

REACTIONS OF REDUCED SULFUR COMPOUNDS WITH OZONE

By

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Abstract of Dissertation Presented to the
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Due to increasing emphasis on the elimination of industrial odors, odor control is a major concern of the kraft pulping industry, and continuous research is needed to evaluate any feasible method that will aid in eliminating this problem. Ozone is one of the most powerful oxidants known, and has been suggested for kraft odor control by gas-phase oxidation of the sulfur compounds. The application of ozone in the kraft industry is near non-existent, and laboratory investigations are very limited and concern primarily only oxidation of hydrogen sulfide.

The purpose of the present study was to evaluate the effectiveness of ozone in gas-phase oxidation of the four malodorous sulfur compounds primarily responsible for the kraft odor problem; namely, hydrogen sulfide, methyl mercaptan, dimethyl sulfide, and dimethyl disulfide. The initial phase of the study involved the use of bottled gases, whereas the last phase evaluated the ozone oxidation of an actual kraft mill source -- smelt tank vent gas.

Experimental data were obtained with the use of a heated, stainless steel reaction tube. Six sampling ports spaced down the length of the tube provided reaction times ranging from approximately 5 to 60 seconds.

For the bottled gases, ozone to sulfur gas ratios of 0.5 to 8.0 were evaluated at reaction tube temperatures of 38° C to 125° C. The effectiveness of ozone oxidation was noted by monitoring the decrease in initial sulfur gas concentrations at various conditions of reaction time, temperature, and concentration ratios. Multiple regression analysis was used to evaluate the data points obtained for each gas, and provide several regression equations representative of the oxidation process for the conditions studied.

Results of the data on bottled gases indicated that concentration ratio and reaction temperature had a much more significant effect on oxidation than did increased reaction time, and to achieve complete oxidation of the malodorous sulfur compounds, ozone concentrations of more than twice the stoichiometric amount would be required for the reaction times and temperatures studied. The percent oxidation achieved in this study for hydrogen sulfide was significantly higher than that reported by other authors, and attributed primarily to the difference in experimental conditions and procedures between the investigations.

For experiments with actual kraft emissions, total reduced sulfur (TRS) of the smelt tank vent gas stream was continuously monitored with an electrolytic titrator. Ozone was effective in eliminating all of the methyl mercaptan, dimethyl sulfide, and dimethyl disulfide from this source at an ozone to TRS ratio of approximately 2.50. These three sulfur compounds accounted for about 52 percent of the TRS as determined by gas-liquid chromatography. In view of the oxidation results with bottled gases, the concentration ratio of 2.5 for a stack source was considered acceptable, recognizing the vast difference in a stack effluent as opposed to a bottled gas source.

Additional studies are needed to further evaluate the ozone oxidation of various kraft mill sources, covering a wide range of stack conditions and reaction times. The current study indicated that complete oxidation of the malodorous compounds would only be achieved with reaction times far exceeding those normally experienced in an emission stack, thus requiring the possible need of holding chambers to achieve adequate mixing. Costs are also of major concern, both for ozone production and additional facilities for increased mixing time, but were not evaluated as part of this study.

CHAPTER I

SCOPE OF RESEARCH PROJECT

Introduction

Ozone is one of the most powerful oxidants known, and is finding increasing use in the field of odor control. Due to its high electro-negative potential (second only to fluorine) the potential applications for ozone as an oxidant are considerable, but have been somewhat limited in the past due to the practical requirements that it be used in its gaseous state, the low concentrations of ozone to parent gas (air or oxygen) delivered by ozone generators, and the cost of ozone in pounds/kilowatt hours. Improvements in ozone generator design and efficiency, the availability of tonnage oxygen at decreased costs, and the emergence of cylinder ozone have expanded the economical applications of this oxidant for various commercial uses.

Gas-phase oxidation of malodorous compounds with ozone for industrial odor control is mentioned by Yocum and Duffee (1) and Turk (2, 3) and is used today for controlling odors from sewage treatment plants, lift stations, and various commercial operations (kitchens, rendering plants, food processing, rubber compounding mill, chemical exhausts, etc.). Its use specifically for controlling malodorous sulfur emissions from sulfate pulping operations has been suggested by Sarkanen, et al. (4), Douglass (5),

and Cromwell (6) and a patent has been issued for the process (7), but application of this method has been very limited. The article by Cromwell (6) describing the experimental use of ozone to treat effluent gases from a sulfate recovery system at a pulp and paper mill in Canada was the only reference found on actual mill effluent application. Ricca (8) reported on the use of ozone to oxidize exhaust gases from a bench-scale, black liquor oxidation system, and Akamatsu (9) studied the use of ozone in deodorizing kraft mill blow gases produced from an autoclave. Laboratory studies on the reaction of ozone with hydrogen sulfide (from cylinders) have been reported by Gregor and Martin (10), Cadle and Ledford (11), Hales (12) and Finlayson, et al. (13).

Due to the decreased costs in tonnage oxygen over the past few years, improved ozone generation, the possibility of on-site production of oxygen for waste treatment systems and oxygen bleaching, and the increasing emphasis and regulations directed toward eliminating industrial odors, additional data are needed on the feasibility of using ozone for odor control in the sulfate pulping industry.

Research Objective

The objective of this study was to evaluate the effectiveness of ozone in gas-phase oxidation of the four major components of kraft mill odors; namely, hydrogen sulfide (H_2S), methyl mercaptan (RSH), dimethyl sulfide (RSR), and dimethyl disulfide (RSSR). The study involved mixing ozone with each of the individual gases (from cylinder sources) at a variety of concentration ratios, temperatures, and reaction times, followed by analysis of the reaction products. Tests were also performed to evaluate

the effectiveness of various ozone concentrations (and reaction times) on actual emissions from a smelt dissolving tank by analyzing the effluent gas prior to and following ozone injection. The range of experimental conditions (sulfur concentrations, reaction temperatures, etc) for the study included those normally found in the kraft pulping industry.

Research Outline

The research was accomplished according to the following outline:

- (1) Review the air pollution problem facing the pulp and paper industry in the elimination of odorous emissions from sulfate pulping operations, the basic approaches to industrial odor control, and the methods currently used by the industry for control of odorous emissions.
- (2) Review the general characteristics and applications of ozone, such as its physical and chemical properties, methods of generation, toxicity, reactions with various compounds, and uses in the treatment of domestic and industrial waste, drinking water purification, etc.
- (3) Perform a literature survey for previous studies and applications of ozone for odor control in the pulp and paper industry, and in other industries or operations with odor problems (sewage treatment plants, food processing, rendering plants, etc.).
- (4) Select and obtain ozone generating equipment and other experimental apparatus required for studying ozone reactions with bottled sulfur gases and kraft mill effluent gases, both at various experimental conditions.

- (5) Perform experiments designed to evaluate the effectiveness of ozone in oxidizing each of the four odorous sulfur gases (from cylinder sources) at various concentration ratios, reaction temperatures, and reaction times.
- (6) Perform experiments designed to evaluate the effectiveness of ozone at various concentrations and reaction times in oxidizing sulfur compounds in an actual kraft mill effluent gas.

CHAPTER 11

ODORS AND THE SULFATE PROCESS

The Odor Problem

Basis of Problem

Since the development of the sulfate process by Dahl in 1879 as a method of making pulp and paper from wood, the operation of the first sulfate (kraft) mill in 1891, and the appearance in the literature of the first papers concerning kraft mill odor around 1900, there has been little doubt that odor control is a major problem of the kraft pulping industry.

Recent evidence of this continuing problem is the number of papers and reviews published in the last few years concerning atmospheric emissions from kraft pulping operations, with the major portion concerning odorous emissions. Literature published prior to 1963 on air pollution and the kraft pulping industry is reviewed in an annotated bibliography by Kenline and Hales (14). Hendrickson (15) edited the proceedings of an international conference on sulfate pulping emissions held in 1964 at Sanibel Island, Florida. Environmental Engineering, Inc. and J. E. Sirrine Co. published a three-volume study in 1970 for the National Air Pollution Control Administration (16) on control of atmospheric emissions in the wood pulping industry, and a 1970 conference in Stockholm (17) on methods for measuring and evaluating odors had several presentations

on odors from the kraft pulping industry. Annual reviews (18-23) of published literature relative to air pollution control in the pulp and paper industry are prepared by the National Council of the Paper Industry for Air and Stream Improvement. Other excellent reviews are by Sarkanen, et al. (4), Adams (24), and Wright (25).

The major components responsible for this characteristic kraft odor are all sulfur compounds (16, 26-28); namely, hydrogen sulfide (H_2S), methyl mercaptan (RSH), dimethyl sulfide (RSR) and dimethyl disulfide (RSSR), and are referred to as reduced sulfur compounds. These four gases were first identified by Klason during a series of studies from 1908-1924 (4), which is another indication of how long the kraft odor problem has been under investigation and how difficult it is to eliminate. Although some of the odor-producing components of the effluent may be associated with non-sulfurous compounds (29), most attempts to control odors are directed to the four sulfur gases mentioned above.

The elimination of these odors is difficult primarily because of their extremely low odor threshold, or minimum detectable concentration. Table I is a summary of odor threshold values reported in the literature for these four gases of interest. The values are for the pure compound, not for the gas in combination with other gases (sulfur and non-sulfur) as would be under actual conditions. Odor thresholds for a combination of these gases may be completely different than those reported, but would not be a simple addition of the threshold values of each component (37). Due to different tests used to determine threshold values, data treatment, purity of the compounds studied, and interpretations of the word "threshold," a range of values are reported for each compound, but

TABLE I
THRESHOLD ODOR VALUES

Compound	Threshold Odor (ppb) ^a	Reference
Hydrogen Sulfide	4.1	30
	6.0-12.0	31
	7.1	32
	4.7	33
	100.0	34
	20.0	35
Methyl Mercaptan	1.0	30
	2.1	33
	10.0	34
	40.0	36
Dimethyl Sulfide	2.0	30
	1.0	33
	50.0	34
Dimethyl Disulfide	5.6	30
	500.0	34

^aParts per billion by volume.

serve to indicate that the odor threshold of each gas is extremely low.

In addition to the problem of low odor threshold values, the fact that kraft odors are released from so many different points throughout a mill is another obstacle in odor control for this industry. To reduce ambient concentrations of these odorous emissions to threshold values in mill localities, each source will have to be investigated and controlled. Although the same basic process is used in each mill and the emission sources are similar, each mill presents its own particular set of problems, and what may be effective at one installation may not be at another without modifications.

Effects of Odorous Emissions

Why are odors objectionable, and why all the concern about them? Odors are intangible, but may be generally described by their odor threshold, intensity of levels above this threshold, acceptability, and their characteristic properties which distinguish them from other odors regardless of intensity or acceptability (38). For air pollution studies, the most important dimension of an odor is its acceptability, or how many people are inconvenienced by the smell and to what extent. Numerous articles (17, 31, 32, 39-48) are found in the literature describing the evaluation of odors for their objectionability, measurement by test panels and community observer corps, description of nuisance effects, differences in human response to odors, measurement by chemical analysis, and needs for future research in the odor field. Since a quantitative measure of inconvenience, objectionability, or acceptability is sometimes hard to determine, the odor threshold value is normally used for evaluation. As shown previously, even this value is subject to large variations.

Odors in themselves have not been shown to be the direct cause of any disease, but various ways in which they may affect a person's well-being are discussed by McCord and Witheridge (49) and Stockman and Anderson (48). These include reduced appetite, nausea, headaches, interference with sleep, and mental stress. Economic effects of odors, such as the lowering of property values, reduced sales and rentals in resort areas, and reduced desirability of a community in which to live are also mentioned. In sufficient concentrations, sulfur emissions common with kraft mills (particularly hydrogen sulfide) are highly toxic and can be fatal (50), but health hazards resulting from the presence of these gases in the atmosphere around sulfate pulping operations are not

considered to be of any concern due to their diluted concentrations (51, 52). Even though not considered a health hazard, discharges from kraft mills have reportedly caused nausea, headaches, eye irritation, and upper respiratory irritation (48). Other detrimental effects attributed to sulfur emissions are corrosion (35, 48, 53) and darkening of paint by hydrogen sulfide (48, 52, 54).

Regardless of the various economic and health effects that have been attributed to odorous sulfur compounds, their nuisance aspect is of primary concern. This is evidenced by the volumes of literature previously mentioned concerning odors and the sulfate pulping industry, and leaves no doubt that the odors are an annoyance to the public, and therefore undesirable.

Source and Quantity of Odorous Emissions

The various process reactions and factors responsible for kraft odor generation are beyond the scope of this study, but are well described in the literature (4, 16, 26, 27, 51, 55-59). As previously mentioned, odorous gases are generated and released at several points in a kraft mill complex, and at varying temperatures and concentrations. Table 2 is a summary of data from the study for NAPCA (16) listing major sources of odor release in a kraft mill, and ranges of temperature, gas flows, and odorous emissions at each source. Similar data are also listed by Hough and Gross (60), Adams (61), and Sarkanen, et al. (4). Considering the amount of total reduced sulfur compounds that may be generated at various points in a 500-1000 ton per day kraft mill complex, the low odor threshold for each of these compounds (Table 1), and increasing emphasis and regulations (62) directed toward eliminating these emissions, the magnitude of the kraft pulping industry's odor control problem becomes readily apparent.

TABLE 2

SUMMARY OF KRAFT EMISSION DATA

Source	Temp. (°C)	Gas Flow (CF/ADT) ^a	Range of Sulfur Gas Concentrations (lb/ADT) ^b			
			H ₂ S	RSH	RSR	RSSR
Digester Relief	49	35	0-.01	.01-1.00	.10-.40	.10-.20
Digester Blow	49	300	.10-.12	.40-.47	1.20-1.40	1.30-1.50
Brown Stock Washers	52	80,000	.01-.12	.10-.25	.01-.02	.01-.02
Oxidation Towers	57	13,000	.01-.02	.05-.10	.02-.08	.05-.15
Multieffect Evap.-0x.	49	35	.01-.02	.10-.30	.05-.15	.05-.15
Multieffect Evap.-Unox.	55	35	.10-3.00	.10-1.50	.05-.08	.01-.02
Recovery Furnace & DCE-0x.	163	400,000	1.00-5.00	.01-.25	.01-.10	.01-.20
Recovery Furnace & DCE-Unox.	163	400,000	5.00-30.00	.50-2.50	.10-.30	.10-.40
Smelt Tank	88	44,500	.02-.05	.02-.05	.01-.02	0-.01
Lime Kiln	82	50,000	.20-.52	.10-.50	.01-.28	0-.08

^aCubic feet per air dried ton of unbleached pulp.

^bPounds per air dried ton of unbleached pulp.

Industrial Odor Control

The control of odorous gases from industrial sources can normally be accomplished with one or more of the following methods (1-3, 63):

- (1) Reducing or eliminating the initial formation of odorous compounds through process modifications or use of a completely new process,
- (2) Use of various techniques, such as adsorption, absorption, condensation, combustion and chemical oxidation, to remove or reduce odorous gases in the effluent stream prior to their emission into the atmosphere,
- (3) dispersion of the odorous gases (usually through tall stacks) to a greater extent so that they are less concentrated upon reaching any point where they may be detected,
- (4) Addition of other odorant gases to the effluent stream so that the resultant odor becomes less objectionable through either odor masking or odor counteraction.

The use of any of the above methods, or their combinations, depends upon several factors, such as volume of the effluent stream, characteristics and concentrations of particulates and odorous gases in the effluent, location of the particular industry, normal atmospheric conditions, and the chemical reactions taking place in the process. The following sections are brief descriptions of each method mentioned above.

Process Modifications or Substitution

Reduction, or elimination, of the initial formation of odorous gases through process modifications or the use of a completely different process would be a major step in any odor control program, and, in many cases,

could be more effective and cheaper than complete abatement procedures at the stack. Just by reducing the initial odor formation, less load would then be imposed on any control equipment downstream.

Odor control through process changes may include an adjustment of process temperature, residence time, or pressure in various operations, substitution of low odor (or odorless) solvents or reactants for highly odorous ones, a change in flow diagrams to prevent contact of odor producing gases and/or liquids, and proper maintenance and housekeeping practices.

Adsorption

Odor control by adsorption results from an interaction between the malodorous gas and a solid due to the phenomena of surface attractions universal with all substances. The forces that hold atoms, molecules, and ions in the solid state exist throughout the solid and also at its surface, and thus are available for binding other molecules which contact the surface or come in close proximity to it. As a result of these forces, any gas, vapor, or liquid will adhere to any solid surface to some degree (64). This phenomenon is called adsorption (or sorption), the adsorbing solid is called the adsorbent (or sorbent), and the adsorbed material is the adsorbate (or sorbate). This process is useful in air pollution control since it provides a means of concentrating malodorous emissions for ultimate disposal or recovery.

Depending upon the adsorbent, the gases of concern (or adsorbate), temperature, etc., various adsorption processes are available. In chemical adsorption (chemisorption), chemical bonds are formed between the gas and the adsorbent, such as the formation of CO and CO₂ when oxygen is adsorbed on activated carbon at ambient temperatures. In physical

adsorption, the adsorbate is chemically unaltered, and the gas-solid bond may be broken by elevation of the temperature. In some cases, the adsorbates are reactive with each other, and, by concentrating them, the adsorbent acts as a catalyst by speeding up their reaction rate. Adsorbents may also be treated with a specially selected catalyst or reactant prior to use in order to increase its capacity, rate, or selectivity for odor removal. Various factors influence the quantity of material that can be adsorbed by a given weight of adsorbent, and are discussed in detail by Turk (64) and Summer (65). For all practical purposes, the control of atmospheric odors by adsorption is limited to the use of activated carbon as the adsorbent (1, 3). It adsorbs all types of odors under almost any condition, performance is not weakened by the presence of moisture, and it can be used without making a careful analysis of odor content. Von Bergen (63) and Lee (66, 67) discuss the applications of activated charcoal in air pollution control and the design of adsorption systems.

Other adsorbents are available, but show greater selectivity than activated carbon due to their polar nature. For this reason, they are more useful than carbon when separations are to be made among different pollutants in an effluent stream, but are not as good for overall odor control applications. Typical of these adsorbents are silica gel, fuller's, diatomaceous, and other siliceous earths, and synthetic zeolites. Metallic oxides are also used, but are even more polar than the siliceous adsorbents listed above. For this reason they are never used directly for source control of airborne pollutants by physical adsorption, but are used as desiccants, catalyst carriers, or catalysts. Activated alumina (aluminum oxide) is typical of this group.

Once the adsorbent is saturated with the odorous material, several means of disposal are available depending upon the various materials involved. The adsorbate may be desorbed and either discarded or recovered (if valuable), the adsorbent and the adsorbate may both be discarded, or the adsorbate may be oxidized on the adsorbent surface.

Absorption

Where odorous gases are soluble in a liquid, with or without chemical reactions, absorption methods may prove useful for odor control. The transfer of an odorous gas from the effluent stream into a scrubbing liquid requires initial contact of the two mediums in some type of wet scrubber, and then separation into a clean gas and contaminated liquid stream. Gaseous transfer is basically through diffusion, moving from a region of high concentration in the gas stream to one of low concentration in the scrubbing medium. The odorous molecules may also be attached (or adsorbed) to particulate matter in which case both would be removed from the gas stream through various particulate collection mechanisms (inertial, gravitational, etc.).

Various methods are used for gas-liquid contact in wet scrubbers, but are divided into two basic categories -- low energy types and high energy type. Low energy scrubbers achieve absorption by flowing gas through spray chambers, or through restricted passages in a plate or packing on which a liquid head is maintained. Examples of this type include open spray towers, packed towers, wet centrifugal or cyclonic, flooded bed, orifice, and wet dynamic (68). The high energy types, or venturi scrubbers, use a venturi for gas-liquid interaction by impacting high velocity gas on the injected liquid streams, and include the ejector venturi, flooded-disc scrubber, and the dry or wet venturi. Additional

details, design information, etc., on liquid scrubbers are given by Imperato (68), Sargent (69), Calvert (70), and Summer (65).

In all types of scrubbers, it is possible to use an absorbing medium other than water to achieve better odor control through chemical reactions between the gas and liquid rather than just physical solution. Of course, this would depend upon the odorants to be removed, origin and disposition of the scrubbing liquid, corrosive effects, etc. As with any odor control system, basic procedures should be followed when considering or evaluating absorption for odorant removal, and are listed by Von Bergen (63) in addition to the above mentioned references (65, 68-70).

Condensation

Many odorous gases can exist as liquids under ambient conditions, and through simple condensation, cooling such vapors can remove much of the odor from an effluent stream. If the odorant gases have an appreciable solubility in water and moisture is present in the exhaust stream, condensation of the water can also reduce the concentration of malodors released to the atmosphere (71, 72).

The two basic types of condensers are surface and contact. Surface condensers rely upon cooled surfaces where the coolant does not come in contact with the odorous vapors. Contact condensers use a mixture of coolant, vapors, condensate, and non condensable gases, and are applicable to a wider range of odor-control problems and less expensive than surface condensers. However, they produce large volumes of contaminated water which can create a water pollution problem, and care must be taken to prevent re-release of the odorous gases further downstream (1).

Condensation is basically the transfer of an air pollution problem to one of water pollution, but can be very beneficial if an efficient utilization or treatment of the aqueous effluent is available.

Oxidation Systems

Complete oxidation of odorous gases is an effective means of odor control since the final products are either odorless (H_2O , CO_2) or have comparatively very high odor threshold values. If oxidation is incomplete, however, the odors may increase as evidenced by incinerators, incomplete combustion in diesel and internal combustion engines, conversion of alcohols to carboxylic acids, etc. (3, 63). Oxidation systems may be classified as combustion (high temperature) or chemical (low temperature).

Combustion Oxidation

The three basic methods used to incinerate waste gases are flame, thermal, and catalytic combustion. Each method requires that the odorous effluent be heated to the point where the combustible contaminants will burn. The only basic difference is the temperature range at which the units operate.

In flame (or direct-combustion) incineration, if the emission concentrations are in the flammable range, they are destroyed by burning as in a flare. For fluctuating process conditions, or for concentrations at the lower flammable limit, auxiliary fuel is used to maintain a burning mixture. Although flame incineration can be used over a wide range of concentrations, it is most economical at high concentrations since the contaminants could be utilized as fuel. Operating temperature of these units is approximately $2500^{\circ} F$.

Normally, the concentration of combustible contaminants in an effluent stream will be considerably below the lower limit of flammability, and thermal incineration is much more economical than flame incineration. In this system a residence chamber is used, and the contaminants are

destroyed by exposure to temperatures of 900-1400° F in the presence of a flame. Although electric heat energy can be used, the presence of a flame is an important factor for contaminant removal. With electric heat, temperatures of 1500-1800° F are required to obtain the same efficiency achieved with a flame system at 900-1400° F. Continuous operation at efficiencies of 90 to 99 percent have been achieved with flame systems (73).

In a catalytic system, the oxidation of odorous effluent occurs directly on the surface of a catalyst, usually composed of a precious metal (platinum), and in the absence of a flame. Temperatures out of the catalyst bed range from 600-1000° F. The basic parts of this system are a preheat burner, catalyst bed, heat exchanger (for temperatures of 800-1000° F), exhaust fan, and control and safety equipment. Even though some oxidation may take place in the presence of the preheat burner flame, the primary function of this component is only to raise the gas stream to the desired operating temperature for entry into the catalyst bed. Efficiencies in the range of 85-92 percent are reported for properly maintained catalyst systems.

Additional details on each of the above combustion systems, such as initial costs, operation and maintenance costs, design variables, operating characteristics, and factors influencing the selection of each method, are reported by Brewer (74) and Pauletta (73).

Chemical Oxidation

Chemical conversion of many organic gases and vapors to odorless compounds is generally accomplished with oxidizing agents such as ozone, chlorine, chlorine dioxide, and potassium permanganate. An important factor in this method of odor control is the fact that these agents do

not always convert organic substances to their most highly oxidized products (CO_2 and H_2O), so the odor of the intermediates may be of concern.

Depending upon the emission process and the character of the odorous effluent (moisture content, temperature, etc.) contact between the oxidizer and odorant may be gas-gas, gas-liquid, or gas-solid.

The only significant examples of gas-phase oxidation have been the use of chlorine and ozone. Due to its possible corrosive effects, residual odor, and toxicity, chlorine is seldom used in this method. Although also toxic, ozone is used in many odor control applications through release into a stack or vent containing odorous effluent, and is discussed in Chapter III.

For gas-liquid contact, chlorine, chlorine dioxide, and potassium permanganate are the principal oxidants and are normally added either to the scrubbing liquid or to the gases entering the scrubber.

Gas-solid contact is achieved in many applications with the use of activated carbon impregnated with various compounds which react with the odorous effluent after initial adsorption by the carbon. Activated alumina and an aqueous potassium permanganate solution are also used in a similar manner (1).

Dispersal

Reducing the concentration of a malodorous effluent to below the sensory threshold by dilution is still one of the most common methods of odor control. Such dilution is normally achieved by collecting and discharging all emissions through a tall stack and/or increasing the temperature and velocity of the effluent, or by locating the source of emissions (such as a plant) at increased distances from any receptor.

Formulas are available (75) to estimate the average downwind, ground-level concentration of a plume discharged from an elevated continuous source (such as a tall stack), and are a function of emission rates, stack height, effluent temperature, and various atmospheric parameters that describe the meteorological situation. Up to distances of a few miles, and for durations up to ten hours, these formulas will predict concentrations that are within a factor of two or three of the observed values most of the time. At greater distances and longer time intervals, the predicted concentration is much more subject to being in error, but generally should not exceed a factor of ten within the plume trajectory (1, 2).

The formulas predict average concentrations over a period of time, but most odor complaints usually result from peak levels. Since even a brief exposure to a peak concentration may be unacceptable to the populace, the degree of dilution needed for adequate deodorization is normally much greater than that predicted by the calculations. Some studies (1, 76) have shown that the distance from a source at which an odor was detected was not even approximately predicted by dilution and dispersion calculations. Large discrepancies were found by Wohlers (76) in comparing odor travel from different plants based on stack-gas dilution calculations. His most extreme sample was from a kraft pulp and paper mill for which the average dilution needed to reach threshold was 32:1, and the maximum 64:1. The minimum dilution of actual stack effluent was calculated to be 990:1; thus predicting that the odors would not be detected at ground level. Field surveys over a six-month period showed that the kraft odor could be detected at distances up to eight miles where the calculated dilution of stack effluent was 840,000:1, and there were some reports of the odor at a distance of 40 miles.

In addition to errors which can be due to various factors used in meteorological dispersion formulas, the variability of odor threshold in humans, and the possible role of cumulative secondary sources, Turk (2, 3) suggests the role of particulate matter in the transfer and/or perception of odors by humans and as a possible explanation to some of the large discrepancies found in previous studies.

Various design factors, cost information, etc., on the construction of tall chimneys are given in an article by Carlton-Jones and Schneider (77). Meteorological influences on mill effluent dispersion are discussed by Wright (78) and Cramer (79).

Odor Masking

Odor masking is a process in which the perception of an offensive odorous gas is obscured by the addition of other odorous material under conditions that do not involve chemical change to either agent. Hopefully, a more pleasant and acceptable odor sensation is created. The masking agent does not affect the composition of the original malodorous gas, and if the two odors are of near equal strength, a blend of the two is observed and both can be identified. If one is considerably stronger than the other, generally it alone is perceived (2, 63).

Various chemicals are used for odor masking, such as vanillin, methyl ionones, eugenols, benzyl acetate, phenylethyl alcohol, and heliotropin, and must be carefully selected for each particular odor problem. Factors which must be investigated include an analysis for (or a lack of) toxic materials in the effluent stream, addition of the masking agent into the exhaust stream, surrounding area, or as an additive to the process, odor compatibility between the masking agent and malodorous

compounds so a more offensive odor will not result, amount of malodorous material in the exhaust stream, temperature and other conditions of the process and stack effluent, and amount of masking agent required. Pilot plant or laboratory experiments should be run to establish ratios that produce a desirable result.

Advantages of using masking agents are minimum or no capital investment for equipment, ease of application, relatively low operation and maintenance costs as compared with other odor control equipment, and immediate availability for common odor problems. The main disadvantage of this method is that the original malodorous gases are not eliminated from the atmosphere, and may be of such magnitude that odor masking is not economically feasible or desirable. Also, additional odors are being injected into the atmosphere, and, although may be initially more acceptable than the original malodors, they are still subject to complaints from the population since individual reactions to odors are quite variable and change from time to time.

In addition to the two references (2, 63) previously cited, a thorough review of masking is also given by Summer (65).

Odor Counteraction

Odor counteraction (neutralization) is a reduction in the intensity of an offensive odor due to the fact that certain pairs of odors in appropriate concentrations are antagonistic, and when sniffed together, both are diminished. This principle of odor control is distinct from that of odor masking in which strong odors tend to mask weaker ones and the perception of the offensive odor is obscured.

Various pairs of counteracting odorous substances were first published in 1895, and, since that time, similar studies have been made where it was

possible to compensate the olfactory effects of various chemicals to a point of total odor disappearance, or close to it. From those studies, it is known that in the group benzene, toluene, xylene, pseudocumene and durene, combinations from this group in the correct proportions can be produced which are almost odorless. Thus, many materials are available for odor counteraction, including the essential oils (63).

Odor counteraction is particularly effective against multiple odor sources (typical of many industrial plants) which form an odorous "pool" that emanates from a plant site through molecular dispersion and general air movement. An atomizing nozzle is used to vaporize the counteractants and inject them into the air stream where they are designed to mix with and follow the odorous pool. The vaporizing points are located either in the exhaust stacks or in the general vicinity of the major odorous sources. Odor counteraction formulas are designed for specific odor groups, and the installations should be made by a specialist who can discriminate between various odors and estimate the intensity of concentrations involved in the overall problem.

As with odor masking, various procedures must be followed to obtain the best results, and are covered in detail by Von Bergen (63) and Summer (65). Advantages and disadvantages of the two techniques are similar also. Effectiveness of the installation must be determined by actual odor perception of the populace, which is actually the criteria for evaluating the success of any odor control program.

Odor Control in the Kraft Pulping Industry

The major odor control methods used by the kraft pulping industry include process modifications (black liquor oxidation, elimination of direct contact evaporator, etc.), proper operation and maintenance of equipment, combustion and chemical oxidation, absorption, and dispersion. Odor masking is used to some extent. Condensation, primarily for heat recovery, does remove malodorous sulfur compounds from the digester and evaporator gas streams, but presents additional problems in odor control and waste treatment.

Brief descriptions of each method and literature references are presented in the following sections.

Black Liquor Oxidation

Typical of a process change developed to prevent initial formation of malodorous sulfur gases is the practice of black liquor oxidation which is extensively employed throughout the world as a partial solution to the kraft odor problem. The main purpose of black liquor oxidation is to oxidize sodium sulfide in the liquor to sodium thiosulfate to prevent liberation of hydrogen sulfide in the direct contact evaporator.

In the direct contact evaporator, black liquor (at approximately 50 percent solids) is brought into direct contact with hot gases from the recovery furnace to increase its solids content to a firing concentration of 65-70 percent solids. With unoxidized black liquor, carbon dioxide and sulfur dioxide in the furnace gases will react with sodium sulfide in the liquor to generate hydrogen sulfide as follows (16):



With oxidized black liquor, however, the sodium sulfide has been converted to sodium thiosulfate which is relatively stable, and will not break down in passing through the direct contact evaporator. Thus, neither of the above reactions will take place and the sulfur will be retained in the system.

Black liquor oxidation can take place prior to the multiple effect evaporators (weak black liquor oxidation) or immediately before the direct contact evaporator (strong black liquor oxidation). Depending on which system is used, oxidation is normally accomplished by reacting the sodium sulfide with oxygen from the air in either a packed tower, bubble tray tower, or air sparged reactor. Various factors affect the choice of a weak or strong black liquor oxidation system and each has distinct advantages and disadvantages. Thorough reviews of black liquor oxidation are by Collins (80), Guest (81), Landry (82), Hendrickson and Harding (83), and Blosser and Cooper (84). The kinetics of oxidation are discussed by Wright (85) and Murray (86), and effects of operating variables on strong black liquor oxidation by Morgan, et al. (87). The use of pure oxygen instead of air for oxidation was studied by Ricca (8), Galeano and Amsden (88) and Fones and Sapp (89). Significance of the direct contact evaporator as a major source of odor and the importance of practically complete black liquor oxidation to prevent these odors is reported by Murray and Rayner (58) and Blosser, et al. (90).

With new recovery furnaces and unit processes designed to eliminate the direct contact evaporator (as discussed in the following section), the requirement for black liquor oxidation would be virtually eliminated in the construction of new mills since it was originally developed to

prevent odor generation in this unit. Although it has been shown that weak black liquor oxidation will reduce sulfur emissions from the multiple-effect evaporators, the disadvantages and difficulties with the system would outweigh this minor contribution. The small volume of the evaporator effluent stream (generally less than 100 cfm) makes collection and burning in the lime kiln a relatively simple matter, and in addition, elimination of black liquor oxidation would also eliminate the need for treating the oxidizer off-gas (91).

Elimination of Direct Contact Evaporation

The direct contact evaporator has been shown to be a major source of malodorous sulfur emissions (51, 58, 90, 92), and elimination of this unit from the kraft recovery process is a major contribution toward odor control in the kraft pulping industry. Operation of recovery furnaces without direct contact evaporators has been practiced in Scandinavian countries for some time (93, 94) and is showing increased interest and application in the United States.

Two basic methods have been employed to increase the black liquor concentration to firing conditions and avoid direct contact with recovery flue gases. Hochmuth (95) describes the Air Contact Evaporator (ACE) system by Combustion Engineering, Inc. (96) in which combustion air for the furnace is preheated by flue gas to approximately 600° F in an air heater. The flue gas is thus cooled from approximately 800° F to 325° F, and discharged to the atmosphere without coming in contact with the black liquor. The stream of preheated air then passes to a direct contact evaporator where it loses sensible heat while evaporating water from the black liquor. Air leaving the direct contact evaporator is

conveyed to the primary and secondary air admission ports of the furnace as combustion air. Any malodorous sulfur gases that may have been formed during the evaporation process are destroyed by incineration in the high temperature combustion zone of the furnace.

