

SOLID REAGENTS
FOR OZONE ANALYSIS

by

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TABLE OF CONTENTS

	page
LIST OF FIGURES	iii
LIST OF TABLES.	iv
I. Introduction.	1
II. Studies of Reagents.	2
Experimental	2
Reagents	3
Procedure.	3
Results and Discussion	8
III. Studies of Solid Ozone Reagents.	15
Experimental	15
Procedure.	18
Results and Discussion	22
Summary.	28
LITERATURE CITED.	29
ACKNOWLEDGEMENTS.	30
VITA.	31

LIST OF FIGURES

	page
II. Studies of Reagents	
1. Testing apparatus	5
2. Liquid sample holder.	6
3. Solid sample holder	7
III. Studies of Solid Ozone Reagents	
4. Apparatus used for interference studies	16
5. Solid sample holder used.	17
6. Modification made to ozone testing apparatus	19
7. Calibration curve for ozone generator	21

LIST OF TABLES

	page
II. Studies of Reagents	
1. Initial Solid Reagent Study	10
2. Organic Solvent Study	12
3. Aqueous Solution Reagents	13
4. Coupling Reactions.	14
III. Studies of Solid Ozone Reagents	
5. Effects of Acid on Reagents	24
6. Interference Study.	26
7. Response at 250 ppb	27

I. Introduction

Ozone is the most reactive form of oxygen. For many years, it has been known that ozone causes rubber to crack and paints to deteriorate. At concentrations less than 2 ppm it has a pleasant characteristic odor, but at higher concentrations can be injurious to humans (1). In humans, ozone can cause local irritation to the eyes and mucous membranes of the nose and lungs. Severe or prolonged exposures can result in pulmonary edema and hemorrhage. Lesser exposure can produce headache, shortness of breath, uneasy listlessness, and drowsiness or languor (2).

Ozone is produced by exposing oxygen to U.V. light or brush discharge. Commercially it is used for bleaching oils, fats, waxes, flour and starch, for the sterilization of drinking water, and for the disinfection of air.

Present analytical methods require the use of bulky apparatus and/or long sampling times. A solid reagent would offer a simple semi-quantitative method for field determinations of ozone levels, and these reagents could conceivably be taken to a laboratory, dissolved, and the ozone concentration measured more accurately. This thesis will deal only with a survey of the reagents themselves. The sampling procedure and later laboratory work-up were left for further research.

II. Studies of Reagents

The present analytical methods utilize oxidation of potassium iodide in aqueous solution for analysis of ozone (3). Other methods reported include non-aqueous colorimetric reactions involving N-phenyl-2-naphthylamine (4), and the oxidation of 1,2-di-(4-pyridyl) ethylene followed by coupling with another reagent (5). Thus the initial studies involved reactions of ozone in both solution and solid state, employing the principles of direct and indirect oxidation, and carbon-carbon double bond oxidation followed by hydrolysis to aldehydes and coupling with another reagent.

Experimental

Apparatus: The instrument used for the production of ozone was a McMillian Electronics Corporation series 1000 ozone generator capable of delivering concentrations of 0 to 1000 ppb ozone at a flow rate of 5 liters per min. This instrument is equipped with four outlet ports. Three ports were left open to maintain atmospheric pressure in the system. The flow rate in the apparatus was maintained below four liters per minute to keep out room air that had not been decontaminated by adsorbers.

The sampling apparatus is shown in Figure 1. It was constructed entirely of Teflon and Pyrex glass. The liquid sample holder, shown in Figure 2, consisted of a glass frit on the end of the glass tube placed inside of a 50 ml round bottom flask with

a 24/40 joint. The solid sample holder, shown in Figure 3, was constructed by joining a 5 mm I.D. glass tube and a 2 mm I.D. glass tube together. A Pyrex glass wool plug was tamped into the junction of the two glass tubes, using a 3 mm Pyrex glass tube, to support the solid sample. The solid sample was then placed in the 5 mm tube, and another Pyrex glass wool plug was inserted to hold the sample in the sample holder during exposure to ozone. The glass wool plugs were replaced prior to each run and removed when the apparatus was used for liquid samples.

Reagents

Except as noted in Tables 1 through 4 all reagents were prepared such that there was 0.1 g of reagent, and 100 ml of solvent.

Procedure

Solid reagents were prepared by pouring a solution of the reagent over the supporting medium (either anionotropic, neutral, cationotropic alumina; silica gel; or paper) until the supporting medium was just covered. The container with this mixture was then swirled for 30 seconds. The excess liquid was then decanted, and the process was repeated a second time. After the excess liquid had been decanted the second time, the sample was then placed in a vacuum oven and dried under vacuum at 50 - 60°C. If more than one coating was desired, the above process was

repeated for each coating. The solid sample holder was filled with about 1 cm of the reagent.

Liquid or solution reagents were simply mixed and poured into the 50 ml round bottom flask. The level of the liquid was never over two-thirds of the volume of the flask, or less than one-fourth inch above the bottom of the glass frit.

Coupling of liquid reagents was done by adding the coupling agent to a test tube containing about 5 ml of the reagent to a test tube containing about 5 ml of the reagent that had been previously exposed to ozone. About 5 ml of distilled and de-ionized water was added to the test tube to hydrolyze the ozonide. This mixture was then placed in a constant temperature aluminum block set at about 60°C for about 20 minutes. The amount of coupling reagent was never measured, but an estimate would be between 0.05 and 0.10 g. The amount was gauged by using the same spatula each time, and withdrawing, as closely as possible the same apparent volume.

All samples were exposed to a stream of air from ozone generator which was set at 1000 ppb. This setting was calibrated after this study was completed and found to correspond to a concentration of 1560 ppb ozone.

