United States
Environmental Protection
Agency

Environmental Sciences Research
Laboratory
Research Triangle Park NC 27711

EPA-600/2-78-104
June 1978

Research and Development

EPA

Generation of Sulfuric Acid Aerosols for Health Effect Studies

RESEARCH REPORTING SERIES

Research reports of the Office of Research and Development, U S. Environmental Protection Agency, have been grouped into nine series. These nine broad categories were established to facilitate further development and application of environmental technology. Elimination of traditional grouping was consciously planned to foster technology transfer and a maximum interface in related fields. The nine series are:

1. Environmental Health Effects Research
2. Environmental Protection Technology
3. Ecological Research
4. Environmental Monitoring
5. Socioeconomic Environmental Studies
6. Scientific and Technical Assessment Reports (STAR)
7. Interagency Energy-Environment Research and Development
8. "Special" Reports
9. Miscellaneous Reports

This report has been assigned to the ENVIRONMENTAL PROTECTION TECHNOLOGY series. This series describes research performed to develop and demonstrate instrumentation, equipment, and methodology to repair or prevent environmental degradation from point and non-point sources of pollution. This work provides the new or improved technology required for the control and treatment of pollution sources to meet environmental quality standards.

This document is available to the public through the National Technical Information Service, Springfield, Virginia 22161.

EPA=600/2-78-104
June 1978

GENERATION OF SULFURIC ACID AEROSOLS FOR HEALTH EFFECT STUDIES

by

Benjamin Y. H. Liu and Jak Levi
Particle Technology Laboratory
Mechanical Engineering Department
University of Minnesota
Minneapolis, Minnesota 55455

Grant No. R801301

Project Officer

Thomas G. Dzubay
Atmospheric Chemistry and Physics Division
Environmental Sciences Research Laboratory
Research Triangle Park, NC 27711

ENVIRONMENTAL SCIENCES RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27711

DISCLAIMER

This report has been reviewed by the Environmental Sciences Research Laboratory, U.S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the U.S. Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

ABSTRACT

An aerosol generator has been developed for producing sulfuric acid particles for animal exposure studies. The generator has been designed to supply sulfuric acid aerosols at 330 liters per minute to an animal exposure chamber of 330 liters internal volume. The sulfuric acid concentration in the chamber ranges from 0.13 to 1.3 mg/m^3. The particle diameter ranges from 0.04 to 0.15 μm, and the geometrical standard deviation of the aerosol is about 1.6.

The generator operates by atomizing a sulfuric acid solution to form a polydisperse spray. The droplets are then vaporized in a tube-furnace and the vapor injected into filtered air at room temperature to form a high concentration of small sulfuric acid particles.

The aerosol generating system has been evaluated by means of several techniques. The particle size distribution was measured by an Electrical Aerosol Analyzer. Four independent techniques were used to measure the aerosol concentration. These include the Electrical Aerosol Analyzer, the Quartz-Crystal Aerosol Mass Monitor, filter collection and weighing, and chemical analysis of collected particle samples. Good agreement has been found.

The particular generator described in this report has been constructed and delivered to the U.S. Environmental Protection Agency for use in its animal exposure experiments.

This report was submitted in fulfillment of Grant No. R801301 by the University of Minnesota under sponsorship of the U.S. Environmental Protection Agency. This report covers a period from September 1, 1976 to March 1, 1978, and work was completed as of March 1, 1978.

CONTENTS

Abstract. iii
Figures vi
Tables. vii
Acknowledgements. viii

1. Introduction 1
2. Design Criteria. 2
3. Theoretical Considerations 3
   Coagulation Limit 3
   Properties of Sulfuric Acid Solution Droplets 6
4. Description of System. 11
   Atomization of the Sulfuric Acid Solution 11
   Evaporation of Solution Droplets. 13
   Condensation and Growth of the Aerosol. 13
   Exposure Chamber. 13
5. Preliminary Experiments. 15
   The Atomizer. 15
   Vaporization Temperature. 16
   Uniformity of the Aerosol in the Exposure Chamber . . .21
6. Performance of the Aerosol Generating System 24
   Mass Concentration. 25
   Size Distribution 31
   Coagulation Chamber 36
7. Final Remarks. 38

References. 39
Appendices

A. Detailed size distribution data obtained by EAA. 41
B. Operating instructions 46
   Introduction. 46
   Unpacking and Setup 46
   Operating Principles and Characteristics of the
     Sulfuric Acid Aerosol Generator 49
   Operating Procedure 54
   Notes on the Operation of the Aerosol Generator 56

FIGURES

Number		Page
1	Coagulation limited mass concentration of aerosols for H_2SO_4 particles at 50% R.H.	5
2	Properties of sulfuric acid droplets.	7
3	Particle size growth factor taking into account the Kelvin effect.	10
4	Schematic diagram of system for generating sulfuric acid aerosols.	12
5	Variation of total EAA current with time during warm-up for a furnace temperature setting of "1o".	18
6	Variation of total EAA current with time during warm-up for a furnace temperature setting of "2".	19
7	Variation of total EAA current with time during warm-up for a furnace temperature setting of "3".	20
8	Location of sampling probe on a horizontal plane within the exposure chamber.	22
9	Schematic diagram of aerosol diluter.	27
10	H_2SO_4 and aerosol mass concentration in exposure chamber as a function of solution normality.	30
11	Aerosol size distribution for 0.1N H_2SO_4 solution.	33
12	Aerosol size distribution for 1.0N H_2SO_4 solution.	34
13	Aerosol particle size as a function of solution normality for primary dilution airflow of 30 lpm.	35
B1	Photograph of evaporator-mixer.	47
B2	Photograph of sulfuric acid aerosol generator installed on the exposure chamber.	47
B3	Calibration curve of orifice meter for total chamber flow.	55
B4	Calibration curve of rotameter for primary dilution flow.	57
B5	Calibration curve of rotameter for atomizer flow.	58
B6	Dimensions of pyrex evaporator tube and mixing nozzle.	59