Clement and Elliott (97) describe the development of a new recovery furnace by The Babcock and Wilcox Co. (98) to operate directly an unoxidized high-solids liquor from multiple-effect evaporators, thus eliminating direct and indirect contact between the furnace flue gases and black liquor for evaporation purposes. American Can Company's new mill at Halsey, Oregon, utilizes a three-section, forced circulation concentrator in addition to a sextuple effect evaporator system to obtain the desired black liquor concentration for firing, and is discussed in detail by Canovali and Suda (99).

Proper Operation, Maintenance, and Housekeeping

Regardless of what process changes or additions are made, adequate odor control will not be achieved unless operations are performed within design capabilities of the equipment, and continued efforts are made to prevent leaks and the accumulation of odor-producing materials. Proper maintenance of control equipment to prevent breakdowns is an absolute necessity also.

Even though the recovery furnace has long been regarded as a major source of kraft mill odor, studies (51, 90) have been made on the relationship between furnace operation and odorous emissions which show that malodorous sulfur compounds at the furnace outlet can be reduced to negligible amounts if the furnace is operated within design capability with enough excess air to provide about 3 percent oxygen in the flue gas,

and if sufficient turbulence is obtained in the furnace oxidation zone. Furnace overloading by excessive black liquor firing rates is the normal cause of high malodorous emissions since the air handling capacity of the furnace is limited by the installation (4).

Combustion Oxidation

Along with black liquor oxidation, combustion oxidation has proven to be one of the most effective means of odor control used in the kraft pulping industry today. Whereas black liquor oxidation prevents the initial formation of odors, combustion oxidation is used for the destruction of malodorous gases generated in various kraft processes. At the present time, this method of odor control is used primarily for the destruction of digester and evaporator noncondensable gases in the lime kiln, and has shown to be virtually 100 percent effective (100). These two gas streams provide a low volume, high concentration source of malodorous sulfur gases, and can be collected and piped to the kiln relatively easily. The lime kiln has proven particularly useful for this method since the temperature (approximately 2000^o F) is sufficient for complete oxidation, air volume is sufficient for dilution, and sulfur dioxide (formed during oxidation) emissions are negligible (91, 100, 101).

Early work on the development and successful operation of burning these gases was done by DeHaas and Hansen (102) using an auxiliary furnace. Adaptation of the system for burning in the lime kiln is reported by Coleman (103). Numerous other articles (91, 99, 101, 104-106) are found in the literature describing the successful use of the lime kiln for destruction of noncondensable gases. Reports on the use of specially designed boilers and incinerators (107-109), recovery furnaces (99, 107, 110), waste wood incineration units (24) and natural gas-fired power boilers (111)

for burning the noncondensable gases are also found in the literature. The report by Canovali and Suda (99) describes the system at American Can Company's new mill in Halsey, Oregon, in which the noncondensable gases can be alternatively admitted to the recovery furnace in case the lime kiln is not in operation. Incineration of brown stock washer hood gases in the recovery furnace is also discussed in this article (99) and by Hisey (110).

Catalytic oxidation of kraft mill odors has been considered and used to some extent. The major problem appears to be related to the particulate loading of the gases and subsequent poisoning of the catalyst by these materials (61). Blosser and Cooper (100) mention the experience of two mills using catalytic furnaces containing a series of porcelain rods coated with a thin film of catalytic alumina and platinum alloy. Complete removal of mercaptan and dimethyl sulfide and more than 85 percent removal of dimethyl disulfide has been observed in one of these units. Maintenance of automatic controls has been a problem, and frequent replacement of catalyst cells may be encountered where removal of condensables is poor. A description of this system is also reported by Landry and Longwell (112) with a cost breakdown.

Catalytic oxidation has been suggested (113) for controlling emissions of organic solvent vapors (from printing and coating operations) but the presence of inorganic materials or catalytic poisons in the gas stream would have to be investigated.

Chemical Oxidation

Gas-liquid chlorination is widely used throughout the kraft industry for the chemical oxidation of malodorous sulfur gases, particularly the digester and evaporator noncondensables. Common practice is to expose

these gases to chlorination stage washer effluent from the bleach plant in either a scrubber or the washer dropleg. Supplemental chlorine may be required if sufficient amount is not available in the washer effluent. In an unbleached pulp mill, chlorine gas would have to be supplied from an outside source. Typical reactions in this process are discussed by Douglass (5) and DeHaas and Clark (34), and indicate that excessive amounts of chlorine are consumed. Ruus (114) reports the chlorine demand to be 2-9 pounds per pound of malodorous compound, and discusses the subsequent high cost of elemental chlorine oxidation if the bleach residues are insufficient.

Thomas, et al. (115) discuss chlorination at the S. D. Warren Kraft Mill in Westbrook, Maine, in which digester blow gases are passed through primary and secondary deodorizing scrubbers utilizing the chlorination stage effluent. As a backup, weak hypo bleach can be added to the secondary unit. Ghisoni (111) discusses chlorine oxidation of recovery boiler effluent gases, and Morrison (106) reports on the use of chlorination as a backup needed when the lime kiln is not in operation for burning the noncondensables. Archibald and Von Donkelaar (116), Lindberg (107), Adams (61), and Trobeck, et al. (117) also discuss chlorination installations.

Gas-phase chlorination of kraft pulp mill gases was studied by Koppe and Adams (118) in laboratory experiments. Gas samples from the recovery furnace, batch digester, multiple-effect evaporators, and lime kiln of a mill were reacted with known volumes of chlorine gas and the reactions recorded by gas chromatography. Concentrations of hydrogen sulfide and dimethyl sulfide did not change, and the methyl mercaptan was oxidized to dimethyl disulfide. The process appears to be of limited value as a

means of kraft odor control since the overall odor reduction of the total gaseous effluent would probably not be sufficient to justify its use on a plant scale. Nevertheless, gas phase chlorination of noncondensables has been used for several years at the Peña Pobre mill in Mexico City. Excellent control of malodorous sulfur gases are claimed for the TLT (117) system, and obviously at reasonable cost. Tirado and Gonzalez (119) explain that the total results at the Peña Pobre mill are a combination of partial results obtained in each of various stages or processes, and that the experiments by Koppe and Adams (118) may have been conducted under too mild conditions. Air oxidation of the noncondensables in the presence of water is used prior to chlorination to reduce chlorine consumption. Following chlorination, a final wash of the gases with white water completes the TLT system.

Absorption

Gas scrubbing is used throughout the industry for odor control, but, in the interrelationship of air and water pollution, using scrubbing to reduce the odor in one gas stream may simply be transferring the problem to some other point in the mill. Unless an effective oxidant is used in the scrubber to convert the malodorous compounds to innocuous products, care must be taken to prevent re-release of the odors. Keeping the absorbing liquid in the process stream is another solution, and most widely used.

Ruus (114) discusses the use of white liquor for absorbing hydrogen sulfide and methyl mercaptan from evaporator noncondensables which keeps them in the liquor cycle and eliminates the need for aqueous effluent disposal. Secondary scrubbing of recovery stack gas with weak wash is reported by Buxton and La Pointe (120) to give hydrogen sulfide recovery

of 90 percent, and Hawkins (121) discusses the successful use of weak wash for scrubbing evaporator gases. At U.S. Plywood-Champion Paper Inc., Pasadena, Texas, scrubbers utilizing weak wash from the causticizing department are used to absorb evaporator noncondensable gases, while gases from the blow tank, tall oil vent, chlorination tower vents, and chlorination stage washer seal box vents are scrubbed with water (122).

Adams (24) discusses the use of an absorption-adsorption combination at a mill in Sweden. The digester noncondensable gases are scrubbed with warm (95° F) white liquor to absorb hydrogen sulfide and methyl mercaptan. The unabsorbed gases then pass through activated charcoal to remove methyl sulfides and methyl disulfides. The charcoal is then steam stripped to recover the organic sulfides.

Pilot plant studies are reported by Oloman, et al. (123) for selective absorption of hydrogen sulfide from kraft stack gases using a solution of sodium carbonate-sodium bicarbonate.

Dispersal

As a sole means of odor control, dilution of malodorous sulfur emissions by dispersion from tall stacks is not always effective for a kraft mill due to the low odor threshold of the gases, changing meteorological conditions, and the varying concentrations of effluent gases. Average stack height for most mills is 200-300 feet, and their effect on odor control is most noticeable in the vicinity of the installation. It is believed that the tallest stack presently in the paper industry is 475 feet high.

Tall stacks are very effective for kraft odor control when used in conjunction with other control methods. Ghisoni (111) reports on the use of a 260-foot stack located on the rim of a 140-foot-deep valley in Milan.

Remaining odorous gases from a pulp mill located in the valley are piped to the stack for release. The mill uses chlorine oxidation and incineration for primary odor control. Walther and Amberg (101) discuss the use of a 310-foot recovery stack to discharge gases from the lime kiln, power boiler, recovery furnace, and black liquor oxidizer at Crown Simpson Pulp Co. in California. Malodorous gases from the continuous digester and multiple-effect evaporators are burned in the lime kiln and scrubbed in a Venturi scrubber prior to release through the recovery stack.

Odor Masking and Counteraction

Odor masking and counteraction are not used as extensively in the kraft pulping industry for odor control as some of the methods previously discussed, and reports concerning their effectiveness are quite varied and limited.

Tremaine (124) describes the application of Alamask (125) for kraft odor control by either (1) spraying, vaporizing, or atomizing it into the odorous gas stream, (2) adding directly to the process, (3) adding to scrubbing liquors, or (4) spreading or floating on contaminated surfaces, and states that addition directly to the odor-producing process is the best application for the pulp and paper industry. DeHaas and Clark (34) report on the use of a masking agent added directly on the chips in the digester (3-4 pints per digester) prior to closing the lid. Experiences at the mill indicated that the masking compounds would control digester odors under ideal conditions (warm temperatures, unlimited ceiling, and strong winds), but effects were not so pronounced under cold, foggy conditions. Costs were also relatively high.

Meuly and Tremaine (126) discuss a joint study between Gulf States Paper Co., Tuscaloosa, Alabama, and DuPont on the use of Alamask as a

masking agent. Results were favorable, but greatly depended upon meteorological conditions, type of wood being pulped, and liquor sulfidity. The effect of meteorological factors on the amount of masking agent required is covered by Zirm (127). Tremaine (128) suggests that a masking agent should be applied to the blow-down heat recovery and concentrated black liquor at the cascade evaporator in addition to the digesters, and lists favorable comments made at five kraft mills using odor masking. U.S. Plywood-Champion Paper, Inc., Pasadena, Texas, has added masking agents since 1952, and presently uses them in the digester and recovery areas at a cost of \$75-\$100 per day (122).

Von Bergen (129) reviews the phenomenon of odor counteraction, and states that a majority of observers in an evaluation test, covering over 30 days at a paper mill, were enthusiastically impressed by the absence of malodors while counteractants were being used.

Condensation

Although not usually considered as part of an odor control program at a kraft mill, condensation has been practiced in the kraft industry probably ever since the operation of the first mill in 1891, and is actually the first step in removing malodorous sulfur compounds from digester and multiple-effect evaporator gas streams.

Condensation of the digester relief (or steaming vessel relief for continuous digesters) and blow gas is primarily for heat recovery, and is accomplished with either surface or spray (barometric) condensers. Surface condensers are normally used to reduce the volume of liquid to be handled. Turpentine recovery is another advantage for condensation of the relief gases. In the multiple-effect evaporators, condensation of the steam from the black liquor in the last body is used to maintain a high vacuum in the system for circulation.

For the purposes of odor control, the result of condensation is two effluent streams -- a condensate stream and a stream of noncondensable gases. Both contain malodorous sulfur compounds, and must be controlled for an effective odor program. Various methods are discussed in previous sections of this paper for odor control of the noncondensable gas stream, and include incineration, chemical oxidation, absorption, and adsorption. For the condensate stream, in addition to possible release of the malodorous sulfur gases, contamination of water courses may present another problem since the organic load of the combined condensates can amount to approximately 50 percent of the total waste load in a mill effluent going to the river or waste treatment plant (34, 53).

Reuse of the condensate within the mill as water makeup, washwater, etc. has proven to be an effective way of keeping the sulfur compounds in the process and alleviating some of the load on liquid waste treatment facilities, but can result in the release of malodorous gases in open systems such as holding tanks and washers (4, 53). Studies by Walther and Amberg (91) show that whenever digester and evaporator condensates are reused for pulp washing or scrubbing, the odor problem is intensified, and that these streams should be completely treated prior to reuse in these applications.

Walther and Amberg (101) discuss the use of air oxidation to reduce the sulfur content of the condensate stream, and also report a 20 percent reduction in BOD and 50 percent reduction of COD in the effluent. Air oxidation is also used in the TLT (Trobeck-Lenz-Tirado) system (117) at the Peña Pobre mill in Mexico City, where both contaminated condensate and noncondensables are reacted with air and water prior to

chlorination. As reported by Tirado and Gonzalez (119) the condensates lose nearly all their H_2S and mercaptan content due to air stripping. Hisey (110) discusses air oxidation at a South African mill in which digester condensates are blown with air into a packed tower, and the effluent is used as make-up water in a spray cooling pond. Odors created are negligible. Stripping of condensate streams with steam (53, 130) and recovery furnace flue gas (61) are also effective for removing malodorous sulfur compounds and producing reusable water. Gaseous effluents from stripping operations must be disposed of similar to other noncondensable gases for effective odor control.

Land disposal of condensates and other mill effluent through spray irrigation has been investigated (131, 132), and could offer an effective and economical method of disposal for some locations. Odor release could still present a problem near populated areas.

CHAPTER III

OZONE CHEMISTRY AND APPLICATIONS

Characteristics, Formation, and Toxicity

Characteristics

Ozone (O_3) is a triatomic allotrope of oxygen with a molecular weight of 48, and exists as a pale blue gas under normal conditions. The molecule is unstable, and slowly decomposes to ordinary oxygen at normal temperatures. Decomposition is accelerated by heat and moisture, and is almost instantaneous at 300-400^o F. Due to its high electro-negative potential of -2.07 V, which is second only to fluorine at -2.1 V (133), ozone is one of the most powerful oxidants known, and its reaction is rapid with most materials..

The scientific discovery (in 1840) of ozone and some of the earliest investigations of its characteristics are attributed to Christian Schonbien of Switzerland. However, ozone was first detected in 1785 by the Dutch chemist Van Maroom who noticed a previously unknown odor appearing in the air during an electrical discharge. He considered this phenomenon to be inherent to electricity. In 1801, Cruikshank of England detected the same odor in oxygen which was liberated during the electrolysis of water, and in 1840, Schonbien reported that the odor obtained during an electrical discharge in oxygen was caused by the appearance of a new

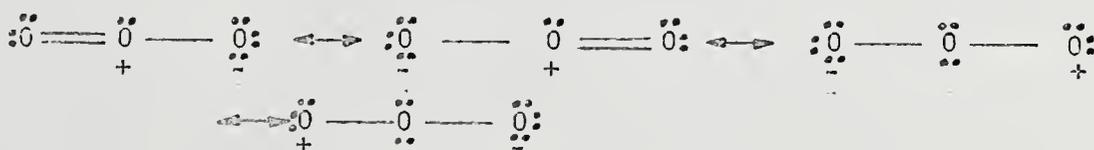
gas which he named ozone. During the period 1845-1860, a number of investigators (Marinyak and Delariv, Fremi and Bekerel, Andrews) attempted to convert pure oxygen into ozone, and made the first characterization of ozone as an allotropic modification of oxygen. In 1867, Soret used measurements of density during diffusion of ozone to introduce the formula of O_3 (134). The word ozone is derived from the Greek "ozon" (smelling), from "ozein" (to smell), and from the base "od" (to smell) as in Latin "odor."

Gas density of ozone at $0^\circ C$ and 1 atmosphere is 2.144 g/liter. At a temperature of $-111.9^\circ C$ ozone thickens and is transformed into a highly unstable fluid of dark blue color. Density of ozone in the liquid state at $-183^\circ C$ is 1.571 g/cc, while in the solid state at $-195.2^\circ C$ is 1.738 g/cc. The melting temperature of ozone is $-192.5^\circ C$. Ozone is absorbed by many liquids (although unstable in most) and its solubility is inversely proportional to temperature. Between 0° and $20^\circ C$ ozone is absorbed in water some 35 times as much as is air. At $50^\circ C$, the absorption is about five times as much as air, and at $60^\circ C$, air absorption is still approximately 16 mg/1000 g H_2O /atm whereas ozone absorption is zero (65).

Although there is some difference in the literature concerning bond dimensions and angles, there is agreement that the ozone molecule is triangular in form with an obtuse apex angle, and a resonance hybrid of at least two structures. According to Mortimer (135), both oxygen-to-oxygen bonds have the same length ($1.26 \overset{O}{\text{Å}}$) which is intermediate between the double bond distance ($1.10 \overset{O}{\text{Å}}$) and the single bond distance ($1.48 \overset{O}{\text{Å}}$), and the ozone molecule is a hybrid of the following two structures:



A reference by Summer (65) indicates an interatomic distance of 1.2 \AA with an obtuse apex angle of 110 degrees. Bailey, et al. (136) and Kozhinov (134) suggest that ozone is a hybrid of the following four structures:



Either way, the ozone molecule is extremely unstable and spontaneously decomposes into an atom and a molecule of oxygen. The reaction is strongly exothermic (34.5 kcal per mole of ozone) which explains the explosive nature of ozone under certain conditions. Chemically pure ozone (100%) explodes violently at the very slightest impulse, and pure liquid ozone at temperatures near its normal boiling point is particularly dangerous (137). In practice, explosion of ozone will not occur if its concentration in the ozone-oxygen mixture or ozone-air mixture does not exceed 10 percent. Such mixtures are safe at pressures of several atmospheres and under any conditions -- during heating or shock and in reactions with traces of organic contaminants (134).

Ozone Formation

Ozone in the earth's atmosphere is generated by the interaction of solar ultraviolet rays and free oxygen atoms. The wavelengths capable of producing ozone naturally fall within the absorption spectrum of oxygen,

or approximately 1100-2400 Å. Ozone is also decomposed by solar radiation, particularly in the Hartley Band (2200-3000 Å), and even at longer wavelengths since the dissociation energy is only 24.6 kcal. As a consequence of this generation and decomposition due to solar radiation, an ozone concentration equilibrium occurs (subject to various meteorological parameters) which results in an ozone profile as a function of altitude (138-140). Although the distribution of ozone in the atmosphere varies from one author to the next, several research projects indicate maximum concentrations at altitudes of 13-16 miles (139, 141). Dependent upon the season and latitude, concentrations of 5-10 ppm can occur in this upper atmosphere. Ozone concentrations at or near sea level are normally in the range of 0.01 to 0.04 ppm, although a concentration of 0.99 ppm was detected during Los Angeles smog conditions in 1956 (142). Processes involved in the generation of atmospheric ozone, both in the upper and lower atmosphere (photochemical oxidation), are well covered in the literature (65, 141, 143).

For laboratory, municipal, and industrial applications, ozone can be produced by three different methods: electrolytic, silent arc discharge, and ultraviolet radiation. Of these, only the latter two have proved practical. since, in the electrolysis of water, ozone yield is severely influenced by thermal destruction resulting from high current densities required at the anode (138).

For high ozone output, silent arc discharge generators are normally used, and was the type used for this study. The generating unit consists of a pair of large area electrodes, either flat or cylindrical, separated by an air gap and a dielectric layer. In many generators, the electrodes

are stainless steel and aluminum, and the dielectric is borasilicate glass. One electrode is contiguous to the glass dielectric, and the gas gap occurs between the dielectric and the other electrode. A common gap distance for voltages below 15000 volts is 1-3 mm (138).

In the presence of high, alternating voltage discharges, ozone is generated from the oxygen in the gap between the two electrodes. Key to the process is the presence (in the air gap) of stray electrons from a previous discharge or background radiation. In a field of sufficient intensity, the electrons move to the positive electrode, thus setting up a series of molecular collisions. Some achieve sufficient velocity to penetrate oxygen molecules, producing additional free electrons or high energy unstable molecules which break down into free radicals -- single oxygen atoms. Most of these single atoms combine with oxygen molecules (O_2) to form ozone (O_3). The process is repeated when polarity is reversed in the second half-cycle, and the electron's movement to the opposite electrode creates new molecular collisions. Thus, there are two productive instants in each cycle, occupying a relatively small portion of the total cycle time. The production efficiency is therefore increased when the cycle is shortened; i.e., when the frequency is raised. Most generating units are designed to operate in the 5000-25,000 volt range (through suitable transformers), and at frequencies up to 1000 Hz, although some designers are exploring the possibilities of higher frequencies for increased production efficiency (144). Normal generator output is 1-3 percent ozone by weight.

The ozone yield of the silent arc discharge generator is a function of the following factors: oxygen purity of the parent gas, oxygen temperature, pressure, and flow, peak voltage, frequency, capacitance of discharge gap,

and capacity of dielectric. For a given configuration generator, ozone output is a function of current density with all other conditions held constant, and the output is approximately doubled when the parent gas is pure oxygen rather than air.

Using oxygen as a feed, various effects have been noted in generator output with different gas diluents. As discussed by Cromwell and Manley (145), the greatest loss in ozone yield is noticed with the presence of less than 1 percent of hydrogen, water, or Freon 12. Up to 50 percent of carbon dioxide or argon reduces the yield to about 85 percent of that expected from pure oxygen. Carbon monoxide or nitrogen, in amounts of less than 10 percent, apparently increase ozone output, but in greater amounts a gradual decrease is noted. Inoue and Sugino (146) studied the inhibiting action of several hydrocarbons on ozone yield by silent arc discharge, and report that the rate of ozone formation varies linearly with the hydrocarbon concentration, regardless of the type of hydrocarbon. Water vapor remains the most common contaminant to be guarded against, however, and can be eliminated by adequate drying of the parent gas (usually specified to -60°C dewpoint) prior to ozone generation.

Additional information concerning ozone generation by electrical discharge is discussed by Lunt (147), Summer (65), Suzuki, et al. (148), Ogden (144), and Fuji and Takemura (149).

Ozone generation by ultraviolet radiation is most commonly used where low ozone concentrations are required, such as laboratory work, air purification, elimination of molds and bacteria, etc. As with the silent arc discharge generator, air or oxygen can be used as the parent gas. Ozone yield is a function of total effective radiation emitted in the

range of 1100-2200 Å, which is in turn dependent upon lamp design, emission area, current density, and oxygen flow, pressure, and temperature (138). The reactions involved are similar to those causing the formation of ozone in the upper atmosphere, and are discussed along with generator design information in the literature (65).

Ozone Toxicity

In an excessive dosage, most any substance is toxic to the human organism. Substances assume the title "toxic," however, when the dosage determined to be excessive is a very low unit quantity. Within the framework of this definition ozone is definitely toxic, since the maximum average concentration for an eight-hour exposure has been set at 0.10 ppm by the American Conference of Governmental Industrial Hygienists (150). With the increasing use of ozone in municipal, commercial, and industrial installations, the occurrence of ozone in smog conditions, and the possible hazards of high altitude flight from atmospheric ozone above 50,000 feet, the toxicity of this gas is an important problem.

Ozone was first recognized as a toxic substance by Andrews in 1874 when he exposed small laboratory animals to high concentrations of ozone, resulting in their death even after a short exposure (151). Since then, numerous toxicity studies have been performed on both animal and human subjects. Naturally, a majority of these investigations have dealt with animals (rats, mice, rabbits, dogs, cats, guinea pigs), and cover a multitude of conditions, ozone concentrations, and exposure times (152-170).

Most of these studies have established an LD₅₀ rate for the various animals, which is the dose of ozone that will, on the average, kill 50

percent of a significant number of animals exposed under specified conditions. Since there are several experimentally simple and statistically sound methods of obtaining LD₅₀ values and various procedures for determining ozone concentration, and due to the multitude of test conditions for the above referenced studies, there is some confusion in the literature on the actual toxicity of ozone. Regardless of the exact toxicity, the studies have left no doubt that ozone in acute exposures is a highly toxic and lethal substance, and that its impact is directed primarily on the soft tissues of the respiratory tract.

Gilgen and Wanner (151) review many of the ozone toxicity studies on animals, and noting the diversity of values, provide a brief summary of the literature. In the case of exposures between 3 and 24 hours, the LD₅₀ for rats and mice varies between 3.8 and 22 ppm. Hamsters, rabbits, and guinea pigs tolerate higher concentrations. Death is caused by pulmonary edema. Small concentrations lead to usually reversible changes of the respiratory organs, to disturbances of respiration, and to changes in the activity of various enzymes. Exposure to low concentrations can also develop a tolerance against subsequent exposure to lethal concentrations. Chronic exposure to ozone causes damage to the respiratory organs (bronchitis and lung emphysema), inhibition of the weight increase of younger animals, and decreased acidity of the urine. The article by Stokinger (165) is also an excellent review of ozone toxicity to animals.

Numerous articles are found in the literature describing controlled experiments on the toxicity of ozone to humans (171-176), and also some effects of ozone from actual working conditions (177-182). A brief review of some of this literature to illustrate the toxicity of ozone

includes a decrease in vital capacity of the lungs after a single exposure to 1.5 ppm for a half hour and a subsequent exposure to 2 ppm for 1.5 hours (176), decrease of the CO diffusion capacity after exposures to 1.2 to 6.0 ppm for 1-2 hours (171), significant reduction in diffusion capacity, vital capacity, and maximum flow in the middle of the expiration phase after inhalation of 0.6 to 0.8 ppm for 2 hours (175), impairment of the upper respiratory passages in welders working with the shielded arc welding process who were exposed to 0.8 - 1.7 ppm ozone every day (180), accelerated pulse, sleepiness, lasting headaches following brief inhalation of 5-10 ppm and impulse to cough and great lassitude after 1.5 hour exposure to 1.0 ppm (182), severe ozone intoxication (dry cough, weak pulse, lowered blood pressure, nearly unconscious) of a crane operator who operated a crane approximately 14 feet above a tank containing 1 percent ozone (181) and lung edema following exposure to ozone concentrations above 4-5 ppm for an hour (171).

The study by Clamann and Bancroft (171) involved five subjects, ranging in age from 19 to 54 years. The highest ozone concentration applied was 6 ppm for 1 hour, and the longest exposure time was 2.5 hours at 1.2 ppm. They concluded that ozone acts only superficially on the wet, soft tissues of the respiratory tract, and is not able to penetrate deeply. A definite impairment on the sense of smell was found at exposures of 2.41 ppm for 1.5 hours and 4.16 ppm for 22 minutes. No effects on blood pressure, pulse rate, and blood itself were observed. Long exposure times and higher concentrations tend to carry injury to the respiratory tract deeper toward the alveoli. In two of their experiments involving inhalation of air with 4.8 ppm ozone, the exhaled air contained practically no ozone, suggesting that ozone decomposes completely in the respiratory

tissues; however, studies by Hallett (174) showed that the expired air of his experimental subjects contained 25-75 percent of the inhaled ozone. The effects of ozone are not limited to the respiratory system according to some authors. Brinkman and Lamberts (183) have described a lowered rate in the release of oxygen from oxyhemoglobin in the skin capillaries, and Lagerwerff (172) reported an impairment of the visual apparatus.

A summary of the biological effects of ozone for concentrations ranging from 0.01 - 10 ppm is shown in Table 3 (65). Similar values are reported by Biget, et al. (141).

TABLE 3
BIOLOGICAL EFFECTS OF OZONE

Concentration (ppm)	Effects
0.01	Threshold odor of pure ozone
0.05	Irritation of the lungs and respiratory mucosae after prolonged inhalation
0.10	Respiratory discomfort, headache
0.15	Eye irritation threshold
0.50	Considerable discomfort, disordered breathing
1-10	Coughing, fatigue, headache, possible coma after prolonged inhalation.
5-10	Stupefaction, body pain, accelerated pulse, dangerous

Tolerance to ozone has been demonstrated in laboratory animals (153, 155, 156, 165-168), but it is still unclear whether a tolerance develops in humans. Gilgen and Wanner (151) and Stokinger (155) suggest the possibility that the population of Los Angeles has developed an ozone tolerance resulting from the often repeated exposures to low ozone concentrations, and due to the fact that the inhabitants have reported no acute pulmonary damages even when the ozone concentration exceeds 0.5 ppm. In the case of welders, ozone concentrations of more than 0.5 ppm led to the development of acute lung damages in every case, but their re-exposures occur after short intervals, thus they are not able to develop a tolerance. Animals always showed the best tolerance when their exposures were separated by an interval of several days.

Various explanations are found in the literature concerning the mechanism of ozone's action on the body (156, 167, 183-189). Fetner (188) and Brinkman and Lamberts (183) suggested the possibility of radio-mimetic effects of ozone. Fetner (185) showed that human cell cultures, which had been exposed for 5-10 minutes to 8 ppm of ozone, exhibited chromosomal cleavages similar to those resulting from an irradiation with 200 roentgens. Zelac (187) reported on chromosome aberrations in circulating blood lymphocytes of Chinese hamsters due to ozone inhalation, and stated that if the results of the study were directly extended to the human case, presently permitted human ozone exposures would be expected to result in break frequencies that are orders of magnitude greater than those resulting from permitted human radiation exposures. An excellent review of possible mechanisms of ozone action is given by Fenn and Rahn (190), and also covers other areas of ozone toxicity (tolerance, factors affecting toxicity, effects on man and animals, etc.).

As stated by Gilgen and Wanner (151) and Fenn and Rahn (190), so far it has not been possible to determine the meaning of the immunochemical changes taking place during the appearance of the ozone effect; therefore, it is impossible to give a meaningful explanation for the pulmonary damages resulting after chronic exposure to ozone. Regardless of its mode of action, controlled studies on animal and human subjects, and actual cases of ozone exposure in working environments, have definitely established that ozone is a highly toxic gas.

Ozone Applications

Waste Treatment

The market for ozone application in the waste treatment field is normally as a polishing agent in conjunction with other accepted waste treatment systems. Studies have shown ozone to be very effective in treating industrial waste streams, particularly those containing cyanide and phenols. The Boeing Company plant at Wichita, Kansas, uses more than 350 pounds of ozone per day as a secondary waste treatment process to cope with cyanide, phenols, oils, detergents, sulphides, and sulphites. The waste is ozonated at approximately 20 ppm and discharged into a lagoon where fish have survived since the beginning of the project in 1957 (144, 191, 192). Reports on the kinetics of ozone-cyanide reactions (193, 194), comparisons of chlorine and ozone treatment of cyanide wastes (195, 196), laboratory and pilot plant studies of the ozone oxidation of phenols (197-201) and others (202-205) describe the feasibility of using ozone for treating industrial waste waters.

Air Reduction Co. (Airco) was awarded a contract by FWPCA to construct a pilot plant at the Washington, D.C. Blue Plains treatment facility to

study tertiary treatment of municipal waste with ozone. Previous work by Airco has demonstrated that ozone treatment of sewage plant effluent destroys organic contaminants, surfactants, and bacteria, and produces a clear, odorless effluent that meets PHS standards for drinking water. Economic evaluations indicate that the ozone treatment will be competitive with activated carbon (206, 207). Similar results were obtained in pilot plant work using effluent from trickling filter waste treatment plants at Totawa and Berkeley Heights, New Jersey (144). Additional studies on ozone treatment of municipal waste effluent are covered in the literature (203, 208-212).

Odor Control

The most prominent use of ozone for odor control is in the treatment of sewage exhaust gases, primarily hydrogen sulfide. Installations have included odor control for sludge storage and supernatant tanks (213), treatment of ventilating and exhaust gases from fully enclosed aeration and settling tanks (6), lift station and wet well exhaust (214), complete underground sewage treatment plant in Atami City, Japan (215), grit removal, bar screens, settling and chlorination buildings in Mamaroneck, New York (191), and treatment plants in Florida (216, 217) and Michigan (218). One of the earliest installations was the Ward's Island Treatment Plant in New York City, installed about 1930 (6). The plant treats an exhaust gas stream of 30,000 cfm with an ozone concentration of 1 ppm, and reports complete elimination of the odor problem.

Other installations using ozone for odor control include a pharmaceutical plant (219), rendering plants (214), fish-processing operations (6), rubber compounding plant exhaust, phenolic odors from felts, and commercial kitchens (215).

Table 4 lists typical ozone concentrations for various installations established from experience by the Welsbach Corp. (220), although exact dosages would depend upon retention times, temperature, humidity, and concentration of the exhaust stream, and nature of the malodorous gases being treated. These figures are based on a contact time of at least 15 seconds.

TABLE 4
OZONE CONCENTRATIONS FOR ODOR CONTROL

Application	Ozone Concentration (ppm)
Restaurants	1
Sewage plants, general	1
Morgues	3
Phenol plants	3-10
Rubber plants	3-10
Fish-processing plants	10
Sludge storage and vacuum filter	10
Rendering plants	10
Paper mills	10-50

Water Treatment

The most widespread application of ozone is in the treatment of drinking water, and the first recorded commercial installation for this purpose began operation at Nice, France, in 1906. Over 20 million gallons of water are sterilized daily with ozone at the water works in this city (221). There are currently more than 500 municipalities using ozone for water treatment in over 50 countries. Its use is definitely more widespread in European

countries who use ozone as the disinfectant of choice, while in the United States, a chlorine residual is required in order to provide a disinfectant at the consumer's tap. In many of these installations, ozone is used in conjunction with other water treatment techniques (chlorination, microstraining, filtration, flocculation, carbon filtration, etc.), and depends upon the raw water and the water quality requirement (211, 222, 223).

