorption is very similar to adsorption. The major difference is that in chemisorption sorbate molecules react with molecules on a solid sorbent and are thus removed from the airstream. The media for these reactions are porous sorbents, such as activated carbon, which have been impregnated with a reactant. The mechanism is selective; only certain pollutants will react with a given sorbent (ASHRAE, 1990). The process is usually not reversible and will only be effective as long as unreacted reactant is present, although physical adsorption by the support material may still be a factor. A potential drawback of chemisorption systems is that the surface reactions may result in the formation of undesirable byproducts (Godish, 1989).

Two factors that may improve chemisorption are increased temperature and the presence of water vapor (ASHRAE, 1990). This is in direct contrast to the effect these factors usually have on the performance of physical adsorption systems.

Limited studies have been done to evaluate the performance of chemisorption systems (Godish, 1989). These systems are generally designed and used for the removal of specific organic and inorganic gases from air and thus may not be an appropriate solution for many indoor air quality problems where a wide range of compounds are present.

2.4.4 Catalysis

Catalysts designed for use at ambient temperatures can also be used to purify indoor air. In this process, reactions between contaminants that are physically adsorbed or chemisorbed occur at the surface of a catalyst (Barnard and Mitchell, 1968a). The catalyst is able to increase the reaction rate by adsorbing the reactants in a form that lowers the activation energy of the reactions involved. The catalyst is not consumed in the process, facilitating the possibility of long service lifetimes. Catalysts can assist reactions in which individual molecules are decomposed into smaller molecules, or reactions in which contaminants are oxidized by a supplied chemical oxidant such as oxygen or ozone. Some catalysts are selective, meaning that they will only catalyze reactions with specific molecules, and some are non-selective meaning that they are effective with a variety of target chemicals (Godish, 1989).

The rate at which a catalyst system oxidizes trace organics can be controlled by any one of several factors associated with the catalysis process. These include the rate of diffusion of the reactants to the catalyst surface, the rate of adsorption of the reactants, the rate of the surface reaction, rate of desorption of the reactants from the catalyst, and rate of diffusion of the reactants from the catalyst surface. Since all of these steps are always present and occur in series, the slowest step in this process is considered the "rate controlling step" (Barnard and Mitchell, 1968a).

Catalysts are widely used in the manufacturing process of industrially important partially oxidized products (Spivey, 1987). These oxidation reactions are generally carried out at high reactant concentration and at temperatures greater than 400 °C (Spivey, 1987). By contrast, catalysts used for the removal of trace organics from air usually operate at much lower temperatures and reactant concentrations. Applications of low temperature (e.g., 200 ° C) catalytic oxidation of trace contaminants include gasoline vapor removal, and VOC removal from processes such as spray painting, offset printing, and coating operations.

There are two general process configurations used for the catalysis of trace organics in air (Spivey, 1987). In the first, direct contact with open flame is used to preheat the gas stream upstream of the catalyst bed. The preheating elevates the gas stream temperature so that catalytic oxidation can occur and effectively oxidizes some of the trace contaminants through free-radical-induced homogeneous reactions. In the second configuration, the gas stream enters the catalyst bed after indirect preheating by passing through a heat exchanger. Conversion in this configuration utilizes only heterogeneous catalytic oxidation reactions. The difference between these two configurations involves the use of direct flame preheating. The free-radical-induced oxidations which take place due to the high temperatures when direct flame is used increase the overall conversion rate of the system but may cause a variety of reactant species to be introduced to the catalyst. These species will not be produced when indirect preheating is used since gas phase reactions are eliminated.

Very few materials are known to be effective catalysts for the destruction of VOCs at normal room temperature (Spivey, 1987). Catalysts designed for use in indoor air cleaning applications must be non-selective and relatively immune to poisoning by the contaminants in the airstream. Activated carbon effectively catalyzes the decomposition of ozone to oxygen and the oxidation of hydrogen sulfide to elemental sulfur in the presence of oxygen (Godish, 1989). Sorbents impregnated with metal chlorides or noble metals have been used for removal of a variety of organic and inorganic gases from air (Godish, 1989; Spivey, 1987). A residential air cleaner developed by Teledyne Water-Pik used a copper chloride/palladium chloride catalyst (Godish, 1989). Evaluation of this system proved it to be very effective at destroying several inorganic gases, including ozone, carbon monoxide, and hydrogen sulfide, but its destruction of benzene was lower (Collins, 1986).

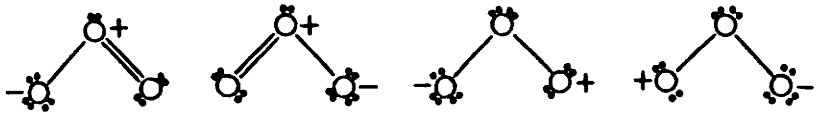
2.5 OZONE ACCELERATED CATALYSIS

2.5.1 Application to Indoor Air Cleaning

In response to the shortcomings of other air cleaning techniques, a novel method for cleaning indoor air has been proposed by Rodberg et al. (1991). This technology is said to "permanently reduce the concentration of a wide variety of volatile organic compounds" and possibly also provide reduction in levels of microbiological aerosols. This process uses the combination of a strong oxidant, ozone, and a proprietary catalyst to oxidize VOCs at room temperature. Air is drawn from the occupied space and ozone is diffused into this airstream. The ozone is allowed to thoroughly mix with the airstream which is then passed over a proprietary hydrocarbon destruction catalyst which oxidizes VOCs to CO_2 and water. The system then uses activated carbon to remove all unreacted ozone from the airstream prior to reintroduction into the occupied space. An evaluation of the effectiveness of the system suggests that as much as 50% of the VOCs in the airstream will be removed per pass. The system was designed to be incorporated into the HVAC system of existing commercial buildings.

2.5.2 Ozone

Ozone is an allotropic form of the element oxygen consisting of three atoms of oxygen per mole of ozone (Oehlschlaeger, 1978). The structure of the ozone molecule is a hybrid of four contributing resonance structures (Oehlschlaeger, 1978):

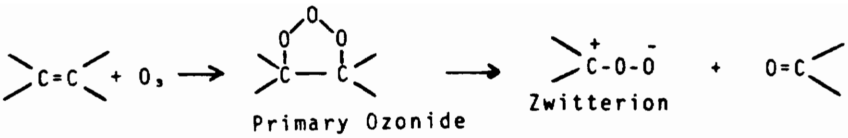


(adapted from Oehlschlaeger, 1978)

Ozone is an extremely powerful oxidant and is used in a variety of industrial processes including the production of pelargonic and azelaic acids from oleic acid and the synthesis of hormonal compounds (Razumovskii and Zaikov, 1984). Since the end of the 19th century, ozone has been used as a disinfectant in water treatment facilities, and has also been used as an oxidant and coagulant (AWWA, 1991).

The ozone molecule will react as a dipole, an electrophilic agent and as a nucleophilic agent (Oehlschlaeger, 1978; AWWA, 1991). Due to its dipolar structure, ozone will react as a 1,3-dipolar cyclo-addition with unsaturated bonds (Oehlschlaeger, 1978). This reaction is commonly known as the Criegee mechanism. The electrophilic reaction occurs at molecular sites with high electron densities, particularly those on specific aromatic molecules. The nucleophilic reaction occurs at molecular sites having an electron deficit and on carbons with electron-withdrawing groups such as halogens, nitro groups, and carbonyl groups (AWWA, 1991; Oehlschlaeger, 1978).

Perhaps the most important reaction of ozone with organic compounds is the reaction of ozone with double bonds. The mechanism generally accepted for this reaction was proposed by Rudolph Criegee in the 1950s. The Criegee mechanism postulates that the initial reaction of ozone with the olefin produces a primary ozonide which rapidly decomposes to yield a reactive zwitterion and a carbonyl fragment (Oehlschlaeger, 1978):



(from Oehlschlaeger, 1978)

If the olefin is unsymmetrical, two different zwitterions and two different carbonyl fragments can be formed (Oehlschlaeger, 1978). If the reaction is carried out in a non-participating solvent, the zwitterion and the carbonyl will re-combine to form the normal ozonide. If the reaction is carried out in a participating solvent, the reactive zwitterion will react with the solvent to form various products. If the solvent is alcohol or water, alkoxy hydroxides and hydroxy hydroperoxides, respectively, are the main products of the zwitterion reactions (Oehlschlaeger, 1978).

Research by Hoigne and Bader (1979) has shown that ozone reacts in the aqueous phase by direct reaction and by formation of the highly reactive hydroxyl radical. The hydroxyl radical is extremely reactive and will attack almost any organic compound (Glaze, 1986). The hydroxyl radical is formed in the atmosphere by photolysis of ozone and is an important factor in the removal of organic compounds from the atmosphere (Atkinson and Carter, 1984; Hendry and Kenly, 1979).

2.5.3 Potential Intermediate Formation

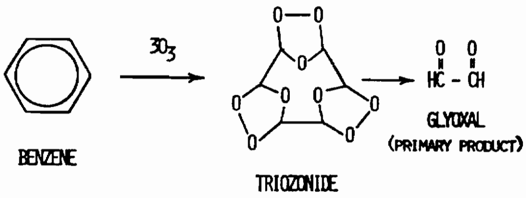
A large number of catalytic oxidation processes have been developed to produce partially oxidized products of industrial importance (Spivey, 1987). In processes such as indoor air cleaners which are designed to destroy unwanted chemical contaminants by complete oxidation to CO_2 and water, any oxygen containing organic intermediate is considered a partial oxidation product. These intermediates may be more toxic than the original compounds and are considered undesirable (Spivey, 1987). In order to effectively evaluate ozone accelerated catalysis the possibility that partial oxidation products may be produced and introduced into the occupied space must be investigated.

It has been established that ozone used for water treatment will produce chemical by-products (Glaze, 1986). As a thesis for this work it was assumed that the proposed air cleaning system could also produce chemical by-products (partial oxidation products). The focus of this literature review was therefore aimed at determining what those by-products could be.

The reactions relevant to this study are the reactions of ozone with the chemicals used to challenge the test air cleaning system (see Chapter 3 for complete description). The chemicals evaluated were benzene and 2-butanol. Gas phase reactions of ozone with these chemicals were of primary interest; however aqueous phase reactions were considered as well. Particularly relevant are studies of the kinetics and mechanisms of ozone reactions in the gas phase which have been conducted to further the understanding of the atmospheric removal processes for organic compounds. Ozone has been used as a disinfectant in water treatment applications for over a hundred years and numerous investigations of by-product formation have been conducted (AWWA, 1991). General research has identified aliphatic aldehydes as common by-products of the reactions of ozone with organics in water (Glaze, 1986). The most common ozone reactions, the ozonolysis of olefins, are known to produce carbonyl containing fragments (Oehlschlaeger, 1978). It has been suggested that the chemistry of ozone attack on reactive chemicals will be the same in the gas and aqueous phases (Bailey, 1972).

Investigations of the kinetics, mechanisms, and products of the reaction of aromatic compounds with ozone have been carried out for both gas and aqueous phase reactions (Bailey, 1958; Waters, 1964; Pate et al., 1976; Oehlschlaeger, 1978; Bailey, 1958). Aromatics are not as reactive towards ozone as olefins (Bailey, 1958; Oehlschlaeger, 1978). Electron releasing substituents such as hydroxy and methoxy groups activate the ring towards ozone (Bailey, 1958). Studies of the kinetics of the reaction of ozone with various aromatic compounds show that benzene is the least reactive aromatic towards ozone (Atkinson and Carter, 1984; Pate et al., 1976; Bailey, 1958).

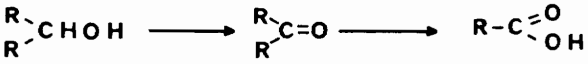
The mechanism of the reaction of ozone with benzene is not well understood but it is postulated to be the same Criegee mechanism governing the reaction of ozone with olefins (Bailey, 1958; Pate et al., 1976; Oehlschlaeger, 1978). Research of the mechanism, carried out in the aqueous phase, postulates that three moles of ozone react with each mole of benzene, cleaving the ring and producing three moles of glyoxal (Bailey, 1958; Waters, 1964; Falk and Moyer, 1978):



(from Falk and Moyer, 1978)

Falk and Moyer (1978), Kou et al. (1978), and Gilbert (1978) have conducted studies to document the products of ozonation of benzene and its reaction products in the aqueous phase. This research has found glyoxal as the initial product of the reaction. Further ozonation oxidizes the glyoxal to glyoxylic acid, oxalic acid, and traces of formic acid (Oehlschlaeger, 1978; Kuo et al., 1978). Ozonation of glyoxal and glyoxylic acid produced oxalic acid prior to complete oxidation to carbon dioxide and water (Kou et al., 1978; Gilbert, 1978).

It is known that the ozonolysis of secondary alcohols will produce ketones with the same number of carbon atoms (Finar, 1963; Bailey, 1958; Waters et al., 1976; AWWA, 1991). Further oxidation of the ketones produced is difficult and slow, but can be accomplished with a strong oxidant, producing carboxylic acids with less carbon atoms than the original ketone (Finar, 1963; Atkinson and Carter, 1984; Oehlschlaeger, 1978). It is suggested that the oxidation reactions of alcohols and ketones are initiated by ozone and then carried out by oxygen (Bailey, 1958; Oehlschlaeger, 1978). Catalytic oxidation of secondary alcohols has been affected by passing oxygen through alcohol solutions in the presence of metal catalysts (Hudlickey, 1990). Bailey (1972) has proposed a pathway for the ozonolysis of alcohols:



(from Laplanche and Martin, 1982)

Several studies have been conducted which document the formation of carbonyls from ozonolysis of alcohols in the liquid phase. In a study of ozonation products in aqueous reactions, Whiting et al. (1968) documented the formation of acetone, acetic acid and formaldehyde upon the ozonation of 2-propanol. Research of ozonation by-products by Kuo et al. (1978) found that ozonation of 2-propanol produced acetone which was in turn oxidized to acetic acid, oxalic acid, formic acid, and formaldehyde. In a review of ozone reactions with various organics, Laplanche and Martin (1982) found that ozonation of a concentrated solution of ethanol produced acetaldehyde, acetic acid, and organic peroxides. The AWWA (1991) also mentions acetaldehyde as a possible product of the ozonation of ethanol.

Research of the ozonation of various secondary alcohols in methylene chloride at 0°C was conducted by Waters et al. (1976) to investigate the usefulness of the process as a synthetic oxidation method. This research found that ozonation of secondary alcohols to ketones was a much slower reaction than the reaction of ozone with the carbon-carbon double bond, and that the ketone products were fairly pure and essentially inert. In addition, the ozonation of acyclic and cyclic alcohols were found to produce minor amounts of mono and di-basic acids, respectively. When the reactions were carried out at higher temperatures, carbon-carbon scission became significant resulting in the production of more impurities. The reactions produced identical products and similar reaction rates when the experiments were duplicated in carbon tetrachloride, chloroform, and acetone, suggesting that solvent effects are minimal. This research was the only study found which specifically mentions the ozonation of 2-butanol; the product of the reaction was butanone.

It appears that the mechanisms and kinetics of the reactions of ozone with benzene and 2-butanol are not clearly understood (Bailey, 1958; Oehlschlaeger, 1978). Some investigations of the products of these reactions have been conducted, and much of the reported literature has focused on uncatalyzed reactions of ozone and organic chemicals. The proposed mechanisms of reactions of ozone with organic compounds, including aldehydes, often involve radical formation (Bailey, 1958; Falk and Moyer, 1978). These radicals may themselves react with molecules and produce a variety of products (Falk and Moyer, 1978). While it appears that the solvent effects are minimal it is not known whether the mechanism of ozonolysis in the gas phase can be assumed to be the same as in the condensed phase. This represents, then, a major gap in the understanding of the relevant chemistry. Nevertheless, the liquid phase mechanism will be considered as an initial guess when considering the results of the present investigation.

CHAPTER 3. METHODS AND MATERIALS

3.1 OVERVIEW AND EXPERIMENTAL DESIGN

3.1.1 Overview

In this chapter, details will be given of the sampling and analysis methods used during the operation of the pre-prototype unit of an indoor-air-pollution-abatement system. The data-analysis procedures will also be presented in detail.

3.1.2 Experimental Design

The purpose of this study was to determine if the air cleaning system produced partial oxidation products, or intermediates, when challenged with selected chemical pollutants. The intermediates investigated were organic compounds known as carbonyls (e.g., aldehydes and ketones). Compounds belonging to this class were of interest because (a) the literature indicated that the potential for their formation is high, (b) they are potentially toxic, and (c) they are likely to be odorous. They are also common indoor air pollutants.

Two chemicals were chosen to challenge the system for the purpose of investigating formation of carbonyl intermediates. The first challenge chemical chosen was benzene. This chemical was chosen because it is commonly found in indoor air, and it is a carcinogen, thereby posing a significant threat to human health. The second challenge chemical chosen was 2-butanol which had the advantages that it has a low odor threshold, is a chemical commonly found in indoor air, and a low toxicity.

Each group of air samples included samples from several stages of the air cleaning process. Samples were collected while operating the system under four test conditions to evaluate which factors affected the concentrations of carbonyls found in the airstream. Data recorded during sampling included air temperature, relative humidity, sample volume, concentration of challenge chemical applied (e.g., benzene or 2-butanol), and concentration of ozone in the airstream. The concentration of challenge chemical applied is a predicted concentration based on the milligrams of pollutant diffused per cubic meter of air in the airstream. Relative humidity was considered to be proportional to partial pressure since temperature variation was minimal over the duration of the air sampling trials.

Carbonyls were extracted from the air stream and analyzed using EPA Method IP-6A (Riggins, 1984). This method is based on the specific reaction of aldehydes and ketones with acidified 2,4-dinitrophenylhydrazine (DNPH). Air samples were pulled through silica cartridges coated with acidified DNPH. Carbonyls in the air sample were trapped in the cartridge and then eluted and analyzed.

Liquid chromatography (LC) combined with diode-array detection was used to identify and quantify carbonyl compounds from the air stream. The aldehydes and ketones detected were quantified with external calibration standards prepared for each compound. Gas chromatography (GC) and combined gas chromatography with mass spectrometry (GC/MS) were also used to confirm identification of carbonyl contaminants found in the air samples.

The carbonyl concentrations from each air sample were calculated and corrected for blank values. This information, along with qualitative data, was used to characterize carbonyl formation during different stages of the air cleaning process under varying operating conditions. An analysis of variance (ANOVA) test was used to determine which factors significantly affected the concentration of carbonyls detected in the airstream.

3.2 SAMPLING SITE DESCRIPTION

3.2.1 Physical Description of Pre-Prototype Indoor Air Pollution Abatement System

To evaluate the air cleaning system, a pre-prototype unit was constructed. The unit was designed, constructed and operated at Virginia Tech through a contract with Union Carbide. Close coordination in the design, construction, and operation was maintained between the College of Architecture (Indoor Environment Program), the College of Engineering (Departments of Civil and Chemical Engineering), and Union Carbide (Drs. George Keller, Joan Rodberg, and Jay Miller). A schematic of the system is shown in Figure 1. The one-pass duct/fan system was capable of handling an airflow of 3500 cubic feet per minute (cfm) and can therefore be considered as a commercial sized unit. The face velocity of 440 feet per minute was typical of conventional air handling units. The unit was approximately sixty feet long and duct sections were 2 feet high by 4 feet wide. The unit was located and operated in a research facility near the town of Blacksburg in rural southwest Virginia.

Outside air was pulled into the duct by the blower whereupon it was passed across a heater and humidifier to provide control of the airstream's temperature and relative humidity. The airstream was then passed through a section containing a diffuser through which the vaporized challenge chemicals entered the duct. The liquid challenge chemical was drawn under vacuum from a container on an electronic gram balance, and delivered through a micrometer needle valve to an atomizer. The challenge chemical was vaporized by the atomizer and then introduced into the air stream through two perforated diffuser pipes transversing the duct cross-section. Measurements from the gram balance and airflow data were used to calculate the concentration of challenge chemical applied to the airstream in the duct. This system provided precise control of the amount of challenge chemical supplied through the diffuser into the duct. Baffles were placed within the duct to facilitate complete mixing of the challenge chemical in the airstream.

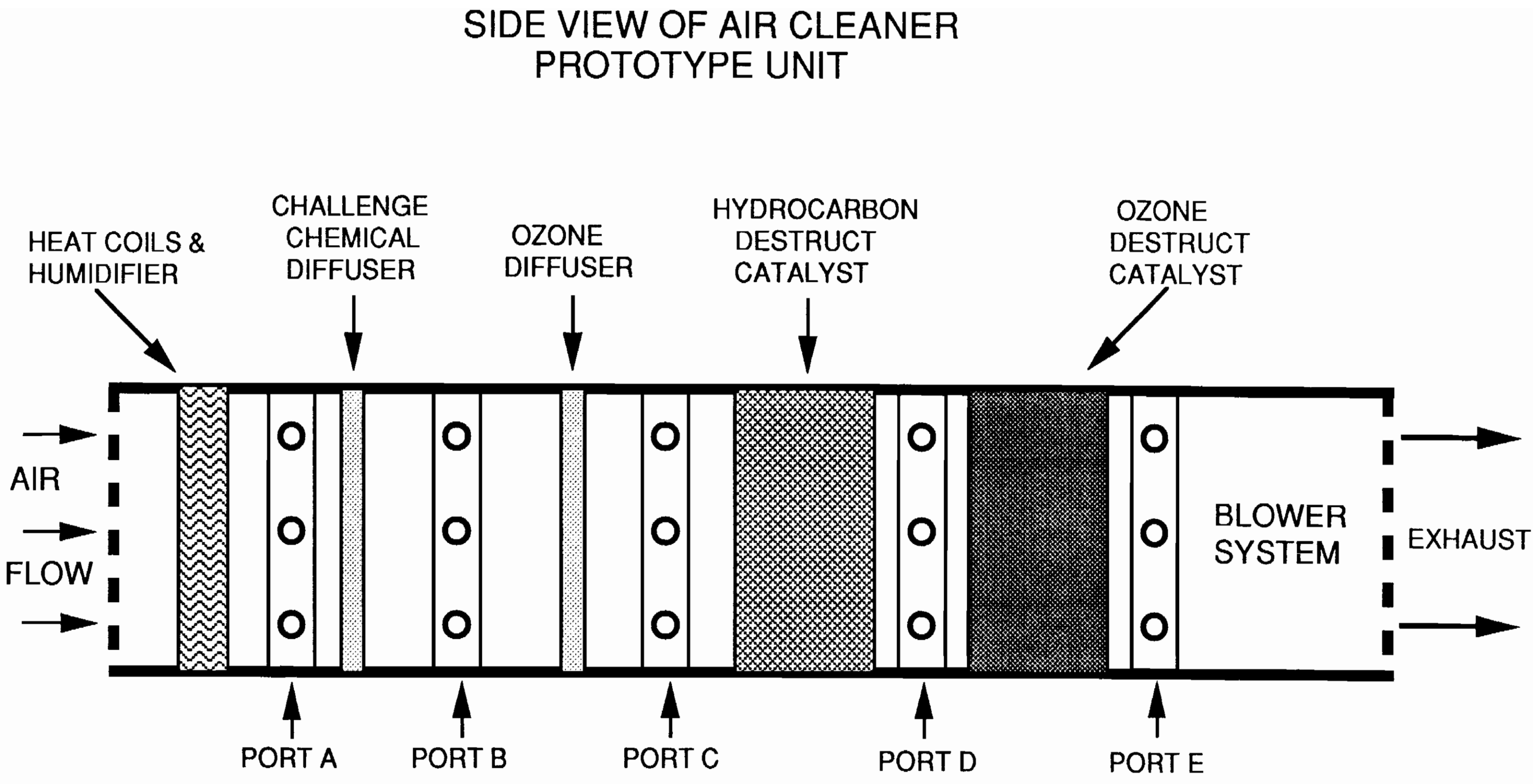


Figure 1. Schematic of air cleaner duct system showing location of sampling ports, diffuser systems, catalyst beds, and blower. Total duct length is approximately 60 feet. Drawing not to scale.

Ozone produced by an air supplied generator was then introduced to the air stream through two perforated diffuser pipes transversing the duct cross section downstream of the hydrocarbon diffuser. The ozone generator, model #G-14, was purchased from PCI Ozone & Control Systems, Inc. (Caldwell, NJ). The amount of ozone introduced to the duct could be carefully controlled. Baffles were placed within the duct to assure complete mixing of the ozone in the airstream.

The air stream was then passed over a proprietary hydrocarbon destruct catalyst which was purchased from UOP (Arlington Heights, IA). This design consisted of twelve parallel, packed catalyst beds. Each catalyst bed was 36 inches long and had a bed depth of 1.25 inches. The catalyst section had a capacity for 7.5 cubic feet of catalyst. The airstream was then passed over an ozone destruction catalyst (i.e., activated carbon) and returned to the outdoors. The ozone catalyst, furnished by Union Carbide, was packed in the same configuration as the hydrocarbon destruct catalyst.

Samples of the airstream could be taken at several locations along the length of the duct allowing chemical characterization of the air stream at different stages of the air cleaning process. The locations of the sampling ports are shown in Figure 1.

Each sampling port was configured to allow detailed cross-plane sampling of the airstream within the duct. Samples were withdrawn from the duct through

1/4" OD stainless steel tubing. Three of these tubes were connected vertically in a fork-like configuration which could be moved to laterally (normal to the direction of air-flow) traverse the duct at each sampling port. Four header lines from each sampling station allowed simultaneous batch VOC analysis, continuous VOC analysis, ozone level monitoring, and subjective analysis. A schematic of the sample tube arrangement is shown in Figure 2.

The pre-prototype unit was constructed in the fall and early winter of 1990-91 in a research facility near Blacksburg, Virginia. The trials which used benzene as the challenge chemical were conducted between April 25 and September 26, 1991. Specifically, benzene trials were conducted on April 25, May 14, September 19, and September 26, 1991. During this time period the system was operated continuously with benzene and ozone being diffused into the airstream. The trials which used 2-butanol as the challenge chemical were conducted between January 15 and March 26, 1992. The 2-butanol trials were conducted on January 15 and 16, February 11, 17 and 19, and March 25 and 26, 1992. During this time period the system was only operated during the daytime on weekdays. The system was operated for several hours under the test conditions prior to collection of air samples.