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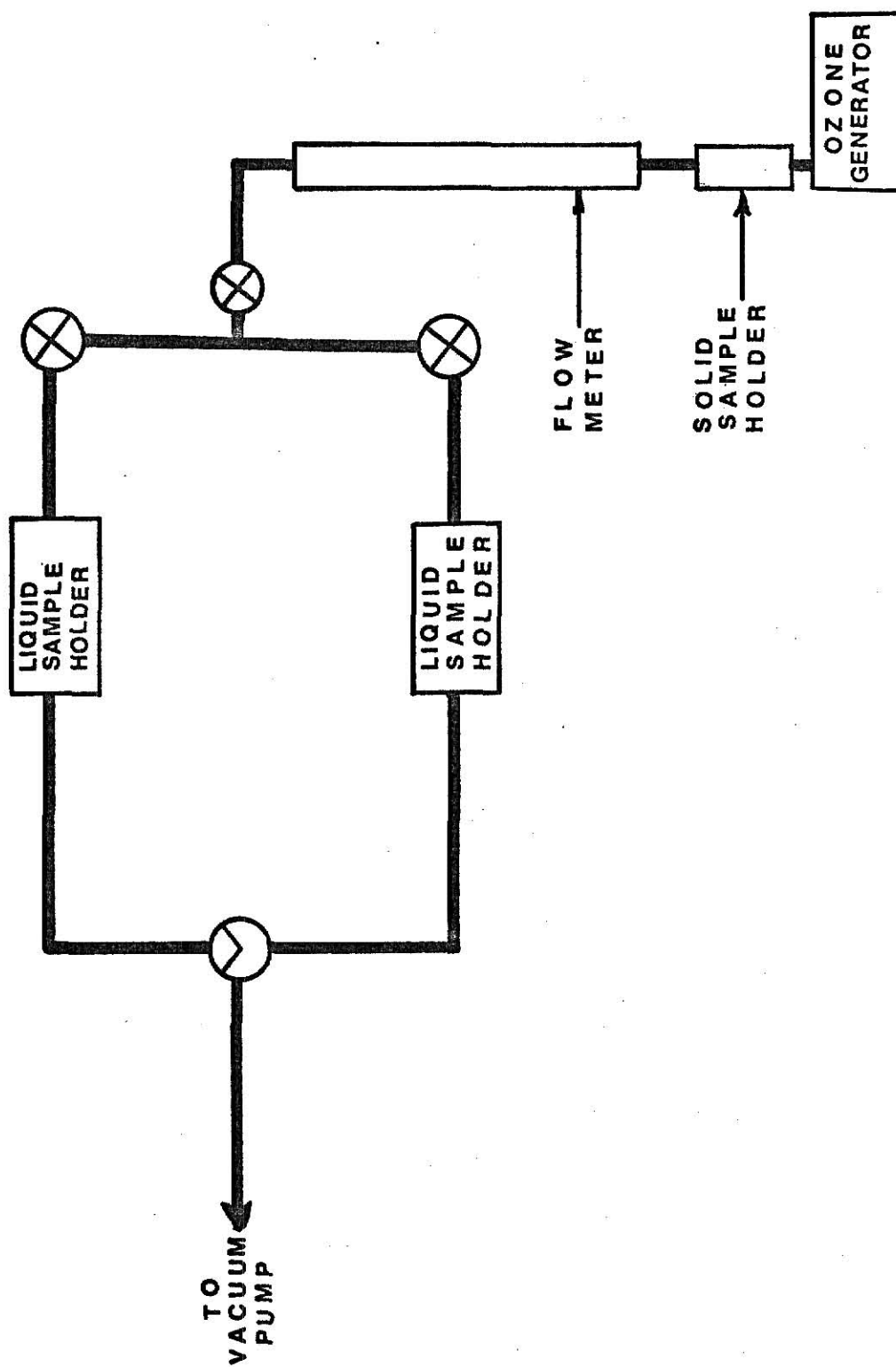