TABLES

Number		Page
1	Variation of Solution pH with Time for Liquid in Atomizer. . . .	16
2	Characteristics of Atomizer.	16
3	Variation of Aerosol Concentration within Exposure Chamber. . . .	23
4	Comparison of Aerosol Mass Measurement by Weighing and by SO_4^{--} Analysis.	28
5	Comparison of Aerosol Mass Concentration Measurement by Several Different Techniques.	29
6	Summary of Aerosol Size Distribution Parameters for Various Generator Operating Conditions.	32
A1	Size Distribution Measurement by EAA.	42
A2	Size Distribution Measurement by EAA (10 lpm primary dilution air).	43
A3	Size Distribution Measurement by EAA (20 lpm primary dilution air).	44
A4	Size Distribution Measurement by EAA (30 lpm primary dilution air).	45
B1	Characteristics of Aerosol Produced by the Sulfuric Acid Aerosol Generator.	50
B2	Aerosol Particle Size as a Function of Coagulation Chamber Volume.	53
B3	Consumption and Concentration of H_2SO_4 Solution by Atomizer as a Function of Time.	53

ACKNOWLEDGEMENTS

The authors of this report wish to thank Dr. Thomas G. Dzubay of EPA for his help in establishing the basic design criteria for the aerosol generator. His interest in the project and his helpful discussions are greatly appreciated. The authors also wish to thank Mr. Mike Kirtz of EPA for providing the animal exposure chamber used in the study. A special word of thanks goes to Dr. David Y. H. Pui of the University of Minnesota for his help in the preparation of the report.

This work is supported by EPA under Grant R801301.

SECTION 1

INTRODUCTION

Under the sponsorship of the Environmental Protection Agency, the Particle Technology Laboratory, University of Minnesota, undertook a study on methods for generating sulfuric acid aerosols. The goal of the study was to develop a generator for producing sulfuric acid aerosols in the 0.01 to 0.1 μm diameter range and at concentration levels that are sufficiently high for studying the health effect of fine sulfuric acid particles.

The impetus for the present research came from the finding that sulfuric acid particles are emitted by modern, catalyst-equipped automobiles. The particles are formed apparently by the catalytic conversion of SO_2 in the exhaust gas due to the combustion of sulfur-containing fuel. Studies conducted by EPA at the General Motors Proving Ground and at Los Angeles freeways concerning this "sulfuric acid problem" (see the recent summary by Maugh, 1977) showed that the particles emitted are very small in size, typically in the 0.01 to 0.1 μm diameter range (Whitby et al., 1977; Wilson et al., 1977). Since small aerosol particles can penetrate deeply into the human respiratory system, the potential health effect of these fine sulfuric acid particles is of some concern. The purpose of the present research is to develop a sulfuric acid aerosol generator for studying the health effect of fine sulfuric acid particles.

SECTION 2

DESIGN CRITERIA

The generator described in this report has been developed specifically for EPA for use in its health effects studies program. The generator has been designed for an animal exposure chamber having an internal volume of 0.33 m^3, and a design flow rate that would provide one complete air exchange per minute in the chamber volume, i.e., 330 liters per minute. Therefore, the principal requirement of the generator is that it must be capable of supplying the test aerosol at a sufficiently high rate to produce an adequate sulfuric acid concentration in the test chamber. The basic design parameters have been set as follows:

Exposure chamber volume: 0.33 m^3

Chamber air flow: 330 liters per minute

Aerosol diameter range: 0.02 to 0.2 μm

Sulfuric acid aerosol concentration: from about 100 $\mu g/m^3$ to a few mg/m^3

Although the aerosol generated does not need to be monodisperse, both the size distribution and aerosol concentration must be stable. In addition, the generator must be capable of unattended operations and be reasonably maintenance- and trouble-free.

SECTION 3

THEORETICAL CONSIDERATIONS

COAGULATION LIMIT

An important consideration in the design of aerosol generating systems to supply highly concentrated aerosols for animal exposure experiments is the following: what is the maximum aerosol concentration that can be obtained? Among the factors limiting the maximum obtainable aerosol concentration is the limit imposed by coagulation, which takes place whenever aerosol is transported from the point of formation to where it is used. In this Section, this limit will be determined.

Consider a monodisperse aerosol undergoing coagulation according to the following equation:

$$\frac{dN}{dt} = - KN^2 \tag{1}$$

where N is the aerosol number concentration and K is the coagulation coefficient. Separating variables and integrating between appropriate limits, we have:

$$\int_{N_o}^{N} - \frac{dN}{N^2} = \int_0^t Kdt \tag{2}$$

$$\frac{1}{N} - \frac{1}{N_o} = Kt \tag{3}$$

where N_o is the initial aerosol concentration and N is the aerosol concentration at the time t. It follows from Equation (3) that,

$$N = \frac{1}{Kt + \frac{1}{N_o}} \tag{4}$$

which can be approximated by

$$N = \frac{1}{Kt} \tag{5}$$

if $N_o > \frac{1}{Kt}$. The above result states that, if the initial aerosol concentration, N_o, is sufficiently high, the aerosol concentration N at time t will be independent of the initial concentration, the concentration N being solely a function of the coagulation time, t.

The coagulation coefficient for monodisperse aerosols is a function of particle size. The following table, taken from Fuchs (1964), gives the coagulation coefficient for various particle sizes:

D_p, μm	0.02	0.04	0.1	0.2
K, cm^3/sec	12×10^{-10}	11×10^{-10}	7.2×10^{-10}	5.2×10^{-10}

Over the particle size range from 0.02 to 0.2 μm, the coagulation coefficient does not vary greatly. For the present purpose of making an estimate of the limiting particle concentration that can be obtained, $K = 10^{-9}$ cm^3/sec will be used as an approximate average for the coagulation coefficient in the above-mentioned size range.

Using Equation (5) and the coagulation coefficient of $K = 10^{-9}$ cm^3/sec, we have for the coagulation-limited number concentrations at various coagulation times:

t, sec	1	10	100
N, cm^{-3}	10^9	10^8	10^7

The corresponding mass concentration of the aerosol is related to the number concentration by:

$$M = \frac{1}{6} \pi D_p^{\ 3} \rho N \tag{6}$$

where ρ is the particle density.