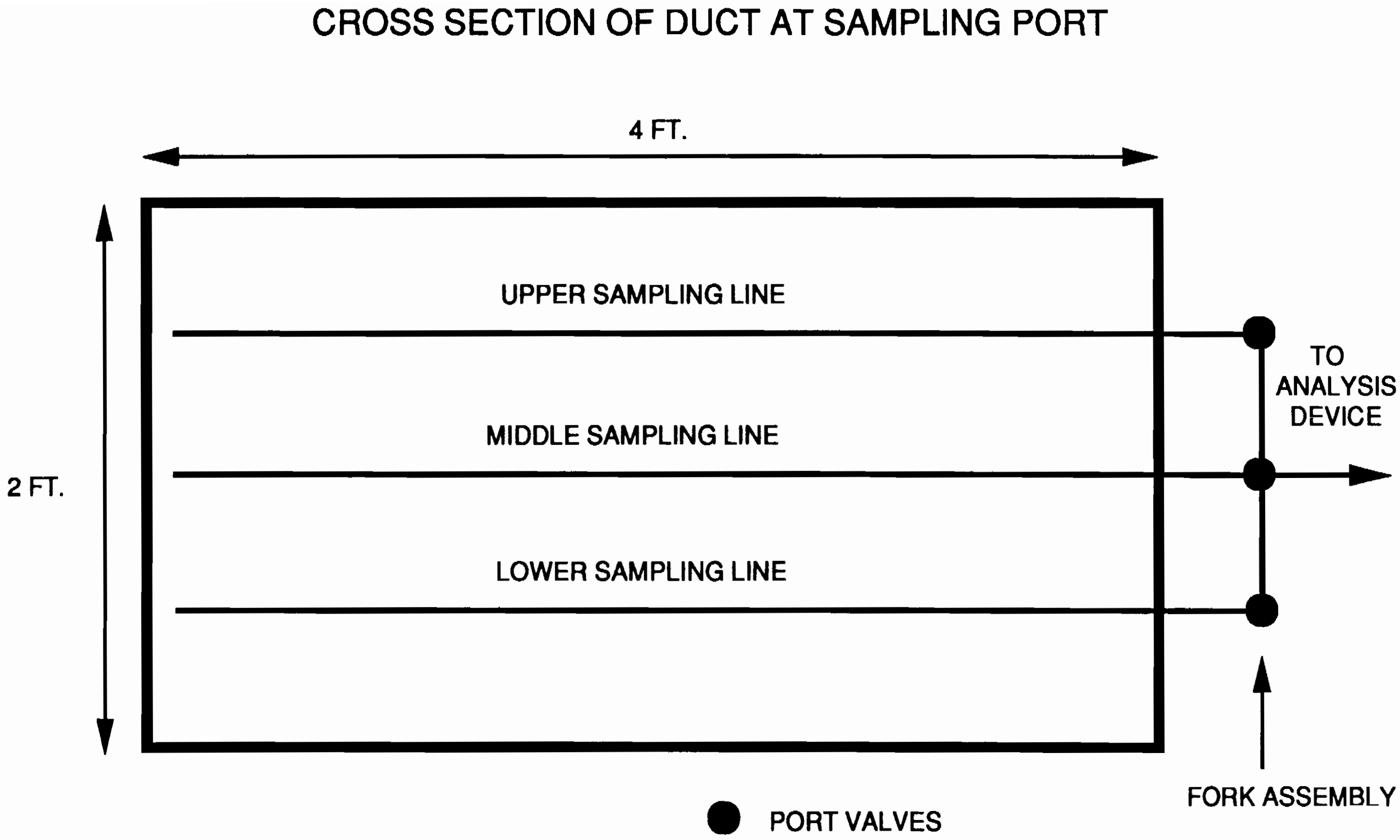


Figure 2. Schematic of sampling tube configuration. Drawing not to scale. Note: Fork assembly moves horizontally to allow cross section characterization. Port valves could be opened/closed with toggle switches so that sampling lines could be analyzed individually.

3.2.2 Sampling Instruments

Ozone levels in the duct were measured using two instruments. A Series 300B Computerized Ozone Analyzer from Environics (Middletown, CT) was used to measure ozone at levels between 1 and 10 ppb. Concentrations of ozone above 10 ppb and below 1500 ppb were measured by a Model #03DM-100 monitor from Ozone Research and Equipment Corporation (Phoenix, AZ). Flow from the duct to the ozone monitors was controlled by pumps within the instruments.

Continuous measurement of the total concentration of volatile organic compounds (TVOCs) in the duct was performed using a flame ionization analyzer. The instrument, model #FIA-23A with analysis section #30121, was purchased from Horiba Instruments Incorporated (Irvine, CA). Samples were withdrawn from the duct using a pump, model #2107CA18-515, produced by Thomas Instruments, Inc. (Sheboygan, WI).

Air samples taken from each port for batch VOC analysis or for carbonyl analysis were withdrawn using a pump, model #2E8666 Speed Air, from Dayton Electric Manufacturing Company (Chicago, IL). Air flow from each sampling port was controlled by a separate needle valve and measured using factory calibrated flow meters obtained from Dwyer Instruments, Inc. (Michigan City, IN). The control valves and flow meters were mounted on a central control panel.

Temperature and relative humidity probes, model # CT-839-A-H19-(0/100F)-(0-100%)-X20-X5 with probe IH-3602-E-8, were purchased from HY-CAL Engineering (El Monte, CA). These probes were located at sampling ports C, D, and E. Output from the probes was displayed on Beckman 500 Series indicators.

3.3 RESEARCH CHEMICALS AND SAMPLING EQUIPMENT

3.3.1 Chemicals

The following chemicals were purchased from Aldrich Chemical Company, Inc. (Milwaukee, WI): 2,4-dinitrophenylhydrazine (70% solid, 30% water) (CAS 119-26-6), formaldehyde(37% wt. in water) (CAS 50-00-0), acetaldehyde (99%) (CAS 75-07-0), butanal (99%) (CAS 123-72-8), 2-butanone (99.7%) (CAS 78-93-3), benzene (99%+) (CAS 71-43-2), and acetone (99.5%) (CAS 67-64-1). HPLC grade acetonitrile (CAS 75-05-8), 2-butanol (99%+) (CAS 15892-23-6), certified ACS Grade potassium iodide (CAS 7681-11-0), and certified ACS Grade hydrochloric acid (CAS 7647-01-0) were obtained from Fisher Scientific (Pittsburgh, PA). Reagent water was processed using a Milli-Q water purification system from Millipore Corporation (Milford, MA). Nitrogen was supplied by Industrial Gas and Supply, Inc. (Radford, VA).

3.3.2 Carbonyl Sampling Supplies

Thermosorb/F air sampling cartridges were purchased from Thermedics, Inc. (Woburn, MA). Sep-Pak DNPH-Silica cartridges were obtained from Waters Division of Millipore Corporation (Milford, MA).

3.4 GLASSWARE

All glassware used was washed in warm water and dish detergent, and then rinsed with distilled water and acetonitrile. Samples and standards were stored in either amber or Raysorb© glassware to prevent decomposition due to exposure to light.

3.5 SAMPLING STRATEGY

3.5.1 Sampling Port Locations

Air samples were collected from five specific sampling ports throughout the course of the study. These ports are labeled as ports A, B, C, D, and E in Figure 1. Each port corresponds to a different phase of the treatment process.

The air sampled at Port A was outdoor air that had been heated and humidified. This air had no chemical additions and is referred to as outdoor air. The challenge chemical was diffused into the duct upstream of sampling Port B.

The concentration of the chemical was fairly uniform throughout the cross section of the duct by the time it reached Port B (Holbrook, 1991). No ozone was present at this stage. Sample Port C was located downstream of the ozone diffusion system. The ozone concentration in the duct was fairly constant throughout the cross section of the duct at this location (Holbrook, 1991). Sample Port D was located just downstream of the hydrocarbon-oxidation catalyst and just upstream of the ozone destruct catalyst. Sample Port E was used to sample the duct air immediately downstream of the ozone destruct catalyst. This was the last stage of the treatment process at which air was sampled.

Samples were removed from a point in the cross section of the duct determined to be representative of the average concentration of the challenge chemical in the cross section at each specific sample port (Holbrook, 1991). The location of this point varied at each sample port but was kept constant for each port for the duration of the study, and was at the height in the duct corresponding to the location of the middle sampling line. For Ports A and D the point of average concentration was at the vertical and horizontal midpoint of the cross-section of the duct. For Port B, this point was displaced six inches horizontally from the cross section midpoint, in the direction away from the side of the duct containing the port. For Port C, this point was displaced 12 inches horizontally from the cross-section midpoint, in the direction towards the side of the duct containing the port. For Port E, this point was displaced 6 inches from the cross-section midpoint, in the direction of the side of the duct containing the port.

3.5.2 Test Conditions Used to Investigate Carbonyl Formation in the Pre-Prototype Indoor Air Pollution Abatement System.

In addition to sampling air from various stages of the air cleaning process, samples were collected while operating the system under four general test conditions. These conditions were used to assist in determining the factors affecting the formation of carbonyls in the airstream during the trials which used 2-butanol as the challenge chemical. Since the same condition was used for all four benzene trials, the four test conditions apply only to the 2-butanol trials. A summary of these test conditions is provided in Table 1; a detailed description follows.

The system was initially operated under conditions designed to simulate typical operating conditions that could be in an indoor environment. Both a challenge chemical (2-butanol) and ozone were diffused into the duct, at controlled concentrations, during these trials. This condition was referred to as "Condition One". The second set of conditions eliminated the use of ozone in the duct. The challenge chemical was diffused into the duct at a controlled rate.

Table 1: Summary of Experimental Conditions

TRIAL	CHALLENGE CHEM. mg/m^3 (ppm)	OZONE mg/m^3 (ppm)	DATE/TIME
BENZENE			
BENZENE-1	3.2 (1.0)	9.8 (5)	4/25/91 10am-2pm
BENZENE-2	3.2 (1.0)	43 (22)	5/14/91 9am-11am
BENZENE-3	3.2 (1.0)	9.8 (5)	9/19/91 12pm-3pm
BENZENE-4	3.0 (0.94)	9.8 (5)	9/26/91 12pm-3pm
2-BUTANOL			
O_3B-1 (Condition 1)	2.33 (.77)	9.8 (5)	1/15/92 10am-1pm
O_3B-2 (Condition 1)	1.63 (.54)	9.8 (5)	1/16/92 11am-3pm
O_3B-3 (Condition 1)	2.3-2.5(.76-.83)	9.8 (5)	2/19/92 10am-2pm
BUTANOL-1 (Condition 2)	2.0-2.6(.65-.85)	Not Applied	2/17/92 10am-1pm
BUTANOL-2 (Condition 2)	3 (1)	Not Applied	3/26/92 12pm-2pm
BUTANOL-3 (Condition 2)	3 (1)	Not Applied	3/26/92 3pm-5pm
OZONE-1 (Condition 3)	Not Applied	9.8 (5)	2/11/92 10am-1pm
OZONE-2 (Condition 3)	Not Applied	9.8 (5)	3/25/92 10am-1pm
OZONE-3 (Condition 3)	Not Applied	9.8 (5)	3/25/92 1pm-4pm
CLEAN-1 (Condition 4)	Not Applied	Not Applied	3/25/92 8am-10am

Note:
Ranges are given for applied 2-butanol concentrations when the applied concentration varied during the sampling period.

This set of conditions was referred to as "Condition Two". Trials were also run while operating only the ozone diffusion system. No challenge pollutant was introduced to the duct during these trials. This condition was referred to as "Condition Three". The system was also operated without the ozone or pollutant being introduced into the duct. This was designed to determine the effects of flushing relatively clean outdoor air through the system without any oxidant, and was referred to as "Condition Four".

Samples were collected in two major groups. The first group of samples was collected while benzene was being used as the challenge chemical. The second group of samples was collected while 2-butanol was being used as the challenge chemical.

During the trials using benzene, the system was only operated using both the challenge chemical (benzene) and ozone. Both benzene and ozone were diffused into the duct continuously during the period of several months during which the benzene trials were conducted. Four trials were conducted , each on a different day. These trials are referred to as Benzene-1, Benzene-2, Benzene-3 and Benzene-4 (Table 1).

A total of ten trials were conducted during the experiments which used 2-butanol as the challenge pollutant. The air cleaner system was not operated at night or on weekends during the 2-butanol trials. At least one trial was conducted under each of the four operating conditions (Table 1).

Three trials were conducted using Condition One. These trials are referred to as O_3B-1, O_3B-2, and O_3B-3. Prior to each of these trials the challenge chemical and ozone were both diffused into the airstream for several hours in an attempt to reach steady state conditions.

The three trials conducted using Condition Two are referred to as Butanol-1, Butanol-2, and Butanol-3. Trials Butanol-2 and Butanol-3 were conducted on the same date but were considered as separate trials and sample sets. Prior to these trials the challenge chemical was diffused into the duct for several hours to achieve steady state conditions.

The three trials conducted using Condition Three are identified Ozone-1, Ozone-2, and Ozone-3. Trials Ozone-2 and Ozone-3 were conducted on the same date but were considered separate trials and sample sets. Prior to these trials outdoor air was allowed to flush through the system for several hours.

One trial was conducted using operating Condition Four. This experiment is identified as trial Clean-1. Prior to this trial outdoor air was flushed through the system overnight.

During each trial an attempt was made to collect at least one sample from each port, but this was not always possible. Occasionally more than one sample was taken from a given port during a trial. All of the samples collected during a given trial, plus the corresponding blanks, comprised the complete sample set. The sample sets for each trial all included a laboratory blank and a field blank, with the exception of Benzene-1, which did not include a laboratory blank. The sample sets from trials Ozone-2 and Ozone-3 shared common laboratory and field blanks. The sample sets from trials Butanol-2, Butanol-3, and Clean-1 also shared common laboratory and field blanks.

The concentration of challenge chemical introduced to the air stream varied between trials that used a challenge chemical as a part of the test conditions (Table 1). During trials conducted with ozone in the system, the concentration of ozone was always 5 ppm, with one exception. In trial Benzene-2, a level of 22 ppm of ozone was used.

3.6 AIR SAMPLE COLLECTION FOR CARBONYL DETERMINATION

3.6.1 Air Sampling Cartridges

All samples obtained during the trials using benzene as the challenge pollutant were collected using Thermosorb/F air sampling cartridges. These cartridges contain a Florisil packing, and were prepared for sampling following the procedures outlined in EPA Method IP-6A.

The preparation of the Thermosorb/F cartridges involved four basic steps. First, solid DNPH was purified by recrystallizing from acetonitrile several times. Next, a coating solution was prepared by acidifying 100 milliliters (mL) of a saturated solution of DNPH with a hundred microliters of concentrated hydrochloric acid. Seven mL of the coating solution were then gravity fed through each unused cartridge. Finally, the cartridges were dried by blowing nitrogen through them for 15 minutes. The purity of the crystals and coating solutions was checked using the LC analysis discussed in the next section. The crystals and coating solutions were considered pure when no impurity peaks were detected using the LC analysis. The prepared cartridges were stored under nitrogen in airtight containers and refrigerated until used.

All samples obtained during the 2-butanol trials were collected using Sep-Pak DNPH-Silica Cartridges. These cartridges were pre-coated with DNPH by the manufacturer, and were used as delivered. They were stored under nitrogen in air-tight containers and refrigerated until used.

3.6.2 Air Sampling Method

Ozone has been shown to interfere with EPA Method IP-6A by reacting with DNPH and its hydrazone derivatives in the sampling cartridge. A scrubber device was used to remove ozone from the sample airstream before it passed through the sampling cartridge. The ozone scrubbers consisted of a three foot length of 1/4 in. OD copper tubing coated on the inside with potassium iodide. Proper performance of the scrubbers was verified prior to sampling using the Environics ozone monitor. Scrubbers were replaced when ozone levels in air passed through them exceeded 40 ppb.

A schematic of the sampling apparatus used is shown in Figure 3. This apparatus was connected to the sampling port using Swagelok fittings. Air was pulled from the duct, and through the ozone scrubber. The air then passed through the air sampler where carbonyls in the air stream were sorbed by reaction with DNPH. Short lengths (< 2 inches) of Tygon© tubing were used to connect the sampling cartridge to the ozone scrubber and to the stainless steel tubing leading to the pump. These connections were sealed with teflon tape. The air was then pulled through the needle valves and flow meters and was vented into the atmosphere.

Normally, two separate air samples were collected from two ports simultaneously, but occasionally one port was sampled alone or three ports were sampled at once (three individual samples collected simultaneously). The sampling period for each sample was long enough to filter approximately 50 liters of air. Since air flow rates through the cartridges were set as close to 1 liter per minute as possible, the sampling period was usually about 50 minutes. The sampling period was defined as the total amount of time a given cartridge spent in the sampling apparatus with duct air being drawn through it.

Initial flows through each cartridge were set as close to 1 liter per minute as possible using the needle valves and flow meters for each sample port. Actual air flow rate was measured at the beginning and end of collection of each sample

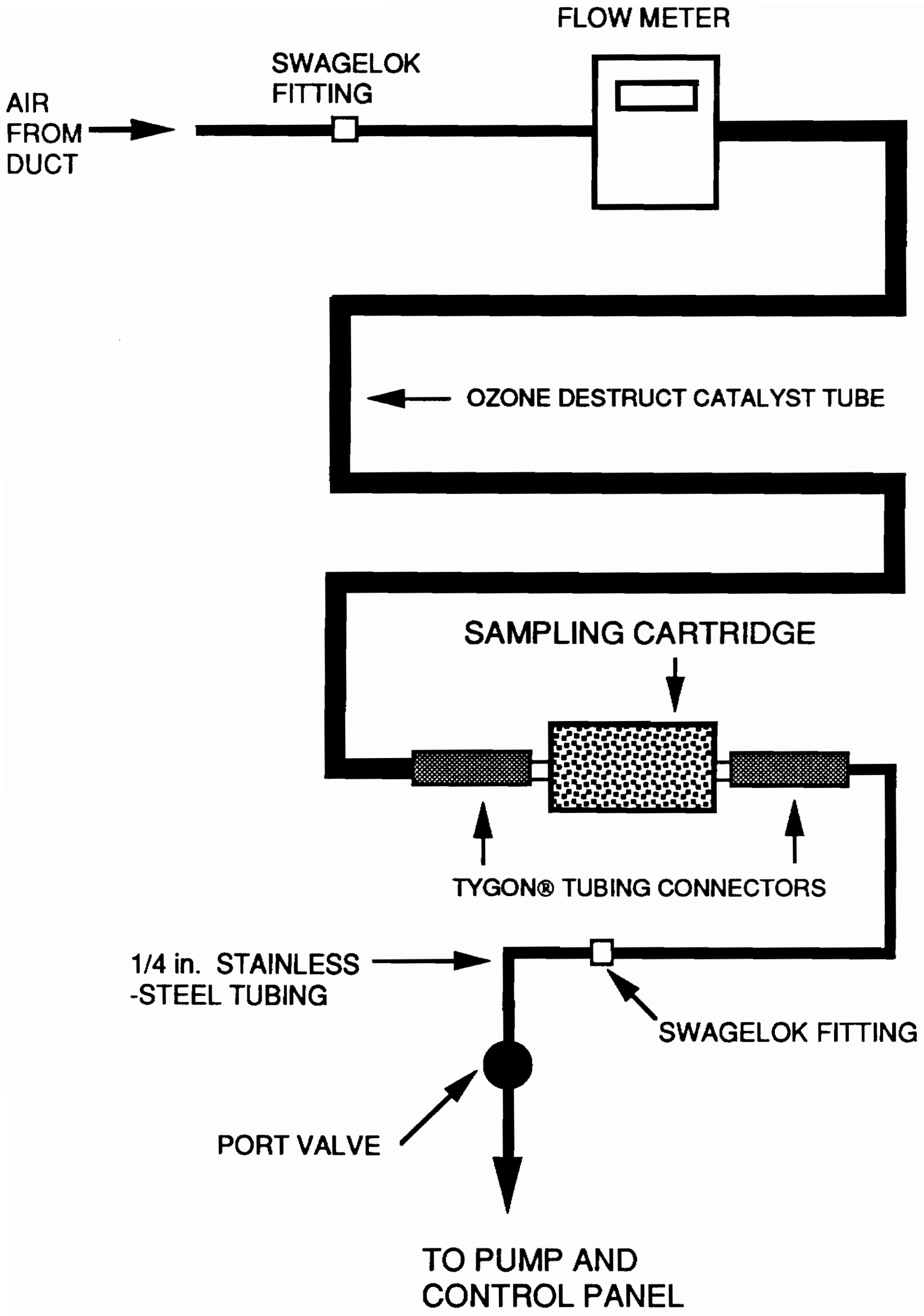


Figure 3. Schematic of sampling apparautus. Drawing not to scale.

using a Mass Flow Meter from Cole Parmer Instrument Company (Chicago, IL). This flow meter was also used to check the sampling apparatus for leaks prior to sample collection. The mass flow meter was installed between the sample port and the ozone scrubber while in use.

If air from only one port was being sampled at a given time, the mass flow meter was left in place throughout the sampling period. If two ports were sampled simultaneously the following method was used to obtain flow rates for each sample.

Both sampling apparatuses were set up and attached to the sampling port, one with the mass flow meter in line. Port valves allowing air to be pulled through the samplers were opened. The flow through the first cartridge was recorded. Port valves were closed. The mass flow meter was switched to the second sampling apparatus. Port valves were once again opened. Flow at the second cartridge was recorded immediately and once again at the end of the sampling period. Port valves were closed. The mass flow meter was switched back to the first sampling apparatus. Port valves were reopened. Final flow rate through the first cartridge was recorded. Port valves were closed. A similar method was used when air from three ports was sampled simultaneously. The possibility of cross contamination of the sampling cartridges was eliminated by using separate sampling apparatuses for each sampling cartridge in use.

Duplicate samples were collected by sampling the airstream at one port location with two cartridges in parallel. This was accomplished by splitting the air stream using a T-fitting and sampling each with a separate cartridge. Air flow rates were measured using the method previously discussed.

At the end of the sampling period the cartridges were removed from the sampling apparatus, plugged with polypropylene plugs, returned to storage in an air-tight container, and refrigerated.

Temperature and relative humidity levels of the airstream in the duct were recorded at the beginning and end of the sampling period for each cartridge. The temperature and relative humidity data for samples collected from sample ports A and B was taken using the probes at sample port C.

3.7 DETERMINATION OF CARBONYLS IN AIR SAMPLES

3.7.1 Sample Elution

Stored samples were eluted and analyzed within one week of sample collection. As per EPA Method IP-6A, each sample cartridge was eluted with 7 milliliters (mL) acetonitrile. Five mL of eluate was collected for analysis. A portion of the eluate was immediately analyzed by HPLC using the methods outlined in Method IP-6A and a portion of it was stored for confirmatory analyses.

3.7.1.1 Preparation of Carbonyl-DNPH Derivatives

It was necessary to prepare solid DNPH hydrazone derivatives for several carbonyls in order to perform qualitative and quantitative analyses of the samples. These solid derivatives were prepared using a modified version of the method suggested by EPA Method IP-6A.

Purified DNPH crystals were dissolved in 100 mL acetonitrile and brought to a boil. While the solution was boiling, drops of the individual carbonyl (e.g., 2-butanone, acetone, acetaldehyde, butanal, formaldehyde) were added with a dropper until the color of the solution was no longer visually changed by additional drops. This solution was then boiled down to a volume of 20 mL and then allowed to cool. The resulting crystals were then rinsed and purified by recrystallization as per Method IP-6A. The purity of the derivative crystals was verified using the LC analysis suggested in EPA Method IP-6A.

3.7.2 Liquid Chromatography (LC) Analysis

The eluate from each of the sample and blank cartridges was analyzed using a Hewlett-Packard 1090 Liquid Chromatograph (HPLC) (Avondale, PA) equipped with a diode array ultraviolet adsorption detector (DAD). The eluates from cartridges used in trial Benzene-1 were analyzed using a C-18 5u 4.6mm ID x 250mm reverse phase HPLC column from Alltech Associates, Inc. (Deerfield IL) in conjunction with a C-135B guard column from Upchurch Scientific Inc. The eluates from all other sampling cartridges used were analyzed using a Zorbax ODS 5u, 4.6mm ID x 250mm reverse phase HPLC column from MAC/MOD Analytical Inc. (Chadds Ford, PA), in conjunction with a C-135B guard column from Upchurch Scientific Inc.

The HPLC operating parameters suggested in EPA Method IP-6A were used for the HPLC analysis of all samples. The parameters used provided excellent peak separations for the carbonyls detected. All of the carbonyls detected had retention times of less than 10 minutes. A sample injection volume of 25 microliters (uL) and an oven temperature of 40°C were used. A mobile phase of acetonitrile and water was used at a flow rate of 1 mL/min. The DAD was programmed to measure absorbance at a wavelength of 360 nanometers (nm). The mobile phase was initially set at a ratio of 60% acetonitrile/40% Milli-$Q_{\circ}$ water. Over the first 30 minutes of the analysis this ratio was increased on a linear gradient until the ratio was 75% acetonitrile/25% water. The remainder of the gradient program was designed to flush the column. This flush sequence was modified for samples collected during 2-butanol testing to allow for shorter analysis time. Total LC run time was 71 minutes for samples from the benzene group and 52 minutes for samples from the 2-butanol group. The result of this analysis was a chromatogram that contained distinct contaminant peaks if carbonyls were present in the air sample. Chromatograms from trial O_3B-2 are shown in Appendix A.