Figure 1. Testing Apparatus

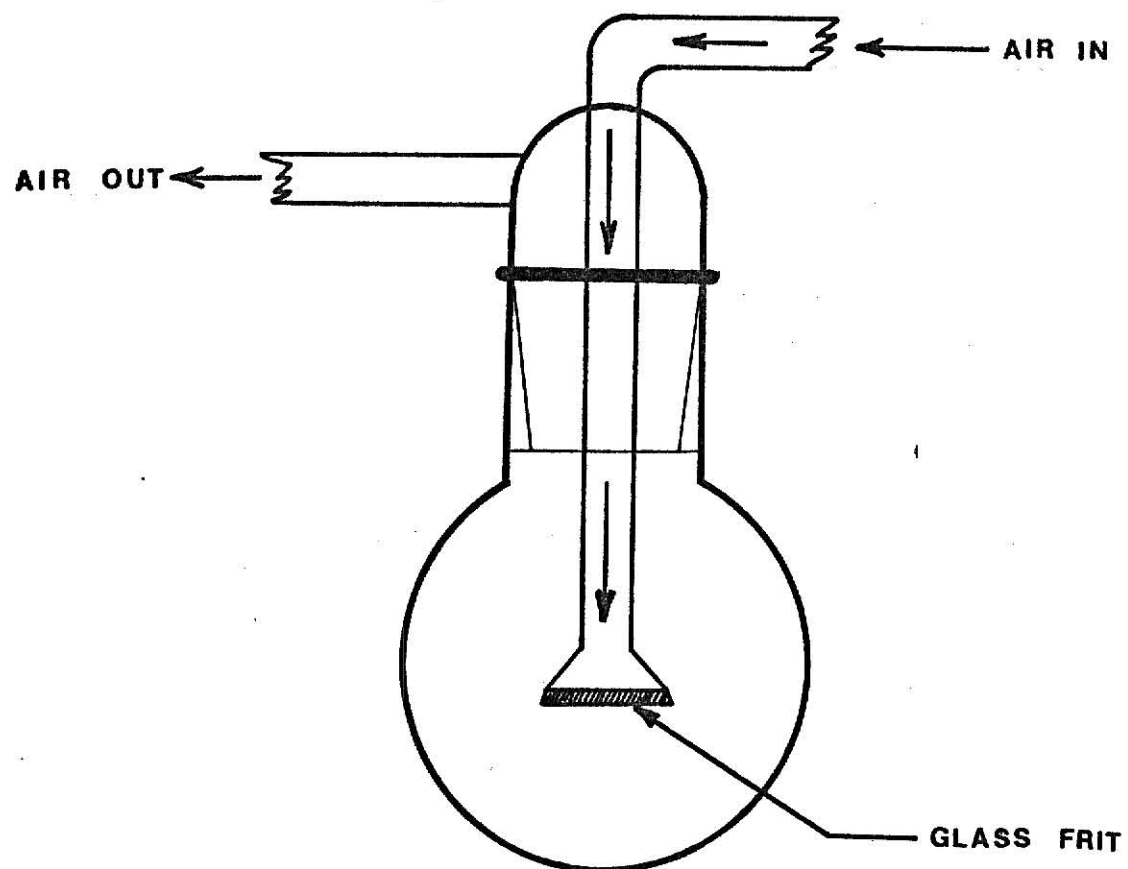


Figure 2. Liquid Sample Holder

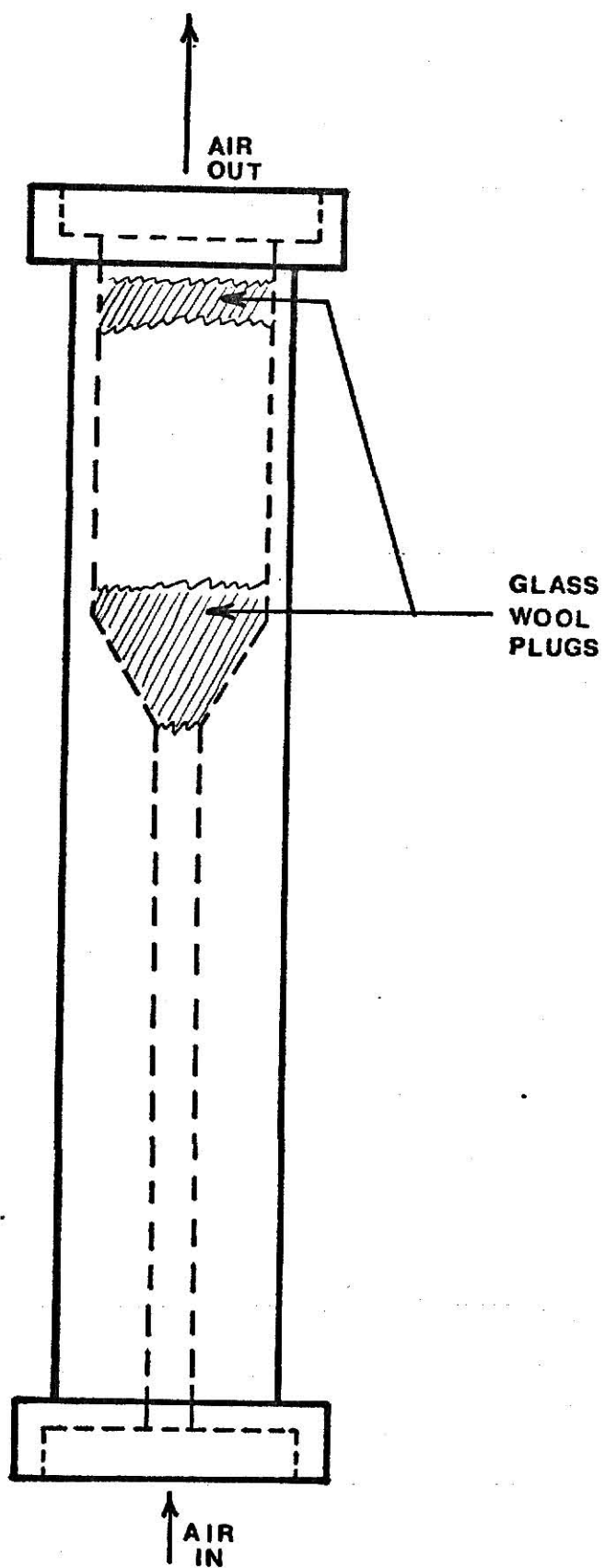


Figure 3..Solid Sample Holder

Results and Discussion

Table 1 shows the results of the solid reagent tests. The brownish color in the samples containing potassium iodide were probably due to the oxidation of potassium iodide in the standard method used for ozone analysis, but the response was poor. Also the reagents appeared to fade in almost every case. The best response was obtained from N-phenyl-2-naphthylamine and iminostilbene.

Table 2 shows the results of a preliminary run to determine suitable solvents for non-aqueous runs.

Table 3 shows the results of some miscellaneous runs in aqueous solutions.

Table 4 shows the results of the coupling reactions. It was impossible to develop a color with both the coupling reagent and the reacting reagent present in the same solution. As it was possible to develop a color by adding the coupling reagent after the reacting reagent had been exposed to ozone, it is concluded that the coupling reagent must react with ozone, and thus be deactivated as a coupling agent. Thus after exposing the reacting solution to ozone, the coupling agent was added to complete the color reaction. This procedure may be used to obtain more accurate readings in the laboratory. The coupling reactions were discarded because there does not appear to be a coupling agent that will couple with aldehydes to give a color and yet not be deactivated by ozone.

The brown color produced with iminostilbene in the solid state (Table 1) with thiobarbituric acid was not characteristic of the compounds that underwent the coupling reactions. Since thiobarbituric acid is also an acid that could form salts with the various amines and imines, and since the color produced by N-phenyl-2-naphthylamine, it appeared that the various arylamines should be studied.

It was possible to cause N-phenyl-2-naphthylamine to turn brown when not coated on a supporting media by exposing it to the ozone stream (1560 ppm ozone) for longer than 24 hours. It took several weeks to cause a sample of about 1 gram to appear to turn completely brown. However, recrystallization from an ethanol-water mixture showed that very little of the starting material had reacted. There was not a sufficient quantity of material for analysis.

