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# **EVALUATION OF METHODOLOGY AND PROTOTYPE TO MEASURE ATMOSPHERIC SULFURIC ACID**



**Environmental Sciences Research Laboratory  
Office of Research and Development  
U.S. Environmental Protection Agency  
Research Triangle Park, North Carolina 27711**

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EVALUATION OF METHODOLOGY AND PROTOTYPE  
TO MEASURE ATMOSPHERIC SULFURIC ACID

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## ABSTRACT

The objective of this research was the development of methodology to selectively assay sulfuric acid in the range of 0.25 to 50  $\mu\text{g}/\text{m}^3$ . Research was oriented toward identifying reagents with which sulfuric acid would react to form sulfur bearing adducts that could be analyzed in the presence of interfering sulfate.

A literature search was undertaken to determine the reactions of sulfuric acid which might be useful for fixation. Theoretical considerations first led to the possibility of using a selective  $\text{H}_2\text{SO}_4$  solvent in which sulfate salts were insoluble to collect the acid. Isopropanol and 1,2-dimethoxyethane were examined and found to be unsuitable because of the relatively high solubility of ammonium sulfate and hydrogen sulfate salts. Selective solubility was rejected as being a method with a low probability of success.

Interest was then focused on volatile amino compounds which could react rapidly with sulfuric acid aerosol in the gas phase to form amine sulfate and bisulfate salts. One such compound, diethylamine, was found to form an adduct which could be decomposed to release  $\text{SO}_2$  at  $200^\circ\text{C}$ , thus eliminating interference from inorganic sulfate salts. Related compounds (hydroxylamines and oximes) were also found to form sulfate salts, which could be selectively decomposed. A sulfuric acid aerosol generator was constructed, and a sample probe was designed, which mixed the aerosol with one of three fixing reagents: diethylamine (DEA), diethylhydroxylamine (DEHA), acetaldoxime (AAO). The adduct thus formed was collected on a Millipore Mitex Filter.

A sample cell with Teflon-coated surfaces was constructed in which the fixed acid samples were heated at  $200^\circ\text{C}$  to liberate  $\text{SO}_2$ . A valve arrangement connected the cell to a flame photometric detector (FPD), which measured the evolved  $\text{SO}_2$ . It was established with this apparatus that the fixation process was very rapid and essentially complete after a few seconds. The thermal stability of the samples was raised by the

fixing process, so that the filter could be dried by heating at 100°C without loss of sample.

Interference was eliminated from ammonium sulfate and other sulfate salts by decomposing the adduct below the decomposition temperatures of these substances. Sulfur dioxide was collected as a reagent-complex on the filter, but was selectively removed by heating at 100°C. Suppression of side-reactions on the collection surface by the fixation process has not been experimentally demonstrated, but is likely from theoretical considerations.

This report was submitted in fulfillment of Contract No. 68-02-2247 by Atlantic Research Corporation under the sponsorship of the U. S. Environmental Protection Agency. The report covers the period June, 1975, through June, 1976, and work was completed June 30, 1976.

## CONTENTS

Abstract . . . . .	iii
Figures. . . . .	vi
Tables . . . . .	vii
1. Introduction. . . . .	1
2. Conclusions . . . . .	3
3. Recommendations . . . . .	5
4. Technical Discussion. . . . .	6
Physical description. . . . .	6
The measurement problem . . . . .	7
Summary of developed method . . . . .	9
Theoretical development of method . . . . .	10
5. Experimental. . . . .	54
Apparatus . . . . .	54
Fixing reagents . . . . .	63
Procedures and results. . . . .	65
Method evaluation . . . . .	70
Interferences eliminated. . . . .	76
Summary of achievements . . . . .	81

## FIGURES

<u>Number</u>		<u>Page</u>
1	Bubbling System. . . . .	30
2	Impactor with Rotating Drum. . . . .	32
3	Filter System With Spray Jets. . . . .	32
4	Absorbance vs. Sulfate Concentration . . . . .	34
5	H <sub>2</sub> SO <sub>4</sub> Filter Collection System (Gas or Vapor Reagent). . . . .	40
6	Dual Collection/Fixation System. . . . .	55
7	Analysis Instrumentation . . . . .	56
8	Early FPD Recordings from Samples. . . . .	58
9	Effect of Injecting Progressively Larger SO <sub>2</sub> Volumes . . . . .	59
10	Quantitative FPD Response to Injected SO <sub>2</sub> . . . . .	61
11	Quantitative Response of FPD to SO <sub>2</sub> . . . . .	62
12	Composite DTA of Potential Interferences . . . . .	64
13	(PDA) <sub>2</sub> SO <sub>4</sub> and Py <sub>2</sub> SO <sub>4</sub> DTA . . . . .	66
14	Completeness of Fixation by AAO. . . . .	69
15	Completeness of Decomposition of AAO/H <sub>2</sub> SO <sub>4</sub> after 5 Min (A) and 15 Min (B) . . . . .	71
16	Typical FPD Trace from AAO-Treated Samples . . . . .	72
17	AAO-Fixed Filter Portions after Heating 5 Min at 200°C . . . . .	74
18	AAO-Treated Sample, Different Sampling Volumes, 5 Min at 200°C . . . . .	75
19	Pairs of AAO-Fixed Samples Collected Simultaneously. . . . .	77
20	Continuous Heating Procedure -FPD Recordings from H <sub>2</sub> SO <sub>4</sub> and Adduct Samples . . . . .	80



## TABLES

<u>Number</u>		<u>Page</u>
1	Variation of Sulfuric Acid Content of Atmospheric Aerosol. . .	8
2	General Reactions of Sulfuric Acid . . . . .	15
3	Chloranilate Absorbance of Sulfate Standards . . . . .	33
4	Chloranilate Absorbance of Successive $(\text{NH}_4)_2\text{SO}_4$ Wash Solutions . . . . .	35
5	Chloranilate Absorbance of Successive $(\text{NH}_4)_2\text{SO}_4$ / 1,2-Dimethoxyethane Wash Solutions. . . . .	36
6	Sensitivity Comparison of Sulfur-Gas Measurement Methods . . .	52
7	Temperature of First FPD Signal from Adducts . . . . .	67
8	Peak Heights of Sample Pairs Collected Simultaneously. . . . .	76
9	Temperature ( $^{\circ}\text{C}$ ) of First FPD Response from Sulfur Gas Reagent Complexes. . . . .	79

## SECTION 1

### INTRODUCTION

The concern regarding environmental sulfuric acid aerosol has been gradually gaining momentum over the years. This is due in part to recent smog disasters in Meuse Valley (1), Donora (2), and London (3). The inability to correlate mortality rates during these disasters with measured levels of sulfur dioxide has raised serious questions as to the real nature of the problem. Leighton (4) has documented that sulfur dioxide, in the presence of oxygen, moisture and sunlight can form sulfuric acid. This fact, coupled with the knowledge that high levels of sulfur dioxide existed during these smog disasters, has made sulfuric acid aerosol a prime suspect for responsibility for the excessive mortality rate. Fricket's (5) correlation between ambient air particulates and mortality rates during the Meuse Valley smog disaster also suggests that aerosols could be responsible for the large number of deaths. Sulfuric acid is known to be a potent irritant that can cause narrowed air passages (6,7) and, thus, be a significant health hazard to people with respiratory difficulties.

The source of most  $\text{H}_2\text{SO}_4$  pollution is fuel, which often contains significant quantities of sulfur. When fuel containing a sulfur component is burned, sulfur dioxide is generated. The sulfur dioxide, in the presence of oxygen, moisture and sunlight, can be further oxidized to sulfuric acid. The process can be accelerated by metal particulates in the air which serve as catalysts.

The current energy crisis suggests that more coal will be used in the future as an energy alternative. Much of our coal resources has a high sulfur content which will cause ambient sulfate levels to rise. The advent of the automobile catalytic converter insures efficient oxidation of  $\text{SO}_2$  to  $\text{H}_2\text{SO}_4$  (or a sulfate salt) and will also add to the problem. Thus, the ambient sulfate situation shows no sign of improvement, but only a steady upward trend can be anticipated.

The hazards that can result from  $\text{H}_2\text{SO}_4$  aerosols in ambient air make it imperative that a reliable method for its measurement be established. Many problems in finding a method for measuring  $\text{H}_2\text{SO}_4$  in air can be foreseen. The primary problem is the diversity of forms in which aerosols exists, i.e., sulfuric acid, ammonium sulfate and metal sulfates, some of which are water soluble ( $\text{Na}_2\text{SO}_4$ ), and some of which are insoluble ( $\text{PbSO}_4$ ). In order to accurately measure sulfuric acid concentration, both the sampling and analysis method must be capable of handling all forms of sulfate efficiently. Other problems which affect the reliability of a method are the collection of small particles, the loss of  $\text{H}_2\text{SO}_4$  by reaction with other particulates, and interferences from various pollutants.

## SECTION 2

### CONCLUSIONS

Gas-phase fixation of sulfuric acid aerosol by a volatile amine or amine-derivative is a convenient and effective method of stabilizing an atmospheric sample. By choosing an appropriate fixing reagent, it is possible to form an adduct which can be selectively decomposed to release  $\text{SO}_2$  at  $200^\circ\text{C}$ . Three compounds which seem to meet this requirement are diethylamine, diethylhydroxylamine, and acetaldoxime.

The evolved  $\text{SO}_2$  can be measured with either a flame photometric detector (FPD), or a West-Gaeke Bubbler. The FPD is preferred, because the higher sensitivity allows for collection of a smaller sample with a correspondingly lower possibility of interfering collection-surface reactions. Sampling volume of a few cubic meters or less are called for, to prevent collection of an overlarge sample, which will saturate the detector. To be quantitatively measured, 0.01 to  $1.0\text{ }\mu\text{g}$  of  $\text{H}_2\text{SO}_4$  must be on the filter as a fixed adduct.

Instrumentation for this method requires only minor modification of existing devices. Any filtration or impaction device can be used, if provision is made for addition of the gaseous reagent to the sample air stream. The analysis instrumentation is essentially the same as devices which have already been developed for direct volatilization of sulfuric acid. The uniqueness of the proposed method arises from its use of a gas-phase fixing reaction, and its choice of reagents which offer a useful compromise between adduct stability and selective analyzability.

### SECTION 3

#### RECOMMENDATIONS

As a result of the past year's effort at Atlantic Research Corporation under Environmental Protection Agency Contract No. 68-02-2247, the following recommendations for further work are made.

- 1) Experimental data is required on the ability of the developed fixing reactions to prevent interfering reactions with common atmospheric particulates, such as  $\text{CaCO}_3$  and  $\text{Fe}_2\text{O}_3$ .
- 2) The interference of representative ambient levels of ammonia must be determined.
- 3) Heating the filter to remove water during sampling should be evaluated as a method for further stabilizing the fixed acid sample.
- 4) More background work, both theoretical and experimental, is needed on the chemical properties of the adducts, specifically their formation under sampling conditions, chemical stability, and thermal decomposition.
- 5) New compounds of the same categories (amines and amine-derivatives) should be evaluated for the desired properties.
- 6) Re-examination of sulfur gas interference at ambient concentration levels should be carried out, with special attention to the possible oxidation of  $\text{SO}_2$  under sampling conditions.
- 7) Effects of the analysis system on the sample (i.e., adsorption on or reaction with reactive surfaces) must be determined and, if possible, eliminated.
- 8) Generation of a reproducible aerosol, which has proved impossible with the Thomas generator, may be attempted with a pneumatic or ultrasonic generator.
- 9) An estimate of collection efficiency must be made in order to calculate the  $\mu\text{g}/\text{m}^3$  value of the FPD response.

- 10) A reliable method of calibrating the FPD needs to be demonstrated, either by injecting  $\text{SO}_2$  or preparing known  $\text{H}_2\text{SO}_4$  samples.
- 11) Precision and accuracy of the proposed methodology must be established.
- 12) Ambient samples need to be collected in areas prone to have  $\text{H}_2\text{SO}_4$  aerosol to validate field use of the methodology.

## SECTION 4

### TECHNICAL DISCUSSION

#### PHYSICAL DESCRIPTION

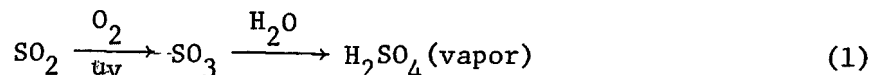
Concentrations of sulfuric acid aerosol in the atmosphere generally range from 2.4 to 48.7  $\mu\text{g}/\text{m}^3$  (8). Toxicity is most directly related to three parameters of the aerosol:

- Droplet size distribution.
- Concentration of acid in the droplet.
- Concentration of droplets in the atmosphere.

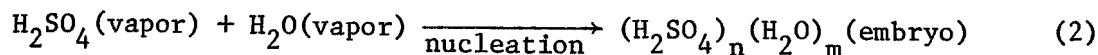
All three of these values can be calculated from the  $\mu\text{g}/\text{m}^3$  measurement, if temperature, humidity, and other factors are known. The average particle diameter of sulfuric acid aerosols has been shown to be 0.35  $\mu$  (9), but varies greatly with humidity. Considerations of droplet size and acid concentration are also important in the development of analytical methods.

Several theoretical and experimental treatments of the aerosol nucleation and growth phenomenon have been published (10-14). Takahashi, et al. (15) proposed a three-step mechanism for formation of the acid aerosol by photo-oxidation of  $\text{SO}_2$ :

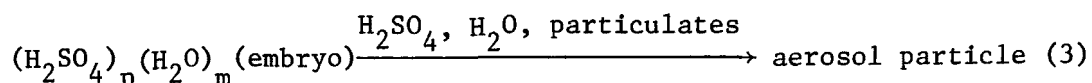
Photo-oxidation of  $\text{SO}_2$  followed by rapid combination with a water molecule,



Nucleation to a critical size by combination with several water and sulfuric acid vapor molecules,



Growth of the embryo to a large aerosol particle through combination with additional water, sulfuric acid and other molecules,



The photo-oxidation rate, the growth of the aerosol particle and, thus, the sulfuric acid concentration in each particle is affected by the relative humidity. During the growth period, sulfuric acid molecules condense on the embryo resulting in an increase in the sulfuric acid concentration. Simultaneously, water molecules are also condensing. The resulting particle will grow until an equilibrium is reached between the water vapor pressure and the ambient relative humidity. The net result is that the concentration of sulfuric acid in each aerosol particle is a function of its radius and the ambient relative humidity. Table 1 shows the sulfuric acid content of an individual aerosol droplet as a function of particle radius and relative humidity. This data is the result of theoretical calculations (16); however, evidence indicates that the concentrations are representative of the real situation.

Inspection of Table 1 shows that the weight percent of sulfuric acid in an individual aerosol particle decreases as the particle size and the relative humidity increase. For aerosols ranging from  $r = 1.0$  to  $0.1 \mu m$ , the average concentration ranges between 45 and 60% for 50% relative humidity, and between 33 and 54% for 75% relative humidity. These concentration ranges will be encountered under normal conditions. However, in areas of high humidity and inversion conditions, the concentration per particle can drop to 18% or below. It is under these high humidity-inversion conditions that high sulfuric acid concentrations in air and resulting fog disasters occur, even though the concentration per particle is low.

#### THE MEASUREMENT PROBLEM

The hazards that result from sulfates in ambient air make it imperative that a reliable method for their measurement in this complex aerosol be established. It is evident from the foregoing discussion that this is not an easy task. A reliable method must collect and measure sub-micron sized particles containing from 90% to less than 18% sulfuric acid in water.



TABLE 1. VARIATION OF SULFURIC ACID CONTENT  
OF ATMOSPHERIC ACROSOLS (16)

<u>Particle radius <math>\mu\text{m}</math></u>	<u>Relative humidity</u>	<u>Mole fraction of <math>\text{H}_2\text{SO}_4</math></u>	<u>Weight % of <math>\text{H}_2\text{SO}_4</math></u>
1.0	100	0.04	18.5
	75	0.086	33.9
	50	0.132	45.3
	25	0.196	57.0
	10	0.258	65.4
0.5	100	0.06	25.8
	75	0.098	37.2
	50	0.140	47.1
	25	0.200	57.6
	10	0.267	66.5
0.2	100	0.104	38.7
	75	0.132	45.3
	50	0.175	53.6
	25	0.225	61.3
	10	0.289	68.9
0.1	100	0.154	49.8
	75	0.179	54.3
	50	0.215	59.9
	25	0.267	66.5
	10	0.327	72.6

The measurement range of 0.25 to 50  $\mu\text{g}/\text{m}^3$  has been established as a goal in this work.

Even more important is the requirement that the method distinguish between sulfuric acid and similar compounds in the atmospheric sample, including sulfate salts [ $\text{NH}_4\text{HSO}_4$ ,  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{PbSO}_4$ ,  $\text{CaSO}_4$ , etc.], sulfur gases ( $\text{SO}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{COS}$ ,  $\text{RSH}$ ), other acid aerosols ( $\text{HCl}$ ,  $\text{HNO}_3$ ,  $\text{H}_3\text{PO}_4$ ), and a wide variety of other organic and inorganic particulates. In addition, since the aerosol must be concentrated by any sampling method that is used, it is necessary to stabilize the acid in some manner to prevent it from reacting with other substances on the collection surface.

No analytical method published to date has succeeded in eliminating all of these interferences simultaneously. The method discussed here and supported by research during the past twelve months shows great promise toward solving this problem.

#### SUMMARY OF DEVELOPED METHOD

The purpose of the sulfuric acid program was to develop methodology and instrumentation for the selective analysis of sulfuric acid aerosol in the range from 0.25 to 50  $\mu\text{g}/\text{m}^3$ . This has been accomplished by the method summarized below:

- 1) An atmospheric sample is first drawn into a glass tube and then through a Millipore Mitex 5 $\mu$  filter by a vacuum pump. Simultaneously, a gaseous organic compound containing reduced nitrogen (amine, hydroxylamine, or oxime) is added to the glass tube through sideports. Sulfuric acid in the sample is thus fixed as a stable adduct (the sulfate or hydrogen sulfate salt of the fixing reagent), and collected on the filter.
- 2) The sample is analyzed by heating the filter to 200°C in a closed cell with non-reactive surfaces. After five minutes, an inert carrier gas flushes the sulfur dioxide evolved from the sample into a flame photometric detector (FPD). The peak height of the FPD recording is a direct measure of the amount of acid originally collected, and may be calibrated by injecting known  $\text{SO}_2$  solutions or by preparing known  $\text{H}_2\text{SO}_4$  standards.

- 3) Only compounds containing sulfur are detected by the FPD; others cannot interfere directly. Sulfate salts, including  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{NH}_4\text{HSO}_4$ , do not interfere because they do not decompose significantly at  $200^\circ\text{C}$ . Sulfur gases, primarily  $\text{SO}_2$ , may be absorbed by the fixing reagent and collected on the filter, but the compound thus formed can be selectively removed from the sample by decomposition at  $100^\circ\text{C}$ . Finally, fixation of the acid as it is collected reduces its acidity and decreases the probability of reaction with other substances on the filter.

#### THEORETICAL DEVELOPMENT OF METHOD

By far the most difficult problem in the development of a method for measuring sulfuric acid aerosol has been the many potential interferences. In fact, this problem has largely determined the direction of research from the inception of the program. Therefore, it is first necessary to discuss in some detail the types of potential interferences and the general requirements to eliminate them.

Interfering substances may be divided into two practical categories: those which artificially enhance the measured acid value; and those which diminish it. To the former we have assigned the term "positive interferences," and to the latter "negative interferences."

#### Positive Interferences

Positive interferences usually result from the failure of an analytical method to distinguish between the desired compound and one which is chemically similar. This is particularly a problem with sulfuric acid measurement, because so many similar forms may be present in the atmospheric sample. Since the different forms are known to have different toxicological properties, it is necessary to be able to distinguish between them (17).

Ammonium sulfate and bisulfate have the greatest chemical similarity to sulfuric acid, and have constituted a severe interference with most previous methods of analysis. These compounds are formed by an equilibrium reaction between ammonia and sulfuric acid, the extent of which seems to be related to climatic conditions (18). In aqueous solution, both sulfate and acidic protons (from hydrolysis of  $\text{NH}_4^+$ ) are present, making it difficult

to distinguish from dilute sulfuric acid. Ammonium sulfate and bisulfate particulates in the atmosphere are generally associated with some moisture, further enhancing the interference by hydrolysis which has already occurred. Some success has been achieved in separating  $\text{H}_2\text{SO}_4$  from the ammonium sulfates by volatilization, since they are stable to about  $235^\circ\text{C}$ .

Many other sulfate salts may be present, some soluble ( $\text{Na}_2\text{SO}_4$ ) and some insoluble ( $\text{CaSO}_4$ ,  $\text{PbSO}_4$ ). These are generally less of a problem than the ammonium sulfates, but may still interfere with a simple sulfate measurement. All but a few require temperatures over  $500^\circ\text{C}$  to cause decomposition, and none decompose under  $250^\circ\text{C}$ .

Ambient sulfur gases, including sulfur dioxide, hydrogen sulfide, carbonyl sulfide, and methyl mercaptan, can generally be separated automatically during collection, if a filtration or impaction system is used. There has been, however, some concern about the catalytic oxidation of  $\text{SO}_2$  to sulfuric acid on certain filter media, particularly glass fiber filters (19). Other atmospheric particulates collected during sampling may also catalyze this reaction (20-22). If a fixing reagent is used to stabilize the acid during collection, as in this method, it is necessary to evaluate the potential interference of these gases as a result of interaction with the fixing reagent.

Also of concern are other strong mineral acids ( $\text{HCl}$ ,  $\text{HNO}_3$ , and  $\text{H}_3\text{PO}_4$ ) which may be present in the atmospheric sample (23-24). These may interfere directly if the analytical method measures only acidity, or they may interfere by reacting with sulfate salts on the collection surface to produce sulfuric acid. In this method, fixation of sulfuric acid by a basic reagent also serves to stabilize other acids and reduces the probability of these reactions.

Finally, a wide variety of substances may interfere with widely used wet chemical methods of sulfate analysis. Most of these methods are based upon precipitation of  $\text{SO}_4^{2-}$ , usually as  $\text{BaSO}_4$ ; thus, other anions which precipitate  $\text{Ba}^{+2}$  may interfere ( $\text{PO}_4^{3-}$ ,  $\text{S}^{2-}$ ). Some metal cations may cause a negative interference by precipitating sulfate ( $\text{Pb}^{+2}$ ,  $\text{Ca}^{+2}$ ), and other species may interfere by complexing indicator reagents. The complex nature of urban aerosols has been dramatized by studies which have found

over 50 elements present in measurable quantities (25). Clearly, a simple sulfate measurement is inappropriate unless the sulfuric acid is first separated from these other species.

### Negative Interferences

Interferences that cause a negative error in analytical measurement generally result from loss of sample. Since sulfuric acid is a highly reactive substance, such a loss may readily occur, if the acid contacts other particulates on the collection surface. Reactions with inorganic salt particulates produce sulfate salts, which must necessarily be excluded from the analytical measurement if positive interferences from these compounds are to be avoided. Ambient ammonia may also cause a negative error, since the collection process tends to mix acid and ammonia to a greater extent than would normally occur. Once again, the product ammonium sulfates must necessarily be excluded from the sulfuric acid measurement.

These interfering side-reactions have been the greatest single obstacle in the development of a reliable measurement method for sulfuric acid aerosol. The volatilization technique for separating the acid from its salts fails to prevent this sample loss; in fact, the loss is increased by the volatilization procedure which brings hot acid vapor into contact with potentially reactive substances. Only by completely preventing these reactions can the interferences be avoided. By using a very sensitive analytical method which requires only a small volume of air to be sampled, the problem can be minimized, but not eliminated. Chemical stabilization of the acid as it is collected seems to be the only solution.