3.7.3 Gas Chromatography (GC) Analysis

Gas chromatography analysis was performed on one sample set from the 2-butanol group to provide confirmation of the qualitative analysis done using LC data. The sample set, O_3B-2, was analyzed on Hewlett-Packard 5890 Gas Chromatograph equipped with a flame ionization detector (FID). A J & W Scientific 30m x 0.25mm DB-5 capillary column with 0.25 μm film thickness was used for the analysis. The injector temperature was set at 280 °C and the detector temperature was set at 300°C. The helium flow rate was set at 20 cm/sec. The initial oven temperature was 140 °C and increased at a rate of 8 C°/min to a final temperature of 280°C. A 2.5uL sample volume was injected using splitless injection.

3.7.4 GC/MS Analysis

Mass spectrometry was used to analyze one sample set from the 2-butanol group to provide additional data on the qualitative analysis of by-products. Sample set O_3B-2 and the DNPH hydrazone derivatives were analyzed using a Hewlett-Packard 5890 Series II Gas Chromatograph coupled to a Hewlett-Packard 5970 Mass Spectrometer. A 2.5 uL injection volume was injected onto a J & W Scientific 30m x 0.25mm DB-5 capillary column using splitless injection. The injector temperature was set at 250°C and the transfer line at 280°C. The helium flow rate was set at 30 cm/sec. The initial oven temperature was 140 °C and increased at a rate of 8 C°/min for twenty minutes to a final temperature of 300°C. The mass spectrometer was operated with 70 eV electrons, data were collected from 45-400 amu mass range with an approximate scan rate of 1 sec/scan. The mass spectrometer was calibrated with difluorotriphenylphosphate (DFTPP).

3.7.5 Qualitative Analysis

Prior to qualitative analysis of the trial samples, standard solutions at a concentration of 10 milligrams per liter (mg/L) were prepared from the DNPH-carbonyl derivative crystals. The chromatograms from LC analysis of the standard solutions for formaldehyde, acetaldehyde, acetone, and butanone are contained in Appendix B. The double peak for the DNPH-butanone derivative is a result of the presence of both cis and trans isomers of butanone.

Qualitative analysis of the carbonyls detected in samples from the trials were performed using the following three methods.

All of the samples and blanks were analyzed using the LC method previously described. The Diode Array Detector produced a chromatogram for each sample which plotted the absorbance of the sample at a wavelength of 360 nanometers (Y axis) versus retention time (X axis). Standard solutions containing potential DNPH-carbonyl derivatives were also analyzed using the LC method discussed earlier. The retention times of contaminant peaks in the chromatogram for each sample were compared to the retention times of the standards. If the retention time of a contaminant peak was within 2-3% of the retention time of one of the carbonyl derivative standards, it was concluded that the contaminant in question was the same compound as the standard. Samples of chromatograms of the standards used in this identification process are located in Appendix A. This procedure provided the initial identification for the contaminants found in each sample.

Gas chromatography was also used to identify contaminants found in samples. Standard solutions of the same DNPH-carbonyl derivatives used in the LC identification technique were analyzed using the GC method discussed earlier. Samples from trial O_3B-2 were subsequently analyzed using the same GC method. The FID chromatogram displayed the retention time for each contaminant detected. The retention times of contaminant peaks in the chromatogram from each sample were compared to the retention times of the standards. If the retention time of a contaminant peak was within 2% of the retention time of a standard, the contaminant was identified as the corresponding standard carbonyl. Sample chromatograms from the GC analyses are contained in Appendix B. It is uncertain why the DNPH-acetaldehyde derivative eluted as a double peak during these analyses. This method confirmed the identifications done using LC analysis.

Gas chromatography/mass spectrometry was also used to provide additional confirmation for qualitative analysis of the samples collected during the 2-butanol trials. The standard solutions of DNPH-carbonyl derivatives (same as described above) were used to provide retention time data for each by-product of interest. The eluate from samples from trial O_3B-2 were used to generate mass spectra and retention times for contaminant peaks. Contaminant peaks in the samples were tentatively identified using the comparative methods previously discussed. The mass spectrum of the contaminant peak was then compared to the mass spectrum of the corresponding standard to positively identify the carbonyl. Mass spectra of the DNPH-carbonyl derivatives for formaldehyde, acetaldehyde, acetone, and butanone are contained in Appendix C.

This combination of methods was used to positively identify several carbonyl compounds found in the air samples collected during the trials.

3.7.6 Quantitative Analysis

The total air volume of each air sample collected was adjusted to give a sample volume at standard temperature (25°C) and pressure (760mm Hg). It was assumed that the pressure in the duct was atmospheric, so correction was done for deviations from standard temperature only. The adjusted volume was calculated using equation (1).

$V_{stp} = V_{measured} * [298/(273 + T)]$ (1)

V_{stp} = volume adjusted for deviation from standard temperature, L

$V_{measured}$ = measured sample volume, L

T = average temperature of air sampled, °C

To facilitate quantification of the carbonyl concentrations detected in the samples collected, four-point standard curves were prepared for the DNPH-carbonyl derivatives of formaldehyde, acetaldehyde, acetone, and butanone. These standard curves were prepared from stock solutions prepared using DNPH-carbonyl derivative crystals. The ranges of concentrations used bracketed the concentrations found in the large majority of the samples. Carbonyl concentrations outside the range of the corresponding standard curve were quantified and a note was made of the circumstance.

A standard linear regression was performed on the data used to create each standard curve using Quatro-Pro© computer software (Tables 4-7). The resulting regression equation was then used with the integrated peak area from the sample chromatogram to determine the concentration of each DNPH-carbonyl derivative detected in the sample eluate. For samples containing butanone, the combined area of the cis and trans isomer peaks was used. Equation (2) was then used to determine the total mass of the contaminant in the sample cartridge.

$W_s = (C_{eluate})(V_s)$ (2)

W_s = total analyte mass in the sample cartridge, ug

C_{eluate} = concentration of the analyte in the sample eluate, ug/mL

V_s = total volume of the sample cartridge eluate, mL

Next, equation (3) was used to determine the total contaminant mass originating in the sampled air volume. The analyte mass found in the field blank for each sample was subtracted from the total analyte mass found in the sample cartridge.

$$W_t = W_s - W_b \qquad (3)$$

W_t = total analyte mass from volume of sampled air, ug

W_b = analyte mass in the field blank, ug

Equation (4) was then used to determine the concentration of the contaminant in the original air sample.

$$C_a = W_t * (MW_{ald}/MW_{der}) * (1000 ng/ug/V_{stp}) \quad (4)$$

C_a = concentration of analyte in the air sample, ng/L

MW_{ald} = molecular weight of the analyte, g/g-mole

MW_{der} = molecular weight of the DNPH derivative of the analyte, g/g-mole

3.7.6.1 Quantification Example

The eluate (5 mL) from a 50 liter air sample (already adjusted for deviation from standard temperature and pressure) was analyzed using the aforementioned LC technique and was found to have a formaldehyde derivative peak with an area count of 200. Using the regression equation from Figure 4, the corresponding concentration in the eluate is determined:

$$C_{eluate} = (\text{Area} - (\text{Y-intercept}))/\text{Slope}$$

Using 200 for the Area variable, and the Y-intercept (-2.784) and Slope (68.507) values found in Figure 4, the value of C_{eluate} is found to be 2.96 ug/ml. Equation 2 was then used to find the total analyte mass in the sample cartridge:

$$W_s = 2.96 \text{ ug/ml} * 5 \text{ ml} = 14.8 \text{ ug}$$

For simplicity, assume that the field blank contained no formaldehyde derivative so that the total analyte mass from the volume of air sample, W_t, was also equal to 14.8 ug. Equation 4 was then used to determine the concentration of formaldehyde in the original air sample:

$$C_a = 14.8 * (30/210) * (1000\text{ng/ug}/50 \text{ L})$$

$$C_a = 42.2 \text{ ng/L}$$

3.8 STATISTICAL ANALYSIS

Standard analysis-of-variance (ANOVA) tests were performed on the carbonyl data using the software package SYSTAT. The purpose of these tests was to determine, if possible, which factors influenced the concentrations of each of the four carbonyl compounds detected. A 90% confidence level was needed for a variable to be considered a significant factor affecting the formation of each carbonyl. Data from all samples collected during the 2-butanol tests were used for these analyses.

Four ANOVAs were performed, one for each carbonyl detected. In each test, the by-product concentration was used as the dependent variable. Independent variables used were temperature (Temperature), relative humidity (Humidity), sampling location in the duct (Port), presence of ozone (Ozone), presence of the challenge chemical (2-butanol), and two interaction variables. The first interaction variable tested the significance of the interaction of the presence of ozone and the presence of 2-butanol (Ozone*2-butanol). The second interaction variable tested the significance of the interaction of three factors: presence of ozone, presence of the challenge pollutant, and the sampling location (Ozone*2-butanol*Port). The variable Port effectively tested the significance of the stage of treatment, since each sample port was located at a different stage of the air cleaning process.

3.9 QUALITY CONTROL AND QUALITY ASSURANCE

3.9.1 System Performance

Prior to LC analysis of each sample set, the LC column was solvent flushed using a set of flush parameters. A 25 uL sample of Milli-Q© water was injected onto the column for the flush cycle. Oven temperature was set at 40°C and a flow rate of 1 milliliter (mL) per minute was used. The mobile phase was initially set at 100% water and ramped to 100% acetonitrile over a period of 10 minutes. Pure acetonitrile was then flushed through the column for two minutes. Over the next four minutes the percent acetonitrile was dropped to 60% and held at that level for four more minutes. This concluded the flush cycle. The mobile phase was then kept at 40% Milli-Q© water/60% acetonitrile until sample analysis.

In addition, on each day the LC was used to analyze samples or standards, a sample of DNPH coating solution was also analyzed. The retention time and area of the DNPH peak were compared to data from previous analyses of the same coating solution to verify that the system performance had not changed. If the retention time and the area count were consistent with previously gathered data, then instrument performance was considered acceptable.

3.9.2 Blanks And Duplicates

Each sample which was collected and analyzed had one field blank and one laboratory blank associated with it, with the exception of samples from trial Benzene-1, which had no laboratory blank. A field blank was carried to the field sampling site during each trial. The package containing the field blank was opened while sampling was conducted with other cartridges, but no air was pulled through it. The field blank was stored and analyzed with the other cartridges in its sample set. Laboratory blanks were stored and analyzed with the other sample cartridges in the sample set but were not brought to the sample site on the date of the trial.

Field blanks generally contained more contamination than lab blanks so they were used to adjust the carbonyl concentrations found in the relevant air samples. All blanks were eluted and analyzed using the same LC method used to analyze the samples from the corresponding sample set.

No duplicate samples were collected during the benzene trials. Duplicate samples were collected at a single sampling port during trials O_3B-2, Ozone-1, and O_3B-3.

3.9.3 Instrument Detection Limits (IDLs) and Limits of Quantification (LOQ)

Instrument detection limits were determined by analyzing a solution containing a low concentration of the DNPH derivative of each carbonyl found in the samples. This concentration was set at approximately five times the expected detection limit. The prepared solution contained 0.1 mg/L concentrations of the DNPH derivatives of formaldehyde, acetaldehyde, acetone, and 2-butanone. Ten aliquots of the solution were analyzed. A blank of acetonitrile was analyzed prior to and immediately following the analysis of each detection limit sample. The area count of each hydrazone peak was adjusted by subtracting off the average of the area counts from the blanks preceding and following each sample. An IDL for each carbonyl was then produced using equation (5). An LOQ for each carbonyl was computed using equation (6).

$$IDL = [\,(C_{STD})(3 * SD)]/Mean \qquad (5)$$

IDL = instrument detection limit, mg/L

$$LOQ = [\,(C_{STD})(10 * SD)]/Mean \qquad (6)$$

LOQ = limit of quantification, mg/L

C_{STD} = Concentration of hydrazone in standard, mg/L

SD = standard deviation of area counts from ten samples

Mean = average of area counts from ten samples

The IDL and LOQ for each carbonyl was converted to units of ng/L using equations (2) and (4). The IDL and LOQ for each carbonyl detected in the air samples are contained in Table 2.

Table 2. **Instrument Detection Limits (IDL) and Limits of Quantification (LOQ) for DNPH derivatives.**

CARBONYL	IDL ng/L (ppb)	LOQ ng/L (ppb)
Formaldehyde	0.49 (0.4)	1.6 (1.3)
Acetaldehyde	0.83 (0.46)	2.7 (1.5)
Acetone	0.83 (0.35)	2.5 (1.1)
Butanone	2.0 (.68)	6.7 (2.3)

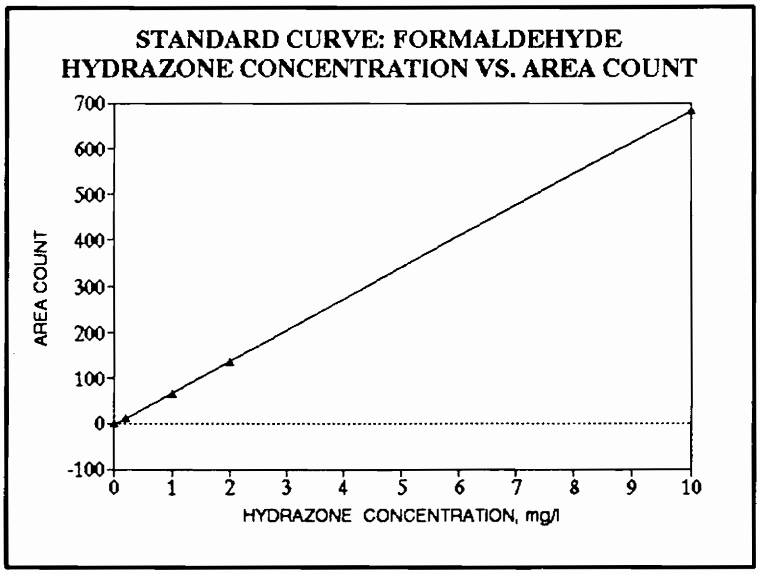
CHAPTER 4. RESULTS

4.1 SUMMARY

In this chapter, the standard curves used for quantitative analysis of the samples from the 2-butanol trials are presented, along with the quantitative and qualitative results of the benzene trials and the 2-butanol trials. No carbonyls were detected in any of the air samples collected during the benzene trials. Four different carbonyls were detected in air samples collected during the 2-butanol trials. All chemical concentrations are reported in volume measurements, i.e., ppbv or ppmv.

4.2 STANDARD CURVES

The standard curves used to quantify the carbonyls found in air samples collected during the 2-butanol trials are presented in Figures 4-7. Figure 4 shows the standard curve for the DNPH-formaldehyde derivative and Figure 5 shows the standard curve for the DNPH-acetaldehyde derivative. Figure 6 shows the standard curve for the DNPH-acetone derivative, and Figure 7 shows the standard curve for the DNPH-butanone derivative. The regression data presented in each figure was used to calculate the concentration of the corresponding carbonyl in each air sample.

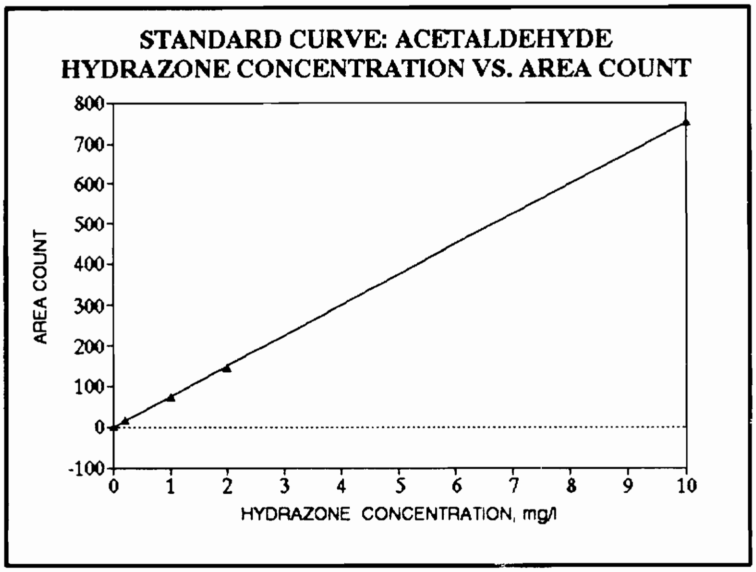


Regression Output:

Constant	-2.78401
Std Err of Y Est	2.255776
R Squared	0.999954
No. of Observations	5
Degrees of Freedom	3

X Coefficient(s)	68.50758
Std Err of Coef.	0.269248

Figure 4. Standard curve and regression data for determination of formaldehyde-DNPH derivative in eluate of air sampling cartridge. Slope = 68.507, Y-intercept = -2.784

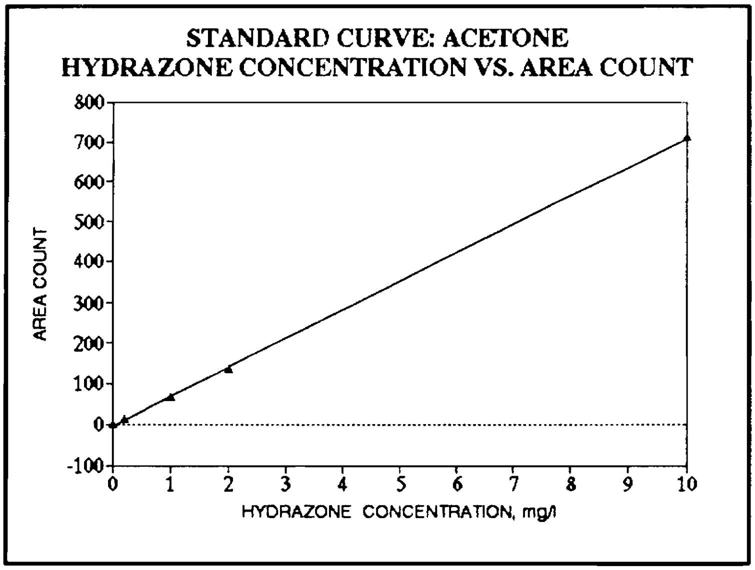


Regression Output:

Constant	-2.29022
Std Err of Y Est	3.175302
R Squared	0.999924
No. of Observations	5
Degrees of Freedom	3

X Coefficient(s)	75.36271
Std Err of Coef.	0.379002

Figure 5. Standard curve and regression data for determination of acetaldehyde in eluate from air sampling cartridge. Slope = 75.363, Y-intercept = -2.29.

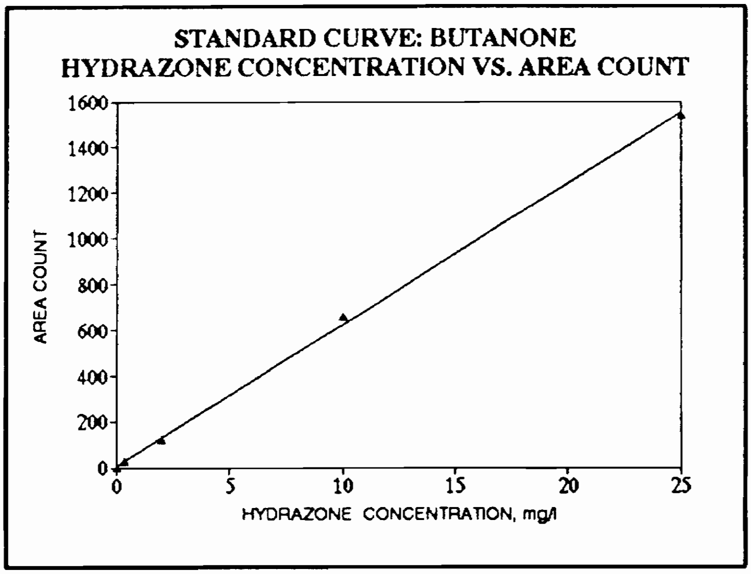


Regression Output:

Constant	-3.52158
Std Err of Y Est	3.948458
R Squared	0.999869
No. of Observations	5
Degrees of Freedom	3

X Coefficient(s)	71.23393
Std Err of Coef.	0.471285

Figure 6. Standard curve and regression data for determination of acetone in eluate of air sampling cartridge. Slope = 71.234, Y-intercept = -3.521.



Regression Output:	
Constant	5.617375
Std Err of Y Est	20.37596
R Squared	0.999276
No. of Observations	5
Degrees of Freedom	3

X Coefficient(s)	61.82959
Std Err of Coef.	0.961165

Figure 7. Standard curve and regression data for determination of butanone in eluate of sampling cartridge. Slope = 61.83, Y-intercept = 5.617.

4.3 RESULTS OF BENZENE TRIALS

Air samples were collected on four different days while both benzene and ozone were being diffused into the system. Analysis of these samples revealed that, once field blank levels were accounted for, no carbonyls were present in the air samples at detectable levels. Concurrent research indicated that benzene levels were reduced by approximately 50% when the inlet concentration of benzene was 1.3 ppm and the ozone concentration was 5.2 ppm (Rodberg et al., 1991). The results of the benzene sampling data are presented in Tables 3-6. The concentration of benzene and ozone used on each sampling date are shown along with the average temperature and relative humidity in the duct during the sampling period.

4.4 RESULTS OF 2-BUTANOL TRIALS

4.4.1 General

Air samples were collected under four test conditions. These included samples taken while 2-butanol and ozone were diffused into the system (Condition One), while 2-butanol alone was diffused into the system (Condition Two), while ozone alone was diffused into the system (Condition Three), and while only conditioned outdoor air was passed through the unit (Condition Four). Samples for carbonyl determination were collected at Ports A, B, C, D, and E. Port E represented air which would be reintroduced to the occupied space after treatment by the indoor air pollution abatement system.

Four carbonyls, including formaldehyde, acetaldehyde, acetone, and butanone, were detected in the airstream within the air cleaning system during the 2-butanol trials. EPA Method IP-6A is capable of detecting 15 carbonyls from 1-carbon (formaldehyde) to 9-carbon (2,5-dimethylbenzaldehyde). Inspection of the HPLC chromatograms did not indicate the presence of other carbonyls in these samples.

The results of each individual trial are presented in a table and a bar graph. The table includes the applied concentrations of 2-butanol and ozone (ppmv), as well as the average temperature and average relative humidity in the duct during the trial. A range of 2-butanol concentrations is given for trials during which the concentration varied. The concentrations of the carbonyls detected at the sampling ports are also presented. The bar graph for each sample set shows the concentration of each carbonyl detected at the various stages of the air cleaning system. The scale on the y-axis of the bar graphs for the Condition One trial results is different than the scale used on the other bar graphs. The concentrations are presented as nanograms per liter (note: nanograms per liter of air are equivalent to micrograms per cubic meter of air). Concurrent research found that experiments conducted under similar conditions in the same time frame showed an average reduction in 2-butanol of 26% (Holbrook, 1991).

Table 3. Summary of Trial Benzene-1: Test conditions and carbonyl concentrations detected.

Trial:	**Benzene-1**		
Date: 4/25/91		Time:	10am-2pm
Benzene Concentration, mg/m³ (ppm):	3.2 (1)		
Ozone Concentration, mg/m³ (ppm):	9.8 (5)		
Average Temperature, °C:	17.8		
Average Relative Humidity, %:	40.6		

	Carbonyl Concentrations ng/L (ppb)			
Port	Formaldehyde	Acetaldehyde	Acetone	Butanone
B	N.D.*	N.D.	N.D.	N.D.
C	N.D.	N.D.	N.D.	N.D.
D	N.D.	N.D.	N.D.	N.D.
E	N.D.	N.D.	N.D.	N.D.

Notes:
Sample was not collected at Sample Port A
* N.D. = Not Detected

Table 4. **Summary of Trial Benzene-2: Test conditions and carbonyl concentrations detected.**

Trial: **Benzene-2**

Date: 5/14/91 Time: 9am-11am

Benzene Concentration, mg/m^3 (ppm): 3.2 (1)

Ozone Concentration, mg/m^3 (ppm): 43 (22)

Average Temperature, °C: 18.8

Average Relative Humidity, %: 40.7

	Carbonyl Concentrations ng/L (ppb)			
Port	Formaldehyde	Acetaldehyde	Acetone	Butanone
B	N.D.*	N.D.	N.D.	N.D.
C	N.D.	N.D.	N.D.	N.D.
D	N.D.	N.D.	N.D.	N.D.

Notes:
Samples were not collected at Sample Ports A and E
* N.D. = Not Detected

Table 5. **Summary of Trial Benzene-3: Test conditions and carbonyl concentrations detected.**

Trial:	**Benzene-3**		
Date: 9/19/91		Time:	12pm-3pm
Benzene Concentration, mg/m^3 (ppm):		3.2 (1)	
Ozone Concentration, mg/m^3 (ppm):		9.8 (5)	
Average Temperature, °C:		24.6	
Average Relative Humidity, %:		45.8	

	Carbonyl Concentrations ng/L (ppb)			
Port	Formaldehyde	Acetaldehyde	Acetone	Butanone
B	N.D.*	N.D.	N.D.	N.D.
C	N.D.	N.D.	N.D.	N.D.
$D_1$$	N.D.	N.D.	N.D.	N.D.
D_2	N.D.	N.D.	N.D.	N.D.
E	N.D.	N.D.	N.D.	N.D.

Notes:
Sample was not collected at Sample Port A
[*] N.D. = Not Detected
[$] Data shown is for two separate samples taken at separate times from Sample Port D during this Trial

Table 6. **Summary of Trial Benzene-4: Test conditions and carbonyl concentrations detected.**

Trial:	**Benzene-4**		
Date: 9/26/91		Time:	12pm-3pm
Benzene Concentration, mg/m^3 (ppm):		3.0 (0.94)	
Ozone Concentration, mg/m^3 (ppm):		9.8 (5)	
Average Temperature, °C:		25	
Average Relative Humidity, %:		31	

	Carbonyl Concentrations ng/L (ppb)			
Port	Formaldehyde	Acetaldehyde	Acetone	Butanone
B	N.D.*	N.D.	N.D.	N.D.
C	N.D.	N.D.	N.D.	N.D.
$D_1$$	N.D.	N.D.	N.D.	N.D.
D_2	N.D.	N.D.	N.D.	N.D.
E	N.D.	N.D.	N.D.	N.D.

Notes:
Sample was not collected at Sample Port A
* N.D. = Not Detected
$ Data shown is for two separate samples taken at separate times from Sample Port D during this Trial

4.4.2 Condition One Trial Results and Trends

Air samples were collected on three days while both 2-butanol and ozone were being diffused into the system. These sample sets were designated O_3B-1, O_3B-2, and O_3B-3.