The reagents shown in Table 3 were chosen at random. The color changes were either bleaching or else the color intensity was not sufficient for use as a coating on supporting media.

TABLE 1
INITIAL SOLID REAGENT STUDY

Solution used for coating (in order of use)	Support medium	Gas flow rate (l/min)	Results
1) $K_3(Fe(CN)_6)$ in water	anionotropic alumina	3.0	light brown ring formed at about 100 seconds
2) 1.5 ml eugenol in 25 ml acetone			
1) $(CdI_4)^-$ 0.45 g KI^+ 0.5 g CdI_2 in 100 ml water	silica gel	3.4	brownish-yellow band formed by 80 seconds started to fade at 150 seconds
2) saturated starch in water			color gone by 400 seconds
N-phenyl-2- naphthylamine (0.1 g in 250 ml $CHCl_3$)	paper	4.0	paper turned light orange- brown by 13 minutes
N-phenyl-2- naphthylamine (0.1 g in 250 ml $CHCl_3$)	neutral alumina	3.0	orange-brown color by 40 sec sample completely colored by 400 sec
1) Saturated starch	neutral alumina	2.5	slight yellowish- brown color at 100 seconds
2) KI			entire sample colored by 700 sec
N-phenyl-1- naphthylamine (0.1 g in 250 ml $CHCl_3$)	filter paper	---	sample decomposed before run could be made
N-phwnyl-2- naphthylamine (no solvent)	none	2.5	no color change after 20 minutes

TABLE 1 (continued)

Solution used for coating (in order of use)	Support medium	Gas flow rate (l/min)	Results
1) KI 2) AgNO_3 (0.11 g in 100 ml water 3) $(\text{HgI}_3)^-$ 0.18 g KI 0.60 g HgI_2 in 100 ml water	anionotropic alumina	3.4	no color developed after 20 minutes
1) $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ 2) KI	cationotropic alumina	2.7	yellowish-brown color after 100 seconds color began to fade at 300 seconds color gone by 600 seconds
iminostilbene thiobarbituric acid salt (1.4 g thiobarbituric acid, 0.2 g iminostilbene in 95% ethanol)	silica gel	3.0	brown color appeared at about 300 seconds
iminostilbene in 95% ethanol	neutral alumina	3.0	no color change after 20 minutes

* water is distilled and deionized water

TABLE 2
ORGANIC SOLVENT STUDY

<u>SOLVENT</u>	<u>REACTION WITH OZONE</u>
CCl_4	passed ozone
CHCl_3	absorbed ozone slightly
$\text{CH}_3\text{CH}_2\text{OH}$	completely absorbed ozone
CH_3OH	passed ozone
$\text{C}_6\text{H}_5\text{NO}_2$	passed ozone
$\text{C}_6\text{H}_5\text{Cl}$	passed ozone

TABLE 3
AQUEOUS SOLUTION REAGENTS

<u>REAGENT</u>	<u>RESULTS</u>
2-hydrazino-4-hydroxy- 6-methyl pyrimidine	solution clear at the start turned pink by the end of two hours
violuric acid	solution clear at start turned pink after two hours
1-(2-hydroxy-1-naphthylazo) -2-naphthol-4-sulfonic acid zinc salt	solution was opaque and purple in color at start turned yellow by the end of two hours
4-(8-hydroxy-5-quinolyazo)- benzene-sulfonic acid	solution was red at start became yellow by the end of two hours
4-amino-3-hydrazino-5- mercapto-1,2,4-triazole	solution started clear turned yellow by the end of two hours
salt prepared by adding 0.288 g thiobarbituric acid to 0.182 g 1,2-di-(4-pyridyl) ethylene	no color change after two hours
salt prepared by adding 0.256 g barbituric acid to 0.182 g 1,2-di-(4-pyridyl) ethylene	no color change after two hours

TABLE 4
COUPLING REACTIONS

REAGENT	SOLVENT	EXPOSURE TIME (HOURS)	COLOR WITH BARBITURIC ACID	COLOR WITH THIOBARBITURIC ACID
cycloheptatriene	CCl ₄	4	orange	not run
1,2-di-(4-pyridyl) ethylene	acetic acid	2	yellow	yellowish- orange
bicyclo(2.2.1) hepta-2,5-diene	acetic acid	4	yellow	deep yellow
acenaphthylene	CCl ₄	4	water layer yellow	water layer red
diaminomalonitrile	acetic acid	2	the sample produced a yellow color during the exposure to ozone	
1,4-cyclohexadiene	acetic acid	2	yellow	orange
angelica lactone	acetic acid	4	light yellow	dark yellow
4,4'-diamino- stilbene-2,2'- disulfonic acid	acetic acid	2	yellow	yellow
iminazole	acetic acid	2	slight yellow	slight yellow
pyrazole	acetic acid	2	yellow	yellow

* The acetic acid was glacial acetic acid of reagent grade.

III. Studies of Solid Ozone Reagents

Bovee and Robinson used a solution of 1% sodium diphenylaminesulfonate to determine ozone concentrations down to 0.1 ppm (6). N-tetramethyldiaminodiphenylmethane has been proposed as an ozone detector in dilute acetic acid medium, and for continuous colorimetric determination in citric acid solution (7). A combination of diphenylamine and oxalic acid can be used as an indicator for oxidants when coated on a silica gel thin-layer chromatography plate (8). Silica gel has been found to adsorb ozone to a great extent (9).