In Figure 1, the mass concentration of a coagulation-limited aerosol based upon the above analysis is shown as a function of particle size for various coagulation times. The particles are sulfuric acid droplets in equilibrium with ambient air at 50% relative humidity. At this humidity, the equilibrium sulfuric acid concentration in the solution is 42.5% by mass,

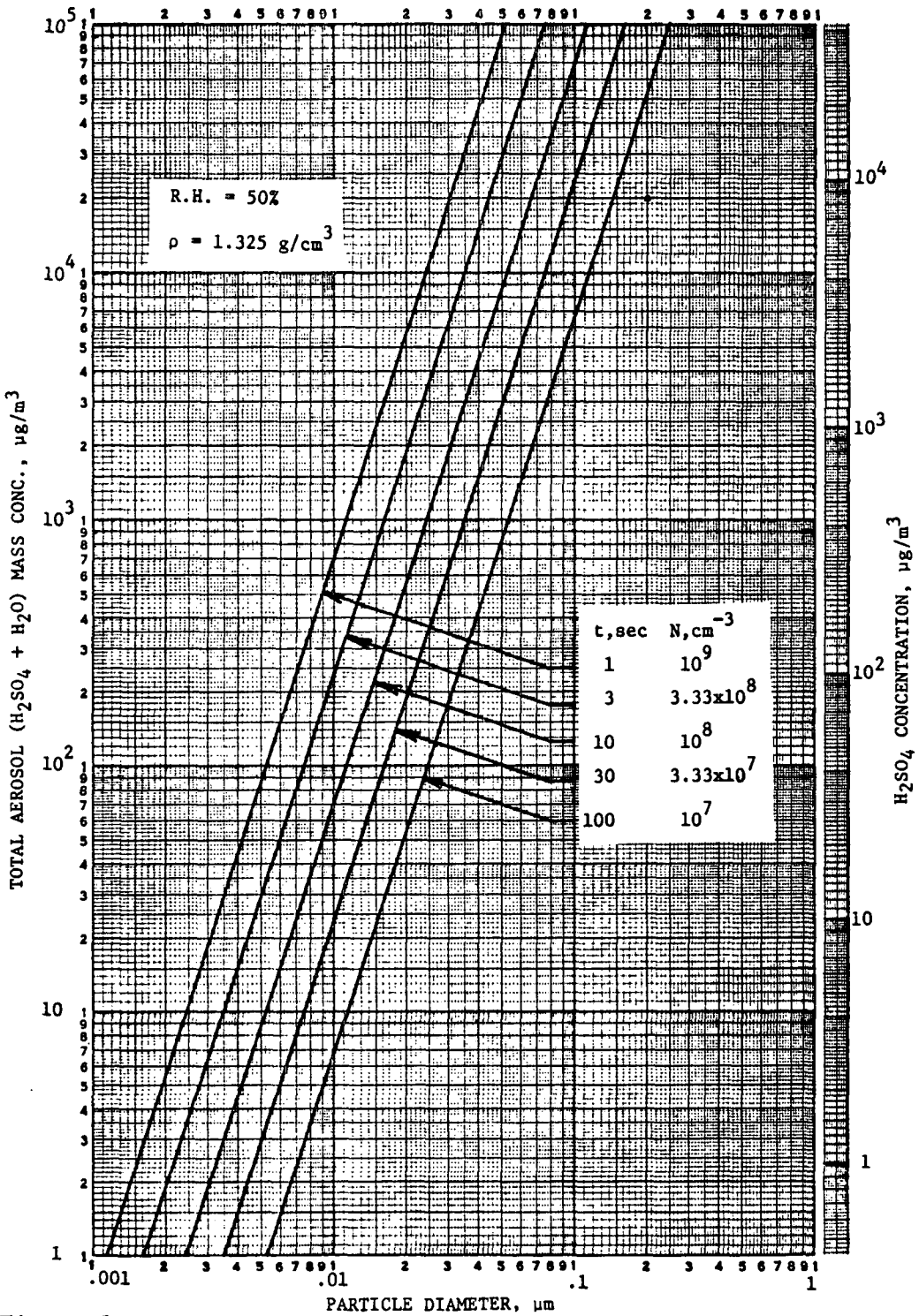

Figure 1. Coagulation limited mass concentration of aerosols for H_2SO_4 particles at 50% R.H.

and the solution density is $\rho = 1.325\ g/cm^3$. Similar graphs for other humidity conditions can easily be constructed.

From the above analysis, it is clear that coagulation imposes a limit on the maximum aerosol concentration that can be obtained. For example, suppose that a certain animal exposure experiment requires that sulfuric acid particles be transported from where they are formed to where they are inhaled by the test animals in 30 seconds. Then, according to Figure 1, the maximum sulfuric acid concentration will be 79 $\mu g/m^3$ if the particle diameter is 0.02 μm. If the ambient relative humidity is 50%, the maximum aerosol mass concentration (sulfuric acid plus associated liquid water) will be 185 $\mu g/m^3$, also from Figure 1. Any attempt to increase the aerosol concentration to a level above these limits would only result in more coagulation and the production of larger particles. This is an important factor that must be taken into account in designing human or animal exposure experiments in health effect studies.

PROPERTIES OF SULFURIC ACID SOLUTION DROPLETS

Sulfuric acid droplets are hygroscopic particles whose size will change in response to changes in ambient humidity. To facilitate calculations, Figure 2 has been prepared (Liu, Pui and Kousaka, 1977).

In Figure 2, the pertinent sulfuric acid solution properties are shown plotted against x, the solution concentration expressed in g H_2SO_4/g solution. Included in the plot are the equilibrium relative humidity over a flat solution surface, the solution density, ρ, the boiling point, B.P., and the surface tension, σ. The data have been taken from the Chemical Engineers Handbook (Perry and Chilton, 1973) and from Sabinina and Terpugow (1935), as indicated in the figure. In addition, several calculated parameters are shown. These include the solution normality, the product, $x\rho$, the particle growth factor, D_p/D_{po}, and the Kelvin effect parameter, $D_{po} \ln \frac{p}{p_\infty}$, which are defined below. To illustrate the use of the various plotted quantities, the following example is given.