The test conditions and results of the laboratory analysis of air samples collected during trial O_3B-1 are contained in Table 7 and Figure 8. No samples were collected from Port A during this trial. No carbonyls were detected in the samples collected at Port B. Note the increase in acetaldehyde to 130 ng/L downstream of the ozone destruct catalyst (ODC) at Port E. Also note that the levels of butanone were several hundred ppbs higher upstream of the hydrocarbon destruct catalyst (HDC) at Port C, downstream of the HDC at Port D, and downstream of the ODC at Port E, than levels detected at Port B.

The test conditions and results of the laboratory analysis of air samples collected during trial O_3B-2 are contained in Table 8 and Figure 9. Note the increased levels of formaldehyde (24 ng/L) and acetaldehyde (130, 170 ng/L) downstream of the HDC at Port E. Also note that the levels of butanone detected upstream of the HDC at Port C (300 ng/L), downstream of the HDC at Port D (300 ng/L), and downstream of the ODC at Port E (79, 93 ng/L) were higher than concentrations detected at Ports A and B.

The test conditions and results of the laboratory analysis of air samples collected during trial O_3B-3 are contained in Table 9 and Figure 10. Note that

Table 7. Summary of Trial O_3B-1: Test conditions and carbonyl concentrations detected.

Trial:	**O_3B-1**		
Date: 1/15/92		Time:	10am-1pm
2-Butanol Concentration, mg/m^3 (ppm):	2.33 (0.77)		
Ozone Concentration, mg/m^3 (ppm):	9.8 (5)		
Average Temperature, °C:	22.2		
Average Relative Humidity, %:	10.5		

	Carbonyl Concentrations ng/L (ppb)			
Port	Formaldehyde	Acetaldehyde	Acetone	Butanone
B	N.D.	N.D.	N.D.	N.D.
C	N.D.	19 (10)	6.7 (2.8)	342 (120)
D	16 (13)	27 (15)	8.0 (3.4)	450 (150)
E	28 (23)	130 (74)	8.8 (3.7)	120 (42)

Notes:
Sample was not collected at Sample Port A
[*] N.D. = Not Detected

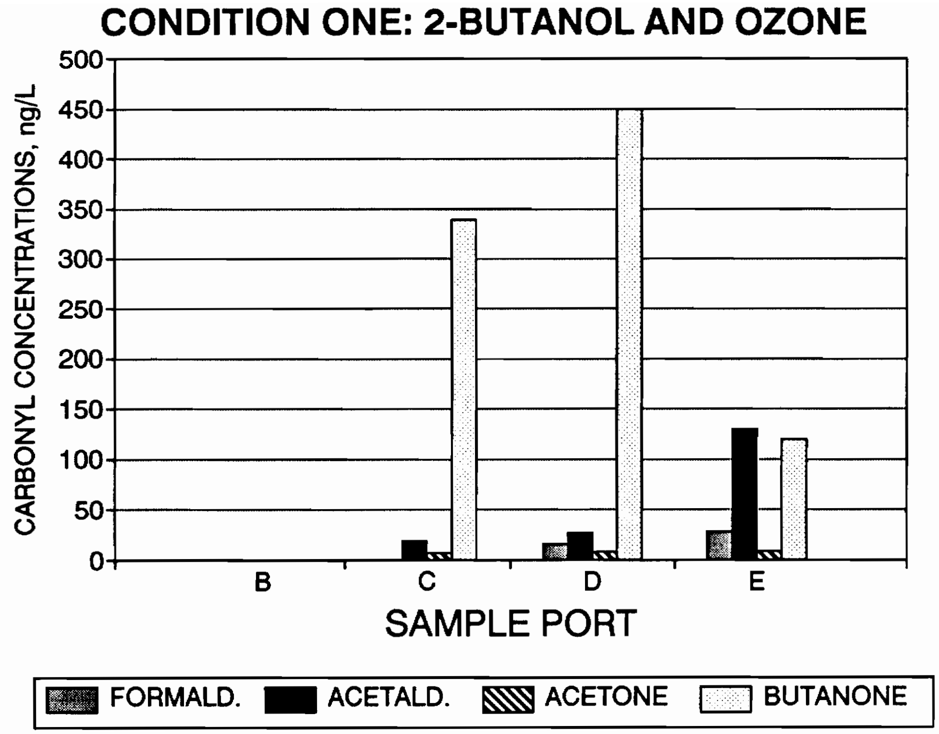


Figure 8. Carbonyl concentrations detected in the duct airstream at sampling ports B, C, D, and E during trial O_3B-1. Note: 1) Sample Port B was located between the challenge pollutant diffuser and the ozone diffuser. Sample C was located just upstream of the hydrocarbon destruct catalyst. Sample Port D was located between the hydrocarbon destruct catalyst and the ozone destruct catalyst. Sample Port E was located downstream of the ozone destruct catalyst. 2) No carbonyls were detected at Port B; Formaldehyde was not detected at Port C.

Table 8. **Summary of Trial O_3B-2: Test conditions and carbonyl concentrations detected.**

Trial:	**O_3B-2**		
Date: 1/16/92		Time:	11am-3pm
2-Butanol Concentration, mg/m^3 (ppm):		1.63 (0.54)	
Ozone Concentration, mg/m^3 (ppm):		9.8 (5)	
Average Temperature, °C:		20.9	
Average Relative Humidity, %:		4.6	

	Carbonyl Concentrations ng/L (ppb)			
Port	Formaldehyde	Acetaldehyde	Acetone	Butanone
A	N.D.*	N.D.	N.D.	48 (16)
B	N.D.	N.D.	N.D.	19 (6.6)
C	N.D.	35 (19)	8.1 (3.4)	300 (100)
D	5.6 (4.5)	17 (14)	6.2 (2.6)	300 (100)
E_1#	24 (19)	170 (94)	8.6 (3.6)	93 (32)
E_2	24 (19)	130 (70)	6.3 (2.6)	79 (27)

Notes:
* N.D. = Not Detected
# Data shown is for duplicate samples collected (in parallel) at Sampling Port E

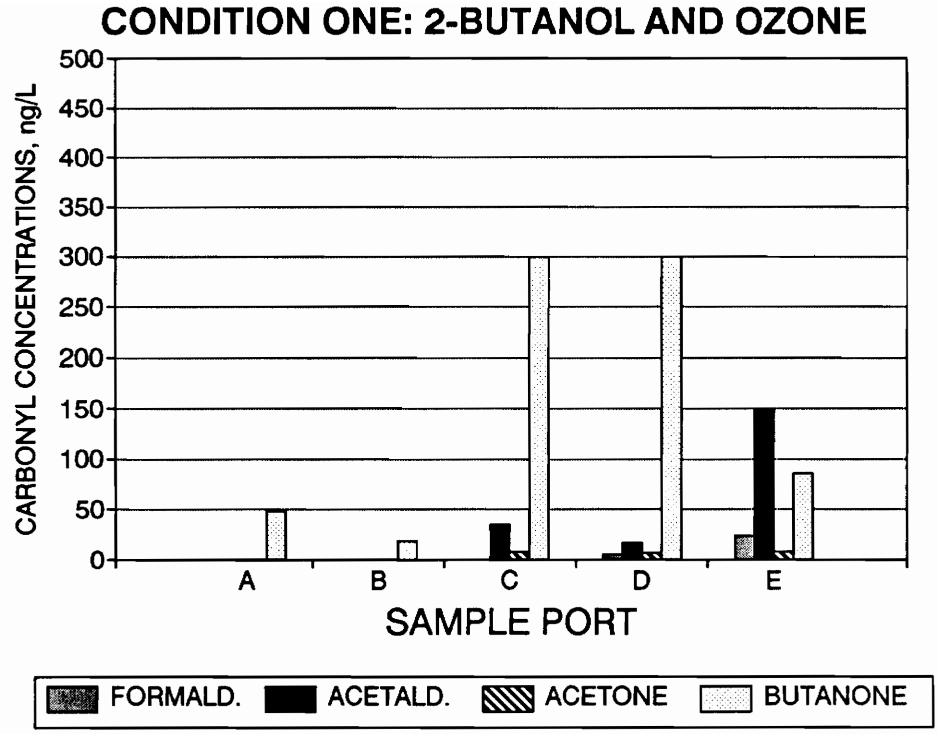


Figure 9. Carbonyl concentrations detected in the duct airstream at sampling ports A, B, C, D, and E during trial O_3B-2. Note: 1) Sample Port A was located upstream of the challenge pollutant diffuser. Sample Port B was located between the chemical pollutant diffuser and the ozone diffuser. Sample Port C was located just upstream of the hydrocarbon destruct catalyst. Sample Port D was located between the hydrocarbon destruct catalyst and the ozone destruct catalyst. Sample Port E was located downstream of the ozone destruct catalyst. 2) Formaldehyde, acetaldehyde, and acetone were not detected at Ports A and B; formaldehyde was not detected at Port C. 3) Data for Port E is average of duplicate samples.

Table 9. Summary of Trial O_3B-3: Test conditions and carbonyl concentrations detected.

Trial: **O_3B-3**	
Date: 2/19/92	Time: 10am-2pm
2-Butanol Concentration, mg/m^3 (ppm):	2.3-2.5 (0.76-0.83)[@]
Ozone Concentration, mg/m^3 (ppm):	9.8 (5)
Average Temperature, °C:	18
Average Relative Humidity, %:	36

	Carbonyl Concentrations ng/L (ppb)			
Port	Formaldehyde	Acetaldehyde	Acetone	Butanone
A	N.D.[*]	N.D.	4.9 (2.1)[&]	N.D.
B	N.D.	N.D.	8.5 (3.6)	N.D.
C_1[#]	5.0 (4)	4.8 (2.7)	8.8 (3.7)	10 (3.6)
C_2	N.D.	N.D.	3.1 (1.3)[&]	19 (6.3)
D_1[$]	16 (13)	29 (16)	73 (31)	260 (89)
D_2	N.D.	20 (11)	8.6 (3.6)	250 (84)
E_1[$]	N.D.	70 (39)	94 (40)	360 (122)
E_2	8.2 (6.7)	63 (35)	19 (8.1)	269 (91)

Notes:

[@] The applied 2-Butanol concentration varied during the sampling period. The applied concentration was 2.5 mg/m^3 (0.83 ppm) during sampling at Sampling Ports A and B. The applied concentration was 2.37 mg/m^3 (0.79 ppm) during sampling at Sampling Port C. The applied concentration was 2.3 mg/m^3

Table 9, Continued.

(0.76 ppm) during sampling at Sampling Ports D and E.

[*] N.D. = Not Detected

[&] Data not bracketed by standard curve used for quantification

[#] Data shown is for duplicate samples collected in parallel at Sampling Port C on this date

[$] Data shown is for two separate samples collected at separate times from Sampling Port D and two separate samples collected at separate times from Sampling Port E

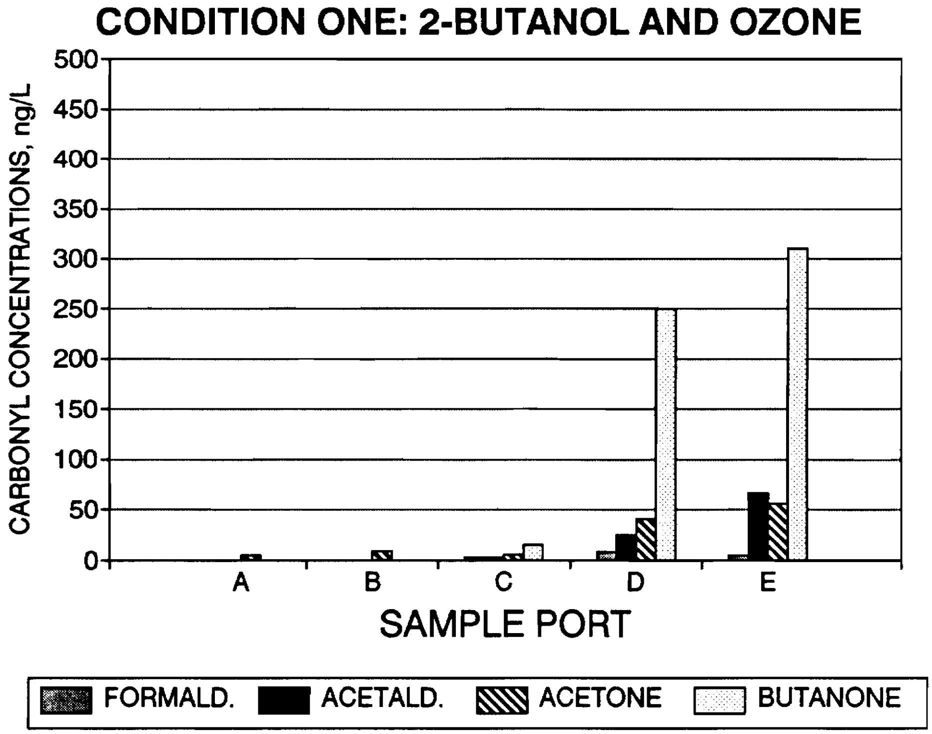


Figure 10. Carbonyl concentrations detected in the duct airstream at sampling ports A, B, C, D, and E during trial O_3B-3. Note: 1) Sample Port A was located upstream of the challenge pollutant diffuser. Sample Port B was located between the chemical pollutant diffuser and the ozone diffuser. Sample Port C was located just upstream of the hydrocarbon destruct catalyst. Sample Port D was located between the hydrocarbon destruct catalyst and the ozone destruct catalyst. Sample Port E was located downstream of the ozone destruct catalyst. 2) Formaldehyde, acetone, and butanone were not detected at Ports A and B. 3) Data for Ports C, D, and E are average values.

acetaldehyde and butanone concentrations increased downstream of the HDC at Port D, and downstream of the ODC at Port E, similar to the results from trials O_3B-1 and O_3B-2.

The results from these three trials show several trends. Formaldehyde was detected prior to the HDC in only one air sample, at a very low level of 5 ng/L. Formaldehyde was present at low levels (less than 30 ng/L) in several air samples collected downstream of the HDC and ODC at Ports D and E. Acetaldehyde was not detected prior to the ozone diffuser, but tended to increase to low levels (5-35 ng/L) downstream of the ozone diffuser at Ports C and D. The acetaldehyde concentrations were higher downstream of the ODC (63-170 ng/L). Levels of acetone in the duct were very low or undetectable regardless of the sampling location. Butanone concentrations in the duct generally increased from low levels (e.g., 19, 48 ng/L) upstream of the ozone diffuser to much higher levels downstream of the ozone diffuser (e.g., 450, 300 ng/L). The levels of butanone detected at Port C were much higher in trials O_3B-1 and O_3B-2 compared to trial O_3B-3. This same trend is noticeable to a lesser degree for acetaldehyde and acetone. The relative humidity during trials O_3B-1 and O_3B-2 (4.6, 10.5 %) was significantly lower than that of trial O_3B-3 (36 %). Butanone concentrations tended to decline somewhat downstream of the ODC during these trials.

4.4.3 Condition Two Trial Results and Trends

Three trials were conducted while diffusing 2-butanol alone into the air cleaning system. These trials were designated Butanol-1, Butanol-2, and Butanol-3.

The test conditions and results of the laboratory analysis of air samples collected during trial Butanol-1 are contained in Table 10 and Figure 11. No sample was collected at sample Port B during this trial. Note the high concentrations of butanone detected in the air samples collected downstream of the HDC at Port D (100 ng/L), and downstream of the ODC at Port E (83 ng/L), relative to the levels detected at Ports A and C.

The test conditions and results of the laboratory analysis of samples collected during trial Butanol-2 are contained in Table 11 and Figure 12.
Note the elevated levels of butanone detected in the air samples collected downstream of the HDC at Port D (78 ng/L), and downstream of the ODC at Port E (54 ng/L), relative to the levels detected at Ports A, B, and C.

The test conditions and results of the laboratory analyses of samples collected during trial Butanol-3 are contained in Table 12 and Figure 13. Note the elevated levels of butanone detected in the air samples collected downstream of the HDC at Port D (73 ng/L), and downstream of the ODC at Port E (62 ng/L), following the trend found in trials Butanol-1 and Butanol-2.

Table 10. **Summary of Trial Butanol-1: Test conditions and carbonyl concentrations detected.**

Trial: **Butanol-1**	
Date: 2/17/92	Time: 10am-1pm
2-Butanol Concentration, mg/m³ (ppm):	2.0-2.6 (0.65-0.85)[@]
Ozone Concentration, mg/m³ (ppm):	Not Applied
Average Temperature, °C:	17.1
Average Relative Humidity, %:	28

	Carbonyl Concentrations ng/L (ppb)			
Port	Formaldehyde	Acetaldehyde	Acetone	Butanone
A	N.D.*	N.D.	N.D.	N.D.
C	N.D.	N.D.	N.D.	N.D.
D	4.4 (3.6)	5.6 (3.1)	N.D.	100 (34)
E	7.4 (6)	9.4 (5.2)	N.D.	83 (28)

Notes:
Sample was not collected from Sample Port B

[@] The applied concentration of 2-Butanol varied during the sampling period. The applied concentration was 2.0 mg/m³ (0.65 ppm) during sampling at Sample Ports A and C. The applied concentration was 2.6 mg/m³ (0.85 ppm) during sampling at Sample Ports D and E.

* N.D. = Not Detected

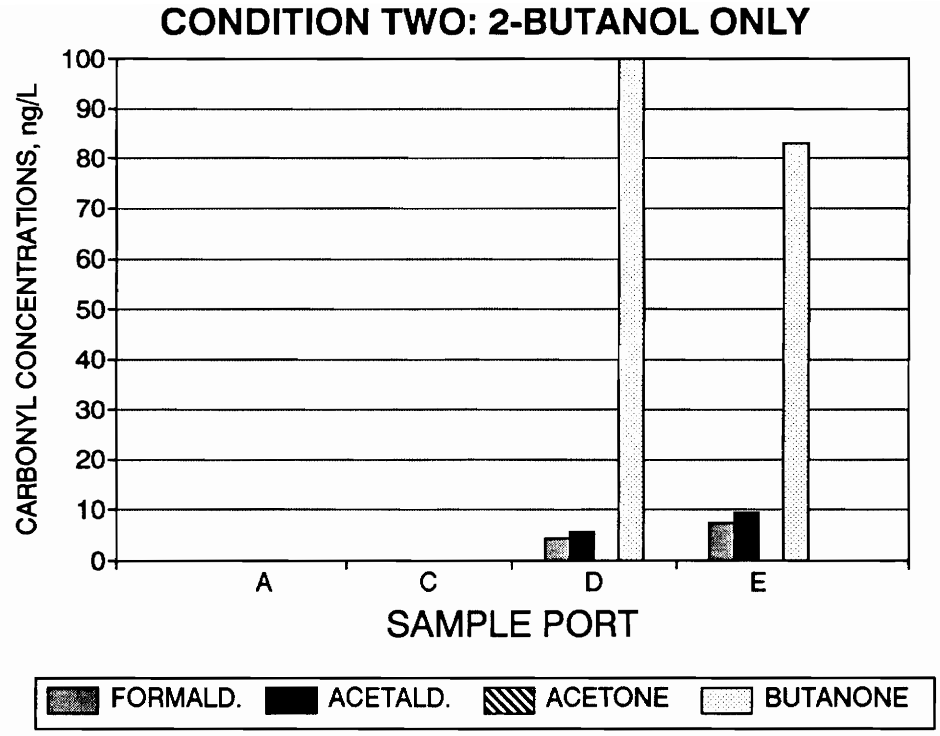


Figure 11. Carbonyl concentrations detected in the duct airstream at sampling ports A, C, D, and E during trial Butanol-1. Note: 1) Sample Port A was located upstream of the challenge pollutant diffuser. Sample Port C was located just upstream of the hydrocarbon destruct catalyst. Sample Port D was located between the hydrocarbon destruct catalyst and the ozone destruct catalyst. Sample Port E was located downstream of the ozone destruct catalyst. 2) No carbonyls were detected at Ports A and C; acetone was not detected at any of the sampling ports.

Table 11. **Summary of Trial Butanol-2: Test conditions and carbonyl concentrations detected.**

Trial: **Butanol-2**	
Date: 3/26/92	Time: 12pm-2pm
2-Butanol Concentration, mg/m^3 (ppm):	3.0 (1.0)
Ozone Concentration, mg/m^3 (ppm):	Not Applied
Average Temperature, °C:	18.3
Average Relative Humidity, %:	40.7

	Carbonyl Concentrations ng/L (ppb)			
Port	Formaldehyde	Acetaldehyde	Acetone	Butanone
A	5.6 (4.6)	N.D.[*]	16 (6.7)	N.D.
B	4.2 (3.5)	N.D.	15 (6.5)	N.D.
C	3.4 (2.8)	N.D.	12 (5.2)	N.D.
D	4.3 (3.5)	3.8 (2.1)[&]	10 (4.4)	78 (26)
E	5.1 (4.2)	5.6 (3.1)	12 (4.9)	54 (18)

Notes:
[*] N.D. = Not Detected
[&] Data not bracketed by standard curve used for quantification

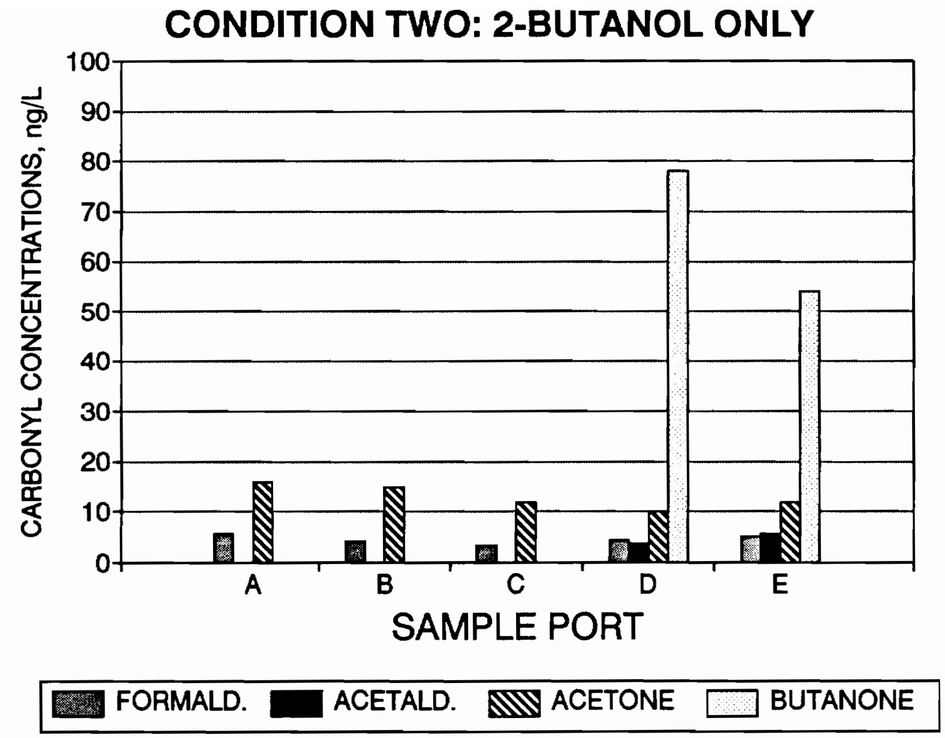


Figure 12. Carbonyl concentrations detected in the duct airstream at sampling ports A, B, C, D, and E during trial Butanol-2. Note: 1) Sample Port A was located upstream of the challenge pollutant diffuser. Sample Port B was located between the chemical pollutant diffuser and the ozone diffuser. Sample Port C was located just upstream of the hydrocarbon destruct catalyst. Sample Port D was located between the hydrocarbon destruct catalyst and the ozone destruct catalyst. Sample Port E was located downstream of the ozone destruct catalyst. 2) Acetaldehyde and butanone were not detected at Ports A, B, and C.

Table 12. Summary of Trial Butanol-3: Test conditions and carbonyl concentrations detected.

Trial: **Butanol-3**	
Date: 3/26/92	Time: 3pm-5pm
2-Butanol Concentration, mg/m^3 (ppm):	3.0 (1.0)
Ozone Concentration, mg/m^3 (ppm):	Not Applied
Average Temperature, °C:	17.5
Average Relative Humidity, %:	40

	Carbonyl Concentrations ng/L (ppb)			
Port	Formaldehyde	Acetaldehyde	Acetone	Butanone
A	6.3 (5.2)	N.D.[*]	7.9 (3.3)	N.D.
B	6.2 (5.1)	N.D.	9.0 (3.8)	N.D.
C	4.0 (3.3)	N.D.	5.5 (2.3)	N.D.
D	4.4 (3.6)	4.0 (2.2)[&]	16 (6.6)	73 (25)
E	5.4 (4.4)	5.8 (3.2)	15 (6.5)	62 (21)

Notes:

[*] N.D. = Not Detected

[&] Data not bracketed by standard curve used for quantification

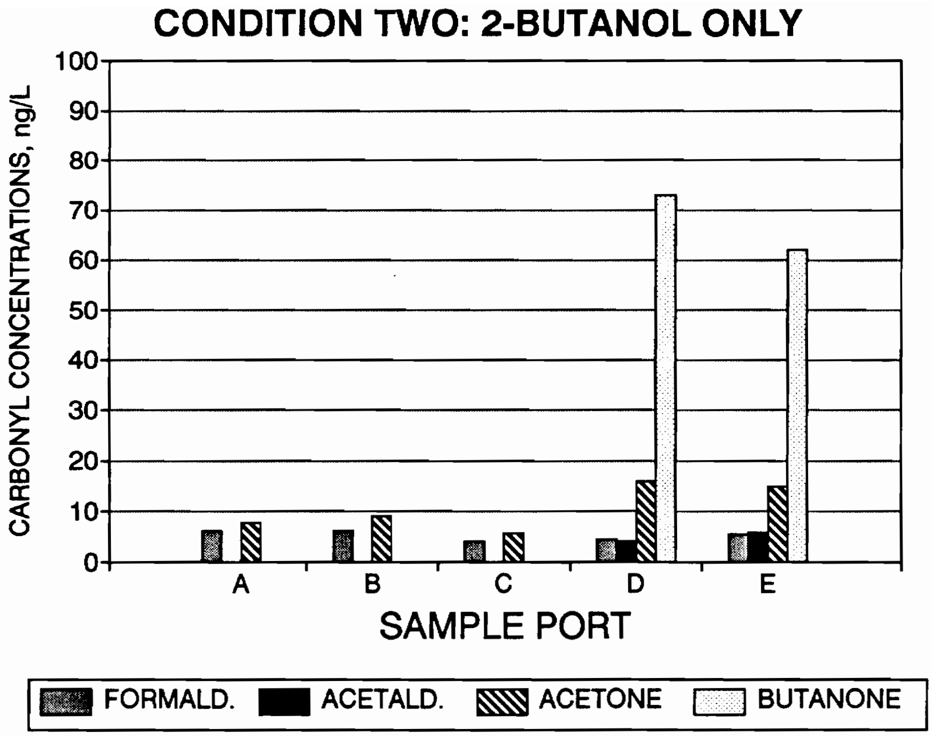


Figure 13. Carbonyl concentrations detected in the duct airstream at sampling ports A, B, C, D, and E during trial Butanol-3. Note: 1) Sample Port A was located upstream of the challenge pollutant diffuser. Sample Port B was located between the chemical pollutant diffuser and the ozone diffuser. Sample Port C was located just upstream of the hydrocarbon destruct catalyst. Sample Port D was located between the hydrocarbon destruct catalyst and the ozone destruct catalyst. Sample Port E was located downstream of the ozone destruct catalyst. 2) Acetaldehyde and butanone were not detected at Ports A, B, and C.