The use of ozone for water disinfection and the removal of tastes, odors, and color is well covered in the literature. Nobert (224) discusses the use of ozone at five water works plants in Quebec to produce good quality water free from tastes and odors, which had not been previously achieved with chlorination and activated carbon. Studies comparing the effectiveness of ozone and chlorine (156, 212, 225-228) for water treatment stress that ozone leaves no residual taste or odor, and reacts more rapidly than chlorine in killing most bacteria. In addition to municipal water treatment, ozone has been used to obtain high quality water for breweries, distilleries, water bottle operations, food processors, carbonated beverage producers, hospitals, laboratories, etc. (144, 222). Additional reports on ozone installations (204, 205, 229), production (230), and methods of mixing for more efficient disinfection (231) are available in the literature.

Miscellaneous

The use of ozone for sterilization of food containers (232), and control of mold and bacteria (65, 156, 233, 234) demonstrate other uses of this oxidant, although in some cases the required concentrations exceed the recommended limit for humans and would limit these ozone applications to certain situations.

Ozone for Kraft Odor Control

Previous Applications and Investigations

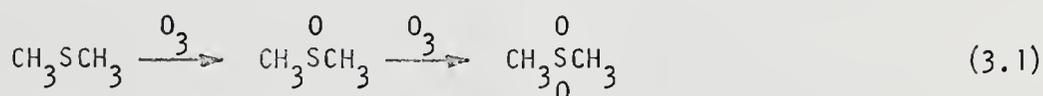
As a method of eliminating odors in kraft pulp mill operations, a patent was issued to Limerick (7) concerning the procedure of conducting ozone to a line discharging odorous stack gases, mixing the ozone with such gases in a proportion from about 10 to 100 ppm of the total gas volume, retaining the ozone and odorous gases in intimate mixture for not less than about two seconds, and thereafter discharging the mixture to the atmosphere.

As mentioned in the introduction of this paper (Chapter 1), literature concerning the application of ozone for kraft odor control is very limited. The only reference found that mentions an actual mill application was by Cromwell (6) who briefly describes the experimental use of ozone to treat effluent stack gases from the sulfate recovery system of a pulp and paper mill in Canada. Ozone was applied to a 100-foot stack at a point 10 feet above the ground, giving a retention time of approximately two seconds for mixing with the effluent gases. Maximum ozone output was 300 pounds per 24 hours, which provided a concentration of 80 ppm in an effluent flow of approximately 50,000 cfm. Concentration of sulfur compounds in the effluent stream was not given, and there was no indication of how effective the ozone application was. A thorough literature search and correspondence (235) failed to provide any additional information on these tests.

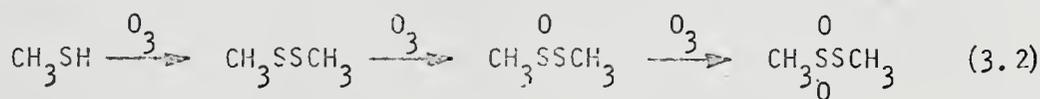
The literature is also somewhat limited on laboratory studies concerning ozonation of the individual sulfur compounds primarily responsible for kraft mill odors; i.e., hydrogen sulfide, methyl mercaptan, dimethyl

sulfide, and dimethyl disulfide. Barnard (236), discussing the reaction of ozone with organic sulfur compounds, showed that the oxidation of monosulfides ($R \cdot S \cdot R$) occurs in two well-defined stages to give, first, the sulfoxide ($R \cdot SO \cdot R$) and then the sulfone ($R \cdot SO_2 \cdot R$), and require somewhat less than the theoretical amount of ozone for their oxidation. With this analogy, disulfides would be expected to yield successively thiosulfinate ($R \cdot SO \cdot S \cdot R$), thiosulphonate ($R \cdot SO_2 \cdot S \cdot R$) or disulfoxide ($R \cdot SO \cdot SO \cdot R$), and disulfone ($R \cdot SO_2 \cdot SO_2 \cdot R$). Ozone-uptake curves did not reveal such stepwise reaction and indicated, for "normal" disulfides, the absorption of 2.5-3.0 moles of ozone. The major product of the reactions was a sulfonic anhydride ($R \cdot SO_2 \cdot O \cdot SO_2 \cdot R$) with small amounts of thio-sulfonate and disulfone, although ozonation of dimethyl disulfide showed the major product to be the thiosulfonate (50 percent) rather than the sulfonic anhydride (39 percent).

Similar results are reported by Douglass (5) using nuclear magnetic resonance (NMR) analytical techniques. Ozone was found to react rapidly with dimethyl sulfide to form the sulfoxide and then the sulfone without evidence of other products being formed (Equation 3.1).



With methyl mercaptan, a stepwise reaction was noted, first forming the disulfide which is oxidized to the thiosulfinate, and then to the thiosulfonate (Equation 3.2).



Bubbling ozone through liquid dimethyl disulfide appeared to convert it entirely to the thiosulfonate ($R \cdot SO_2 \cdot S \cdot R$), and attempting to distill

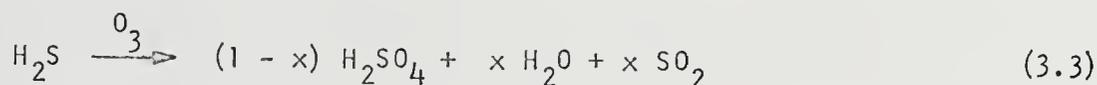
the thiosulfonate thus obtained gave a mixture of thiosulfonate and sulfonic anhydride ($R \cdot SO_2 \cdot O \cdot SO_2 \cdot R$).

Ozone oxidation of kraft pulp mill blow gases (from an autoclave) was studied by Akamatsu (9) and indicated that most of the odor could be eliminated; however, concentrations of sulfur compounds in the blow gas or ozone concentrations used for odor control were not mentioned. Results showed that ozone converts the methyl disulfide and methyl mercaptan of the blow gas to a "mild odored" oxide. Akamatsu, et al. (237) also studied the ozone oxidation of dimethyl sulfide, and showed that 75 percent of this malodorous gas could be oxidized to dimethyl sulfoxide and the remainder to dimethyl sulfone, similar to the studies by Barnard (236) and Douglass (5).

During a study on the oxidation of kraft black liquor with oxygen, Ricca (8) evaluated the effects of oxygen enriched with 1/50 ppm ozone. The reaction rate of dissolved hydrosulfide was not increased but the mercaptan odor of the black liquor was eliminated, thus indicating that ozone was more effective in oxidizing gaseous odors than black liquor. Additional tests showed that the black liquor oxidation exhaust gases could be effectively deodorized with 100-150 ppm ozone (at 78° C).

Reactions between ozone and hydrogen sulfide have been reported on by several authors. Gregor and Martin (10) studied the reaction at ambient temperature and illumination by injecting known quantities of each gas into glass reaction vessels, and allowing them to stand for 16 hours to insure complete reaction. Results of their work indicated that when hydrogen sulfide and ozonized oxygen are mixed under initially anhydrous conditions, reaction occurs with water, sulfur dioxide and sulfuric acid being formed as end products.

Under their reaction conditions, the percentage of hydrogen sulfide actually oxidized steadily increased with an increase in the ozone to hydrogen sulfide ratio, and complete oxidation only occurred at ratios in excess of 9 to 1 (Figure 1). At ozone to hydrogen sulfide ratios below 9 to 1, sulfur dioxide was the principal product, and at ratios above this, sulfuric acid became the predominant product. At a ratio of 18 to 1, oxidation of all the initial hydrogen sulfide to sulfuric acid was considered complete (Figure 2). The overall stoichiometry of the reaction (under the test conditions) was represented by the equation



where $0 \leq x \leq 1$ and $x \rightarrow 0$ as the initial ratio of $\text{O}_3/\text{H}_2\text{S} \rightarrow 18$ or greater.

Cadle and Ledford (11) also studied the gas-phase reaction of ozone with hydrogen sulfide, and when the reaction was allowed to go to completion in the cell of an infrared spectrometer, the only products found were sulfur dioxide and water. Sulfuric acid was not detected as reported by Gregor and Martin (10). The stoichiometry corresponded approximately to the equation



A summary of Cadle and Ledford's data is given in Table 5, indicating a maximum ozone to hydrogen sulfide ratio of approximately two, which is somewhat less than the maximum studied by Gregor and Martin.

At the low concentration ratios, the data of Gregor and Martin (Figures 1 & 2) also show the major reaction product to be sulfur

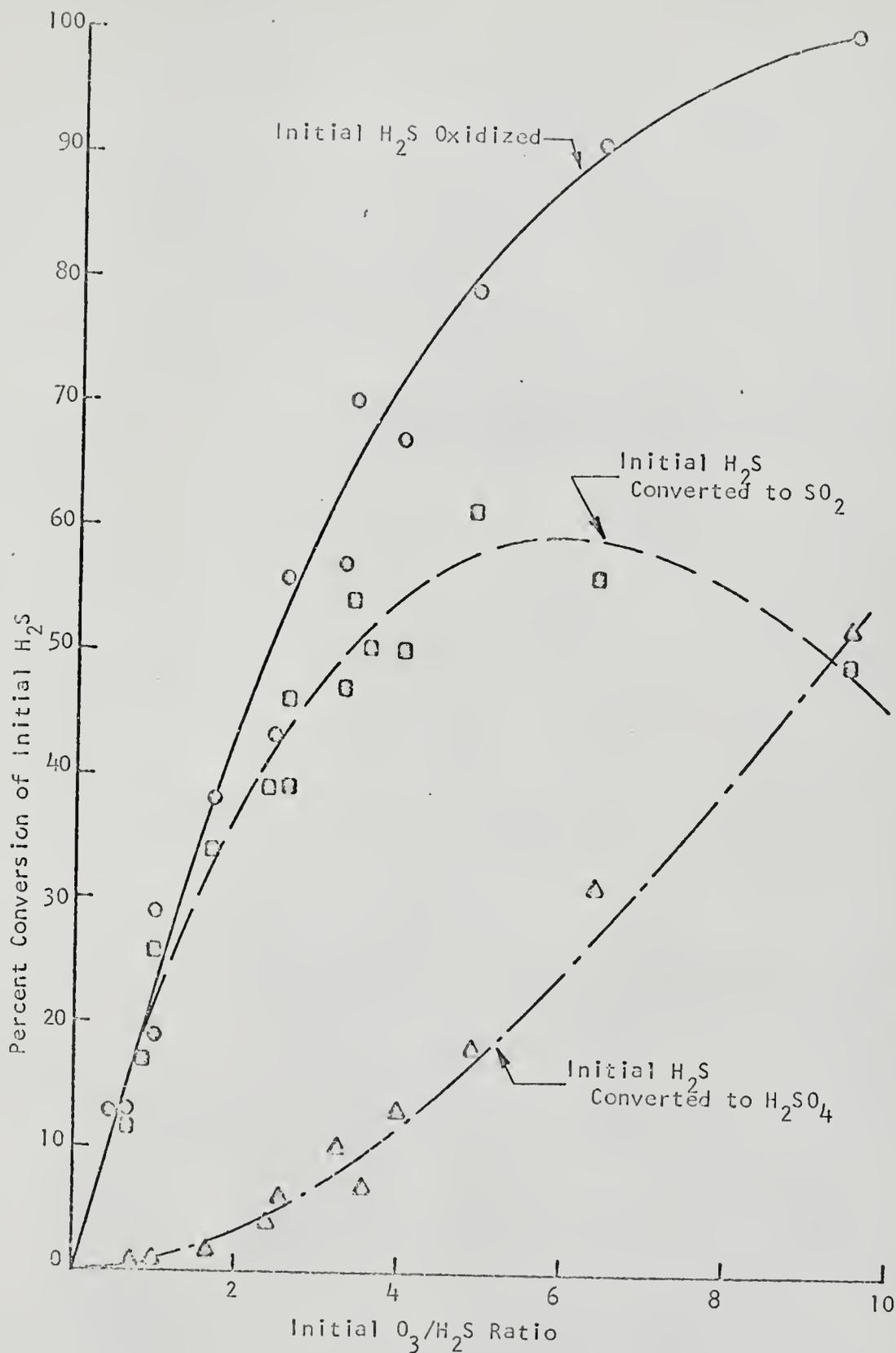


Figure 1. -- Conversion of Initial H_2S to SO_2 and H_2SO_4 (Gregor and Martin).

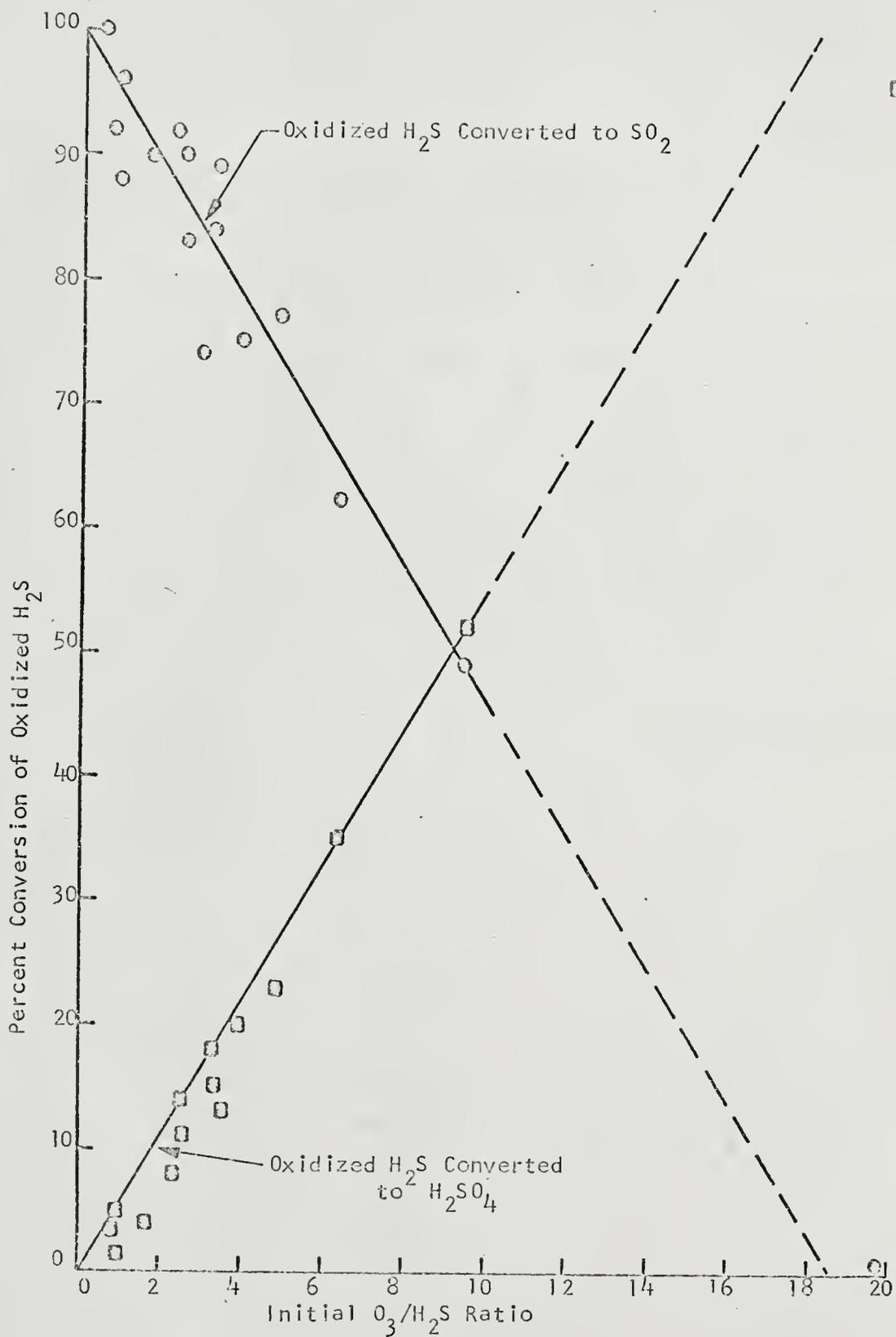


Figure 2. -- Conversion of Oxidized H₂S to SO₂ and H₂SO₄ (Gregor and Martin).

TABLE 5

REACTION DATA OF CADLE AND LEDFORD FOR THE GAS PHASE REACTION
OF OZONE AND HYDROGEN SULFIDE

Initial H ₂ S	Concentrations (moles × 10 ⁻⁸ /cm ³)	
	Initial O ₃	Final SO ₂
78	30	19
31	30	23
78	30	18
16	30	18

dioxide, with only small amounts of sulfuric acid. Also, since the oxidation of sulfur dioxide to sulfur trioxide is known to be very slow (238), it is possible that sulfuric acid did not have sufficient time to form in the study by Cadle and Ledford since reaction time was not mentioned, whereas 16 hours were allowed in the work by Gregor and Martin.

Considering data from both studies (10, 11), it would appear that the stoichiometry represented by Equation 3.4 is valid for low ozone to hydrogen sulfide ratios, and for all ratios at minimum reaction times.

Cadle and Ledford (11) also studied the kinetics of the ozone-hydrogen sulfide reaction using a 1-meter long reaction tube constructed of 16 mm Pyrex tubing. Maximum residence time in the reactor was about 3 seconds. Tests were run at 26^o, 65^o, and 100^o C with ozone concentrations ranging from about 245-7350 ppm and hydrogen sulfide concentrations of 245-19,600 ppm. It was determined that the reaction had orders near zero and 1.5 in hydrogen sulfide and ozone respectively, and followed the rate expression

$$\frac{dc_{O_3}}{dt} = - 2.5 \times 10^8 \exp (-8300/RT) c_{O_3}^{1.5} \frac{\text{moles}}{\text{ml sec}} . \quad (3.5)$$

The homogeneity of the reaction was examined by placing several pieces of Pyrex tubing in the reactor which increased the surface to volume ratio four-fold. The overall reaction rate was about double that of the original system, indicating significant wall effects. No attempt was made to quantify these effects. It was concluded that the reactions in the system were at least partially heterogeneous, and the rate law (based on a purely homogeneous reaction) could be used to estimate upper limits for the rate of reaction between ozone and hydrogen sulfide in the atmosphere.

Hales (12), considering the significance of simultaneous bulk and wall reactions, and based upon the information and experiences of Cadle and Ledford (11), performed additional studies on ozone-hydrogen sulfide reactions in laminar flow reactors. Measurements were made at 28.5° and 48° C in the absence of light, and involved a number of reactant concentration ratios. The reaction was observed to be almost totally homogeneous, and described by the expression

$$\frac{dc_{SO_2}}{dt} = 22.8 \exp (-6500/RT) c_{H_2S}^{0.5} c_{O_3}^{1.5} \frac{\text{micromoles}}{\text{liter min}} \quad (3.6)$$

for the range of variables studied. All evidence obtained during the experiments indicated that Equation 3.4 represents the true stoichiometry of the reaction for the conditions studied.

Although the rate equations (3.5 and 3.6) are similar in that they indicate a reaction order of 1.5 in ozone, they differ in the reaction order of hydrogen sulfide and in the activation energy. Also, reactions

observed by Hales were thought to be almost totally homogeneous, whereas Cadle and Ledford observed significant wall effects in their system. Various possibilities for these differences were investigated by Hales, and it was concluded that the disagreements stem mainly from a nitric oxide quench used by Cadle and Ledford which, among other things, could have conditioned the reactor wall in such a way that it became catalytically active. This would also offer some explanation to the fact that the absolute rates predicted by Cadle and Ledford (Equation 3.5) are about two orders of magnitude higher than those of Hales (Equation 3.6) over the range of hydrogen sulfide concentrations studied (12).

Noting that Equation 3.6 applies to rather specialized conditions and that care should be exercised in its application to practical situations, Hales considers a hypothetical odor control situation involving the emission of hydrogen sulfide at 500 ppm from a 150° C stack. Assuming no spontaneous ozone decay and a stack residence time of 10 seconds, Equation 3.6 predicts that only about 2 percent of the hydrogen sulfide will be oxidized upon applying a stoichiometric quantity of ozone. Although recognizing the limits of his rate equation, and the complexity of the ozone-hydrogen sulfide reaction mechanism and the stack environment itself, Hales concludes that the effect of ozone for odor control is due more to its odor-masking properties than to actual oxidation of the hydrogen sulfide.

Because ozone is a powerful oxidizing agent, its classification as a masking agent is subject for argument (213), since a true masking compound does not enter into chemical reactions with the malodorous substance being masked. Naturally, if excessive amounts of ozone are injected into an effluent gas stream, and/or adequate reaction time is

not provided, ozone could be emitted into the atmosphere and act as a masking agent due to its own "sweet" odor. The inhibitory effect of ozone on the sense of smell would also tend to negate the effect of a malodorous compound, but its use in this manner, or as a pure masking agent, could result in serious problems due to the known toxic effects of ozone.

Basis of Present Study

Various methods used for odor control in the kraft pulping industry were reviewed in Chapter 2. The referenced literature indicated that proper application of these methods would permit a mill to comply with most any current or proposed emission standard. What the future regulations will be concerning odor compounds is not known. Additional odor control steps may be required to completely eliminate the malodorous emissions, for whether these gases are released in concentrations of 5, 10, or 100 ppm, if they can be detected by the public and create a nuisance, they are still too great.

The application of ozone as a polishing agent following a major piece of odor control equipment is a possibility. Older mills may not find it feasible to make major process changes and/or additions (black liquor oxidation, elimination of DCE, etc.) to prevent initial odor formation, but find it easier to treat the malodorous compounds at the emission points by injecting ozone into the gas stream. If a mill has effective recovery furnace control and incineration of the noncondensables, some of the emissions which were once considered unimportant now become major odor sources and may be suitable for ozone oxidation, such as the brown-stock washer hood vents, knotter hood vents, and washer seal tank vents.

Is ozone effective for controlling odors in the kraft pulping industry, for which effluent gases, and under what conditions? A relatively few laboratory studies investigating a limited range of conditions, no reported results of ozone installations in kraft mills, and conflicting reports on the effectiveness of ozone for odor control have not tended to provide suitable answers for these questions, although ozone has been shown to be effective in other applications (water and wastewater treatment) and for other malodorous installations.

In almost every investigation regarding either the sole use of ozone, or comparing it with other oxidizing agents (chlorine, chlorine dioxide, etc.) for water treatment, wastewater treatment, or odor control, the cost of ozone production was invariably mentioned as its main disadvantage. In many instances, it has been shown to be more effective and faster acting than chlorine, and without the residual effects sometimes experienced with chlorine. With the anticipated decrease in cost of ozone production (as discussed in Chapter 1), its effectiveness for kraft odor control needs to be established.

The end products resulting from ozone oxidation of the four malodorous sulfur compounds of interest have been established by previous investigators (5, 9-12, 236) and shown to be relatively odorless. Kinetics of ozone-hydrogen sulfide reactions were studied by Cadle and Ledford (11), resulting in a rate expression based on the depletion of ozone. Hales (12) also studied the ozone-hydrogen sulfide reaction kinetics to resolve some of the difficulties experienced by Cadle and Ledford, and derived a rate expression based on the generation of sulfur dioxide.

For the present study, ozone oxidation of all four of the major malodorous sulfur compounds was studied, and the effectiveness of the

ozone treatment was based on the depletion of the malodorous compounds themselves rather than measurement of the end products or ozone uptake. Although partial oxidation of some compounds, such as butanol (mild odor) to butyric acid (very bad odor), can result in an odor increase (63), this does not pose a problem in ozone oxidation of these four sulfur gases of interest since their reaction products have a much higher odor threshold than the original compound. Of course, the first step in the ozone oxidation of methyl mercaptan is dimethyl disulfide, but the formation and subsequent depletion of this compound was monitored along with the destruction of the original methyl mercaptan.

CHAPTER IV
EXPERIMENTAL APPARATUS

Description of Test Stand

Basic Flow Pattern

As mentioned in Chapter I, the initial phase of this study was to evaluate the effectiveness of ozone in oxidizing bottled sulfur gases at various temperatures, reaction times, and concentration ratios. The equipment, flow diagrams, and techniques for this part of the study were slightly different than those required for oxidation of actual stack effluent. Descriptions in this chapter are directed primarily toward the initial phase of the study, and any variations required for the stack gases will be described in Chapter VI. Both phases of the study were conducted from the NCASI Mobile Laboratory since a majority of the analytical equipment used for the experiments is permanently mounted in this trailer. A brief description of these units is given in a later section of this chapter.

With the exception of a few components (primarily the analytical equipment mentioned above), all the experimental apparatus used for the study was mounted on a test panel as shown by Figures 3 and 4. This panel was designed and constructed to (1) allow for changes in reaction tube temperature, sulfur gas concentrations, ozone concentrations, and residence time with a minimum time delay, (2) provide ease of handling for

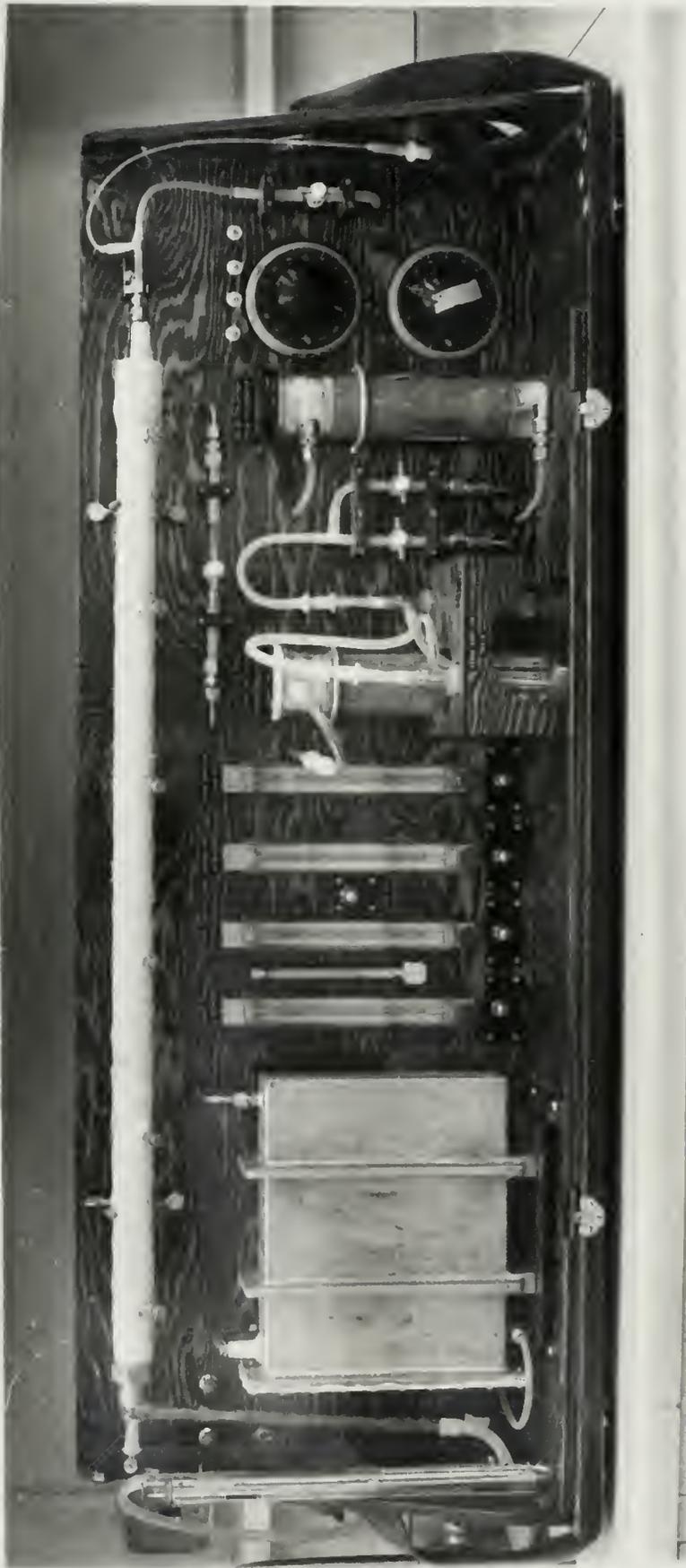


Figure 3. -- Front View of Test Panel.

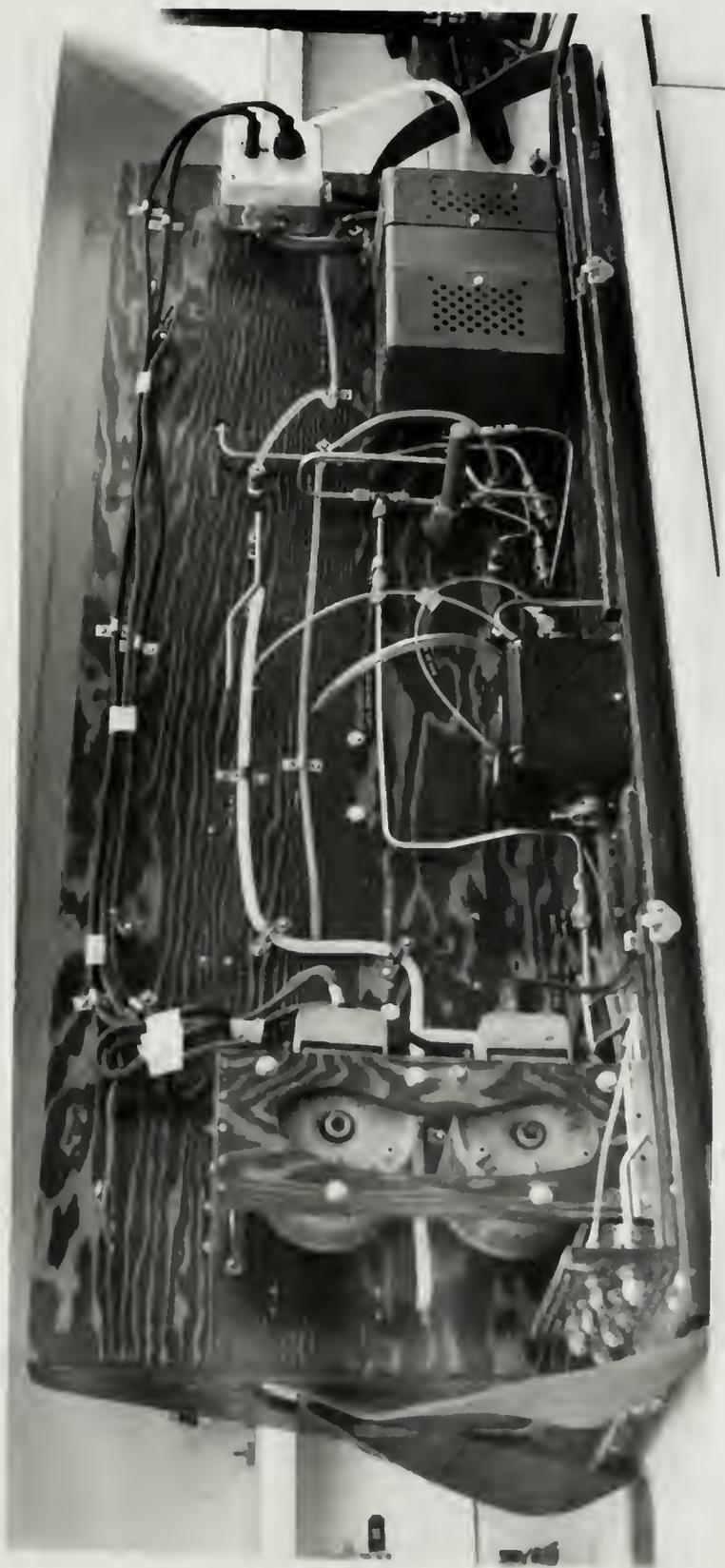


Figure 4. -- Rear View of Test Panel.

all the components with subsequent minimum set-up and take-down time, (3) provide ease of operation by concentrating all the necessary controls in a relatively small area, and (4) require a minimum area for operation due to the limited space in the NCASI Mobile Laboratory.

A schematic of the complete system used for the initial phase is shown by Figure 5 and indicates the components attached to the test stand. As shown by the schematic, pure oxygen was released from a cylinder source, passed through a moisture trap of silica gel, through a flowmeter, and into an Ozonator Corporation (239) Model 4000 Ozone Generator where ozone was produced by silent arc discharge. The ozone-oxygen flow from the ozone generator was then directed to the heated reaction tube or wasted to the atmosphere as required.

Nitrogen was used as a carrier gas for the sulfur compounds and was admitted to the system from a cylinder also. Sulfur compounds were injected into the nitrogen stream using a spinning syringe, and the nitrogen-sulfur gas mixture combined with the ozone-oxygen flow in a mixing chamber attached to the end of the heated reaction tube. The extent of ozone oxidation was monitored with a gas chromatograph through sampling ports spaced down the reaction tube to provide various mixing times. Waste gases were vented to the outside of the mobile laboratory.