Experimental

The apparatus used for the tests was the same one described in Chapter II. Only solid samples were run. The support medium used was exclusively silica gel (specifications: ICN Pharmaceuticals Inc., Woelm, 0.05 - 0.20 mm, for column chromatography). All other reagents were of reagent grade or higher purity. The apparatus used for the interference studies was constructed of Pyrex glass, with Teflon needle valves. This apparatus is shown in Figure 4. The sample holder consisted of a 6 mm Pyrex glass tube with two small indentations to support the sample, shown in Figure 5. A quartz glass wool plug was tamped flat onto the indentations, using a 3 mm Pyrex glass tube, to support the

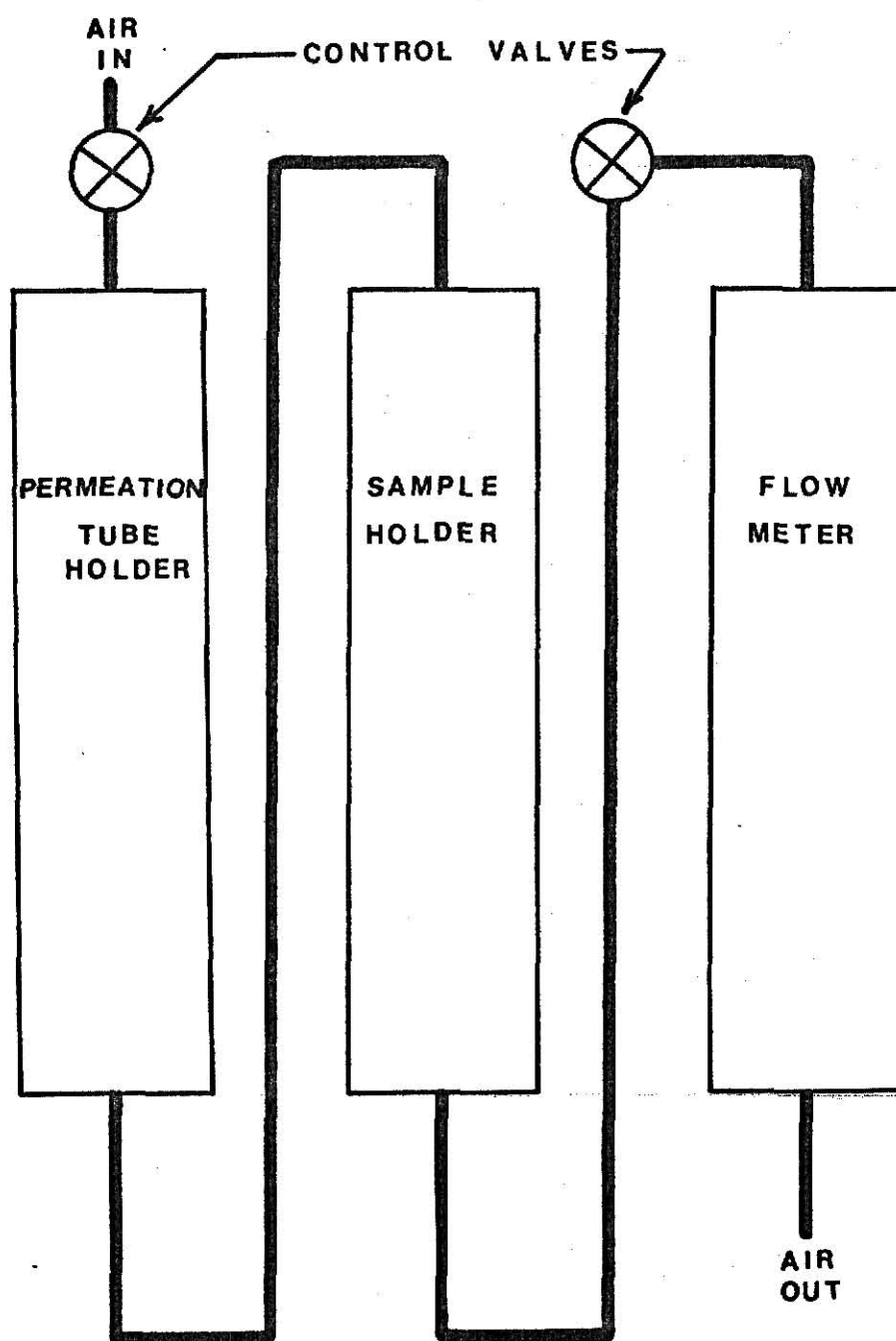


Figure 4. Apparatus used for interference runs.

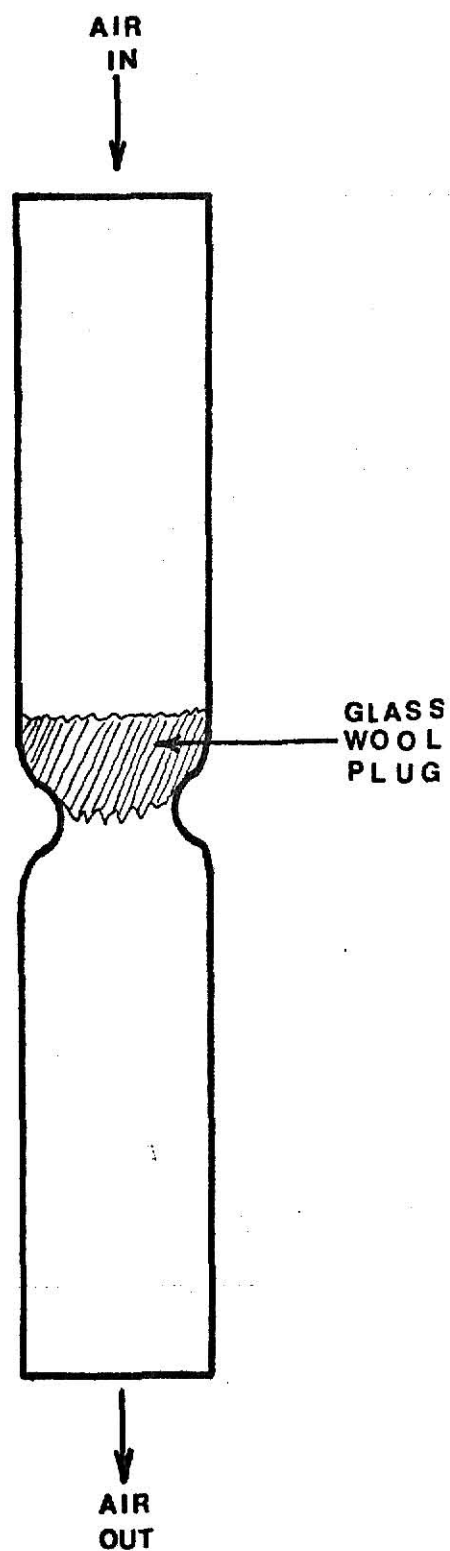


Figure 5. Solid sample holder used.

sample. A new sample holder was used for each run. The ozone apparatus was modified to accept this type of solid sample holder, prior to the interference studies, as shown in Figure 6.