The carbonyl data collected during the Condition Two trials exhibited several trends. Formaldehyde and acetone were detected at all stages of the air cleaning process at low levels (3.4 - 16 ng/L). Acetaldehyde was detected at low levels downstream of the HDC (3.8 - 5.6 ng/L) and downstream of the ODC (5.6 - 9.4 ng/L) but was not detected upstream of the HDC. Butanone was not detected prior to the HDC but levels increased sharply downstream of the HDC before declining to somewhat lower levels downstream of the ODC.

4.4.4 Condition Three Trial Results and Trends

Three trials were conducted while ozone alone was diffused into the duct. These trials were designated Ozone-1, Ozone-2, and Ozone-3.

The test conditions and results of the laboratory analyses of air samples collected during trial Ozone-1 are reported in Table 13 and Figure 14. No samples were collected at sample Port A during this trial. Note the higher levels of formaldehyde detected downstream of the HDC at Port D (14, 19 ng/L) and downstream of the ODC at Port E (22 ng/L), compared to the concentrations detected at Ports B and C. Acetaldehyde levels were also higher at Port D (16, 18 ng/L) and Port E (43 ng/L) than at Ports B and C. Butanone levels followed this same general trend with 95 and 98 ng/L detected at Port D and 67 ng/L detected at Port E.

The test conditions and results of the laboratory analyses of air samples collected during trial Ozone-2 are contained in Table 14 and Figure 15. No sample was collected at Port B during this trial. Note the elevated concentrations of acetaldehyde and butanone detected in the air samples collected downstream of the HDC at Port D (16 and 51 ng/L, respectively) and downstream of the ODC at Port E (23 and 23 ng/L respectively).

The test conditions and results of the laboratory analysis of samples collected during trial Ozone-3 are contained in Table 15 and Figure 16. No sample was collected at Port B during this trial. Note the elevated levels of formaldehyde and acetaldehyde detected downstream of the ODC at Port E (14 and 34 ng/L respectively), and the elevated levels of butanone detected downstream of the HDC and ODC at Ports D and E (50 and 23 ng/L respectively).

There were several trends from the Condition Three trials worth noting. Formaldehyde and acetaldehyde levels in the duct generally increased downstream of the HDC. Acetone levels were either very low or undetectable at all of the sampling locations. Butanone was not detected upstream of the HDC but higher concentrations were detected downstream of the HDC at Ports D (50-98 ng/L) and E (23-67 ng/L).

Table 13. **Summary of Trial Ozone-1: Test conditions and carbonyl concentrations detected.**

Trial:	**Ozone-1**
Date: 2/11/92	Time: 10am-1pm
2-Butanol Concentration, mg/m^3 (ppm):	Not Applied
Ozone Concentration, mg/m^3 (ppm):	9.8 (5)
Average Temperature, °C:	18
Average Relative Humidity, %:	25.4

	Carbonyl Concentrations ng/L (ppb)			
Port	Formaldehyde	Acetaldehyde	Acetone	Butanone
B	12 (9.8)	4.2 (2.3)[&]	6.7 (2.8)	N.D.[*]
C	9.8 (8.0)	5.3 (2.9)	8.4 (3.5)	N.D.
D_1[#]	14 (12)	16 (9.2)	11 (4.6)	95 (32)
D_2	19 (16)	18 (9.8)	14 (6.0)	98 (33)
E	22 (18)	43 (24)	12 (5.1)	67 (23)

Notes:
Sample was not collected at Sample Port A
[*] N.D. = Not Detected
[#] Data shown is for duplicate samples collected (in parallel) at Sampling Port D
[&] Data not bracketed by standard curve used for quantification

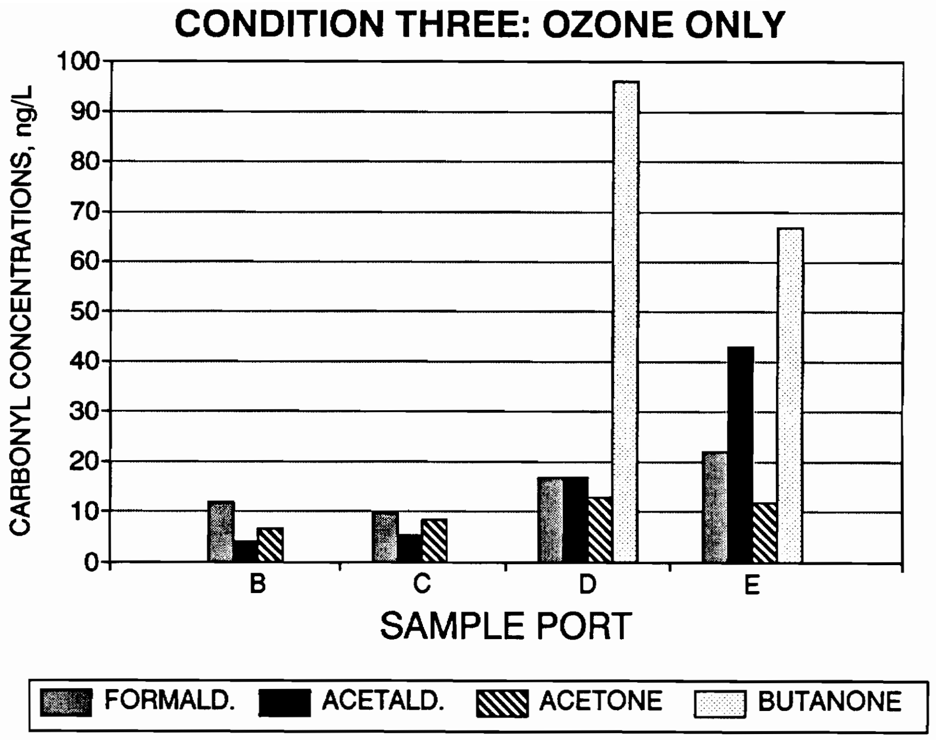


Figure 14. Carbonyl concentrations detected in the duct airstream at sampling ports B, C, D, and E during trial Ozone-1. Note: 1) Sample Port B was located between the challenge pollutant diffuser and the ozone diffuser. Sample C was located just upstream of the hydrocarbon destruct catalyst. Sample Port D was located between the hydrocarbon destruct catalyst and the ozone destruct catalyst. Sample Port E was located downstream of the ozone destruct catalyst. 2) Butanone was not detected at Ports B and C. 3) Data shown for Port D is average of duplicate samples.

Table 14. Summary of Trial Ozone-2: Test conditions and carbonyl concentrations detected.

Trial: **Ozone-2**	
Date: 3/25/92	Time: 10am-1pm
2-Butanol Concentration, mg/m^3 (ppm):	Not Applied
Ozone Concentration, mg/m^3 (ppm):	9.8 (5)
Average Temperature, °C:	18
Average Relative Humidity, %:	21.8

	Carbonyl Concentrations ng/L (ppb)			
Port	Formaldehyde	Acetaldehyde	Acetone	Butanone
A	5.1 (4.1)	N.D.	N.D.	N.D.
C	N.D.*	N.D.	N.D.	N.D.
D	13 (11)	16 (9.0)	10 (4.4)	51 (17)
E	5.7 (4.7)	23 (13)	N.D.	23 (7.7)

Notes:
Sample was not collected from Sample Port B
* N.D. = Not Detected

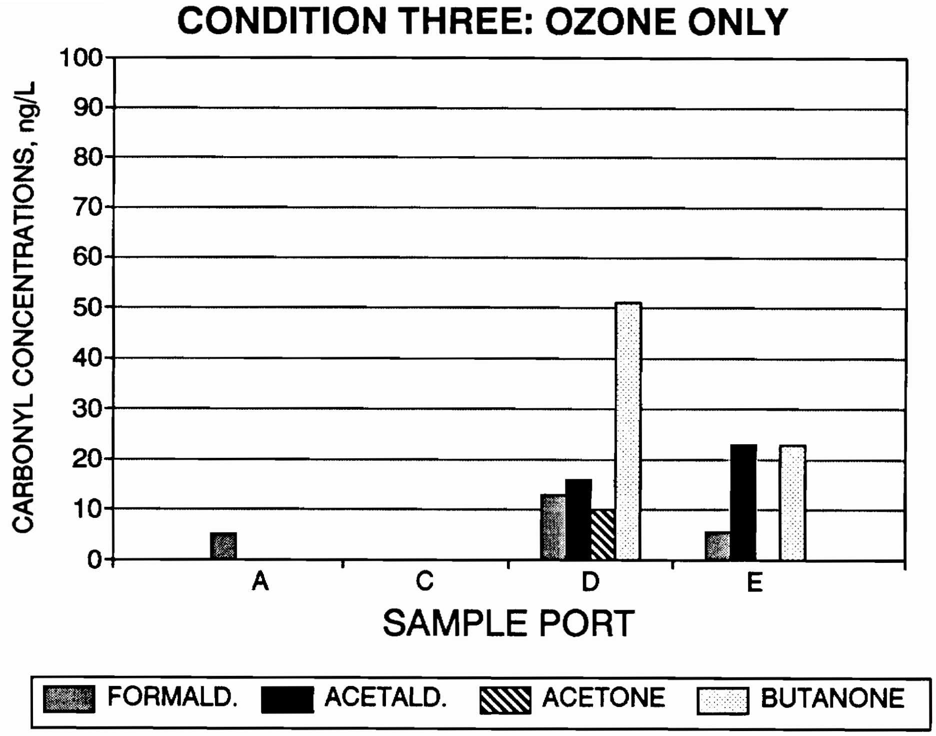


Figure 15. Carbonyl concentrations detected in the duct airstream at sampling ports A, C, D, and E during trial Ozone-2. Note: 1) Sample Port A was located upstream of the challenge pollutant diffuser. Sample Port C was located just upstream of the hydrocarbon destruct catalyst. Sample Port D was located between the hydrocarbon destruct catalyst and the ozone destruct catalyst. Sample Port E was located downstream of the ozone destruct catalyst. 2) Acetaldehyde, acetone, and butanone were not detected at Port A; no carbonyls were detected at Port C.

Table 15. **Summary of Trial Ozone-3: Test conditions and carbonyl concentrations detected.**

Trial: **Ozone-3**	
Date: 3/25/92	Time: 1pm-4pm
2-Butanol Concentration, mg/m³ (ppm):	Not Applied
Ozone Concentration, mg/m³ (ppm):	9.8 (5)
Average Temperature, °C:	18.1
Average Relative Humidity, %:	25.4

	Carbonyl Concentrations ng/L (ppb)			
Port	Formaldehyde	Acetaldehyde	Acetone	Butanone
A	4.7 (3.8)	N.D.	N.D.	N.D.
C	N.D.*	N.D.	5.3 (2.2)&	N.D.
D	11 (9.2)	12 (6.7)	4.5 (1.9)&	50 (17)
E	14 (12)	34 (19)	N.D.	23 (7.7)

Notes:

Sample was not collected from Sample Port B

* N.D. = Not Detected

& Data not bracketed by Standard Curve used for quantification

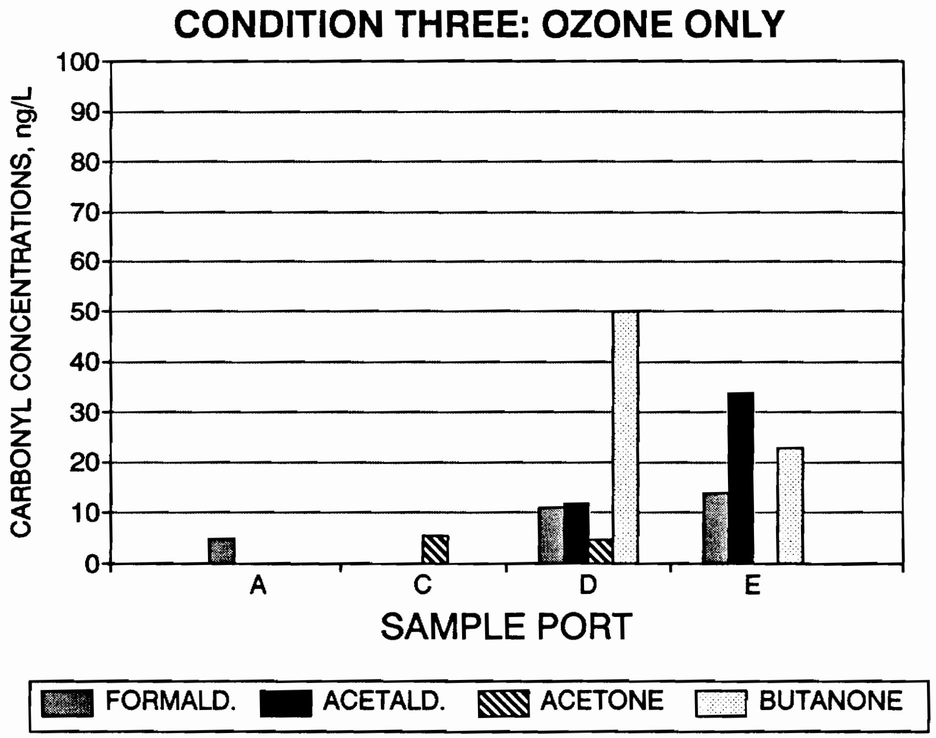


Figure 16. Carbonyl concentrations detected in the duct airstream at sampling ports A, C, D, and E during trial Ozone-3. Note: 1) Sample Port A was located upstream of the challenge pollutant diffuser. Sample Port C was located just upstream of the hydrocarbon destruct catalyst. Sample Port D was located between the hydrocarbon destruct catalyst and the ozone destruct catalyst. Sample Port E was located downstream of the ozone destruct catalyst. 2) Acetaldehyde, acetone, and butanone were not detected at Port A; formaldehyde, acetaldehyde, and butanone were not detected at Port C.

4.4.5 Condition Four Trial Results and Trends

Samples were collected on one day while outdoor air alone was flushed through the system. It had been several days since 2-butanol had been diffused into the system, and 16 hours since ozone had been diffused into the system. This sample set was designated Clean-1. The test conditions and results of the laboratory analyses of air samples collected during trial Clean-1 are reported in Table 16 and Figure 17. No sample was collected at Port B during this trial. Acetaldehyde was detected at very low levels downstream of the HDC and the ODC at Ports D (6.6 ng/L) and E (6.5 ng/L). Acetone was detected at very low levels at all stages of the air cleaner at which samples were collected. Butanone was not detected in air samples collected upstream of the HDC; levels had increased downstream of the HDC at Port D (74 ng/L) and remained at about the same level downstream of the ODC at Port E (65 ng/L).

4.4.6 Overall Carbonyl Concentration Trends in Pre-Prototype Air Cleaner System

A comparison of the carbonyl concentrations formed under each test condition revealed some interesting trends. Formaldehyde levels in the airstream were very low regardless of the test condition or sample location with two exceptions. When either ozone alone or both ozone and 2-butanol were diffused into the system, formaldehyde levels appeared to increase slightly downstream

Table 16. Summary of Trial Clean-1: Test conditions and carbonyl concentrations detected.

Trial: **Clean-1**

Date: 3/26/92	Time: 8am-10am
2-Butanol Concentration, mg/m^3 (ppm):	Not Applied
Ozone Concentration, mg/m^3 (ppm):	Not Applied
Average Temperature, °C:	18.4
Average Relative Humidity, %:	40.3

	Carbonyl Concentrations ng/L (ppb)			
Port	Formaldehyde	Acetaldehyde	Acetone	Butanone
A	N.D.*	N.D.	6.3 (2.6)	N.D.
C	4.9 (4.0)	N.D.	6.8 (2.9)	N.D.
D	N.D.	6.6 (3.7)	8.4 (3.5)	74 (25)
E	N.D.	6.5 (3.6)	8.1 (3.4)	65 (22)

Notes:
Sample was not collected from Sample Port B
* N.D. = Not Detected

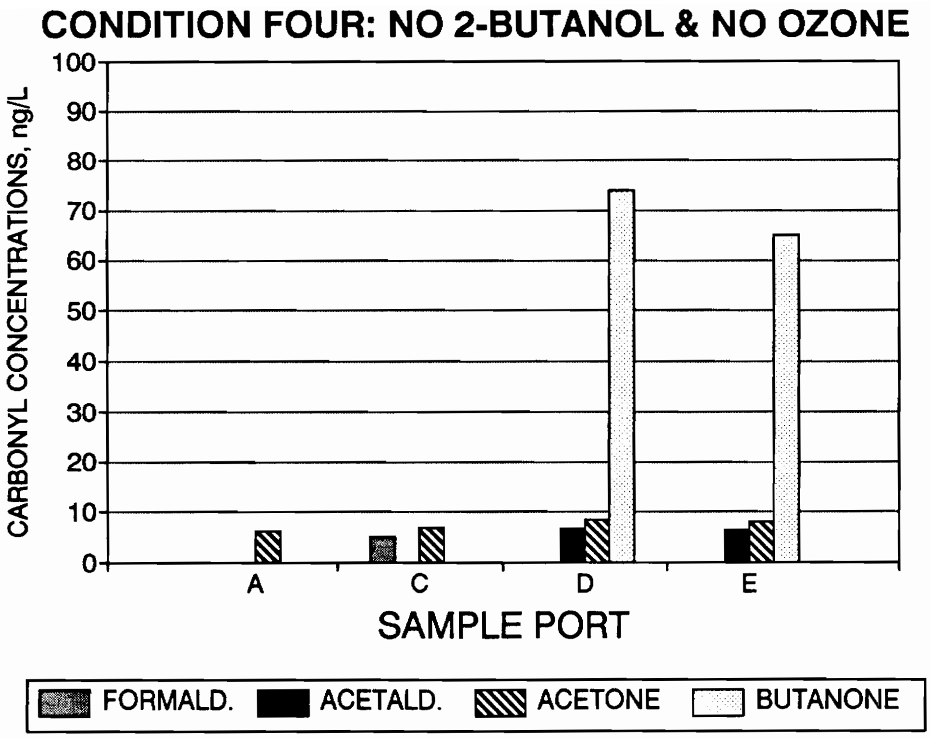


Figure 17. Carbonyl concentrations detected in the duct airstream at sampling ports A, C, D, and E during trial Clean-1. Note: 1) Sample Port A was located upstream of the challenge pollutant diffuser. Sample Port C was located just upstream of the hydrocarbon destruct catalyst. Sample Port D was located between the hydrocarbon destruct catalyst and the ozone destruct catalyst. Sample Port E was located downstream of the ozone destruct catalyst. 2) Formaldehyde was not detected at Ports A, D, and E; acetaldehyde and butanone were not detected at Ports A and C.

of the HDC at Ports D and E. Acetaldehyde levels upstream of the HDC were very low (Not detected - 35 ng/L) regardless of the test conditions. When either ozone alone or both ozone and 2-butanol were delivered to the system acetaldehyde levels appeared to increase downstream of the HDC at Ports D and E. The concentrations detected at these sample locations increased to a somewhat higher level when the combination of ozone and 2-butanol was used. The levels of acetone in the airstream appeared to remain around 10 ng/L at all sampling stations regardless of the test conditions. With the exception of two samples collected during trial O_3B-2, butanone was not detected prior to the ozone diffuser (Ports A and B). Butanone was detected between the ozone diffuser and the HDC (Port C) when ozone and 2-butanol were delivered to the system simultaneously. In trials O_3B-1 and O_3B-2, when relative humidity was very low, butanone was detected at high levels at Port C (300, 342 ng/L); the concentration of detected at Port C in trial O_3B-3 when relative humidity was higher (36%) was much lower (10, 19 ng/L). Butanone was detected downstream of the HDC at Ports D and E under all of the test conditions. Butanone levels from Ports D and E were highest in samples collected while ozone and 2-butanol were delivered to the duct simultaneously (79-450 ng/L).

The results indicated that the concentrations of the carbonyls in the airstream were similar during the outdoor air condition trial (Clean 1) and the trials conducted using 2-butanol alone. When ozone was used alone in the system, or when ozone and 2-butanol were used together, the levels of formaldehyde and acetaldehyde detected downstream of the HDC at Ports D and E appeared to increase. Butanone levels were similar at corresponding sampling ports for all test conditions except when ozone and 2-butanol were used together. When this test condition was used the levels of butanone found downstream of the ozone diffuser at Ports C, D, and E were markedly increased.

In summary, butanone was the most abundant carbonyl detected in the system. Levels of butanone increased at sampling ports located downstream of the ozone diffuser (Ports C, D, and E) when ozone and butanone were delivered to the duct simultaneously. Formaldehyde and acetaldehyde appeared to be more plentiful when ozone was present in the airstream. Acetone concentrations appeared to be the least affected by the test conditions.

4.5 STATISTICAL ANALYSIS OF 2-BUTANOL RESULTS

An ANOVA test was performed for each carbonyl detected in the 2-butanol trials, to determine which test conditions and factors significantly affected carbonyl concentrations in the duct. p-Values from the four ANOVAs, with the corresponding independent system variables, are shown in Table 17. A 90% confidence level was used in determining the significance of each independent variable in affecting the concentrations of the carbonyls in the duct.

For formaldehyde, significant variables included the presence of ozone, the interaction of the presence of 2-butanol and the presence of ozone, and the temperature in the duct. Formaldehyde concentration was also slightly affected by the triple interaction variable of the presence of ozone, the presence of 2-butanol, and the sample location. Acetaldehyde concentration in the duct was significantly affected by temperature and the triple interaction of the presence of ozone, the presence of 2-butanol, and the sample location. The only factor significantly affecting the concentration of acetone in the duct was the relative humidity. The concentration of butanone in the duct was significantly affected by the triple interaction of the presence of ozone, the presence of 2-butanol and the sample location; butanone concentration was slightly affected by the interaction of the presence of ozone and the presence of 2-butanol.

Table 17. p-Values From the ANOVA Tests Performed to Determine the Factors Having a Significant Effect on the Concentration of Each Carbonyl Detected in the Air Cleaning System.

	p-Values			
Variable	Formaldehyde	Acetaldehyde	Acetone	Butanone
Ozone	**0.006**	0.280	0.468	0.829
2-Butanol	0.155	0.806	0.494	0.982
Ozone*2-Butanol	**0.003**	0.778	0.387	**0.060**
Port	0.835	0.590	0.687	0.294
Temperature	**0.004**	**0.001**	0.241	0.825
Humidity	0.807	0.219	**0.002**	0.801
Ozone*2-Butanol *Port	**0.098**	**0.001**	0.434	**0.020**

Note: Boldfaced values indicate variables which are significant at the 90% confidence level in the formation of the corresponding carbonyl.

CHAPTER 5. DISCUSSION

5.1 OVERVIEW

In this chapter, the results of the benzene trials and 2-butanol trials will be discussed. The trends in the data will be reviewed, system operating conditions will be discussed, and operational difficulties of the study will be mentioned.

5.2 DISCUSSION OF BENZENE TRIAL RESULTS

There are several inferences which can be made based upon the results of the benzene trials. Concurrent research which found a decrease in the benzene concentration as the air moved through the system indicated that a reaction of ozone and benzene was occuring. The fact that no carbonyls were detected in the airstream during these trials leads directly to the conclusion that the air cleaning system did not contribute to the formation of carbonyl by-products when benzene was used to challenge the system under the test conditions used.

There are two likely explanations for the absence of carbonyls detected in the airstream during these trials. The first is that the ozone accelerated catalysis system completely oxidized all of the benzene adsorbed on the catalyst to carbon dioxide and water. The second possibility is that the mechanism of oxidation of the benzene molecule did not produce carbonyl intermediates. Both of these explanations likely have some merit.

It is possible that the catalyst used in the system was particularly suited to the catalytic ozonation of benzene, resulting in the complete oxidation of the benzene molecules adsorbed on the catalyst surface. This would have been due to chemical or physical properties of the catalyst, including the ability to strongly chemisorb or physically adsorb benzene and ozone, and/or the ability to greatly increase the rate of the reaction between ozone and benzene. Strong adsorption (i.e., chemisorption) of ozone and benzene on the catalyst bed would facilitate the reaction between ozone and benzene, increasing the probability of complete oxidation. Research by Barnard and Mitchell (1968b) found that benzene was strongly adsorbed by two noble metal catalysts, palladium and platinum. If the properties of the catalyst greatly increased the kinetics of the ozonation of benzene, the probability of complete oxidation would also increase. Benzene molecules which passed through the catalyst bed without being adsorbed were most likely not oxidized owing to the extremely slow kinetics associated with non-catalyzed ozone attack (i.e., gas-phase reactions) on benzene.