System Details

Ozone production was controlled by varying the voltage to the ozone generator with a voltage regulator (Variac). As shown by the schematic (Figure 5), a constant voltage transformer was installed prior to the variac to dampen out any line fluctuations, and provide a steady 118 volts to the variac. By regulating voltage with the variac, output of the 6000

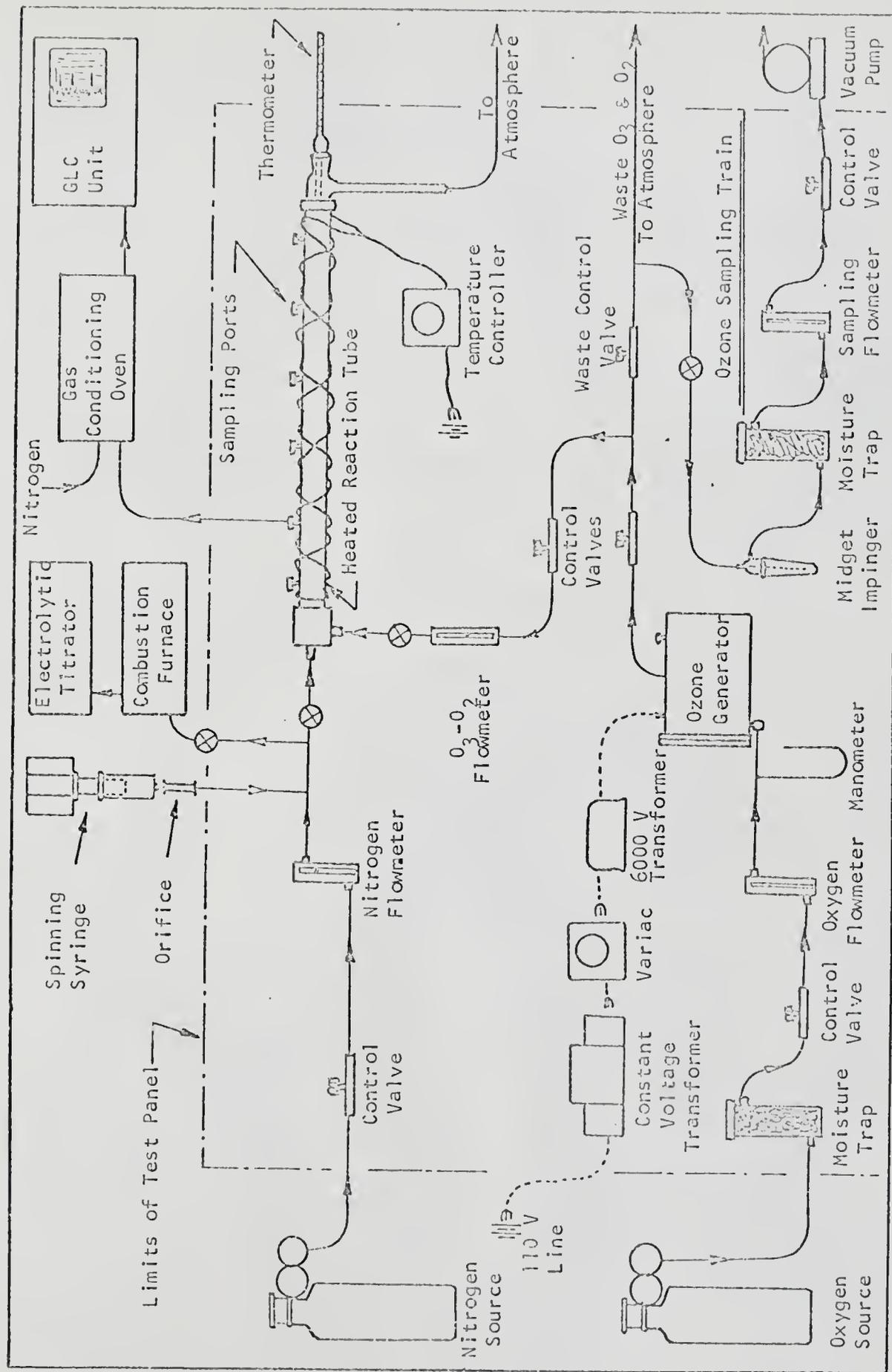


Figure 5. -- System Schematic for Oxidation of Bottled Gases.

volt transformer (supplied with the Model 4000 Ozone Generator) was controlled, thus controlling ozone production in the ozone generator. Oxygen flow to the ozone generator, which can also affect ozone production, was maintained at a constant 350 cc/min, and pressure in the generator was held at 34.0 in Hg. Voltage settings for desired ozone production were determined from a calibration curve as described in Appendix A.

From the ozone generator, 80 cc/min of ozone-oxygen mixture was directed to the heated reaction tube. The remaining 270 cc/min was discharged to the atmosphere through a waste line. An ozone sampling train, set to pull 150 cc/min, was connected to the waste line. This allowed the ozone output of the generator to be checked simultaneously with an experimental run to verify the actual ozone concentration entering the reaction tube. The neutral potassium iodide method was used for ozone sampling, and is described in Appendix A.

Nitrogen flow to the reaction tube was 320 cc/min, and was used as a carrier gas for the sulfur compounds. The spinning syringe used for injecting sulfur compounds into the nitrogen stream is shown in Figure 6, and flow rates from the syringe could be varied by changing orifice sizes at the syringe outlet. Additional details and calibration data for this apparatus are given in Appendix A. Sulfur concentrations in the syringe were varied by diluting known bottled gases to different sulfur/air ratios, and were checked periodically with the electrolytic titrator and gas chromatograph.

The reaction tube and mixing chamber used for the study were fabricated from 316 stainless steel. A diagram of this apparatus is shown by Figure 7. The mixing chamber was designed to provide thorough interaction between the ozone and sulfur gases prior to the first sampling

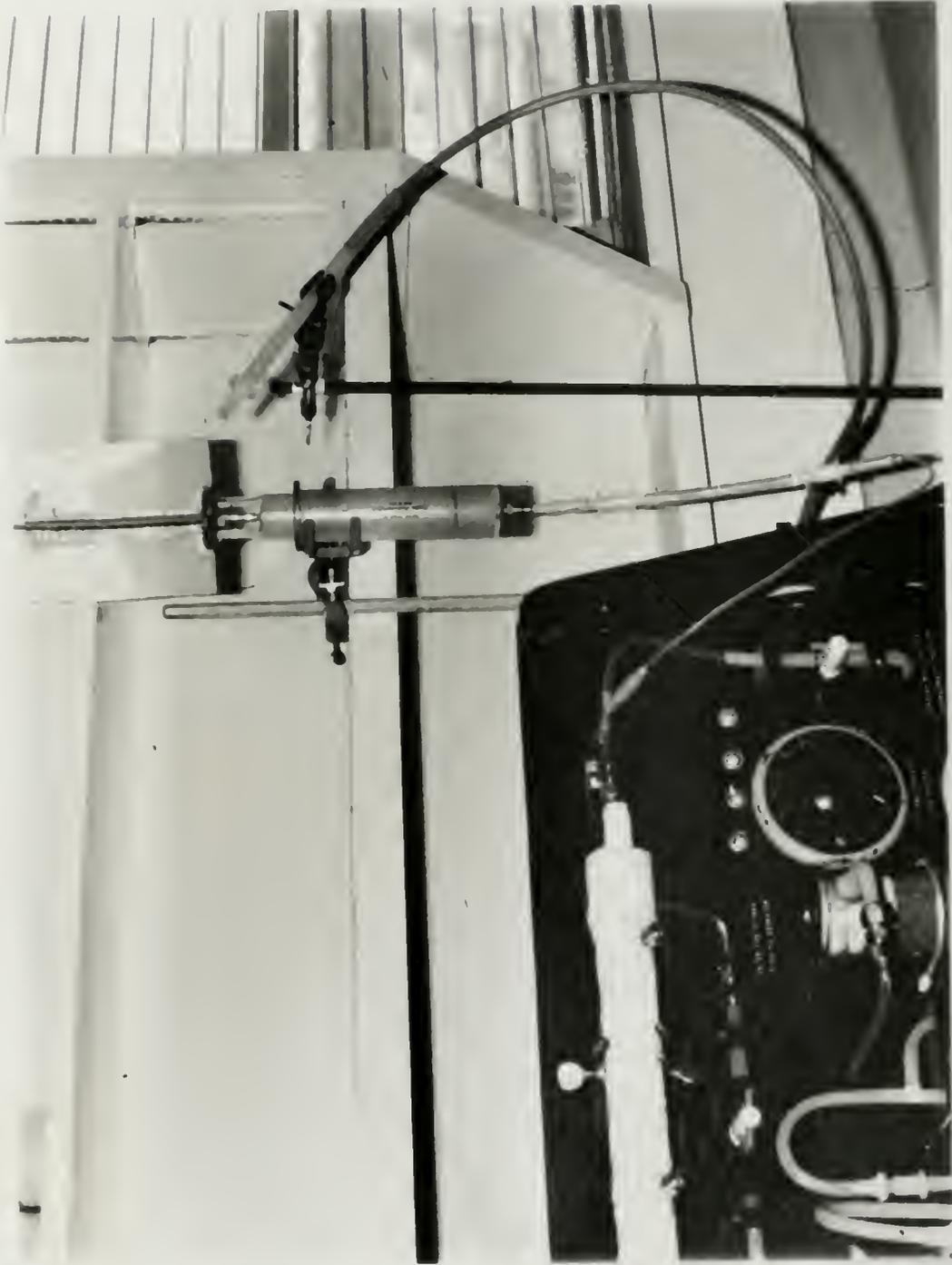


Figure 6. -- Injection of Sulfur Gases with Spinning Syringe.

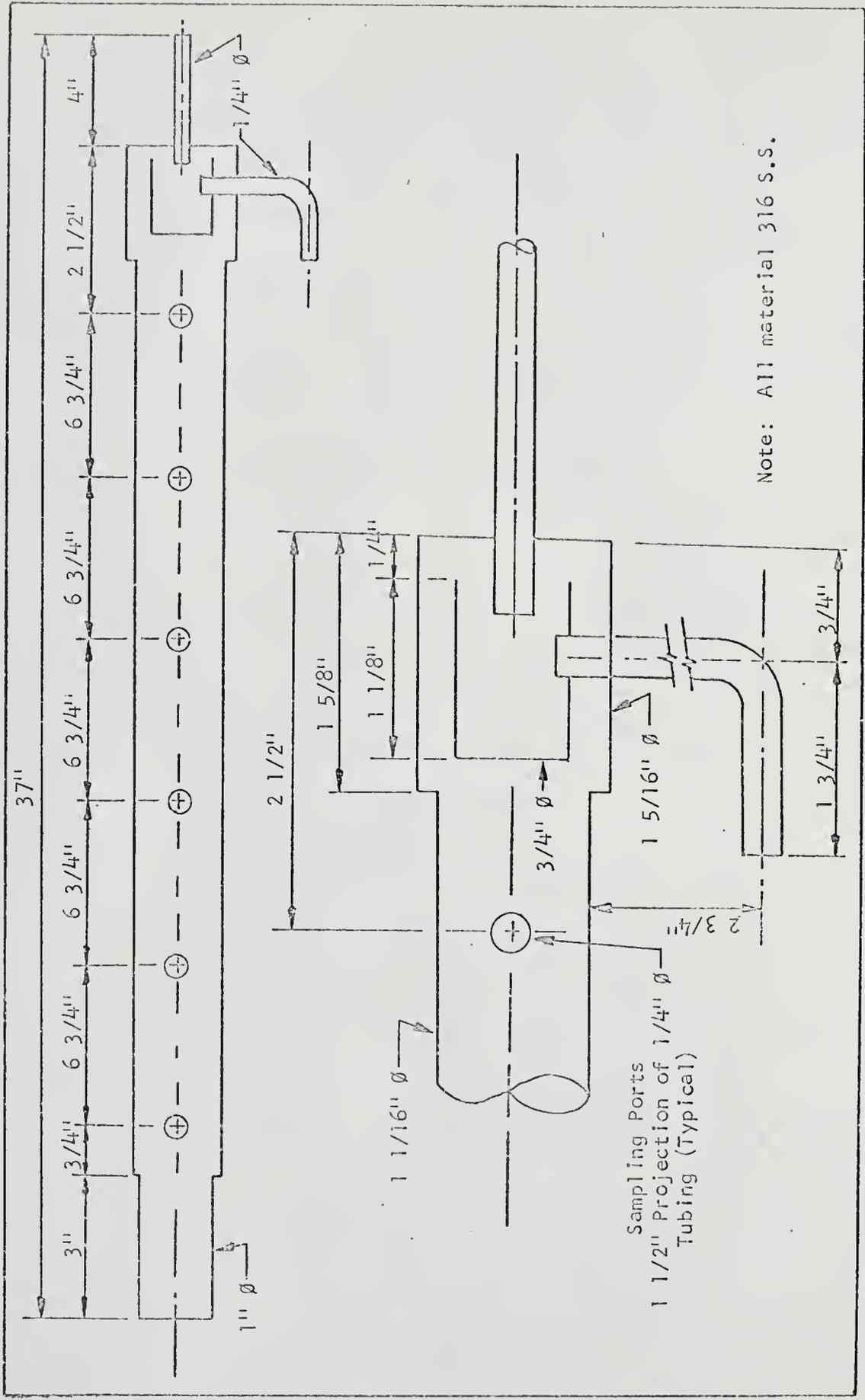


Figure 7. -- Diagram of Reaction Tube.

port. Volume of the reactor to the first port was 39.4 cc which provided a residence time of 5.9 seconds based on a total gas flow of 400 cc/min (80 cc/min ozone-oxygen and 320 cc/min nitrogen) at 25° C. Residence time to the last port was 61.5 seconds for the same conditions.

For heating purposes, the tube was wrapped with 1 x 1/8-inch asbestos tape followed by evenly spaced (at 1/4 inch), 18 gauge ni-chrome wire. This was covered with two more layers of asbestos tape. With a voltage regulator, a temperature range of ambient to 125° C was achieved, and was monitored with a thermometer inserted through a glass fitting (with a ground-glass joint) at the reactor outlet. The glass piece allowed visual observation of any deposits formed during the ozone-sulfur gas reactions.

Oxidation of the sulfur compounds was monitored with a gas chromatograph. Samples were pulled through a heated 1/8-inch Teflon line from the various sampling ports, depending upon the particular residence time desired. Exhaust from the reactor was discharged to the atmosphere through the previously mentioned glass fitting into 1/2-inch polyethylene tubing which extended outside the mobile laboratory.

NCASI Mobile Laboratory Equipment

General Description of Mobile Laboratory

The NCASI Mobile Laboratory is a modified, 19-foot travel trailer containing the necessary sampling and analytical equipment needed to investigate the emission sources in a kraft mill complex. The trailer facilitates the transportation of equipment from one mill to another and the location of it in close proximity to the emission source under

investigation. It also provides a suitable working environment while making a study. The basic equipment includes an all Teflon-stainless steel heated gas sampling system, combustion furnace, electrolytic titrators, and a gas-liquid chromatography unit (GLC). These components are supplemented with gas-flow measuring equipment, calibration systems, and miscellaneous laboratory supplies, chemicals, tools, etc.

All the equipment in the mobile laboratory was not utilized for the initial phase of the study since sampling and oxidation of actual stack gases were not required. As shown by the schematic (Figure 5), only the electrolytic titrator, gas conditioning box, and GLC unit were used in the initial phase. Extra bottles of nitrogen and oxygen were available in the trailer for connection to the test panel also.

Electrolytic Titrator and Combustion Furnace

As mentioned in the previous section of this chapter, a Barton Model 286 Electrolytic Titrator (240) was used to check concentrations of the sulfur gases prior to entering the reaction tube. The use of this instrument in the kraft pulping industry is well documented. Thoen, et al. (51) and Thoen and DeHaas (241) report on the use of a Barton Titrator to monitor the operation of kraft recovery furnaces. Blosser and Cooper (242) evaluate it as a method for the continuous monitoring of various process emission sources in the sulfate pulping operations, and Thoen, et al. (243) describe its use in the analysis of sulfur compounds in samples drawn from various points in the kraft process.

The operation of the Barton Titrator, using bromide coulometry, depends on reactions between oxidizable sulfur gases from the syringe (or from an emission source) and bromine in the titrating cell. These reactions, and additional details on the operation of a Barton Titrator, are thoroughly

described in the literature (51, 243). The major interfering compound in the bromine titration is alpha-pinene, usually emitted at some points in the sulfate process, but definitely not of concern using known bottled gases. However, interference has not been noticeable in the analysis of kraft effluent gases (243).

Sensitivities of the Barton Titrator as reported by Thoen, et al. (243) are 7-10 ppb for hydrogen sulfide, 10-12 ppb for methyl mercaptan, and 40-50 ppb for dimethyl sulfide. Previous applications of this instrument, and its use in NCASI investigations, have shown it to be dependable, simple to operate, and requiring minimum maintenance.

A combustion furnace, operating at 1750° F, was used in conjunction with the titrator for measuring the sulfur gas concentrations. The purpose of the furnace was to oxidize all forms of reduced sulfur to sulfur dioxide, and oxidize organic compounds (such as terpenes) that interfere with the titrator's response to carbon dioxide and water. Although not necessary while using bottled gases, the furnace was used since it is included in the normal gas flow pattern of the mobile laboratory, and only one set of calibration data (that of sulfur dioxide) was needed to determine sulfur gas concentrations from the syringe.

Gas Conditioning Oven

The gas conditioning oven, or dilution box, is primarily for use in the sampling and analysis of moisture laden, kraft mill effluent gases. It is constructed of 3/4-inch asbestos board and houses an electric heater, thermostat, and air circulation fan. In addition, it contains valves, flowmeters, and tubing and fittings necessary to control, monitor, dilute, and distribute the gas flow. For a clearer understanding of the function and location of the gas conditioning oven in the mobile laboratory,

Figure 8 shows a simplified flow diagram of the system while sampling stack gases. By maintaining a temperature of 100° - 110° C in the box, condensation is prevented in the lines, valves, flowmeters, etc., and by diluting the flow to the electrolytic titrator, the dewpoint can be reduced below ambient temperature and condensation prevented in those lines.

For the initial phase of this study with the bottled gases, the conditioning oven was used primarily to transfer a sample from the reaction tube, or spinning syringe, to the gas chromatograph through the GLC sampling valve. The sampling valve has eight ports, and is pneumatically operated with nitrogen by a solenoid valve. Sample gases from either the reaction tube, or spinning syringe, continually pass through the valve as does the GLC carrier gas (nitrogen). Also connected to the sampling valve are two sections of Teflon tubing (sampling loops) having identical volumes. At any given time, one sampling loop is in series with the sample gas flow and the other with the carrier gas flow. When the solenoid valve is activated, the relative positions of the sampling loops are changed with respect to the two gas flows. Thus, the GLC carrier gas sweeps the sample trapped in one loop into the GLC system for analysis.

Sampling loops of three different volumes were used depending upon concentrations in the sample gas and are listed in Table 6.

TABLE 6
GLC SAMPLING LOOPS

Loop	Length (in)	O.D. (in)	Concentration Range (ppm)
Small	2 1/2	1/16	100-2000
Medium	3 1/4	1/8	50-500
Large	22	1/8	1-60

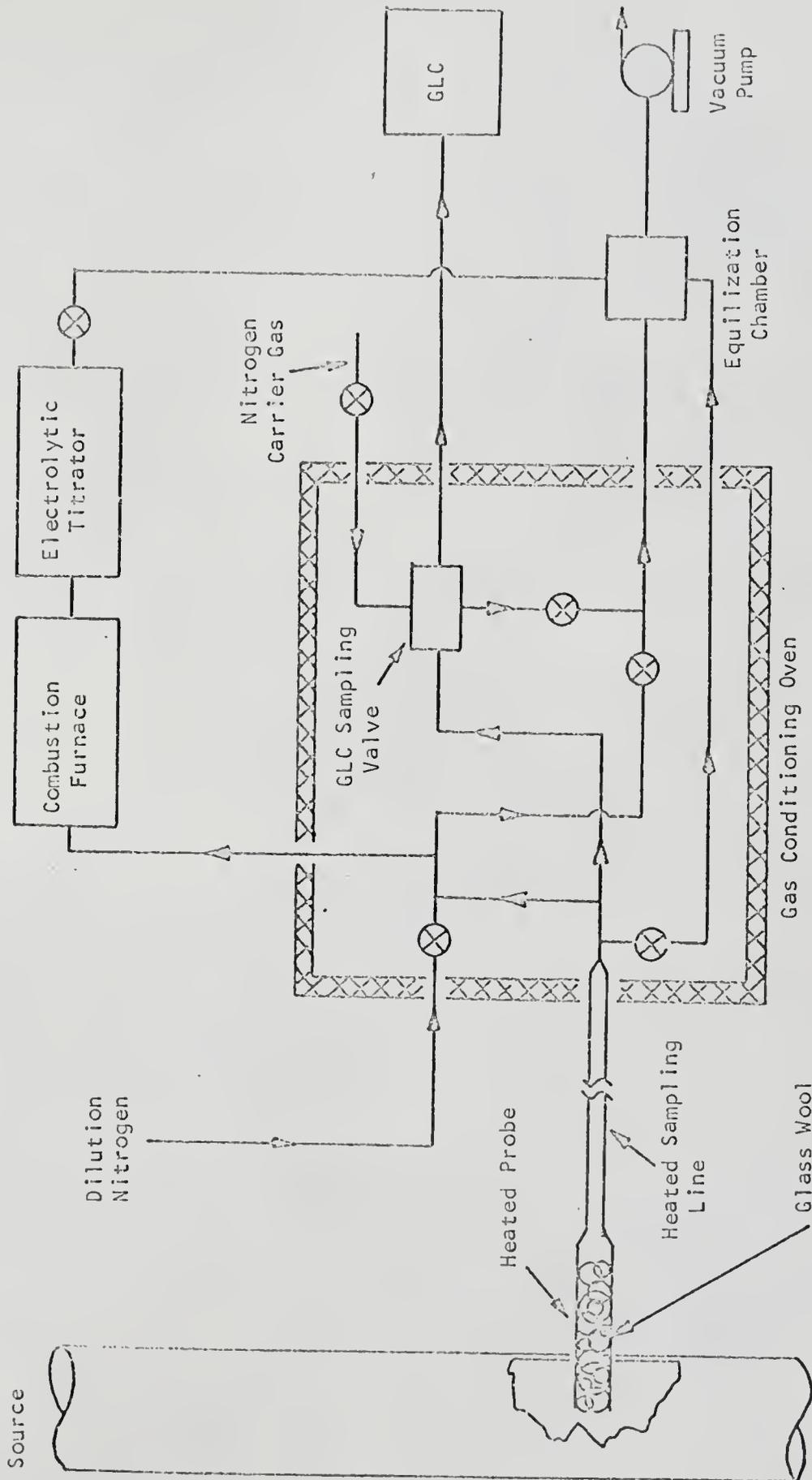


Figure 8. -- Mobile Laboratory Flow Diagram.

Gas-Liquid Chromatography System

The use of gas chromatography for the analysis of sulfur gases from kraft mills is also covered extensively in the literature (12, 39, 244-251). The unit contained in the mobile laboratory is a F & M Model 720 Gas Chromatograph (252) with a Melpar Model 65-34A Flame Photometric Detector (253). Two analytical columns are utilized in the separation and analysis of gaseous sulfur compounds. One is a 33-foot x 1/8-inch Teflon column packed with 30/60 mesh Haloport F (Teflon), and coated with 5 percent polyphenyl ether (5-ring). The other column is constructed of identical materials, but is only five feet long. The longer column is for analyzing hydrogen sulfide, sulfur dioxide, methyl mercaptan and dimethyl sulfide, while the five-foot column is for dimethyl sulfide and disulfide. A valve allows the selection of either column, and samples are introduced to the column selected through the GLC sampling valve previously described in the gas conditioning oven. Both columns operate at a temperature of 50° C with the carrier gas (nitrogen) set at 50 cc/min. Under these conditions the elution time of each column is as shown in Table 7.

TABLE 7
GAS CHROMATOGRAPH COLUMN ELUTION TIMES

Sulfur Compound	Long Column	Short Column
Hydrogen Sulfide	2 minutes	--
Sulfur Dioxide	3 minutes	--
Methyl Mercaptan	4-5 minutes	--
Dimethyl Sulfide	7-8 minutes	48 seconds
Dimethyl Disulfide	--	4-5 minutes

From either column, the sample enters the Melpar Flame Photometric Detector where it is mixed with oxygen, hydrogen and nitrogen and burned. The burning sulfur emits a blue light which is detected by a photomultiplier tube. The current output is proportional to the light produced, and is displayed on a strip chart recorder. With the use of calibration curves, the sulfur gas concentration is determined. Additional details on the flame photometric detector are covered by Brody and Chaney (254). Calibration of the GLC unit is discussed in Appendix A.

CHAPTER V

EXPERIMENTS AND RESULTS WITH BOTTLED SULFUR GASES

Experimental Procedures

To study the effectiveness of ozone in oxidizing the malodorous sulfur gases of interest, measured amounts of ozone and individual sulfur gases were injected into the heated reaction tube and allowed to react for a specified period of time. The products of the reaction were analyzed by the GLC unit, and the percent reduction in the malodorous sulfur gas noted. Specific details on operation of the test panel are covered in Appendix A, and describe the procedures used to obtain specific ozone to sulfur gas ratios, to change operating conditions (ratios, reaction times, temperature), and other necessary operations to run the experiments.

As discussed in Chapter IV (and Appendix A), reaction times in the heated reaction tube were controlled by using different sampling ports along the tube to withdraw samples for the GLC unit. Space times, or residence times, to each sampling port along the reactor are listed in Table 15 (Appendix A) for the various temperatures used during the study. Since a quench was not used at the sampling port to stop the oxidation process, any residual ozone in the sample would continue to oxidize the sulfur gas while in the transfer line to the GLC unit, thus resulting in an actual reaction time longer than those listed in Table 15.

Due to the fact that the transfer line was maintained at the same temperature as the reaction tube, the assumption was made that any reaction in the line would proceed similar to that in the reactor, and that the additional reaction time would be based only on flow and volume of the transfer line. At a flow of 200 cc/min through the transfer line, approximately four seconds of additional reaction time would have to be included. Table 8 reflects this additional transfer time, and lists the total reaction time associated with each sampling port.

TABLE 8
TOTAL REACTION TIME FOR OZONE OXIDATION

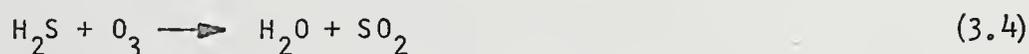
Sampling Port	Total Reaction Time (sec)				
	25°C	38°C	55°C	76°C	125°C
1	9.9	9.7	9.4	9.0	8.4
2	21.1	20.4	19.5	18.6	16.8
3	32.4	31.2	29.8	24.3	25.3
4	43.4	41.8	39.9	37.7	33.6
5	54.5	52.4	49.8	47.1	41.8
6	65.5	63.0	59.9	56.5	50.0

The experimental procedures used for each of the four gases were basically the same, the only difference being the concentration ratios evaluated for some of the experiments. As discussed in Chapter III, a majority of the laboratory investigations concerning ozone oxidation of malodorous sulfur compounds have dealt only with hydrogen sulfide. The range of conditions studied has been somewhat limited, thus restricting the practical application of the investigation's results. Based upon the data of Table 2 (Chapter II), which summarize kraft emission sources,

stack temperatures, and sulfur gas concentrations, a series of experimental tests were established for this study to cover a wide range of conditions representative of the kraft pulping industry. The following sections describe the experimental conditions established for each of the four malodorous sulfur gases, and the resulting data obtained at these conditions.

Hydrogen Sulfide

Cadle and Ledford (11) and Hales (12) agreed that the true stoichiometry of the ozone oxidation of hydrogen sulfide is represented by Equation 3.4, shown here again for convenience.



Theoretically then, an ozone to hydrogen sulfide ratio of 1.0 would achieve complete oxidation to sulfur dioxide. However, studies by Gregor and Martin (10) indicated that a ratio of 9.0 was necessary for complete oxidation of all the initial hydrogen sulfide, even for reaction times of 16 hours. Regardless of this, experimental conditions were established to study low concentration ratios and reduced reaction times since extremely high ratios and large holding chambers would be impractical from a cost viewpoint. Table 9 lists the conditions established to study the ozone oxidation of hydrogen sulfide.

Experimental data obtained on hydrogen sulfide oxidation are listed in Tables 18, 19, 20 and 21 (Appendix B), and show the remaining hydrogen sulfide at each sampling port for specific concentration ratios and temperatures. As noted in the data tables, the exact concentration ratios

TABLE 9
HYDROGEN SULFIDE EXPERIMENTAL CONDITIONS

Initial H ₂ S Concentrations (ppm)	O ₃ /H ₂ S Ratios	Temperatures (°C)
10	0.5, 1.0, 2.0, 5.0	38, 76, 125
50	" " " "	" " "
250	" " " "	" " "
500	" " " "	" " "
1000	" " " "	" " "
2000	" " " "	" " "

varied slightly from those proposed in Table 9 due to variations in ozone generator output and sulfur concentrations in the spinning syringe (as discussed in Appendix A -- Test Stand Operating Procedures).

Percent reduction of the initial hydrogen sulfide concentration for each temperature, sampling point, and concentration ratio (236 data points) is listed in Table 22 (Appendix B). Data from this table were used for a multiple regression analysis of the hydrogen sulfide oxidation. The data were fit to six different models (equations), using combinations of the variables ozone-hydrogen sulfide ratio (O_3), temperature (Te), residence time (Time), ratio squared (O_3^2), ratio-Te ($O_3 \times Te$), ratio-time ($O_3 \times Time$), and temperature-time (Te x Time). The object was to find a relatively simple equation with a high coefficient of determination (R^2), which indicates the percent of data variance accounted for by the particular equation, thus giving a high multiple correlation coefficient (R).

The three equations resulting in a high R^2 value and with minimum variables are as follows:

$$y = B_0 + B_1 O_3 + B_2 O_3^2 \quad , \quad (5.1)$$

$$y = B_0 + B_1 O_3 + B_2 Te + B_3 O_3^2 \quad , \quad (5.2)$$

$$\text{and } y = B_0 + B_1 O_3 + B_2 Te + B_3 \text{ Time} + B_4 O_3^2 \quad (5.3)$$

where y = percent reduction of initial hydrogen sulfide,

B_0, B_1, B_2, \dots = regression coefficients

O_3 = ozone-hydrogen sulfide ratio,

Te = temperature ($^{\circ}K$),

Time = reaction time (seconds).

The R^2 values for the above equations are 0.7958, 0.8261, and 0.8422 respectively. As expected with these high coefficients, the "F" statistic for each equation was highly significant (***) indicating a relatively small amount of variance in the data due to error.

Using each of the above equations, estimated values for percent reduction of hydrogen sulfide were calculated for concentration ratios of 0.5, 1.0, 2.0, and 3.0, reaction times of 10, 30, and 60 seconds, and for a temperature of $82^{\circ}C$. The temperature of $82^{\circ}C$ ($180^{\circ}F$) is typical of various kraft emission sources, and residence times of 10, 30, or 60 seconds could be obtained for many sources to insure good oxidation. Estimates for the above conditions, their standard error, regression coefficients, and other data on each equation are listed in Tables 23, 24, and 25 of Appendix B.

Using the data of Table 25, which estimate percent reduction using Equation 5.3, the effects of increased concentration ratios and reaction times are shown by Figure 9 for $82^{\circ}C$. This equation estimates a reduction of approximately 44 percent for 60 seconds' reaction at a concentration ratio of 1.0, whereas the data of Gregor and Martin (Figure 1, Chapter 3)

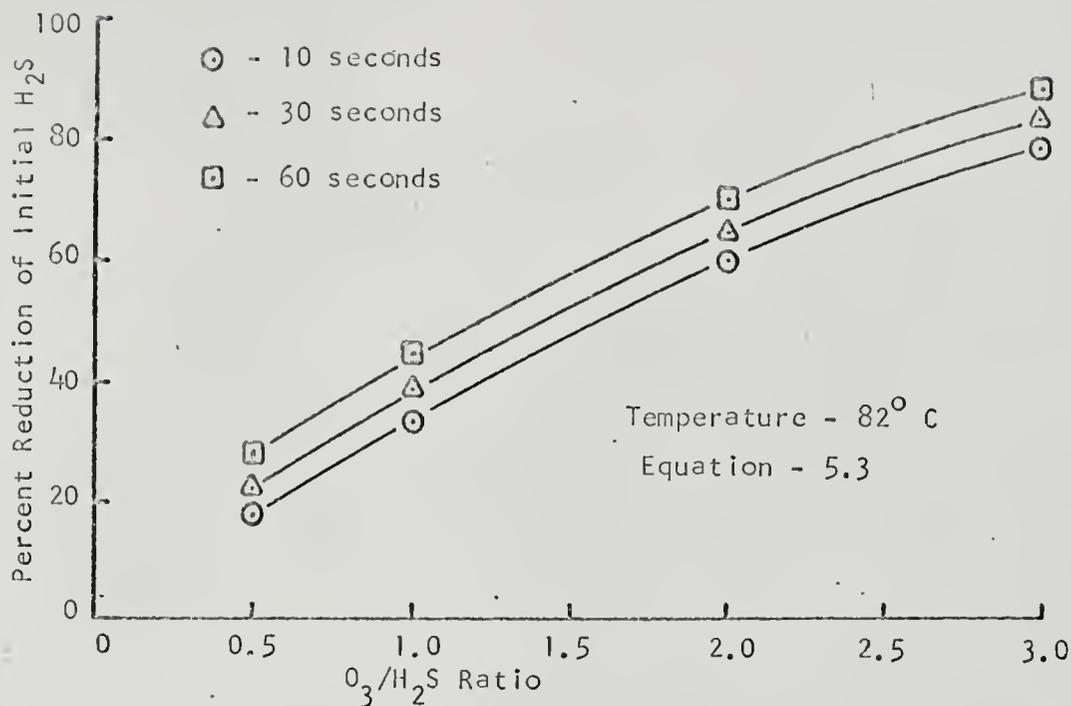


Figure 9. -- Ratio and Time Effects on H_2S Oxidation.

