1974

The Measurement of Sulfuric Acid Aerosol and the Total Sulfate Content of Ambient Air.

Ray Frank Maddalone
Louisiana State University and Agricultural & Mechanical College

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THE MEASUREMENT OF SULFURIC ACID AEROSOL
AND THE TOTAL SULFATE CONTENT OF AMBIENT AIR

A Dissertation

Submitted to the graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of

Doctor of Philosophy

in

The Department of Chemistry

by

Ray F. Maddalone
B.S., University of Notre Dame, 1970

December, 1974

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TABLE OF CONTENTS

	<u>PAGE</u>
ACKNOWLEDGEMENTS.....	ii
LIST OF TABLES.....	v
LIST OF FIGURES.....	vi
ABSTRACT.....	vii
PART I -- INTRODUCTION.....	2
CHAPTER I. Sulfuric Acid Aerosol as an Air Pollutant....	3
A. Background and Emission Sources of Sulfuric Acid	3
B. Characterization and Health Effects of Sulfuric Acid Aerosol.....	4
CHAPTER II. Previous Attempts at Measuring Sulfuric Acid Aerosol.....	8
A. Measurement of Sulfuric Acid Aerosol as Protons.	9
B. Measurement of Sulfuric Acid Aerosol as Sulfate.	11
PART II -- MEASUREMENT OF SULFURIC ACID AEROSOL.....	13
CHAPTER III. Separation of Sulfuric Aerosol from the Gross Filter Sample.....	14
A. Previous Attempts at the Separation of Sulfuric Aerosol from the Gross Filter Sample.....	14
B. Microdiffusion of Sulfuric Acid Aerosol from Various Filter Media.....	16
1. Experimental.....	16
a. Reagents.....	16
b. Apparatus.....	17
c. Procedure.....	18
2. Results and Discussion.....	21
a. Microdiffusion from Glass Plates.....	21
b. Microdiffusion from Glass Fiber Filters.	28
c. Microdiffusion from Other Filter Media..	32
3. Conclusions.....	40

	<u>PAGE</u>
CHAPTER IV. Reduction of Sulfate to Sulfur Dioxide via Thermal Degradation of Perimidyl- ammonium Sulfate.....	41
A. Previous Attempts at Sulfate Reduction.....	41
1. Experimental.....	42
a. Reagents.....	42
b. Apparatus.....	43
c. Procedure.....	49
B. Results and Discussion.....	50
CHAPTER V. Measurement of Sulfuric Acid Aerosol and the Total Sulfate Content of the Ambient Air.	65
A. Previous Attempts at Measuring Sulfuric Acid in the Air.....	65
1. Experimental.....	66
a. Reagents.....	66
b. Apparatus.....	66
c. Procedure.....	67
i. Extraction Procedure (Total Sul- fate Method).....	68
ii. Diffusion-Pyrolysis Method (Sul- furic Acid Aerosol Method).....	69
B. Results and Discussion.....	70
1. Total Sulfate Method.....	70
2. Sulfuric Acid Aerosol Method.....	71
C. Summary.....	81
REFERENCES.....	82
APPENDIX I.....	86
VITA.....	87

LIST OF TABLES

<u>TABLE</u>		<u>PAGE</u>
I.	Diffusion at 195° from Glass Plate Using Polished Petri Dishes - Effect of Time.....	22
II.	Results of Diffusion from a 16 mm Disc of Gilman A Glass Fiber at 195° After Various Washes.....	29
III.	Amount of Sulfuric Acid Found on Glass Plate for Different Size Petri Dishes and 8 mm Filter.....	34
IV.	Precision of the Pyrolytic Sulfate Method.....	63
V.	Coefficient of Variance for the Extraction Procedure Analysis of Generated Aerosol Samples at Several Concentrations.....	72
VI.	Coefficient of Variance for the Diffusion-Pyrolysis Analysis of Generated Aerosol Samples at Several Concentrations.....	79

LIST OF FIGURES

<u>FIGURE</u>		<u>PAGE</u>
1.	Microdiffusion Apparatus.....	20
2.	Microdiffusion of Sulfuric Acid from Glass Plates <u>vs.</u> Temperature.....	25
3.	Microdiffusion from Polished <u>vs.</u> Unpolished Petri Dishes.....	27
4.	Microdiffusion from Poco Graphite Filters for 3 Hours at 195°.....	37
5.	Microdiffusion from Mitex Teflon Filters for 3 Hours at 195° (Δ) and for 6 Hours at 125° (⊙).....	39
6.	Combustion Tube and Injector.....	46
7.	Combustion Train.....	48
8.	Differential Thermal Analysis and Differential Scanning Calorimeter of (PDA) ₂ SO ₄	53
9.	Pyrolysis Scheme.....	56
10.	Total Sulfur Analyzer Flow System Diagram.....	59
11.	Pyrolysis Calibration Curve.....	62
12.	Diffusion from Fluoropore Filters for 6 Hours at 125° Using Sulfuric Acid Solutions.....	75
13.	Diffusion from Fluoropore Filters for 6 Hours at 125° Using Generated Sulfuric Acid Aerosols.....	78

ABSTRACT

The advent of the energy crisis has placed a greater reliance on coal and other high sulfur fuels. When any sulfur-containing fuel is burned, sulfur dioxide is released as a by-product. By burning additional amounts of coal, we will be introducing greater amounts of sulfur dioxide into the air. Sulfur dioxide is a toxic pollutant in its own right, but by the action of air, sunlight, and moisture, sulfur dioxide is converted to sulfuric acid aerosol. The main problem with an aerosol is its lack of mobility as compared to a gas such as sulfur dioxide. The low mobility of the acid aerosol raises the possibility of high localized concentrations.

This Dissertation will discuss the measurement of sulfuric acid aerosol, including sampling, separation, and analytical finish. It was evident early in our work that most sulfate methods would not perform properly at the levels necessary (1 to 50 μg). A new method for determining sulfate was developed where sulfate was precipitated as the perimidylammonium sulfate $[(\text{PDA})_2\text{SO}_4]$. When the $(\text{PDA})_2\text{SO}_4$ was heated at 500° in a nitrogen-purged oven, sulfur dioxide is quantitatively evolved. The West-Gaeke procedure was used to measure the evolved sulfur dioxide.

The sampling of the acid was accomplished by using a 0.5 μ Fluoropore Teflon filter. Once a sample was collected, the sulfuric acid was separated from the gross air sample by heating the filter to 125° for 2 hours. A small petri dish was placed over the air sample and the acid was trapped on the inside of the dish by using a suitable

absorbant. It was found that the amount recovered was dependent on the concentration of acid on the filter. There was, however, a plateau reached when 5 or more micrograms of acid were collected. By operating on this plateau, 86% of the sulfuric acid was recovered from the filter. By coating the inside of the petri dishes with perimidylammonium bromide (PDA-Br), $(\text{PDA})_2\text{SO}_4$ was formed directly. Without any further treatment, the petri dishes were heated in the pyrolysis oven and the sulfur dioxide evolved and measured.

The total sulfate content of a filter was determined by extracting a filtered air sample with a 50% methanol-water solution. The sulfate was precipitated by addition of PDA-Br, and the $(\text{PDA})_2\text{SO}_4$ formed was pyrolyzed. By knowing the sampling flowrate and time of sampling, the ambient concentration of sulfuric acid or total sulfate could be calculated from the amount of sulfur dioxide evolved.

PART I

INTRODUCTION

INTRODUCTION

Modern man prides himself on his accomplishments in taming the world and molding it after his fashion. Some feel this progress has been but a shallow victory in light of the price the environment has paid. The problem of pollution, however, is an old one, as early man can verify. He, too, probably turned from those first cooking fires with tears in his eyes and a gag in his throat and asked, "Is this progress?"

CHAPTER I. SULFURIC ACID AEROSOL AS AN AIR POLLUTANT

A. Background and Emission Sources of Sulfuric Acid

In 1273, the English thought London's air was so bad that they banned the burning of sea coal. In 1661, John Evelyn submitted to Charles II a pamphlet entitled, "Fumifugium, or the Smoake (sic) of London Dissipated", in which he predicted many of the problems we have today.¹ The Londoner's distress was due to burning coal in poorly designed furnaces. The resulting smoke contained near-toxic, toxic, and odoriferous components of which sulfur dioxide was one of the more toxic products. Since the energy crisis is upon us, the shortage of domestic gas and oil supplies will force us to use greater amounts of coal. Even low sulfur coal contains more sulfur than a clean fuel like natural gas, and the most plentiful sources of coal in the United States are not of the low sulfur variety. Thus, the United States Congress is debating an upward revision of the maximum allowable sulfur dioxide emission concentrations in order to take advantage of the large coal reserves in the United States. Any retreat from present standards will allow widespread use of coal which previously wasn't possible due to its sulfur content. The revision of the Air Quality Act will also benefit industrial procedures like coke production and ferrous and non-ferrous metallurgical processes which emit sulfur dioxide as a by-product.² All industries will be able to use cheaper, higher sulfur fuels with less pollution control of sulfur dioxide. The net result will be an increase of the sulfur dioxide introduced into the environment.

Sulfur dioxide by itself is harmful, but it has been well documented that in the presence of oxygen, moisture, and sunlight,

sulfur dioxide is converted to sulfuric acid.³ The toxicity of sulfuric acid is much greater than that of sulfur dioxide, and at the same time the sulfuric acid is in the form of a mist. While the sulfur dioxide emitted from any given source will be dissipated in a large volume of air because of its mobility as a gas, the sulfuric acid mist will be much less mobile, and its effect will be localized at the point of its formation. The low mobility and the localized effect of sulfuric acid mist is especially significant when one realizes that some sulfuric acid is produced directly by most sulfur dioxide sources, the amount produced varying according to operational conditions.

Looming on the horizon is a new source of sulfuric acid aerosol, the catalytic converter. Though designed to convert carbon monoxide to carbon dioxide, the catalytic converter has recently⁴ been shown capable of oxidizing sulfur dioxide to sulfur trioxide. The sulfur trioxide in the humid atmosphere of a car's exhaust system would be emitted as sulfuric acid. The danger here is one of localized increases of sulfuric acid causing harm to pedestrians near heavily traveled roads. As of this writing, plans are still set to equip cars with catalytic converters in the 1975 model year.