Procedure

The samples were prepared by dissolving 0.1 g of the reagent to be tested in 100 ml of 95% ethanol (except the samples for the interference studies where methanol was used). For the runs with acids, the acid was added after the reagent to be studied had dissolved. The solid acids were added on an equal molar basis to the reagent alcohol solution. Hydrochloric acid was added by pouring 10 ml of concentrated hydrochloric acid into the reagent mixture; the excess was removed by the drying process. The silica gel was coated as described in chapter II. Sample drying was carried out at room temperature in a vacuum oven, as heating seemed to affect some of the reagents slightly.

The samples were allowed to dry overnight and were stored under vacuum between tests. The vacuum system employed for all but the interference studies was a water aspirator which pulled a vacuum of about 25 inches of mercury. A vacuum pump was installed for the interference studies, and a vacuum of 29 inches of mercury was obtained.

The ozone generator output was calibrated by inserting two impingers in the line in place of the solid sample holder. The second impinger was used as a scrubber. The first impinger was filled with a 25 ml aliquot of a potassium iodide solution (10.0 g KI + 4.0 g NaOH in 1 liter of water). The air from the

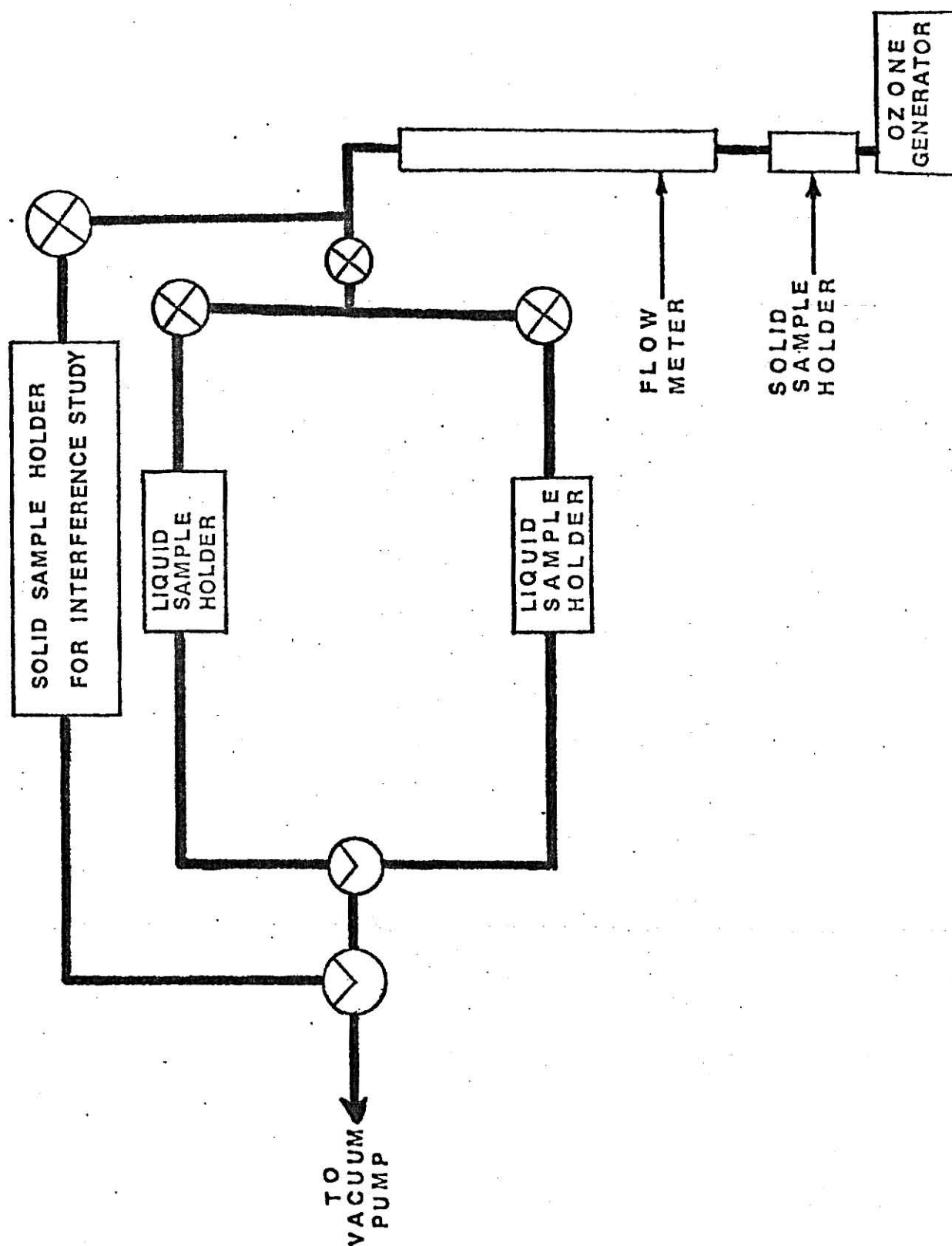


Figure 6. Modification made to ozone testing apparatus

ozone generator was passed through the impinger at 900 ml/min, the same rate used for all samples in this chapter. After a sufficient time, the contents of the first impinger were transferred quantitatively to a 50 ml volumetric flask. Two ml of a 6:1 dilution of glacial acetic acid was added to the sample, and the sample diluted to volume. The mixture was allowed to stand for at least four minutes, and the absorbance then measured at 352 nm. A standard curve (Figure 7) was prepared using potassium iodate standards and calculations were made following the procedure set down in the Byers and Saltzman method (3). The only change was that 6:1 dilution of glacial acetic acid was substituted for the phosphoric acid. All reagents were tested for response time at a setting of 300 ppb (this corresponds to an actual output of 250 ppb).