### Approach to Problem

From the foregoing discussion, it is evident that any solution to the selective measurement problem has several special requirements. In order to eliminate positive interferences, the method must be highly selective. Simple acid or sulfate measurement is not adequate unless sulfuric acid is first separated from other acids and sulfates in the atmospheric sample. To prevent negative interferences, the method must be highly sensitive (so that only a small sample need be collected), and it must employ a process for chemically stabilizing the acid as it is collected. Of course,

the adduct thus formed must be selectively analyzable.

It is also evident that every aspect of this problem is intimately related to every other aspect. The goal was to develop a combination of fixation, sampling, and analysis techniques which, working together, eliminated all interferences. No one of these three aspects could be regarded as separate from the other two, since a decision in any one area would limit possibilities for the others. The remaining discussion on theoretical development of the proposed method is divided into three sections: fixing reactions, sampling techniques, and sample analysis; but reference must continually be made to all three, as was necessary during the actual development of the method.

#### H<sub>2</sub>SO<sub>4</sub> Fixing Reactions

At the beginning of the program, the following general requirements were established for the fixing reagent:

- 1) React between 0 and 100°C.
- 2) Reagent must be chemically stable under sampling conditions.
- 3) Reagent must react with sulfuric acid to render it in a chemically stable and non-volatile configuration under sampling conditions.
- 4) Kinetics and thermodynamics of the reaction must be such that sulfuric acid is fixed quantitatively, immediately, and nonreversibly under sampling conditions.
- 5) Preferably, the reagent should react only with sulfuric acid. In reality, this may not be possible. In this case, the sulfuric reaction product must be separable in some manner from other reaction products. Possible recognized interferences, depending upon reagent, are  $\text{SO}_4^{=}$ ,  $\text{SO}_3$ ,  $\text{SO}_2$ ,  $\text{H}_2\text{S}$ , organic sulfur compounds, acids, particulates, and possibly nitrogenous compounds.
- 6) Reagent must come in physical contact with the sulfuric aerosol.
- 7) Reagent must be present in sufficient quantities to assure that all the sulfuric acid will be fixed.

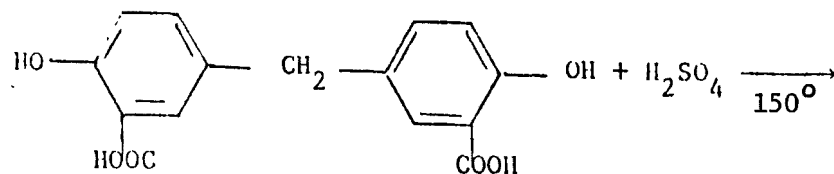
- 8) Reagent should be non-toxic and non-carcinogenic.
- 9) Reagent should be relatively inexpensive.
- 10) Reagent must form an  $\text{H}_2\text{SO}_4$ -adduct which is demonstrably less reactive toward common atmospheric particulates on the filter than unfixed  $\text{H}_2\text{SO}_4$ .

With regard to finding an appropriate fixing reaction, a general survey of the reactions of sulfuric acid was undertaken. Table 2 is an outline of these reactions, as discussed in the following sections.

#### Oxidation/Condensation

Sulfuric acid is frequently used in organic reactions where a non-specific catalyst is required. In general, these reactions are neither specific for sulfuric acid nor quantitative for the amount of acid present. Feigl (26), however, developed a fairly selective test for sulfuric acid which makes use of the fact that this acid is both an oxidizing agent and a dehydrating agent.

Methylenedisalicylic acid reacts with  $\text{H}_2\text{SO}_4$  at  $150^\circ\text{C}$  in a combined oxidation-dehydration reaction to form the red quinoidal formaurindicarboxylic acid:



(11)

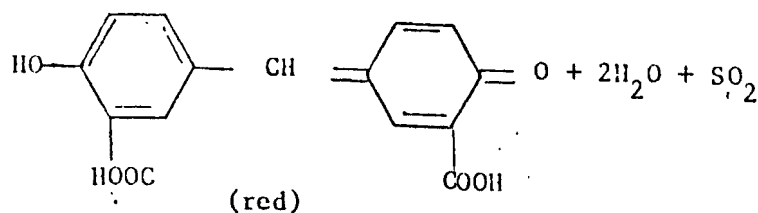
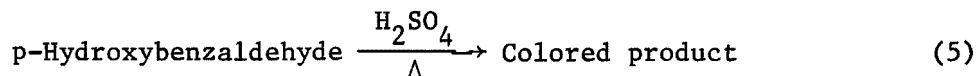
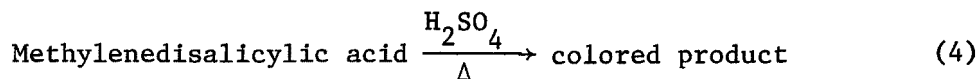


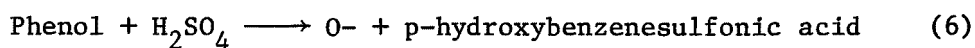
TABLE 2. GENERAL REACTIONS OF SULFURIC ACID

I. Oxidation/Dehydration

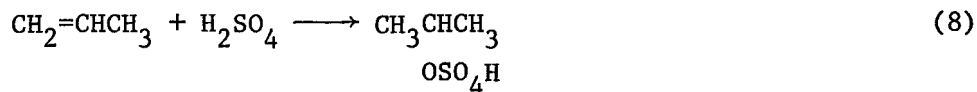
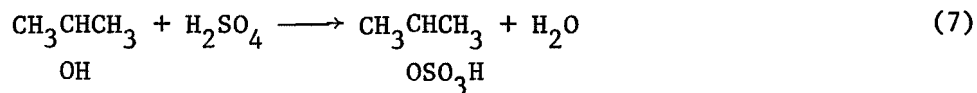


II. Sulfonation

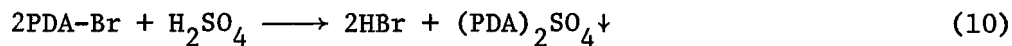
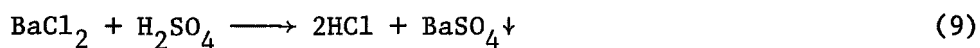
A. Electrophilic Aromatic Substitution



B. Formation of Sulfate Esters



III. Precipitation of Insoluble Sulfate



IV. Acid Base Neutralization/Salt Formation

A. Formulation of Inorganic Salts

1. Acid-metal reactions
2. Acid-salt reactions

B. Formation of Organic Salts

1. Oxonium salts
2. Amine and amine-derivative salts



Our goal in studying this reaction was not to fix the acid itself, but to form a stable, stoichiometrically related derivative, which in this case could be measured spectrophotometrically. A minimum of  $2.5 \mu\text{g H}_2\text{SO}_4$  can be detected by this method. Feigl (26) also found that p-hydroxybenzaldehyde undergoes a similar reaction, with formation of a green-colored quinoidal compound.

Experiments were performed with p-hydroxybenzaldehyde in ethylene glycol to determine selectivity of this method for sulfuric acid. First, 3 drops of 20% sulfuric acid in water were added to 25 ml of ethylene glycol in which 0.5 g of p-hydroxybenzaldehyde had been dissolved. The mixture was slowly heated to boiling, and a green color rapidly appeared when the temperature reached  $\sim 160^\circ\text{C}$ . When phosphoric or hydrochloric acids were used instead of  $\text{H}_2\text{SO}_4$ , no color developed. Nitric acid produced a red color at a lower temperature ( $100^\circ\text{C}$ ), but in combination with phosphoric acid, a green color appeared. Undried ammonium sulfate crystals also produced a green color when added to the solution and heated.

Since this reaction utilizes the combined oxidation/dehydration properties of sulfuric acid, it is not surprising that the combination of an oxidizing acid ( $\text{HNO}_3$ ) and a dehydrating acid ( $\text{H}_3\text{PO}_4$ ) gives the same product. Considering the immense variety of substances in the atmospheric sample, it is not unlikely that two compounds with these properties will be collected together. This finding leads to a generalization regarding the fixing reaction and the specificity of the analytical method. The adduct which is formed during sampling and measured during analysis must incorporate at least part of the sulfuric acid molecule. It is impossible to form a unique sulfuric acid adduct unless this is done, because the reactions of sulfuric acid in themselves are not sufficiently distinct from those of other acids.

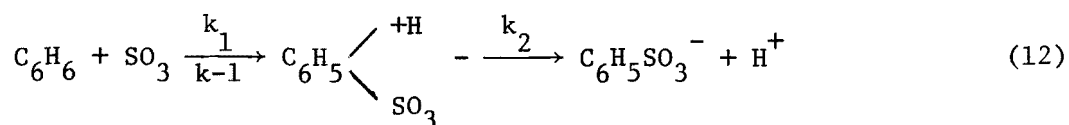
Another problem arose from the observation that ammonium sulfate also gave a green color under test conditions. There was some question whether this was due to a direct action of ammonium sulfate on the reagent, or to the solvent ethylene glycol dissolving a significant amount of salt. Subsequent work (see page 37) indicated that the second factor may be most important.

Oxidation-condensation reactions do not appear to be feasible for fixation of atmospheric  $\text{H}_2\text{SO}_4$ . The reaction is not sufficiently specific for sulfuric acid to form a unique adduct which could not be duplicated by other substances. Even if this interference is allowed, the problem of preventing sulfate salts from dissolving in the collection medium remains. This involves a selective solvent approach, which is discussed in detail on page 37.

#### Sulfonation of Organic Compounds --

This category of reactions includes all those in which sulfur from sulfuric acid becomes covalently bonded to an organic group.

Electrophilic Aromatic Substitution--One of the reaction types which sulfuric acid undergoes is electrophilic substitution on an aromatic ring (sulfonation). The mechanism of this substitution is postulated to be:

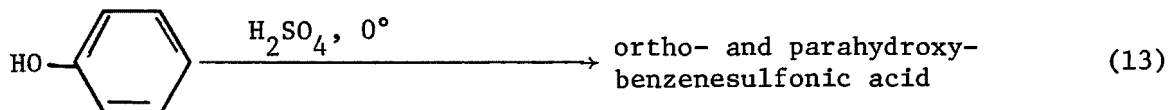


As with all electrophilic aromatic substitutions, the sulfonation position and the kinetics of the reaction are controlled by other substituents on the ring. With electron releasing substituents, such as  $-\text{NH}_2$ ,  $-\text{OH}$ ,  $-\text{OCH}_3$ ,  $-\text{NHCOCH}_3$ ,  $-\text{C}_6\text{H}_5$ , and  $-\text{CH}_3$ , the rate of substitution is increased over that of benzene due to increased stabilization of the carbonium ion intermediate. The substitution occurs in either the ortho or the para position. With electron withdrawing groups, the rate of substitution is slower than with benzene, and the substitution takes place in the meta position. Thus, from a kinetic point of view, it would be more desirable to use a substituted aromatic, such as phenol, in preference to benzene.

Sulfonation reactions differ from other electrophilic aromatic substitution reactions in that they are reversible and  $k-1 \approx k_2$ . The reaction rate for sulfonation is inversely proportional to the square of the water concentration. Thus, the attacking species,  $\text{SO}_3$ , must be in high concentration in order to drive the reaction toward the formation of the sulfonic acid. Concentrations of  $\text{SO}_3$  sufficient for the sulfonation

to occur are found only in concentrated sulfuric acid (98%) or oleum solutions.

At 0°C, phenol reacts with sulfuric acid to give a mixture of ortho- and parahydroxybenzenesulfonic acids (27):



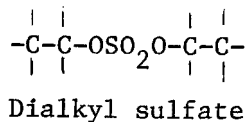
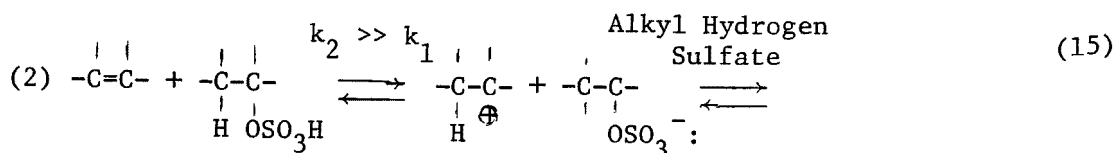
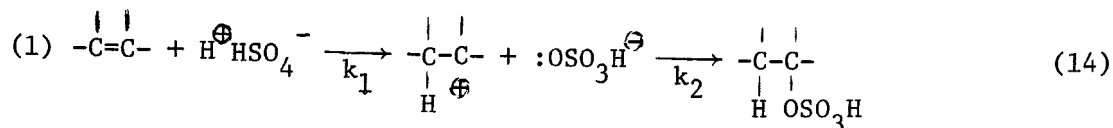
Of course, sampling cannot be carried out at 0° if the acid has to be heated to achieve the necessary concentration. It was found that at room temperature or above, phenol is rapidly oxidized by sulfuric acid to a bright red quinoidal compound. Sulfuric acid is very likely reduced to  $\text{SO}_2$  and lost in the process, as was seen in comparable reactions in the preceding section. Whatever sulfonation does occur is far from uniform, existing as many sulfonated isomers of phenol and its oxidation products. Resorcinol (m-hydroxyphenol) gave comparable results. In both cases, the color change was also affected by nitric acid, indicating that oxidation is involved, rather than sulfonation. Aniline, another highly activated ring, is also readily oxidized to a variety of products.

Unfortunately, it appears that most highly activated rings are also most easily oxidized by sulfuric acid. Less reactive compounds, such as benzene and toluene, generally require refluxing with concentrated  $\text{H}_2\text{SO}_4$  to achieve sulfonation. Such reactions do not appear suitable for the purpose of fixing sulfuric acid, since the heating that would be necessary to concentrate the acid would also cause some to be volatilized before the relatively slow reaction could occur.

Formation of Sulfate Esters--Sulfuric acid reacts with alkenes and alcohols to form alkyl hydrogen sulfate and dialkyl sulfate esters. These compounds are hygroscopic and readily hydrolyzed to alcohols and sulfuric acid. Because they are so difficult to isolate, the chief concern with them in this program was in the theoretical mechanism by which sulfuric acid dissolves in liquid alkenes and alcohols. The practical possibility of using these solvents to collect sulfuric acid and separate it from its salts is discussed more fully on page 37. This section contains a discussion of the chemical reactions which occur when sulfuric

acid is added to these reagents.

Alkenes--The mechanism by which sulfuric acid dissolves in an alkene is postulated to be:



Product distribution is dependent upon H<sub>2</sub>O concentration, but it was reported (28) that very little of the dialkyl sulfate is formed in the presence of any appreciable amount of H<sub>2</sub>O.

Polymerization and hydrolysis are major interfering side-reactions. Acid-catalyzed and free-radical polymerization of alkenes are well-known reactions, and there is evidence (28) that this may also result from the decomposition of alkyl hydrogen sulfate with time in the reaction mixture. In addition to affecting the distribution of the two sulfate esters, water in the mixture may also hydrolyze the esters to an alcohol. The acid thus liberated may then react with more alkene, a polymer of the alkene, or the alcohol just formed.

Consequently, dissolution of H<sub>2</sub>SO<sub>4</sub> in an alkene yields a very complex mixture, with the original acid existing in a variety of chemical forms. This fact does not disqualify alkenes as potential fixing reagents, however, as long as the acid can be reproducibly recovered. A problem does appear to exist, however, in the slow rate at which the reaction occurs.

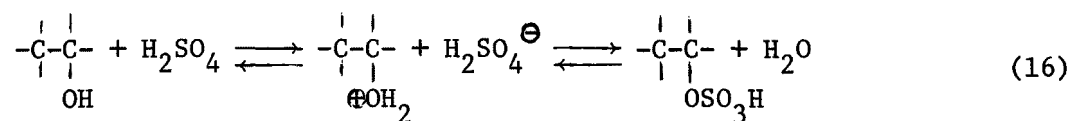
The reaction of sulfuric acid with alkenes proceeds best when

electron-donating groups are next to the double bond. Since a carbonium ion is formed in the rate determining step, compounds capable of forming stable carbonium ions react faster and under milder conditions. For example, ethylene requires 98% sulfuric acid for the reaction to proceed, while propylene and isobutylene required 80% and 63%, respectively.

Concentrated sulfuric acid, however, does not dissolve immediately when added to isobutylene at room temperature; the mixture must be agitated for several minutes. Styrene, an alkene with the powerful electron-donor phenyl group next to the double bond, does not react noticeably faster. Heating the mixture shortens the reaction time, but it also increases the extent of polymerization. Unfortunately, these relatively reactive alkenes also undergo other reactions involving a carbonium ion intermediate more readily, including polymerization and hydrolysis of the sulfate esters.

These findings cast doubt on the theoretical usefulness of alkenes as fixing reagents. Practical problems also arise regarding the control of water collected from the aerosol into a water-immiscible solvent. This will be taken up in the section on selective solvent approach (page 37).

Alcohols--Concentrated sulfuric acid dissolves immediately when added to an alcohol, even if the alcohol is not completely water soluble. This fact made the alcohols much more attractive than alkenes as potential collection/fixation media. In order to dissolve an alkene, sulfuric acid must take the difficult step of forming a carbonium ion. Dissolution in an alcohol is accomplished simply by protonating oxygen to form an "oxonium salt" which is soluble in the alcohol. If the acid concentration is high, the alkyl hydrogen sulfate ester may be formed (29):



Under conditions of heat and high acid concentration, the alcohol can also be dehydrated to an alkene. Normal sampling conditions, however, should not allow this reaction to occur.

Thus, at first sign, alcohols seem to satisfy many of the requirements for a fixing reagent. Although the adduct (a distribution of oxonium salt

and sulfate ester) cannot be isolated as such, in solution the acid is diluted and its acidity reduced immediately upon collection. The feasibility of using alcohols depends primarily upon the extent to which the acid can be separated from interfering substances. This question was dealt with experimentally, and the results are discussed on page 37.

Another approach to the alcohol- $\text{H}_2\text{SO}_4$  reaction is the sulfonation of -OH groups in carbohydrates (30-33). This reaction has been widely used in carbohydrate analysis, but most previous work is not applicable to the problem at hand. The acid must be quite concentrated in order to react, and the product is subject to rapid hydrolysis. Polymerization and dehydration of the carbohydrate have been observed as side-reactions. Analysis of cholesterol and other sterols has also been accomplished by similar reactions with  $\text{H}_2\text{SO}_4$  (34-38), but once again concentrated acid is required. It has been determined that even concentrated acid reacts slowly at room temperature, while heating the mixture causes extensive dehydration and decomposition. These compounds do not seem to be adequate as sulfuric acid fixing reagents.

Summary--Of the various sulfate ester-forming reactions of sulfuric acid, only the reaction with simple liquid alcohols seemed very promising. In this case, the adduct was not strictly a sulfate ester, but was a distribution between it and an oxonium salt. Rather than isolating these adducts, it seemed most advantageous to use their solubility in excess alcohol to separate them from potential interferences, i.e., sulfate salts.

#### Precipitation of Insoluble Sulfate --

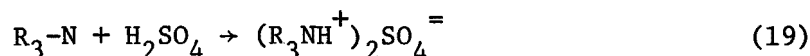
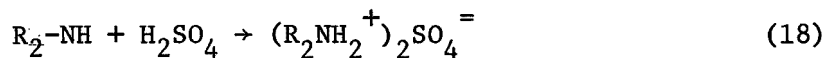
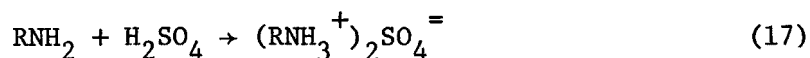
Another manner in which to fix sulfuric acid aerosol is to bring it into contact with a reagent which causes the sulfate to be precipitated as an insoluble salt. The overriding advantage of an insoluble adduct is that the fixing reaction is not greatly affected by the dilution of the acid. Moreover, the reaction is virtually instantaneous for even very dilute acid. From the standpoint of fixation alone, adduct formation by precipitation seemed to be ideal.

There are, however, other considerations in the development of the total method. Primarily, the adduct must be selectively analyzable. An


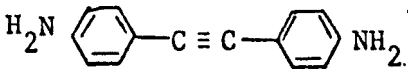
insoluble adduct cannot be separated from other insoluble sulfate salts by selective solubility. The only possibility for selective analysis is if the adduct can be thermally decomposed, releasing  $\text{SO}_2$  for analysis, at a lower temperature than these other sulfates. Unfortunately, insoluble sulfate salts seem to have very high decomposition temperatures, which are not surprising, if their insolubility is taken as an indication of high stability. Thus, although precipitation is a highly desirable fixing reaction, it may not be suitable for other reasons.

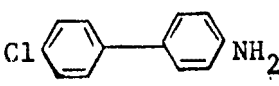
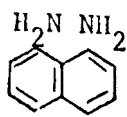
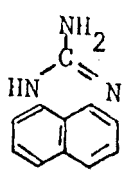
The most common method for precipitating sulfate is as the highly insoluble barium sulfate,  $\text{BaSO}_4$ . A soluble barium salt, such as the chloride, is conveniently used for this purpose. As previously discussed, however, there does not appear to be any way to separate the product  $\text{BaSO}_4$  from other insoluble sulfates in the sample, since it is thermally stable to over  $1500^\circ\text{C}$ .

Much attention has been paid to the formation of insoluble amine sulfates. The amino group in organic compounds is a moderately strong base which readily reacts with mineral acids to form "ammonium salts:"



The reaction is virtually instantaneous, and if the product salt is insoluble, it precipitates out of solution. Most organic amine sulfates are water-soluble, but several organic amines have been investigated which are distinguished by the very low solubilities of their sulfate salts in both aqueous and non-aqueous solvents. These compounds are listed below:

<u>Compound</u>	<u>Formula</u>	<u>Solubility of Sulfate Salt, g/l</u>
Benzidine (39)		0.098 ( $25^\circ\text{C}$ )
4:4'-diaminotolane (39)		0.059 ( $25^\circ\text{C}$ )

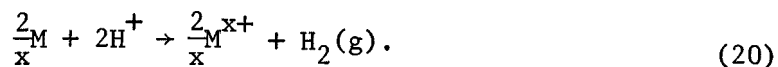
<u>Compound</u>	<u>Formula</u>	<u>Solubility of Sulfate Salt, g/l</u>
2-amino-4'-chlorodiphenyl (40)		0.155 (25°C)
1,8-diaminonaphthalene (41)		0.222 (25°C)
2-aminoperimidine (41) or perimidylammonium bromide (42)		-0.020 (18°C)

Unfortunately, these compounds have the same problem as  $\text{BaSO}_4$ : their thermal stability is too high for selective analysis. Thomas, *et al.*, (43) found that the insoluble perimidylammonium sulfate must be heated to 400°C to cause thermal reduction. They impregnated a filter with the soluble bromide salt of this compound and showed that the acid was collected and stabilized as the insoluble sulfate. During analysis at 400°C, however, inorganic ammonium sulfate and ammonium hydrogen sulfate interfered totally. Theoretically, this interference could be eliminated by washing soluble sulfates out of the sample with water; but with such trace amounts of sample to be measured, the potential handling error makes this approach unfeasible.

#### Acid-Base Neutralization/Salt Formation --

This section discusses the general salt-forming reaction of sulfuric acid not already mentioned under another more specific category. The discussion is divided into reactions with inorganic and organic reagents.

Formation of Inorganic Salts--Sulfuric acid reacts with active metals which lie above hydrogen in the redox potential series to yield metal sulfates. The following oxidation reduction reaction occurs in this case:



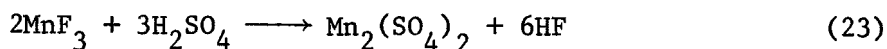
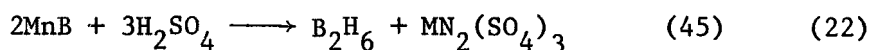
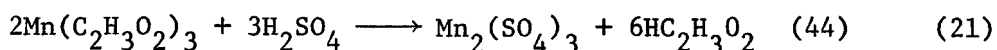
Many metals react in this manner, but the reaction rate is highly dependent upon concentration of the acid. The metal collection surface would then have to be heated in order to complete the reaction.