B. Characterization and Health Effects of Sulfuric Acid Aerosol

Since air pollution studies were initiated, sulfuric acid has been identified in the atmosphere. The toxicity of sulfuric acid in gross quantities is well known, but until recently the effect of sulfuric acid aerosol has not been investigated. Amdur^{5,6} exposed laboratory animals to various amounts of sulfuric acid aerosol. She found

that exposure to sulfuric acid resulted in narrowed air passages caused by bronchostenosis, mucosal swelling or increased secretion. As a result of these effects, people who already have trouble breathing (the old, asthmatic, or heart patients) can be killed not by the direct corrosive qualities of sulfuric acid, but by the respiratory strain that sulfuric acid aerosol places on an already stressed person.

The correlation between high concentrations of sulfuric acid aerosol and deaths resulting from respiratory distress was not immediately apparent. In most air pollution episodes many other pollutants were present at high levels. For example, during the Meuse Valley fog⁷ of 1930, sulfur dioxide levels as high as 8 ppm were found. That level was high, but not fatally toxic, yet 63 people were killed in a 5-day period. Fricket⁷ was the first to note that only those areas that were subjected to emissions from heavy industry and fog exhibited excess mortality rates. Fricket also found that in previous fogs, excess mortalities (deaths above statistical average for a given period of time) occurred during times of industrial activity. Fricket warned that if the same event happened in London, death rates as high as 3,200 could be expected.

The disaster that Fricket predicted took place in London in 1952. For the period of December 5 through 9 a total of 3,500 to 4,000 excess mortalities was recorded. The sulfur dioxide levels only reached 1.34 ppm, but the suspended particulate matter⁸ was found to be 4,500 $\mu\text{g}/\text{m}^3$. This extremely high concentration of suspended material, and the fact that all deaths were characterized by respiratory tract irritation, implicated some agent other than sulfur dioxide. The prime candidate was sulfuric acid which as we have already stated can be formed in the atmosphere by photo-oxidation of sulfur dioxide. The end

result is the formation of a highly toxic atmospheric aerosol which contains sulfuric acid by itself or attached to suspended particulate matter.

Another facet of the sulfuric acid toxicity problem is the result of the relationship between particle size and depth of penetration into the lungs. Particles above $2\ \mu$ in diameter are normally trapped in the upper respiratory tract and expelled, while particles in the $0.1\ \mu$ to $2\ \mu$ range will penetrate deep into the lung, where the most damage can occur. Several researchers⁹⁻¹² have studied the particle size distribution for sulfate aerosols. Their results are in good agreement as a range of 0.35 to $0.45\ \mu$ for the mass median diameter was found. One study¹¹ commented that 80 to 90% of the sulfate measured was in the respirable range. Amdur⁵ confirmed that the effect of the aerosol depended on particle size. She found as the particle size was decreased, an increase was noted in the flow resistance to respiration in animals. Other sulfates produced similar results. A comparison of zinc ammonium sulfate, zinc sulfate and ammonium sulfate showed zinc ammonium sulfate to be the worst irritant. When zinc ammonium sulfate and sulfuric acid aerosol of equal particle size were compared, sulfuric acid was the greater irritant.*

This dependence on particle size was aptly illustrated by the Donora, Pennsylvania fog (1948) which killed 17, and left 43% of the 14,000 people affected.¹³ Though other air pollution episodes have occurred in the U.S. (Detroit¹⁴ and New York¹⁵), the Donora episode

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*This comparison has not been explored completely. For some of the added problems involved in the comparison, see Amdur ref. 5.

was unique since the calls for assistance ceased on the fifth day even though the fog remained quite dense. It is quite possible that the fog droplets containing sulfuric acid underwent a physical change. A simple maturation of the fog droplets due to a change in meteorological conditions could easily have converted the small toxic droplets to large non-toxic droplets. Thus the fog remained, but its toxicity decreased.

The lack of any suitable method to measure sulfuric acid as such precludes any direct statement on the actual agent responsible for the deaths in the above air pollution episodes. The weight of evidence strongly suggests that sulfuric acid aerosol was the killer.

CHAPTER II. PREVIOUS ATTEMPTS AT MEASURING SULFURIC ACID AEROSOL

Once sulfuric acid and sulfates were implicated as severe respiratory irritants, investigators began to look for sulfuric acid in the air samples with a variety of methods. The accuracy of their results not only depended on the skill of the investigator, but more often on his or her luck in making the proper assumption. Most investigators assumed that either the total acidity or the total sulfate found was due to the sulfuric acid. In some samples this assumption would be valid, but in most it would not. Thus, the literature is littered with terms like "acid sulfate", "particulate acid" or "fixed soluble sulfate", depending upon whether the method employed measured protons or the sulfate anion. Such terms only hide the fact that there is no method available today for the measurement of sulfuric acid as an identifiable species. The numbers that have been obtained are the result of fairly complicated or tedious procedures. In order to appreciate the problem better, one must realize that in a city like Pittsburgh a typical summer air sample would contain approximately 12-16 $\mu\text{g}/\text{m}^3$ of sulfuric acid aerosol.¹⁰ Sulfuric acid aerosol was measured by the same method in London, and concentrations of 7 $\mu\text{g}/\text{m}^3$ and 18 $\mu\text{g}/\text{m}^3$ were found in summer and winter, respectively.¹⁸ Thus, any method used must be quite sensitive unless extremely large air samples are to be collected.

The above values can only be used to indicate the concentration of sulfuric acid found in the atmosphere. Because of the sampling procedure used (collection on Whatman No. 1 filter paper), alkaline materials present in the air sample would react with the sulfuric acid collected on the filter's surface, and reduce the amount of acid measured.

One must understand that an air sample is mostly particulate matter of which sulfuric acid comprises less than 1%. The possibility of topographical chemical reactions occurring between carbonates, metal oxides or fly ash, and sulfuric acid increases as the unused surface of the filter is decreased during prolonged sampling. Thus, if large samples are taken, the possibility of interference is increased and the results of the method is suspect. A short review of sulfuric acid aerosol methods based on proton or sulfate measurements follows.

A. Measurement of Sulfuric Acid Aerosol as Protons

Early investigators using the measurement of acidity as a measure of sulfuric acid concentration assumed that the acidity found was directly related to sulfuric acid aerosol. As information on the make-up of air samples grew, investigators realized that other acidic compounds existed in the atmosphere. Later methods employed corrections for this possibility. Coste and Courtier¹⁷ removed the sulfur dioxide from an air sample and then saturated the resultant air stream with water vapor. The sulfuric acid aerosol particles would act as nuclei, so that sulfuric acid could be condensed in a flask immersed in ice. The acidity was measured by direct titration. One of the drawbacks of this approach was the small sample (1 m^3) collected over a long period of time (24 hours). Goodeve¹⁸ recommended filtering air samples with asbestos-packed Gooch crucibles, but that method was too slow and the filtration efficiency varied. Mader, *et al.*,¹⁹ used Whatman No. 4 filters, that had been washed in copious amounts of distilled water and then dried, to sample the Los Angeles atmosphere. After a sample was collected, the filters were placed in a

flask and macerated, the pH was measured. Mader found sulfuric acid aerosol concentrations to be 0.036 ppm or $36 \mu\text{g}/\text{m}^3$. This number is high, and probably is the result of sulfur dioxide adsorbing on the filter surface and then oxidizing to sulfuric acid. Mader mentioned this as a drawback, especially in humid air samples.

Commings¹⁸ proposed a method for measuring sulfuric acid aerosol by titration to pH 7 with acid after a known excess of sodium tetraborate was added. Commings' method took into account interferences such as sulfur dioxide and basic gases, but it could not differentiate between sulfuric acid and other acid components.

Acid indicators have been used in a variety of ways for qualitative measurements of acidity in air samples. Waller²⁰ collected London air by impaction on glass slides coated with gelatin containing thymol blue. When viewed under a microscope, strongly acidic droplets were seen as pink spots. Derre and Pfeifer²¹ used a similar approach except the plates were coated with nitrocellulose and 5,5'-methylene-disalicylic acid. After exposure to the atmosphere, the plates were heated producing red spots where the acid droplets landed. Horstman and Wagman²² collected sulfuric acid aerosol on a slide coated with iron deposited by vacuum distillation. The particle size was estimated by viewing the size of the reaction site on the iron film. Honma and Sakito²³ used a photo-electric colorimeter to quantitatively measure the sulfuric acid aerosol collected on the metal film.

In summary, most of these methods make the assumption that all acidity is due to sulfuric acid in the atmosphere. Those methods that attempt to measure sulfuric acid specifically, require complicated or tedious procedures.

B. Measurement of Sulfuric Acid Aerosol as Sulfate

In this section a review of sulfate methods will be presented. Some researchers who applied these methods to an air sample made the assumption that all sulfate present was due to sulfuric acid. Andronov, et al.,²⁴ simply washed a filter with aqueous-acetone or ethanol mixtures and measured the "sulfuric acid" as sulfate with barium rhodizionate. Obviously the sulfate measured did not correspond to sulfuric acid, but was a measure of the total sulfate content of the air sample. Capkeviciene²⁵ collected an air sample in distilled water. The sulfate was precipitated by addition of benzidine. The benzidine sulfate was isolated and coupled with thymol to produce a red product. The intensity of the coloration was proportional to the amount of benzidine sulfate isolated. Bavika, et al.,²⁶ measured sulfuric acid by impingement in distilled water followed by the addition of ammonium vanadate, which produced a yellow solution.