The water referred to in this chapter was distilled and deionized.

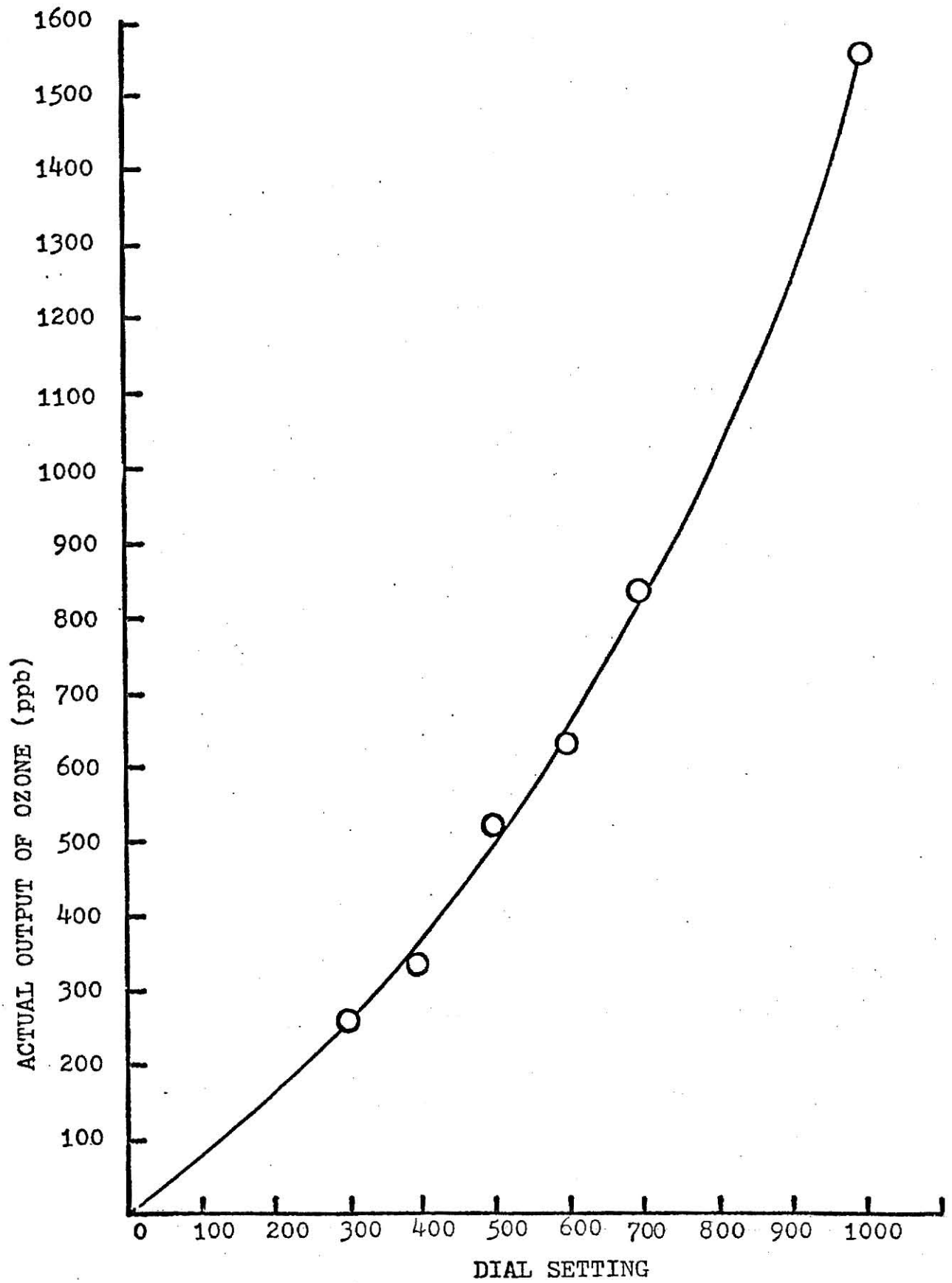


Figure 7. Calibration curve for ozone generator

Results and Discussion

The effects of acid on the response of the reagent can be seen in Table 5. Generally the response is increased with the addition of an acid. The most suitable acid was hydrochloric acid, because of the ease of sample preparation and the fact that reagents appeared to give a slightly better response with hydrochloric acid. Hydrochloric acid caused a better response than oxalic acid, but both hydrochloric and oxalic acid performed better than sulfamic acid. Sulfuric, nitric, and phosphoric acids were not tested because of problems in removing the excess acid.

Six reagents were deemed suitable for ozone analysis. They are the following: carbazole; N-phenyl-2-naphthylamine; iminostilbene; diphenylamine; iminobenzyl; and diphenylamine sulfonic acid sodium salt. The criteria for this choice was based on the fact that these compounds gave immediate and definite color changes when exposed to the 1560 ppb ozone stream. The main interferences with ozone reagents are chlorine, nitrogen dioxide, and sulfur dioxide. Chlorine interference studies were not carried out since there was no apparatus available to do so. Nitrogen dioxide and sulfur dioxide interference studies were made. Sulfur dioxide proved to enhance rather than interfere with the sensitivity of the reagents. Several reagents actually seemed to have better response after exposure to sulfur dioxide. Nitrogen dioxide is somewhat of an interferent. All six compounds showed a color when exposed to nitrogen dioxide. However, the

colors produced were different from the colors produced from exposure to ozone in every case. Table 6 shows the results of the interference study. Table 7 shows the results of the response study at 250 ppb.