It is also possible that the reason no carbonyls were detected in the airstream during these trials is that the mechanism of the ozonation of benzene on the catalyst surface did not produce carbonyl products or intermediates. Studies investigating the mechanisms and products of the reaction of benzene and ozone consistently found the major product of the reaction to be glyoxal, a di-carbonyl (Bailey, 1958; Waters, 1964; Falk and Moyer, 1978). The secondary products of the reaction have been found to be oxalic acid, glyoxylic acid, and formic acid (Oehlschlaeger, 1978; Kuo et. al., 1978). No studies were found which mentioned carbonyl products of the reaction, other than glyoxal, and ozonation of this reaction product is not expected to produce carbonyls. It is possible that partial oxidation products other than carbonyls (probably carboxylic acids) were produced. This possibility would have to be researched further, as this study was only concerned with monitoring for carbonyls in the airstream.

5.3 DISCUSSION OF 2-BUTANOL TRIAL RESULTS

Four different carbonyls were detected in the airstream within the air cleaning system during the 2-butanol trials. These included formaldehyde, acetaldehyde, acetone, and butanone. The HPLC chromatograms did not indicate the presence of other carbonyls at detectable levels. The factors affecting the concentrations of each will be discussed in turn.

5.3.1 Formaldehyde

The ANOVA test (Table 17) performed using the concentration of formaldehyde as the dependent variable found that four factors contributed significantly to this variable. These factors were the presence of ozone, the combination of the presence of ozone and the presence of 2-butanol, and increased air temperature. The combination of the presence of 2-butanol, the presence of ozone and sample location was slightly significant (p=0.098). It is possible that the trace levels of formaldehyde formed by surface reactions on the catalyst were not high enough (above background levels) for the triple interaction variable to be found more significant by the ANOVA. The presence of elevated levels of formaldehyde in air samples collected downstream of the HDC during the trials which used the combination of 2-butanol and ozone suggested that the catalyst contributed to the formation of trace levels of formaldehyde. This information supports the finding of significance of the triple interaction variable.

The fact that the presence of ozone and the presence of 2-butanol and the triple interaction variable were significant factors implies that formaldehyde is a product of catalyzed reactions of ozone with 2-butanol or oxidation products of 2-butanol. Previous research does not indicate that formaldehyde is a product of the ozonation of 2-butanol but the mechanisms and products of these reactions have not been thoroughly researched under conditions simulating those used in the trials. Research suggests that the liquid-phase ozonation of hydrocarbons with saturated carbon-carbon bonds including aldehydes, ketones, and alcohols are very slow reactions which are initiated by ozone and then carried out by oxygen (Bailey, 1958; Oehlschlaeger, 1978). While the mechanisms of ozone-accelerated catalyst-based reactions with these compounds are expected to be different than liquid-phase reactions, they could produce carbonyls such as formaldehyde. Formaldehyde has been found to be a product of the ozonation of another alcohol in the liquid-phase, 2-propanol (Whiting et. al.,1978; Kuo et. al., 1978). This suggests that ozonation of 2-butanol in the presence of the proprietary catalyst could also produce formaldehyde. The formaldehyde could also be a product of the reaction of ozone and/or oxygen with molecules resulting from the partial oxidation of 2-butanol. It is not likely that formaldehyde was formed during radical-induced reactions in the gaseous phase, since these reactions would not be expected to occur at the temperatures used in the air cleaning system (Spivey 1987). The fact that formaldehyde is generally very easily oxidized to formic acid (Finar, 1963), combined with the fact that the reactions leading to the formation of formaldehyde are likely to proceed very slowly (Bailey, 1958; Oehlschlaeger, 1978), likely explains why higher levels were not detected in the air samples.

Formaldehyde was detected at both ports downstream of the HDC (Ports D and E) in several air samples from trials other than those which used the combination of ozone and 2-butanol. This evidence suggests that previously sorbed formaldehyde was desorbing from the catalysts and re-entering the airstream during these trials. This, in turn, suggests an explanation of why temperature was found to be a significant factor. Higher temperatures would increase desorption of formaldehyde previously sorbed on the catalysts, thereby increasing formaldehyde levels in the airstream.

Air samples from the Condition Three trials (ozone-only) contained elevated levels of formaldehyde downstream of the HDC. This evidence suggests that 2-

butanol and other molecules sorbed on the catalysts were being re-emitted to the airstream during these trials and subsequently oxidized by ozone and/or oxygen to form formaldehyde. This would explain why the presence of ozone was found to be a significant variable by the ANOVA.

Since the presence of ozone combined with the presence of 2-butanol and the sample location were circumstances directly related to the operation of the air cleaning system, it is suggested that the pre-prototype air cleaning system contributed to the formation of formaldehyde under the test conditions. The conclusion is supported by the fact that formaldehyde levels in the airstream were very low except when ozone alone or ozone and 2-butanol were delivered to the system. Under these conditions the levels of formaldehyde downstream of the catalysts were elevated somewhat. It is concluded from the results of this research that the ozonation of 2-butanol over the proprietary catalyst produced formaldehyde as a partial oxidation product. As a result the prototype air cleaning system caused increased levels of formaldehyde in the airstream when challenged with 2-butanol under the test conditions.

The levels of formaldehyde detected during these trials were in the low ppb range. These levels were below the recommended Threshold Limit Value (TLV) (1 ppm) and Time Weighted Average (TWA) concentration (1 ppm) for commercial and industrial workplaces (ASHRAE, 1989). However, the levels of formaldehyde produced in the pre-prototype unit may be different under operating conditions other than those used in this research.

5.3.2 Acetaldehyde

The ANOVA test (Table 17) for acetaldehyde found that increased temperature and the combination of the presence of ozone, the presence of 2-butanol, and sample location were factors affecting the formation of this chemical. The fact that the triple interaction variable was significant indicates that the combination of ozone and the catalysts contributed to the formation of acetaldehyde when challenged with 2-butanol under the test conditions used.

No studies were found in the literature which specifically mentioned acetaldehyde as a product of the ozonation of 2-butanol but the mechanisms of the ozone accelerated catalytic oxidation of secondary alcohols have not been well investigated. Two studies were found which specifically document finding acetaldehyde as a product of the ozonation of another alcohol, ethanol (AWWA, 1991; Laplanche and Martin, 1982). It is suggested that the catalytic ozonation of 2-butanol under the specific test conditions could possibly result in formation of acetaldehyde and that this is in fact what occurred. It is not likely that acetaldehyde was formed during radical-induced reactions since these reactions would not be expected to occur at the temperatures used in the air cleaning system (Spivey, 1986). The fact that acetaldehyde is very easily oxidized (Finar, 1963), combined with the fact that the reactions leading to the formation of acetaldehyde are likely to proceed very slowly (Bailey, 1958; Oehlschlaeger, 1978), probably explains why higher levels were not detected in the air samples.

Acetaldehyde was detected at both ports downstream of the HDC (Ports D and E) in several air samples from trials other than those which used the combination of ozone and 2-butanol. This evidence suggests that previously sorbed acetaldehyde was desorbing from the catalysts and re-entering the airstream during these trials. This acetaldehyde was most likely sorbed on the catalysts during prior trials conducted using Condition One. If this was the case, it offers a possible explanation for why increased temperature was found to significantly affect acetaldehyde levels in the duct. Increased temperatures would increase desorption of acetaldehyde previously sorbed on the catalysts, thereby increasing acetaldehyde levels in the airstream. It is also possible that elevated acetaldehyde levels detected at Ports D and E during the Condition Three trials (ozone only) were the result of ozone reacting with 2-butanol previously sorbed on the HDC bed.

The presence of ozone, the presence of 2-butanol, and sample location were all found to significantly affect the concentration of acetaldehyde found in the air samples collected. Because these factors are directly related to the operation of the air cleaner, the fact that they were found to be significant suggests that the air cleaning system contributed to the formation of acetaldehyde when challenged with 2-butanol. The conclusion is supported by the trial data showing increased levels of acetaldehyde downstream of both catalysts when ozone and 2-butanol were delivered to the duct airstream simultaneously, compared to the levels found otherwise. It is concluded from the results of this research that the ozonation of 2-butanol over the proprietary catalyst produced acetaldehyde as a partial oxidation product. As a result the prototype air cleaning system caused increased levels of acetaldehyde in the airstream when challenged with 2-butanol under the test conditions.

The levels of acetaldehyde detected in the air samples collected from the pre-prototype unit were far below the recommended TLV (100 ppm) and TWA (200 ppm) for acetaldehyde in industrial workplaces (Sax, 1984). It is uncertain whether the pre-prototype system would produce the same acetaldehyde levels if used in a commercial building.

5.3.3 Acetone

The results of the ANOVA test (Table 17) for acetone indicated that the only factor which significantly affected the concentration of this chemical in the duct was relative humidity. Since none of the variables directly associated with the operation of the air cleaning system (presence of ozone, sample location, presence of 2-butanol, and both interaction variables) were found to be significant, it can be concluded that the air cleaning system, as operated for these studies, did not contribute to the formation of acetone. The indifference of acetone concentration to varying test conditions also supports this conclusion. There were no studies found which indicated that acetone would be produced from the ozone accelerated catalysis of 2-butanol or any other oxidation of 2-butanol. The fact that acetone is difficult to oxidize is probably why the catalysts had little effect on the acetone concentration.

The second conclusion is that the source of acetone detected in the duct is probably a combination of outdoor air and internal sources such as acetone previously sorbed on surfaces including the catalysts, which has desorbed and re-entered the airstream. Many samples collected at Port A contained acetone, supporting the conclusion that outside air was a source.

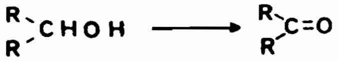
The relative humidity probably affected acetone concentrations by saturating hydrophilic surfaces and occupying spaces on which acetone molecules present in the outdoor air could be sorbed. This would have the effect of increasing the concentration of acetone in the airstream. It is also possible that ozone attacked and destroyed acetone except in the presence of water. This possibility is supported by the data from the Condition One trials which suggests that 2-butanol is attacked by ozone (producing butanone) in the gaseous phase unless relative humidity is high.

5.3.4 Butanone

The results of the ANOVA test of butanone data indicated that the combination of the presence of ozone, the presence of 2-butanol, and the sample location in the duct significantly affected the concentration of butanone in the airstream. To a lesser degree, the combination of the presence of 2-butanol and the presence of ozone also affected butanone concentrations ($p=0.060$). The fact that these factors are directly related to the operation of the air cleaning system suggests that, under the test conditions used, the operation of the air cleaning system contributed to the formation of butanone when challenged with 2-butanol. The conclusion is supported by the trial data showing a large increase (e.g., greater than 6X increases) in levels of butanone at sample ports downstream of the ozone diffuser when ozone and 2-butanol were delivered to the duct simultaneously (Figures 8, 9, and 10). The research by Waters et al. (1976), which documents the formation of relatively inert butanone upon ozonation of 2-butanol, also lends support to the conclusion.

In the two trials conducted at low relative humidity levels, butanone was detected in the airstream prior to the catalyst at concentrations of 342 and 300 ng/L. Research by Ryan and Koutrakis (1993) reported the reaction of ozone with organics in the presence of water and a surface. This suggests that any surface in the system could promote a reaction of ozone with 2-butanol, producing carbonyls and other byproducts. It is suggested that in humid air the 2-butanol reacts with hydroxyl radicals formed in the in the air and on surfaces, and is completely oxidized instead of forming butanone.

The oxidation of secondary alcohols to form ketones is a well known reaction. The 2-butanol in the duct would be expected to react with ozone to form butanone according to the following mechanism (Bailey 1972):



$$\mathrm{RR'CHOH} \longrightarrow \mathrm{RR'C{=}O}$$

(taken from Laplanche and Martin, 1982)

The fact that the ketones formed by these reactions are difficult to oxidize likely explains why larger concentration of butanone were found than any other carbonyl (Bailey, 1958; Waters et al., 1976; Oehlschlaeger, 1978). Butanone was detected at elevated levels at sample locations downstream of the hydrocarbon destruct catalyst in the trials other than those which used the combination of both ozone and 2-butanol. This evidence suggests that previously sorbed butanone was desorbing from the catalysts during these trials. This butanone was most likely sorbed on the catalyst beds during prior trials using ozone and 2-butanol simultaneously. The butanone detected during ozone only trials might also have been produced by ozone reacting with 2-butanol previously sorbed on the HDC bed.

It is concluded from the results of this research that the ozonation of 2-butanol over the proprietary catalyst and in the gaseous phase produced butanone as a partial oxidation product. As a result the prototype air cleaning system caused increased levels of butanone in the airstream when challenged with 2-butanol under the test conditions.

The levels of butanone detected in the air samples collected from the pre-prototype unit are well below the recommended TLV (200 ppm) and TWA (200 ppm) for butanone in industrial workplaces (Sax, 1984). It is uncertain whether the pre-prototype system would produce the same butanone levels if used in a commercial building.

5.4 COMPARISON OF BENZENE TRIAL AND 2-BUTANOL TRIAL RESULTS

No carbonyls were detected in the duct airstream during the benzene trials while carbonyls were detected in many of the samples collected during the 2-butanol trials. This contrast is probably due to several factors. First, the reaction of benzene with ozone is not expected to produce carbonyls as ultimate oxidation products, while the reaction of 2-butanol with ozone is expected to produce 2-butanone. It is also possible that the catalyst bed adsorbed benzene more strongly than 2-butanol allowing for more complete oxidation of the benzene molecules. The catalyst may also increase the rate of the benzene reaction to a greater degree than the reaction with 2-butanol. This would also result in more complete oxidation of benzene and a lower probability that partial oxidation products would be produced.

Another factor which may have contributed to the contrast in benzene and 2-butanol trial results is the fact that the catalyst was new during the benzene trials and may have had a higher destruct efficiency. The appearance of the catalyst was observed to change during the 18 month period of testing and visual inspection of the beds indicated that channeling was occurring during the 2-butanol trials (Holbrook, 1991). The possibility that catalyst performance may have decreased during the test period should be investigated further. The continuous operation of the system during the trials compared to more sporadic operations during the 2-butanol trials may have also affected the trial results.

5.5 OPERATIONAL CHARACTERISTICS OF THE PRE-PROTOTYPE AIR CLEANER

A discussion of the operating characteristics of the air cleaning system is appropriate due to the effect of these characteristics on the study. Ideally, when a challenge chemical was initially introduced to the system, the amount of the chemical adsorbed on the catalysts would eventually reach an equilibrium, allowing the system to be operated at steady state. At steady state the rate of the adsorption of the challenge pollutants by the catalyst would be equal to the rate of desorption plus the rate of destruction reactions. If the system could be operated at steady state, destruction efficiencies could then be accurately determined.

System tests conducted using benzene and 2-butanol destruction efficiency data indicated that the hydrocarbon destruct catalyst never reached a steady state condition with respect to the challenge chemical adsorbed on the catalyst (Holbrook, 1991). This condition was probably caused by noncontinuous operation of the system, and continuously changing temperature and humidity conditions which affected the equilibrium condition of the catalyst beds. The presence of oxidation products in the duct may also have affected the adsorption characteristics of the catalyst by being preferentially adsorbed and forcing the challenge chemical back into the airstream.

While the lack of steady state operating conditions could have implications concerning the interpretation of the results of the study, it is suggested that the most serious complication caused by the lack of steady state operating conditions was a reduction in the ability to determine the destruction efficiency of the catalyst. Since these data were not used in this study and the objectives of the study do not concern catalyst destruction efficiency, the situation was considered bearable, if not unavoidable. The system was operated in a manner designed to allow the system to approach steady state, if not achieve it, prior to the trials in order to minimize any adverse effects (as noted in Chapter II).

Unpublished data collected by other researchers during the course of this study are worth noting. An effort was made to determine the destruction efficiency of the system for benzene and 2-butanol. This was exceedingly difficult, however, due to the steady state situation previously discussed and only approximate values could be obtained. The data did show that a significant level of destruction was occurring for both benzene and 2-butanol. Ozone levels were also monitored and showed significant decreases after mixing with the challenge chemical and after passing over the hydrocarbon destruct catalyst. This data supported the notion that the challenge chemicals were in fact reacting with ozone within the system and producing carbonyls, and that ozone was attacking 2-butanol in the gas phase under dry conditions.

Data were also collected which lends support to the conclusion that chemicals were adsorbed on the beds and desorbed later. Data collected by Holbrook (1991) using GC analysis for 2-butanol indicated that 2-butanol was desorbing from the catalyst beds 1-2 weeks after discontinuation of the 2-butanol diffuser. Similar data collected during rainy outdoor conditions showed significantly increased desorption of both 2-butanol and butanone.

5.6 RECOMMENDATIONS FOR THE FUTURE

There are several insights gained from this study that could benefit the design and execution of future studies. These include the need for a mass balance approach, catalyst destruction efficiency data, knowledge of the adsorption/desorption characteristics of the catalysts, and more sample collection and analysis.

The use of a mass balance approach in the present study would have been ideal. Using this approach, all inputs (chemicals) would have been measured along with a measure of the chemicals flowing out of the system. The destruction efficiency could then be easily determined, along with many other parameters, including by-products formed. The problem with this approach was that it would have required a great deal more resources, in the form of monitoring systems, than were available. In addition a very clear understanding of the destruction, adsorption, and desorption characteristics of the catalyst would have been necessary to effectively use a mass balance approach.

Catalyst destruction efficiency data was not collected during the sampling trials. This information would have been necessary to attempt a mass balance approach to the study. A lack of knowledge of the adsorption/desorption characteristics of the catalyst combined with the inability to operate the system at steady state made destruction efficiency a difficult parameter to determine.

A larger quantity of samples under each of the test conditions would have been preferable. Only one trial was conducted while operating the system with clean air. A larger number of samples would lend credence to the results and conclusions. Unfortunately, due to lengthy sampling and analysis procedures and other concurrent research projects, the number of trials that could be conducted was curtailed.

The conclusion that formaldehyde, acetaldehyde, and butanone levels were increased by the operation of the air cleaning system is cause for concern. Formaldehyde and butanone have received a significant amount of attention from regulatory and health agencies and are considered to be significant health threats. This and the fact that other partial oxidation products may be produced (or may have been produced and were not detected) leads to the recommendation that the safety of this system be thoroughly evaluated under a wide variety of conditions and stresses.

CHAPTER 6. CONCLUSIONS

The following conclusions were drawn from the data collected during tests of the pre-prototype unit an indoor air pollution abatement system which utilized ozone accelerated catalysis to treat artificially polluted air. As such, the conclusions may not apply to bench-scale, prototype, commercial, or other versions of the system. The fact that the system was not operated at steady state with respect to saturation of the catalysts was not considered significant to invalidate the results of the study. If system parameters such as temperature and humidity could be better controlled, operating the system at steady state would be more feasible, and the interpretation of data from the system would be easier.

1. The pre-prototype air cleaning system did not contribute to the formation of carbonyls in the airstream when operated using benzene as the challenge chemical under the test conditions.
2. Under the conditions tested, the pre-prototype air cleaning system contributed to the formation of formaldehyde and acetaldehyde in the airstream when operated using 2-butanol as the challenge chemical. The concentration of butanone in the airstream was significantly increased.

3. Butanone was the most prevalent intermediate formed during the operation of the pre-prototype air cleaning system while using 2-butanol as the challenge chemical.
4. The presence of the hydrocarbon destruct catalyst was influential in the formation of acetaldehyde and butanone, and was likely a factor affecting the formation of formaldehyde, when 2-butanol was applied.
5. Carbonyls were most likely adsorbed by both the hydrocarbon and ozone destruct catalysts during trials which used both 2-butanol and ozone, and were re-emitted to the airstream during other trials.
6. The use of ozone accelerated catalysis for indoor air cleaning systems must be investigated further to fully evaluate the effectiveness and safety of the technology.

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CHAPTER 8. APPENDICES

APPENDIX A

HPLC CHROMATOGRAMS

Figures A.3.-A.9. - Sample Chromatograms
Figures A.10.-A.13. - Chromatograms for Standards

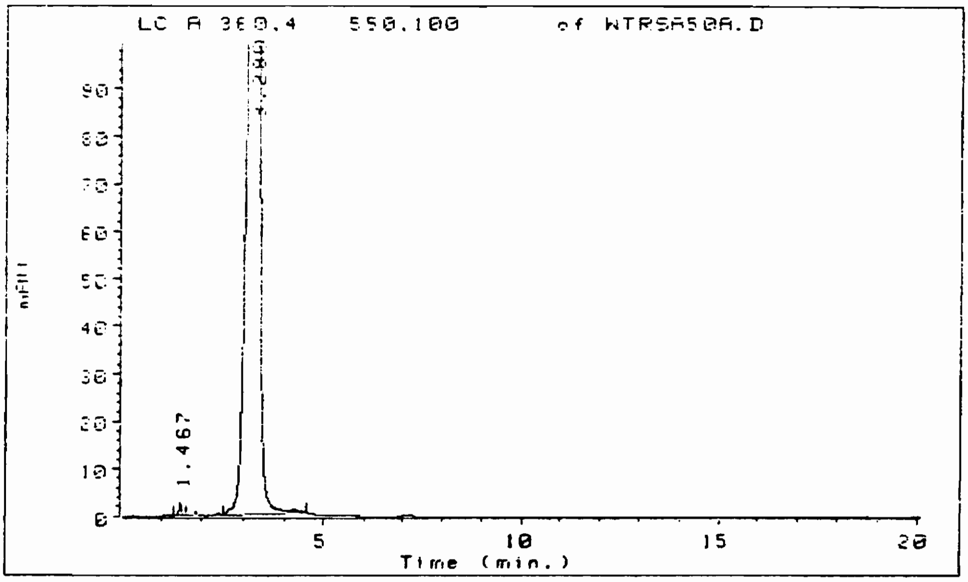

Figure A.1. Liquid chromatogram of laboratory blank for trial O_3B-2. DNPH peak is large peak located at 3.28 minutes.

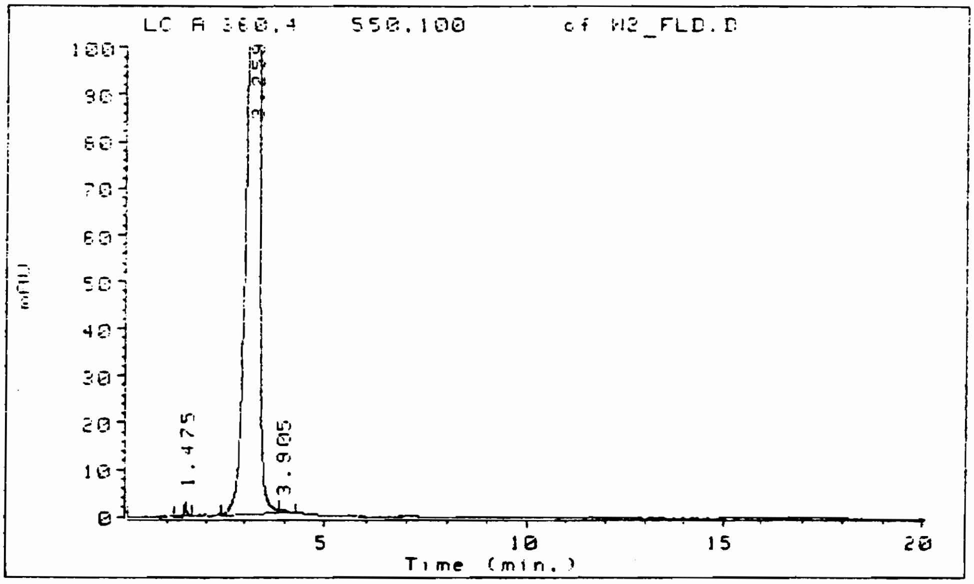

Figure A.2. Liquid chromatogram of field blank for trial O_3B-2. DNPH peak is large peak located at 3.259 minutes.

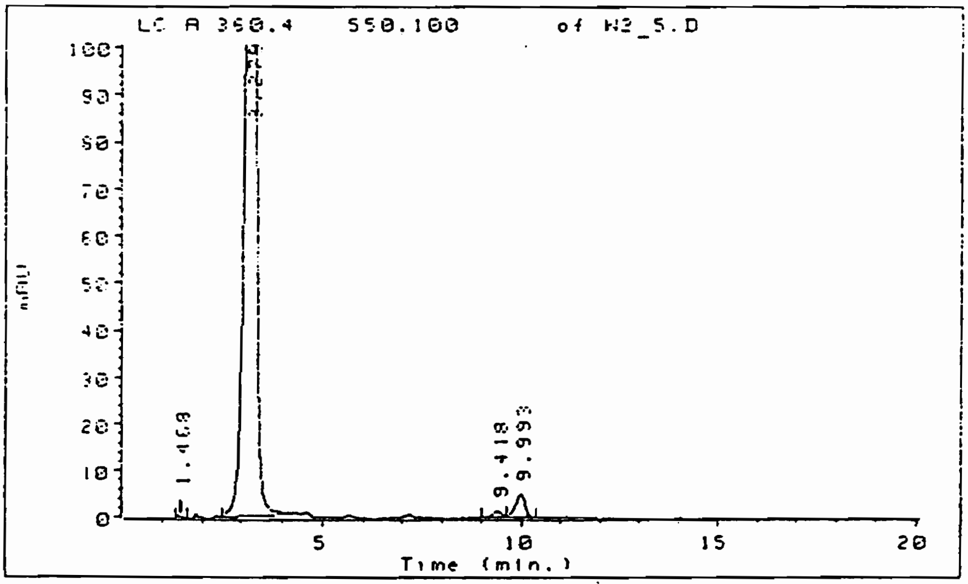

Figure A.3. Liquid chromatogram from sample collected at Port A during trial O_3B-2. DNPH peak is large peak located at 3.278 minutes. The peaks located at 9.418 and 9.993 minutes represent the cis and trans isomers of butanone.