Ellis²⁷ passed an air sample through a bubbler containing hydrogen peroxide. Any sulfur dioxide present in the air sample would be collected and oxidized to sulfate, while any particulate acid (i.e., sulfuric acid) would be scrubbed from the air flow. The same air was analyzed for its sulfur dioxide content by a redox reaction with iodine. The sulfate content of the hydrogen peroxide trap was determined, and the amount of sulfate due to the oxidation of sulfur dioxide was subtracted. The value left was considered by Ellis to be the sulfuric acid content of the air sampled. Ellis overlooked (or did not know in 1931) that soluble sulfates were present in an air sample. Even sulfates like calcium sulfate are soluble at the microgram level. Thus,

without a prior separation step to remove the sulfuric acid from the gross air sample, the measurement of the sulfate content will only provide data on the total sulfate content of the sample.*

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*For a further summary of sulfate methods see references 28 through 32.

PART II

MEASUREMENT OF SULFURIC ACID AEROSOL

CHAPTER III. SEPARATION OF SULFURIC ACID AEROSOL FROM THE GROSS FILTER SAMPLE

A. Previous Attempts at the Separation of Sulfuric Acid Aerosol From The Gross Filter Sample

As was shown in the previous Chapter, values found for the acidity or sulfate content of an air sample are not a true measure of the concentration of sulfuric acid. Simply measuring the acidity or sulfate content of a collected air sample will only give values for the net acidity (since other acidic or alkaline materials are present) or total sulfate (since other sulfate species are present). The preferred mode of analysis would be to analyze for sulfate, since the sulfate will always be there, while protons tend to find a base and react before they have been determined. But before one could analyze for sulfuric acid as sulfate, a separation step must be applied to remove the sulfuric acid from the gross air sample. The lack of an adequate pre-analysis separation step has prevented the measurement of sulfuric acid aerosol as sulfate.

Several investigators have attempted to separate sulfuric acid aerosol from the gross air sample either by extraction or by selective distillation. Barton and McAdie^{33,34} have published papers dealing with glass fiber filter pretreatment, as well as on the selective extraction of sulfuric acid from Nucleopore polycarbonate membrane filters. Their method, using 1-propanol, looked extremely promising, but recently³⁵ 1-propanol has been shown to extract ammonium sulfate and possibly other sulfates. Experiments described in this Dissertation have confirmed that 1-propanol will not selectively extract sulfuric

acid. Also, Barton and McAdie's method of pretreating glass fiber filters was found to be inadequate. The evidence for this will be discussed in the following section.

Recently Leahy, et al.,³⁶ have proposed benzaldehyde as a selective solvent for sulfuric acid. Separations based on the use of this solvent appear to be free of interferences, and open the door to the use of any common sulfate method, once the sulfuric acid is removed from the gross sample. The separation procedure, however, was tested using samples well above normal environmental levels.

Since sulfuric acid is volatile compared to most compounds present in a filtered air sample, Dubois, et al.,³⁷ sought to isothermally distill or micro-diffuse the sulfuric acid from the surface of the filter. Their method consisted of taking a 47 mm diameter disc from an 8 x 10-inch glass fiber filter. This filter disc was covered by a petri dish whose inside top had been coated with sodium hydroxide. The whole apparatus was placed in a nitrogen-purged oven and heated overnight at 195°. The sulfuric acid diffused from the glass fiber to the sodium hydroxide, and was trapped. The following morning the tops were washed with a small amount of water, and the sulfuric acid was determined as sulfate by any one of a number of methods. Since this approach showed promise, we initiated a tracer study to investigate whether some sulfuric acid could have been lost in the sampling procedure, and whether or not an absolute amount of sulfuric acid was separated from the filter.

B. Microdiffusion of Sulfuric Acid Aerosol from Various Filter Media

1. Experimental

a. Reagents

Absorbing Solution - Two grams of reagent grade sodium hydroxide were dissolved in 5 ml of water and made up to 100 ml with absolute ethanol. This solution was made fresh daily.

Sodium Hydroxide - Reagent grade, low in carbonate from Fisher Scientific Company.

Ammonium Sulfate - Reagent grade from Fisher Scientific Company.

Ethanol - Absolute ethanol from U. S. Industrial Chemicals Company.

$H_2^{35}SO_4 + H_2SO_4$ Solutions - Portions of a 1 ml carrier-free $H_2^{35}SO_4$ solution containing 5 mc/ml from New England Nuclear were added to 0.01 $\mu\text{g}/\mu\text{l}$, 0.1 $\mu\text{g}/\mu\text{l}$ and 1.0 $\mu\text{g}/\mu\text{l}$ sulfuric acid solutions to give an appropriate activity ($\sim 40,000$ to $70,000$ cpm). The sulfuric acid was reagent grade from Mallenckrodt Chemical Works.

p--Dioxane - Reagent grade from Matheson, Coleman and Bell.

Naphthalene - Recrystallized from ethanol, reagent grade naphthalene was obtained from Matheson, Coleman and Bell.

2,2'-p-Phenylenebis-(5-phenyloxazole) - the POPOP was scintillation grade from Matheson, Coleman and Bell.

2,5-Diphenyloxazole - the PPO was scintillation grade from Matheson, Coleman and Bell.

Scintillation Cocktail - 300 g of naphthalene, 15 g of PPO and 0.15 g POPOP were placed in 3 liters of p-dioxane. To 17 ml of

this solution, 3 ml of water rinses were added, bringing the total volume in the scintillation vial to 20 ml.

b. Apparatus

Oven - Sargent Analytical Oven (low gradient) equipped with a nitrogen purge.

Pyrex Petri Dishes - Petri dish bottoms (Corning No. 3160) approximately 49 mm ID x 14 mm were used. The bottoms were used as purchased but with the edges ground to give a smooth seal with the glass plates.

Glass Vials - Vials of 15 mm, 19 mm, and 25 mm OD were cut ~ 5 mm from the bottom to provide dishes of various ID's. Also, several more dishes were made from Pyrex tubing of 8 and 11 mm diameter.

Scintillation Vials - Disposable 20 ml capacity scintillation vials of Kimble No. 74500 or equivalent were used.

Plate Glass - Single strength window pane glass was cut into 63 mm squares.

Pipets - Radioactive solutions were pipetted with an Eppendorf 10 or 50 μ l capacity pipet.

Liquid Scintillation Counters - All counting was done on either a Beckman Liquid Scintillation System II or Beckman LS-250 Liquid Scintillator.

Thermogravimetric Analyzer - Dupont 950 TGA.

Filters - The following filters were tested for their micro-diffusion qualities:

Mitex (Teflon) from the Millipore Corporation (5.0 μ)
Solvinert from the Millipore Corporation (0.5 μ)
Nucleopore from General Electric (1.0 μ)

Graphite filter from Spectrogram Corporation; North
Haven, Connecticut

Whatman 41

Gelman A glass fiber filter from Gelman Instrument Com-
pany.

c. Procedure

In order to approximate a sulfuric acid aerosol, 10 to 50 μ l of the appropriate $\text{H}_2\text{S}^{35}\text{O}_4$ solution were placed on the glass plate or the filter media and dried for 15 min. at 80° . No $\text{H}_2\text{S}^{35}\text{O}_4$ was lost, although the water was removed.

The apparatus used (Figure 1) differed slightly from that of Dubois.³⁷ Instead of using both a top and bottom petri dish, only one dish was used (as the top) and a treated glass plate served as a bottom. This configuration approximated that of Dubois while allowing the entire inside of the petri dish to be coated.

The preheated (60°) petri dish was coated with 0.15 ml of the sodium hydroxide solution just before it was used. This minimized absorption of carbon dioxide from the air. After the tops were placed over the glass plates or filter media, the entire apparatus was placed in an oven at an appropriate temperature and time. The oven was constantly purged with nitrogen and a vent line was run into a bottle of 1 M sodium hydroxide to prevent any contamination of the laboratory from volatilized $\text{H}_2\text{S}^{35}\text{O}_4$.

Labeled standards were placed on the glass plates or on the filter media and treated the same as the samples except they were not microdiffused. All data on the percentage recovery on sodium hydroxide as well as mass balance data were based on a comparison to these non-microdiffused standards.

FIGURE 1
MICRODIFFUSION APPARATUS

DIFFUSION APPARATUS

The samples were removed from the oven, and still covered, allowed to cool to room temperature. The petri dish and glass plate were then rinsed with 3 milliliters of water and the washings placed in a scintillation vial. Filter media were placed directly into the scintillation vial and the 3 milliliters of water were added. The petri dishes and the glass plates were then air-dried, broken, and placed into separate scintillation vials to determine mass balance data. The smaller dishes were simply dropped into the vial and 3 ml of water added. The scintillation vials were then filled with 17 ml of the scintillation cocktail and counted for 10 min. or to 0.5% error, whichever came first.

Although the general procedure remained the same, the individual experiments varied in regard to temperature, time and filter media. Specific changes such as filter media size and petri dish diameter will be noted in the discussion.

2. Results and Discussion

a. Microdiffusion from Glass Plates

Before testing filter media for diffusion properties, a study of the microdiffusion apparatus was undertaken. A 63 mm piece of single strength window glass was used as the bottom and a 49 mm ID x 14 mm Pyrex petri dish as the top (Figure 1). The chemical composition of the window glass approximated that of the glass fiber in the filters. Thus, apparatus design and diffusion conditions could be projected. The relative utility of polished and unpolished petri dish rims was studied.

Table I summarizes the initial experiments. Quite unexpectedly, only 40% of the sulfuric acid was found to diffuse from the untreated

TABLE I
 DIFFUSION AT 195° FROM GLASS PLATE
 USING POLISHED PETRI DISHES - EFFECT OF TIME

-----% Recovered on Petri Dish----- Time (hr.)					Avg. Mass Balance	Treatment of Plate
1	2	4	6	Avg.		
38.0	43.0	39.0	43.9	41.0	96.6	None
-	-	71.8	71.1	71.5	87.5	Conc. H ₂ SO ₄ Baked at 195° C
47.6	48.0	50.2	54.3	50.0	97.8	Boiled in 1:1 H ₂ SO ₄ , H ₂ O Rinse

glass. Even after placing several drops of concentrated sulfuric acid on the plate, heating in an oven at 195° to evaporate the sulfuric acid and then placing spiked sulfuric acid on the treated area, only 71% diffused and the total amount recovered dropped to 87%. As an alternate choice, the glass plates were boiled in 1:1 sulfuric acid and rinsed in water. This was chosen as the preferred treatment for all of the glass plates. Figure 2 gives a summary of results of diffusion at temperatures of 100° , 125° , 150° , 175° and 195° using polished petri dishes, and averaging the results of the 1, 2, 4 and 6 hour runs for each temperature.