TABLE 5

EFFECTS OF ACID ON REAGENTS (1560 ppb ozone)

<u>REAGENT</u>	<u>ACID</u>	<u>RESULTS</u>
iminostilbene	oxalic	reagent is yellow; formed brown ring immediately after exposure to ozone
	HCl	same as oxalic acid
N-phenyl-2-naphthylamine	HCl	immediate formation of a brown ring upon exposure to the ozone stream
	sulfamic	brown color formed after 1 min
trimethylamine	HCl	No color produced
2,4-quinolinediol	HCl	sample slowly formed a deep yellow color
2-hydrazino-4-hydroxy-6-methyl-pyrimidine	HCl	no color developed after 3 hours
	oxalic	slowly formed pink color
4,4'-methylene-bis-(n,n-dimethyl aniline)	HCl	immediately turned blue when exposed to ozone the entire sample turned blue while setting on top of the desk in a 1 dram vial
di-2-naphthylamine	oxalic	brown ring formed after 1 minute
triphenylamine	HCl	showed brown ring after 5 minutes
iminodibenzyl	HCl	formed greenish ring after 1 min
N-(1-naphthyl)-ethylenediamine	HCl	turned reddish brown after 1 min
diphenylamine-sulfonic acid sodium salt	none	sample turned yellow-orange after 1 minute
	HCl	sample immediately turned yellow then green, and finally black

TABLE 5 (continued)

<u>REAGENT</u>	<u>ACID</u>	<u>RESULTS</u>
phenoxazine	none	turned dirty brown after 1 min
	HCl	immediately began to form brown color
phenazine	none	no color after 20 minutes
	HCl	no color after 20 minutes
pheonthioazine	none	turned reddish-brown after 1 minute
	HCl	sample almost immediately began to turn brown
carbazole	none	slowly turned brown
	HCl	sample developed a blue color which quickly turned brown

TABLE 6

INTERFERENCE STUDY

SO₂ concentration 282 ppb; NO₂ concentration 749 ppb; ozone concentration 250 ppb

<u>REAGENT(+HCl)</u>	<u>INTERFERENCE</u>	<u>RESULTS</u>	<u>OZONE RUN</u>
carbazole	NO ₂ /1135 sec	light green color	color at 150 sec
	SO ₂ /1017 sec	no change	not run
N-phenyl-2-naphthylamine	NO ₂ /1105 sec	bright yellow	color at 157 sec
	SO ₂ /3685 sec	no change	not run
iminostilbene	NO ₂ /1500 sec	deep yellow	color at 150 sec
	SO ₂ /1003 sec	no change	not run
iminodibenzyl	NO ₂ /1003 sec	bright green	no color after 3 minutes
	SO ₂ /1007 sec	no change	color at 100 sec
diphenylamine	NO ₂ /300 sec	dark green	color at 30 sec
	SO ₂ /1007 sec	no change	color at 30 sec
diphenylamine sulfonic acid sodium salt	NO ₂ /300 sec	yellow	color at 170 sec
	SO ₂ /1165 sec	no change	color at 170 sec

TABLE 7

RESPONSE AT 250 ppb

<u>REAGENT(+HCl)</u>	<u>INITIAL COLOR</u>	<u>RESULTS</u>
iminostilbene	light yellow	produced a brown ring at bottom by 75 sec
diphenylamine	white	produced a greenish-yellow color at bottom by 60 sec
diphenylamine-sulfonic acid	white	formed a purple-blue ring at bottom by 60 sec
carbazole	very light blue	light brown color formed at bottom by 160 sec
N-phenyl-2-naphthylamine	very light tan	brown ring formed at bottom by 90 sec
iminodibenzyl	green	brown ring formed at bottom by 90 sec

Summary

From the interference study it would appear that iminostilbene is an excellent reagent for ozone when coupled with hydrochloric acid. Further, the response at 250 ppb shows that iminostilbene has almost as good a response as any of the other reagents.

Although this survey is complete, there is still much work that can be done. First, thin layer chromatography plates should be coated and their response checked against the loose silica gel. Also a static system should be designed. The system used in this thesis was a dynamic system, which means that diffusion was neglected. In factory or other enclosures the air would more closely approach the static system. In which case diffusion would become more important and response may change. The use of selective membranes would make the reagents responsive to partial pressures of the ozone. This method would require the study of many membranes to determine which membranes would pass ozone.

The solid reagent offers a quick and easy method of semi-quantitative measurement since color charts can be prepared and used for comparison. Precise determinations could be made when the sample is returned to the laboratory and more accurate reading obtained with a spectrophotometer. More work is needed to find a method for eluting the reagent off the silica gel and reading the absorbance of the sample.

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VITA

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AN ABSTRACT OF A MASTER'S THESIS

submitted in partial fulfillment of the
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Department of Chemistry

KANSAS STATE UNIVERSITY
Manhattan, Kansas

1976

New reagents for quantitative analysis of ozone are proposed. Two methods are explored. The first uses the coupling of barbituric and thiobarbituric acids with the aldehyde; formed by the reaction of ozone with a carbon-carbon double bond and followed by hydrolysis of the ozonide. This method employs solution chemistry.

The second method employs solid media. Phenyl- and naphthylamine are found to turn brown when coated on silica gel. Acid salts of the amines are found to have greater sensitivity. The following six reagents are found to have suitable sensitivity for ozone analysis: diphenylamine-sulfonic acid sodium salt; carbazole; N-phenyl-2-naphthylamine; ininostilbene; iminodibenzyl; and diphenylamine. These reagents work best when combined with hydrochloric acid. Subsequent treatment of the arylamine salts with sulfur dioxide appeared to enhance the response of the reagents.