Consider a 1 μm diameter sulfuric acid solution droplet in equilibrium with relative humidity at 50%. Using the curve denoted by R.H. in Figure 2,

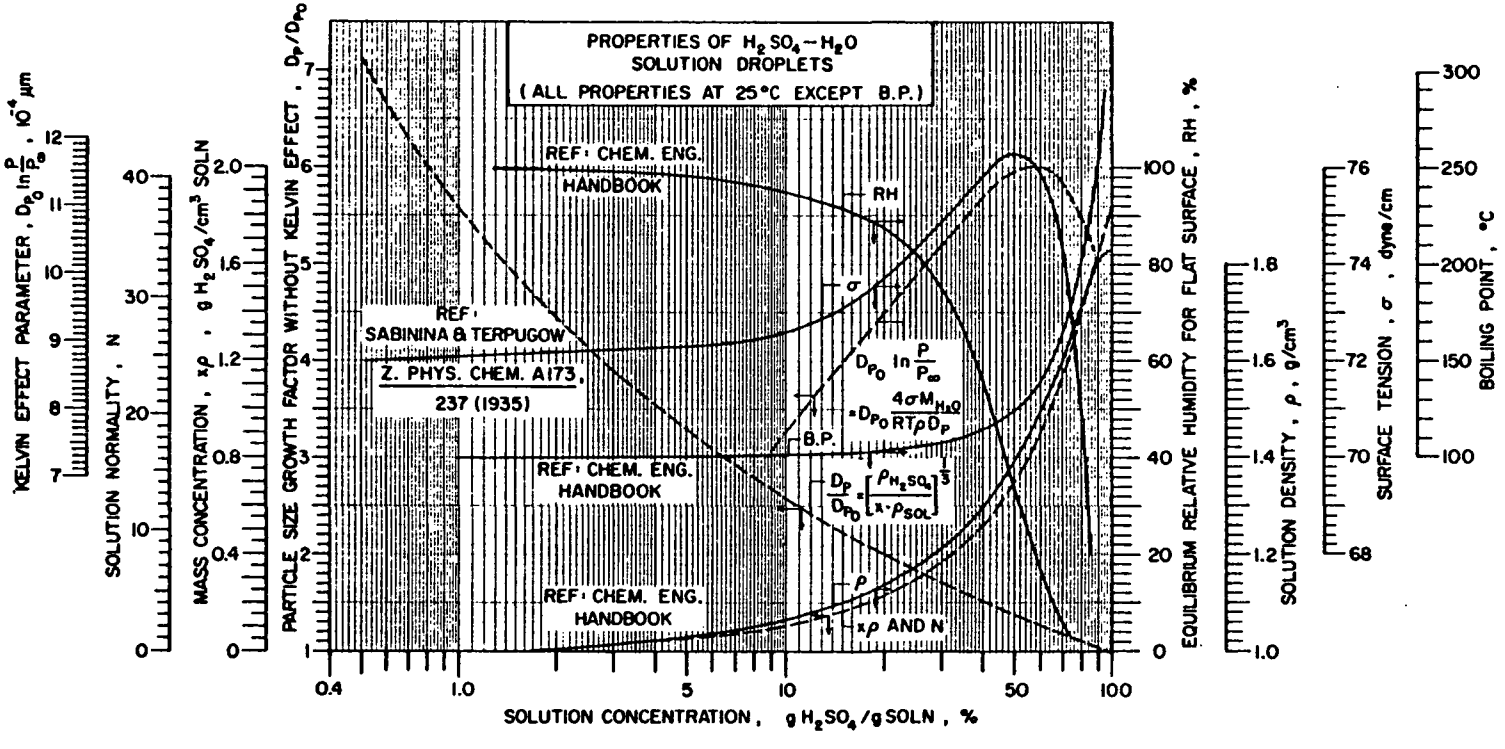

Figure 2. Properties of sulfuric acid droplets.

we find that the solution concentration, x, is 0.425 g of H_2SO_4 per g of solution, or a concentration of 42.5% by mass. At this concentration, the solution has a density, ρ, of 1.32 g/cm^3, a boiling point, B.P., of 115°C, a surface tension, σ, of 76 dyne/cm, a normality of 11N, and a mass concentration, $x\rho$, of 0.55 g H_2SO_4 per cm^3 of solution. The particle size growth factor, D_p/D_{po}, is 1.48, and the Kelvin effect parameter, $D_{po}\ \ln(p/p_\infty)$, is 11.3×10^{-4} μm. The last two parameters are explained in more detail below.

The particle size growth factor, D_p/D_{po}, shown in Figure 2, is the ratio of the actual diameter of the particle, D_p, to the diameter of the particle, D_{po}, if the water associated with the droplet is completely removed. In the example given above, the 1 μm diameter sulfuric acid solution droplet will become a droplet of pure sulfuric acid of 1/1.48 = 0.68 μm if water is removed. Similarly, if the ambient humidity is now increased to 90%, then according to Figure 2, the equilibrium solution concentration is 17% by mass and the particle size growth factor is 2.12. Consequently, the 1 μm diameter particle at 50% R.H. will now become a particle of (2.12/1.48) (1) = 1.43 μm diameter at 90% R.H. Thus, the particle size growth factor can be used to predict changes in particle size when ambient relative humidity around the particles is changed.

In the above discussion of particle size change, the Kelvin effect has been ignored. The Kelvin effect relates the increase in equilibrium vapor pressure, p, over a curved surface to that over a flat surface, p_∞,

$$\ln(p/p_\infty) = \frac{2\ \sigma\ M}{RT\ \rho\ a} \tag{7}$$

where σ is the surface tension of the solution, M is the molecular weight of water, R is the gas constant for water, T is the absolute temperature, ρ is the solution density, and a is the particle radius. The quantity plotted in Figure 2 is the ratio $D_{po}\ \ln(p/p_\infty)$ which, according to Equation (7), is:

$$D_{po}\ \ln(p/p_\infty) = \frac{4\sigma M}{RT\rho}\left(\frac{D_{po}}{D_p}\right) \tag{8}$$

where D_{po} has the same meaning as that discussed above. It should be noted that the quantity on the right-hand side of Equation (8) involves only solution and vapor properties, which are functions of x, the solution

concentration. Consequently, the Kelvin effect parameter is also a function of x.