As can be seen, the best percentage of separation occurred at 125° . One possible reason for the decrease in diffusion as the temperature was increased from 125° to 195° could be the result of a trade-off between vaporization vs. chemical reactivity. Referring to Table I, time had little effect on the amount diffused. The average range of separation for all temperatures between 1 and 6 hours was 6%. Since vaporization (at or above 125°) is immediate, the added temperature apparently served only to increase the rate of attack of sulfuric acid toward the glass plate.

Figure 3 compares the 2-hour data at various temperatures for unpolished and polished petri dishes. The data for the polished petri dishes did not include data from the 1, 4 or 6-hour runs as Figure 2 does. Consequently, neglecting the points at 150° for unpolished petri dishes and at 125° for polished petri dishes, the results are linear indicating that the unpolished are better than the polished petri dishes. The mass balance, however, for the unpolished petri dishes is 5 to 10% less than the polished petri dishes. In subsequent studies, only petri dishes with unpolished rims were used.

FIGURE 2

MICRODIFFUSION OF SULFURIC ACID FROM
GLASS PLATES VS. TEMPERATURE

FIGURE 3
MICRODIFFUSION FROM POLISHED VS.
UNPOLISHED PETRI DISHES

b. Microdiffusion from Glass Fiber Filters

After the design of the separation apparatus was optimized and some of the operating parameters were established, a study of glass fiber filters was initiated. Several surprising problems were disclosed.

Experiments were made using 16 mm circular discs cut from an untreated 8 x 10-inch sheet of Gelman A glass fiber filter. A 49 mm ID x 14 mm petri dish and a glass plate were used as described in the Experimental Section. Ten microliters of spiked 1 $\mu\text{g}/\mu\text{l}$ sulfuric acid were placed on the center of a disc and dried. The first separations were attempted using a purged oven at 125° for 6 hours. No diffusion occurred. Consequently, the filter was washed in various acids and the experiment was repeated. In all cases the results were negative.

Because 125° was 70° below the temperature at which Dubois, et al.,³⁷ did their work, the experiments were repeated at 195°. Again no diffusion was observed (Table II).

Barton and McAdie³⁴ have published a method based on the pre-treatment of the glass fiber with sulfuric acid, water, 80% isopropanol, and finally acetone. When their system was used, a small amount of diffusion was noted, but the results were insufficient to warrant further study (Table II).

It was possible that the affinity of the glass fiber for sulfuric acid was such that the sulfuric acid did not diffuse. On the other hand, it was possible that a neutralization was occurring on the surface of the glass fibers. To test the latter hypothesis, 50 μl of a spiked 1 $\mu\text{g}/\mu\text{l}$ sulfuric acid solution were placed on three 16 mm discs of Gelman A glass fiber that had been treated by the Barton and McAdie method.

The three discs were extracted with 3 ml of warm distilled water. One milliliter of the extract was centrifuged to remove the

TABLE II
RESULTS OF DIFFUSION FROM A 16 mm DISC OF
GELMAN A GLASS FIBER AT 195° AFTER VARIOUS WASHES

Treatment	Time	Activity on NaOH
Untreated	6 hr.	0.034%
Boiled in H ₂ O, blotted and dried at 80° C	6 hr.	0.051%
Boiled in 1:1 CH ₂ O, blotted and dried at 80° C	6 hr.	0.30%
Boiled in 1:1 HCl	6 hr.	0.32%
Boiled in 1:1 H ₃ PO ₄ , rinsed in 1% H ₃ PO ₄ and dried at 80° C	6 hr.	1.0%
Soaked in 20% H ₂ SO ₄ for 3 days; boiled for 10 min.; rinsed in H ₂ O, 80% isopropanol, and acetone; then air dried.	6 hr.	3.5%
Soaked in 20% H ₂ SO ₄ for 3 days; boiled for 10 min.; rinsed in H ₂ O, 80% isopropanol, and acetone; then air dried.	12 hr.	4.0%

solids. Fifty microliters of this centrifuged extract were then diffused from a treated glass plate using an unpolished 49 mm x 14 mm petri dish for 6 hours at 125°. As previously shown (Figure 2), approximately 65% of the sample should have diffused; however, no diffusion occurred.

The lack of diffusion could be attributed to the neutralization of the sulfuric acid by the glass fiber filter. In order to measure the glass fiber filter's capacity to neutralize the sulfuric acid, 50 μ l aliquots of an unspiked 1 μ g/ μ l of sulfuric acid were placed on the untreated 16 mm glass fiber filter disc and dried. Ten microliters of the spiked 1 μ g/ μ l sulfuric acid solution were then placed on the disc, dried and diffused.

Even 200 μ g of sulfuric acid did not neutralize the available alkaline sites. A possible explanation for these results is the penetration ability of the sulfuric acid solution to the alkaline sites. It must be remembered that neutralization products (sodium chloride, sodium sulfate, sodium phosphate or sodium acetate), depending on what acid is used to pre-treat the filter, are soluble in water. A solution of sulfuric acid could dissolve and expose new alkaline sites underneath the neutralized layer. Furthermore, solutions tend to spread over the glass fibers in a thin film. Consequently, more of the sulfuric acid solution is exposed to the alkaline sites. On the other hand, the lack of wetting power of concentrated acids prevents the natural sulfuric acid aerosol from penetrating to the alkaline sites under the neutralized layer. Rather they tend to coalesce into droplets leaving only the bottom edges exposed to the filter surface.

It is possible, therefore, that the first few hours of a high volume sampling serves to neutralize most of the alkaline sites. Sulfuric acid aerosol acid then can sit on a neutralized layer and for the above reasons not penetrate to new alkaline sites. Dubois, et al.,³⁸ have also used this reasoning to explain why the concentration of sulfates in air depends on the sampling volume.

Before turning to other types of filters, investigations were made regarding the volatility of ammonium sulfate and the use of isopropanol as a selective solvent for sulfuric acid.

Dubois, et al.,³⁷ mentioned that ammonium sulfate could be used as a standard for diffusion at 195°. Consequently, this species would be an interference if it were present in an air sample. A thermal gravimetric analysis was made of a finely ground reagent grade ammonium sulfate in nitrogen atmosphere. Decomposition started at 250° and a second slope occurred after 340°. Erdey, et al.,³⁹ reported similar results and also included a differential thermal analysis. They reported the following reactions at the indicated temperature ranges:

Using a scan rate of 5°/min. no loss of sample was observed until 250°. An isothermal TGA run at 175° and 205° showed a 1.8% and 8.2% weight loss for a 3-hour period. Assuming this weight loss to be linear, a loss of 9.6% and 43.7% at 175° and 205°, respectively, for overnight (16 hours) heating would be expected. Proper choice of time and temperature can minimize the effect of ammonium sulfate as an interferant.

Finally, 10 μ l of a spiked 1 μ g/ μ l solution of sulfuric acid were placed on two 16 mm discs of glass fiber and dried at 80° for 5 min. The discs were placed in separate scintillation vials, and 3 mls of isopropanol added. After shaking the vials for several minutes, the isopropanol was poured off into another vial. The extract, filters and standards were counted and it was found that 50% of the activity was in the extract. From our previous results we believed the 10 μ g of sulfuric acid to be completely neutralized and consequently, the isopropanol in this crude extraction removed 50% of the sulfuric acid as a salt. It appears that at this concentration, isopropanol is not a selective solvent for sulfuric acid.

c. Microdiffusion from Other Filter Media

Several other filter papers and membranes were tested. Included in the group were: Nucleopore, Whatman 41, Solvinert, Spectrogram Corporation 47-XA3 Poco Graphite filter (experimental) and Mitex (Teflon). The glass apparatus shown in Figure 1 was also used in these experiments.

Nucleopore was tested at 100° for 6 hours with no diffusion observed. Both Whatman 41 and Solvinert were run at 125° for 6 hours. Whatman 41 exhibited no diffusion while the Solvinert had 13.5% diffusion. In both cases, 10 μ g samples of spiked sulfuric acid were used. Whatman 41 and Nucleopore both had a 49 mm ID petri dish as the absorbing dish while a 13 mm ID x 5 mm dish was used for the Solvinert study.

The Poco graphite filter was tried next. The filters were 47 mm in diameter, brittle yet slightly flexible. Using a stainless steel cork borer mounted on a drill press, 8 mm diameter discs were cut from the 47 mm disc. Using the standard 49 mm ID petri dish and glass

plate, 10 μ l of the 1 μ g/ μ l spiked sulfuric acid solution were placed on the filter disc. The water was driven off at 80° for 10 min. and then diffused at 195° for 6 hours. The results were encouraging as only 1.6% was left on the filter and 60% microdiffused to the sodium hydroxide. Another temperature was tried (150°/6 hrs.) but the amount of sulfuric acid left on the filter increased to 9.2% while the microdiffused portion was 57%. A time plot of 1, 2, 4 and 6 hours at 195° was run and it was found that 3 hours was sufficient to reduce the amount left on the filter to ~ 3%.

In doing a mass balance on the above systems, it was found that 30% of the activity was left on the glass plate. Since the filter only covered a small part of the glass plate under the petri dish, the 49 mm ID petri dish was replaced with a 13 mm and 9 mm ID dish, both approximately 10 mm high. The experiment (195°/3 hrs.) was repeated with the 8 mm graphite filter. The results (Table III) showed that the amount of sulfuric acid found on the glass plate was directly related to the area of the exposed glass plate beneath the petri dish. In order to minimize the loss of sulfuric acid to the glass plate, the ID of the petri dish should nearly match the diameter of the filter disc used.