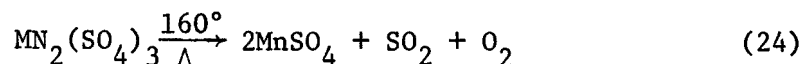
Many salts will also react with sulfuric acid by forming a sulfate salt and another acid. One of three requirements must be met before a reaction of this type will go to completion. Either the product sulfate must be insoluble (page 21), or the product acid must be either weaker or more volatile than sulfuric acid. Each condition serves to remove one product from the equilibrium reaction so that it goes to completion. If the product acid is more volatile than sulfuric acid but water soluble, such as the HX acids, it may again be necessary to heat the collection surface in order to remove water and product acid, thereby driving the reaction to completion.

Reactions of this type are quite promising for fixation of  $\text{H}_2\text{SO}_4$ , but their practical usefulness depends upon the ability to form an adduct sulfate salt which can be selectively analyzed in the presence of common atmospheric sulfates. As with the insoluble sulfates previously discussed, this, in turn, depends upon the ability to decompose the sulfate adduct at a relatively low temperature. A search of the literature found four sulfate salts which decompose between  $150^\circ\text{C}$  and  $200^\circ\text{C}$ : manganese, ceric, thallium, and hydroxylamine sulfates. The decomposition temperatures and liberation of  $\text{SO}_2$  were verified by DTA and FPD in the manner discussed on page 60.

Manganic sulfate is formed by the reaction of sulfuric acid with  $\text{Mn}(\text{C}_2\text{H}_3\text{O}_2)_3$  or  $\text{MnB}$  according to the following equations:



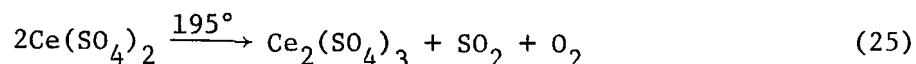
When heated, thermal reduction to the more stable  $\text{Mn}^{+2}$  salt occurs with release of  $\text{SO}_2$ :



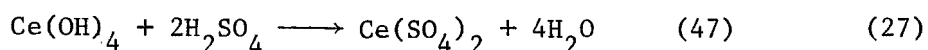
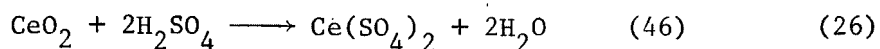
Unfortunately,  $\text{Mn}^{+3}$  salts are not very stable, and may decompose upon standing. Of particular concern is the possibility that they may catalyze the

oxidation of  $\text{SO}_2$  to  $\text{SO}_4^{-2}$  during sampling. Therefore, although the decomposition temperature is ideal,  $\text{Mn}^{+3}$  salts may not be suitable fixing reagents.

Ceric sulfate also decomposes in the desired range:

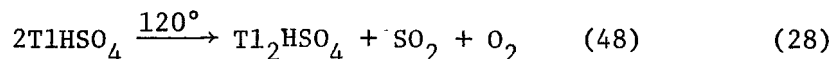


It is formed from the reaction of sulfuric acid with any of several  $\text{Ce}^{+4}$  salts:



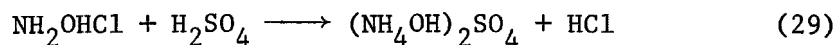
The  $\text{Ce}^{+4}$  salts are more stable than  $\text{Mn}^{+3}$  salts and will not spontaneously decompose at room temperature. However, ceric sulfate is very slow to decompose at  $300^\circ\text{C}$ ; a 100 mg sample requires several hours at this temperature to completely decompose.

Thallium hydrogen sulfate decomposes at  $120^\circ\text{C}$  to the normal sulfate, releasing  $\text{SO}_2$  in the process:



The major problem with this adduct is insuring that excessive amounts of the normal sulfate are not formed during sampling in preference to bisulfate.

Hydroxylamine sulfate (considered an inorganic salt) is most conveniently prepared from the chloride:



This sulfate decomposes rapidly at  $180^\circ$  (explosively if a large amount is present). Hydroxylamine can be either an oxidizing or reducing agent, so there is some concern that  $\text{H}_2\text{SO}_4$  may be lost as  $\text{SO}_2$ , or  $\text{SO}_2$  oxidized to  $\text{SO}_4^{-2}$ . Additionally, any decomposition to  $\text{NH}_3$  would produce  $(\text{NH}_4)_2\text{SO}_4$  and acid would be lost from analysis.

Despite the problems raised, inorganic sulfate adducts hold significant theoretical promise as fixed forms of sulfuric acid. It seems more desirable to use a salt fixing reagent than a metal foil, because of the faster reaction rate and lower multiplicity of products. Nevertheless, the practical problems of impacting collected aerosol on a salt surface, and decomposing the adducts in the presence of excess reagent salt, led to placing more importance on the reactions discussed in the following section.

Organic Salt Adducts--Oxygen and nitrogen in organic compounds are usually sufficiently basic to become protonated by a strong mineral acid. Formation of oxonium salts by protonation of the -OH group in alcohols was discussed on page 14. In fact, concentrated sulfuric acid dissolves in almost any organic compound containing oxygen by the same mechanism: carbonyl compound, ethers, etc. However, these oxonium salts are not sufficiently stable to isolate as such; they are useful only as soluble forms of sulfuric acid in organic solvents.

Organic nitrogen (excluding nitro-, nitroso-, and quaternary ammonium compounds) is more strongly basic than oxygen because its unshared electron pair is more available for protonation due to the lower electronegativity of this element. Consequently, "amine sulfates" are more stable than oxonium sulfates and can be isolated as ionic solids. This can be demonstrated by adding concentrated  $\text{H}_2\text{SO}_4$  to diethylamine, which produces rapid precipitation of a white solid.

As discussed on page 22, most amine sulfates are soluble and completely ionized in aqueous solution. Hydrolysis of the protonated amine produces a fairly acidic solution, so it would seem desirable to heat the sample collection surface to remove water and form dry amine sulfate crystals. This would not be necessary for an insoluble amine sulfate; however, the thermal stability of these compounds seems to be too high for selective analysis.

Even water soluble amines seem to be at the limit of selective analyzability. Diethylamine sulfate does decompose slowly at  $200^\circ\text{C}$  and releases  $\text{SO}_2$  more quickly than ammonium sulfate at the same temperature. Other amine sulfates, however, such as pyridinium sulfate (from pyridine), require a higher temperature at which the inorganic sulfates interfere.

For this reason, experiments were begun with amine-derivatives in which oxygen is bonded to nitrogen : hydroxylamines and oximes:



The primary effect of oxygen in these compounds is to reduce the base strength of nitrogen. As a result, the corresponding sulfate salts tend to be less stable and decompose at a lower temperature than the basic amine. An analogous difference is observed in the decomposition temperatures of ammonium sulfate and hydroxylamine sulfate:



Of course, many factors beside base strength are involved in the decomposition temperature, but this seems to be a useful generalization.

The main advantage of these adducts over the inorganic salts discussed in the previous section is that they allow greater flexibility of sampling techniques. Reagents containing the appropriate functional groups can be prepared as solid, liquid, or gaseous compounds at ambient temperatures. The possibility of using a gaseous reagent to partially stabilize the acid, even before it reaches the collection surface, was particularly interesting. Huygen (49) demonstrated that diethylamine vapor is rapidly absorbed by  $\text{H}_2\text{SO}_4$  on a filter, although his purpose was not to fix the acid, but to measure total acidity by a wet-chemical analysis of the amount of amine absorbed. By applying a more selective analytical technique, both acid fixation and selective measurement were demonstrated in our laboratories with this vapor-absorption method.

#### Summary of $\text{H}_2\text{SO}_4$ Fixing Reactions --

The preceding discussion has focused on reactions of sulfuric acid which may be theoretically useful as fixing reactions. Little experimental

data was given, since this is better discussed in the context of the actual collection and analysis procedures used. Some conclusions, however, were drawn regarding the usefulness of these reactions from considerations of theoretical specificity of adduct formation and reaction rate.

Oxidation/dehydration and other reactions where sulfuric acid is not incorporated in the adduct to be measured were rejected as lacking specificity. Sulfonation of aromatic rings was too slow, required too high a concentration of acid, and produced too many side-products by oxidation of activated rings. Sulfate ester formation was too slow for alkenes, and polymerization was seen to be a major problem. Alcohols showed more promise in this reaction, although the adduct would probably consist of more oxonium salt than sulfate ester. Precipitation of insoluble sulfate was seen as an ideal fixing reaction, but selective analysis of the adduct seemed to be practically impossible. Formation of inorganic sulfates from metal or other inorganic salts was regarded as promising, if somewhat difficult procedurally, and several adducts were suggested which may be selectively analyzed by thermal decomposition. Oxonium salts, from alcohols and other oxygen-containing organic compounds, were potentially very useful if inorganic sulfates could be sufficiently separated in such solvents. Amine and amine-derivative sulfates were given the highest priority, particularly in the use of a gas-phase reagent to fix sulfuric acid as it is collected.

#### Collection/Fixation Methods - Physical State of Fixing Reagent

The theoretical fixing reactions discussed in the last section are useful only if they can be applied in a practical manner. This section describes general techniques for collecting and fixing sulfuric acid in terms of the physical state of the fixing reagent: liquid, solid, and gas. Since most of the reagents previously mentioned are limited in this aspect, the present discussion will serve to further illustrate the relative usefulness of the various fixing reactions.

Methods for collecting and fixing sulfuric acid will be divided into three categories. The first category covers bubbler and impinger methods in which the acid aerosol is collected in a liquid medium. Second will be

methods of filtration and impaction in which the acid aerosol is brought into contact with a solid fixing reagent on the collection surface. Third will be methods in which a gaseous fixing reagent is mixed with the aerosol prior to filtration or impaction.

#### Liquid Phase Reagent --

Selective Solubility - Theory--When sulfuric acid aerosol is collected into a liquid medium in which it is soluble, the acid is immediately diluted so that reaction with other collected substances is unlikely. Of course, it is necessary that positive interferences from other sulfates and acids be avoided. For this reason, water is unsuitable as a collecting solvent, since these interfering species would dissolve and be indistinguishable from the original sulfuric acid. However, a solvent in which sulfuric acid is soluble, but sulfate salts are not, would avoid this interference. In fact, there are many organic solvents which fulfill this requirement on first examination.

In considering solubility, it is necessary to distinguish between concentrated sulfuric acid and dilute aqueous sulfuric acid, which is the form in which an atmospheric aerosol exists. Concentrated acid is immediately soluble in almost any organic solvent containing oxygen: alcohols, ethers, and carbonyl compounds. The mechanism of this solubility is seen as the formation of an oxonium salt, which is soluble in the solvent. (See page 17.) Similarly, concentrated acid will dissolve immediately in many amino compounds, although the amine sulfate is often insoluble in this solvent and precipitates out of solution. Additionally, concentrated sulfuric acid is soluble within a few minutes in alkenes and activated aromatic compounds, by forming sulfate esters and sulfonic acids, respectively.

Dilute aqueous acid, however, is very similar to  $H_2O$  in its solubility properties, even if the acid constitutes 50% of the mixture. Like water, dilute acid is soluble only in organic solvents which are quite polar, particularly low-molecular weight alcohols and carbonyl compounds. Thus, if the aerosol is to dissolve immediately in the collecting solvent, one of these compounds must be used. On the other hand, a water-immiscible solvent may be used, if the formation of an aqueous layer can be avoided (which

would dissolve sulfate salts and retain much of the  $\text{H}_2\text{SO}_4$ ). Heating the solvent during collection to concentrate the acid is one approach, but may cause volatilization loss of acid and troublesome side reactions (polymerization, oxidation, etc.).

The ideal collecting solvent is one in which dilute acid (essentially  $\text{H}_2\text{O}$ ) is immediately soluble, but sulfate salts are not sufficiently soluble to interfere. This must remain true, even after the solvent has absorbed some moisture from the air. A typical bubbling system utilizing the liquid collection medium is illustrated in Figure 1.

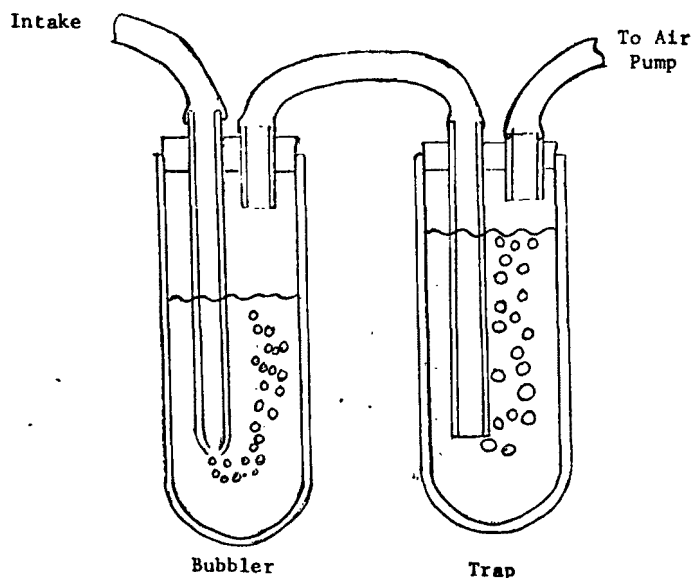


Figure 1. Bubbling system

Fixing Reactions in Liquid Collection Medium--Dissolution of the acid in an appropriate solvent is a fixing reaction of sorts, since the high dilution makes subsequent interfering reactions unlikely. However, it is conceivable that another substance may be dissolved in the solvent which will selectively react with the acid, thereby further stabilizing the sample and possibly making analysis easier.

One example of this approach is the method described on page 14, using p-hydroxybenzaldehyde in ethylene glycol, although the reaction was not sufficiently specific, for  $\text{H}_2\text{SO}_4$  and ammonium sulfate interfered. An organic sulfate precipitation agent dissolved in methanol, such as PDA-Br

(page 21), would immediately fix the acid as it is collected, but other slightly more soluble sulfates would slowly form  $(\text{PDA})_2\text{SO}_4$ .

It can be seen that the same requirements hold as in ordinary dissolution of the acid; it must be immediately soluble, and other sulfate salts must be so highly insoluble that they do not measurably interfere. If a solvent which meets these requirements cannot be found, then no fixing reaction in a solvent can have the necessary selectivity for sulfuric acid. Figure 2 illustrates the manner in which a liquid medium might be utilized with an impaction device, while figure 3 illustrates the use of a liquid reagent utilized with a filter collection device.

Experimental Evaluation of Selective Solvents--Because of the importance of finding a selective solvent for use in the above techniques, experiments were undertaken to determine the solubility of ammonium sulfate in various organic solvents. The barium chloranilate method developed by Bertolacini and Barney (50) was used with some modifications to measure total sulfate in solution. Barium chloranilate is an insoluble salt of the highly-colored chloranilic acid. On contact with sulfate in solution, the even more insoluble  $\text{BaSO}_4$  is precipitated and acid chloranilate is quantitatively released. The UV-visible absorbance of chloranilate in solution is, therefore, a measure of the amount of sulfate originally present.

Isopropanol--Sulfuric acid aerosol has been collected in isopropanol using the Greenburg-Smith Impinger and various modifications of this device. One such method, described in the Federal Register (51), collects sulfuric acid aerosol and sulfur trioxide into 80% isopropanol, allowing the sulfur dioxide to pass on into a hydrogen peroxide collection solution. An obvious modification is to use absolute alcohol rather than 80%, since this would decrease the solubility of particulate sulfates.

First, a standard absorbance curve was obtained from known  $\text{H}_2\text{SO}_4$  standards. A 4 ml volume of each standard was buffered by adding 1 ml of 0.05 M potassium hydrogen phthalate. To this was added 5 ml of isopropanol and the solution mixed. Then, 0.03 g of barium chloranilate was added, and the solution magnetically stirred for 15 minutes. The mixture was centrifuged and absorbance of the solution was read at  $\lambda_{\text{max}}$  of the UV



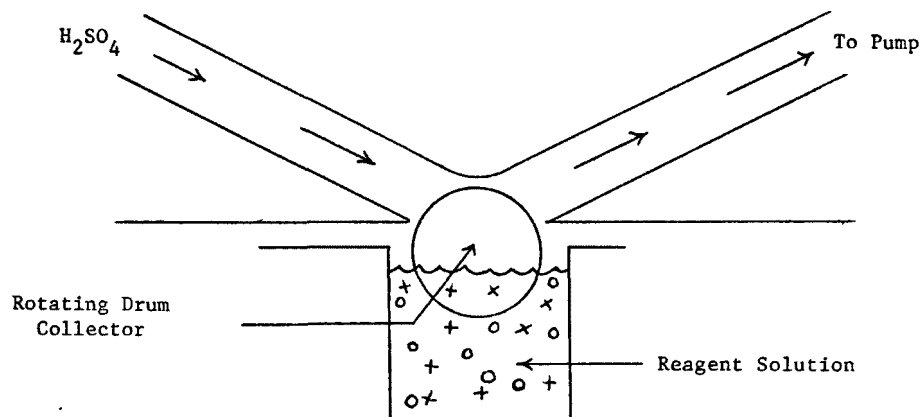


Figure 2. Impactor with rotating drum.

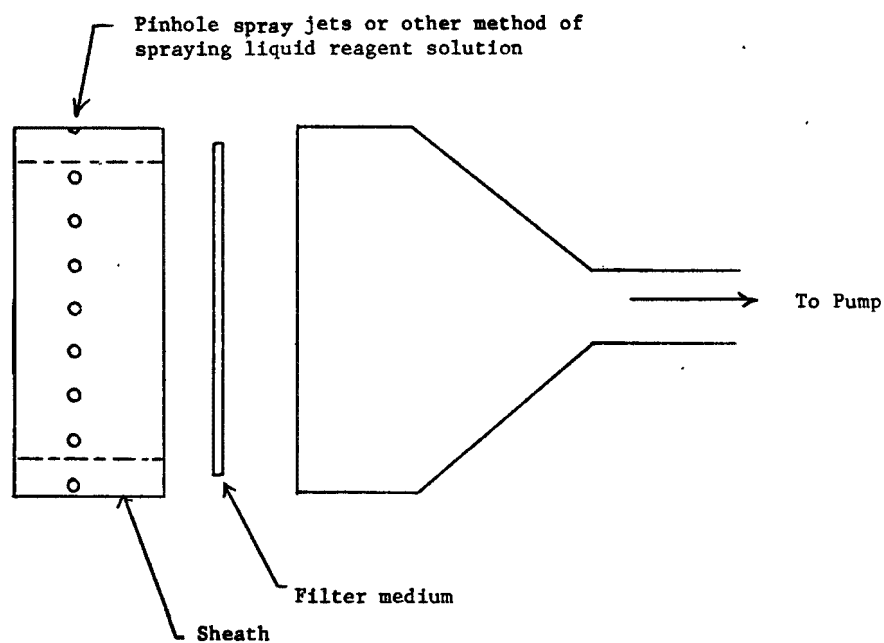


Figure 3. Filter system with spray jets.

band 310-350 nm, using a Beckman DK-1 spectrophotometer. A blank reference solution was prepared and further diluted so that a blank sample would have a small positive absorbance. Table 3 gives the results of the experiment.

TABLE 3. CHLORANILATE ABSORBANCE OF SULFATE STANDARDS

<u>ppm SO<sub>4</sub><sup>-2</sup></u>	<u>Absorbance %</u>
20	1.47
15	1.04
10	0.72
5	0.43
1	0.20
0.5	0.19
Blank	0.19

These results agree well with the reported sensitivity limit of the method, about 2 ppm. Figure 4 shows the relationship is linear.

To determine the solubility of ammonium sulfate in isopropanol, a quantity of this salt was added to the alcohol and let stand for 15 minutes. Afterwards, the salt crystals were removed by centrifugation and a 5 ml portion of this alcohol was added to 4 ml water and 1 ml phthalate solution. Analysis was carried out by the barium chloranilate method previously described. Absolute isopropanol was taken directly from the reagent bottle with no additional effort to dry it, since this would more closely approximate real sampling conditions.

In the first experiment, 1 g of ammonium sulfate taken directly from the reagent bottle was added to 25 ml isopropanol. To eliminate the effects of moisture on the crystals causing hydrolysis, a second sample of ammonium sulfate was dried at 150°C in a dessicator oven for 3 hours. Results are shown below.

<u>Sample</u>	<u>A(%)</u>
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> from bottle	0.99
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> dried	0.83
Blank	0.21

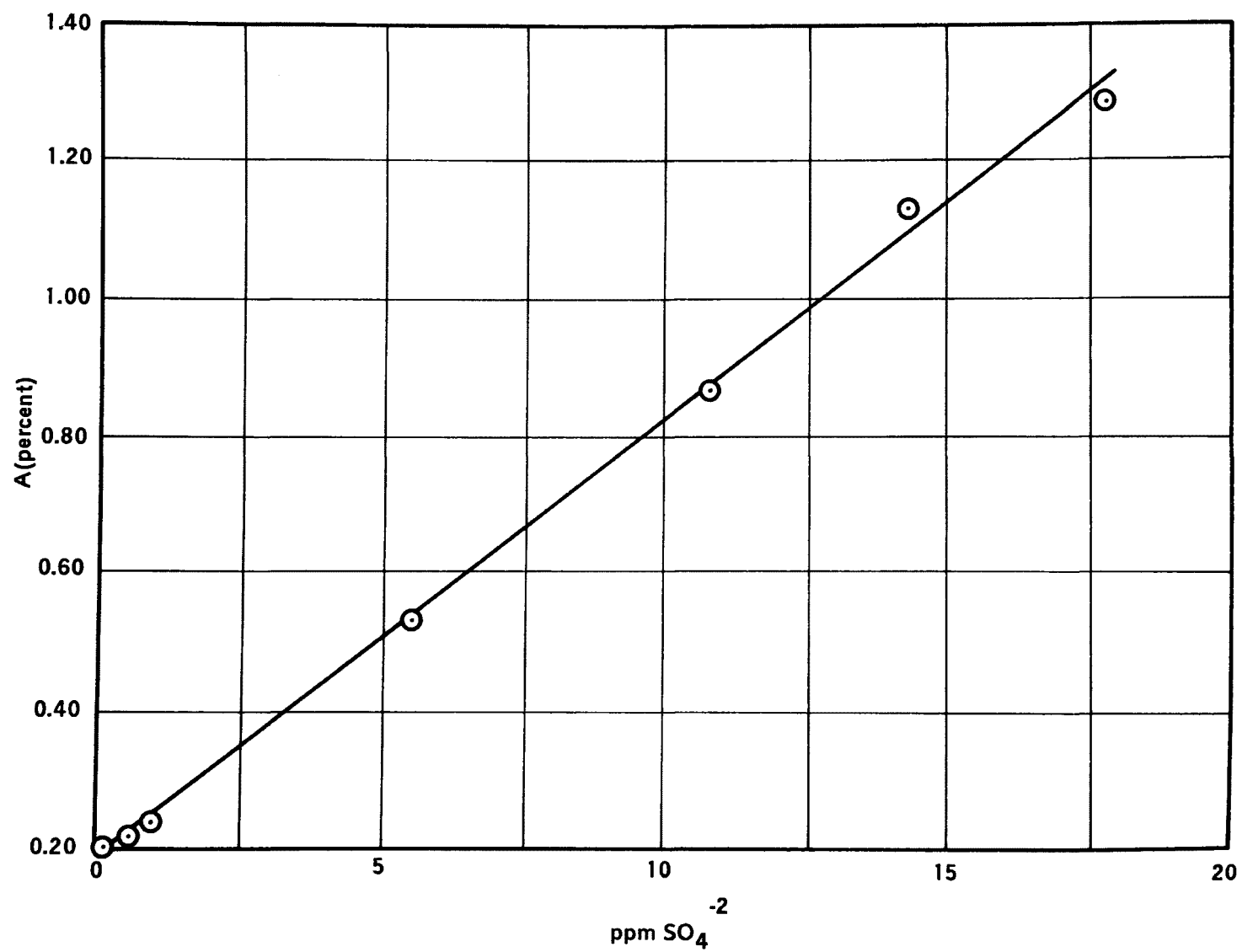


Figure 4. Absorbance vs. sulfate concentration.