To illustrate the use of the Kelvin effect parameter, let us consider the example discussed earlier, viz. the 1 μm diameter sulfuric acid solution droplet at 50% R.H. Since D_{po} = 0.68 μm, and the Kelvin effect parameter is 11.3×10^{-4} μm, we have $\ln(p/p_\infty) = 11.3 \times 10^{-4}/0.68 = 16.62 \times 10^{-4}$. Consequently, $p/p_\infty = 1.00166$. For this case, the Kelvin effect is negligible; the increase in water vapor pressure is only 0.166% above that for a flat surface.

Let us now consider a 0.01 μm diameter sulfuric acid particle at 50% humidity. Since $D_{po} = 0.01/1.48 = 0.0068$ μm in this case, we have $\ln(p/p_\infty) = 11.3 \times 10^{-4}/0.0068 = 0.166$, which gives $p/p_\infty = 1.18$. Consequently, the Kelvin effect will cause the equilibrium vapor pressure over the curved droplet surface to be 18% higher than that over a corresponding flat surface. Thus, the effect is substantial and generally cannot be ignored. In Figure 3, the particle size growth factor, D_p/D_{po}, taking into account the Kelvin effect has been calculated and shown as a function of the relative humidity.

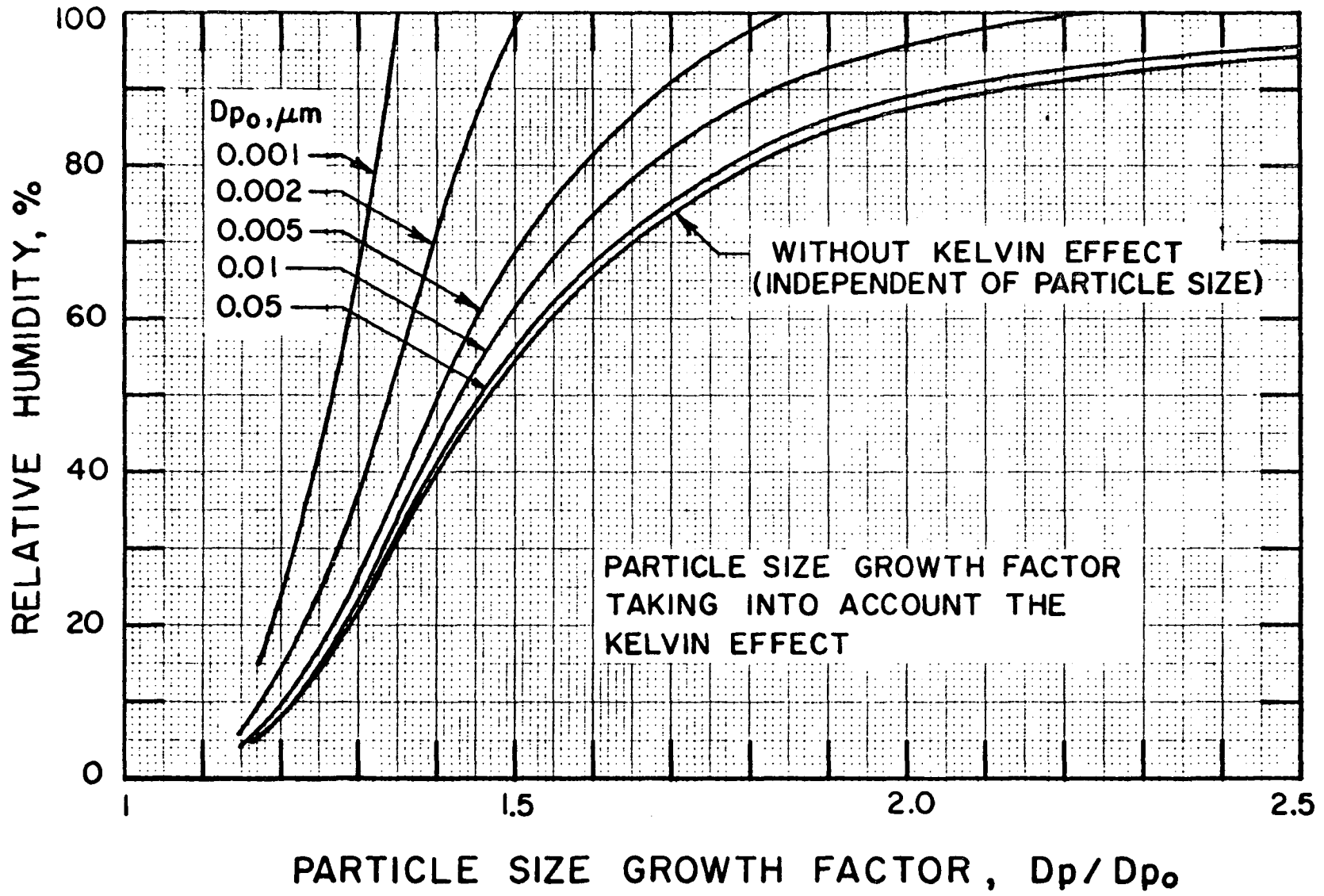

Figure 3. Particle size growth factor taking into account the Kelvin effect.

SECTION 4

DESCRIPTION OF SYSTEM

There are three main steps involved in the method chosen for generating H_2SO_4 particles, and they can be summarized as follows:

(a) Atomization of the sulfuric acid solution

(b) Evaporation of the solution droplets

(c) Condensation and growth of the aerosol

The complete system is shown in Figure 4.

ATOMIZATION OF THE SULFURIC ACID SOLUTION

Since sulfuric acid is to be used in the experiments, it is necessary that the aerosol generator be made of an acid-resistant material. Also, it is very important that under steady state conditions, the concentration of the particles should remain constant at the outlet of the atomizing device used. The atomizer shown in Figure 4 proved to be most reliable in this respect. The atomizer is made of 304 stainless steel, and all other parts in contact with the acid solution are made of either polyethylene or Teflon. The basic atomizer design has been adapted from that described by Liu and Lee (1975). The only difference is that in the system described by Liu and Lee, a syringe pump is used to feed the liquid continuously to the atomizer, whereas in the present case, the liquid is drawn into the atomizer head by suction, and the excess, non-aerosolized liquid is returned to the same liquid reservoir. The atomizer is normally operated with dry, filtered compressed air at 35 psig (241 kPa). At this pressure, the flowrate through the atomizer is 2.4 lpm, as measured downstream of the atomizer as shown in Figure 4.