At first these results seemed surprising, but they can be understood in terms of a diffusion controlled reaction. The sulfuric acid vaporizes uniformly throughout the diffusion system. The filter is inert and only minimal amounts remain there while the soft glass plate and the sodium hydroxide offer excellent neutralization sites. Consequently, after subtracting the area covered by the filter, the sulfuric acid uniformly spreads itself about the inside area. As will

TABLE III
AMOUNT OF SULFURIC ACID FOUND ON GLASS PLATE
FOR DIFFERENT SIZE PETRI DISHES AND 8 mm FILTER

ID of Petri Dish	Exposed Glass Plate as % of Total Inside Area	% Sulfuric Acid on Glass Plate
49 mm	31.0	31.1
13 mm	11.4	12.9
9 mm	3.1	5.1

be seen in Chapter V, it will be necessary to trap the sulfuric acid on the absorber, so in this and all future work the entire inside of the petri dish was coated with an absorber.

The Mitex Teflon filters were tested next. In this case a 13 mm ID x 5 mm dish was used. The 47 mm diameter disc was cut into quarters and 10 μ l of a spiked 1 μ g/ μ l solution of sulfuric acid was placed on the filter. The sodium hydroxide coated dish was centered over the dried solution and then diffused.

The first temperature tried was 125° and heating was carried out for 3 and 6 hours with 79% and 85% of the sulfuric acid applied respectively, diffused to the sodium hydroxide with approximately 9% left on the filter. Under the same arrangement the filters were heated at 195° for 3 hours. In this case, 82% microdiffused while 6% remained on the filter. Both temperatures seemed to work equally well so it was decided to run a calibration curve from 0.1 to 50 μ g sulfuric acid for the Mitex filter at 125° for 6 hours and at 195° for 3 hours. Concurrently, a similar calibration curve was run for the Poco graphite filter at 195° for 3 hours. The results of these studies are shown in Figures 4 and 5.

The graphs show a distinct cut-off for the lower limit of diffusion. For the system of 13 mm ID dishes, the value was 10 μ g. At first, it was believed that a neutralization was again affecting the system. It is, however, unlikely that two unrelated filter materials would show the same neutralization characteristics. Neutralization is also unlikely as increasing the temperature from 125° to 195° increased the amount of sulfuric acid microdiffused at 5 μ g from 3 to 19% for the Mitex filter (Figure 5). Later experiments presented in Chapter V will clarify the situation further.

FIGURE 4
MICRODIFFUSION FROM POCO GRAPHITE FILTERS
FOR 3 HOURS AT 195°

FIGURE 5

MICRODIFFUSION FROM MITEX TEFLON FILTERS

FOR 3 HOURS AT 195° (Δ) AND FOR 6 HOURS AT 125° ($\odot$)

3. Conclusions

From these investigations the following observations can be made:

1. Since the sulfuric acid diffuses throughout the entire inside of the apparatus, the microdiffusion apparatus should be modified to a system in which the absorbing substance covers the entire inside surface except that area covered by the filters.
2. The inner diameter of the cover dish should exactly (within 1 mm) match the diameter of the filter media.
3. Glass fiber filters should not be used as a sulfuric acid sampling medium.
4. Suitable filters for collecting sulfuric acid aerosol can be made of pure Teflon or graphite.
5. Isopropanol should not be considered to be a selective solvent for sulfuric acid.

The application of these results awaited only a proper analytical finish. The development of this new approach to sulfate analysis will be discussed in the following chapter.

CHAPTER IV. REDUCTION OF SULFATE TO SULFUR DIOXIDE
VIA THERMAL DEGRADATION OF PERIMIDYLAMMONIUM SULFATE

A. Previous Attempts at Sulfate Reduction

Once a separation procedure had been worked out, the next step in the determination of sulfuric acid aerosol was the development of a suitable analytical finish for sulfate. Since both the West-Gaeke⁴⁰ and the flame photometric⁴¹ approach offered specific and sensitive methods for measuring sulfur dioxide, the catalytic reduction of sulfate to sulfur dioxide appeared to be an attractive approach. A search of the literature showed that several investigators had attempted to reduce sulfates or oxidize sulfur to sulfur dioxide.

Heslinga, in 1925⁴² determined sulfur by burning samples in a quartz tube and completing the combustion by passing the gases over hot quartz chips. The sulfur gases were absorbed in a hydrogen peroxide solution, and the sulfur titrated as sulfuric acid. Other investigators refined the apparatus of Heslinga.⁴³⁻⁴⁵

Kristen⁴⁶ volatilized residual sulfur from the ash of certain biological materials by heating the sample in a combustion tube with vanadium pentoxide. Hagerman and Faust⁴⁷ used vanadium pentoxide fusion to measure sulfur in refractory materials, while Larsen, et al.,⁴⁸ employed the same approach to analyze uranium trioxide, sodium zirconium fluoride and hydrofluoric acid. The interesting part of Larsen's work was the reduction of the initially produced sulfur trioxide over copper at 950°. The sulfur dioxide produced was trapped in tetrachloro-mercurate(II) and measured by the West-Gaeke procedure.

The measurement of sulfuric acid aerosol was attempted by Scaringelli and Rehme.⁴⁹ Sulfuric acid (vaporized from glass fiber filters) or sulfur trioxide (produced when copper impactors were heated) was reduced over copper at 500°. Aside from its drawbacks in measuring sulfuric acid aerosol (see Chapter V), the method required complicated equipment and extremely tedious procedures. Except for sulfuric acid, ammonium sulfate, ammonium hydrogen sulfate and copper sulfate,⁴⁹ the remaining sulfates decomposed above 400°.

For a flexible sulfate determination, a system was sought which would not require drastic heating for reduction. A search was initiated for an organic amine which would both precipitate sulfate and upon heating, promote the reduction of sulfate to sulfur dioxide. In early 1970, Stephen³¹ proposed a new nephelometric sulfate determination based on the precipitation of sulfate by perimidylammonium chloride (PDA-Cl). The solubility of the precipitated perimidylammonium sulfate $[(\text{PDA})_2\text{SO}_4]$ is somewhat less than that of barium sulfate. This low solubility made $(\text{PDA})_2\text{SO}_4$ the most insoluble organic amine sulfate known. McClure⁵⁰ synthesized Stephen's reagent via cyanogen bromide and 1,8-diaminonaphthalene, producing the bromide salt which was used in all of our studies.

1. Experimental

a. Reagents

Perimidylammonium Bromide, 0.5% - Fifty milligrams of PDA-Br synthesized according to McClure⁵⁰ and recrystallized twice from methanol was added to 10 ml of distilled water. This solution was made fresh daily.

Potassium Sulfate Stock Solution - 1.81 grams of freshly dried reagent grade potassium sulfate were added to 1 liter of distilled water to give a solution 1 $\mu\text{g}/\mu\text{l}$ as sulfate. Solutions containing 0.1 $\mu\text{g}/\mu\text{l}$ of sulfate were made up by dilution of the stock solution.

Sodium Tetrachloromercurate(II), 0.1 M - Reagent grade mercury(II) chloride (27.2 g) and reagent grade sodium chloride (11.2 g) were dissolved and diluted with distilled water.

Formaldehyde Solution, 0.2% - 0.5 ml of 40% formaldehyde solution was added to 100 ml of distilled water. This solution was made fresh daily.

Pararosaniline Hydrochloride - 0.64 g of reagent grade pararosaniline hydrochloride was added to 240 ml of concentrated HCl, and diluted to 1 liter with distilled water. Twenty-five ml of this solution were diluted to 100 ml with distilled water to provide the working solution.

Nitrogen - Pre-purified.

Oxygen - Pre-purified.

b. Apparatus

Spectrophotometer - Beckman DB.

Sulfur Dioxide Permeation Tubes - Six mm ID x 120 mm Teflon tubes containing liquid sulfur dioxide and stoppered at both ends with Teflon plugs were placed in a controlled temperature cell. At constant temperature the rate of permeation of sulfur dioxide through the Teflon tube was also constant. The permeation rate was determined by repeated weighing of the tubes over an extended time period. In this case the permeation rate of sulfur dioxide was found to be 10.07 $\mu\text{g}/\text{min}$.

Pyrolysis Oven - A Sargent microcombustion furnace (S-21580) was modified to accept a 25 to 33 mm OD quartz tube. The original heating coils were retained, but a No. 50122-Type 1708-KSP Lindburg cylindrical heating block was added to the top hinge of the oven. The Lindburg was controlled by a separate Variac.

Combustion Train - At one end of a 25 mm OD x 65 mm quartz tube a 33 mm OD 3/4/45 female ground glass joint was attached. The other end of this 25 mm OD quartz tube was fitted with an 11 mm OD x 60 mm 18/9 Vycor male ball joint. A bubbler was connected to the quartz tube via 6 mm ID Teflon tubing, glass tubing and a Pyrex 18/9 female ball joint (see Figures 6 and 7).

Injector System - A 3/4/45 Pyrex male ground glass joint was fitted on its center line with a 12 mm OD x 30 mm Pyrex tube. This tube was blown with an inside depression half-way down its length enabling it to accept a Viton high temperature O-ring (11 mm OD). A 9.5 mm OD Teflon sleeve with a 6.5 mm center tap was inserted into the 12 mm OD tube. A 6 mm OD x 80 mm quartz rod with a fork designed to hold a 15 mm OD dish at one end was inserted through the Teflon sleeve. By means of another Viton O-ring (6 mm ID) and Teflon washer, the system was made air-tight. Finally, at 90° to the center line of the 3/4/45 male joint, a 10 mm piece of 7 mm OD Pyrex tubing was added to the side of the joint to act as an inlet/outlet port (see Figure 6).

Flame Photometric Detector - A Bendix Model 8300 and a Meloy SA-102 Total Sulfur Analyzer were used as SO₂ monitors.

Pipets - Solutions were pipetted with a 10 or 50 µg Eppendorf pipet.

FIGURE 6
COMBUSTION TUBE AND INJECTOR

COMBUSTION TUBE & INJECTOR

FIGURE 7
COMBUSTION TRAIN

COMBUSTION TRAIN

Glass Dishes - Soft glass vials, 15 mm OD x 120 mm, were cut 15 mm from the bottom to provide dishes for the precipitation of standard sulfate solutions.

Thermogravimetric Analyzer and Differential Scanning Calorimeter - Dupont 950 TGA and DSC was used.