With reference to figure 4, this corresponds to about 10 ppm  $\text{SO}_4^{-2}$ .

In order to determine whether this was a direct dissolution of ammonium sulfate, or a surface moisture effect, the same ammonium sulfate crystals were repeatedly washed with isopropanol and each of the wash solutions was analyzed for sulfate. If a surface moisture effect was operating, the measurements should fall to the blank level after several washings. Table 4 shows the results.

TABLE 4. CHLORANILATE ABSORBANCE OF SUCCESSIVE  
 $(\text{NH}_4)_2\text{SO}_4$  ALCOHOL WASH SOLUTIONS

<u>Sample</u>	<u>A(%)</u>
1	0.72
2	0.54
3	0.55
4	0.50
5	0.57
6	0.59
Blank	0.43

It can be seen that sulfate levels did not decrease after the first washing, and remained significantly above blank. This must, therefore, be due to a direct dissolution of ammonium sulfate in isopropanol. From these results, the solubility can be estimated at 5 to 10 ppm. Subsequent runs gave comparable results.

1,2-dimethoxyethane--An effort was made to evaluate the solubility of ammonium sulfate in 1,2-dimethoxyethane. Since its solubility in isopropanol was unacceptably high, it was reasoned that the less polar ether group might make a more selective solvent.

The procedure was to place ammonium sulfate in a test tube, add 1,2-dimethoxyethane, shake, and let stand for 15 minutes. The liquid was then separated, filtered, and 5 ml taken for analysis. This volume was used in place of the isopropanol in the established chloranilate procedure. More ether was added to the same ammonium sulfate, and the process repeated. A total of three washings was carried out.

Absorbance of all three samples was measured, first using a blank reference containing chloranilate but no sulfate, then against a solution of the original blank diluted with an ether-water mixture. Table 5 gives the results.

TABLE 5. CHLORANILATE ABSORBANCE OF SUCCESSIVE  
(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>/1,2-DIMETHOXYETHANE WASH SOLUTIONS

<u>Sample</u>	<u>A(% at 320 mμ)</u>
Blank Reference First Washing	0.40
Second Washing	0.52
Third Washing	0.75
Blank	0.03
Diluted Reference First Washing	1.14
Second Washing	1.30
Third Washing	1.56
Blank	0.75

The results show that all samples were significantly higher than the blank. Furthermore, the sulfate concentration appeared to increase with successive washings, possibly as a result of the solvent absorbing water. No quantitative comparison can be made to the isopropanol calibration curve, because a different solvent was used; however, the SO<sub>4</sub><sup>-2</sup> concentration must be over the sensitivity limit of the technique, at least 5 ppm.

Discussion--The solubility behavior of a salt in a given solvent can usually be best described in terms of a solubility product. If the equilibrium equation is  $CA \rightarrow C^+ + A^-$ , then the equilibrium expression (with constant [CA] omitted) is  $[C^+][A^-] = K_p$ . The solubility product,  $K_p$ , sets a limit on the maximum concentration of dissolved species, regardless of how much excess solid remains. For this reason, it is arbitrary to report the data by taking the weight of dissolved species as a percent of the amount originally added. Rather, it is meaningful to report the sulfate concentration of a solution in equilibrium with excess solid, for a given solvent and temperature.

From the results given above, ammonium sulfate seems to be able to generate an  $\text{SO}_4^{2-}$  level of about 5 ppm in isopropanol at 25°C. This corresponds to  $5 \mu\text{g}/\text{m}^3$  or  $50 \mu\text{g}/10 \text{ ml}$  (since 10 ml is about the smallest collection volume possible). Thus, in order for the potential measurement elevation to be no more than 5%, 1,000  $\mu\text{g}$  of  $\text{H}_2\text{SO}_4$  would have to be collected. This is an unrealistic requirement when the lower goal detection limit is  $0.25 \mu\text{g}/\text{m}^3$ , since it would require  $4,000 \text{ m}^3$  of sample air. In most cases, however, the amount of  $(\text{NH}_4)_2\text{SO}_4$  collected will not reach the maximum value, so the interference is quantitative.

Barton and McAdie (52) demonstrated that hydrogen sulfate salts, as well as ammonium sulfate, are measurably extracted by isopropanol. Maddalone, *et al.* (53), also concluded that isopropanol is not sufficiently selective as a solvent for sulfuric acid.

This supports the work accomplished here, which seems to cast grave doubt on the feasibility of the selective solvent approach. Acid sulfate salts can also protonate basic functional groups, in this case to form the soluble oxonium salt. Apparently, the mechanism by which sulfuric acid dissolves in these solvents is available to other acid sulfates as well.

It is not very likely that another solvent will be able to achieve the necessary separation. Leahy, *et al.* (54), have proposed benzaldehyde as a selective solvent, but their data is either ambiguous because lower sensitivity limits are not stated, or inapplicable to this problem because of the sample size used. Moreover, benzaldehyde is not very water-soluble, so elaborate precautions must be taken to prevent formation of an aqueous layer by collected water in the aerosol.

As a result of these findings and considerations, we concluded that the selective solvent approach is not feasible. Any solvent which rapidly dissolves dilute  $\text{H}_2\text{SO}_4$ , also dissolves enough ammonium sulfate and hydrogen sulfate salts to constitute an unacceptable interference.

#### Solid-Phase Reagent --

Another method for fixing  $\text{H}_2\text{SO}_4$  is to collect it on a filter or impactor surface which is coated with a solid fixing reagent. This method has both advantages and limitations, but in general seems more useful than liquid-phase fixation.

Advantages and Limitations--The main advantage of this approach to sampling over the liquid-phase method is that interfering reactions are less likely to occur in the absence of a reaction medium. Sulfate salts were an interference in a solvent because trace amounts dissolved and formed more sulfuric acid adduct. Dry sulfate particulates, however, do not react when collected on a dry surface of the fixing reagent, since a reaction medium is lacking. Similarly, if sulfuric acid is stabilized as dry adduct crystals on the collection surface, there is very little tendency to react with other dry particulates that may contact the filter.

However, some limitations also result from the reduced reagent-acid contact with this method. In order to minimize "matting" on the collection surface by the collected aerosol, it is desirable to collect as small a sample as possible. Additionally, it is necessary that the fixing reaction be very rapid, to reduce the possibility of subsequently collected particulates reacting with unfixed acid. Of course, there is still a statistical probability that an acid droplet may strike and react with a previously collected particle; but a rapid fixing reaction will reduce the extent of this interference. Finally, the collection surface must be heated to remove water, which would act as a medium for interfering reactions, and to speed the fixing reactions as discussed below. It would, of course, be necessary to show that no acid is lost by volatilization prior to fixation under sampling conditions.

Solid Fixing Reagents--Regardless of the type of fixing reagent used, the adduct must be dried (by heating) before the acid is fixed in the most stable form possible. However, it is desirable that the acid be somewhat stabilized immediately upon contact with the reagent, even before drying has occurred. In this respect, the three types of solid-phase fixing reactions described on page 23 can be ranged from the most to least desirable.

The most desirable type of fixing reaction is one in which an insoluble sulfate is formed, as in the  $(\text{PDA})_2\text{SO}_4$  precipitation (page 21). Here sulfate is fixed immediately upon contact and is not likely to react further, even before drying has occurred. Drying is still necessary, however, because collected water will also allow sulfate salts to be precipitated as the adduct. This reaction may be most desirable from the standpoint of fixation,

but a serious problem with selective analysis of the adduct results from the high thermal stabilities of insoluble sulfates. If the adduct cannot be selectively analyzed, the fixation is worthless.

A fixing reaction in which the product acid is weak is the second most desirable type. An example is the reaction of sulfuric acid with a basic amino compound to produce a soluble amine sulfate, which is a weak acid in aqueous solution. With this reaction, acidity of the aerosol is reduced immediately, since the acidic protons are held more strongly by basic nitrogen of the fixing reagent. The aqueous solution, however, is still somewhat acidic, so the sample must be dried to achieve the most stable configuration.

The final and least desirable fixing reaction is one in which the product acid is strong and volatile, such as an HX acid. When sulfuric acid reacts with a soluble chloride salt, the product acid, HCl, is strong and completely ionized in aqueous solution. Consequently, no reduction in acidity occurs on contact, and the sample must be heated to remove water and volatile HCl before stable adduct crystals are formed. For this reason, if amino compounds are used as fixing reagents, it is more advantageous to use them in the basic form than as the HCl salts.

Conclusions--The solid fixing reagent approach was not rejected outright, but offered less advantages than the gas reagent method ultimately adopted. Matting was the principal problem, which was minimized by collecting as small a sample as possible, but could not be avoided altogether. Of the fixing reactions, the second alternative offered more possibilities for analysis.

#### Gas-Phase Reagent --

Figure 5 illustrates the use of a gaseous fixing reagent to stabilize the acid aerosol prior to collection on a filter. The fixing gas is added to the sample probe at a point in front of the filter, and excess reagent simply passes through the filter. This method was ultimately adopted as most useful for collection/fixation of sulfuric acid.



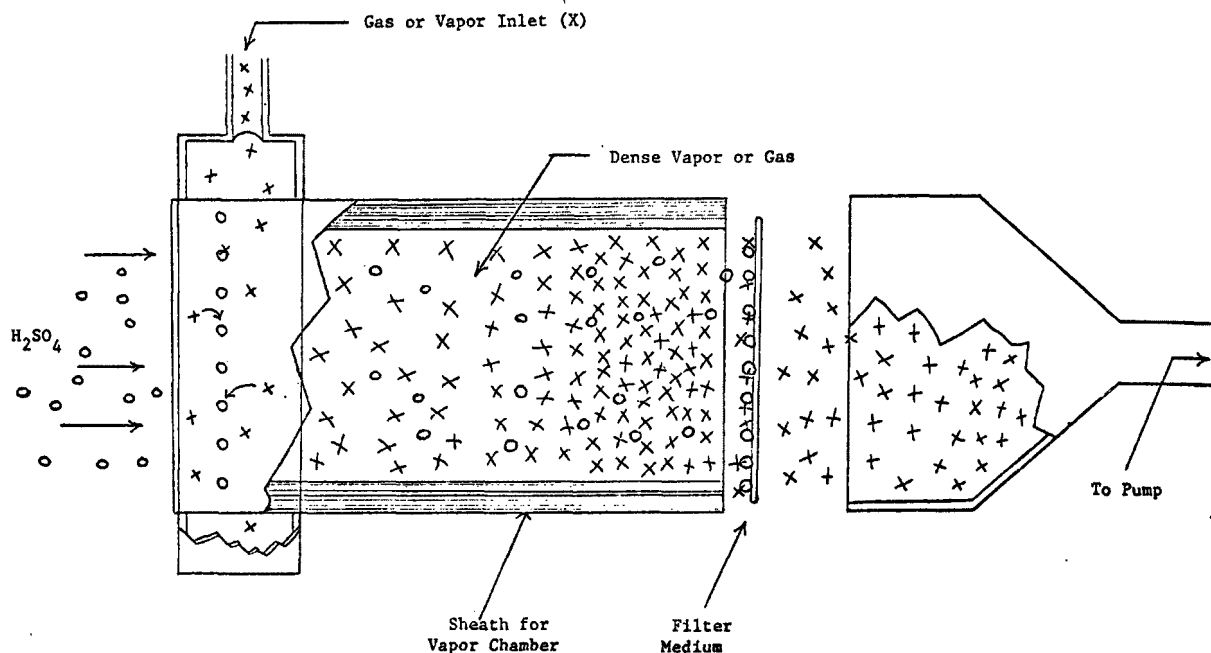


Figure 5.  $\text{H}_2\text{SO}_4$  filter collection system.  
(Gas or vapor reagent)

Theoretical Advantages--The gas-phase reagent method combines the advantages of the two previously discussed methods. It allows good acid-reagent contact without providing a medium for interfering collection surface reactions. If the fixing reaction is very rapid, the acid is significantly stabilized even before contacting the filter. Thus, the danger of acid reacting with pre-collected particulates is reduced. Particulate sulfates are collected unchanged on the filter, since there is no solvent in which they can dissolve. Of course, it is necessary to show that ambient sulfur gases do not become an interference as a result of interaction with the fixing reagent.

Potential Gaseous Fixing Reactions--This method of fixation limits potential fixing reagents to those which can be generated in a vapor phase at ambient temperatures. Inorganic salts are immediately ruled out. (An aerosol powder would not provide enough reagent-acid contact prior to filter contact, and excess reagent could not be removed.) Of the amino compounds

which are known to form insoluble sulfates, none are sufficiently volatile to use in this manner. The only potential fixing reagents previously discussed, which have sufficient volatility are alkenes, alcohols, and amines; but the adducts formed from alkenes and alcohols are too unstable to be useful out of solution, and the reaction rate may be slow.

Volatile amines and amine-derivatives, however, seem to be ideal for this purpose. In the basic form, many of the low molecular weight compounds are either gaseous or liquid with a high vapor pressure at room temperature. During the first phase of fixation, the gaseous reagent dissolves in the droplet and reduces its acid strength by forming an aqueous solution of the amine sulfate. Robbins and Cadle (55) found that the rate of the analogous reaction between sulfuric acid droplets and ammonia was controlled by the speed of product diffusion into the droplets. After 4 seconds at 28°C, droplets of 0.2 $\mu$  and 0.9 $\mu$  diameters were reacted 100% and 60%, respectively. Huygen (49) demonstrated that 2 minutes of contact with an air stream containing diethylamine vapor was sufficient to react completely with microgram quantities of sulfuric acid on a filter. The kinetics of this reaction seem to be sufficient for rapid fixation of the acid.

After the first phase of fixation is complete, the adduct exists as an aqueous solution of the amine sulfate, which is still somewhat acidic. To further reduce the chance of interfering collection-surface reactions, it is probably advantageous to heat the filter in order to drive off water, leaving the adduct as dry amine sulfate crystals. In this form, the sulfuric acid is stabilized until analysis in the laboratory.

Experimental--Several preliminary experiments were carried out in establishing the validity of the gas-phase fixation method. The procedure is much simpler than the solid reagent technique, since special preparation of the collection surface is unnecessary, and excess reagent is automatically removed.

Although alkenes were not considered very promising fixing reagents, the first experiments were performed with propylene gas. The gas was passed for several minutes through a glass fiber filter containing concentrated H<sub>2</sub>SO<sub>4</sub>. A variety of chemical changes occurred on the filter, as higher hydrocarbons (from polymerization of propylene) were identified and

a series of oxidation products appeared upon standing in air for several hours. These results confirmed the earlier conjecture that alkenes form a variety of products in contact with sulfuric acid, without fixing the acid in a significantly more stable form.

Experiments then proceeded with the volatile compound, diethylamine, in place of propylene. A full description of experiments and results with this and related compounds is presented in Section 6. In general, however, it was demonstrated that the adducts formed rapidly (less than 15 seconds of exposure to concentrated vapor was required), were more stable than sulfuric acid, and could be selectively analyzed by thermal decomposition at 200°C. As a result, gas-phase fixation of  $\text{H}_2\text{SO}_4$  was ultimately selected for the proposed method.

#### Summary - Collection/Fixation Methods --

The preceding discussion on collection/fixation methods attempted to place the theoretical fixing reactions described under  $\text{H}_2\text{SO}_4$  Fixing Reactions (page 13) in a practical framework. On this basis, several were eliminated as impractical. As a net result of the experiments, it was concluded that dilute sulfuric acid cannot be separated from ammonium sulfate in the low microgram range by selective solubility. This ruled out any attempt to collect the acid directly into a liquid medium via a bubbler or impinger system. Since sulfate esters and oxonium salts are not stable out of solution, this finding also ruled out alkenes, alcohols, and other oxygen-containing organic compounds as fixing reagents. Thus, from the original survey of potential fixing reactions, only those which result in the formation of stable sulfate salts (by precipitation or acid base reaction) are still viable.

Collection of the acid aerosol onto a solid fixing reagent is still feasible, provided one of the three criteria discussed on page 37 apply: the product sulfate is insoluble, the product acid is weak, or the product acid is volatile. In any case, heating is required to dry the collection surface in order to minimize interfering reactions. Potential problems with this method include incomplete fixation (from the limited acid-reagent contact), matting-over of the reagent surface by collected material, and analysis problems associated with the large amount of excess reagent on the filter.

Gas-phase fixation holds the most promise and was ultimately adopted as part of the proposed method. The only volatile fixing reagents which are suitable in speed of reaction and stability of adducts are amines and amine derivatives. This method avoids the problems of solid-phase fixation by providing better acid-reagent contact, preventing matting of the collection surface by continuously applying fresh reagent, and automatically removing excess reagent.

#### Analysis Methods

The final criterion to be considered in this discussion of the theoretical development of the method is the sample analysis methodology. Just as the available collection/fixation techniques placed constraints upon the theoretical fixing reactions that could be utilized, so it will be seen that the available analytical techniques further limit the choice of fixing reagents and collection methods.

Relevant analytical methods include not only ways of measuring sulfuric acid, but also means to measure any conceivable stoichiometrically related adduct. Of course, the choice of adducts has already been greatly limited in previous discussion by chemical or sampling criteria. However, for the sake of a logical argument, the present discussion will deal with all of the analytical possibilities implied in the original listing of potential fixing reactions (Table 2).

#### Non-incorporative $\text{H}_2\text{SO}_4$ Derivatives --

It is essential to a successful analytical method that the substance which is actually measured be a unique product of sulfuric acid. There does not seem to be any means of satisfying this requirement without incorporating at least part of the  $\text{H}_2\text{SO}_4$  molecule in the adduct to be measured. Specifically, sulfur from the acid must be contained in the adduct if it is to be measurably distinct from other products of the fixing reagent.

This conclusion was drawn from the results of experiments on the oxidation-dehydration reaction of sulfuric acid with p-hydroxybenzaldehyde (page 14). Even this relatively specific reaction could be duplicated by other substances which may be in the atmosphere. The product does not incorporate sulfur from sulfuric acid, so it is not a unique product.

Evidently, the reactions of sulfuric acid are not sufficiently unique in themselves to form a distinct non-incorporative adduct; sulfur from the acid must be included as an indication of its origin.

As a result, the number of relevant analytical techniques is greatly reduced. Since the uniqueness of the adduct is based upon the incorporation of part of the  $\text{H}_2\text{SO}_4$  molecule, it follows that the analysis method must measure this portion of the adduct. Thus, the analysis problem is reduced to measuring a closely related derivative of sulfuric acid without interference from other similar compounds.

#### $\text{H}^+$ Measurement --

Simple acidity measurement is not appropriate for  $\text{H}_2\text{SO}_4$  analysis, unless it can be separated from other substances which may affect pH. So many substances have this property that such a separation seems impossible. This characteristic of sulfuric acid is not sufficiently unique to serve as the basis for selective analysis.

#### $\text{SO}_4^{-2}$ in Solution Measurement --

Greater selectivity may be achieved by measuring the sulfate portion of sulfuric acid, rather than its acidic protons. However, this is still inadequate, unless the acid can be first separated from sulfate salts. Selective solubility in an organic solvent has been ruled out as an effective separation method (page 29), which eliminates both direct collection in a solvent and extraction of a filter sample by a solvent as viable alternatives. Sulfate measurement may still be useful, however, if a more effective separation technique is successfully employed. This section discusses several wet-chemical and instrumental methods of measuring sulfate in solution.

Gravimetry--The classical, though seldom used, method for analysis of sulfate is by precipitation of barium sulfate from a hot, slightly acid solution by the addition of barium chloride:  $\text{SO}_4^{=2} + \text{Ba}^{++} \rightarrow \text{BaSO}_4\downarrow$ . The precipitate must be digested, filtered, the paper ignited, and the residue weighed as  $\text{BaSO}_4$ . The procedure is long and tedious, and subject to many interferences, due to coprecipitation of other substances. Interfering substances are largely cations such as lead, strontium, and calcium, which

form insoluble sulfates, although anions of weak acids, nitrates, chlorates, and heavy metal ions interfere, if care is not taken to remove them (56).

Titrimetry--There are many modifications of titrimetric methods of sulfate determinations. Most of the methods involve the pretreatment of the solution by passing it through a cation exchanger, or addition of suitable reagents to eliminate interferences from metal ions. Direct titrations with a barium salt, either barium chloride ( $\text{BaCl}_2$ ) or barium nitrate ( $\text{Ba}[\text{NO}_3]_2$ ), have been reported using various indicators, such as diphenylcarbazone, sodium alizarinsulfonate (57), and nitrochromeazo (58), etc. Potentiometric titrations using both barium and lead salts have been reported as well. Probably the most satisfactory titrimetric method is an indirect determination accomplished by adding a known amount of barium, strontium, or lead salt, and titrating the excess with a suitable reagent, such as ethylenediaminetetraacetic acid (EDTA) (59).

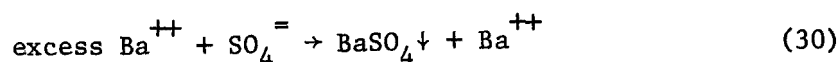
The prescribed EPA method for sulfate determination is titration of the sample with a known  $\text{Ba}(\text{ClO}_4)_2$  solution, using thorin as indicator. When all  $\text{SO}_4^{2-}$  is precipitated as  $\text{BaSO}_4$ , excess  $\text{Ba}^{++}$  forms a colored complex with thorin. Hevel, Protzmann, Davis and Knarr (60) report an indistinct endpoint using this method and prefer to titrate with  $\text{Ba}(\text{ClO}_4)_2$  solution using solfonazo III as indicator.

Eastman Chemical Abstracts 122 and 124 give titrimetric methods for sulfate determination following precipitation by benzidine. Belcher, Nutten and Stephen (40) suggest 4-amino-4-chlorodiphenyl hydrochloride as a precipitating agent to form an amine sulfate which is less soluble than benzidine. The only interference is phosphate, which can be removed as the Ca or Zn salt. Precipitation is analyzed by titration with standard NaOH.

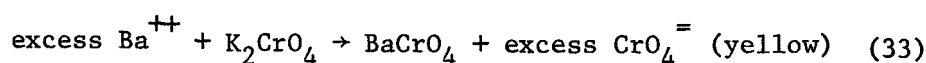
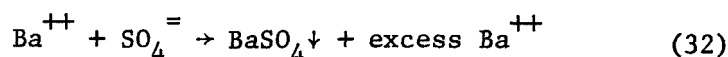
Colorimetry--Colorimetric methods for sulfate determinations follow the same general outline as found in gravimetry, in that barium is added to precipitate barium sulfate. The methods usually involve one of three general procedures:

- 1) A known amount of barium salt is added to the sulfate solution and the excess barium is complexed with a reagent such as methylthymol blue (61). The remaining barium is then determined

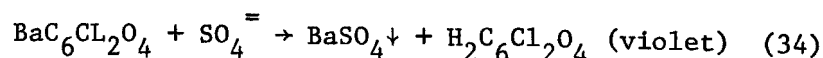
colorimetrically, thus allowing the amount of sulfate to be calculated:



- 2) A known amount of barium is added to precipitate the sulfate followed by addition of a known amount of potassium chromate to precipitate the excess barium. The amount of sulfate present is determined by measuring the absorbance of the excess chromate:



- 3) In the method described on page 29, the insoluble barium chloranilate is allowed to exchange with the unknown sulfate solution to form barium sulfate and the highly colored acid chloranilate ion. The intensity of the color of the chloranilic acid is proportional to the amount of sulfate present (50).