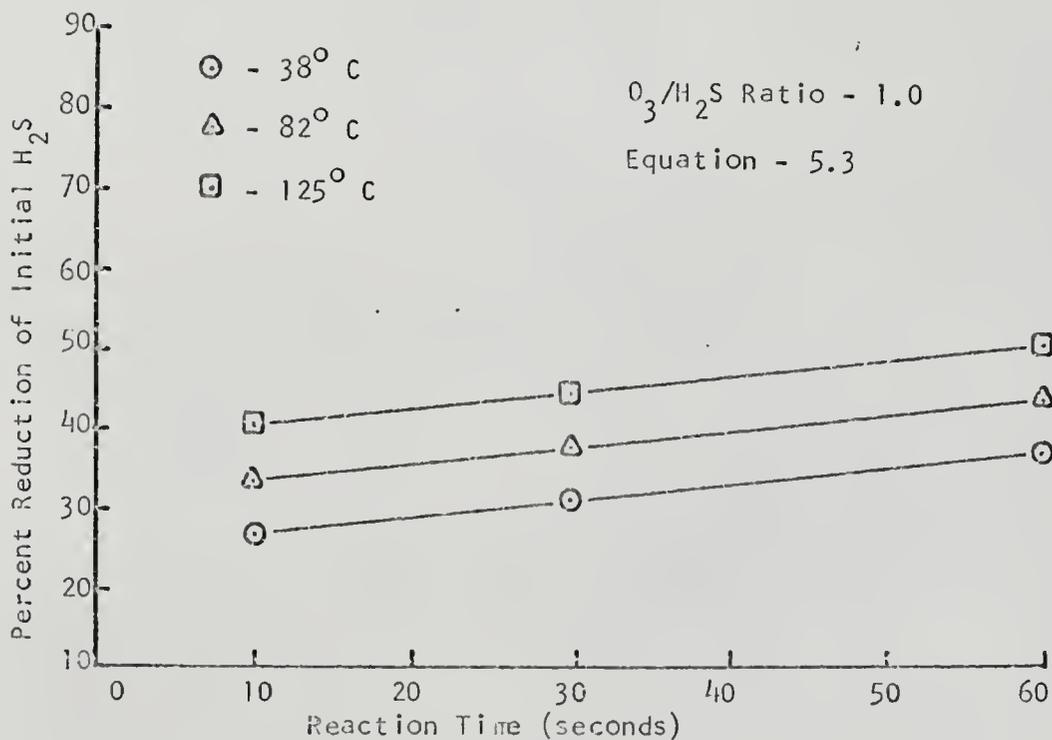


Figure 10. -- Temperature and Time Effects on H_2S Oxidation.

show only a 23 percent reduction for the same ratio. Of course, the data of Gregor and Martin were taken at ambient temperature, whereas the current reduction is based on 82°C which would account for some of the difference. This effect of temperature is illustrated in Figure 10, which plots percent reduction of initial hydrogen sulfide versus increased reaction times for three temperatures. As noted by this plot (at a ratio of 1.0), a reduction of about 37 percent is indicated at the low temperature (38°C), which is still somewhat higher than the 23 percent determined by Gregor and Martin. Thus, for the conditions of this study, the theoretical ratio of 1.0 needed for complete conversion to sulfur dioxide resulted in a maximum reduction of only 50 percent (125°C and 60 seconds). An estimated reduction of 96 percent could be achieved by increasing the ratio to 3.0 for the same conditions.

Although not indicated by any of the three equations selected for hydrogen sulfide oxidation, some of the initial data indicated that for concentration ratios of 2.0 and below, increased reaction times had very minor effects on the oxidation process. This would indicate that the ozone was being reduced very rapidly upon entering the reaction tube, thus eliminating any further reaction down the tube. Also, at these low concentration ratios, ozone was very rarely detected (by smell) at any of the sampling ports. The variable ' $\text{O}_3 \times \text{Time}$ ' was evaluated in one of the discarded equations, but was not determined to be significant. It should be noted, however, that Equation 5.2 does not include the 'Time' variable, yet has a R^2 value of 0.8261 which is only slightly lower than Equation 5.3. This indicates that for the conditions of this study, time was not nearly as significant as concentration ratio and temperature in the oxidation of hydrogen sulfide.

Methyl Mercaptan

Prior to starting the experimental tests with methyl mercaptan, a preliminary analysis of the hydrogen sulfide data indicated that the effectiveness of ozone oxidation in the reaction tube was independent of the initial hydrogen sulfide concentration as long as the concentration ratios remained the same. For this reason, approximately half of the data points were eliminated for methyl mercaptan and the remaining gases since only three initial sulfur gas concentrations (rather than six) were evaluated at varying concentration ratios. As reported by Douglass (5), oxidation of a mole of methyl mercaptan to thiosulfonate would require three moles of ozone as indicated by Equation 3.2 (Chapter 3). Based on the two above conditions, experimental tests were established for the ozone oxidation of methyl mercaptan, and are shown in Table 10.

TABLE 10
METHYL MERCAPTAN EXPERIMENTAL CONDITIONS

Initial RSH Concentrations (ppm)	O ₃ /RSH Ratios	Temperatures (°C)
50	1.0, 2.0, 4.0, 8.0	38, 125
250	1.0, 2.0, 4.0, 8.0	38, 125
1000	1.0, 2.0, 4.0, 8.0	38, 125

As previously mentioned, the experimental procedures used in obtaining the desired concentration ratios, reaction times, and temperatures are described in Appendix A. Concentrations of the bottled methyl mercaptan gas used during the tests are shown in Table 17 (Appendix A).

Experimental data obtained on the oxidation of methyl mercaptan are listed in Tables 26 and 27 (Appendix B), and show the remaining methyl mercaptan for each concentration ratio and reaction time, and also the amount of dimethyl disulfide found in the reaction products. As indicated by Equation 3.2, the formation of dimethyl disulfide is the first step in ozone oxidation of methyl mercaptan, and complete oxidation to thiosulfonate would require an ozone to methyl mercaptan ratio of 3.0. As shown by the data in Table 26 (Appendix B) for reactions at 38° C, approximately 100 percent removal of the methyl mercaptan is achieved at ratios of 3.0 - 4.0, but ratios of more than 7.0 are required for simultaneous oxidation of all the dimethyl disulfide for reaction times of at least one minute. Naturally, lower ratios could have achieved complete oxidation with longer reaction times than those evaluated during these tests since residual ozone was detected at various sampling ports at ratios above 2.0, indicating that additional reaction time would provide more complete oxidation. The data also indicated that for ratios of approximately 2.0 and below, increased reaction times have little effect on the oxidation process, suggesting that the available ozone is reduced very rapidly upon mixing with the sulfur gas, and leaves no residual for continued oxidation down the reaction tube. Similar results were noted, and previously discussed, in the oxidation of hydrogen sulfide.

The effect of increased temperature on methyl mercaptan oxidation is evidenced by the data of Table 27 (Appendix B), which indicate near complete removal of the initial methyl mercaptan at an ozone to sulfur gas ratio of approximately 2.0 for 125° C, whereas ratios of about 4.0 were required for similar results at 38° C. The data also indicated

approximately 100 percent removal of the dimethyl disulfide at ratios of approximately 4.0 for this higher temperature, whereas ratios of 7.0 (or larger) were required for reactions at 38° C. Assuming the final product of this oxidation process was thiosulfonate (which was not monitored by the GLC), the ratio of 4.0 would still exceed that predicted by Equation 3.2, although the reaction times allowed for this study were much shorter than those studied by Barnard (236) and Douglass (5) in formulating Equation 3.2.

Percent reduction of the initial methyl mercaptan for each concentration ratio, reaction tube temperature, and reaction time is shown in Table 28 (Appendix B), and was used as input data for the regression analysis of the ozone-methyl mercaptan reactions. The regression equations accounting for the largest percentages of the data variance are as follows:

$$y = B_0 + B_1 O_3 + B_2 Te + B_3 Time \quad , \quad (5.4)$$

$$y = B_0 + B_1 O_3 + B_2 Te + B_3 Time + B_4 O_3^2 \quad , \quad (5.5)$$

$$\text{and } y = B_0 + B_1 O_3 + B_2 Te + B_3 Time + B_4 O_3^2 + B_5 O_3 Te \quad . \quad (5.6)$$

Coefficients of determination (R^2) for the above equations are 68.53, 70.89, and 71.11 percent respectively, and are somewhat lower than values achieved for the other three gases. This is possibly due to a reduced amount of data for the 125° C experiments resulting from the rapid oxidation of methyl mercaptan at low concentration ratios for this temperature. Nevertheless, the above coefficients are considered adequate to describe the oxidation reactions for the test conditions studied, and to predict estimated removal of methyl mercaptan from a gas stream at these conditions.

The regression coefficients for each equation, along with other data, are given in Tables 29, 30, and 31 (Appendix B). These tables also include estimated reduction of initial methyl mercaptan for various concentration ratios and reaction times based on the regression equation listed with the table. The standard error associated with each estimate is also given.

Using the data of Table 30, which describe Equation 5.5, Figure 11 shows the regression lines for three reaction times and concentration ratios at 38° C. Although this equation does not have the highest R^2 value of those evaluated, it is very close, and contains one less variable than Equation 5.6 (the highest R^2). The effect of temperature is shown by Figure 12 for a concentration ratio of 1.0, and indicates the difference in oxidation achieved at 38° C and 82° C for various reaction times.

Dimethyl Sulfide

As reported by Barnard (236) and Douglass (5), and shown in Equation 3.1 (Chapter 3), ozone reacts with dimethyl sulfide to form the sulfoxide and then the sulfone. The studies by Barnard showed that the oxidation process required somewhat less than the theoretical amount (two moles) of ozone per mole of dimethyl sulfide. Assuming complete oxidation would be achieved at a ozone to sulfur gas ratio of 2.0, the experimental conditions shown in Table 11 were established to evaluate the ozone oxidation of dimethyl sulfide.

Data obtained on the ozone oxidation of dimethyl sulfide are shown in Tables 32 and 33 of Appendix B. Using these basic data, percent

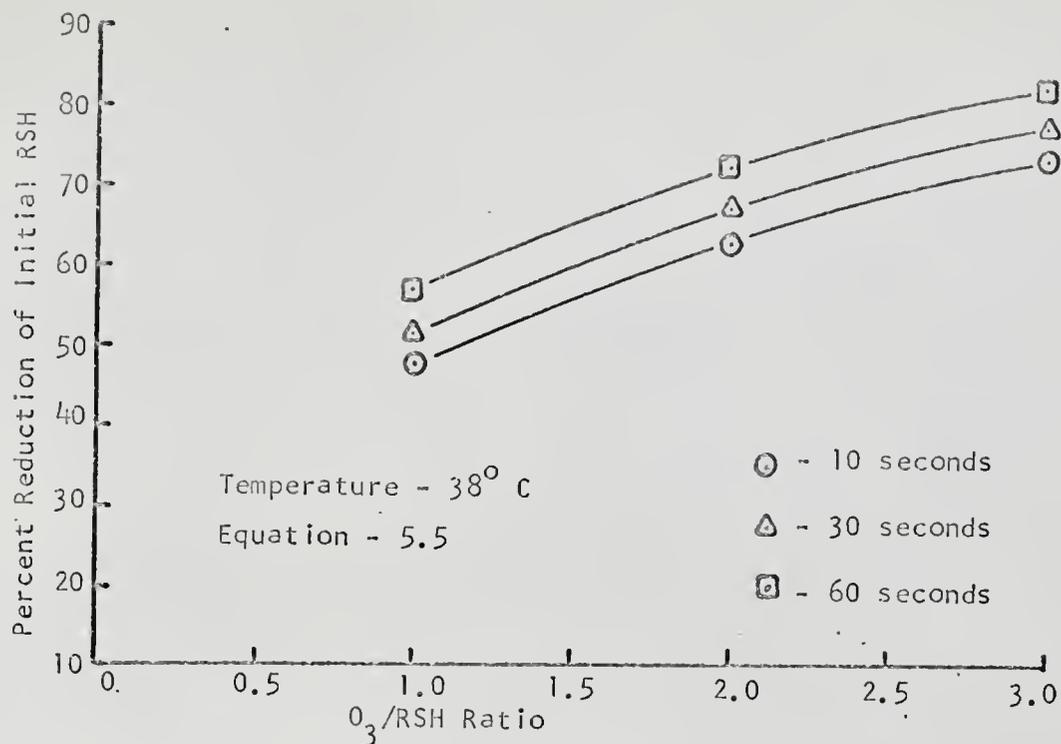


Figure 11. -- Ratio and Time Effects on RSH Oxidation.

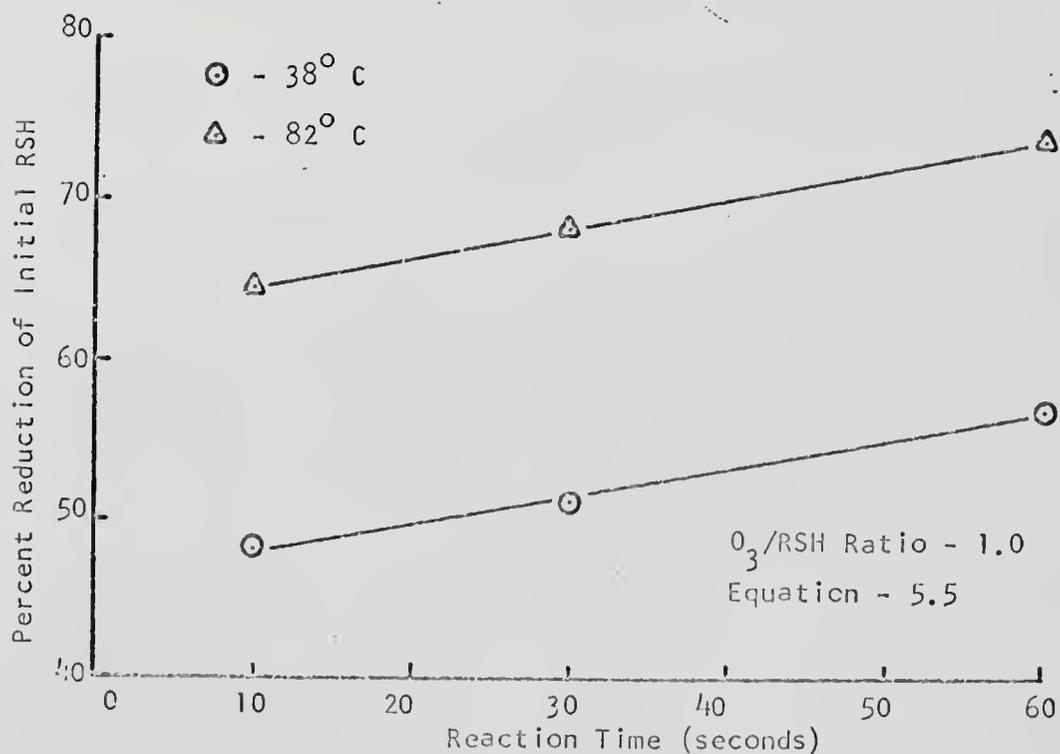


Figure 12. -- Temperature and Time Effects on RSH Oxidation.

TABLE 11
DIMETHYL SULFIDE EXPERIMENTAL CONDITIONS

Initial RSR Concentrations (ppm)	O ₃ /RSR Ratios	Temperatures (°C)
50	0.5, 1.0, 2.0, 4.0	38, 125
250	0.5, 1.0, 2.0, 4.0	38, 125
1000	0.5, 1.0, 2.0, 4.0	38, 125

reduction at each experimental condition was calculated (Table 34), and resulted in the following three regression equations:

$$y = B_0 + B_1 O_3 + B_2 O_3^2 \quad , \quad (5.7)$$

$$y = B_0 + B_1 O_3 + B_2 Te + B_3 Time + B_4 O_3^2 \quad , \quad (5.8)$$

$$\text{and } y = B_0 + B_1 O_3 + B_2 Te + B_3 O_3^2 + B_4 O_3 Te \quad . \quad (5.9)$$

Coefficients of determination (R^2) for the above equations are 0.7038, 0.7160, and 0.7279 respectively. Regression coefficients, "F" values, and other data relative to each equation are given in Tables 35, 36, and 37 of Appendix B. Similar to the R^2 values for methyl mercaptan, the above listed values are not as high as those achieved for hydrogen sulfide, but each equation has a highly significant "F" statistic, and is considered completely adequate for the conditions studied. As with the methyl mercaptan tests, approximately 60 combinations of experimental conditions were used as input for the regression analysis, whereas 236 were used for the hydrogen sulfide analysis. In many cases, the absence of data was due to the rapid oxidation of dimethyl sulfide at the elevated temperature (125° C) and the lower concentration ratios. For complete oxidation (100 percent removal) of the initial dimethyl sulfide at any specific

condition, the data were not used as input for the regression analysis since the exact ratio needed to achieve 100 percent reduction had not been determined, i.e., if a concentration ratio of 2.5 resulted in 100 percent reduction, the exact ratio needed to achieve reduction may have been only 2.1. For this reason, progressions of ratios and reductions were desired for data input, but were not always attainable due to the varying experimental conditions (ozone generation and syringe dilutions).

Estimated reductions of dimethyl sulfide at 82^o C for various concentration ratios and reaction times are given in Tables 35, 36, and 37 for the three equations. To show the relatively minor effects of time and temperature on the oxidation reactions of this gas, Figure 13 shows percent reduction versus reaction times for three temperatures. For these test conditions, no increase in oxidation is noted with increased reaction times, and the differences in percent reduction for the three temperatures is relatively small when compared to those noted for hydrogen sulfide and methyl mercaptan. The reduced effect of temperature is also shown by Figure 14 in a plot of percent reduction versus concentration ratios for the three temperatures. As reported by Douglass (5), the initial oxidation step of dimethyl sulfide to the sulfoxide is very rapid, and would account for at least a part of the reduced effects of time and temperature noted at these test conditions.

As shown by Figure 14, the theoretical concentration ratio of 2.0 needed for complete oxidation resulted in an estimated reduction of only 67 percent for this study (at 82^o C). By increasing the ratio to 3.0, the reduction is increased to approximately 84 percent for the same temperature, and for the limited reaction times evaluated.

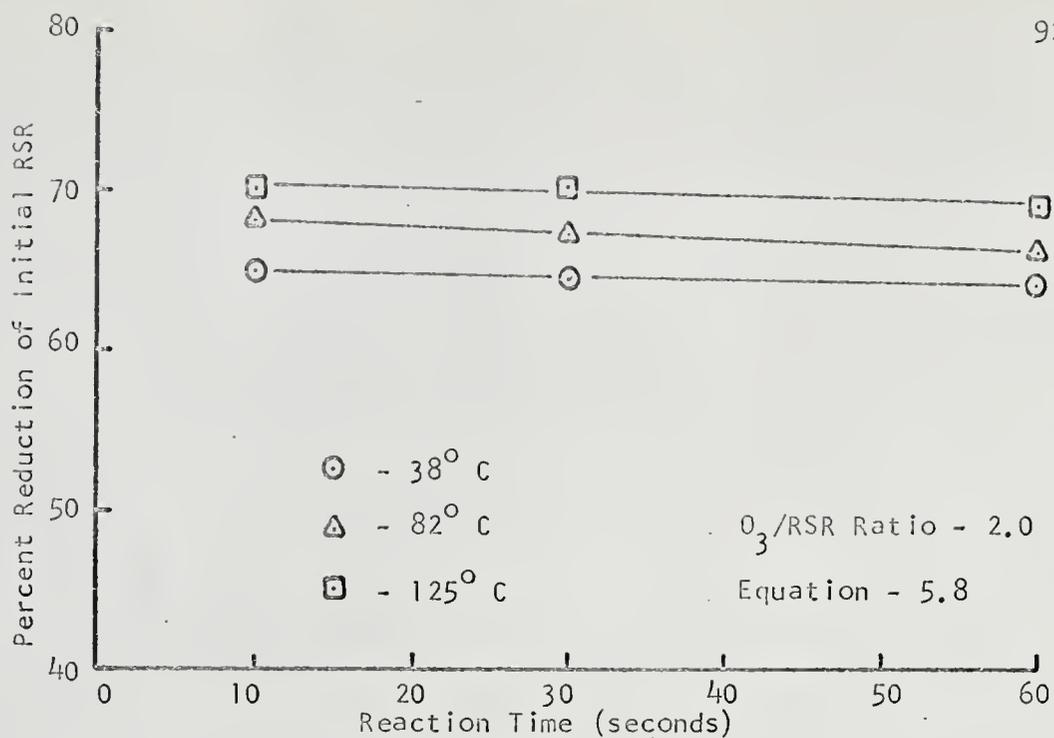


Figure 13. -- Temperature and Time Effects on RSR Oxidation.

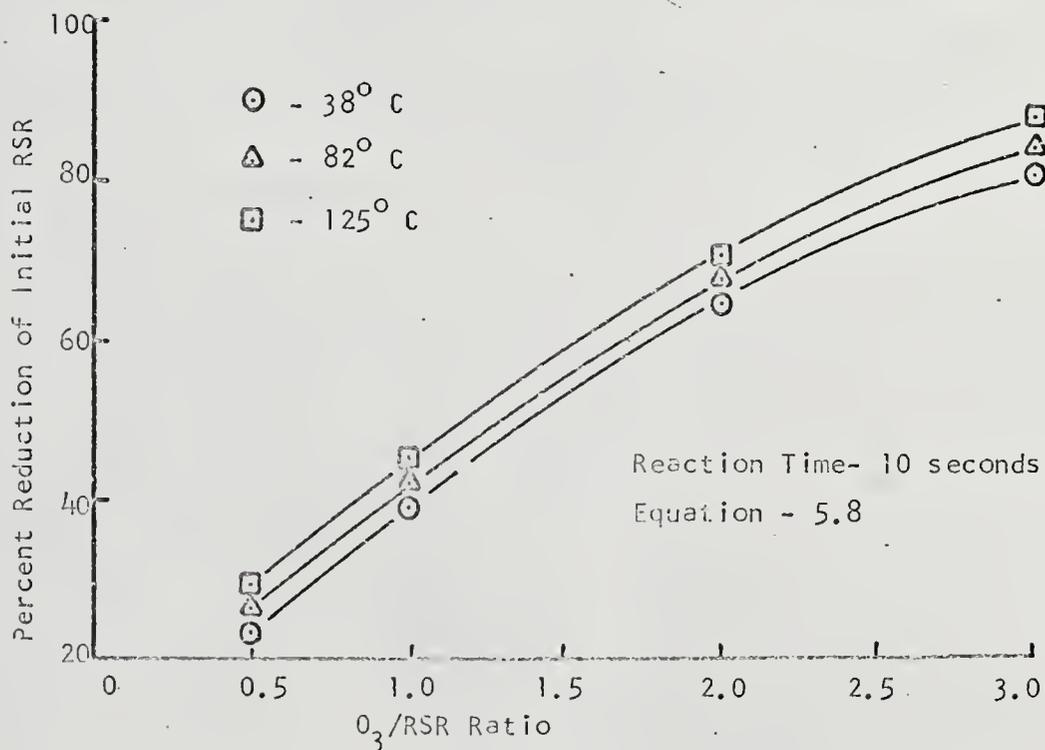


Figure 14. -- Ratio and Temperature Effects on RSR Oxidation.

Dimethyl Disulfide

As reported by Barnard (236), and discussed fully in Chapter III, tests on the oxidation of "normal" disulfides showed the absorption of 2.5 - 3.0 moles of ozone per mole of disulfide. These ratios are also indicated by Douglass (5) discussing the oxidation of methyl mercaptan in which dimethyl disulfide is the first product formed, and further oxidation to the thiosulfonate and sulfonic anhydride would require 2.0 - 3.0 moles of ozone per mole of dimethyl disulfide. Based on the above discussion, the experimental conditions of Table 12 were established.

TABLE 12
DIMETHYL DISULFIDE EXPERIMENTAL CONDITIONS

Initial RSSR Concentrations (ppm)	O ₃ /RSSR Ratios	Temperatures (°C)
50	0.5, 1.0, 2.0, 3.0, 5.0	38, 125
150	1.0, 2.0, 3.0, 5.0	38, 125
350	1.0, 2.0, 3.0, 5.0	38, 125

Initial data taken at approximately these conditions are shown in Tables 38 and 39 of Appendix B. From these data, percent reduction of the initial dimethyl disulfide was calculated for each experimental condition (75 data points), and listed in Table 40 (Appendix B). Regression equations computed from the data are as follows:

$$y = B_0 + B_1 O_3 + B_2 Te + B_3 O_3^2 + B_4 O_3 Te, \quad (5.10)$$

$$y = B_0 + B_1 O_3 + B_2 Te + B_3 Time + B_4 O_3^2 + B_5 O_3 Te, \quad (5.11)$$

$$\text{and } y = B_0 + B_1 O_3 + B_2 \text{Te} + B_3 \text{Time} + B_4 O_3^2 + B_5 O_3 \text{Te} + B_6 O_3 \text{Time} \\ + B_7 \text{Te Time} \quad (5.12)$$

Coefficients of determination (R^2) for each equation are 0.8544, 0.8734, and 0.8952 respectively which are the highest for any of the four gases studied. More data points were evaluated (75 versus 60) for this gas than for dimethyl sulfide or methyl mercaptan, and the slower oxidation process resulted in a more uniform progression of concentration ratios and percent reduction.

Estimated reductions at various experimental conditions are listed in Tables 41, 42, and 43 (Appendix B) for each regression equation along with the regression coefficients, "F" values, and other equation information. Data from Table 42 (Equation 5.11) were used to show the effects of temperature, reaction time, and concentration ratios on the oxidation process. In Figure 15, the effect of reaction time and temperature is noted at a concentration ratio of 3.0, which would theoretically achieve 100 percent oxidation at optimum conditions. As indicated by this plot, a maximum reduction of 67 percent is estimated for 125° C and 60 seconds reaction time.

Figure 16 shows the effect of increasing the concentration ratio and reaction temperature for the 10 second reaction time. Even by increasing the concentration ratio to 5.0, a maximum reduction of only 83 percent is estimated for the 125° C reactions. Further analysis of the data and equations of Table 42 indicates that by increasing the reaction time from 10 to 60 seconds, an estimated 92 percent reduction would be achieved at the higher temperature.

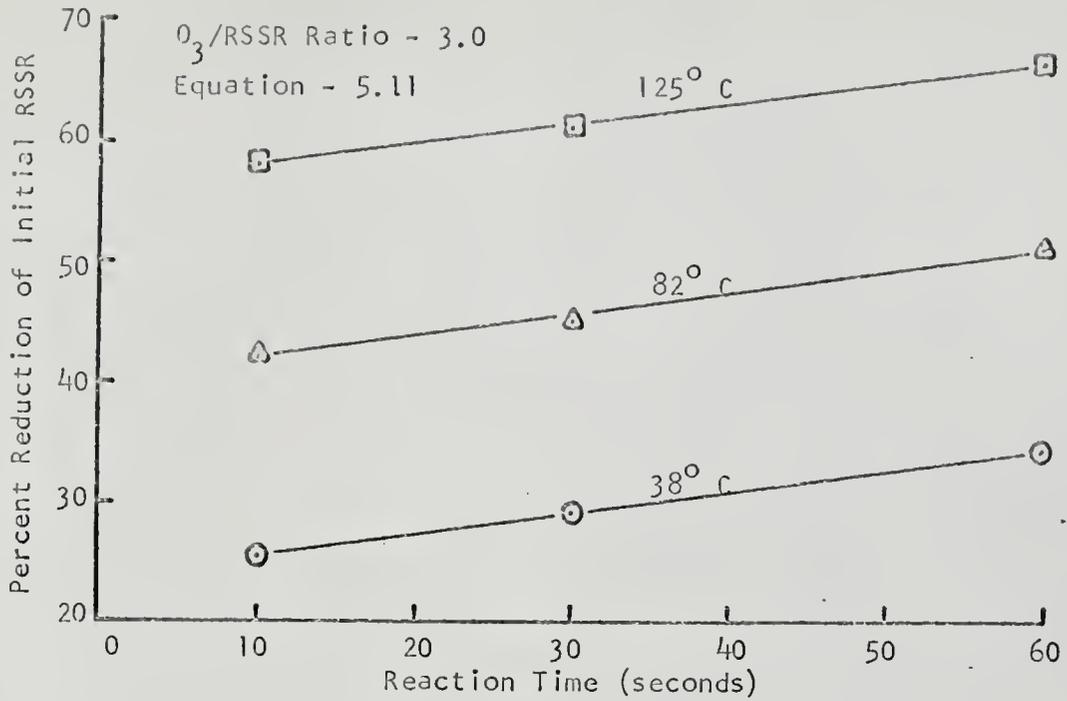


Figure 15. -- Temperature and Time Effects on RSSR Oxidation.

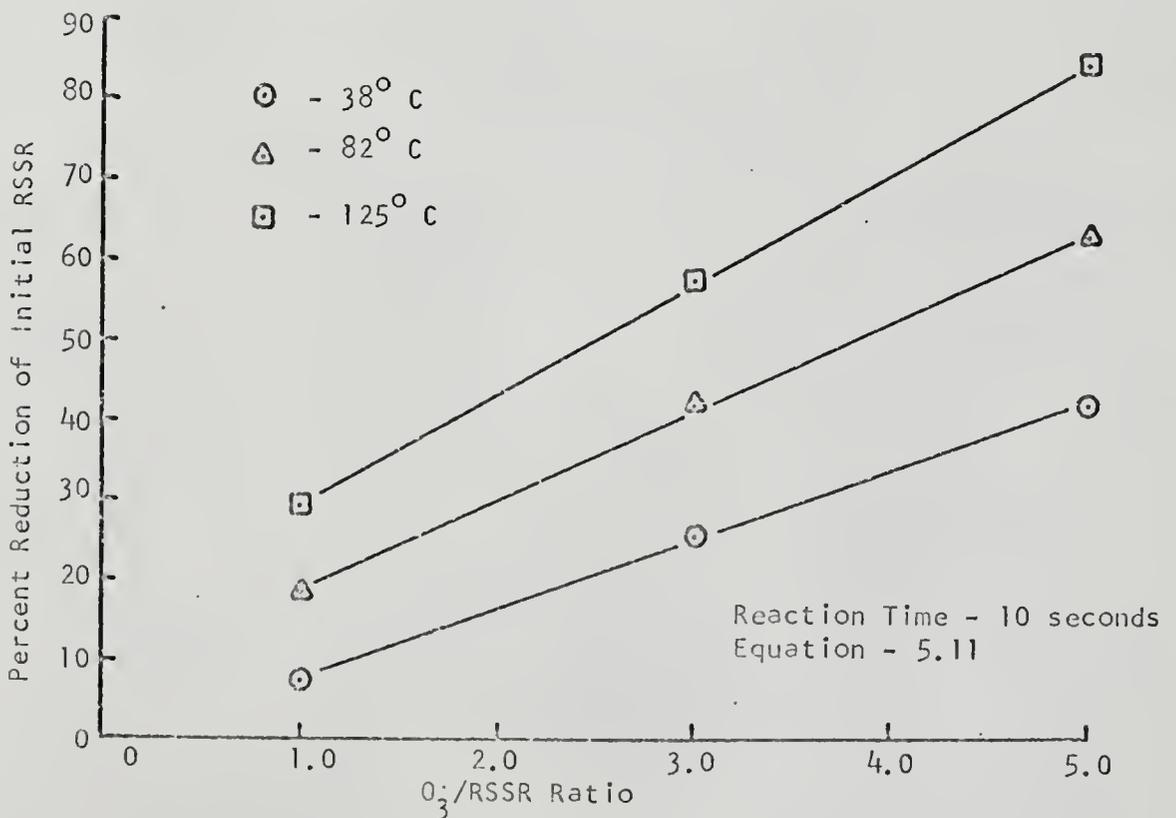


Figure 16. -- Ratio and Temperature Effects on RSSR Oxidation.

CHAPTER VI

EXPERIMENTS AND RESULTS WITH KRAFT MILL EFFLUENT GASES

System Modifications

Upon completing the tests with bottled sulfur gases, the experimental system was modified slightly in order to study the reaction between ozone and actual kraft mill effluent gases. Figure 8 (Chapter IV) shows the normal flow pattern in the mobile laboratory while sampling stack gases. In order to use the reaction tube to study the ozone oxidation of a stack gas, the flow pattern inside the gas conditioning oven was changed so that a measured portion of the stack effluent could be drawn through the tube. Figure 17 shows the basic flow patterns of the modified system.

The electrolytic titrator was used to continually monitor total sulfur gas concentrations (TRS) in the effluent stream prior to ozone injection. As mentioned in Chapter IV, a combustion furnace was used in conjunction with the electrolytic titrator, and all sulfur gases were read as sulfur dioxide. The gas chromatograph was used to analyze the effluent gas for hydrogen sulfide, methyl mercaptan, dimethyl sulfide, dimethyl disulfide, and sulfur dioxide prior to ozone injection (for baseline data), and then analyze for the same gases of interest following ozone mixing to determine the extent of oxidation.