Flowmeters - Lab-crest rotameters of appropriate ranges were used. These were accurate to $\pm 2\%$ of full scale.

c. Procedure

Samples of sulfate were placed in 15 mm OD x 15 mm glass dishes, and 200 μ l of a 0.5% PDA-Br water solution were added. A silky white precipitate was immediately formed. After precipitation was complete (approximately 10 minutes), the dishes were placed in an oven set at 80° to evaporate the excess liquid. With the pyrolysis oven set at 500°, the nitrogen flowrate at 500 ml/min., and 10 ml of 0.1 M tetrachloromercurate(II) in the bubbler, the samples were ready to be pyrolyzed.

By proper manipulation (see Figure 7) of the 4-way valves and a 3-way stopcock, the nitrogen flow was fed through the injector, past the hot zone, and into the West-Gaeke trap (pyrolysis mode), or the flow was reversed so the nitrogen would pass through the 3-way stopcock, back through the oven, and out the injector male joint (backflush mode). This flow system allowed the oven to operate continually while a nitrogen blanket was maintained in the quartz combustion tube.

A typical pyrolysis cycle would be:

1. Pull the injector rod out of the hot zone.
2. Remove the tetrachloromercurate(II) solution from the bubbler.

3. Reverse the nitrogen flow to the backflush mode.
4. Remove the entire injector system at the 34/45 joint.
5. Place a fresh sample on the injector fork.
6. Replace the injector in the 34/45 joint.
7. Place the nitrogen flow in the pyrolysis mode.
8. Replace the tetrachloromercurate(II) solution in the bubbler.
9. Slide the injector rod into the center of the oven.
10. Heat the sample for 2.5 minutes.

This entire cycle, including replacing the West-Gaeke trap, would take approximately 3.5 minutes.

After several pyrolysis runs, the quartz tube immediately outside of the oven on the bubbler side of the oven collected a small amount of organic debris. The Teflon and glass tubing leading to the bubbler were also coated with this material. The sulfur dioxide evolved during the pyrolysis was not adsorbed on this material, but as a precaution the quartz tube was periodically cleaned. The quartz tube was disconnected from the system at the ball joint, and retracted into the oven. At the same time oxygen was fed into the quartz tube, and the temperature was raised to 700°. While the quartz tube was being heated, the rest of the combustion train was rinsed with acetone and allowed to air dry. Within 10 minutes, the combustion train was ready for use.

B. Results and Discussion

In order to check the efficiency of the reduction of sulfate to sulfur dioxide, a standard curve of net absorbance versus micrograms of sulfur dioxide was established for the West-Gaeke procedure. A dry

air stream was passed through the thermostated cell containing the sulfur dioxide permeation tube, and was scrubbed in a bubbler containing 10 ml of 0.1 M tetrachloromercurate(II). The contents of the bubbler were diluted to 250 ml with 0.1 M tetrachloromercurate(II) to provide a stock solution containing 2.5 μg sulfur dioxide in each milliliter. Using this stock solution, a standard curve was plotted from 0 to 20 μg of sulfur dioxide.

Following McClure's⁵⁰ procedure, a sufficient quantity of PDA-Br, though light and moisture sensitive, could be stored up to a month before an increase in the blank values was noted. Solutions of PDA-Br were normally made fresh daily, but if kept in an amber bottle, they could be used for a week.

A 0.5% solution of PDA-Br was made as suggested by Stephen,³¹ and was mixed with small amounts of sulfate in a test tube. The precipitate was collected by centrifugation, and was washed several times in methanol to remove the excess PDA-Br and water. After the $(\text{PDA})_2\text{SO}_4$ was dried in an oven at 80° , a Thermogravimetric Analysis and a Differential Scanning Calorimeter studies were conducted. Figure 8 shows the results of the DSC and TGA. The DSC showed an endothermic peak at 450° , while the TGA confirmed that this peak was not just a phase change, but a reaction with the formation of a new product. Because the new product was volatile, an exact value for the molecular weight loss could not be determined. Several TGA's were run, and the results indicated that a molecular weight loss of 115 occurred. From this datum it was not possible to determine directly whether sulfur dioxide or sulfur trioxide was being formed. However, the West-Gaeke procedure is specific for sulfur dioxide, and thus if formed it could be measured.

FIGURE 8

DIFFERENTIAL THERMAL ANALYSIS AND DIFFERENTIAL
SCANNING CALORIMETER OF $(\text{PDA})_2\text{SO}_4$

DSC - (PDA)₂ SO₄

TGA - (PDA)₂ SO₄

The pyrolysis products were tested for evidence of sulfur dioxide formation by pyrolyzing samples of $(\text{PDA})_2\text{SO}_4$ in the quartz combustion tube (Figure 6). The effluent gases were bubbled through 10 ml of 0.1 M tetrachloromercurate(II), and the color was developed by addition of formaldehyde and p-rosaniline. The appearance of a deep violet-purple color, when $(\text{PDA})_2\text{SO}_4$ was pyrolyzed and the absence of color when PDA-Br was pyrolyzed, confirmed the reduction of sulfate to sulfur dioxide (Figure 9).

Stephen reported an extensive survey of PDA-Br reactions with other anions, and concluded that a 10-fold excess of most common anions would not interfere with the precipitation of $(\text{PDA})_2\text{SO}_4$. This, however, did not preclude the possibility that various salts of PDA exhibit a blank when pyrolyzed. Ten micrograms each of phosphate, carbonate and nitrate were placed in separate dishes, and 200 μl of 0.5% PDA-Br were added. After the excess water was evaporated, these dishes were pyrolyzed in the combustion tube, and the effluent gases passed through the tetrachloromercurate(II) trap. No change was noted over the blank value obtained for PDA-Br alone.

During the pyrolysis cycle, organic debris was seen bubbling through the tetrachloromercurate(II) trap. Several other samples of $(\text{PDA})_2\text{SO}_4$ were pyrolyzed, and the effluent gases were passed through a 5 μl Solvinert filter to collect some of the organic debris. Mass spectral analysis proved that this slightly yellow material was 2,2'-diperimidylamine.

The next step was to optimize the operational parameters. The effect of increasing the temperature of the pyrolysis was investigated first. Increasing the temperature above 500° failed to provide

FIGURE 9
PYROLYSIS SCHEME

PYROLYTIC SULFATE METHOD

PERIMIDYL AMMONIUM
BROMIDE (PDA)

(PDA)₂ SO₄

any significant increase in recovery. In fact, recovery and especially the precision, fell with pyrolysis oven temperatures over 600°. As the TGA showed, a plateau exists between 450° and 600° after which a second slow decomposition ensues. Higher temperatures would favor reaction via the second step of decomposition which does not produce sulfur dioxide. Since the sample in the glass dish requires a finite time to reach the operating temperature of the oven, the completeness of conversion from sulfate to sulfur dioxide will depend on the time the sample stays below 600° when the pyrolysis oven is set above 600°. For these reasons, a pyrolysis temperature of 500° was selected to provide the quickest heat-up while avoiding any secondary thermal reactions.

The pyrolysis time and nitrogen flow rate were set by considering the reaction rate and dead volume in the oven. The minimum reaction time was estimated by the cessation of fumes coming from the bubbler. This estimate was later verified by using a Total Sulfur Analyzer (TSA) connected to a recorder. Figure 10 shows the flow diagram using either a Meloy SA-120 or a Bendix 8300 Total Sulfur Analyzer. Both instruments were designed to operate on an atmospheric sample, so an artificial air mixture was produced by adding oxygen to the nitrogen stream at the 3-way stopcock. These instruments confirmed that the sulfur dioxide was evolved in a sharp peak after 30-45 seconds of heating at 500°, and lasted for 30 seconds after the reaction started. Since the oven chamber and combustion train contained approximately 150 ml of dead volume, a flow rate of 500 ml/min. was chosen to provide an adequate purge during the 2.5 minute pyrolysis cycle used.

Once these experimental conditions were established, a calibration curve was made using the West-Gaeke procedure to measure the

FIGURE 10
TOTAL SULFUR ANALYZER FLOW SYSTEM DIAGRAM

sulfur dioxide. Figure 11 shows the results of pyrolysis of 1 to 30 μg of sulfate following the cycle in the Procedure Section. In order to maintain linearity, the procedure for samples containing more than 20 μg of sulfate was modified by adding an additional 10 ml of tetrachloromercurate(II) after the pyrolysis product was trapped. The formaldehyde and p-rosaniline additions were also doubled. This procedure produced a linear and broad range curve. Pyrolysis of 50 μg of sulfate was attempted with no loss in linearity. Table IV shows the results of precision and sensitivity studies. Defining the sensitivity as 2.5 times the standard deviation of the blank, the sensitivity, using the West-Gaeke procedure, would be 0.1 μg of sulfate. The most significant fact of the $(\text{PDA})_2\text{SO}_4$ pyrolysis is the efficiency of conversion of sulfate to sulfur dioxide. Using the standard sulfur dioxide curve for the West-Gaeke procedure, the sulfur dioxide trapped during the pyrolysis was compared with expected sulfur dioxide output from a specific amount of sulfate as $(\text{PDA})_2\text{SO}_4$. In all cases from 1 to 50 μg the sulfate, as $(\text{PDA})_2\text{SO}_4$, was converted to sulfur dioxide with 100% efficiency.