Other less familiar colorimetric procedures for the determination of sulfates are given below:

- a. Barabas and Kaminski (62) formed a purple-colored sulfonic acid derivative of pararosaniline which was analyzed by colorimetry. This method detects  $\text{SO}_2$  as well.
- b. Goguel (63) added excess  $\text{Fe}^{+3}$  to the sample to form the soluble  $\text{FeSO}_4^-$  complex, which is determined colorimetrically. Phosphate, fluoride, chloride, and other anions also complex with  $\text{Fe}^{+3}$ , but some correction can be made.

Turbidimetry and Nephelometry--In these methods for sulfate determination, barium chloride, 4,4'-diaminotolane, 2-aminoperimidine, or benzidine, etc. are used to form a fine precipitate with sulfate. The basis of both measurements is the interaction of light with a fine suspension of particles. The differences in the methods are in the way this interaction is measured. In nephelometry, the radiation that is scattered by the particles is measured perpendicular to the axis of incident light. Turbidimetry, on the other hand, measures the amount of radiation that passes through the suspension, and thus, the measurement is made along the axis of the incident light. Both of these methods are very sensitive to small amounts of sulfate, if the proper reagent is used.

Potentiometry--Hebel, et al. (64) titrated a sample with  $\text{Pb}(\text{ClO}_4)_2$  using an Orion lead specific ion electrode as an indicator. When all  $\text{SO}_4^{2-}$  is precipitated by  $\text{Pb}^{+2}$ , excess  $\text{Pb}^{+2}$  is sensed by electrode.

X-ray Fluorescence--X-ray fluorescence depends upon the excitation of secondary x-rays characteristic of each element by absorption of primary x-rays. The identification of these characteristic wavelengths and the measurement of their intensities constitute a method for qualitative and quantitative analysis. Elements from atomic number 12 and up in solid and liquid matrices may be determined routinely by x-ray fluorescence. Liquid samples should exceed a depth which will appear infinitely thick to the primary x-ray beam.

Quantitative analysis by x-ray fluorescence requires the use of a known standard for count comparison. Before the comparison of the standard and the sample can be made, it is necessary to correct for matrix effects. The correction for matrix effects can be accomplished by diluting the sample with a material having a low absorption, or by applying an internal standard technique. The internal standard technique is valid only if the matrix elements affect both the reference line and the analytical line in exactly the same way. The internal standard line and the analytical line ratio is not a true measurement of the concentration of the element to be determined, if the reference line or the analytical line is selectively absorbed or enhanced by a matrix element.

Since x-ray fluorescence is responsive to an element, no matter in what



state it is, it would be necessary to separate the  $\text{H}_2\text{SO}_4$  adduct from other species containing the same element to be measured prior to analysis. Sulfur would, of course, be the element measured, and this method would be a wholly-instrumental way of measuring total sulfate in solution. Other sulfur-specific instrumental methods require that the sulfate-containing solution be atomized or vaporized, and these are discussed in the following section.

#### Separation from Interferences by Decomposition/Volatilization --

None of the methods for sulfate measurement described in the preceding section can solve the selective analysis problem alone. In every case, it is necessary that sulfuric acid be separated from sulfate salts and other potential interferences prior to sulfate measurement. If this cannot be done during the collection process, then it must be done as part of the analytical procedure.

Volatilization (Microdiffusion) of  $\text{H}_2\text{SO}_4$  --The only physical property in which sulfuric acid differs greatly from sulfate salts is volatility. Sulfuric acid is often considered non-volatile at room temperature, but it does have a measurable vapor pressure and, when heated over  $100^\circ\text{C}$ , can be volatilized quite rapidly. In contrast, sulfate salts are truly non-volatile until their decomposition temperature is reached, and even the lowest-decomposing sulfate (ammonium hydrogen sulfate) is stable to at least  $230^\circ\text{C}$ .

Dubois, et al. (65) first used this property to separate  $\text{H}_2\text{SO}_4$  from glass fiber filters by microdiffusion (volatilization). Maddalone, et al. (53) studied the efficiency of microdiffusion from various filter media at  $100^\circ\text{C}$  to  $195^\circ\text{C}$  using  $^{35}\text{S}$ -labeled  $\text{H}_2\text{SO}_4$  and concluded that Mitex Teflon and Paco graphite filters had the best diffusion characteristics. Scarin-gelli and Rehme (66) reduced the acid vapor to  $\text{SO}_2$  over hot copper, which was subsequently measured with the flame photometric detector (FPD) or the West-Gaeke bubbler (65). Dharmarajan, et al. (68) collected the volatilized acid onto a surface coated with the sulfate-precipitation agent, perimidyl-ammonium bromide, and reduced the resulting sulfate to  $\text{SO}_2$  at  $500^\circ\text{C}$  for measurement by the West-Gaeke bubbler. Further elaboration of the micro-diffusion technique by a research group at the Cabot Corporation [Richards

(69)] led to the development of a prototype instrument which collects the aerosol onto a filter and volatilizes it into an FPD for analysis. This instrument has been further developed by Mudgett, Richards, and Roehrig (70) into a fully automatic unit.

The microdiffusion technique does effectively separate sulfuric acid from sulfate salts on the filter, but at the expense of another serious interference. Acid on the filter is free to react with other collected particulates. In fact, during the volatilization process, it may be expected that any substances on the filter capable of reacting with the hot acid vapor will have ample opportunity to do so.

Selective Decomposition of  $H_2SO_4$  Adduct--This deficiency of direct volatilization schemes is widely recognized among researchers in the field, as is the need for fixation of the acid as it is collected in order to eliminate these side reactions. To date, the only published attempt to solve this problem was made by Thomas, et al. (43), who collected sulfuric acid on a glass fiber filter impregnated with the sulfate-precipitating reagent, perimidylammonium bromide (PDA-Br). Unfortunately, the insoluble  $(PDA)_2SO_4$  thus formed was too stable to be thermally decomposed apart from ammonium sulfate. (See Page 21.)

In this area, the requirement of selective analysis seems to be at odds with that of fixation. If the acid is not fixed, it may be lost through side reactions on the collection surface; but, if it is fixed, the separation from other interfering substances may be impossible. West (53) has made the interesting suggestion that an enzymatic reduction of  $(PDA)_2SO_4$  may be possible, but no work on this technique has been published. The only alternative is to find a different fixing reagent which satisfies both requirements by stabilizing the acid as an adduct which can be selectively decomposed.

The solution is necessarily a compromise between adduct stability and selective analyzability. Insoluble sulfates are ideal adducts from the viewpoint of stability, but that same stability makes their decomposition temperatures too high to avoid interference from common atmospheric sulfates. The present method proposes adducts which are water-soluble, and thus chemically stable, but can be selectively decomposed. It is this compromise

solution which is unique to the method considered here.

Measurement of Evolved Gas--Once the adduct has been selectively decomposed, a system for measuring the evolved gases must be employed to complete the analytical procedure. From the discussion on page 43, it is evident that the system must be specific for sulfur, if interferences are to be avoided. With some analytical methods, however, the oxidation state of sulfur in the evolved gas is also an important consideration.

When sulfuric acid is volatilized directly, the evolved gas (loosely termed "sulfuric acid vapor") probably consists of a mixture of  $\text{SO}_2$ ,  $\text{SO}_3$  and  $\text{H}_2\text{O}$  vapor. The hydrated  $\text{SO}_2$  and  $\text{SO}_3$  molecules are extremely reactive and may be lost during the volatilization procedure. When the acid is fixed as dry acid crystals, the evolved gas favors  $\text{SO}_2$  more strongly, and it is much less reactive in the absence of water, since no acidic protons are generated.

Of the two sulfur gases, the one which is favored depends upon temperature, pressure, oxygen content in the chamber, and the presence of catalysts. A mixture may be converted entirely to  $\text{SO}_3$  (71), or to  $\text{SO}_2$  (66) by the appropriate catalytic conditions. With this in mind, there are several possible methods for analyzing the evolved gas.

If the gas is predominantly  $\text{SO}_3$ , it may be dissolved in water to form sulfuric acid, which can then be analyzed by a standard method for sulfate. (See page 44.) This is less attractive than other alternatives for several reasons. First,  $\text{SO}_3$  is more easily lost by side reactions than  $\text{SO}_2$ ; specifically, it has a stronger affinity for water and produces a stronger acid when hydrated. Secondly, many of the wet-chemical sulfate methods (those based upon precipitation of  $\text{BaSO}_4$ ) are sensitive only to the low ppm range. If the detection limit is 5 ppm (or 5  $\mu\text{g}/\text{ml}$ ), and the collecting volume 10 ml, 50  $\mu\text{g}$  of acid would have to be collected before it was detected. With a measurement goal of 0.25  $\mu\text{g}/\text{m}^3$  sulfuric acid in air, 200  $\text{m}^3$  of air would have to be sampled. This may be reduced somewhat by concentrating the  $\text{SO}_3$ -collecting solution, but it is more desirable to use a method with higher sensitivity which will allow a smaller air sample volume. Finally, some of the wet-chemical methods are subject to non-sulfur interferences which may be present in the decomposition gas, such as oxides of phosphorus and

nitrogen, particularly when such a large sample is taken.

If the evolved gas consists predominantly of  $\text{SO}_2$ , it can be measured by the West-Gaeke bubbler (67). In this method,  $\text{SO}_2$  is collected in an aqueous solution of 0.1 M sodium tetrachloromercurate where it is fixed as the stable disulfitomercurate (II) ion. When a p-rosaniline hydrochloride-hydrochloric acid mixture and formaldehyde are added, a violet color is produced proportional to the amount of fixed  $\text{SO}_2$  present. The absorption maximum at 560 m $\mu$  is used for a spectrophotometric measurement. This method will detect the equivalent of 1  $\mu\text{g}$   $\text{H}_2\text{SO}_4$  converted to  $\text{SO}_2$  and dissolved in a 10 ml collection solution. Therefore, the sensitivity is adequate. Nitrogen dioxide and ammonia (72) may interfere, but will probably not be present to a significant extent in the decomposition gas. The West-Gaeke bubbler would be the best method for measuring  $\text{SO}_2$  in the decomposition gas, if more rapid instrumental methods were not available.

Several instrumental methods for sulfur measurement are available which make use of atomic emission and absorption characteristics. The one which is most convenient for measurement of a gas containing sulfur is the flame photometric detector (FPD). Sample gas is fed onto an air- $\text{H}_2$  flame which causes sulfur atoms to emit their characteristic spectrum. A 374 nm optical filter selectively allows the sulfur light emission to reach a photomultiplier tube (older units use 395 nm filters, but these are subject to interference from hydrocarbons). This detector responds to any sulfur present, regardless of the oxidation state. The main advantage is the sensitivity, which ranges from the low nanogram range of about 1  $\mu\text{g}$  of  $\text{H}_2\text{SO}_4$ . Saturation occurs at the upper limit, because excess sulfur atoms reabsorb the emitted light (73).

It is evident from Table 6 that the higher sensitivity of the FPD allows a much smaller sample to be collected than with the other methods. Thus, less distortion of the atmospheric sample occurs by concentration on the collection surface. Measurement by FPD is also much more rapid than the West-Gaeke bubbler. The only theoretical advantage of the bubbler is that it allows the evolved gas to be rapidly separated from the sample and concentrated elsewhere. With the FPD, the gas must be held for at least several minutes before flushing into the detector. If loss of sample during this period is

significant, it may be advantageous to concentrate the gas in another manner, prior to FPD Analysis.

TABLE 6. SENSITIVITY COMPARISON OF SULFUR-GAS MEASUREMENT METHODS

<u>Method</u>	<u>Min. wt. H<sub>2</sub>SO<sub>4</sub> (μg)</u>	<u>Min. Sample Volume (m<sup>3</sup>)*</u>
SO <sub>4</sub> <sup>-2</sup> wet-chemical†	50	200
SO <sub>2</sub> West-Gaeke bubbler	1	4
FPD	0.01	0.04

\*For 0.25 μg/m<sup>3</sup> sensitivity.

†Assuming 10 ml analysis solution.

#### Summary of Analysis Method --

It was determined that the analysis method must be specific for sulfur, either as SO<sub>4</sub><sup>-2</sup>, SO<sub>2</sub>, or both. Since selective solubility is not a very promising approach, it was determined that selective thermal decomposition of the adduct at 200°C or below was the only feasible method for separating interferences.

Three methods of measuring the evolved sulfur-containing decomposition gas were discussed: wet-chemical SO<sub>4</sub><sup>-2</sup> analysis, the West-Gaeke SO<sub>2</sub> bubbler and the FPD. Of the three, the FPD had the greatest advantage in sensitivity and flexibility, responding to all forms of sulfur regardless of oxidation state. Thermal decomposition of the adduct and FPD measurement of the evolved gas was, therefore, adopted into the Atlantic Research method.

#### Summary: Theoretical Development of Atlantic Research's Method

The preceding discussion has attempted to illustrate the manner in which the proposed method evolved from the main possibilities for fixation, sampling, and analysis of sulfuric acid aerosol. Rapid formation of the adduct and convenience of sampling required a gaseous amine or amine-

derivative fixing reagent. Considerations of selective analysis added the requirement that the adduct decompose at 200°C by releasing a sulfur gas.

All of these conclusions were supported by experimental work, some of which has been briefly described. The following sections contain a more detailed discussion of experimental work relating to the developed method.

## SECTION 5

### EXPERIMENTAL

#### APPARATUS

##### Aerosol Generator

The sulfuric acid aerosol generator used in these experiments was based upon the atomizer-burner model described by Thomas, et al. (74). In this model, a dilute  $\text{H}_2\text{SO}_4$  solution is aspirated into an  $\text{H}_2\text{-O}_2$  flame, where it decomposes to  $\text{H}_2\text{O}$  and  $\text{SO}_3$ . Recombination occurs to yield sulfuric acid aerosol.

A Beckman 4060 Large Bore Atomizer Burner Assembly was mounted at the base of a glass stack 1.2 M (4 ft) high by 15.2 cm (6 in.) diameter. Burner gas back-pressures were set at 1.4 kN (0.2 psi) for  $\text{H}_2$  and 1.4 kN/m<sup>2</sup> (10 psi) for  $\text{O}_2$ . The aspirated solution was 10%  $\text{H}_2\text{SO}_4$  by weight.

##### Collection of Aerosol

A glass sample probe was positioned at the top of the stack and drew the aerosol into a glass mixing vessel, where it was divided into two equal streams. Each stream was drawn through a Millipore Mitex filter in a nylon filter holder by a large vacuum pump, and added at a point 7.6 cm (3 in.) above the filter holder. Figure 6 illustrates the complete system.

Sampling was carried out for 2 to 4 minutes with about 5 ml of solution aspirated during that period. Total volume sampled (measured by a wet test meter) was 0.003 to 0.1 m<sup>3</sup>. The position of the probe inlet at the top of the stack was found to be crucial for collection of a suitable amount of sample. If placed in the center of the stack, the sample would be too large and saturate the detector, while if placed outside the stack perimeter, a measurable amount would not be collected. At the median position, a suitable amount of sample was collected in a few minutes.

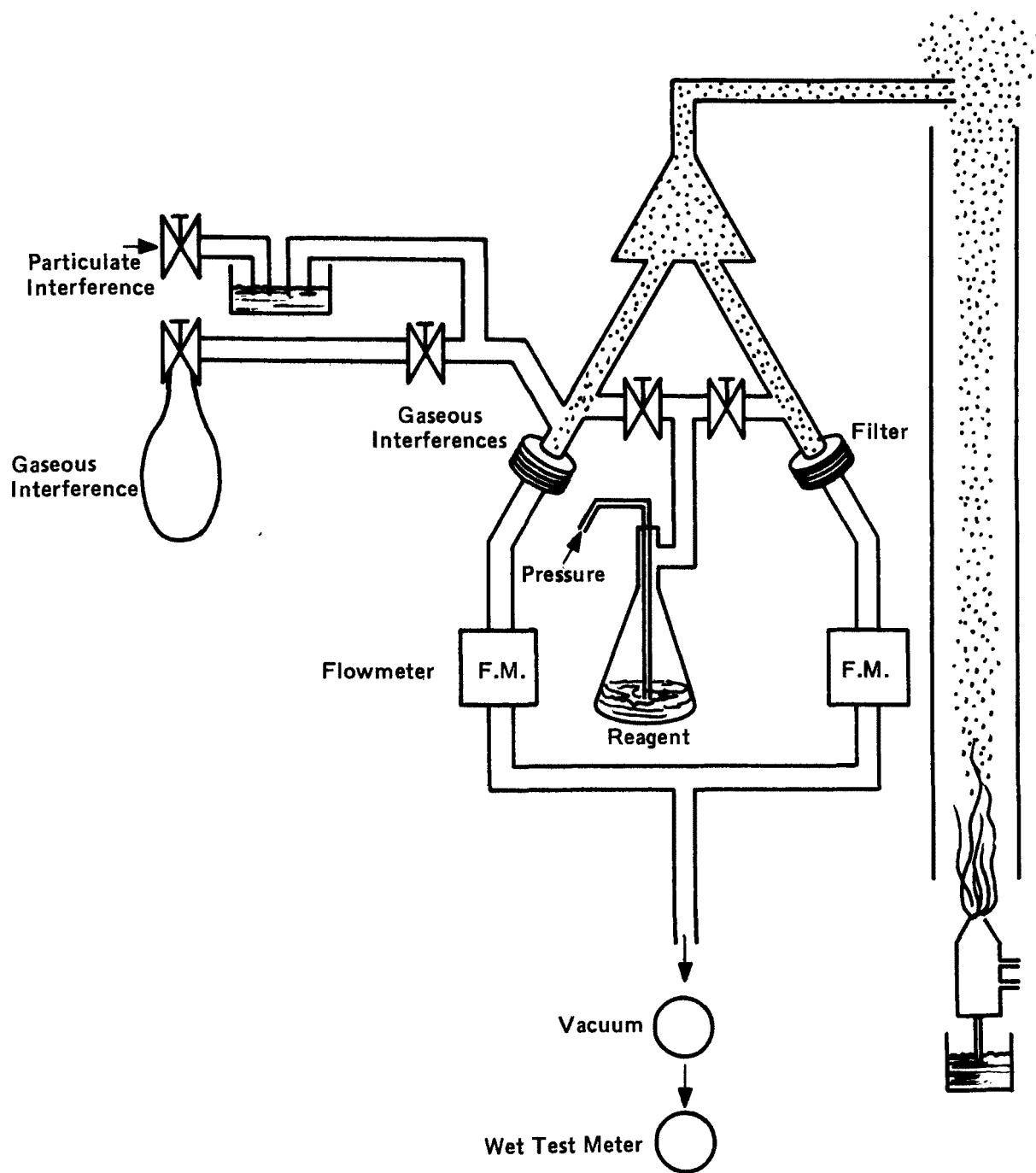


Figure 6. Dual collection/fixation system.



## Analysis of Samples

### Decomposition Apparatus

The instrument constructed to analyze the samples consisted basically of a heated cell to thermally decompose the sample, and a valve arrangement by which helium carrier gas was delivered to the FPD, either through the cell, or through a bypass line. Figure 7 is a schematic diagram of the system.

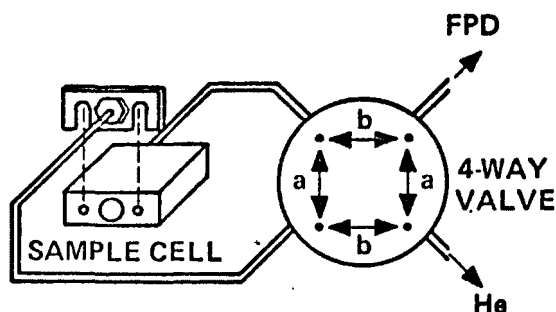


Figure 7. Analysis instrumentation.

The sample cell was machined from a block of aluminum  $5.7 \text{ cm}^2 \times 5.7 \text{ cm}^2 \times 2.54 \text{ cm}$  (2-1/4 in.  $\times$  2-1/4 in.  $\times$  1 in.). The large central cavity for the sample was 1.59 cm (5/8 in.) ID and coated with Teflon. One end of the cavity was tapped to accommodate an aluminum NPT fitting, and a groove was cut around the other end to hold a Viton O-ring. On the breech end, an Allen screw was placed on either side of the cavity to hold the breech cover in place. The cell was opened by loosening these two screws and sliding the cover off the screw shafts. An airtight seal was provided by the O-ring, and all surfaces in contact with the sample were Teflon-coated aluminum. The cell was heated by two implanted cartridge heaters (not shown) on either side of the cavity. Asbestos tape was wrapped around the cell for insulation.

The valve was a Valco 4-way valve constructed of Carpenters C-20 alloy, which is recommended for reactive gases such as  $\text{SO}_2$ . This valve could be heated to  $300^\circ\text{C}$  without damage. All connecting tubing was 0.16 cm (1/16 in.)

ID Teflon-lined aluminum. The sample gas lines and valve were wrapped with Nichrome ribbon (sandwiched between glass fiber tape) which could be heated independently of the sample cell.

#### Flame Photometric Detector (FPD) --

The FPD used in these experiments was a Melpar Model 100 with a 374 nm optical filter. When samples from the aerosol generator were first run on this system, very peculiar FPD recordings were obtained. The main peak was extremely broad, requiring several hours to tail to baseline, and was often preceded by a small sharp peak. Figure 8 illustrates some of these recordings. It was suspected that these recordings were artifacts of a saturated detector. As a result, several experiments were carried out with known SO<sub>2</sub>-air mixtures to clarify the response characteristics of the FPD.

For these experiments, the sample cell was removed and the carrier line was connected directly to the detector inlet. A silicon rubber septum was inserted in the line for injecting SO<sub>2</sub> with a syringe. The source of SO<sub>2</sub> was a compressed-gas lecture bottle, fitted with a valve and a silicon rubber septum. Dilutions of SO<sub>2</sub> in air were carried out in a 305 cc siliclad-coated, glass vessel fitted with a rubber septum. Two syringes with Teflon pressure-lock valves were used, with maximum volumes of 100 µl and 500 µl. Several blank injections were made after each sample injection to insure that the syringes were clean of residual SO<sub>2</sub>.

Microliter amounts of pure SO<sub>2</sub> from a gas cylinder were injected in the first experiments. Figure 9 shows the effect of injecting progressively larger volumes of SO<sub>2</sub>. There was a slight increase in peak width and in separation between the two peaks, but these were not proportional to changes in the SO<sub>2</sub> level. It was evident that all of these peaks were resulting from a saturated detector.

When these peak heights were compared to those previously obtained from samples (Figure 8), it was evident that the samples had been saturating the detector. The smallest volume injected, 10 µl, corresponds to about 3 µg of SO<sub>2</sub> and even this seemed to be considerably over saturation level.

In order to bring the sample size down to the quantitative response range, 1 cc of pure SO<sub>2</sub> was injected into the clean 305 cc dilution vessel.