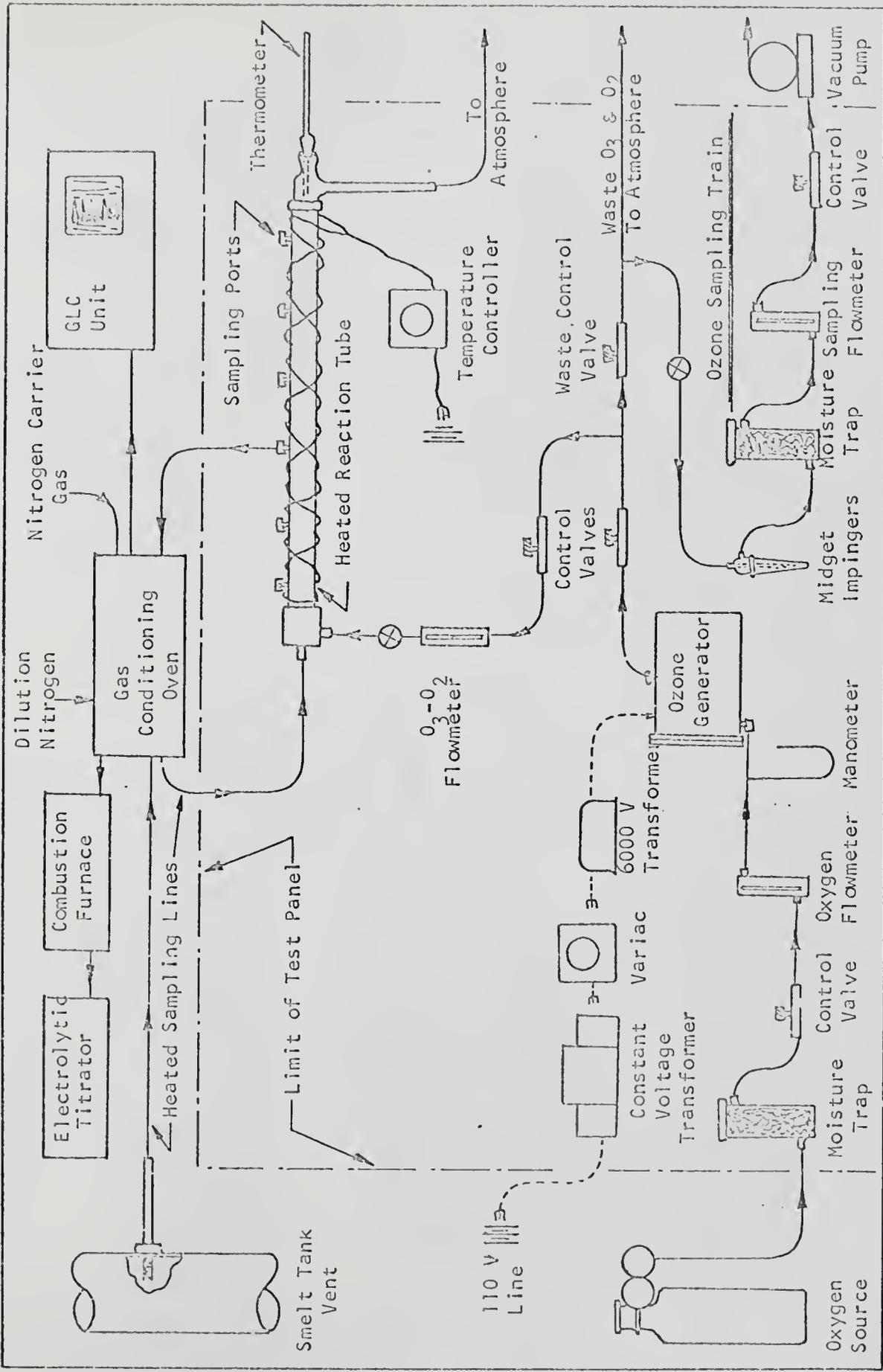


Figure 17. -- System Schematic for Oxidation of Stack Gases.

Effluent Gas Source

Smelt tank vent gas was used to evaluate the effectiveness of ozone oxidation. At the particular mill where this study was conducted, evaporator condensate is used as make-up water for the smelt tanks, and due to the amount of sulfur compounds normally released from the evaporators, it was felt that the condensate would carry a sufficient amount of sulfur compounds to the smelt tank to provide a good evaluation of ozone's oxidation potential on the various gases of interest. Prior to selecting the smelt tank vent, the black liquor oxidation tower vent was checked for total sulfur content (TRS) with the electrolytic titrator for possible experimental runs, but did not contain a sufficient amount for proper evaluation at various ozone-sulfur ratios. Initial checks on the smelt tank vent showed 90 ppm TRS of which 26 ppm was dimethyl disulfide.

Experimental Procedures

For emission inventories at various mills, the NCASI Mobile Laboratory contains 200 feet of heat-traced, Teflon sampling line and several stainless steel probes. Temperature of the sampling line and probe is normally maintained at 100^o C with voltage regulators. For this study, the line was deployed to the smelt tank vent, and connected to the probe installed in a convenient sampling port. As shown by Figure 8 (Chapter IV) and Figure 17, gases were pulled into the gas conditioning oven. A portion was diluted with nitrogen, passed through the combustion furnace, and recorded as TRS by the electrolytic titrator. Of the remainder, a flow of 450 cc/min was directed through the reaction tube for ozone oxidation. Prior to each experimental run (at a specific ozone concentration), the stack gas was analyzed by the GLC unit to determine concentrations of each sulfur compound of interest for baseline data.

Operating procedures for the ozone generator were the same as for the bottled gases, and are described in Appendix A. An ozone-oxygen flow of 50 cc/min was directed to the reaction tube, resulting in a total flow through the tube of 500 cc/min. Actual ozone concentrations in the reaction tube were 24, 47, 191, and 414 ppm respectively for the four experimental runs made on smelt tank vent gases. Reaction tube temperature was maintained at 100° C. Since total flow in the reactor had increased to 500 cc/min (instead of 400 cc/min for the bottled gas experiments), space times to sampling ports 1, 3, and 6 were reduced to 3.8, 18.2, and 39.3 seconds respectively. With the additional time allowed for the sampling transfer line, total reaction times for the three sampling ports (1, 3, and 6) were 7.8, 22.2, and 43.3 seconds.

Results of Ozone Oxidation

Data recorded for this portion of the study are shown in Table 44 (Appendix B). As previously mentioned, the smelt tank vent gases were treated with four different ozone concentrations (24, 47, 191, and 414 ppm) in order to evaluate the effectiveness of varying ozone to sulfur gas ratios in eliminating any of the four major malodorous sulfur gases found in the vent gas.

As shown by the data in Table 44, the TRS values recorded by the electrolytic titrator were quite variable during the experimental runs, with values ranging from 85 to more than 275 ppm. Due to the normal emission variations from both smelt tanks and evaporators (as shown by Table 2, Chapter 11), these erratic values of TRS in the smelt tank vent gases were expected. Naturally, the individual values of methyl mercaptan,

dimethyl sulfide, and dimethyl disulfide varied also. Hydrogen sulfide was not detected during these experimental runs.

The effectiveness of ozone oxidation was evaluated by noting the decrease in the three malodorous sulfur compounds mentioned above at different ozone to TRS ratios. Of course, with the ever changing value of TRS, the ozone to TRS ratio could not be held constant, but was recorded for each series of tests. By increasing ozone concentrations (from 24 to 414 ppm), ratios of 0.19 to 3.48 were achieved. As mentioned, data were taken on the vent gas with the GLC prior to ozone injection to get a baseline reading on the concentration of each malodorous sulfur gas. For all the baseline data (points A, B, I, J, K, L, S, U, BB - Table 44), the summation of methyl mercaptan, dimethyl disulfide, and dimethyl sulfide accounted for approximately 51.5 percent of the TRS value. The values recorded for dimethyl disulfide were doubled to calculate this percentage since one mole of this compound would yield two moles of sulfur dioxide after passing through the combustion furnace and prior to analysis by the electrolytic titrator.

By injecting known amounts of ozone into the vent gas stream and measuring the remaining sulfur compounds, the extent of ozone oxidation was monitored by observing any reduction in the 51.5 percent value which would indicate removal of the three sulfur gases of interest. It should also be noted that baseline data on the vent gas showed no sulfur dioxide, but the amount of this gas steadily increased as the ozone to TRS ratio increased. Table 13 is a summary of the data taken during the experimental runs, and shows the percent reduction (from the original 51.5 percent) of the three sulfur gases from the vent gas stream at varying ozone concentrations. Figure 18 is a plot of these data showing percent reduction of

TABLE 13
SUMMARY OF OZONE-SMELT TANK VENT GAS DATA

Run No.	Point	Vent Gas TRS (ppm) ^a	Ozone (ppm)	O ₃ /TRS Ratio	Sampling Port	GLC Analysis		
						Total Sulfur (ppm) ^b	Percent of TRS	Percent Reduction ^c
43	C	104	24	.23	1	48.2	46.4	9.9
48	D	120	24	.20	1	56.2	46.9	8.9
48	E	127	24	.19	3	59.1	46.6	9.5
48	F	116	24	.21	3	54.8	47.3	8.1
48	G	102	24	.24	6	46.6	45.7	11.3
48	H	93	24	.26	6	39.5	42.5	17.5
49	M	162	47	.29	1	69.1	42.7	17.1
49	N	152	47	.31	1	56.0	36.8	28.5
49	O	157	47	.30	3	63.7	40.6	21.2
49	P	186	47	.25	3	50.1	26.9	47.8
49	Q	210	47	.22	6	98.3	46.8	9.1
49	R	127	47	.37	6	45.9	36.1	30.0
50	V	182	191	1.05	1	35.4	19.5	62.1
50	W	210	191	.91	1	42.8	20.4	60.5
50	Y	197	191	.97	3	45.0	22.9	55.5
50	Z	166	191	1.15	6	34.0	20.5	60.2
50	AA	157	191	1.22	6	29.0	18.5	64.1
51	CC	148	414	2.80	1	0	0	100
51	DD	119	414	3.48	1	0	0	100
51	EE	177	414	2.34	3	7.0	4.0	92.3
51	FF	157	414	2.64	3	2.0	1.3	97.5
51	GG	160	414	2.59	6	0	0	100
51	HH	174	414	2.38	6	4.2	2.4	95.5

^aTotal Reduced Sulfur read as SO₂ by electrolytic titrator prior to ozone injection.

^bDoes not include SO₂ value, but summation of RSH, RSR, and twice RSSR value.

^cPercent reduction from baseline figure of 51.5 percent. Data used to plot Figure 18.

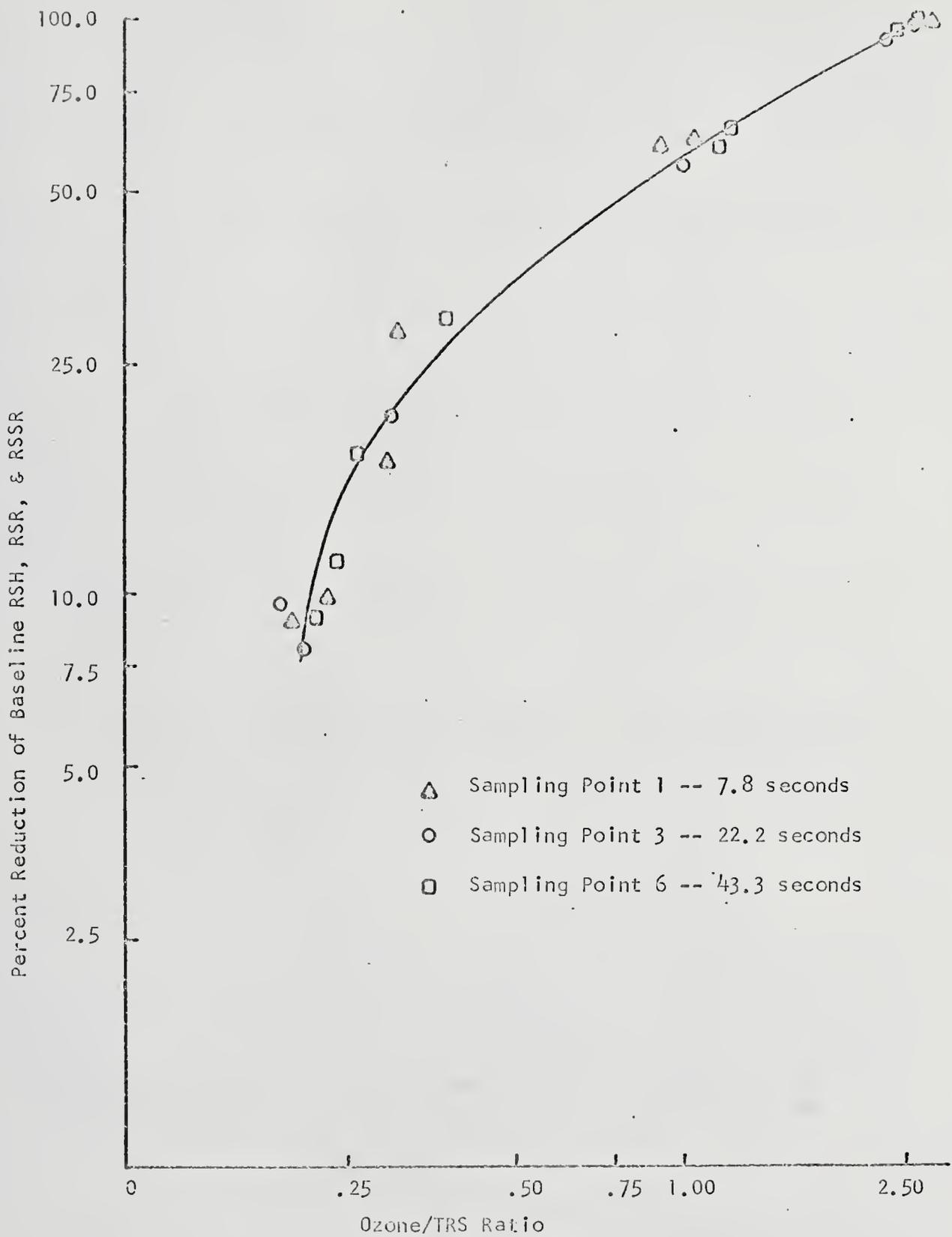


Figure 18. -- Ozone Oxidation of Smelt Tank Vent Gas.

total methyl mercaptan, dimethyl sulfide, and dimethyl disulfide for increasing ozone to TRS ratios. As noted by this plot, and in Table 13, residence time in the reaction tube does not indicate any effect on the percent reduction. This was also noted during the study with bottled gases, particularly at low ozone to sulfur ratios and high temperatures, where the ozone was reduced very rapidly in the reaction tube and no further oxidation was detected at subsequent sampling ports down the tube.

Complete removal of the three malodorous compounds was achieved at an ozone to TRS ratio of approximately 2.5, although this value must be considered particular for the conditions of this study since the ozone demand of the remaining TRS (approximately 48%) was not known. The actual amount of methyl mercaptan, dimethyl sulfide, and dimethyl disulfide found in the vent gas stream varied between 26 and 63 ppm as shown by the baseline data. At the final ozone concentration of 414 ppm (where approximately 100 % oxidation of the three gases was achieved) and using the 26-63 ppm range mentioned above, ozone to sulfur ratios of 6.7 to 15.9 would have been reached; therefore, the ozone demand of the remaining TRS must have been significant since complete oxidation of all the bottled gases was achieved at ratios much lower than these at the elevated temperature. Granted, there was quite a difference in test conditions involving bottled gases and those with actual stack gases which could account for some increase in the amount of ozone required for complete oxidation, but would not appear to justify ratios as large as those mentioned.

Due to the variability in TRS of the vent gas, and also the varying amounts of methyl mercaptan, dimethyl sulfide, and dimethyl disulfide recorded as baseline data and following ozone injection, no attempt was

made to determine the percent reduction for each individual gas at varying ozone concentrations. However, the data of Table 44 (Appendix B) do indicate a significant reduction of methyl mercaptan and dimethyl sulfide at an ozone to TRS ratio of about 1.20, which is less than half of the 2.5 ratio required for complete removal of all three malodorous compounds. This agrees with data obtained on experiments with the bottled sulfur gases in that the percent reduction of methyl mercaptan and dimethyl sulfide was significantly higher than that of dimethyl disulfide at every concentration ratio studied.

Thermal Decay of Ozone

As mentioned in Chapter III, the decomposition of ozone is accelerated by heat, and is almost instantaneous at several hundred degrees Centigrade. In addition to the reduction of ozone due to oxidation of the sulfur compounds, the thermal decay resulting from the heated reaction tube was also of interest since a majority of all applications for kraft odor control would involve emission sources at elevated temperatures, such as the smelt tank vent gas.

Hales (12) reported less than 1 percent decay at 25.5° C in his experimental reactor, and as much as 4 percent at 48° C. As a result, none of his experiments were run above 48° C. For this study, ozone concentrations were checked in the waste line, and then at sampling ports 1, 3, and 6 down the heated reactor for 38° C and 125° C. A summary of these data is listed in Table 45 (Appendix B), and was used to plot Figure 19. As noted by Figure 19, several initial ozone concentrations were checked, and, as expected, gave basically the same results. At 38° C, no significant decrease in ozone concentration was noted down the reactor, whereas at

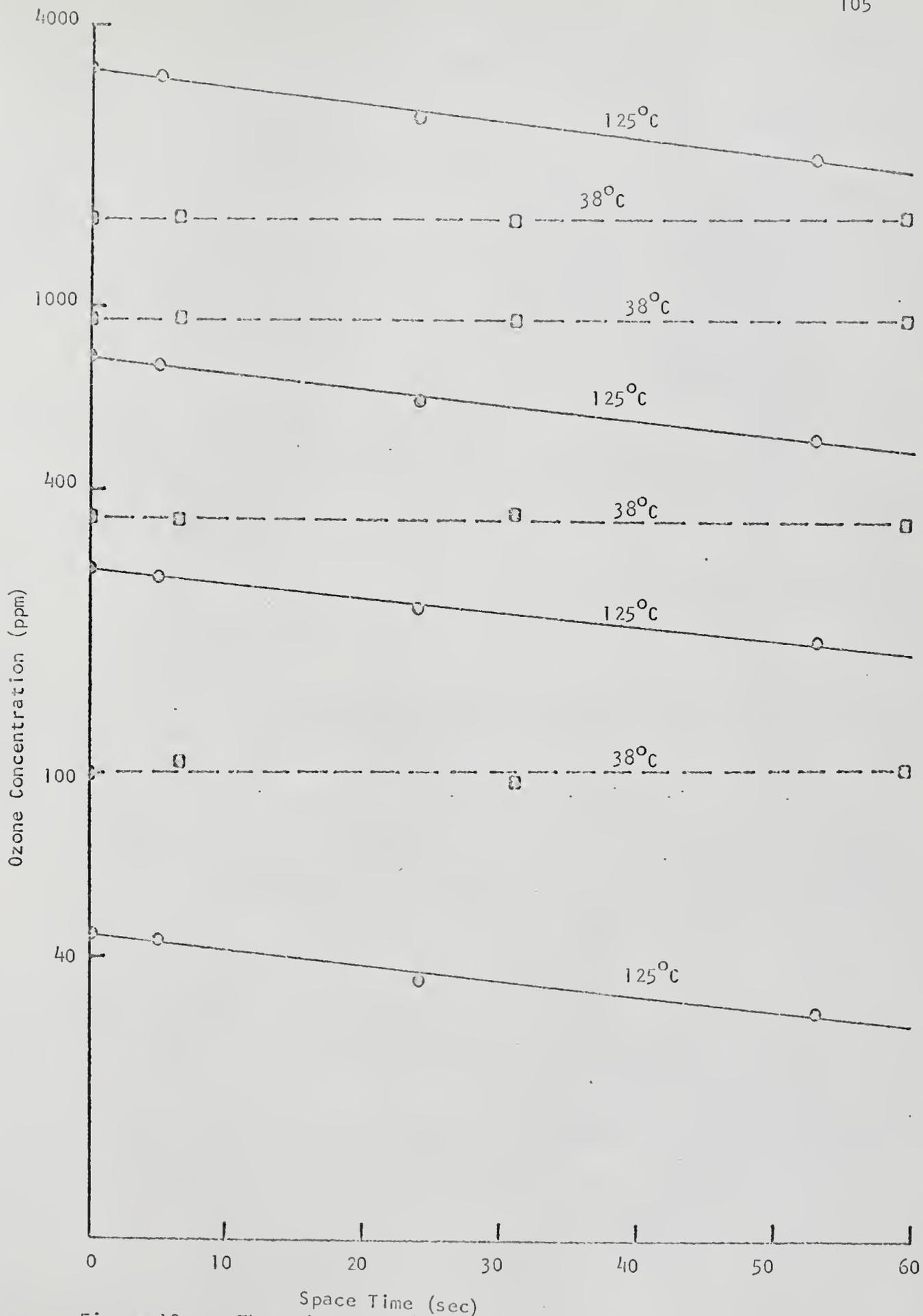


Figure 19. -- Thermal Decay of Ozone in Reaction Tube.

125° C, reductions of approximately 4, 18, and 29 percent were noted at sampling ports 1, 3, and 6 respectively.

This fact would initially indicate that there is a considerable loss in the oxidation potential of the ozone-oxygen mixture due to thermal decay of the ozone, and would help to explain why increased time in the reactor had no significant effect on further oxidation of the smelt tank vent gases (as shown by Figure 18). Actually, in its accelerated decomposition to a molecule and atom of oxygen, the molecule of ozone should still tend to exhibit the same oxidation potential in the sulfur gas stream as it would at a reduced temperature.

Even though there may be a considerable loss of ozone due to thermal decay, the experimental data on bottled gases showed that much lower ozone concentrations were required for complete oxidation of the sulfur gas at higher temperatures. This would indicate that any reduction in the oxidation potential of the ozone molecule due to thermal decay is not too significant, although recognizing the fact that an elevated temperature alone could increase the reaction rate to such an extent that a loss of ozone would not be reflected in the overall oxidation process.

Experimental Error

There were several sources of possible experimental error during this study, both during the oxidation of smelt tank vent gas and the oxidation of bottled sulfur gases. One of the initial sources would be control of flow rates throughout the system, including the ozone-oxygen and nitrogen (or vent gas) flow to the reactor, ozone sampling flow rates, and the injection of sulfur gases into the carrier gas (nitrogen). Due to the calibration procedures used for all the flowmeters governing these flows

and the periodic checks made during the experimental runs, any errors from this portion of the system were not considered significant when compared to other sources.

Another source of possible error was the measurement of ozone and sulfur gas concentrations since all the experimental runs were evaluated on the basis of concentration ratios, both for the smelt tank vent gas and bottled gases. The neutral buffered-potassium iodide method for determining ozone concentrations has been shown to be highly accurate in the absence of interfering gases, particularly sulfur dioxide and hydrogen sulfide. Clean glassware is also a necessity due to the effects of reducing dusts. Sampling efficiency of the midget impinger is also very high, and two impingers were normally used in series to prevent any possible error due to high ozone concentrations. As mentioned previously (and in Appendix A), ozone concentrations were checked a minimum of three times during each experimental run for comparison with the calibration curve. Sulfur gas concentrations, both in the vent gas stream and from the spinning syringe, were continually monitored with the electrolytic titrator and GLC unit. Possible errors due to the measurement of these gases (titration, dilution of bottled gases, analysis of electrolytic titrator and GLC charts, flowmeter readings, and calibration, etc.) were estimated to be 3-5 percent. The thermal decay of ozone in the reaction tube (previously discussed) was not considered as a possible error in calculating concentration ratios, since the basis of the study was percent reduction of the sulfur gases resulting from the initial concentration ratio injected into the reactor.

The major source of possible error in the study was the reaction time calculated for each experimental data point. Naturally, the space time in the reactor was based on tube volume and flow rates, which are subject

to error as previously mentioned. The area of concern was the additional reaction occurring in the line from the reaction tube, through the gas conditioning oven, and to the GLC unit, and the assumption that any additional reaction in this line would proceed similar to that in the reaction tube. Any error resulting from this assumption would be increased at high ozone concentrations and when sampling from the first sampling port since these conditions would tend to leave residual ozone in the sample leaving the reactor. At low ozone concentrations and extended reaction times, all the ozone would be reduced by the sulfur gases in the reaction tube. This was evidenced by the fact that ozone was only detected (by smell) at concentration rates above 2.0 and normally at the first three sampling ports. Since an additional four seconds were allowed for reactions in the transfer line, the percent error would naturally be larger for the first sampling port (approximately 5 seconds' space time) than the last (approximately 60 seconds' space time).

Due to the amount of data points recorded during the study and the relatively few times that ozone was detected at the sampling ports, any error arising from the assumptions discussed above was not thought to exceed 15 percent for high ozone concentrations and/or low reaction times, and would be much lower for a majority of the experimental runs (low concentration ratios and increased reactor space times).

Recognizing these sources of error, the data obtained on the bottled sulfur gases and the resulting regression equations are considered representative of the oxidation reactions for the range of conditions studied. As evidenced by the regression equations for each gas, a highly significant 'F' statistic and large coefficients of determination (R^2) were obtained when the 'Time' variable was not even evaluated in the

equation, thus indicating that the major effects on oxidation resulted from concentration ratios and temperature.

Results of ozone oxidation of smelt tank vent gas were also considered representative since even lower concentration ratios were evaluated, and the effect of increased reaction time was not significant for the conditions studied.

CHAPTER VII

SUMMARY AND CONCLUSIONS

Summary

Odor control is one of the major problems of the kraft pulping industry. Various methods are used to both eliminate the initial formation of odors in the kraft process, and to destroy them once formed and prior to release to the atmosphere. Kraft mills that are "near odorless" have been reported in the literature, and new developments in kraft odor control are making a completely odor-free mill more and more a possibility.

Still, with increasing emphasis on the elimination of odors as a nuisance problem, the number of older mills that need odor control methods for their existing sources, and the extremely low odor threshold of the sulfur compounds, continuous research is needed to evaluate any feasible method that will aid in eliminating this problem. Gas-phase oxidation of malodorous sulfur gases with ozone has been suggested as an odor control method, but application in the kraft industry has been near non-existent. Laboratory data are also limited.

The purpose of this study was to evaluate the effectiveness of ozone in oxidizing malodorous sulfur gases associated with the kraft odor problem; namely, hydrogen sulfide, methyl mercaptan, dimethyl sulfide, and dimethyl disulfide. The oxidation of each gas (from a bottled source) was evaluated at a variety of ozone to sulfur gas ratios, temperatures,

and reaction times. The range of experimental conditions was selected to be representative of actual kraft emissions. The effectiveness of ozone in oxidizing an actual emission source was also evaluated by injecting known quantities of ozone into smelt tank vent gases and measuring any reduction in the malodorous sulfur gases of interest.

A multiple regression analysis of the data resulting from the oxidation of each bottled gas was performed, and three regression equations were evaluated (with different variables) for each individual gas. Using a representative equation for each gas, estimated values for percent reduction at various concentration ratios, temperatures, and reaction times were calculated, and are listed in Table 14 for conditions covered by the individual equations. Figure 20 is a plot of percent reduction versus concentration ratios for a typical stack temperature of 82° C and reaction time of 10 seconds, and illustrates the difference in oxidation achieved for hydrogen sulfide, dimethyl sulfide, and dimethyl disulfide. Due to the rapid oxidation of methyl mercaptan, sufficient data points were not obtained at elevated temperatures and high concentration ratios to continue the plot.

Tests on the oxidation of smelt tank vent gases were based on the ozone to total reduced sulfur (TRS) ratio, and the percent reduction of methyl mercaptan, dimethyl sulfide, and dimethyl disulfide in the gas stream. The baseline data did not indicate the presence of hydrogen sulfide. Baseline data indicated that the three gases mentioned above accounted for approximately 52 percent of the TRS. Complete removal of these malodorous gases was achieved at an ozone to TRS ration of approximately 2.5. Since the ozone demand of the remaining TRS (48 percent)

TABLE 14

SUMMARY OF REGRESSION ANALYSIS DATA FOR BOTTLED SULFUR GASES

Concentration Ratio	Reaction Time (sec)	% Reduction at 38°C			% Reduction at 82°C			% Reduction at 125°C				
		H ₂ S	RSH	RSR	H ₂ S	RSH	RSR	H ₂ S	RSH	RSR		
0.5	10	11	-- ^a	24	18	--	26	--	25	--	29	--
0.5	30	15	--	23	22	--	26	--	29	--	28	--
0.5	60	21	--	22	28	--	25	--	35	--	28	--
1.0	10	27	48	40	34	65	42	18	40	81	45	29
1.0	30	31	51	39	38	68	42	22	44	85	44	33
1.0	60	37	57	38	44	74	41	27	50	90	43	38
2.0	10	53	63	65	60	--	68	30	66	--	70	44
2.0	30	57	67	64	64	--	67	34	71	--	70	47
2.0	60	63	72	64	70	--	66	39	77	--	69	53
3.0	10	72	73	82	79	--	85	42	85	--	87	58
3.0	30	76	77	81	83	--	84	45	89	--	87	61
3.0	60	82	82	81	89	--	83	51	95	--	86	67
5.0	10	--	--	--	--	--	--	63	--	--	--	84
5.0	30	--	--	--	--	--	--	67	--	--	--	86
5.0	60	--	--	--	--	--	--	72	--	--	--	93

^aExperimental conditions not covered by regression equation.

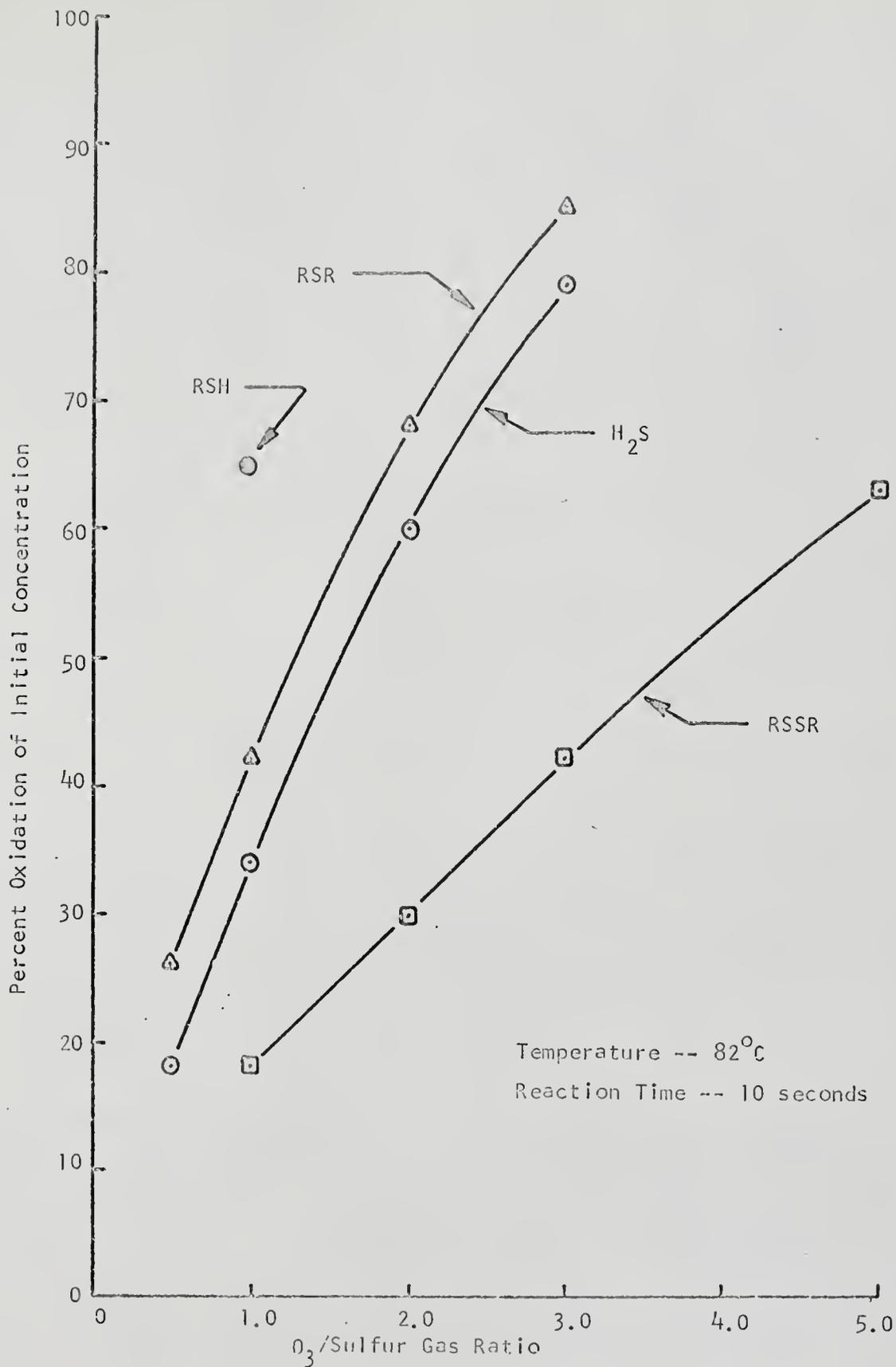


Figure 20. -- Ratio Effects on Oxidation of Reduced Sulfur Compounds.

was not known, the exact amount of ozone required for oxidation of only the sulfur gases of interest could not be determined.

Conclusions

Based on the range of conditions evaluated for both bottled sulfur gases and smelt tank vent gases, and the data resulting from the experimental runs, the following conclusions can be drawn from this research project:

(1) Multiple regression analysis of the data points obtained for each bottled sulfur gas yielded regression equations that adequately described the oxidation process of each gas over the range of variables studied. All regression equations had coefficients of determination (R^2) between .68 and .89, a highly significant "F" statistic, and gave estimated reduction values with standard errors of less than 5 percent.

(2) As long as the ozone to sulfur gas ratios remained basically the same, observed oxidation reactions in the heated, stainless steel reaction tube were not significantly affected by changes in initial sulfur gas concentrations.

(3) The ozone demand required to achieve complete oxidation of the sulfur gases primarily responsible for kraft odors was more than twice the theoretical amount predicted, even in the relatively uniform and controlled conditions of a reaction tube and using pure bottled gases.

(4) Provided a minimum reaction time (10 seconds) between ozone and bottled sulfur gases, the concentration ratio and reaction temperature had a much more significant effect on the oxidation process than increased reaction time, particularly for dimethyl sulfide for which no increase

in oxidation was noted with increased reaction time for some of the conditions studied.

(5) The initial oxidation step of methyl mercaptan to dimethyl disulfide was achieved at a concentration ratio only slightly above that predicted, but subsequent oxidation of the dimethyl disulfide for complete odor control created the total ozone demand mentioned in (3) above.

(6) By using high concentration ratios to achieve complete oxidation, reaction times far exceeding those normally experienced in an effluent stack would be required to insure adequate time for the oxidation process. Even with concentration ratios slightly above stoichiometric conditions, extended reaction times would significantly increase oxidation of the sulfur gas.

(7) There was no apparent loss of ozone oxidation potential due to thermal decay at elevated temperatures since significant increases in the oxidation process were observed for each gas as the reaction tube temperature was increased.

(8) The percent oxidation achieved in this study for hydrogen sulfide was significantly higher than that reported by Gregor and Martin (10) and Hales (12). This was attributed primarily to the large difference in experimental conditions and procedures involved in the three studies. Laboratory investigations on the other three gases were not found in the literature, other than predicted and observed products of the ozone-sulfur gas reaction. As indicated by (3) above, the ozone demand observed during this study was more than double that predicted in the literature for these gases.