Both the Bendix and the Meloy Total Sulfur Analyzers were used in an attempt to provide real time analysis and increase the sensitivity. The Meloy SA-120 was more flexible than the Bendix 8300, since the range of the detector could be chosen by selecting the proper amplifier range on the front of the instrument. Both were equipped with exponential amplifiers, so the output of the instruments was linear over the entire range of 0.01 to 1 μg of sulfur dioxide. Figure 10 shows the flow system for pyrolysis when a Total Sulfur Analyzer was used as the detector. Surprisingly, the precision varied from ± 6 to

FIGURE 11
PYROLYSIS CALIBRATION CURVE

TABLE IV
PRECISION OF THE METHOD

Blank Absorbance Values	10 μ g Net Absorbance Values
0.033	0.299
0.034	0.272
0.036	0.305
0.035	0.269
0.034	0.260
0.033	0.292
0.038	0.272
0.033	0.269
0.034	0.260
0.036	0.279
<u>0.033</u>	<u>0.266</u>
Avg. = 0.034	Avg. = 0.276
σ = 0.002	σ = .015
Coefficient of Variance = 5.9%	Coefficient of Variance = $\pm$ 5.3%

$\pm 10\%$ at $0.5 \mu\text{g}$ of sulfate. Two factors, the organic debris and the flow system, were responsible for the poor precision. The organic debris tended to clog the Teflon filter and vary the flow into the hydrogen flame. The nitrogen and oxygen rotameters were not able to maintain the flow rate any better than $\pm 5\%$. As a result of these fluctuations, the precision of the Total Sulfur Analyzers was lower than that of the West-Gaeke procedure. To take advantage of the flexibility of these instruments, a higher degree of sophistication in the flow system would be required.

The appeal of this method lies in simplicity and flexibility. Although the chemistry involved is somewhat sophisticated, the equipment is not. A Variac and two Lindberg heating cylinders would work quite well as a simple constant temperature oven. By using the West-Gaeke procedure to determine the sulfur dioxide evolved in the pyrolysis, the only instrument required was a typical laboratory spectrophotometer. Finally, as we will see in the next Chapter, the use of the thermal degradation of $(\text{PDA})_2\text{SO}_4$ greatly simplifies the sulfuric acid determination problem.

CHAPTER V. THE MEASUREMENT OF SULFURIC ACID AEROSOL AND THE TOTAL SULFATE CONTENT OF THE AMBIENT AIR

A. Previous Attempts at Measuring Sulfuric Acid Aerosol

The foregoing chapters have shown the lack of a method for measuring sulfuric acid aerosol. Most methods for determining sulfuric acid aerosol now available require a great deal of a technician's time in extracting^{33,35} or in titrating¹⁶ the acid content of the air sample. Several methods have features that, if combined with the right analytical finish or separation step, could become useful.

As we have seen, Dubois, et al.,³⁷ separated sulfuric acid aerosol by microdiffusion from glassfiber filters to a petri dish coated with sodium hydroxide. After the acid was collected on the sodium hydroxide, the petri dishes were rinsed and the sulfate titrated. Though the separation was simple, the analytical finish was tedious and required extremely large samples.

Scaringelli and Rehme⁴⁹ have proposed a unified approach to sulfuric acid aerosol determination, but their method has several problems. Either glass fiber filters or copper impactors were used to collect the sample. As pointed out previously, glass fiber filters (Chapter III) will partially neutralize sulfuric acid aerosol while the collection efficiency of copper impactors is doubtful, especially for smaller droplets. Once a sample was collected, sulfuric acid (vaporized from glass fiber filters) or sulfuric trioxide (produced when copper impactors were heated) was reduced over copper at 500°. The apparatus used required pre-conditioning with sulfuric acid, had less than 100% conversion efficiency, and had a positive interference from ammonium sulfate.

The successful development of a method for sulfuric acid aerosol determination depends on the proper combination of collection, separation, and determination of the acid from a gross air sample. The problem of the separation was discussed in Chapter III. It was found that sulfuric acid could be separated from the filter by microdiffusion to a suitable trapping medium. During the process of heating the filter, the problem of topochemical reactions occurring on the surface of the filter between the collected particulate matter and sulfuric acid was noted. The probability of topochemical reactions occurring increases as the amount of sample collected increases, so a decision was made to collect a small air sample. By collecting small samples, the possibility of interfering reactions was reduced, but a sensitivity problem was created. Most methods become highly unreliable at the low concentrations of sulfuric acid expected when small (1 m^3 or less) air samples are collected. In Chapter IV, a new method for sulfate determination having a sensitivity limit of $0.1 \text{ } \mu\text{g}$ was described. In the present chapter, the combination of microdiffusion to PDA-Br coated dishes, and subsequent pyrolysis of the $(\text{PDA})_2\text{SO}_4$ formed, will be proposed as a specific sulfuric acid aerosol method.

1. Experimental

a. Reagents

Refer to Chapters III and IV.

b. Apparatus

In addition to the equipment listed in Chapters III and IV, the following apparatus was employed for the analysis of air samples for sulfuric acid and total sulfate.

Tape sampler---Gelman Instrument Company, Model 23000-1 tape sample was modified by the addition of a 17 mm diameter stainless steel mesh, a 12 mm ID (16 mm OD) O-ring, an 8 mm ID (11 mm OD) O-ring, and an 11 mm diameter stainless steel mesh. These parts were layered in the sampling port in the order listed to provide support for the Fluoropore filters. Without this build-up support, the filters would collapse under the pressures produced by the sampling rate employed. With the sample port modified in this manner, samples were collected over an effective diameter of approximately 12 mm.

Glass dishes---Soft glass vials, 15 mm ID X 120 mm, were cut 3 mm from the bottom to provide microdiffusion dishes.

Vacuum desiccator---Corning No. 3118 or equivalent.

Filters---Fluoropore Teflon filters (47 mm) of 0.5 μ pore size were used to collect the sulfuric acid aerosol.

Teflon block---A 14 cm X 7 cm X 1 cm Teflon block was used to support the filters during microdiffusion.

Ultrasonic cleaner---Fisher ultrasonic generator, Model CT, and cleaner, Model SS-O, were used to sonicate the air samples.

c. Procedure

The sulfuric acid generator of Thomas, et al.,⁵¹ was used to produce a standard aerosol to test the recovery of the diffusion-pyrolysis method at different levels of sulfuric acid. The resultant aerosol was sampled using a slightly modified Gelman tape sampler to produce samples containing from 2 to 40 μ g of sulfuric acid on the sample spot.

The Gelman tape sampler is normally expected to operate with a 2.5 cm paper tape as the sampling medium. A 47 mm Fluoropore filter

cut in half was slid into the collection zone, and the sulfuric acid was collected on a 12 mm spot. A flowrate of approximately 4.0 l/min was maintained throughout the sampling period. Normally, 10 samples were collected containing like amounts of aerosol, so that 5 samples could be analyzed by the extraction procedure (Total Sulfate Method) and 5 by the diffusion-pyrolysis method (Sulfuric Acid Aerosol Method).

1. Extraction Procedure (Total Sulfate Method)

After the sulfuric acid samples were collected on the Fluoropore filter, a 16 mm diameter cork borer was used to cut away the excess filter surrounding the 12 mm sample spot. This filter disc was placed in a 10 ml beaker and approximately 0.5 to 1.0 ml of the extraction solvent was added. These beakers, along with a beaker containing a blank sample of Fluoropore, were placed in a Fisher ultrasonic cleaner and sonicated for 3 minutes.

After sonication, the extract and a 0.5 ml rinse were transferred to a 5 ml volumetric flask. The sonication was repeated a total of 3 times for each sample.

Methanol will extract most hydrogensulfate salts and sulfuric acid.³⁶ Since the laboratory samples contained only sulfuric acid, methanol was used as the extraction solvent. Besides the hydrogensulfate salts, an actual air sample may contain ammonium sulfate, sodium sulfate, and possible small amounts of calcium sulfate. The total sulfate can be extracted with a 50% methanol-water (v/v) solution. This mixed solvent is easier to evaporate than water alone, and will extract all the soluble sulfates present in the air sample.

After the samples have been extracted, 2 ml of the 5 ml extract were put into a 15 mm X 15 mm ID dish containing 250 μ l of a 0.5%

methanol solution of PDA-Br. The samples were allowed to stand for 10 minutes before they were placed in a vacuum desiccator, maintained at 80°. A water aspirator was used to produce a vacuum and remove the solvent. The dry samples were then pyrolyzed according to the procedure outlined in Chapter IV, except that a quartz tube of the same design but with a 33 mm OD was used. The sulfate content of the samples was obtained by multiplying the weight of sulfur dioxide collected by 3.75.*

ii. Diffusion-Pyrolysis Method (Sulfuric Acid Aerosol Method)

A 15 mm ID X 3 mm dish was filled with 250 µl of a 0.5% methanol solution of PDA-Br. The solvent was evaporated in an oven at 80°, leaving a thin crystalline coating on the inside of the dish. A small amount of PDA-Br will crystallize on the rim of the dish, and should be removed with a cotton swab wetted with methanol. The crystalline coating was extremely cohesive and resistant to mechanical shock up to its melting point (265°).

The filter containing the sample was placed on a Teflon block and the sample spot was covered with one of the inverted PDA-Br coated dishes. The Teflon block, filter, and dish were placed in a nitrogen purged oven at 125° for 2 hours, after which the dishes were removed and directly pyrolyzed (see Chapter IV). By knowing the amount of sulfur dioxide produced, the diffusion efficiency, and the sampling rate,

---

*
$$\left(\frac{5.0 \text{ ml}}{2.0 \text{ ml}}\right) \left(\frac{\text{m.w. SO}_4}{\text{m.w. SO}_2}\right) = 3.75$$

the concentration of sulfuric acid aerosol in the ambient air could be calculated.

B. Results and Discussion

1. Total Sulfate Method

Though the Total Sulfate Method is quite simple, there are several points to be considered while performing the procedure. It is important to insure that the filter disc is placed sample side down in good contact with the extracting solution. If methanol is used (to remove only sulfuric acid and the common hydrogensulfates), no special precautions are necessary, since it will wet the Fluoropore.

Another significant step is the evaporation of the solvent once the sulfate has been precipitated. Although 2 ml of solvent can be removed easily in the heated vacuum desiccator, smaller aliquots are desirable. A water solution of $(\text{PDA})_2\text{SO}_4$ will decompose slightly upon extended heating above 80° in air. The results obtained by pyrolyzing these samples will be lower than expected. Thus, if any discoloration of the precipitate occurs during the solvent removal, the samples should be discarded. Since there is no lack of sensitivity with the pyrolysis method, the size of the aliquot for most environmental samples can be adjusted downward. A working range of 1 to 50 μg sulfate in the aliquot is recommended.