Relative FPD Responses, Amps  $\times 10^{-9}$

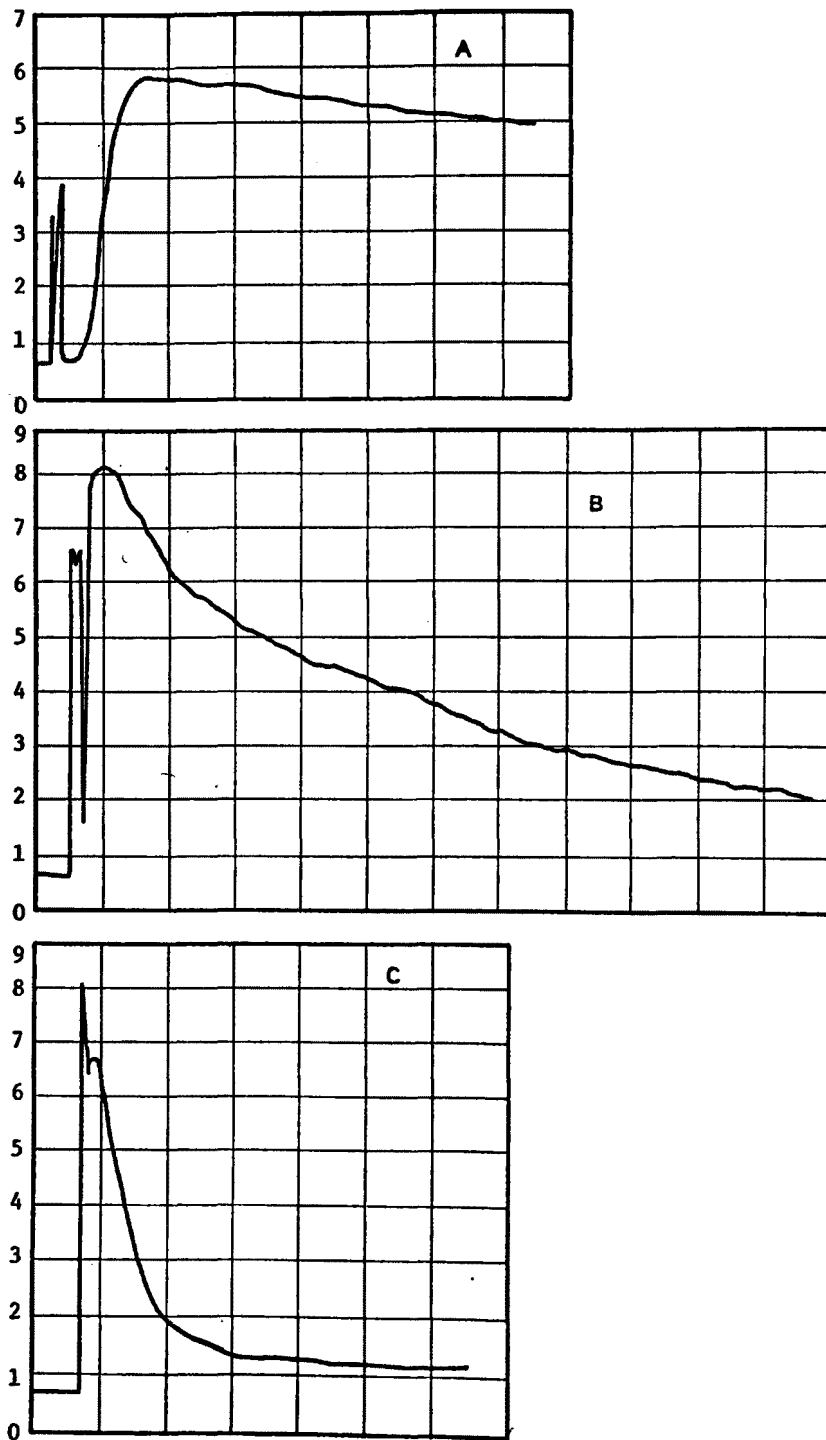


Figure 8. Early FPD recordings from samples.

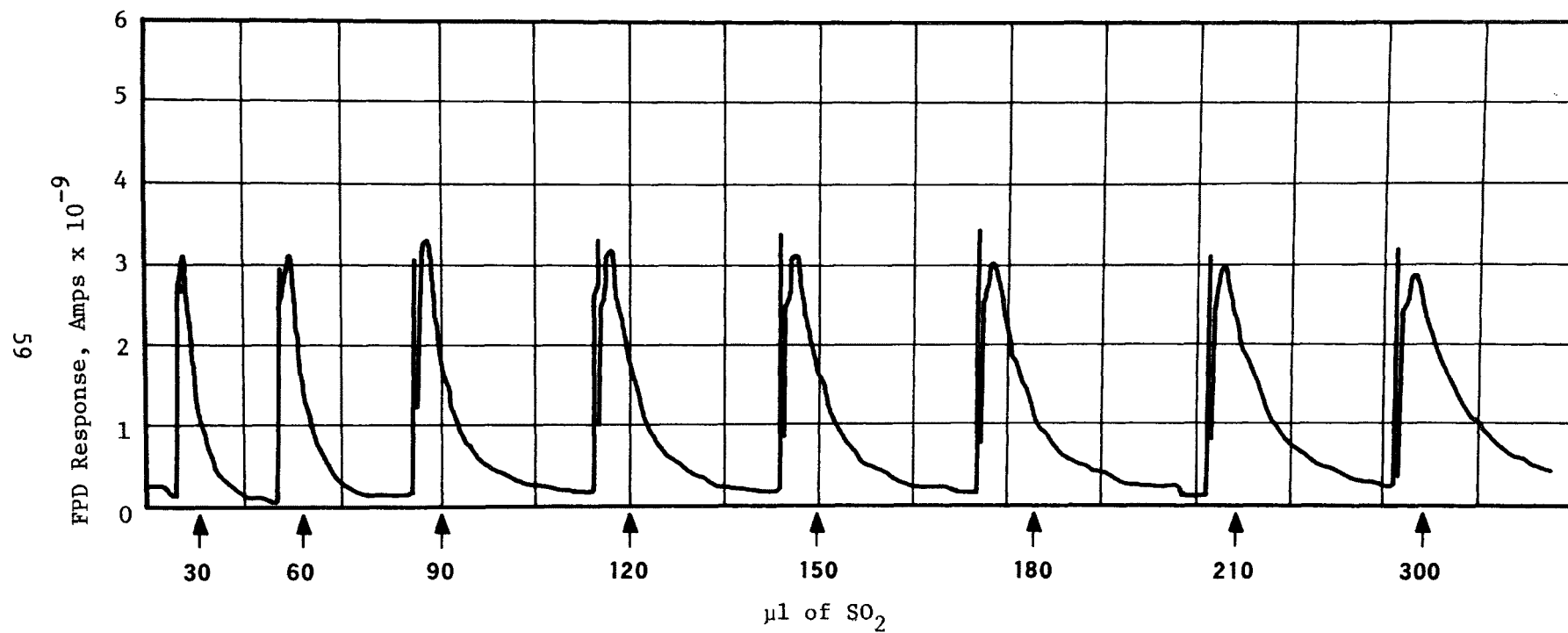


Figure 9. Effect of injecting progressively larger  $\text{SO}_2$  volumes.

The resulting mixture was about 3300 ppm  $\text{SO}_2$ . When microliter volumes of this dilution were injected, the peaks were much sharper and their heights were related to the amount injected as figure 10 shows. The response was fairly linear from at least 0.1  $\mu\text{g}$  up to about 0.6  $\mu\text{g}$ , beyond which there was no further consistent increase in peak height. It was established on other electrometer settings that the saturation level always occurred at about 0.6  $\mu\text{g}$  of  $\text{SO}_2$  and did not depend upon the electronics of the instrument.

If the saturation level of the detector is 0.6  $\mu\text{g}$   $\text{SO}_2$ , the corresponding amount of  $\text{H}_2\text{SO}_4$  is 0.9  $\mu\text{g}$ . It is, therefore, not surprising that the large acid aerosol samples which gave the FPD recordings of figure 8, and were estimated to contain 20 to 30  $\mu\text{g}$   $\text{H}_2\text{SO}_4$  (by an independent pH measurement), did indeed saturate the detector.

To look at the lower end of the scale, a new  $\text{SO}_2$ -air dilution was made, which was one-tenth as concentrated as the last one (330 ppm). Sensitivity of the electrometer was increased by setting the range at 10 and attenuation at 32. As figures 10 and 11 show, the response was fairly linear from 10 to 100  $\mu\text{l}$  of the injected sample. There was some difference observed between the two syringes, the smaller one producing less response from the same volume of sample. This was possibly due to the greater surface-to-volume ratio of the smaller syringe, causing retention of  $\text{SO}_2$  by glass surfaces to be greater. Both sets of data are shown.

These experiments, in which  $\text{SO}_2$  was injected into the FPD, were crucial in the interpretation of the FPD recordings from aerosol samples. It was established that the peaks of figure 8 were saturation artifacts. The delay between the first sharp peak and the second broad one was due to signal suppression by excess sulfur atoms in the flame reabsorbing the emitted light. In subsequent runs, sampling procedures were modified to collect smaller samples and the resulting peaks resembled the unsaturated  $\text{SO}_2$  peaks. The linearity of the response was somewhat puzzling, since it is supposed to be a square function of the sample size. No explanation has been suggested for this observation.

Supporting Instrumental Analysis --

Instruments other than the FPD were used to obtain information

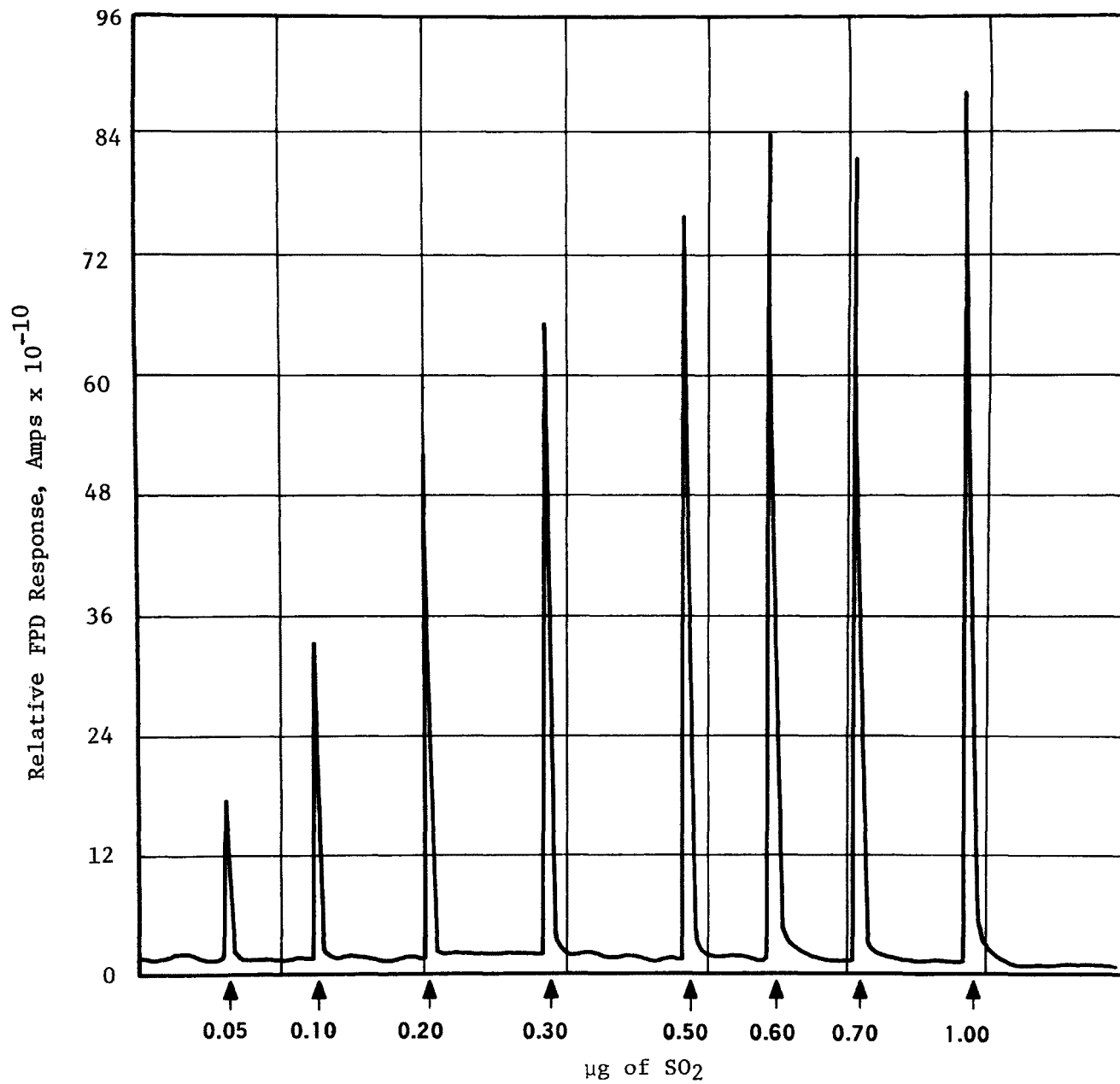


Figure 10. Quantitative FPD response to Injected  $\text{SO}_2$ .

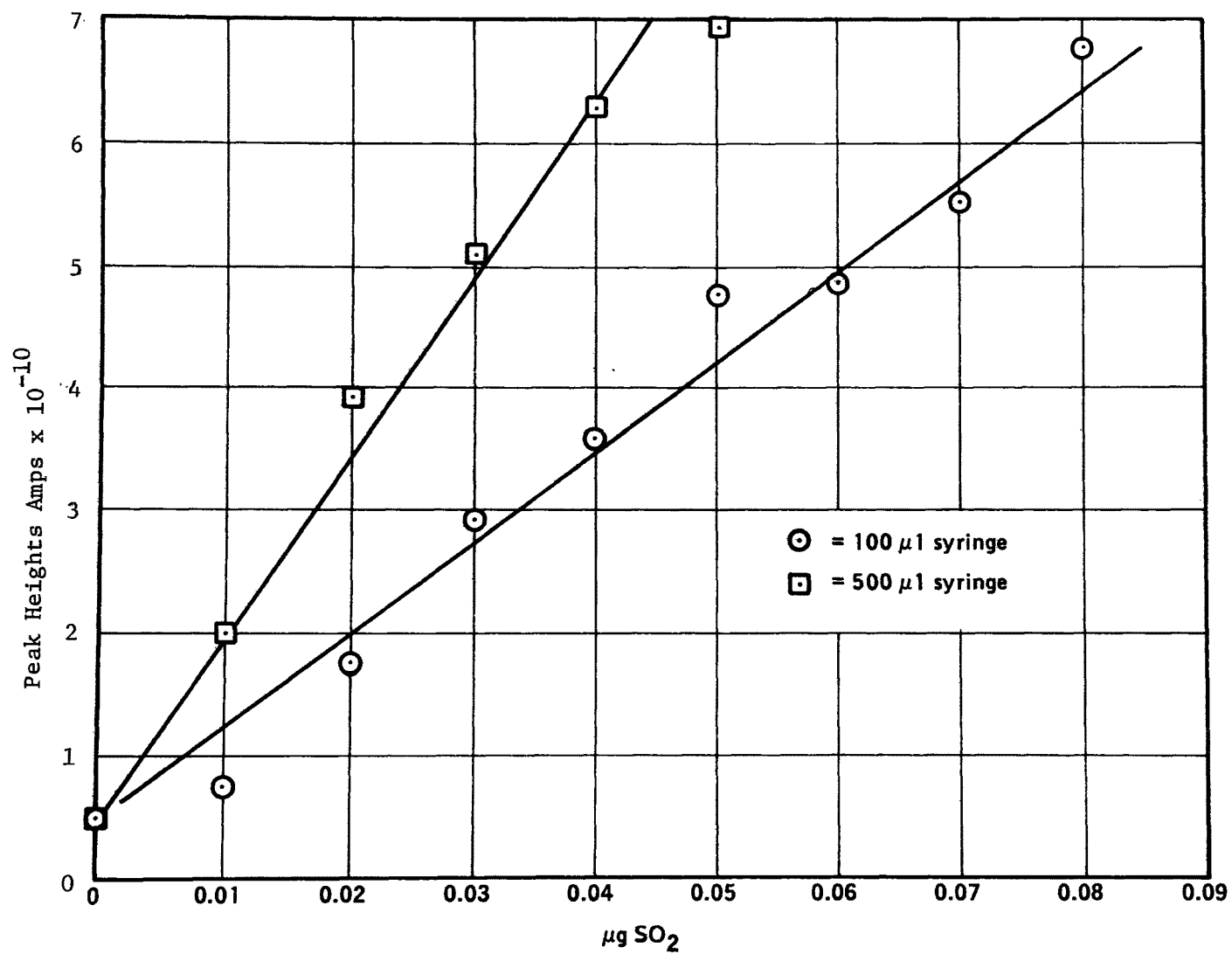


Figure 11. Quantitative response of FPD to  $\text{SO}_2$ .

concerning decomposition of the adducts, although these instruments were not considered adequate for analysis of real samples.

Differential Thermal Analysis (DTA)--DTA was used to obtain information about the temperatures at which candidate adducts and potential interfering substances decomposed. This instrument operates by amplifying and recording the temperature difference between a quantity of the sample substance and an inert reference (ground glass) as they are slowly heated in a baffle. When an endothermic or exothermic process occurs in the sample, it is recorded as a peak at the temperature of the baffle.

Figure 12 is a composite DTA recording of several common sulfates which have relatively low decomposition temperatures. All are above 200°C, except for the melting (sharp peak) of  $\text{KHSO}_4$  at 180°C, and a slight decomposition of  $\text{CuSO}_4$  at 200°C. More importantly, ammonium sulfate and ammonium hydrogen sulfate are stable to 250°C and 230°C, respectively. This indicates that an adduct which decomposes and releases  $\text{SO}_2$  at 200°C may be analyzed without interference from these substances.

Mass Spectrometry--Mass spectrometry was utilized to identify the gases released by the decomposing adducts. All of the adducts discussed in the next section were found to release  $\text{SO}_2$  at 200°C, but no detectable  $\text{SO}_3$ . There was some ambiguity in these results, however, because even unreacted  $\text{H}_2\text{SO}_4$  gave predominantly  $\text{SO}_2$  at this temperature.

#### FIXING REAGENTS

The fixing reagents used in this method have been described as volatile amines and amine-derivatives (hydroxylamines and oximes). One compound in each category was evaluated, although this is not to imply that the compound chosen is necessarily the most desirable one. The compounds were:

$(\text{C}_2\text{H}_5)_2\text{NH}$	$(\text{C}_2\text{H}_5)_2\text{NOH}$	$\text{CH}_3\text{CH=NOH}$
Diethylamine (DEA)	Diethylhydroxylamine (DEHA)	Acetaldoxime (AAO)

All are liquids at room temperature, but are sufficiently volatile to generate a substantial vapor from a bubbler.

#### Reactions of $\text{H}_2\text{SO}_4$

The functional groups of the compounds DEA, DEHA, and AAO are all



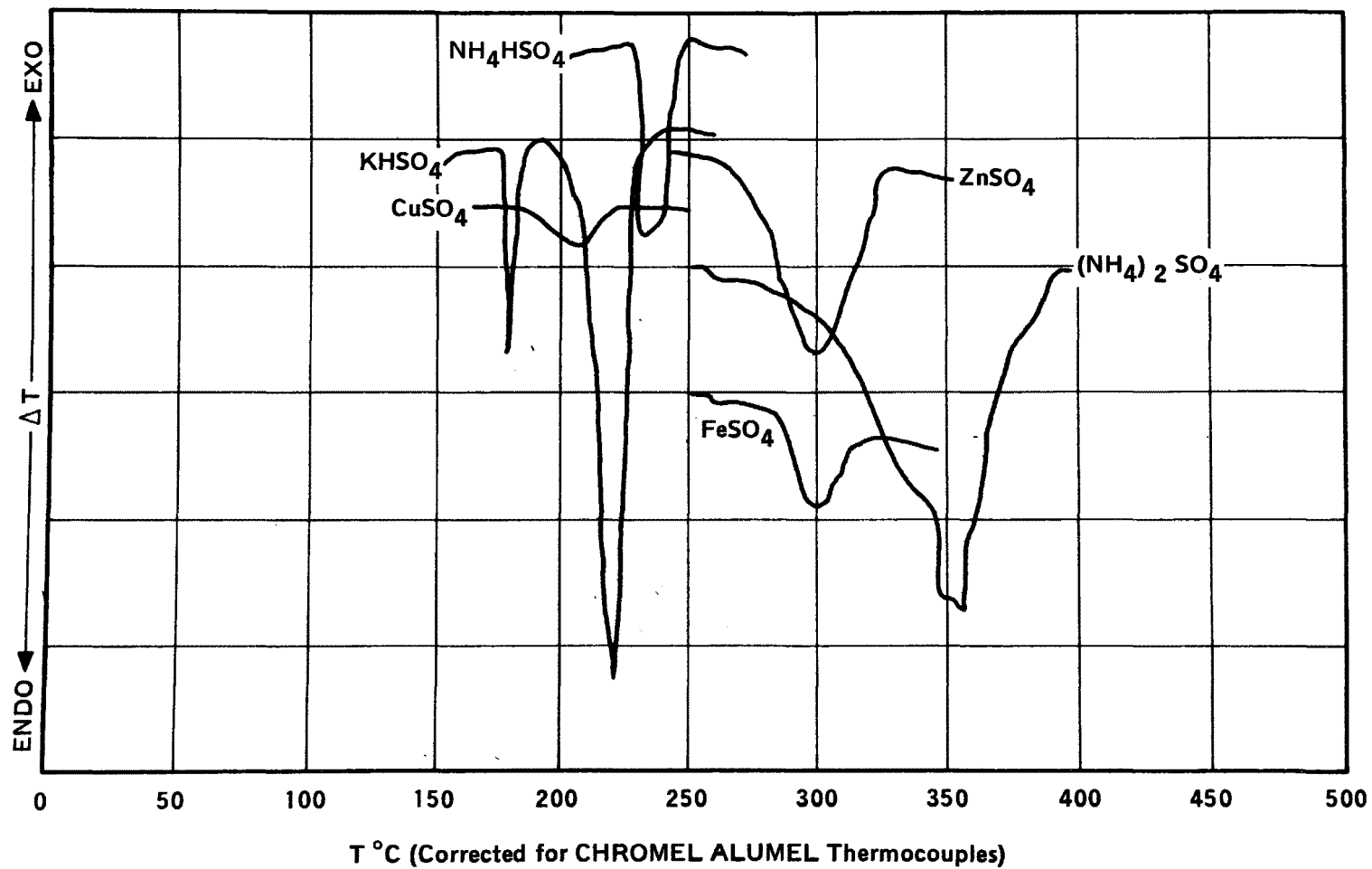


Figure 12. Composite DTA of potential interferences.

sufficiently basic to form the bisulfate salt from sulfuric acid. Base strength decreases in the order: DEA > DEHA > AAO. When concentrated  $\text{H}_2\text{SO}_4$  was added to excess DEA or AAO, white crystals immediately formed and crystallized out of solution. They were water-soluble and turned black when heated. These physical properties, as well as IR spectral evidence, strongly suggested an ionic sulfate or bisulfate salt. DEHA formed a very viscous yellow oil when  $\text{H}_2\text{SO}_4$  was added, but this oil was also water-soluble and decomposed when heated. A peak at  $1650\text{ cm}^{-1}$  in the IR spectrum of this oil, which was absent in the unreacted reagent and acid, suggested an N-H bending vibration from protonation of nitrogen, as postulated in the formation of the bisulfate. NMR did not give any information on the position of the acidic proton, because of exchange with the solvent.

Thus, it appears that these compounds do react with sulfuric acid rapidly, by forming a sulfate or bisulfate salt. There is no reason to suppose that the product would be different when formed under sampling conditions.