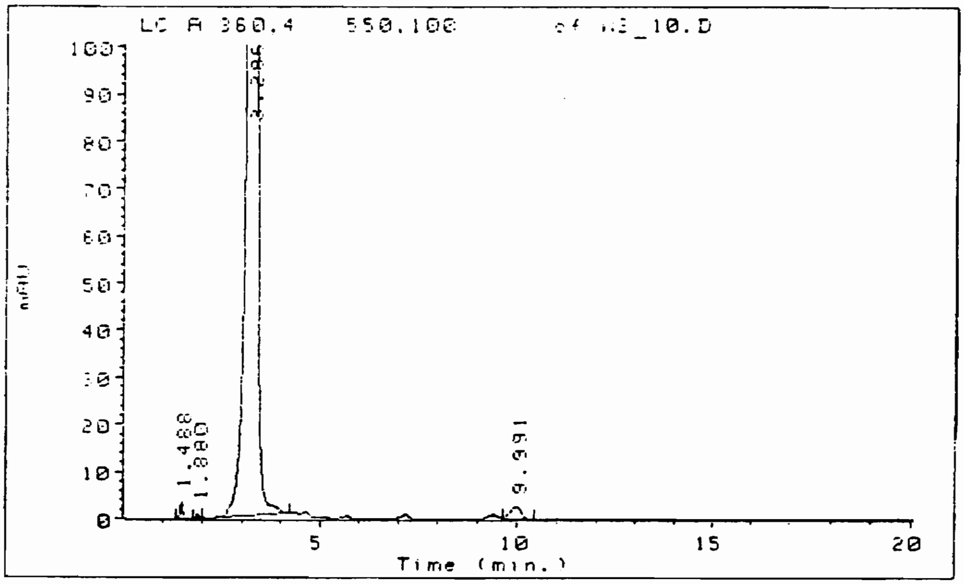

Figure A.4. Liquid chromatogram from sample collected at Port B during trial O_3B-2. DNPH peak is large peak located at 3.286 minutes. The peak located at 9.991 minutes represents cis and trans isomers of butanone.

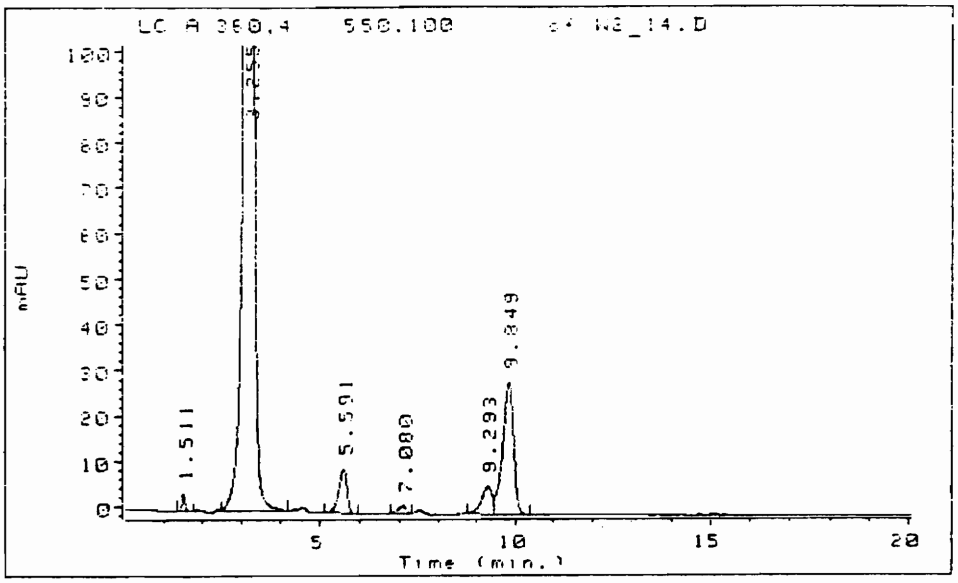

Figure A.5. Liquid chromatogram from sample collected at Port C during trial O_3B-2. DNPH peak is large peak located at 3.255 minutes. The peak located at 5.591 minutes is acetaldehyde. The peak located at 7.080 minutes represents acetone. Peaks located at 9.293 and 9.849 minutes represent cis and trans isomers of butanone.

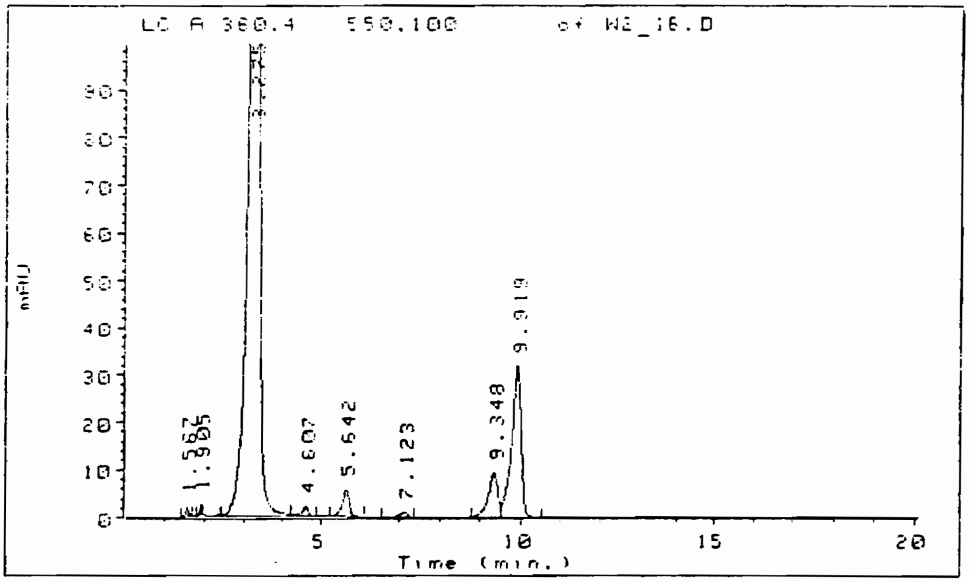

Figure A.6. Liquid chromatogram from sample collected at Port D during trial O_3B-2. DNPH peak is large peak located at 3.275 minutes. The peak located at 4.607 minutes represents formaldehyde. The peak located at 5.642 minutes is acetaldehyde. The peak located at 7.123 minutes represents acetone. Peaks located at 9.348 and 9.919 minutes represent cis and trans isomers of butanone.

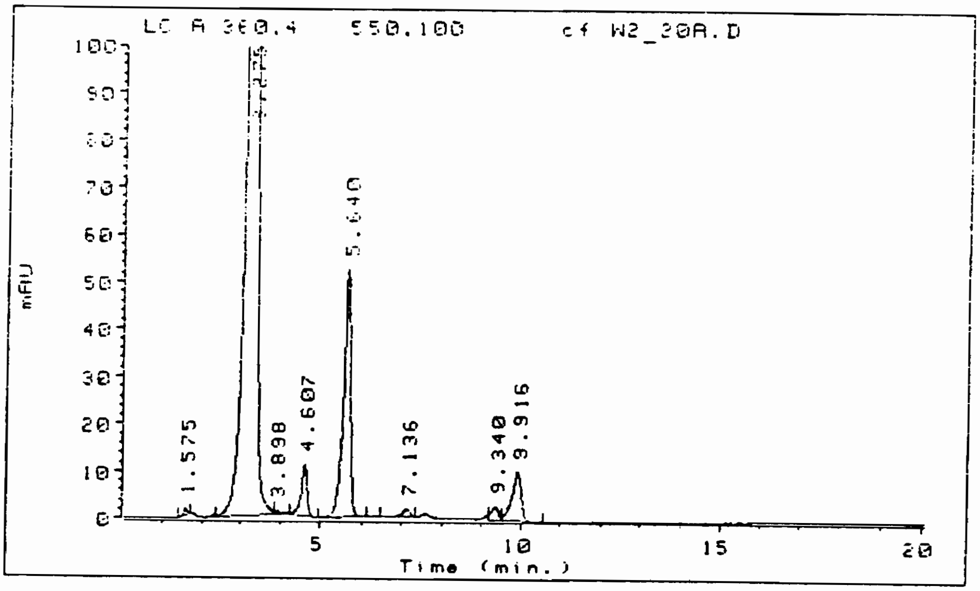

Figure A.7. Liquid chromatogram from sample collected at Port E during trial O_3B-2. DNPH peak is large peak located at 3.275 minutes. The peak located at 4.607 minutes represents formaldehyde. The peak located at 5.640 minutes is acetaldehyde. The peak located at 7.136 minutes represents acetone. Peaks located at 9.340 and 9.916 minutes represent cis and trans isomers of butanone.

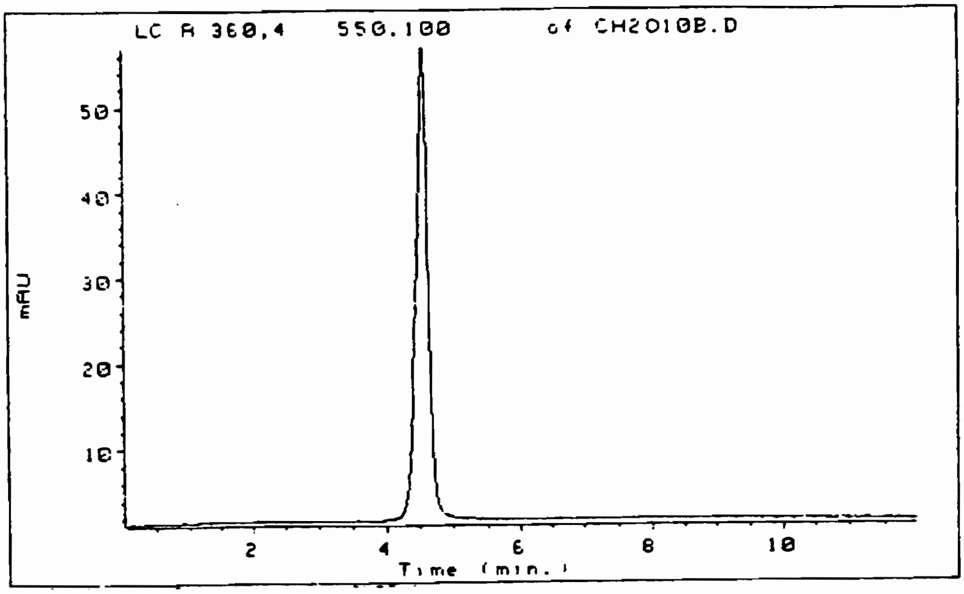

Figure A.8. Liquid chromatogram of standard containing 10 ppm DNPH-formaldehyde derivative in acetonitrile. Retention time of the DNPH-formaldehyde derivative is 4.571 minutes.

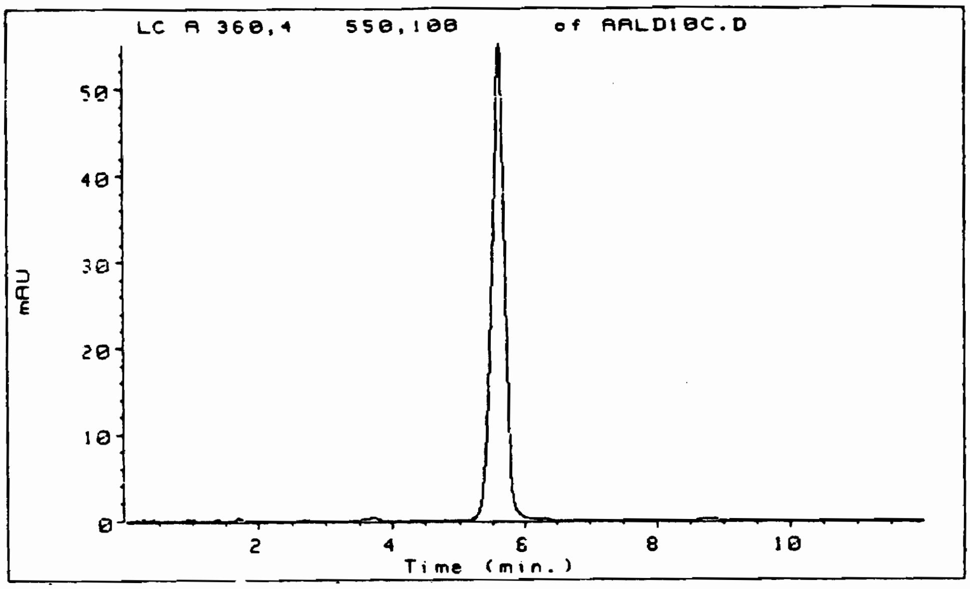

Figure A.9. Liquid chromatogram of standard containing 10 ppm DNPH-acetaldehyde derivative in acetonitrile. Retention time of the DNPH-acetaldehyde derivative is 5.616 minutes.

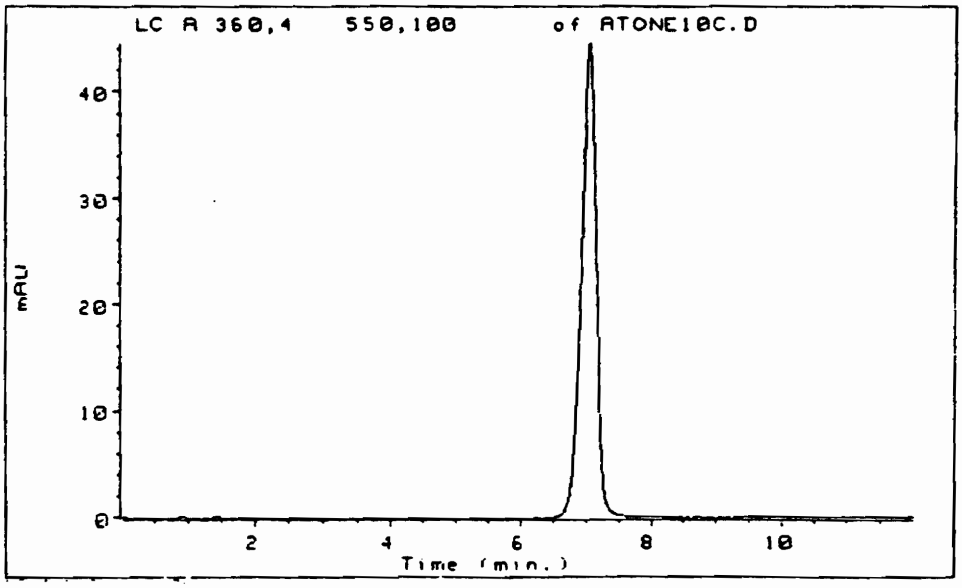

Figure A.10. Liquid chromatogram of standard containing 10 ppm DNPH-acetone derivative in acetonitrile. Retention time of the DNPH-acetone derivative is 7.052 minutes.

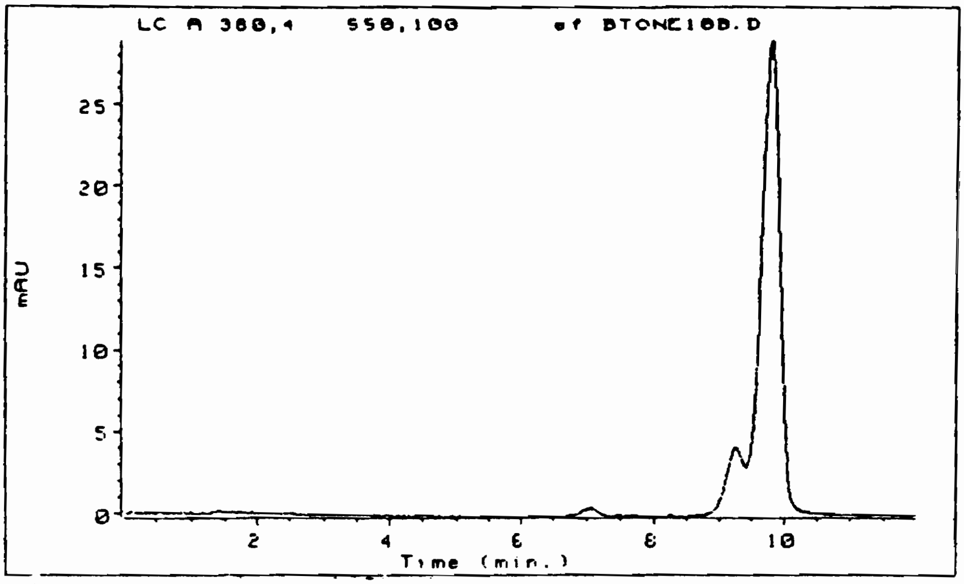

Figure A.11. Liquid chromatogram of a standard containing 10 ppm DNPH-butanone derivative in acetonitrile. Retention times of the DNPH-butanone derivative peaks (cis and trans isomers) were 9.25 and 9.803 minutes.

APPENDIX B

GAS CHROMATOGRAMS OF STANDARDS

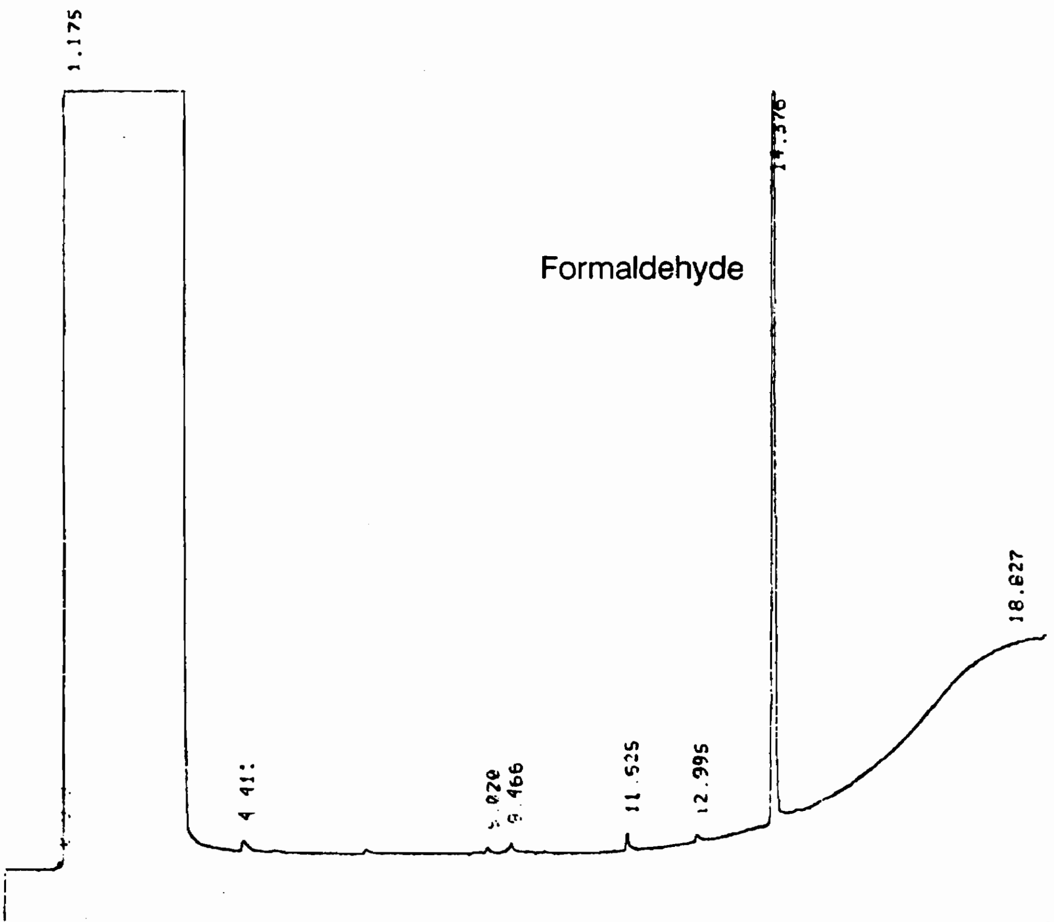

Figure B.1. Gas chromatogram of standard containing DNPH-formaldehyde derivative in acetonitrile. The DNPH-formaldehyde derivative peak is located at 14.376 minutes.

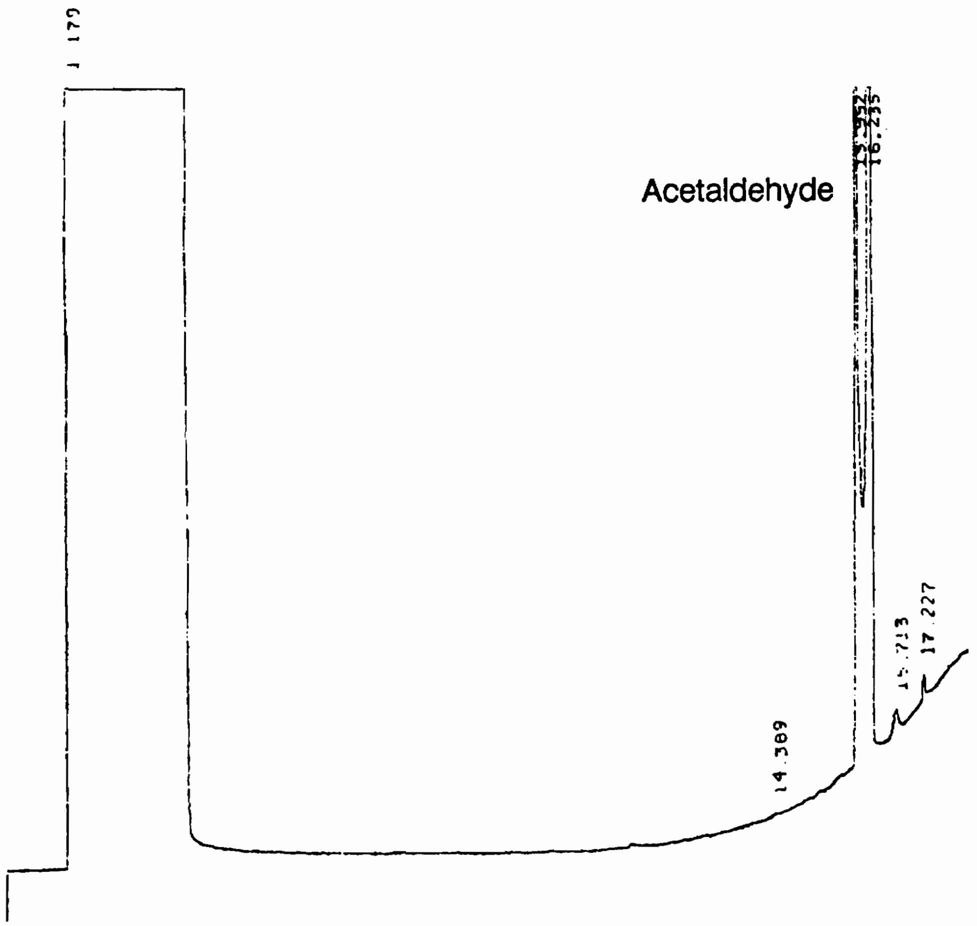

Figure B.2. Gas chromatogram of standard containing DNPH-acetaldehyde derivative in acetonitrile. The DNPH-acetaldehyde derivative peaks are located at 15.952 minutes and 16.235 minutes.

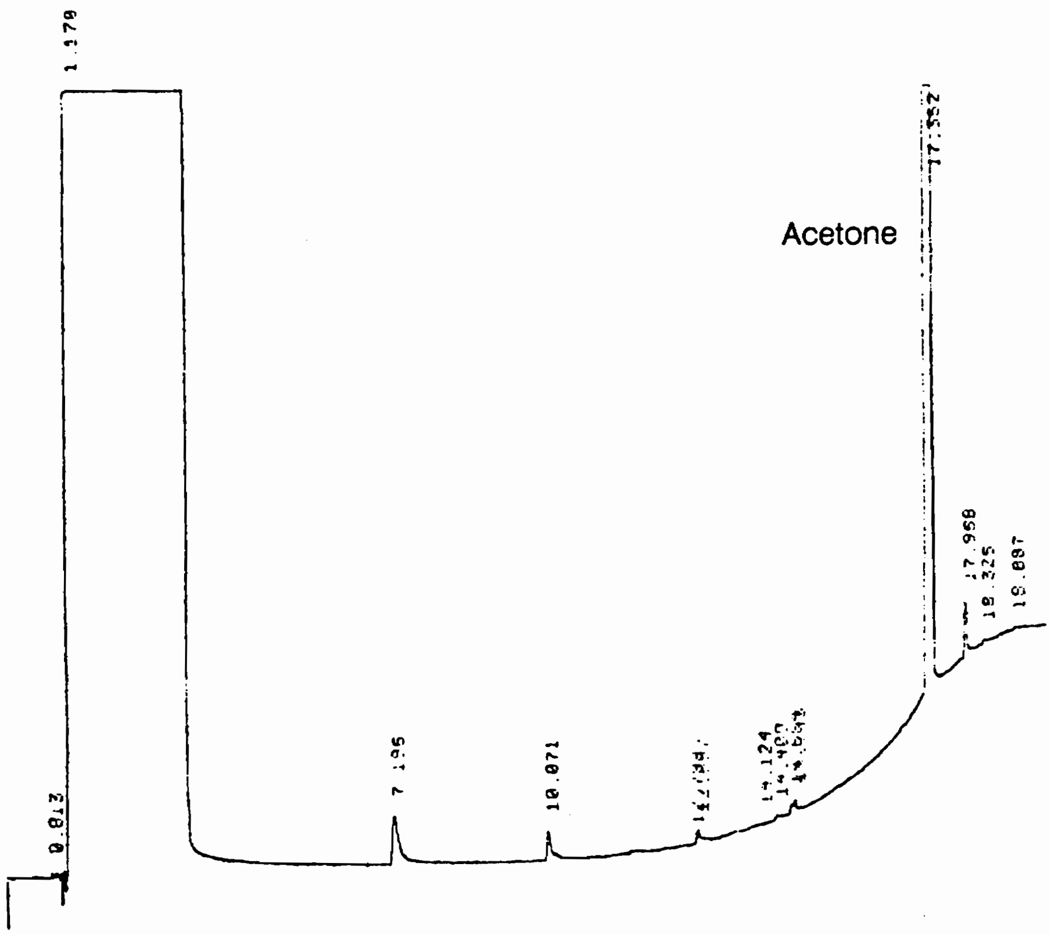

Figure B.3. Gas chromatogram of standard containing DNPH-acetone derivative in acetonitrile. The DNPH-acetone derivative peak is located at 17.352 minutes.