To test both the accuracy and precision of the extraction procedure, 10 μl of a 1 $\mu\text{g}/\mu\text{l}$ (as sulfate) sodium sulfate solution were added to one-quarter of a 47 mm Fluoropore filter. There was some difficulty removing the last drops of the sulfate solution, since the

Teflon surface is hydrophobic, and the pipet tips are designed to be emptied partially by capillary action. This problem was overcome by placing approximately 50 μ l of de-ionized water on the filter, before adding the sulfate solution. Approximately 10 μ l of the water-sulfate solution were pulled into the pipet tip and flushed out. Once the sulfate solution was on the filter, the water was evaporated in an oven at 80°, and the sulfate then extracted using 50% methanol solution.

The results of the extraction were quite good, as 105% of the sulfate was recovered with a coefficient of variance of $\pm 3.6\%$. The recovery was greater than 100%, since the sample pipet tips were rinsed while the standard pipet tips did not appear to require any additional rinsing. The results obtained using generated sulfuric acid aerosol are summarized in Table V. These values compare favorably with results obtained with sample spikes, since the precision of the generated aerosol samples is not better than $\pm 4\%$. Due to the composition of most air samples, the probability of encountering any anions that would interfere with the pyrolysis of the extract is low. The sulfate content of most air samples exceeds possible interferants such as phosphate, carbonate, or nitrate. If, during the extraction procedure, the dust collected becomes dislodged, a filtration step should be added to remove large quantities of suspended matter.

2. Sulfuric Acid Aerosol Method

The first step in measuring ambient levels of sulfuric acid is to separate it from the gross air sample. The microdiffusion work discussed in Chapter III has been expanded to include another filter, Fluoropore.

TABLE V
COEFFICIENT OF VARIANCE FOR EXTRACTION PROCEDURE ANALYSIS
OF GENERATED AEROSOL SAMPLES AT SEVERAL CONCENTRATIONS

μg Sulfuric Acid Extracted	Coefficient of Variance (%)
5	± 5.4
9	± 8.2
38	± 6.8

Fluoropore offers about the same chemical stability as Mitex Teflon filters, but Fluoropore comes in much smaller pore sizes. Thomas, et al.,⁵¹ have made a comparison of Millipore-MF, Whatman 41, Poco Graphite, and Mitex Teflon using their sulfuric acid aerosol generator. The results showed Mitex Teflon to be the least efficient filter. This result was expected, since the Millipore filter's pore size was $0.45\ \mu$ compared to $5\ \mu$ for Mitex. When a similar comparison of filter efficiency between $0.45\ \mu$ MF-Millipore and $0.5\ \mu$ Fluoropore was made, they were found to have equivalent filtration efficiencies.

Once the relative efficiency of the $0.5\ \mu$ Fluoropore was established, a study was undertaken to determine the diffusion efficiency for sulfuric acid for various concentrations. A 47 mm Fluoropore filter was cut into quarters and solutions of $1\ \mu\text{g}/\mu\text{l}$ sulfate as sulfuric acid were placed on the surface. The excess liquid was evaporated, and a PDA-Br coated 15 mm ID X 3 mm dish was centered over the sample spot. The dish, filter, and supporting glass plate were placed in an oven at 125° for 6 hours. Figure 12 summarizes the results from diffusing 1 to 50 μg of sulfuric acid to the PDA-Br coated dishes, and directly pyrolyzing them after they had been removed from the diffusion oven. The data obtained were similar to the Mitex results (Figure 5), although the Fluoropore exhibited much better recovery at the 5 μg level.

In all the tests discussed so far, solutions have been evaporated to leave a residual spot of sulfuric acid on the filter. The development of an aerosol generator by our research group offered the opportunity to test the diffusion-pyrolysis method with a more representative sample. As discussed earlier (Chapter III), the spherical

FIGURE 12

DIFFUSION FROM FLUOROPORE FILTERS FOR 6 HOURS
AT 125° USING SULFURIC ACID SOLUTIONS

structure of an aerosol droplet means that there will be a high mass to surface contact area ratio. Consequently, since less acid is in contact with the surface of the filter, a higher percentage recovery is expected for a dispersed aerosol than for a spot of sulfuric acid. The diffusion-pyrolysis method outlined in the Procedure Section was followed except the samples were diffused for 6 hours instead of 2 hours. The results of the diffused and pyrolyzed aerosol samples are displayed in Figure 13. The bars indicate the precision of both the extraction (horizontal bars) and the percentage recovery (vertical bars). The 15% not recovered was due to the diffusion process, since whatever sulfuric acid evaporates will reach the PDA-Br. It has already been demonstrated that the pyrolysis of $(\text{PDA})_2\text{SO}_4$ is 100% efficient for the range employed. Further evidence that the diffusion step is the limiting factor was demonstrated by the discoloration of the surface of the Fluoropore filter after heating in the diffusion oven.

The precision of the diffusion-pyrolysis method was extremely good for points lying on the plateau (5 to 50 μg). For artificial samples (i.e., evaporated sulfuric acid solutions), the precision was $\pm 5.1\%$ (coefficient of variance) for the diffusion-pyrolysis system. The precision of the diffusion-pyrolysis analysis of the generated sample is summarized in Table VI. On the whole, the precision for the diffusion-pyrolysis method is slightly more precise than the extraction procedure.

Figure 13 indicates that about 1 μg of sulfuric acid can be detected. In order to obtain accurate information on the ambient concentration of sulfuric acid, at least 5 μg of sulfuric acid aerosol should be collected. The volume of air needed to reach the recovery

FIGURE 13
DIFFUSION FROM FLUOROPORE FILTERS FOR 6 HOURS
AT 125° USING GENERATED SULFURIC ACID AEROSOLS

TABLE VI
COEFFICIENT OF VARIANCE FOR THE DIFFUSION PYROLYSIS ANALYSIS
OF GENERATED AEROSOL SAMPLES AT SEVERAL CONCENTRATIONS

μg Sulfuric Acid Diffused	Coefficient of Variance (%)
4	± 5.4
8	± 1.7
33	± 3.0

plateau can be estimated from previous results or a sample of several cubic meters should be taken. The guiding principle in collecting an air sample is simply that the larger the volume of air sampled, the greater the possibility of neutralizing the sulfuric acid on the filter. Consequently, the smaller the volume of air sampled (within the above considerations), the better.

Because of the diffusion step, very few interferants reach the PDA-Br. Only volatile species of the air sample would be expected to reach the PDA-Br, and of these compounds only the ammonium sulfates would interfere. In Chapter III, isothermal TGA's of ammonium sulfate were conducted at 175° and 205°. The weight loss amounted to 1.8% and 8.2%, respectively, for a 2-hour heating. In an effort to minimize both the chemical activity of sulfuric acid and the volatility of ammonium sulfates and hydrogensulfates, the diffusion temperature was reduced to 125°. An isothermal TGA of ammonium sulfate and ammonium hydrogensulfate confirmed the fact that these compounds exhibit no volatility at 125°, and consequently, they would not be expected to interfere with the diffusion-pyrolysis method.

All previous diffusion studies were done on treated glass plates (Chapter III). Normally, these plates were used once and discarded, but in terms of a practical procedure this practice was wasteful. Furthermore, it was reasoned that a more inert support might allow the recovery of the 5% sulfuric acid normally lost to the glass plate. For these reasons a Teflon block of sufficient thickness to prevent warping under heating was used to support the filter during diffusion. While no significant increase in recovery was noted over the treated glass plates, the Teflon block could be used repeatedly.

Previous diffusion studies presented in this Chapter and in Chapter III used a 6-hour diffusion period at 125°. Later data proved that the average recovery after 1 hour and 3 hours of diffusion was identical to the recovery obtained at 6 hours. The precision, however, for the 1-hour diffusion was slightly lower, so, as a compromise, a 2-hour diffusion was recommended.

C. Summary

The results of this Chapter show that the measurement of sulfuric acid can be accomplished in a simple yet efficient procedure. By diffusing the acid to a PDA-Br coated dish, the need for further sample treatment has been eliminated. As a result, technicians are freed from tedious procedures that require ion exchange, extraction, or titration steps prior to or during the determination.

The equipment involved can be found in most analytical labs. Though the equipment presented here was optimized for laboratory conditions, any variation in design is acceptable as long as the oven can reach 500° and be purged with nitrogen. Larger sampling orifices can be used allowing faster flow rates and a shorter sampling period. It is hoped that the sensitivity of this method will foster the collection of hourly samples rather than the customary 24 hour high volume samples. In this way the acid content of the ambient air can be charted in greater detail, thus significantly increasing our knowledge of the atmospheric sulfur cycle.

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APPENDIX I

STATISTICS

These formulas were used in calculating standard deviation(s) and coefficient of variance.

$$\text{Standard Deviation}(s) = \left[\frac{1}{n-1} \sum (x-\bar{x})^2 \right]^{\frac{1}{2}}$$

$$\text{Coefficient of Variance} = \frac{s}{\bar{x}} \times 100\%$$

VITA

Ray F. Maddalone was born in Hammond, Indiana, in November of 1948. After graduating from Mt. Carmel High School in Chicago, he entered the University of Notre Dame in 1966. While at Notre Dame, he was a member of the fencing team, earning two monograms. In 1970, he received his B.S. in Chemistry. Since September of 1970, he has attended Louisiana State University in Baton Rouge until his graduation in December of 1974 with a Ph.D. in Chemistry.

During his undergraduate education, his summer jobs included working as a consultant in Europe for Industra Products of Ft. Wayne, Indiana; a general laborer for Stauffer Chemical Company in Hammond, Indiana; and a summer assistant in the Chicago research labs of Nalco Chemical Company. Currently, Mr. Maddalone is employed by TRW Systems, Incorporated, in Redondo Beach, California.

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EXAMINATION AND THESIS REPORT

Candidate: Ray F. Maddalone

Major Field: Chemistry

Title of Thesis: The Measurement of Sulfuric Acid Aerosol and the Total Sulfate
Content of Ambient Air

Approved:

Major Professor and Chairman

Dean of the Graduate School

EXAMINING COMMITTEE:

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_____

Date of Examination:

_____

September 23, 1974

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