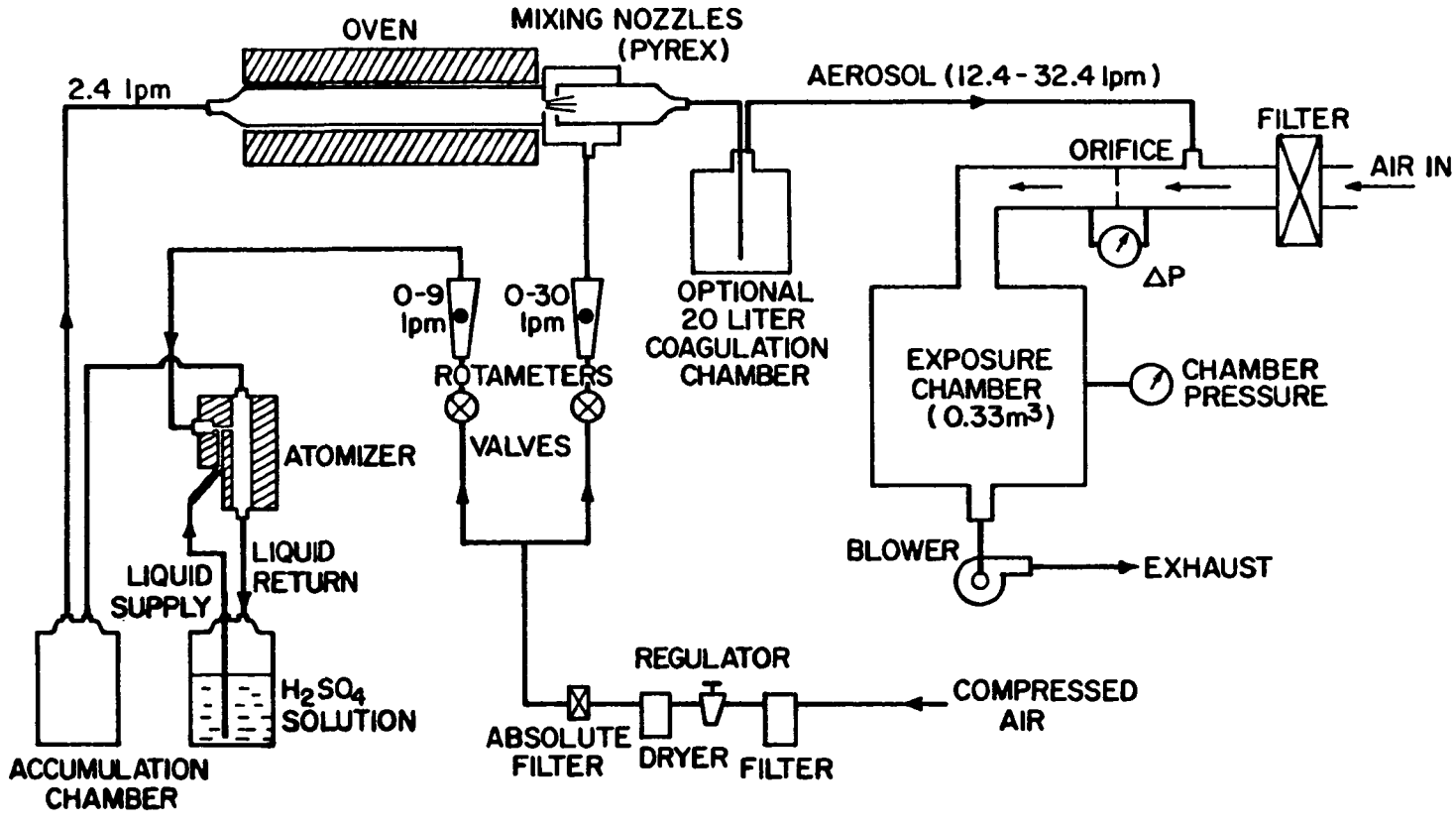

Figure 4. Schematic diagram of system for generating sulfuric acid aerosols.

EVAPORATION OF SOLUTION DROPLETS

The atomizer produces a spray of solution droplets, which are polydisperse and relatively coarse. This spray is passed through an accumulation chamber to remove the liquid collecting on the walls of the connecting tubing, and then introduced into a Pyrex evaporator tube. The evaporator tube is placed within a tube furnace, which is kept at a constant temperature of about 400°F (204°C). The residence time of the flow in the tube is three seconds, and the gas is heated to a temperature of approximately 220°F (104°C) at the exit. At this temperature, the solution droplets are completely vaporized. The specific furnace used is the Lindberg Model 55035 (Solar Basic Industries, 304 Hart St., Watertown, WI 53094). Under normal operation, the furnace temperature control is set to "lo" in order to produce the required furnace temperature of 400°F (204°C) at steady state.

CONDENSATION AND GROWTH OF THE AEROSOL

The hot gas leaving the evaporator is injected through a small orifice at the end of the evaporator tube to form a turbulent jet, which is then mixed with the primary dilution air at room temperature. The dilution air is obtained from a filtered air supply and is metered to the mixing nozzle through a 0 - 30 lpm rotameter, as shown in Figure 4. The rapid mixing of the two streams causes the nucleation and condensation of the vapor and the subsequent coagulation and growth of the sulfuric acid particles.

The aerosol is then introduced into the exposure chamber by means of a 1.27 cm i.d., 60 cm long Tygon tubing. The volume of the flow passages between the point where the hot gas first comes in contact with the dilution air to where the aerosol is further diluted by the exposure chamber air flow is 125 cm^3. This results in a residence time of 0.25 sec for a primary dilution air flow of 30 lpm. This residence time is normally too short to cause substantial particle growth by coagulation. If further coagulation is desired, an optional coagulation chamber can be used, as shown in Figure 4, to increase the size of particles produced.

EXPOSURE CHAMBER

The exposure chamber is roughly cubical in shape, and has an internal volume of 0.33 m^3. An exhaust blower at the chamber outlet provides the

needed air flow of 330 lpm. This air flow is metered by an orifice meter of 1" (2.54 cm) diameter at the chamber inlet. The aerosol is introduced into the chamber just upstream of the orifice. The rapid mixing of the aerosol with the main chamber flow quickly dilutes the aerosol and causes the aerosol size distribution to be "frozen" at that point. Since the total chamber flow of 330 lpm is much higher than the aerosol flow of 12.4 to 32.4 lpm, the humidity of the aerosol in the exposure chamber is approximately the same as the humidity of air at the chamber inlet. In the experiments described below, the main chamber air was taken from the air-conditioned laboratory room, and the relative humidity was between 42 and 48%, with a mean of 45%.