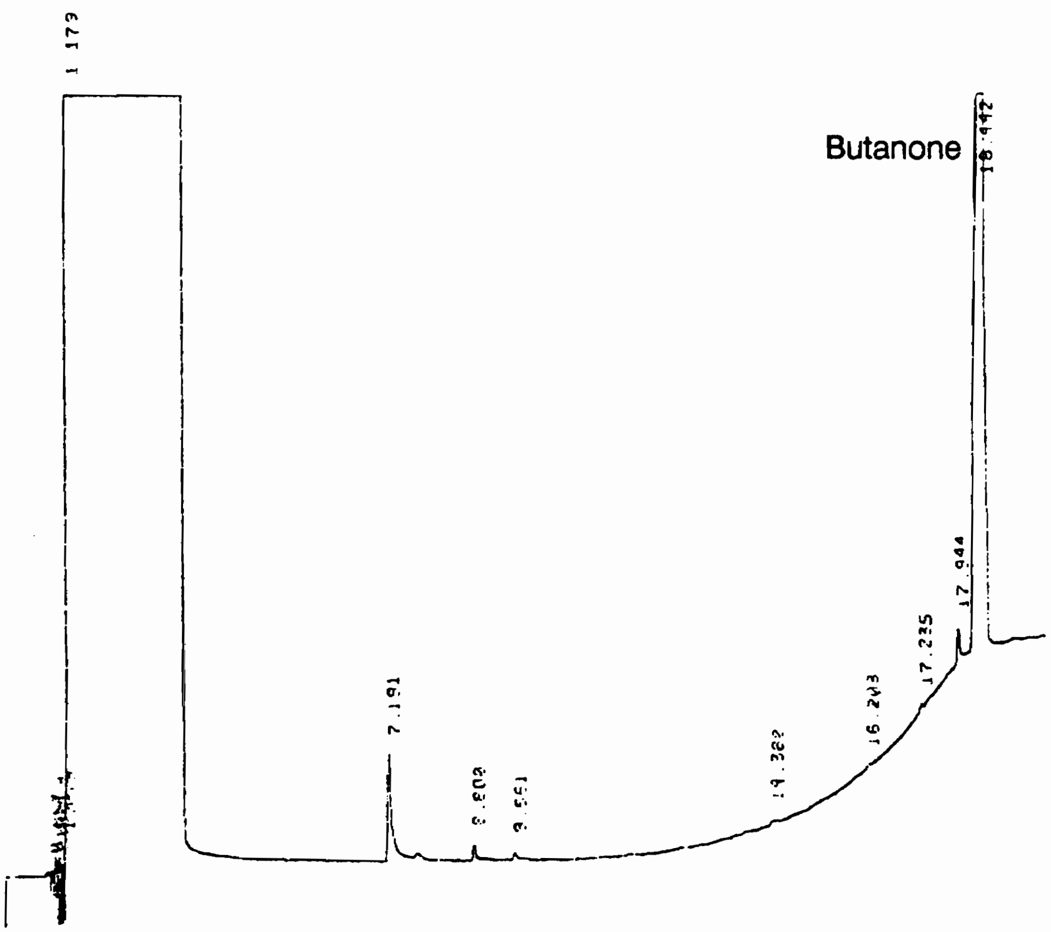

Figure B.4. Gas chromatogram of standard containing DNPH-butanone derivative in acetonitrile. The DNPH-butanone derivative peak is located at 18.442 minutes.

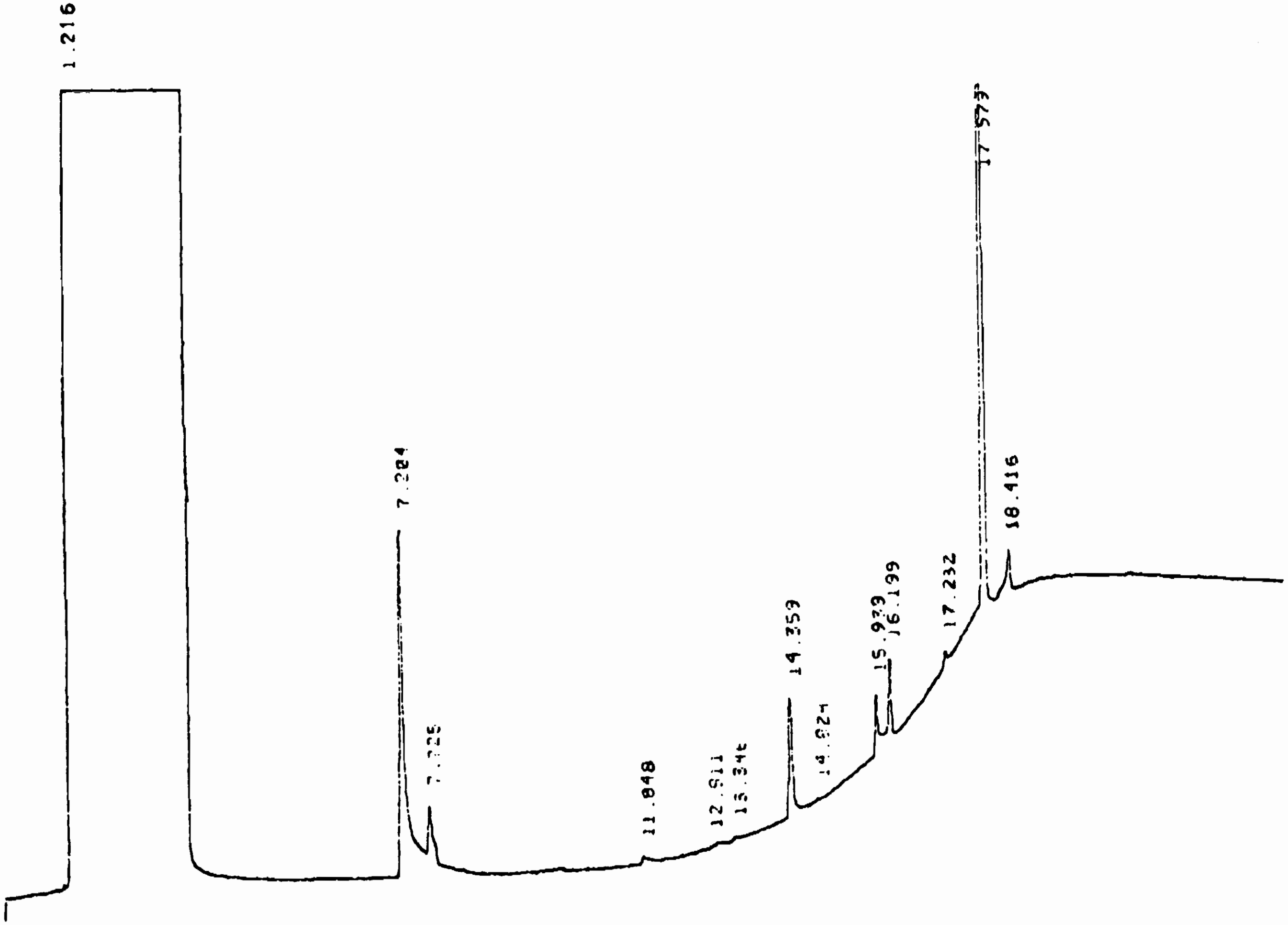

Figure B.5. Flame Ionization Gas Chromatogram of eluate from sample collected at Port E during trial O3B-2. The formaldehyde peak is at 14.359 minutes, the acetaldehyde peaks are at 15.939 and 16.199 minutes, the acetone peak is at 17.232 minutes, and the butanone peak is at 18.416 minutes.

APPENDIX C

MASS SPECTRA OF STANDARDS AND SAMPLES

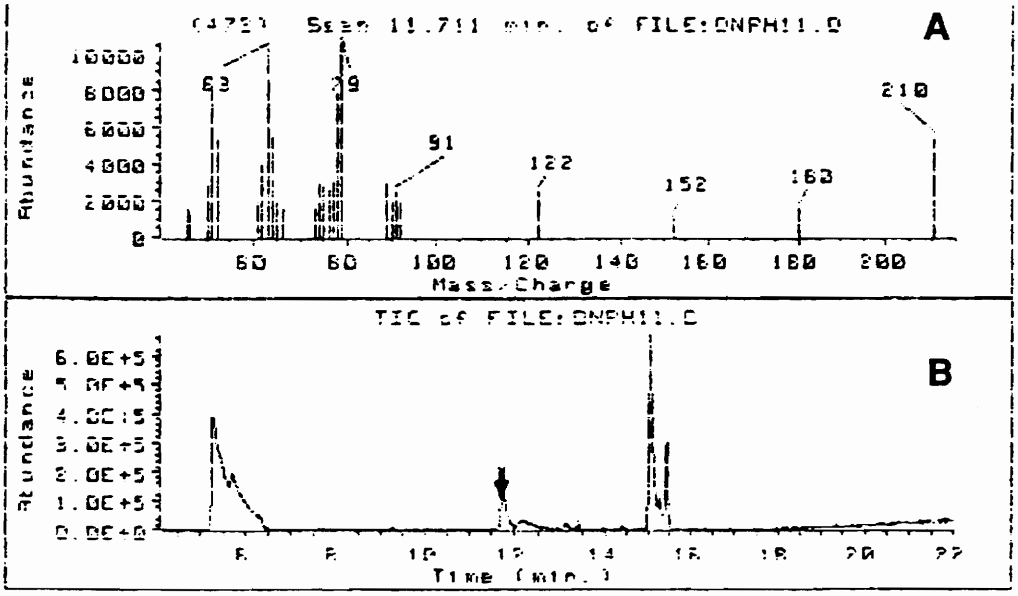

Figure C.1. Mass spectrum of DNPH-formaldehyde derivative MW 210 (A) indicated on the Total Ion Chromatogram (B), from sample collected at Port C during trial O_3B-2.

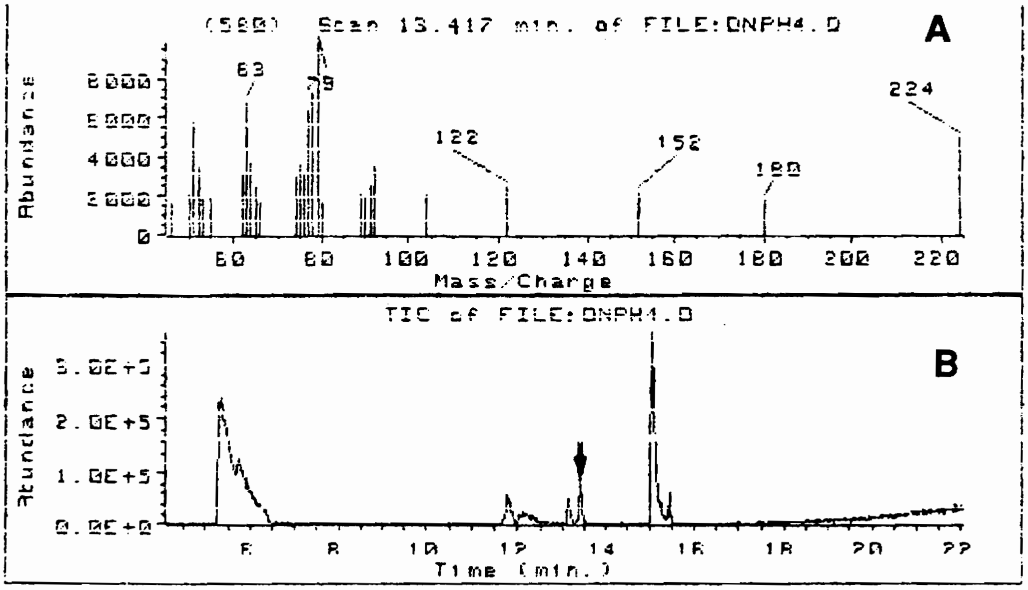

Figure C.2. Mass spectrum of DNPH-acetaldehyde derivative MW 224 (A), indicated on the Total Ion Chromatogram (B), from sample collected at Port E during trial O_3B-2.

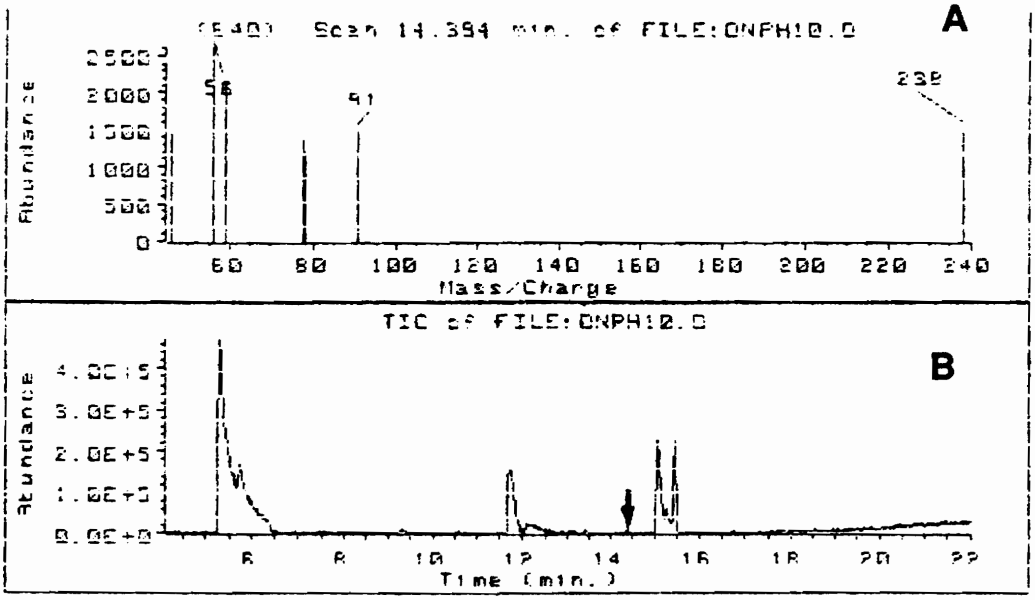

Figure C.3. Mass spectrum of DNPH-acetone derivative MW 238 (A), indicated on the Total Ion Chromatogram (B), from sample collected at Port D during trial O_3B-2.

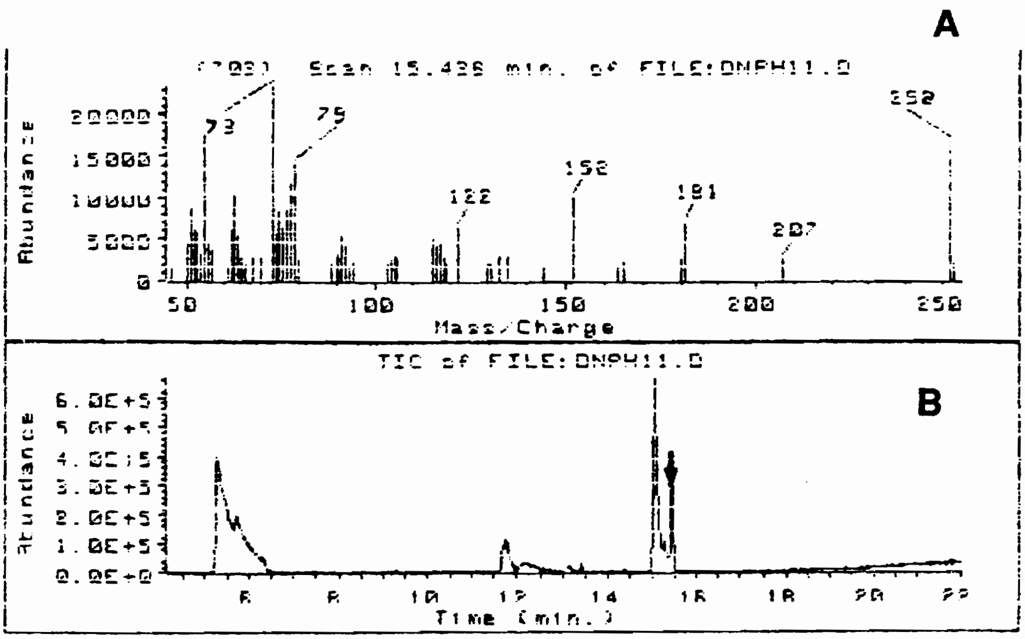

Figure C.4. Mass spectrum of DNPH-butanone derivative MW 252 (A), indicated on the Total Ion Chromatogram (B), from sample collected at Port C during trial O_3B-2.

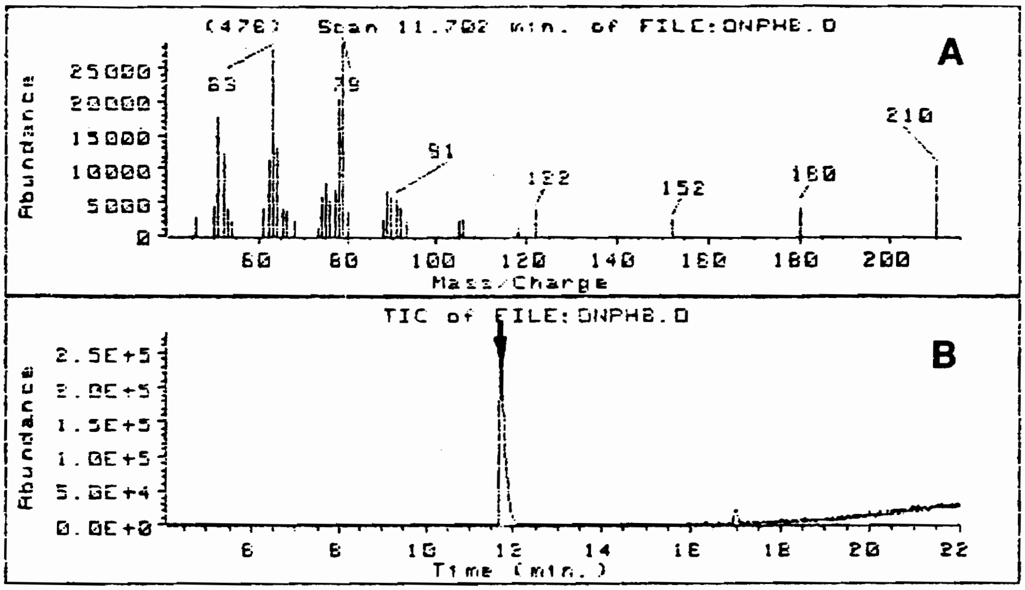

Figure C.5. Mass spectrum of standard DNPH-formaldehyde derivative MW 210 (A) indicated on the Total Ion Chromatogram (B).

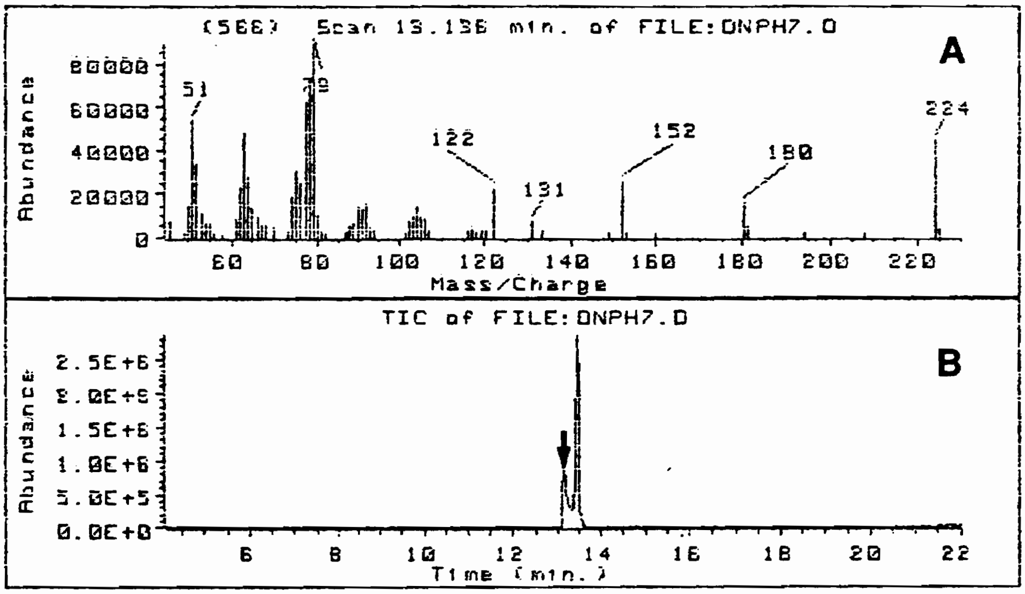

Figure C.6. Mass spectrum of standard DNPH-acetaldehyde derivative MW 224 (A) indicated on the Total Ion Chromatogram (B).

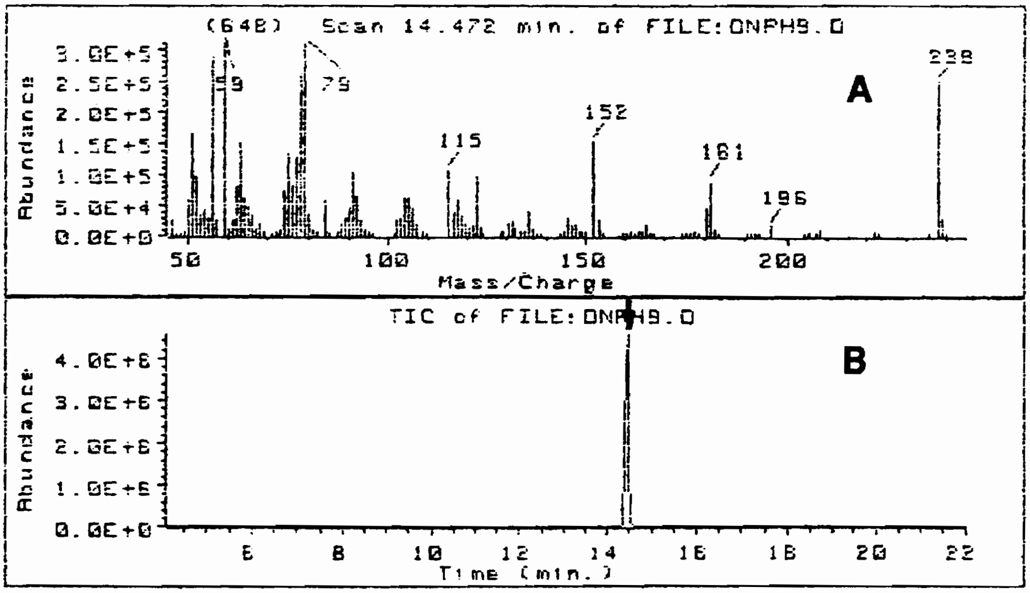

Figure C.7. Mass spectrum of standard DNPH-acetone derivative MW 238 (A) indicated on the Total Ion Chromatogram (B).

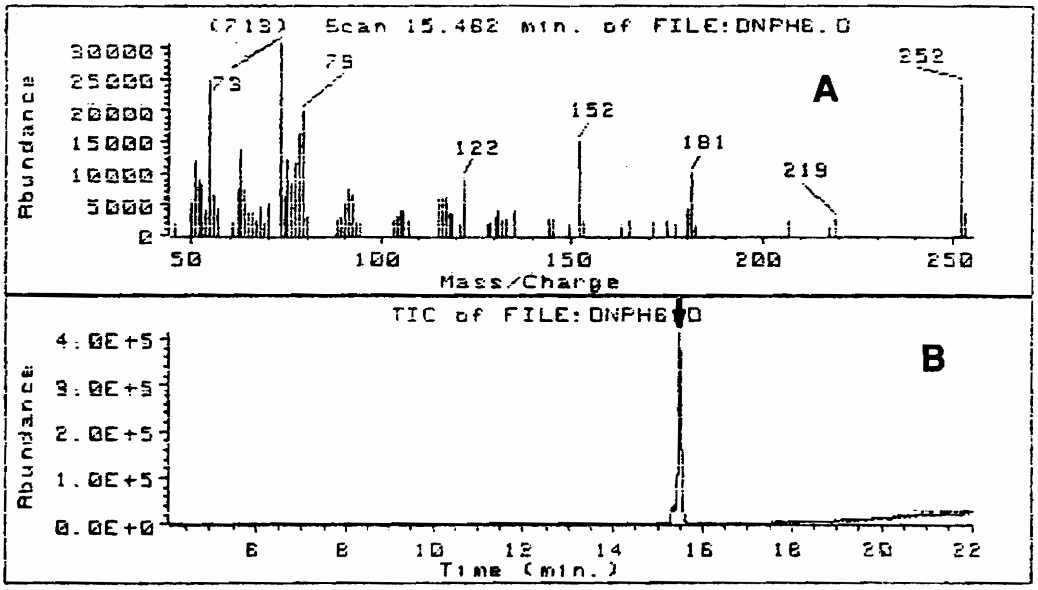

Figure C.8. Mass spectrum of standard DNPH-butanone derivative MW 252 (A) indicated on the Total Ion Chromatogram (B).

VITA

Kevin James Bald was born on October 11, 1967 in Philadelphia, Pennsylvania. Born into a military family, he moved frequently during his childhood, and was afforded the opportunity to visit many places most people only hear about or see on television. He was raised to appreciate the wonders of nature, culture, and history, and for this he is eternally grateful. Kevin settled in Springfield, Virginia long enough to attend and graduate from West Springfield High School in late spring of 1985. In 1985 he enrolled at Virginia Polytechnic Institute and took residence in Blacksburg in the beautiful rolling hills and forests of Southwest Virginia. There he remained until 1992, obtaining a B.S. in Industrial Engineering and an M.S. in Environmental Engineering. While at VPI he exercised his love for the outdoors as often as possible, fishing the New River, hiking the Appalachian Trail, or just wandering the campus. He joined the brotherhood of Delta Kappa Epsilon, and will always treasure the friendships and adventures he found in their midst. He developed a keen interest in the history of our Civil War and found his calling in the environmental field after pursuing several false leads. In July 1992 Kevin moved to Arlington, Virginia and began his career as an environmental engineer and the rest of what has already been a great life.