#### Decomposition of Adduct

DTA's of the white solids obtained from DEA and AAO, as described above, were not very informative because of the multiplicity of peaks, both over and under  $200^\circ\text{C}$ . Release of a sulfur gas at  $200^\circ\text{C}$  was confirmed for all three adducts by heating in the FPD sample cell previously described. Mass spectra indicated that  $\text{SO}_2$  was the main gas, and this was supported by the West-Gaeke bubbler (which does not detect  $\text{SO}_3$  or  $\text{SO}_4^{-2}$ ).

Some other amine sulfates were examined by DTA: perimidylammonium sulfate (an insoluble salt) and pyridinium sulfate (from pyridine). The DTA's indicated (Figure 13) that no decomposition occurred under  $250^\circ\text{C}$ . Consequently these are probably not suitable as adducts.

#### PROCEDURES AND RESULTS

The FPD analysis apparatus described on page 56 was used to analyze fixed aerosol samples from the aerosol generator by two major procedures. In the rising temperature procedure, the sample filter was inserted into the analysis cell at room temperature. With carrier gas flowing through the cell to the FPD, the cell temperature was then slowly raised. In the

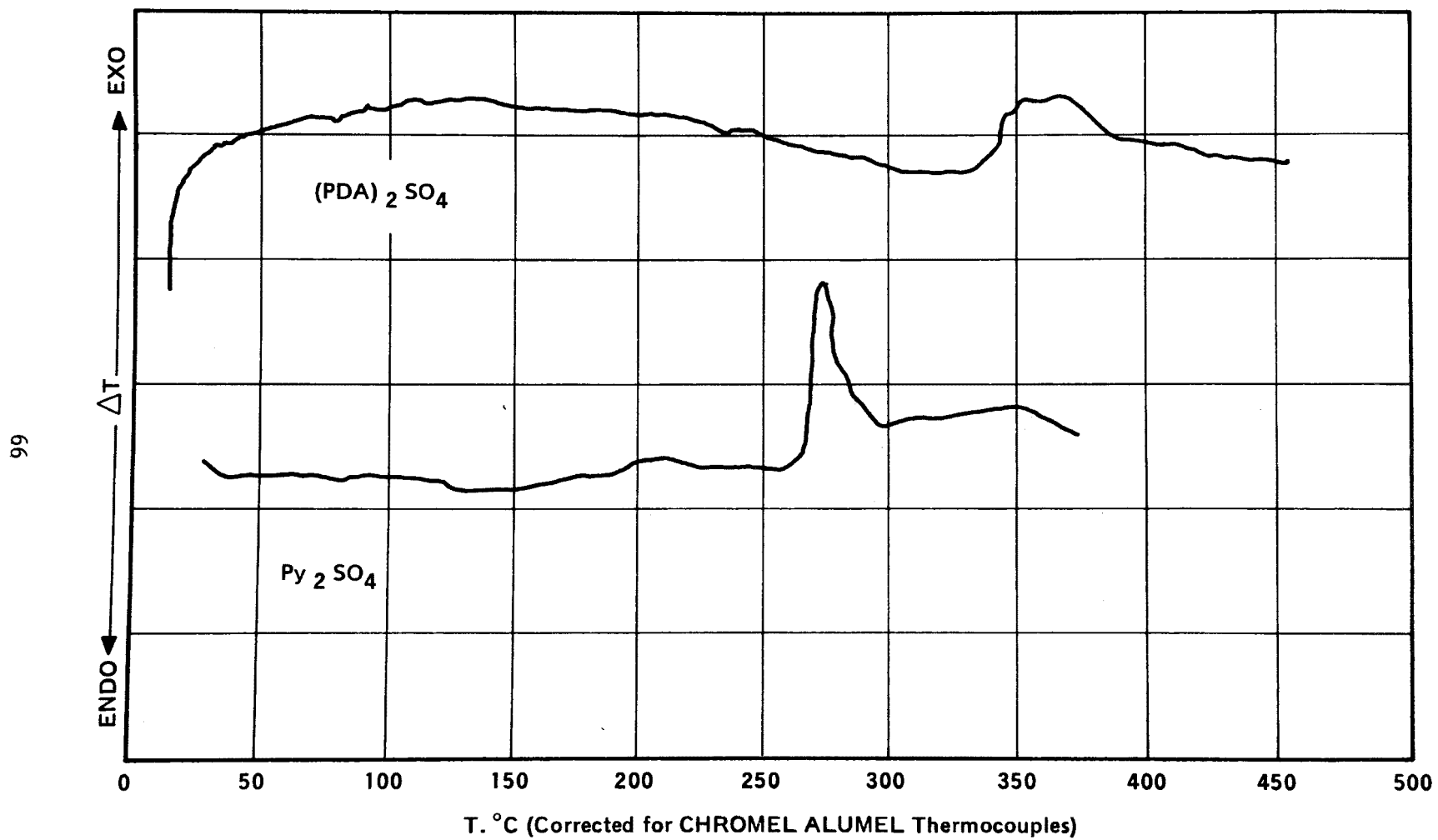


Figure 13.  $(PDA)_2SO_4$  and  $Py_2SO_4$  DTA.

fixed temperature procedure, the sample was inserted at 120°C, and rapidly raised to 200°C, with the carrier gas bypassing the cell. After five minutes at 200°C, the valve was switched to sweep gas evolved from the sample to the FPD. Using these two procedures, different kinds of information were obtained.

#### Rising Temperature Procedure

This procedure was used to determine the temperature at which a sulfur gas was first evolved from the sample. As the cell temperature rose, it was marked on the FPD chart and the temperature at which the pen rose sharply from baseline was taken as the decomposition point. Large aerosol samples were taken when this procedure was used to insure that the beginning of decomposition was detected, although the peaks became saturated at a higher temperature.

The results strikingly revealed the effects of fixation on the collected aerosol. As shown in Table 7, the evolution of SO<sub>2</sub>, in every case, occurred at higher temperature with the fixed samples than with the unfixed H<sub>2</sub>SO<sub>4</sub>.

TABLE 7. TEMPERATURE OF FIRST FPD SIGNAL FROM ADDUCTS

	°C
H <sub>2</sub> SO <sub>4</sub> alone	90
H <sub>2</sub> SO <sub>4</sub> + AAO	140
H <sub>2</sub> SO <sub>4</sub> + DEHA	190
H <sub>2</sub> SO <sub>4</sub> + DEA	190

This was not an indirect effect of excess reagent on the filter, since the same results were obtained when the samples were thoroughly flushed with clean air prior to analysis. Of the three reagents, it appears that AAO forms the adduct which is easiest to thermally decompose.

#### Fixed Temperature Procedure

By holding the evolved SO<sub>2</sub> in the sample cell for several minutes before sweeping it into the FPD, the gas evolved over that period is concentrated. This procedure is, therefore, more sensitive to small samples

than the previous procedure. If care is taken to collect samples that are not too large, the peaks obtained when the valve is switched are sharp, and their height may be taken as a measure of the  $\text{H}_2\text{SO}_4$  collected. This procedure, therefore, was adopted for the quantitative analysis of samples.

The complete technique for analyzing samples with the FPD-decomposition cell device is described by the following steps:

- 1) Bring cell temperature to  $120^\circ\text{C}$ .
- 2) With the carrier gas switching valve on bypass, open the cell and insert the sample filter (rolled). Reseal the cell.
- 3) Maintain the cell temperature at  $120^\circ$  for 5 minutes, then switch the valve to sample and record the peak (if any).
- 4) Switch the valve back to bypass after two minutes and rapidly raise the cell temperature to  $200^\circ\text{C}$ .
- 5) Maintain the cell at  $200^\circ$  for 5 minutes, then switch the valve to sample and record the peak. After 20 minutes, switch back to bypass.
- 6) Clean the cell between runs by heating to  $250^\circ\text{C}$  for 10 minutes with the valve on sample.

Since the adducts are all stable at  $120^\circ\text{C}$ , inserting the sample at this temperature prevents any loss before the breech is closed. Moreover, this step dries the sample so that the  $\text{SO}_2$  evolved later is less reactive. If any unfixed  $\text{H}_2\text{SO}_4$  is present, it will also produce a peak at  $120^\circ\text{C}$ . With the present cartridge heater arrangement, the cell temperature can be raised to  $200^\circ\text{C}$  in 3 minutes. Once this temperature is reached, Step (5) may be repeated several times in order to estimate the completeness of sample decomposition each time.

The results of the rising temperature procedure were confirmed by this method. When the acid was not fixed, it gave a peak at the  $120^\circ\text{C}$  step and could be completely removed by heating for an hour at this temperature. When the sample was fixed with AAO, there was no peak at  $120^\circ\text{C}$ , but a pronounced peak appeared at  $200^\circ\text{C}$ . Figure 14 illustrates these results, which reaffirmed the thermal stabilization produced by fixation. It also demonstrated that the acid was fixed completely and rapidly, since no

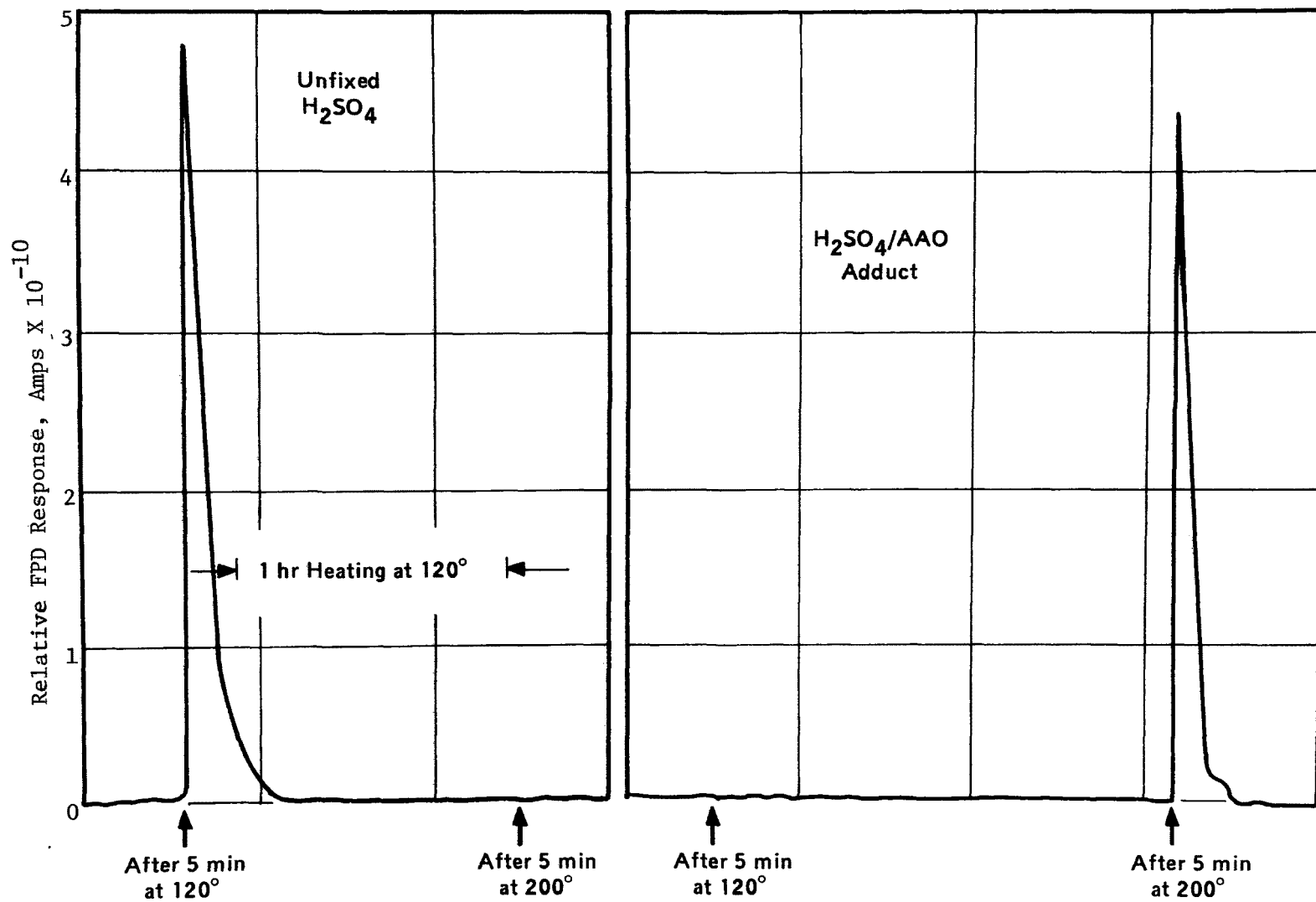


Figure 14. Completeness of fixation by AAO.

120°C peak appeared, even when only 15 seconds of reagent-acid contact was allowed after aerosol collection.

In addition, the speed of decomposition of the AAO-adduct at 200°C was evaluated. The procedure was to repeat the heating period with the valve on bypass several times, with progressively smaller peaks produced from each sample. As figure 15 shows, the second peak was proportionately smaller when the first heating period was 15 minutes than when it was 5 minutes. In other words, decomposition was more complete after 15 minutes (about 80%) than after 5 minutes (about 50%). When a particularly small (<20 ng) sample was analyzed, decomposition seemed to be essentially complete after the first 5 minute period as shown in figure 16.

From these experiments, it is evident that gas-phase fixation with these reagents occurs rapidly and completely, as indicated by a higher thermal stability of the fixed acid on the filter. The AAO-adduct is stable at 120°C, but is approximately 50% decomposed after 5 minutes of heating at 200°C. Finally, the FPD peak height appears to be a quantitative measure of the amount of acid originally collected.

#### METHOD EVALUATION

##### Accuracy

The accuracy of an analytical method is defined as the degree to which the measurements obtained agree with the true values, as determined by an independent method of known accuracy. Since there is no independent method of known accuracy for analysis of atmospheric  $\text{H}_2\text{SO}_4$ , this requirement cannot be strictly fulfilled. Moreover, the unpredictability of the type of aerosol generator used makes it impossible to calculate how much acid is deposited.

One indication of accuracy which can be shown is that the measurement accurately reflects the difference between two samples of known size relationship to one another. The experiments described on page 67 gave some data of this type, since each successive peak from the same sample was smaller, presumably due to the lessened amount of adduct each time. It was desirable, however, to show the validity of the technique with different samples as well, since this would be its practical use.

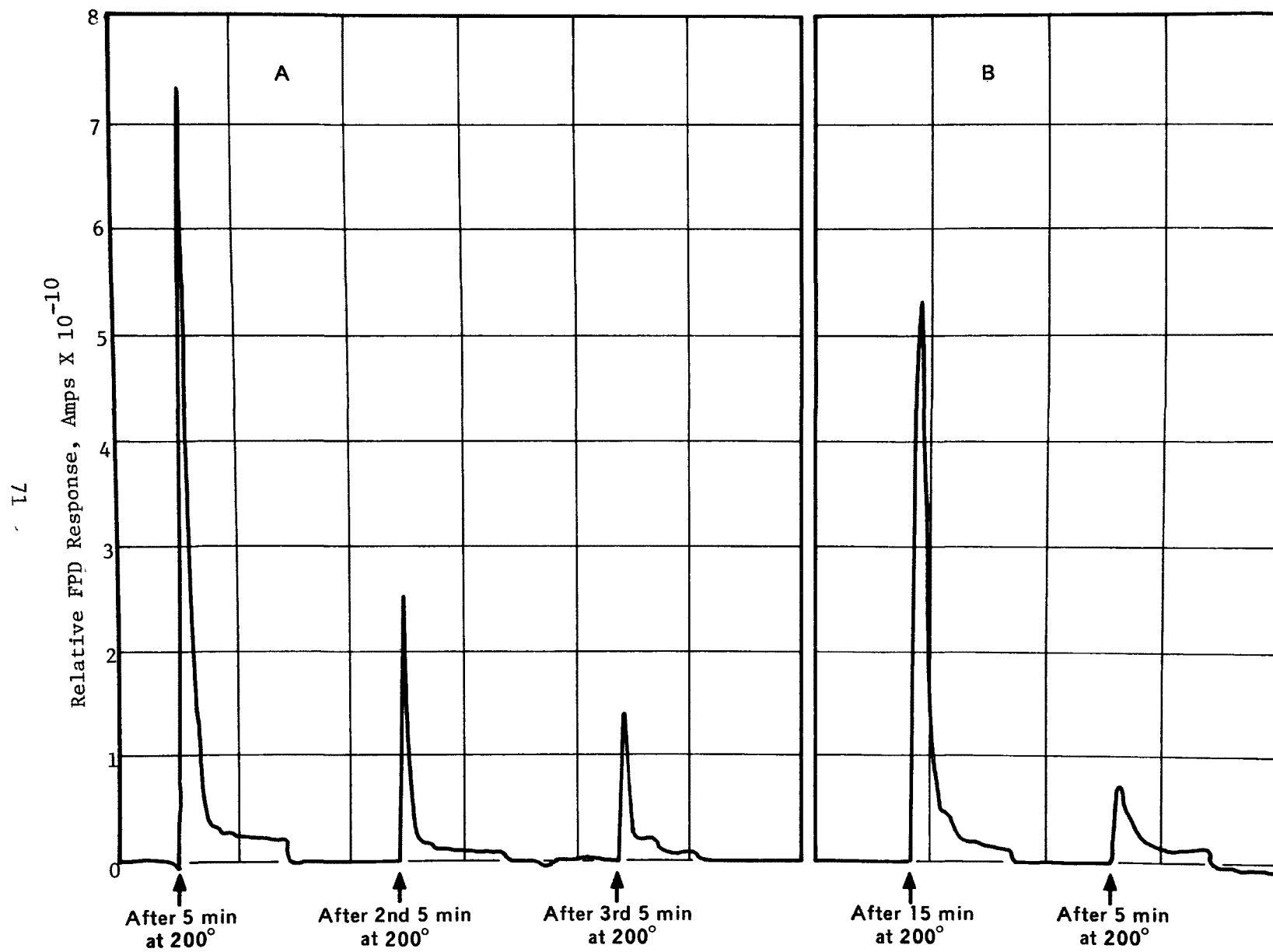


Figure 15. Completeness of decomposition of AAO/H<sub>2</sub>SO<sub>4</sub> adduct after 5 min (A) and 15 min (B).



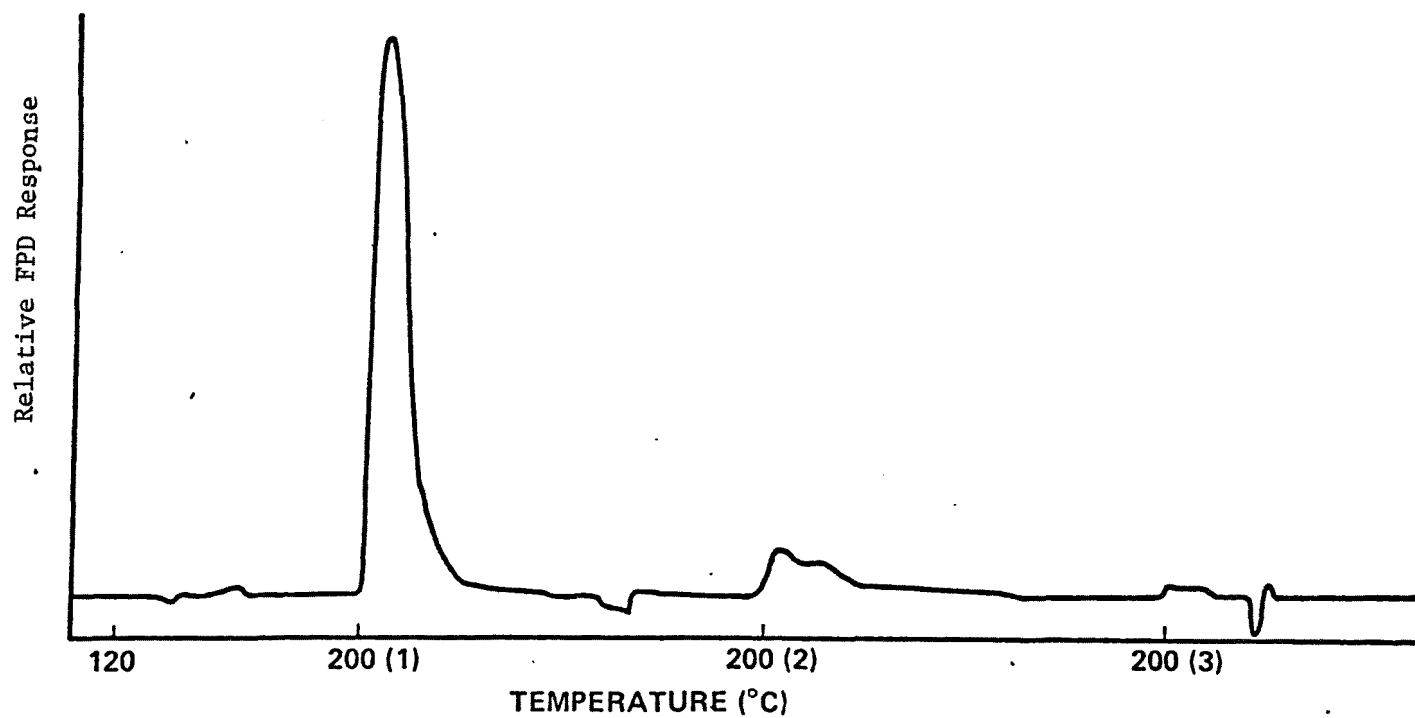


Figure 16. Typical FPD trace from AAO-treated sample.

The simplest way to produce samples of a known size relation was to cut a whole sample into halves, then one section in half again, etc. Figure 17 shows the FPD trace obtained from each segment after 5 minutes at 200°C. The peak heights definitely showed the size order of the corresponding samples, although the order magnitude was not precisely uniform. This may have been due to nonuniform distribution of adduct on the filter, unsymmetrical cutting, or random sample loss during handling.

As a final test of validity, several different samples were generated by collecting different volumes from the aerosol generator (i.e., varying sampling time). Those which had filtered the largest volume of air also produced the largest peaks, as was expected. Figure 18 shows data from these runs.

It was concluded from this data that peak height was an accurate measurement of the amount of acid adduct in a sample. The only possible way to independently verify this measurement would be to make samples by a different method, with which the amount of acid placed on the filter would be known. Many researchers have employed micropipet deposition of dilute  $\text{H}_2\text{SO}_4$ -methanol or -acetone solutions for this purpose. There is, however, still no independent way of verifying the amount of acid calculated to be on the filter, and this method is certainly less representative of real atmospheric aerosols than the Thomas generator method.