(9) Ozone was effective in eliminating methyl mercaptan, dimethyl sulfide, and dimethyl disulfide from an actual kraft mill source (smelt

tank vent gas). Complete removal of these three gases was achieved at an ozone to TRS ratio of approximately 2.50 which is not considered out of line with the bottled gas data, especially due to moisture conditions in the vent gas and any ozone demand exerted by other gases in the effluent stream.

(10) Ozone is considered an effective oxidizing agent for the gas-phase oxidation of kraft mill gases, although the cost of ozone production needed to achieve complete oxidation of a gas stream could be prohibitive. Its use as a polishing agent following a major piece of odor control equipment may be feasible in order to remove enough additional sulfur compounds to reach an acceptable odor level.

Pilot scale studies to further evaluate the effectiveness of ozone in oxidizing actual stack gases over a wide range of conditions are suggested, along with cost evaluations for ozone use. As a result of the present study, additional analytical equipment should be used to analyze the effluent source continuously, both prior to and following ozone injection in order to evaluate the actual reduction of each malodorous gas due to ozone oxidation. Continuous recording instrumentation to monitor ozone generator output would also be beneficial. Provisions should be made to provide adequate mixing chambers to fully evaluate a wide range of concentration ratios, and reaction times, since a requirement for extremely long reaction times would eliminate the use of ozone for many odor sources due to their high emission rate.

APPENDICES

APPENDIX A

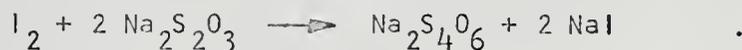
OZONE ANALYSIS, EQUIPMENT CALIBRATION, AND
TEST STAND OPERATING PROCEDURES

Ozone Analysis

The neutral buffered-potassium iodide method was used for ozone analysis, both for initial calibration of the ozone generator and for checking ozone concentrations during experimental runs. This method is described by Saltzman (255), and is based on the liberation of iodine from a 1 percent, neutral buffered-potassium iodide absorbing solution in midget impingers. A slight modification to the procedures described by Saltzman was used, in that the ozone concentrations were determined by titration of the scrubbing solution with standard sodium thiosulfate rather than using a spectrophotometer for color measurement. As discussed by Byers and Saltzman (256), titration is recommended for high ozone concentrations (as used in this study) since it eliminates the extreme dilutions required to permit use of a spectrophotometer.

Sampling flow rate was maintained at 150 cc/min. Depending upon ozone concentrations, sampling times varied between 0.5 minutes (for 12,000 - 15,000 ppm) and 5 minutes (for 65 - 400 ppm) in order to prevent loss of iodine from the absorbing solution but still provide sufficient amount for titration purposes. Two impingers were used in the sampling train for concentrations above 5,000 ppm to insure complete absorption of the ozone.

Reactions important in the sampling and analysis of ozone are as follows:



Ozone concentrations were computed from the following formula:

$$\text{Ozone (ppm)} = \frac{(\text{normality thiosulfate}) (\text{ml titrant}) (12.25) (10^6)}{(\text{sampling time -- min}) (\text{sample flow rate -- cc/min})}$$

Equipment Calibration

Flowmeters

All flowmeters used on the test panel were Brooks Sho-Rate, Model 1355 (257), with stainless steel or glass floats. Each was calibrated in the system at the temperature and pressure for which it would be used, and for the particular gas (oxygen or nitrogen). Calibration was done with a bubble-tube flowmeter, and was checked periodically during experimental runs to insure that static electrical charges, as reported by Hales (12) while using sapphire floats, were not causing erroneous indications.

Ozone Generator

Due to the multitude of ozone concentrations required for this study, the length of time required for the ozone generator to reach equilibrium following a change in conditions (pressure, oxygen flow, voltage), and the time required for a sample analysis to check a new concentration, it was necessary to develop a procedure in which ozone generator output could be varied as quickly as possible and with minimum changes to the overall system.

Since oxygen flow and voltage were the main variables affecting ozone generation, it was decided that oxygen flow to the ozone generator would be held constant, and ozone generation varied solely by voltage changes. The flow of 350 ml/min was established since it permitted an adequate supply to the reaction tube and a sufficient amount in the waste line for sampling purposes. The system was initially plumbed with the ozone generator at atmospheric pressure (through the reaction tube). With this arrangement, the flowmeter measuring oxygen to the ozone generator became unreadable (due to rapid fluctuations of the float) when power was applied to the generator. The plumbing was changed, and the ozone generator arbitrarily put under two psig. This corrected the bouncing float in the oxygen flowmeter, so the generator remained at this pressure setting.

Since a continuous recording ozone monitor was not available to cover the range of ozone concentrations required for the study, it was necessary to calibrate the ozone generator so that when a new ozone output was desired, the voltage regulator could be set to produce this desired concentration, or close to it. Thus, the ozone generator output was determined for various voltage settings at an oxygen flow of 350 cc/min and a barometric pressure of 34.0 in Hg. absolute. The resulting calibration curve is shown by Figure 21. Ozone concentrations were determined by the neutral buffered-potassium iodide method previously described.

With the calibration curve, an ozone concentration close to the desired concentration could be produced, and was close enough to start an experimental run after allowing approximately 15 minutes for the ozone generator to reach equilibrium. The exact concentration (for calculating the exact ozone to sulfur gas ratio) was then determined during the experimental run with the sampling train.

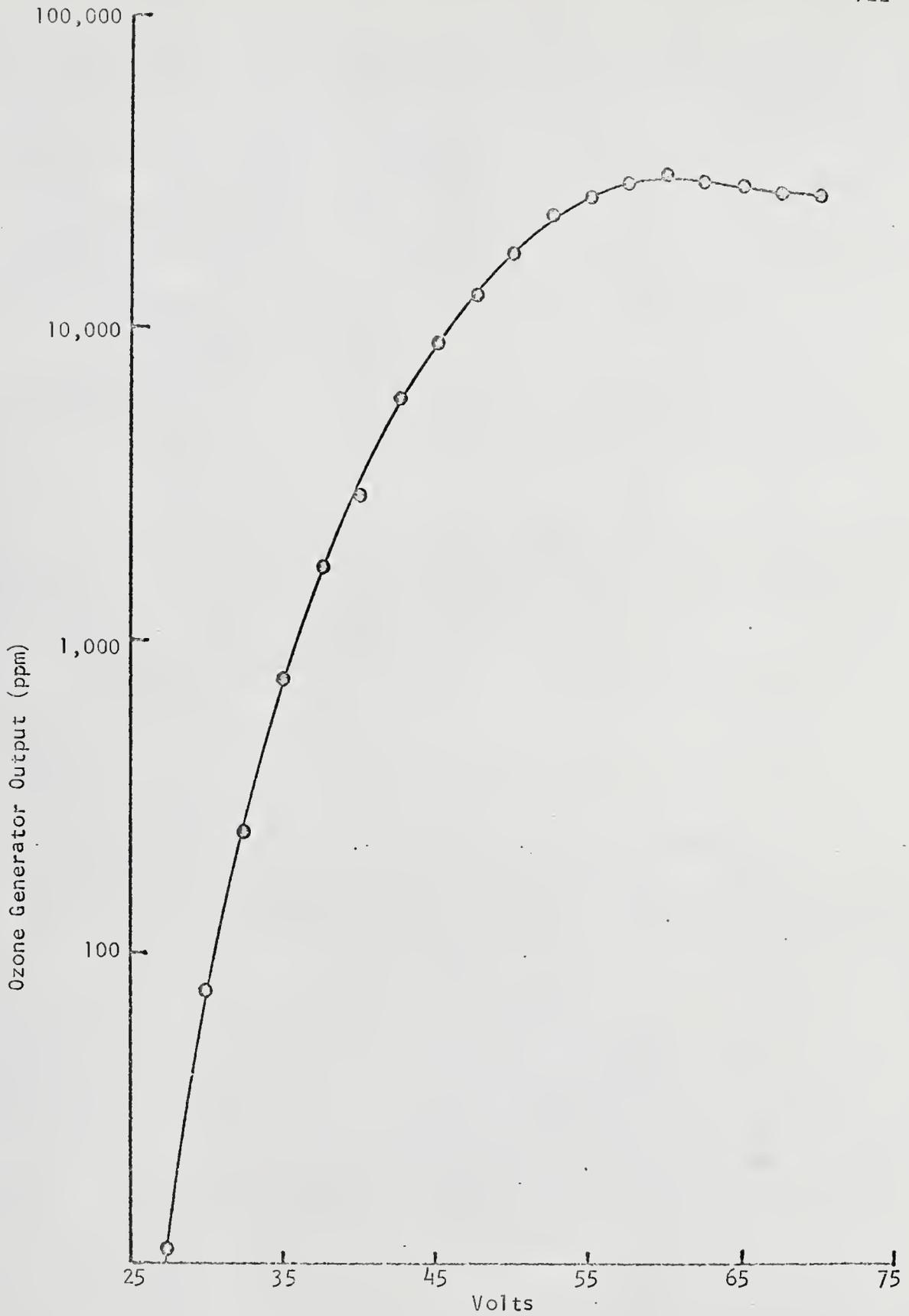


Figure 21. -- Ozone Generator Calibration Curve.

Spinning Syringe

As indicated by the system schematic (Figure 5, Chapter IV), the bottled sulfur gases were injected into the nitrogen stream with a spinning syringe. As described by Blosser and Cooper (242), the spinning syringe consists of a 100 ml glass syringe with ground-glass plunger and seat. Plexiglass (or cardboard) vanes, the length of the plunger, are fixed to the top of the plunger with epoxy glue. The plunger is rotated by directing an air stream against the vanes. The rotation of the plunger assures uniform and minimal friction while the weight of the plunger results in a constant pressure, yielding a uniform delivery of gas through an orifice attached to the exit. The orifice can be fabricated from a length of thermometer tubing, and must be calibrated for flow rate and checked periodically. All connections and tubing must be of inert material.

For this study, four orifices were made with varying lengths of thermometer tubing, and were calibrated with the bubble tube device shown in Figure 22. The apparatus consists of a tee, soap container (rubber suction bulb), and a 1 ml graduated pipet (with the tip broken off). Orifice flow rate is determined by noting the time required for a bubble to pass through a given volume of the pipet. Resulting flow rates were 1.61, 2.12, 3.85, and 5.29 ml/min, and were specific for the particular syringe and gas used for calibration. Since the sulfur gas concentrations from the syringe would be checked with the electrolytic titrator and the gas chromatograph prior to mixing with ozone, and the sulfur gas concentration in the syringe never exceeded 5 percent during the study, the orifices were calibrated with air rather than with each of the four sulfur compounds

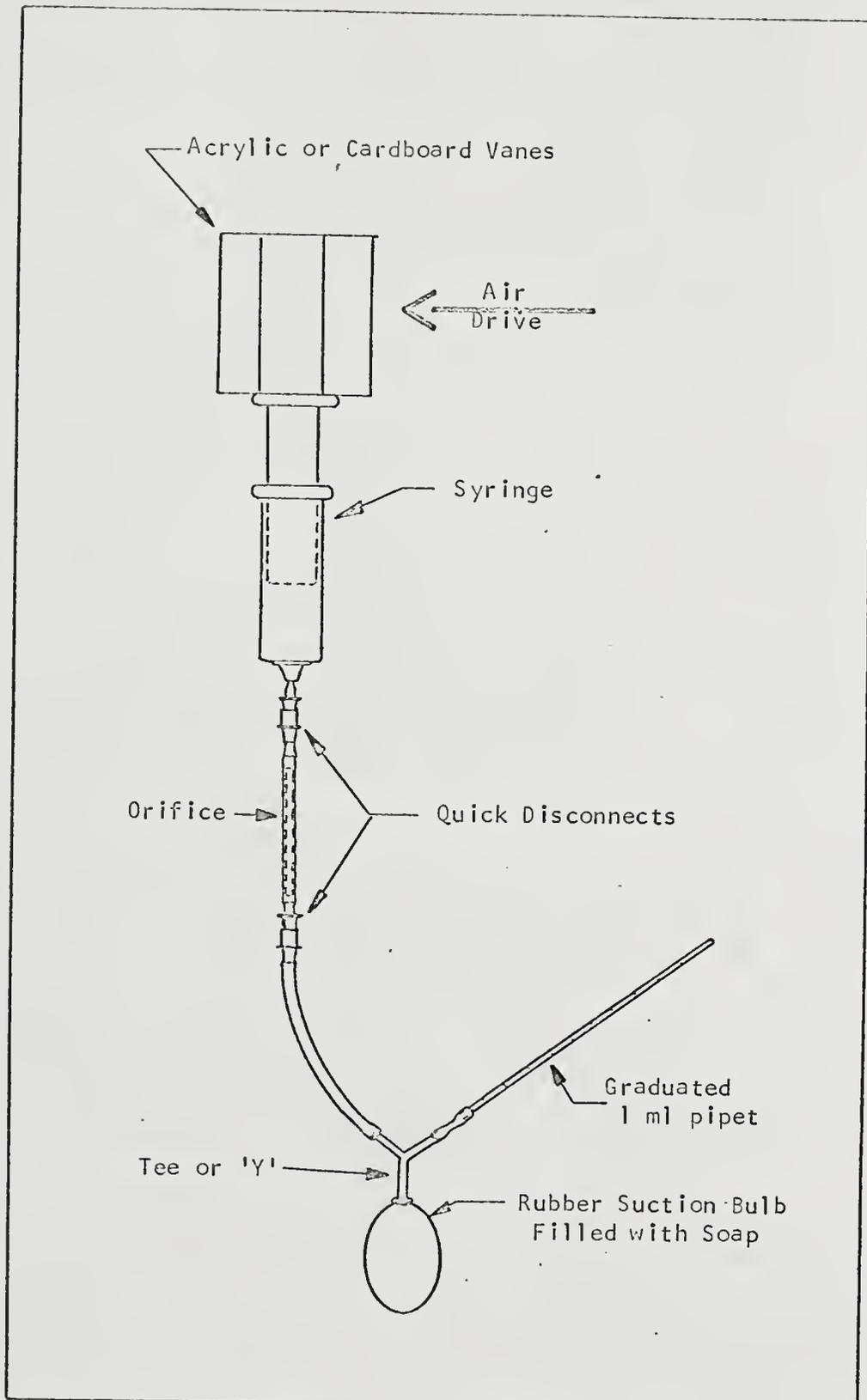


Figure 22. -- Spinning Syringe Calibration Device.

used in the study. The calibrated flow rates with air were close enough for calculating desired sulfur concentrations from the syringe. Whenever possible, these calculations were based on use of the 1.6l ml/min orifice since it permitted the longest delivery time for the syringe.

Barton Electrolytic Titrator

The Barton Titrator was calibrated for sulfur dioxide, hydrogen sulfide, methyl mercaptan, dimethyl sulfide, and dimethyl disulfide. Procedures for this calibration are outlined in the literature (242), although a complete calibration for all the above gases was not performed for this study since the instrument remains in near constant use with the mobile sampling laboratory, and is checked periodically for this work.

Several calibration checks were made on the instrument during this study with known syringe concentrations. The response was verified by previous calibration data and also by the second electrolytic titrator carried in the mobile laboratory. As mentioned in Chapter IV, the titrator was used in conjunction with a combustion furnace which oxidized all sulfur gases to SO_2 prior to entering the titrating cell.

Gas Chromatograph

As with the Barton Titrator, calibration data on the four sulfur gases of interest were available for the gas chromatograph from previous use of the instrument in kraft emission studies. These data were also checked periodically during the ozone study with known syringe concentrations and against the electrolytic titrator.

Calibration of this instrument was based on peak height measurement. Additional information concerning calibration of the unit is given by Tucker (258).

Reaction Tube

The reaction tube was designed to provide approximately five seconds for ozone-sulfur gas reaction prior to the first sampling port and one minute at the last port based upon a total gas flow of 400 cc/min at standard conditions. The volume to each port was determined by filling the tube with water. Resulting reaction time (or space time) to each port for a flow of 400 cc/min at one atmosphere and 25° C is shown in Table 15 for each temperature investigated during the study, and is based upon the following equation:

$$\text{Space time (seconds)} = \frac{(\text{Tube Volume} - \text{cc}) (\text{Room Temp.} - ^\circ\text{K}) (60)}{(400) (\text{Reaction Tube Temp.} - ^\circ\text{K})}$$

TABLE 15
REACTION TUBE SPACE TIME

Sampling Port	Tube Volume (cc)	Space Time (sec)				
		25° C	38° C	55° C	76° C	125° C
1	39.4	5.9	5.7	5.4	5.0	4.4
2	113.9	17.1	16.4	15.5	14.6	12.8
3	189.4	28.4	27.2	25.8	24.3	21.3
4	263.0	39.4	37.8	35.9	33.7	29.6
5	336.7	50.5	48.4	45.8	43.1	37.8
6	410.0	61.5	59.0	55.9	52.5	46.0

After wrapping the tube with asbestos tape and ni-chrome wire as previously described, uniformity of temperature throughout its length was verified for various voltages and gas flows by inserting copper-constantan thermo-couples (connected to a multi-point recorder) in each sampling port and through each end of the tube.

A trial and error method was used to determine what voltage setting would yield the desired reaction tube temperatures needed for the study. A gas flow of 400 ml/min was established in the tube, and the voltage regulator set and corrected as necessary to produce the desired temperatures inside the reaction tube for 25° C ambient conditions. Resultant voltage settings are listed in Table 16.

TABLE 16
REACTION TUBE TEMPERATURE CONTROL

Reaction Tube Temperature (C°)	Voltage Regulator Setting (volts)
38	44
55	63
76	83
125	120

Gases

The bottled sulfur gases used during the study were from Matheson Gas Products (259). Diluted gases were ordered to contain approximately 5 percent sulfur gas with the balance nitrogen. Concentrations obtained for this study are listed in Table 17.

TABLE 17
SULFUR GAS TANK ANALYSIS

Gas	Tank Concentrations (% Vol.)
Hydrogen Sulfide	3.3 & 100
Methyl Mercaptan	2.1 & 100
Dimethyl Sulfide	4.32

Tank analyses were performed as described by Tucker (258). A gas mixture of dimethyl disulfide (from a liquid) was prepared and analyzed as described by Blosser and Cooper (242), and determined to be 2.60 percent sulfur gas.

Test Stand Operating Procedures

Each experimental run was made at a specific reaction tube temperature, ozone concentration, and sulfur gas concentration. For these conditions, samples were drawn off the reaction tube at the different sampling ports to allow varying reaction times between the ozone and sulfur gas. The concentration ratio and reaction tube temperature for each particular experiment and for each sulfur gas were established, and are described in Chapter V. Knowing these conditions, the test panel instruments could be set, and proper dilutions of sulfur gases made in the spinning syringe.

The first step in the procedure was to turn on the heating wires to the reaction tube, and set the voltage regulator to the setting required for the desired tube temperature (Table 16, Appendix A). Approximately 30 minutes was required for the tube to reach equilibrium. Nitrogen flow to the reaction tube was turned on, and initially set at 400 cc/min. Next, oxygen flow to the ozone generator was set at 350 cc/min, and ozone generator pressure regulated to 34.0 in Hg. Knowing the total flow in the reaction tube would be 400 cc/min (of which 80 cc/min would be ozone-oxygen), and the desired ozone concentration in the reaction tube, the ozone generator output was calculated from the following relationship:

$$(400 \text{ cc/min}) (\text{Desired } O_3 \text{ Conc-ppm}) = (80 \text{ cc/min}) (\text{Ozone Generator Output - ppm}).$$

Assuming a desired ozone concentration of 100 ppm in the reaction tube, the ozone generator output had to be 500 ppm. From the ozone generator calibration curve (Figure 21, Appendix A), a setting of 34 on the voltage regulator would produce this concentration. The ozone generator was then turned on, and set at the required voltage. Total flow from the ozone generator was initially directed through the waste line -- none to the reaction tube.

While the reaction tube temperature and ozone generator were coming to equilibrium, a dilution of sulfur gas was made in the spinning syringe for delivery to the carrier gas (nitrogen). As stated in a previous section on calibration of the spinning syringe, four different orifices were fabricated to give varying delivery rates from the syringe, and whenever possible, the 1.61 cc/min orifice was used. Using this orifice, knowing the desired sulfur gas concentration in the reaction tube, and a total flow in the tube of 400 cc/min, the required sulfur gas concentration in the syringe itself was calculated as follows:

$$(400 \text{ cc/min}) (\text{Desired Sulfur Conc-ppm}) = (1.61 \text{ cc/min}) (\text{Syringe conc-ppm}).$$

Assuming a desired sulfur gas concentration of 100 ppm in the reaction tube, the syringe concentration had to be 24,850 ppm. From Table 17 (Sulfur Gas Tank Analysis), using hydrogen sulfide at 3.3 percent concentration, the proper dilution for the syringe to obtain 24,850 ppm would be approximately

$$\frac{24,850}{33,000} = 75 \text{ percent.}$$

Thus, the 100 ml syringe was filled with 75 percent hydrogen sulfide and 25 percent air (by drawing the plunger back to the 100 ml mark). Smaller syringes were used to inject the sulfur gases into the 100 ml

syringe for less than 20 percent concentrations. The syringe was set up, air blower turned on, and the sulfur gas was injected into the 400 cc/min nitrogen flow. The calculated concentration was then checked by the electrolytic titrator and gas chromatograph prior to any ozone mixing. After completing the concentration check, the nitrogen flow was reduced to 320 cc/min.

Having allowed at least 15-25 minutes for the ozone generator to reach equilibrium, a sample was taken from the ozone-oxygen waste line with the sampling train to check ozone output. Once the sample was taken, 80 cc/min of the ozone-oxygen mixture was directed to the reaction tube, thus making a total flow through the tube of 400 cc/min to start the experimental run. Another sample was taken during the experimental run (from the remaining 270 cc/min in the waste line) and one taken at the conclusion of the test to verify ozone output. Actual ozone to the reaction tube was determined by averaging the three sample concentrations since the calibration curve was only an estimate. Actual sulfur gas concentration to the reaction tube was taken as the electrolytic titrator reading. Thus, a desired ozone to sulfur gas ratio of 1.0 may have been slightly more or less than this figure depending upon how close the syringe dilution and ozone output was to that predicted.

Various concentration ratios were thus achieved by making up different spinning syringe dilutions of sulfur gases, and by changing voltage settings on the ozone generator to produce different ozone concentrations. The initial sample of oxidized sulfur gas from the reaction tube was normally taken at the first sampling port (approximately 5-second space time) through a 1/8-inch Teflon line. All sampling ports

were not used on each experimental run, but were selected according to the progress of the ozone-sulfur gas reaction (percent reduction of the sulfur gas) as monitored by readings on the gas chromatograph recorder. For high ozone to sulfur gas ratios, where the sulfur gas may be oxidized very rapidly, the first three sampling ports were usually checked. For lower concentration ratios, ports 1, 3, and 6 were normally monitored.

APPENDIX B
EXPERIMENTAL DATA

TABLE 18

OZONE-HYDROGEN SULFIDE REACTION DATA AT 38° C
Date: 5-5-71

Run No.	Initial H ₂ S (ppm)	O ₃ /H ₂ S Ratio	Final H ₂ S (ppm) @ Sampling Port No.				
			1	2	3	4	6
7	7.0	.55	6.3	--	6.2	--	6.2
	7.0	1.09	4.9	4.8	4.9	--	3.6
	7.0	2.17	3.4	--	2.7	--	2.6
	7.0	5.44	2.6	.4	.3	--	0
8	49	.48	36	--	37	36	36
	49	.97	32	32	32	--	30
	49	1.89	21	17	16	--	16
	49	4.74	6	.4	--	--	--
9	260	.46	225	230	223	220	218
	260	.92	200	--	200	205	200
	260	2.55	92	57	24	19	21
	260	6.35	47	5	--	--	--
10	540	.55	460	455	455	--	455
	540	1.10	380	355	312	--	275
	540	1.87	260	215	210	--	90
	540	4.68	230	143	46	0	--
11	1250	.42	1030	1040	1030	--	1035
	1250	.83	980	925	880	--	850
	1250	1.45	720	700	630	--	540
	1250	3.64	580	380	170	16	--
12	1580	.49	1300	--	1280	1280	1280
	1580	.97	1230	1200	1120	--	1080
	1580	2.18	1030	840	700	--	480
	1580	5.46	500	140	7	--	--

TABLE 19

OZONE-HYDROGEN SULFIDE REACTION DATA AT 55° C
Date: 5-3-71

Run No.	Initial		Final H ₂ S (ppm) @ Sampling Port No.		
	H ₂ S (ppm)	O ₃ /H ₂ S Ratio	1	3	6
5	5.6	.81	4.3	4.3	4.3
	5.6	1.63	4.0	3.1	3.1
	5.6	3.25	2.8	.7	0
	5.6	8.13	2.4	.5	0
6	25.0	.67	23.0	23.0	23.0
	25.0	1.67	16.0	16.5	16.0
	25.0	1.67	--	17.2	17.5
	25.0	3.35	6.2	0	0
	25.0	8.35	1.3	0	0

TABLE 20
 OZONE-HYDROGEN SULFIDE REACTION DATA AT 76° C
 Date: 5-10-71

Run No.	Initial		Final H ₂ S (ppm) @ Sampling Port No.			
	H ₂ S (ppm)	O ₃ /H ₂ S Ratio	1	2	3	6
21	7.5	.46	6.7	--	4.5	4.0
	7.5	.93	5.8	4.6	3.9	3.7
	7.5	1.84	3.0	3.2	2.2	1.7
	7.5	4.60	1.4	.5	0	--
22	44	.46	42	--	40	38
	44	.91	37	34	34	33
	44	1.80	20	13	11	9
	44	4.50	3	1	--	--
23	245	.31	230	--	220	225
	245	.77	190	195	180	183-
	235	2.74	37	17	0	--
	235	6.90	15	0	--	--
24	550	.64	400	--	400	380
	550	1.28	290	280	--	250
	550	1.99	175	142	88	72
	550	4.96	98	60	16	--
25	1000	.53	750	--	760	750
	1000	1.06	660	625	600	590
	1000	2.12	420	390	325	225
	1000	2.65	420	350	225	250

TABLE 21

OZONE-HYDROGEN SULFIDE REACTION DATA AT 125° C
Date: 5-6-71

Run No.	Initial		Final H ₂ S (ppm) @ Sampling Port No.			
	H ₂ S (ppm)	O ₃ /H ₂ S Ratio	1	2	3	6
13	9.0	.52	--	--	6.6	6.5
	9.0	1.04	6.7	--	6.9	6.6
	9.0	2.60	3.0	2.9	2.8	--
14	57	.32	49	--	50	46
	57	.63	47	--	41	41
	57	2.10	23	24	21	22
	57	5.30	0	--	--	--
15	280	.47	192	--	185	185
	280	.95	145	150	147	140
	280	2.40	29	0	--	--
	280	5.90	0	--	--	--
16	520	.52	360	--	375	375
	520	1.05	275	290	270	270
	520	1.93	63	0	--	--
	520	4.82	0	--	--	--
17	1050	.53	840	--	780	830
	1050	1.06	650	650	650	--
	950	2.26	160	28	19	--
	950	2.26	130	52	27	--
	950	5.66	130	9	--	--
	950	5.66	90	--	--	--
18	1800	.56	1230	--	1230	1250
	1800	1.14	980	--	900	900
	1800	1.14	1000	--	--	950
	1800	2.11	400	245	185	155
	1800	2.11	--	--	190	--
	1800	5.28	150	45	0	--

TABLE 22

DATA FOR REGRESSION ANALYSIS OF OZONE-HYDROGEN SULFIDE REACTIONS

Run No.	% H ₂ S Reduction	O ₃ /H ₂ S Ratio	Temp. (°K)	Reaction Time (sec)
7	10	.55	311	9.7
7	30	1.09	311	9.7
7	51	2.17	311	9.7
7	63	5.44	311	9.7
7	31	1.09	311	20.4
7	95	5.44	311	20.4
7	11	.55	311	31.2
7	30	1.09	311	31.2
7	61	2.17	311	31.2
7	96	5.44	311	31.2
7	11	.55	311	63.0
7	49	1.09	311	63.0
7	62	2.17	311	63.0
7	100	5.44	311	63.0
8	27	.48	311	9.7
8	35	.97	311	9.7
8	57	1.89	311	9.7
8	88	4.74	311	9.7
8	35	.97	311	20.4
8	65	1.89	311	20.4
8	99	4.74	311	20.4
8	25	.48	311	31.2
8	35	.97	311	31.2
8	67	1.89	311	31.2
8	27	.48	311	41.8
8	25	.48	311	63.0
8	39	.97	311	63.0
8	67	1.89	311	63.0
9	13	.46	311	9.7
9	23	.92	311	9.7

TABLE 22 (Continued)

Run No.	% H ₂ S Reduction	O ₃ /H ₂ S Ratio	Temp. (°K)	Reaction Time (sec)
9	65	2.55	311	9.7
9	82	6.35	311	9.7
9	12	.46	311	20.4
9	78	2.55	311	20.4
9	98	6.35	311	20.4
9	14	.46	311	31.2
9	23	.92	311	31.2
9	91	2.55	311	31.2
9	15	.46	311	41.8
9	21	.92	311	41.8
9	93	2.55	311	41.8
9	16	.46	311	63.0
9	23	.92	311	63.0
9	92	2.55	311	63.0
10	15	.55	311	9.7
10	30	1.10	311	9.7
10	52	1.87	311	9.7
10	57	4.68	311	9.7
10	16	.55	311	20.4
10	34	1.10	311	20.4
10	60	1.87	311	20.4
10	74	4.68	311	20.4
10	16	.55	311	31.2
10	42	1.10	311	31.2
10	61	1.87	311	31.2
10	92	4.68	311	31.2
10	16	.55	311	63.0
10	49	1.10	311	63.0
10	83	1.87	311	63.0
11	18	.42	311	9.7
11	22	.83	311	9.7
11	42	1.35	311	9.7

TABLE 22 (Continued)

Run No.	% H ₂ S Reduction	O ₃ /H ₂ S Ratio	Temp. (°K)	Reaction Time (sec)
11	54	3.64	311	9.7
11	17	.42	311	20.4
11	26	.83	311	20.4
11	44	1.45	311	20.4
11	70	3.64	311	20.4
11	18	.42	311	31.2
11	30	.83	311	31.2
11	50	1.45	311	31.2
11	86	3.64	311	31.2
11	99	3.64	311	41.8
11	18	.42	311	63.0
11	32	.83	311	63.0
11	57	1.45	311	63.0
12	18	.49	311	9.7
12	22	.97	311	9.7
12	35	2.18	311	9.7
12	68	5.46	311	9.7
12	24	.97	311	20.4
12	47	2.18	311	20.4
12	91	5.46	311	20.4
12	19	.49	311	31.2
12	29	.97	311	31.2
12	56	2.18	311	31.2
12	99	5.46	311	31.2
12	19	.49	311	41.8
12	19	.49	311	63.0
12	32	.97	311	63.0
12	70	2.18	311	63.0
21	10	.46	349	9.0
21	23	.93	349	9.0
21	60	1.84	349	9.0
21	81	4.60	349	9.0

TABLE 22 (Continued)

Run No.	% H ₂ S Reduction	O ₃ /H ₂ S Ratio	Temp. (°K)	Reaction Time (sec)
21	39	.93	349	18.6
21	57	1.84	349	18.6
21	93	4.60	349	18.6
21	40	.46	349	28.3
21	48	.93	349	28.3
21	71	1.84	349	28.3
21	47	.46	349	56.5
21	51	.93	349	56.5
21	77	1.84	349	56.5
22	5	.46	349	9.0
22	16	.91	349	9.0
22	55	1.80	349	9.0
22	93	4.50	349	9.0
22	23	.91	349	18.6
22	70	1.80	349	18.6
22	100	4.50	349	18.6
22	9	.46	349	28.3
22	23	.91	349	28.3
22	75	1.80	349	28.3
22	14	.46	349	56.5
22	25	.91	349	56.5
22	80	1.80	349	56.5
23	6	.31	349	9.0
23	22	.77	349	9.0
23	84	2.74	349	9.0
23	94	6.90	349	9.0
23	20	.77	349	18.6
23	93	2.74	349	18.6
23	10	.31	349	28.3
23	27	.77	349	28.3
23	8	.31	349	56.5
23	25	.77	349	56.5

TABLE 22 (Continued)

Run No.	% H ₂ S Reduction	O ₃ /H ₂ S Ratio	Temp. (°K)	Reaction Time (sec)
24	27	.64	349	9.0
24	47	1.28	349	9.0
24	68	1.99	349	9.0
24	82	4.96	349	9.0
24	49	1.28	349	18.6
24	74	1.99	349	18.6
24	89	4.96	349	18.6
24	27	.64	349	28.3
24	84	1.99	349	28.3
24	97	4.96	349	28.3
24	31	.64	349	56.5
24	55	1.28	349	56.5
24	87	1.99	349	56.5
25	25	.53	349	9.0
25	34	1.06	349	9.0
25	58	2.12	349	9.0
25	58	2.65	349	9.0
25	38	1.06	349	18.6
25	61	2.12	349	18.6
25	65	2.65	349	18.6
25	24	.53	349	28.3
25	40	1.06	349	28.3
25	68	2.12	349	28.3
25	78	2.65	349	28.3
25	25	.53	349	56.5
25	41	1.06	349	56.5
25	78	2.12	349	56.5
25	75	2.65	349	56.5
13	27	.52	398	25.3
13	23	1.04	398	25.3
13	75	2.60	398	25.3
13	28	.52	398	50.0

TABLE 22 (Continued)