SECTION 5

PRELIMINARY EXPERIMENTS

Several preliminary experiments were performed in order to establish the performance characteristics of the major system components, and the best operating conditions for the system. These are described below, together with the results obtained.

THE ATOMIZER

The flowrate of the atomizer was measured by connecting a rotameter downstream of the atomizer and operating the atomizer with compressed air at 35 psig (241 kPa). The flowrate was found to be 2.4 liters per minute.

Next, the atomizer was operated for 24 hours, and the quantity of liquid consumed was measured. The rate of liquid consumption was found to be 6.4 ml/hr.

Since not all the liquid consumed by the atomizer was aerosolized -- some was lost through evaporation -- an experiment was performed to determine the evaporative loss of liquid from the reservoir. This was done by placing 200 ml of the nominal 0.1 N H_2SO_4 stock solution in the atomizer and measuring the pH of the solution in the reservoir as a function of time. The pH was measured by periodically withdrawing 1 ml samples from the reservoir, diluting the sample by a factor of 1000 with distilled water, and measuring the resulting pH with a high resolution (0.001 pH) pH meter (Model 701, Orion Research, Inc., 11 Blackstone St., Cambridge, MA 02139). The result is shown in Table 1. It is seen that as water evaporated, the solution in the reservoir became more concentrated, resulting in a lowering of the pH, and an increase in the solution normality. The rate of evaporation of water was calculated and found to be 1.9 ml/hr, or 30% of the total liquid consumption rate of 6.4 ml/hr.

TABLE 1. VARIATION OF SOLUTION pH WITH TIME FOR LIQUID IN ATOMIZER

Time, hr	Vol. of Solution in Reservoir, ml	pH (1000:1 dilution)
0	200	3.83
7	---	3.71
20	---	3.58
24	46	3.54

The liquid consumption and evaporation rates determined above were obtained by operating the atomizer with dry, filtered compressed air at 35 psig (241 kPa). The relative humidity of the air, after expanding to atmospheric pressure, was found to be 20%.

In Table 2, the principal atomizer characteristics are summarized.

TABLE 2. CHARACTERISTICS OF ATOMIZER

Operating Pressure:	35 psig (241 kPa)
Flowrate:	2.4 liters per minute
Liquid Consumption Rate:	6.4 ml/hr.
Liquid Evaporation Rate:	1.9 ml/hr.
Reservoir Capacity:	1,000 ml

VAPORIZATION TEMPERATURE

To determine the furnace temperature needed to vaporize the sulfuric acid solution droplets, the following experiments were performed. All experiments were carried out with a 0.1 N solution in the atomizer reservoir.

First, a steady flow was established in the system by turning on the compressed air supply and the exhaust blower. An Electrical Aerosol Analyzer (EAA) (Model 3030, TSI Inc., P. O. Box 3394, St. Paul, MN 55165) was then used to monitor the aerosol in the exposure chamber.

Next, the furnace was turned on, and the total EAA current was recorded on a strip chart. The temperature, as indicated by the furnace temperature indicator, was also recorded at regular intervals up to the maximum attainable temperature.

The furnace was then allowed to cool down to room temperature. A thermocouple introduced into the exit orifice of the evaporator tube provided the gas temperature at that point. The furnace was then turned on, and the gas temperature, as sensed by the probe, was recorded on a strip chart on the same time scale as before. Recordings from the two runs were mapped to give the EAA current variation with time and with furnace and gas temperatures. The runs were repeated for three furnace settings, resulting in three steady state temperatures. The plots are shown in Figures 5, 6, and 7. From these plots, the following observations or conclusions can be made:

1) As the furnace began to warm up, there was initially no change in the total EAA current, indicating that the size distribution of the aerosol was not affected by the initial warming of the furnace. This initial warming period varied between 33 minutes, for a furnace temperature setting of "lo", and 9 minutes, for a higher temperature setting of "3".

2) At an exit gas temperature of 138°F (54°C), the total EAA current began to rise sharply, reaching a peak at a gas temperature of 180°F (82°C). Thereafter, the EAA current decreased and then finally stabilized. The variation in EAA current was due to the fact that the instrument sensitivity is a function of particle size, and that as sulfuric acid droplets vaporized and recondensed, the size distribution of the aerosol was changed. The result indicates that the minimum vaporization temperature for sulfuric acid droplets was 130°F (59°C), and that complete vaporization of the droplets could be obtained at a somewhat higher temperature.

3) The time for the EAA current to become steady varied from 50 minutes for a furnace temperature setting of "3" to 130 minutes for a temperature setting of "lo". Thus, sufficient time should be allowed