### Precision

Precision is the degree to which the values obtained by an analytical method are reproducible. Evaluation of precision placed stringent demands on the ability to generate known samples. Specifically, it was necessary to generate two or more samples containing the same amount of adduct with as little variation as possible. The similarity in peak heights from the identical samples was then a measure of precision. The type of  $\text{H}_2\text{SO}_4$  aerosol generator used in these experiments was known to have poor reproducibility from one run to another. The problem was approached by designing the generator's sampling probe so that two samples could be collected simultaneously, and would, therefore, be identical. \*

Several flow adjustments were required before the rates through the

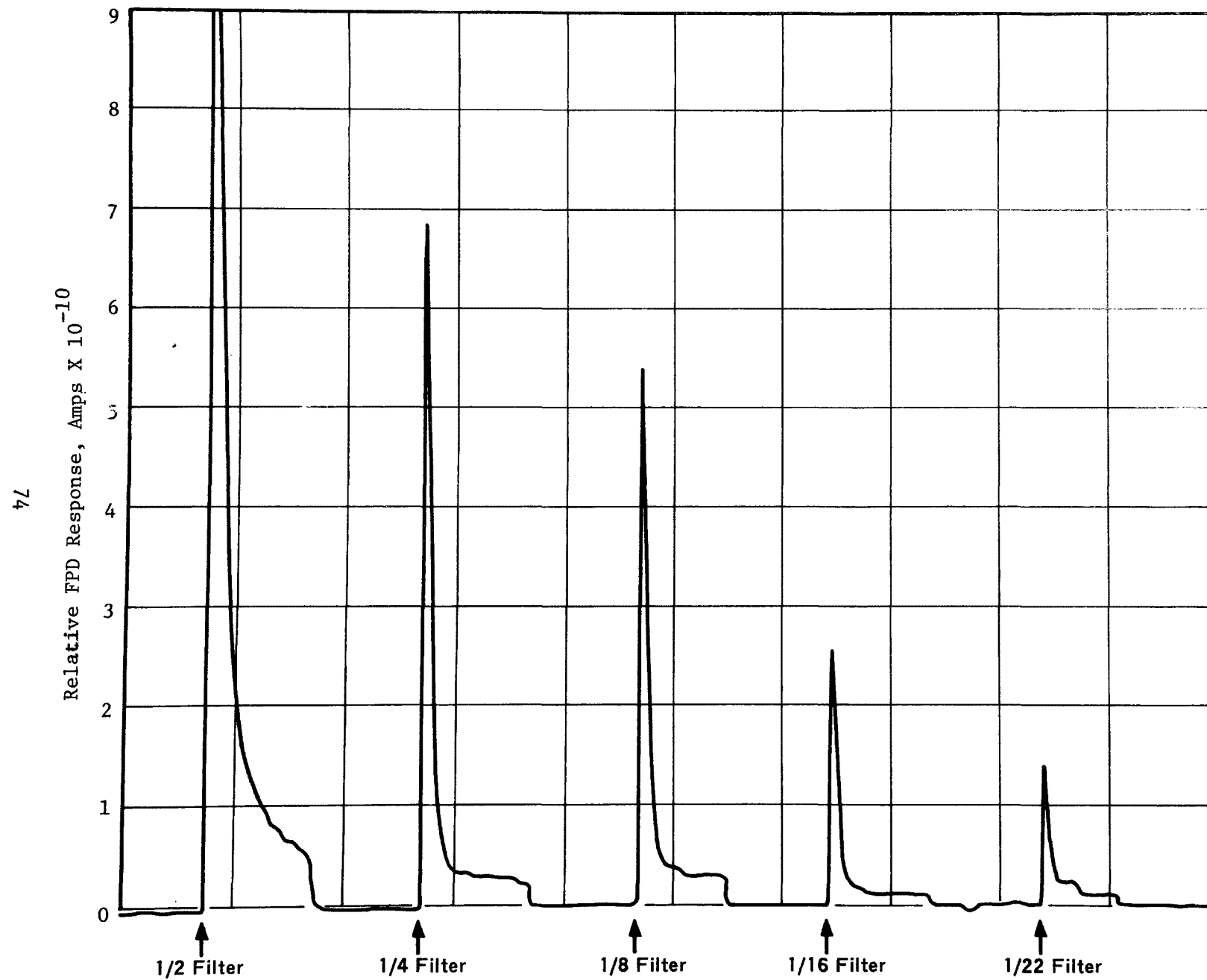


Figure 17. AAO-fixed filter portions after heating 5 min at 200°C.

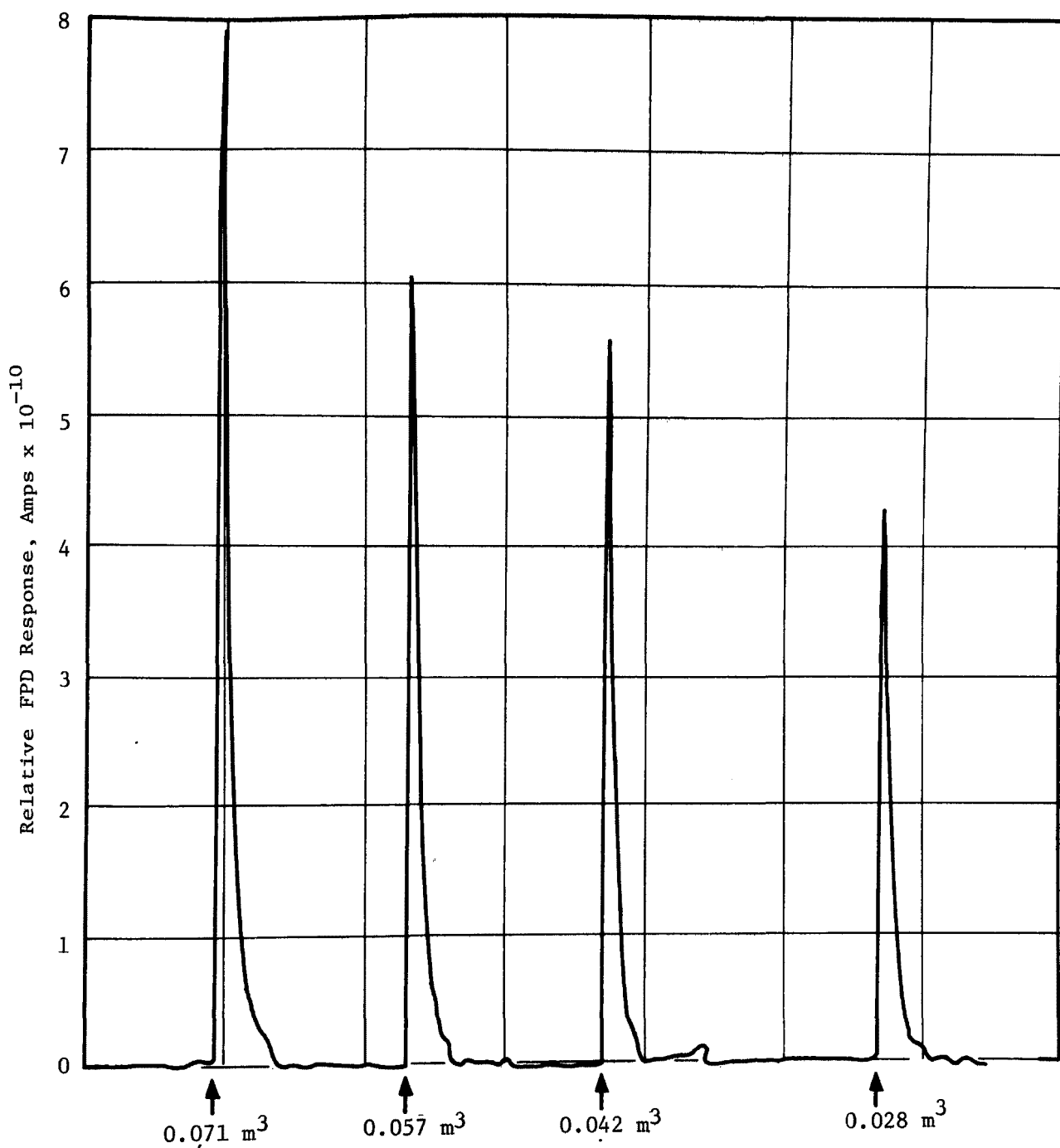


Figure 18. AAO-treated samples, different sampling volumes, 5 min at 200°C.

two holders were equivalent. The last set of data, from a series of three runs, is shown in Figure 19 and summarized in Table 8.

TABLE 8. PEAK HEIGHTS OF SAMPLE PAIRS  
COLLECTED SIMULTANEOUSLY

Run	Peak Height		% Difference
	Sample #1	Sample #2	
1	3.3	3.0	9.5
2	8.3	7.6	8.8
3	5.4	5.8	7.2

For each pair of samples, the variation in peak height is less than 10%. It was concluded from this evidence, however, that reliability is no less than 90% and is probably greater.

#### Calibration

Calibration of the FPD peak height to the amount of acid in the sample is a very complex problem. As a crude approximation, the sample peaks could be compared to those produced by injecting known amounts of  $\text{SO}_2$ . Obviously, the two procedures are not directly comparable. Known samples could be prepared by micropipet deposition, but even with this procedure, the FPD response may not be comparable to that of real aerosol samples.

It is also necessary to determine how much sample adduct is lost, either by failing to decompose during the heating period, or by reacting with surfaces in the sample cell. And finally, in order to calculate the  $\mu\text{g}/\text{m}^3$  figure, it is necessary to know the sampling efficiency, including the amount of acid lost on the walls of the sample probe.

These problems are not impossible to solve, but will require additional research. Presently, a rough estimate of the sample size is made by comparison to the  $\text{SO}_2$  injection peaks previously obtained.

#### INTERFERENCES ELIMINATED

#### Ammonium Sulfate and Bisulfate

DTA's of ammonium sulfate and bisulfate previously presented indicated

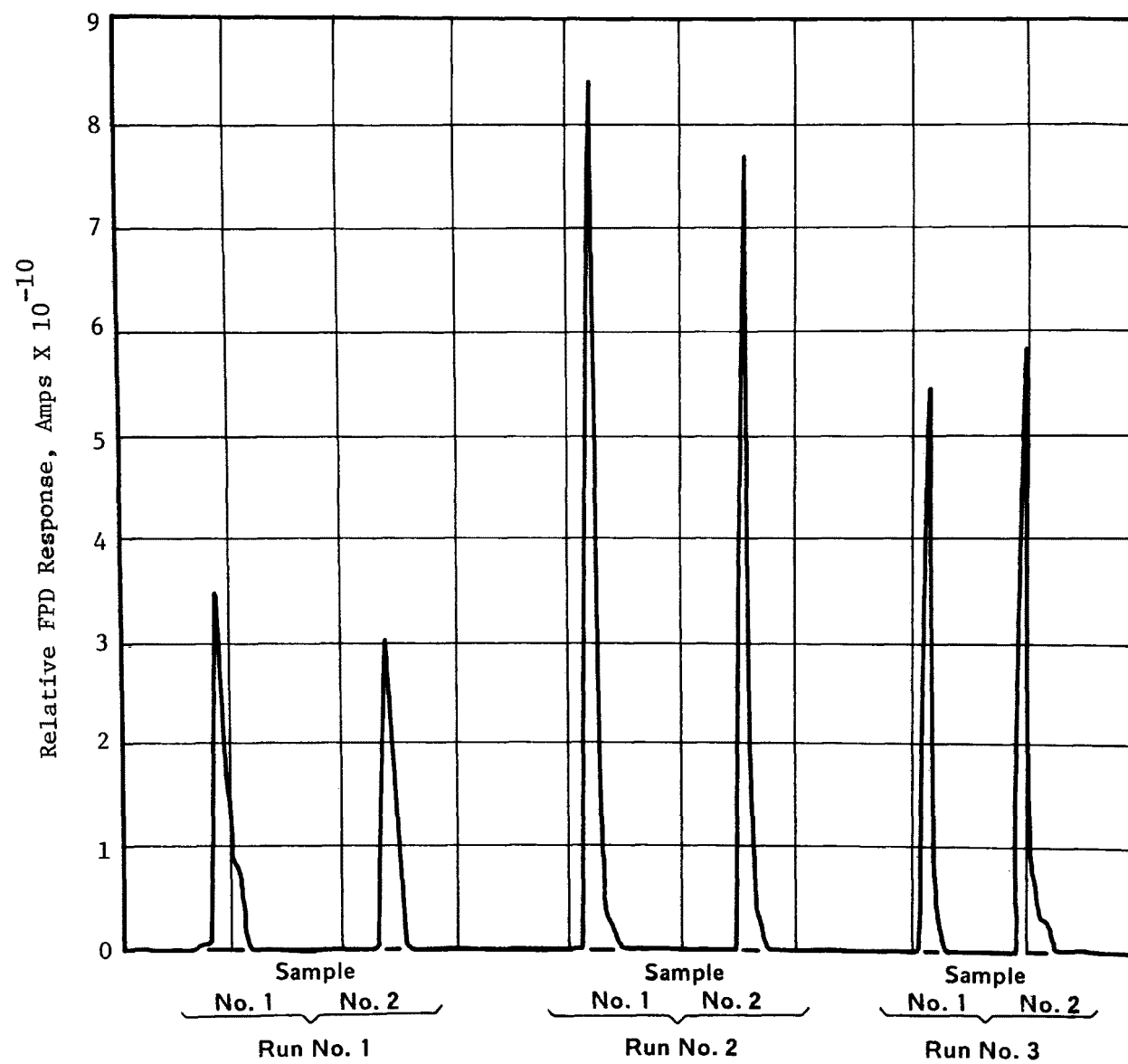
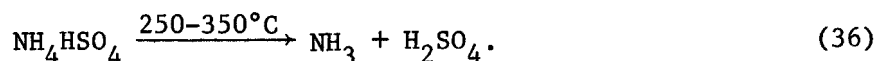
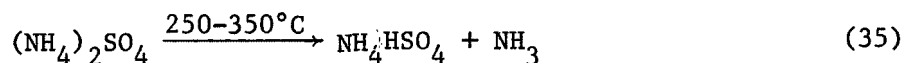


Figure 19. Pairs of AAO-fixed samples collected simultaneously.

that these two salts are stable to at least 250°C and 230°C, respectively. The temperature at which these compounds release a sulfur-containing vapor in significant quantities is the subject of some dispute. Dubois, et al. (65) discussed the use of  $(\text{NH}_4)_2\text{SO}_4$  as a standard for diffusion at 195°C. Maddalone, et al. (53), however, reported that a thermal gravimetric analysis (TGA) of  $(\text{NH}_4)_2\text{SO}_4$  indicated no significant decomposition until 250°C, in agreement with our DTA's. Erdey, et al. (75) have reported the following reactions:



Experiments with the FPD indicated that no volatile sulfur species were released by either of these salts until at least 240°C, and there was some ambiguity when a signal was recorded at this higher temperature, due to background sulfur in the system. Ammonium sulfate and bisulfate, finely ground from a reagent, gave no signal at 200°C with either of the procedures described in the preceding section. When ammonia was passed through a filter on which the acid aerosol had been collected unfixed, no signal was detected at 200°C. Interference from this source has apparently been eliminated.

### Sulfur Gases

Since the FPD responds to sulfur in any form, it was recognized that the ambient sulfur gases,  $\text{SO}_2$ ,  $\text{H}_2\text{S}$ , and  $\text{COS}$ , may interfere by reacting with the gaseous reagent. They may then be collected on the filter as a sulfur gas-reagent complex. These sulfur gas-reagent complexes would interfere with  $\text{H}_2\text{SO}_4$  adduct measurement, if their thermal stability was similar to that of the adduct.

To test this possibility, each of these gases was mixed with reagent vapor in a glass "Y" and drawn through a filter for several minutes. The filter was analyzed by the rising temperature procedure in order to determine both the presence of a volatile sulfur species and the temperature at which it was produced.

As shown in Table 9, of the three gases, only  $\text{SO}_2$  was significantly collected, and in every case, the  $\text{SO}_2$ -reagent complex had a very low thermal stability compared to the  $\text{H}_2\text{SO}_4$ -adduct. This was independently verified by mass spectral evidence. Figure 20 compares the FPD recordings obtained using the rising temperature procedure for unfixed acid, AAO-fixed acid, AAO- $\text{SO}_2$  complex, and  $(\text{NH}_4)_2\text{SO}_4$ .

TABLE 9. TEMPERATURE ( $^{\circ}\text{C}$ ) OF FIRST FPD RESPONSE FROM SULFUR GAS-REAGENT COMPLEXES

	<u><math>\text{SO}_2</math></u>	<u><math>\text{H}_2\text{S}</math></u>	<u><math>\text{COS}</math></u>
DEA	25	60*	-
DEHA	25	-	-
AAO	30	-	-

\*Very little absorbed

First, it appears that a fairly high concentration of  $\text{SO}_2$  (>25 ppm) must be present before a significant amount is collected. Sulfur dioxide was being produced by the aerosol generator in low concentration (5 ppm by Dräger tubes), but none was ever detected at the  $120^{\circ}\text{C}$  step during routine runs. Second, even if the necessary concentration is present, the collected complex can be rapidly and selectively removed from the sample at  $100^{\circ}\text{C}$ , prior to  $\text{H}_2\text{SO}_4$ -adduct analysis.

The chemical nature of these compounds is uncertain. Grundnes, *et al.* (76) have examined the formation of charge-transfer (CT) complexes in the gas phase reaction of  $\text{SO}_2$  with amines. Studies of the analogous reaction between  $\text{SO}_2$  and  $\text{NH}_3$  have found mostly sulfite and bisulfite salts (77,78). It may be possible, however, for the collected  $\text{SO}_2$  to be oxidized to  $\text{SO}_4^{-2}$ , if catalytic conditions are present (78). For this reason, it might be desirable to heat the filter during collection, so that  $\text{SO}_2$ -reagent complexes are immediately decomposed and removed.

#### Negative Interferences

The rationale for fixation was given as the necessity of preventing the acid from reacting with other particulates on the filter. Experimental



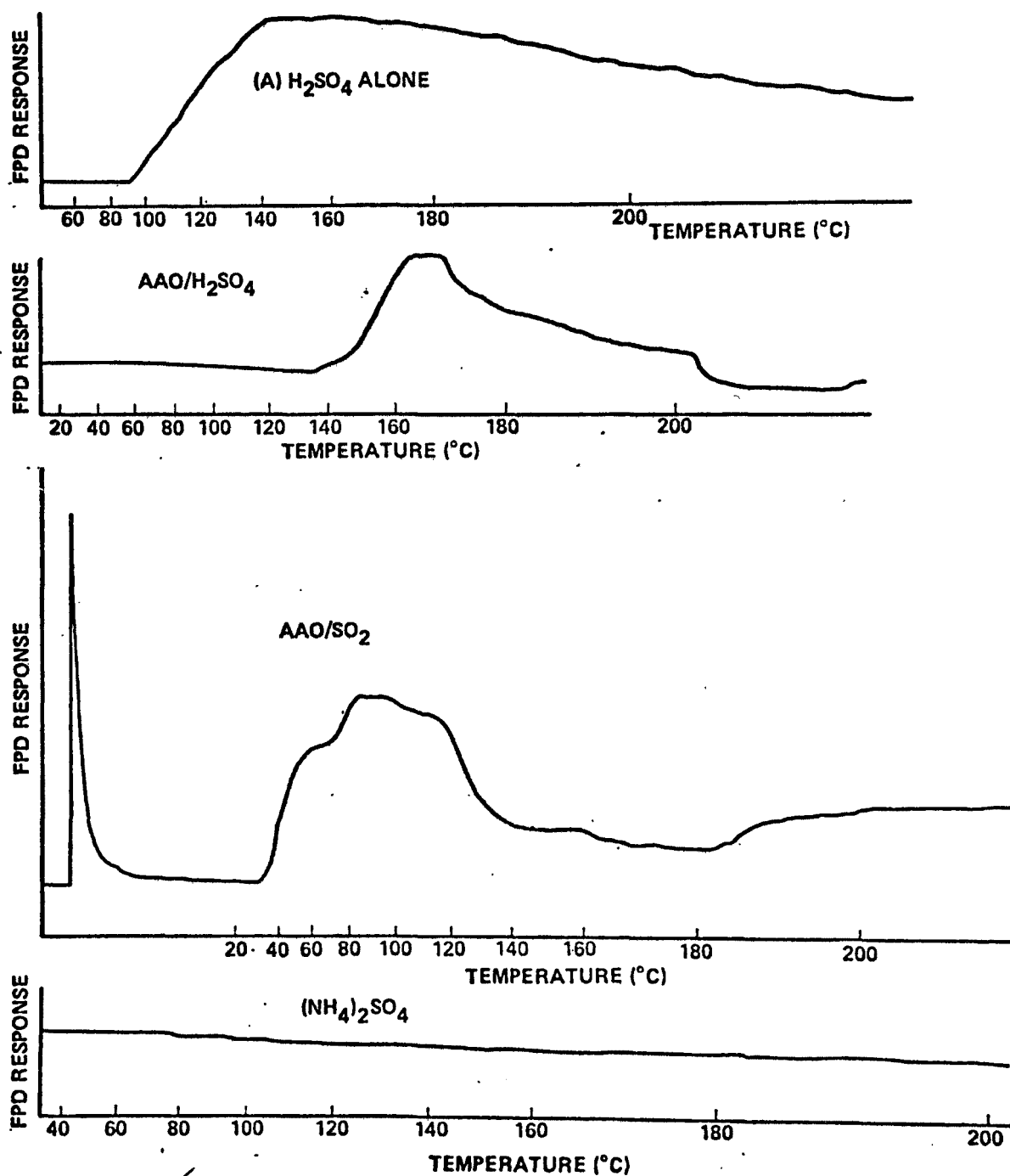


Figure 20. Continuous heating procedure -  
FPD recordings from  $H_2SO_4$  and adduct samples.

evidence for the effectiveness of the proposed method of fixation is not presently available, since research to date has focused on formation of the adducts, their properties and potential positive interferences. In the theoretical discussion of the use of volatile amines for this purpose, it was suggested that the filter be heated during collection to remove water. Since an aqueous solution of an amine (or amine-derivative) sulfate is still quite acidic, drying the adduct should form less reactive solid crystals. It was demonstrated that even the least stable of the three adducts from AAO could be heated at 102°C without decomposition, which is more than sufficient for the purpose of drying.

A related problem concerns the loss of evolved  $\text{SO}_2$  during analysis by reaction with particulates on the filter and surfaces in the system. It has been hypothesized that the dry  $\text{SO}_2$  evolved during this procedure is less reactive than the acid vapor produced by direct volatilization. More experimental work is needed in this area, however.

Finally, the effect of ammonia must be examined in representative concentrations. It was found that highly concentrated ammonia reacted with undried adduct on a filter, which is not surprising, since ammonia is a stronger base than any of the proposed reagents. With the reagent in such large excess, however, low ambient levels of ammonia should not pose an insurmountable problem.

#### SUMMARY OF ACHIEVEMENTS

The most important achievements of the past twelve months' research are summarized below:

- 1) Three candidate reagents for fixation of  $\text{H}_2\text{SO}_4$  were identified.
- 2) The corresponding adducts were isolated and their likely composition determined.
- 3) It was established that  $\text{SO}_2$  is released by decomposing the adducts at 200°C.
- 4) Formation of adduct by treatment of sample with reagent vapor was demonstrated by two different temperature-programming techniques.

- 5) The FPD was calibrated by injection of known  $\text{SO}_2$ -air standards, and the quantitative range of the detector was determined.
- 6) Sample size was adjusted to give analyzable FPD peaks.
- 7) A specific procedure for analyzing samples by the FPD was established.
- 8) Ammonium sulfate and ammonium hydrogen sulfate were shown not to be interferences.
- 9) The sulfur gases,  $\text{SO}_2$ ,  $\text{H}_2\text{S}$ , and  $\text{COS}$ , were shown not to be interferences where a preheating step was used to remove  $\text{SO}_2$ -reagent complexes.
- 10) The  $\text{AAO-H}_2\text{SO}_4$  adduct was shown to be at least 50% decomposed after 5 minutes of heating at  $200^\circ\text{C}$ .
- 11) Peak height of the FPD trace was shown to be an accurate measure of the acid on a filter.
- 12) Two identical samples were collected and shown to produce the same FPD peak heights, with a reliability of greater than 90%.

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16. ABSTRACT  A method is being developed to selectively assay ambient sulfuric acid aerosol. The method utilizes the vapor of a volatile amine (or amine derivative) to neutralize the acid as it is collected on a Teflon filter. The amine sulfate thus formed is thermally decomposed at 200°C to release sulfur dioxide, or other stoichiometrically related sulfur containing adduct, which is measured by a flame photometric detector. Immediate chemical fixation of the acid lessens the chance of side reactions with other substances on the filter, while the relatively low decomposition temperature eliminates particulate interferences such as ammonium sulfate. Sulfur dioxide is also collected as a reagent complex on the filter but is selectively removed by heating at 100°C.		
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