Run No.	% H ₂ S Reduction	O ₃ H ₂ S Ratio	Temp. (°K)	Reaction Time (sec)
13	27	1.04	398	50.0
13	26	1.04	398	8.4
13	73	2.60	398	8.4
13	74	2.60	398	16.8
14	14	.32	398	8.4
14	18	.63	398	8.4
14	60	2.10	398	8.4
14	58	2.10	398	16.8
14	12	.32	398	25.3
14	28	.63	398	25.3
14	63	2.10	398	25.3
14	19	.32	398	50.0
14	28	.63	398	50.0
14	61	2.10	398	50.0
15	32	.47	398	8.4
15	48	.95	398	8.4
15	89	2.40	398	8.4
15	47	.95	398	16.8
15	34	.47	398	25.3
15	48	.95	398	25.3
15	34	.47	398	50.0
15	50	.95	398	50.0
16	31	.52	398	8.4
16	47	1.05	398	8.4
16	88	1.93	398	8.4
16	44	1.05	398	16.8
16	28	.52	398	25.3
16	48	1.05	398	25.3
16	28	.52	398	50.0
16	48	1.05	398	50.0
17	20	.53	398	8.4
17	38	1.06	398	8.4

TABLE 22 (Continued)

Run No.	% H ₂ S Reduction	O ₃ H ₂ S Ratio	Temp. (°K)	Reaction Time (sec)
17	83	2.26	398	8.4
17	86	5.66	398	8.4
17	38	1.06	398	16.8
17	96	2.26	398	16.8
17	99	5.66	398	16.8
17	26	.53	398	25.3
17	38	1.06	398	25.3
17	98	2.26	398	25.3
17	21	.53	398	50.0
18	32	.57	398	8.4
18	44	1.14	398	8.4
18	78	2.11	398	8.4
18	92	5.28	398	8.4
18	86	2.11	398	16.8
18	98	5.28	398	16.8
18	32	.56	398	25.3
18	50	1.14	398	25.3
18	90	2.11	398	25.3
18	90	2.11	398	33.6
18	31	.57	398	50.0
18	50	1.14	398	50.0
18	47	1.14	398	50.0
18	91	2.11	398	50.0
18	89	2.11	308	25.3
18	46	1.14	308	8.4
17	90	5.66	398	8.4
17	86	2.26	398	8.4
5	23	.81	328	9.4
5	29	1.63	328	9.4
5	50	3.25	328	9.4
5	58	8.13	328	9.4
5	23	.81	328	29.8

TABLE 22 (Continued)

Run No.	% H ₂ S Reduction	O ₃ H ₂ S Ratio	Temp. (°K)	Reaction Time (sec)
5	45	1.63	328	29.8
5	88	3.25	328	29.8
5	23	.81	328	59.9
5	45	1.63	328	59.9
6	8	.67	328	9.4
6	35	1.67	328	9.4
6	75	3.35	328	9.4
6	95	8.35	328	9.4
6	8	.67	328	29.8
6	34	1.67	328	29.8
6	31	1.67	328	29.8
6	8	.67	328	59.9
6	36	1.67	328	59.9
6	30	1.67	328	59.9

TABLE 23

OZONE-HYDROGEN SULFIDE REACTION EQUATION 5.1

$$\text{Equation: } ^a y = B_0 + B_1 O_3 + B_2 O_3^2$$

Total S.S. = 177694.75

F = 453.9**

Regression S.S. = 141400.72

 $R^2 = .7958$

$O_3=O_3/H_2S$ Ratio	Te = Temperature (°K)	Time (sec)	y = Estimated Reduction (%)	Standard Error
0.5	355	10	21.18	1.26
1.0	355	10	36.46	0.92
2.0	355	10	61.72	1.11
3.0	355	10	79.89	1.47
0.5	355	30	21.18	1.26
1.0	355	30	36.46	0.92
2.0	355	30	61.72	1.10
3.0	355	30	79.89	1.47
0.5	355	60	21.18	1.26
1.0	355	60	36.46	0.92
2.0	355	60	61.72	1.11
3.0	355	60	79.89	1.47

$^a B_0 = 4.12$

$B_1 = 35.89$

$B_2 = -3.54$

TABLE 24

OZONE-HYDROGEN SULFIDE REACTION EQUATION 5.2

$$\text{Equation:}^a y = B_0 + B_1 O_3 + B_2 T_e + B_3 O_3^2$$

Total S.S. = 177694.75

F = 367.5**

Regression S.S. = 146802.25

 $R^2 = .8261$

$O_3=O_3/H_2S$ Ratio	$T_e = \text{Temperature}$ (°K)	Time (sec)	y = Estimated Reduction (%)	Standard Error
0.5	355	10	22.14	1.17
1.0	355	10	37.49	0.86
2.0	355	10	62.93	1.04
3.0	355	10	81.35	1.38
0.5	355	30	22.14	1.17
1.0	355	30	37.49	0.86
2.0	355	30	62.93	1.04
3.0	355	30	81.35	1.38
0.5	355	60	22.14	1.17
1.0	355	60	37.49	0.86
2.0	355	60	62.93	1.04
3.0	355	60	81.35	1.38

$$^a B_0 = -43.89$$

$$B_1 = 35.97$$

$$B_2 = 0.14$$

$$B_3 = -3.51$$

TABLE 25

OZONE-HYDROGEN SULFIDE REACTION EQUATION 5.3

$$\text{Equation: } ^a y = B_0 + B_1 O_3 + B_2 T_e + B_3 \text{Time} + B_4 O_3^2$$

Total S.S. = 177694.75

F = 308.3**

Regression S.S. = 149663.35

R² = .8422

O_3/H_2S Ratio	T_e = Temperature (°K)	Time (sec)	y = Estimated Reduction (%)	Standard Error
0.5	355	10	18.00	1.40
1.0	355	10	33.65	1.14
2.0	355	10	59.68	1.20
3.0	355	10	78.69	1.43
0.5	355	30	22.00	1.12
1.0	355	30	37.64	0.83
2.0	355	30	63.67	1.00
3.0	355	30	82.68	1.34
0.5	355	60	27.99	1.64
1.0	355	60	43.64	1.51
2.0	355	60	69.66	1.70
3.0	355	60	88.67	2.00

$$^a B_0 = -56.80$$

$$B_1 = 36.55$$

$$B_2 = 0.16$$

$$B_3 = 0.20$$

$$B_4 = -3.51$$

TABLE 26

OZONE-METHYL MERCAPTAN REACTION DATA AT 38° C
Date: 5-17-71

Run No.	Initial RSH (ppm)	O ₃ /RSH Ratio	Final RSH & RSSR (ppm) @ Sampling Port No.							
			1		2		3		6	
			RSH	RSSR	RSH	RSSR	RSH	RSSR	RSH	RSSR
26	63	.87	28	5	--	--	29	3	28	4
	63	1.74	17	5	3	3	20	5	17	4
	63	3.48	17	4	4	4	18	4	14	5
	63	8.73	0	2	--	2	0	2	0	2
27	180	1.06	97	0	--	--	88	0	97	0
	180	2.13	78	0	--	--	85	0	70	0
	180	4.25	53	50	--	--	47	48	20	40
	180	6.85	0	31	--	--	0	28	0	21
28	830	1.06	470	85	--	--	470	75	335	60
	830	2.13	260	85	--	--	160	64	0	55
	830	4.25	0	15	--	--	0	10	0	0
	53	1.05	33	2	2	2	29	3	29	3
34	53	2.14	22	3	3	3	17	4	11	3
	53	4.29	10	2	2	2	7	2	0	2
	53	7.72	0	1	1	1	0	1	0	1
	167	.92	91	41	44	44	77	49	54	72
35	167	1.84	58	43	43	43	49	42	36	49
	167	3.67	30	37	39	39	25	33	0	35
	167	7.40	0	21	20	20	0	19	0	21
	850	3.75	0	0	--	--	--	--	--	--

TABLE 27

OZONE-METHYL MERCAPTAN REACTION DATA AT 125° C
Date: 5-16-71

Run No.	Initial RSH (ppm)	O ₃ /RSH Ratio	Final RSH & RSSR (ppm) @ Sampling Port No.							
			1		2		3		6	
			RSH	RSSR	RSH	RSSR	RSH	RSSR	RSH	RSSR
31	1080	.95	450	90	400	90	280	65	280	78
	1080	1.90	0	45	0	41	0	18	0	14
	1080	3.78	0	15	0	11	0	10	0	8
	1080	7.56	0	1	0	1	--	--	--	--
32	180	1.03	0	50	0	52	0	52	0	51
	180	2.06	0	37	0	37	0	37	0	36
	180	4.05	0	0	--	--	--	--	--	--
	47	.66	9	11	5	10	5	11	5	10
33	47	1.33	4	8	0	6	0	8	0	7
	47	2.66	0	1	0	1	0	1	0	1
	1050	1.01	230	165	--	--	83	170	75	155
29	1050	1.01	210	130	--	--	--	--	--	--

TABLE 28

DATA FOR REGRESSION ANALYSIS OF OZONE-METHYL MERCAPTAN REACTIONS

Run No.	% RSH Reduction	O ₃ /RSH Ratio	Temp. (°K)	Reaction Time (sec)
34	38	1.05	311	9.7
34	59	2.14	311	9.7
34	81	4.29	311	9.7
34	43	1.05	311	20.4
34	61	2.14	311	20.4
34	82	4.29	311	20.4
34	46	1.05	311	31.2
34	69	2.14	311	31.2
34	86	4.29	311	31.2
34	46	1.05	311	63.0
34	80	2.14	311	63.0
34	100	4.29	311	63.0
35	46	.92	311	9.7
35	65	1.84	311	9.7
35	82	3.67	311	9.7
35	51	.92	311	20.4
35	68	1.84	311	20.4
35	88	3.67	311	20.4
35	54	.92	311	31.2
35	71	1.84	311	31.2
35	85	3.67	311	31.2
35	68	.92	311	63.0
35	78	1.84	311	63.0
35	89	3.67	311	63.0
33	82	.66	398	8.4
33	91	1.33	398	8.4
33	89	.66	398	16.8
33	100	1.33	398	16.8
33	89	.66	398	25.3

TABLE 28 (Continued)

Run No.	% RSH Reduction	O ₃ /RSH Ratio	Temp. (°K)	Reaction Time (sec)
33	89	.66	398	50.0
31	58	.95	398	8.4
31	63	.95	398	16.8
31	74	.95	398	25.3
31	74	.95	398	50.0
29	78	1.01	398	8.4
29	80	1.01	398	8.4
29	92	1.01	398	25.3
29	93	1.01	398	50.0
26	55	.87	311	9.7
26	73	1.74	311	9.7
26	73	3.48	311	9.7
26	78	1.74	311	20.4
26	75	3.48	311	20.4
26	54	.87	311	31.2
26	68	1.74	311	31.2
26	71	3.48	311	31.2
26	55	.87	311	63.0
26	73	1.74	311	63.0
26	78	3.48	311	63.0
27	46	1.06	311	9.7
27	57	2.13	311	9.7
27	71	4.25	311	9.7
27	51	1.06	311	31.2
27	53	2.13	311	31.2
27	74	4.25	311	31.2
27	46	1.06	311	63.0
27	61	2.13	311	63.0
27	89	4.25	311	63.0
28	43	1.06	311	9.7
28	69	2.13	311	9.7
28	43	1.06	311	31.2
28	81	2.13	311	31.2
28	60	1.06	311	63.0

TABLE 29

OZONE-METHYL MERCAPTAN REACTION EQUATION 5.4

$$\text{Equation: } ^a y = B_0 + B_1 O_3 + B_2 Te + B_3 \text{Time}$$

Total S.S. = 15935.08

F = 42.82**

Regression S.S. = 10920.00

 $R^2 = .6853$

$O_3=O_3/\text{RSH}$ Ratio	Te = Temperature (°K)	Time (sec)	y = Estimated Reduction (%)	Standard Error
1.0	355	10	65.46	1.85
1.0	355	30	68.91	1.55
1.0	355	60	74.09	2.48
1.0	311	10	49.85	2.29
2.0	311	10	59.98	1.87
3.0	311	10	70.11	2.02
1.0	311	30	53.30	1.87
2.0	311	30	63.43	1.34
3.0	311	30	73.56	1.57
1.0	311	60	58.48	2.50
2.0	311	60	68.61	2.15
3.0	311	60	78.73	2.31

$$^a B_0 = -72.30$$

$$B_1 = 10.13$$

$$B_2 = 0.35$$

$$B_3 = 0.17$$

TABLE 30

OZONE-METHYL MERCAPTAN REACTION EQUATION 5.5

$$\text{Equation: } ^a y = B_0 + B_1 O_3 + B_2 T_e + B_3 \text{Time} + B_4 O_3^2$$

Total S.S. = 15935.08

F = 35.3***

Regression S.S. = 11296.91

R² = .7089

$O_3=O_3/RSH$ Ratio	$T_e = \text{Temperature}$ (°K)	Time (sec)	y = Estimated Reduction (%)	Standard Error
1.0	355	10	64.61	1.84
1.0	355	30	68.23	1.53
1.0	355	60	73.68	2.41
1.0	311	10	47.64	2.44
2.0	311	10	62.93	2.26
3.0	311	10	73.26	2.44
1.0	311	30	51.27	2.04
2.0	311	30	66.56	1.94
3.0	311	30	76.89	2.16
1.0	311	60	56.72	2.56
2.0	311	60	72.00	2.61
3.0	311	60	82.34	2.79

$$^a B_0 = -94.31$$

$$B_1 = -22.71$$

$$B_2 = 0.39$$

$$B_3 = 0.18$$

$$B_4 = -2.48$$

TABLE 31

OZONE-METHYL MERCAPTAN REACTION EQUATION 5.6

$$\text{Equation: } ^a y = B_0 + B_1 O_3 + B_2 T_e + B_3 \text{Time} + B_4 O_3^2 + B_5 O_3 T_e$$

Total S.S. = 15935.08

F = 28.06**

Regression S.S. = 11331.68

 $R^2 = .7111$

$O_3=O_3/RSH$ Ratio	$T_e =$ Temperature (°K)	Time (sec)	y = Estimated Reduction (%)	Standard Error
1.0	355	10	64.30	1.91
1.0	355	30	67.88	1.63
1.0	355	60	73.25	2.51
1.0	311	10	47.41	2.48
2.0	311	10	63.20	2.34
3.0	311	10	73.71	2.54
1.0	311	30	50.99	2.10
2.0	311	30	66.87	2.01
3.0	311	30	77.29	2.25
1.0	311	60	56.36	2.63
2.0	311	60	72.24	2.64
3.0	311	60	82.66	2.85

$$^a B_0 = -123.13$$

$$B_1 = 52.11$$

$$B_2 = 0.47$$

$$B_3 = 0.18$$

$$B_4 = -2.73$$

$$B_5 = -0.09$$

TABLE 32

OZONE-DIMETHYL SULFIDE REACTION DATA AT 38° C
Date: 6-7-71

Run No.	Initial RSR (ppm)	O ₃ /RSR Ratio	Final RSR (ppm) @ Sampling Port No.		
			1	3	6
36	38	.48	36	33	34
	38	.97	32	31	31
	38	1.94	23	20	19
	38	3.88	8	5	5
39	170	.58	130	130	126
	170	1.16	95	90	82
	170	2.31	34	31	24
	170	4.62	0	--	--
40	1160	.40	850	860	900
	1025	.40	725	750	--
	1160	.80	355	460	500
	1350	.80	480	700	--
	1160	1.61	0	--	--
	1160	3.22	0	--	--

TABLE 33

OZONE-DIMETHYL SULFIDE REACTION DATA AT 125° C
Date: 6-8-71

Run No.	Initial		Final RSR (ppm) @ Sampling Port No.		
	RSR (ppm)	O ₃ /RSR Ratio	1	3	6
37	38	.48	30	33	32
	38	.97	29	26	27
	38	1.94	15	12	10
	38	3.88	1	0	--
38	190	.72	115	120	120
	190	1.42	72	56	58
	190	2.90	1	0	--
	190	5.80	0	--	--
41	1160	.40	900	970	1000
	1160	.80	470	600	660
	1160	.80	--	560	--
	1160	1.61	0	0	--
	1160	1.61	0	--	--

TABLE 34

DATA FOR REGRESSION ANALYSIS OF OZONE-DIMETHYL SULFIDE REACTIONS

Run No.	% RSR Reduction	O ₃ /RSR Ratio	Temp. (°K)	Reaction Time (sec)
36	5	.48	211	9.7
36	16	.97	311	9.7
36	39	1.94	311	9.7
36	80	3.88	311	9.7
36	21	.97	311	20.4
36	39	1.94	311	20.4
36	13	.48	311	31.2
36	18	.97	311	31.2
36	47	1.94	311	31.2
36	87	3.88	311	31.2
36	10	.48	311	63.0
36	18	.97	311	63.0
36	50	1.94	311	63.0
36	88	3.88	311	63.0
39	24	.58	311	9.7
39	44	1.16	311	9.7
39	80	2.31	311	9.7
39	24	.58	311	31.2
39	47	1.16	311	31.2
39	82	2.31	311	31.2
39	26	.58	311	63.0
39	52	1.16	311	63.0
39	86	2.31	311	63.0
40	27	.40	311	9.7
40	69	.80	311	9.7
40	26	.40	311	31.2
40	60	.80	311	31.2
40	22	.40	311	63.0
40	52	.80	311	63.0
40	29	.40	311	9.7
40	65	.80	311	9.7

Run No.	% RSR Reduction	O_3 /RSR Ratio	Temp. (°K)	Reaction Time (sec)
40	27	.40	311	31.2
40	48	.80	311	31.2
37	21	.48	398	8.4
37	25	.97	398	8.4
37	61	1.94	398	8.4
37	99	3.88	398	8.4
37	66	1.94	398	16.8
37	100	3.88	398	16.8
37	13	.48	398	25.3
37	32	.97	398	25.3
37	68	1.94	398	25.3
37	16	.48	398	50.0
37	29	.97	398	50.0
37	74	1.94	398	50.0
38	40	.72	398	8.4
38	62	1.45	398	8.4
38	99	2.90	398	8.4
38	37	.72	398	25.3
38	71	1.45	398	25.3
38	37	.72	398	50.0
38	70	1.45	398	50.0
41	22	.40	398	8.4
41	59	.80	398	8.4
41	16	.40	398	25.3
41	48	.80	398	25.3
41	14	.40	398	50.0
41	43	.80	398	50.0
41	51	.80	398	25.3

TABLE 35

OZONE-DIMETHYL SULFIDE REACTION EQUATION 5.7

$$\text{Equation:}^a y = B_0 + B_1 O_3 + B_2 O_3^2$$

Total S.S. = 38771.22

F = 66**

Regression S.S. = 27287.95

 $R^2 = .7038$

$O_3 = O_3 / RSR$ Ratio	Te = Temperature (°K)	Time (sec)	y = Estimated Reduction (%)	Standard Error
.5	355	10	25.44	2.76
1.0	355	10	41.43	2.12
2.0	355	10	66.95	3.49
.5	355	30	25.44	2.76
1.0	355	30	41.43	2.12
2.0	355	30	66.95	3.49
.5	355	60	25.44	2.76
1.0	355	60	41.43	2.12
2.0	355	60	66.95	3.49

$$^a B_0 = 7.30$$

$$B_1 = 38.44$$

$$B_2 = -4.30$$

TABLE 36

OZONE-DIMETHYL SULFIDE REACTION EQUATION 5.8

$$\text{Equation: } ^a y = B_0 + B_1 O_3 + B_2 Te + B_3 \text{Time} + B_4 O_3^2$$

Total S.S. = 38771.22

F = 34**

Regression S.S. = 27759.38

 $R^2 = .7160$

O_3/O_3 RSR Ratio	Te = Temperature (°K)	Time (sec)	y = Estimated Reduction (%)	Standard Error
.5	355	10	26.40	3.36
1.0	355	10	42.26	2.85
2.0	355	10	67.65	3.92
.5	355	30	25.87	2.77
1.0	355	30	41.72	2.12
2.0	355	30	67.12	3.48
.5	355	60	25.06	4.08
1.0	355	60	40.92	3.68
2.0	355	60	66.31	4.65

$$^a B_0 = -13.43$$

$$B_1 = 38.02$$

$$B_2 = 0.06$$

$$B_3 = -0.03$$

$$B_4 = -4.21$$

TABLE 37

OZONE-DIMETHYL SULFIDE REACTION EQUATION 5.9

$$\text{Equation: } ^a y = B_0 + B_1 O_3 + B_2 Te + B_3 O_3^2 + B_4 O_3 Te$$

Total S.S. = 38771.22

F = 36**

Regression S.S. = 28222.57

 $R^2 = .7279$

$O_3 = O_3 / \text{RSR}$ Ratio	Te = Temperature (°K)	Time (sec)	y = Estimated Reduction (%)	Standard Error
.5	355	10	25.49	2.72
1.0	355	10	41.59	2.08
2.0	355	10	67.52	3.41
.5	355	30	25.49	2.72
1.0	355	30	41.50	2.08
2.0	355	30	67.52	3.41
.5	355	60	25.49	2.72
1.0	355	60	41.59	2.08
2.0	355	60	67.52	3.41

$$^a B_0 = 15.13$$

$$B_1 = 14.80$$

$$B_2 = -0.02$$

$$B_3 = -4.19$$

$$B_4 = 0.07$$

TABLE 38
 OZONE-DIMETHYL DISULFIDE REACTION DATA AT 38° C
 Date: 6-9-71

Run No.	Initial		Final RSSR (ppm) @ Sampling Port No.		
	RSSR (ppm)	O ₃ /RSSR Ratio	1	3	6
42	48	.52	41	41	41
	48	1.04	41	41	42
	48	2.08	41	39	40
	48	3.13	38	33	32
	48	5.94	29	22	21
44	150	.89	113	125	130
	150	1.79	125	123	130
	150	2.98	123	114	110
	150	5.06	110	93	82
46	245	.73	220	230	225
	245	1.03	222	225	225
	245	2.05	190	200	185
	245	2.93	160	160	142
	245	5.56	110	80	53

TABLE 39

OZONE-DIMETHYL DISULFIDE REACTION DATA AT 125° C
Date: 6-10-71

Run No.	Initial RSSR (ppm)	O ₃ /RSSR Ratio	Final RSSR (ppm) @ Sampling Port No.		
			1	3	6
43	48	.52	31	34	27
	48	2.08	24	21	17
	48	3.13	14	10	6
	48	5.94	6	1	0
45	150	.89	125	122	125
	150	1.79	110	90	90
	150	2.98	80	52	56
	150	5.06	46	0	--
47	255	1.03	200	180	182
	255	2.05	170	125	120
	255	2.93	126	83	85
	255	5.56	52	17	0

TABLE 40

DATA FOR REGRESSION ANALYSIS OF OZONE-DIMETHYL DISULFIDE REACTIONS

Run No.	% RSSR Reduction	O ₃ /RSSR Ratio	Temp. (°K)	Reaction Time (sec)
42	15	.52	311	9.7
42	13	1.04	311	9.7
42	15	2.08	311	9.7
42	21	3.13	311	9.7
42	40	5.94	311	9.7
42	15	.52	311	31.2
42	15	1.04	311	31.2
42	19	2.08	311	31.2
42	31	3.13	311	31.2
42	54	5.94	311	31.2
42	15	.52	311	63.0
42	13	1.04	311	63.0
42	17	2.08	311	63.0
42	33	3.13	311	63.0
42	56	5.94	311	63.0
44	13	.89	311	9.7
44	17	1.79	311	9.7
44	18	2.08	311	9.7
44	27	5.06	311	9.7
44	12	.89	311	31.2
44	18	1.79	311	31.2
44	24	2.98	311	31.2
44	38	5.06	311	31.2
44	13	.89	311	63.0
44	13	1.79	311	63.0
44	27	2.98	311	63.0
44	45	5.06	311	63.0
46	10	.73	311	9.7
46	9	1.03	311	9.7
46	22	2.05	311	9.7

TABLE 40 (Continued)

Run No.	% RSSR Reduction	O ₂ /RSSR Ratio	Temp. (°K)	Reaction Time (sec)
46	35	2.93	311	9.7
46	55	5.56	311	9.7
46	6	.73	311	31.2
46	8	1.03	311	31.2
46	18	2.05	311	31.2
46	35	2.93	311	31.2
46	67	5.56	311	31.2
46	8	.73	311	63.0
46	8	1.03	311	63.0
46	24	2.05	311	63.0
46	42	2.93	311	63.0
46	78	5.56	311	63.0
43	35	.52	398	8.4
43	50	2.08	398	8.4
43	71	3.13	398	8.4
43	88	5.94	398	8.4
43	29	.52	398	25.3
43	56	2.08	398	25.3
43	79	3.13	398	25.3
43	99	5.94	398	25.3
43	44	.52	398	50.0
43	65	2.08	398	50.0
43	87	3.13	398	50.0
45	17	.89	398	8.4
45	27	1.79	398	8.4
45	47	2.98	398	8.4
45	69	5.06	398	8.4
45	99	5.06	398	16.8
45	19	.89	398	25.3
45	40	1.79	398	25.3
45	65	2.98	398	25.3
45	17	.89	398	50.0
45	40	1.79	398	50.0

TABLE 40 (Continued)

Run No.	% RSSR Reduction	O ₃ /RSSR Ratio	Temp. (°K)	Reaction Time (sec)
45	64	2.98	398	50.0
47	22	1.03	398	8.4
47	33	2.05	398	8.4
47	51	2.93	398	8.4
47	80	5.56	398	8.4
47	29	1.03	398	25.3
47	51	2.05	398	25.3
47	68	2.93	398	25.3
47	93	5.56	398	25.3
47	29	1.03	398	50.0
47	53	2.05	398	50.0
47	67	2.93	398	50.0

TABLE 41

OZONE-DIMETHYL DISULFIDE REACTION EQUATION 5.10

$$\text{Equation: } ^a y = B_0 + B_1 O_3 + B_2 T_e + B_3 O_3^2 + B_4 O_3 T_e$$

Total S. S. = 46678.67

F = 102.6**

Regression S.S. = 39879.94

 $R^2 = .8544$

$O_3=O_3/RSSR$ Ratio	$T_e = \text{Temperature}$ (°K)	Time (sec)	y = Estimated Reduction (%)	Standard Error
1.0	355	10	22.19	1.71
3.0	355	10	45.49	1.83
5.0	355	10	66.28	2.02
1.0	355	30	22.19	1.71
3.0	355	30	45.49	1.83
5.0	355	30	66.28	2.02
1.0	355	60	22.19	1.71
3.0	355	60	45.49	1.83
5.0	355	60	66.28	2.02

$$^a B_0 = -57.36$$

$$B_1 = -5.85$$

$$B_2 = 0.19$$

$$B_3 = -0.31$$

$$B_4 = 0.05$$

TABLE 42

OZONE-DIMETHYL DISULFIDE REACTION EQUATION 5.11

$$\text{Equation: } ^a y = B_0 + B_1 O_3 + B_2 Te + B_3 \text{Time} + B_4 O_3^2 + B_5 O_3 Te$$

Total S. S. = 46678.67

F = 95.25***

Regression S.S. = 40771.75

 $R^2 = .8734$

$O_3=O_3/RSSR$ Ratio	Te = Temperature (°K)	Time (sec)	y = Estimated Reduction (%)	Standard Error
1.0	355	10	18.38	1.99
3.0	355	10	41.84	2.05
5.0	355	10	63.27	2.11
1.0	355	30	21.91	1.61
3.0	355	30	45.37	1.72
5.0	355	30	66.81	1.91
1.0	355	60	27.22	2.24
3.0	355	60	50.68	2.35
5.0	355	60	72.11	2.62

$$^a B_0 = -64.80$$

$$B_1 = -7.82$$

$$B_2 = 0.19$$

$$B_3 = 0.18$$

$$B_4 = -0.25$$

$$B_5 = 0.06$$

TABLE 43

OZONE-DIMETHYL DISULFIDE REACTION EQUATION 5.12

$$\text{Equation: } ^a y = B_0 + B_1 O_3 + B_2 Te + B_3 \text{Time} + B_4 O_3^2 + B_5 O_3 Te + B_6 O_3 \text{Time} + B_7 Te \text{Time}$$

Total S.S. = 46678.67

F = 81.77**

Regression S.S. = 41787.64

R² = .8952

$O_3=O_3/\text{RSSR}$ Ratio	Te = Temperature (°K)	Time (sec)	y = Estimated Reduction (%)	Standard Error
1.0	355	10	20.35	2.07
3.0	355	10	40.17	1.95
5.0	355	10	59.34	2.34
1.0	355	30	22.32	1.49
3.0	355	30	45.96	1.60
5.0	355	30	68.95	1.86
1.0	355	60	25.28	2.54
3.0	355	60	54.64	2.44
5.0	355	60	83.36	3.92

$$^a B_0 = -10.65$$

$$B_1 = -18.89$$

$$B_2 = 0.06$$

$$B_3 = -1.12$$

$$B_4 = -0.08$$

$$B_5 = 0.08$$

$$B_6 = 0.10$$

$$B_7 = 0.01$$

TABLE 44
 OZONE-SMELT TANK VENT GAS REACTION DATA

Date: 6-11-71

Run No.	Point	Vent Gas TRS (ppm) ^a	Ozone (ppm)	O ₂ /TRS Ratio	Sampling Port	GLC Analysis (ppm)					Percent of Vent Gas ^b
						RSH	RSR	RSSR	SO ₂		
--	A	90	---	--	--	0	0	26.0	0	57.8	
--	B	96	--	--	--	6.0	1.0	23.0	0	55.2	
48	C	104	24	.23	1	5.7	2.5	20.0	0	46.4	
48	D	120	24	.20	1	7.0	3.2	23.0	0	46.9	
48	E	127	24	.10	3	6.5	2.6	25.0	3.8	46.6	
48	F	116	24	.21	3	4.5	2.3	24.0	2.6	47.3	
48	G	102	24	.24	6	4.0	2.6	20.0	1.9	45.7	
48	H	93	24	.26	6	9.2	2.3	14.0	2.4	42.5	
--	I	85	--	--	--	3.4	2.6	22.0	0	58.8	
--	J	139	--	--	--	4.6	2.8	31.0	0	50.0	
--	K	162	--	--	--	19.0	2.5	27.0	0	46.6	
--	L	148	--	--	--	15.0	2.2	26.0	0	46.7	
49	M	162	47	.29	1	15.7	3.4	25.0	2.9	42.7	
49	N	152	47	.31	1	14.0	2.0	20.0	2.8	36.8	
49	O	156	47	.30	3	5.2	2.5	28.0	2.7	40.6	
49	P	186	47	.25	3	1.3	2.8	23.0	11.0	26.9	
49	Q	210	47	.22	6	2.5	3.8	46.0	85.0	46.8	
49	R	127	47	.37	6	0	1.9	22.0	49.0	36.1	

--	S	128	--	--	--	0	2.6	28.0	0	45.8
--	T	215	--	--	--	4.8	4.2	off scale	0	--
--	U	191	--	--	--	21.0	2.9	40.0	0	54.5
50	V	182	191	1.05	1	2.8	2.6	15.0	50.0	19.5
50	W	210	191	.91	1	19.0	3.2	10.3	50.0	20.4
50	X	275	191	--	3	21.0	2.5	34.0	11.0	--
50	Y	197	191	.97	3	0	1	22.0	18.0	22.9
50	Z	166	191	1.15	6	0	4	15.0	84.0	20.5
50	AA	157	191	1.22	6	0	1	14.0	51.0	18.5
--	BB	206	--	--	--	25	1.0	37.0	0	48.5
51	CC	148	414	2.80	1	0	0	0	57.0	0
51	DD	119	414	3.48	1	0	0	0	65.0	0
51	EE	177	414	2.34	3	0	0	3.5	43.0	4.0
51	FF	157	414	2.64	3	0	0	1.0	42.0	1.3
51	GG	160	414	2.59	6	0	0	0	74.0	0
51	HH	174	414	2.38	6	0	0	2.1	62.0	2.4

^aTotal Reduced Sulfur read as SO₂ by electrolytic titrator prior to ozone injection.

^bDoes not include SO₂ value, but summation of RSH, RSR, and twice RSSR value.

^cRepresents baseline data on vent gas -- no ozone.

TABLE 45
THERMAL DECAY OF OZONE IN REACTION TUBE

Ozone Generator Output (ppm)	Ozone Remaining at Sampling Port ^a		
	1	3	6
	<u>38° C</u>		
101	107	97	104
355	351	359	347
950	954	944	943
1552	1573	1539	1565
	<u>125° C</u>		
46	44	36	31
278	262	229	192
785	759	632	521
3290	3122	2540	2090

^aSpace times based on 350 cc/min flow in reaction tube.

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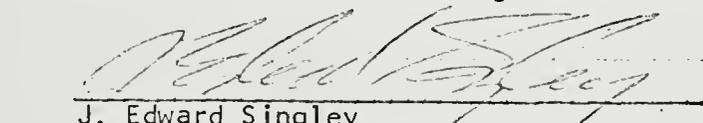
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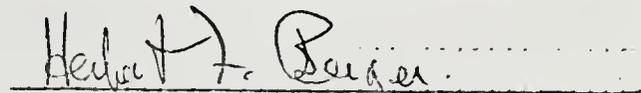
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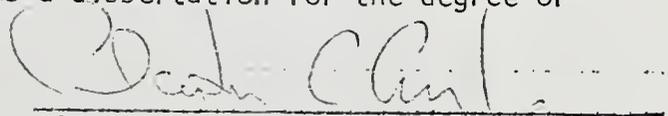
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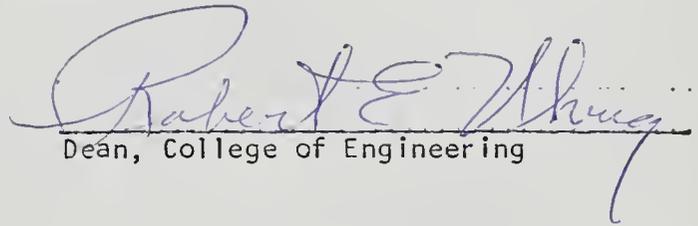
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December, 1971


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