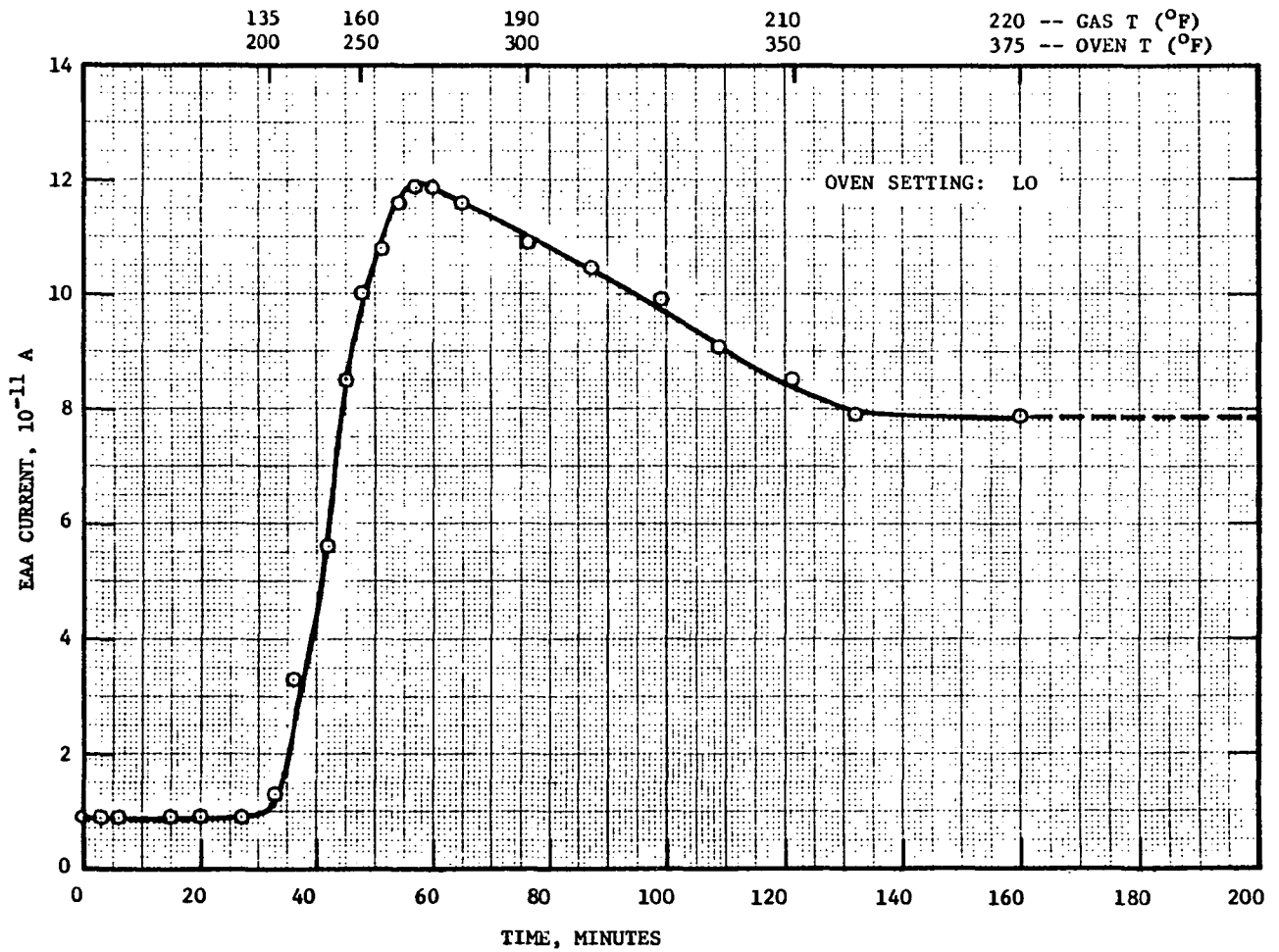

Figure 5. Variation of total EAA current with time during warm-up for a furnace temperature setting of "lo".

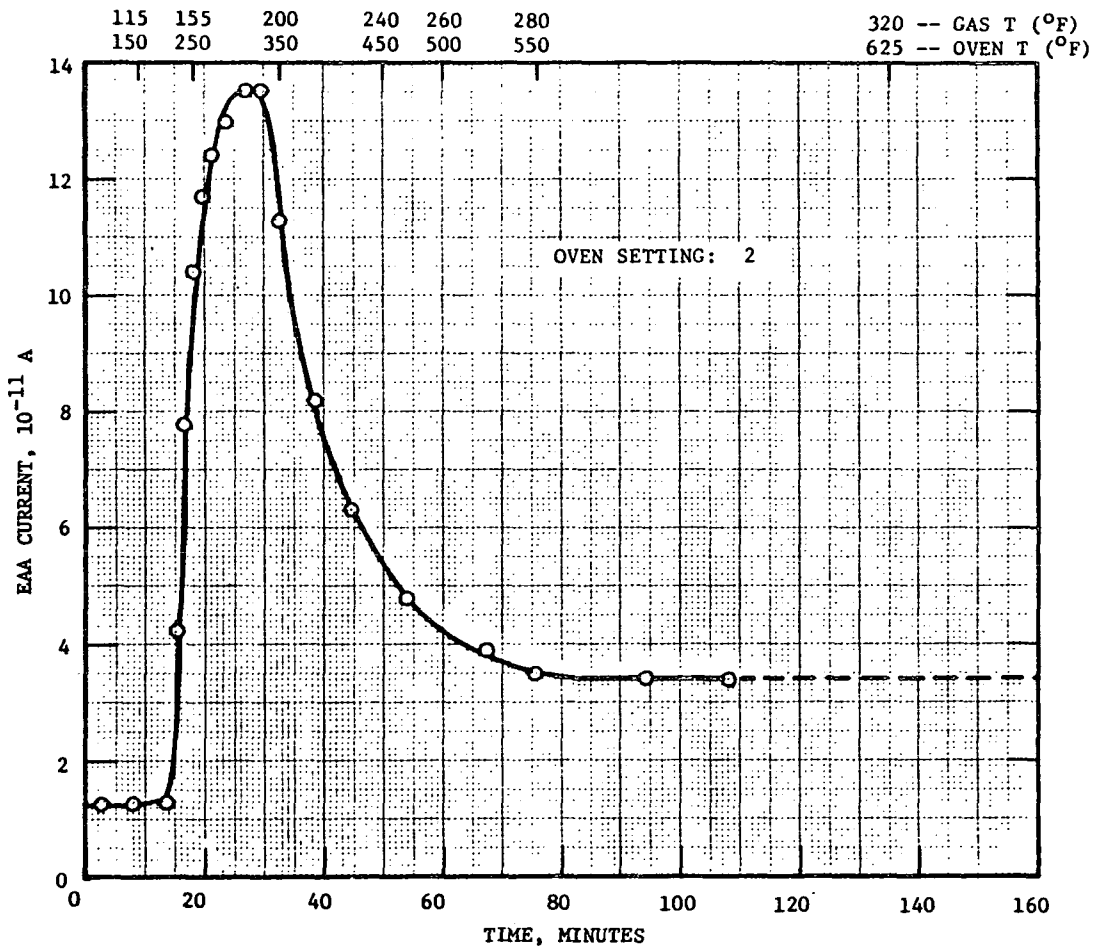

Figure 6. Variation of total EAA current with time during warm-up for a furnace temperature setting of "2".

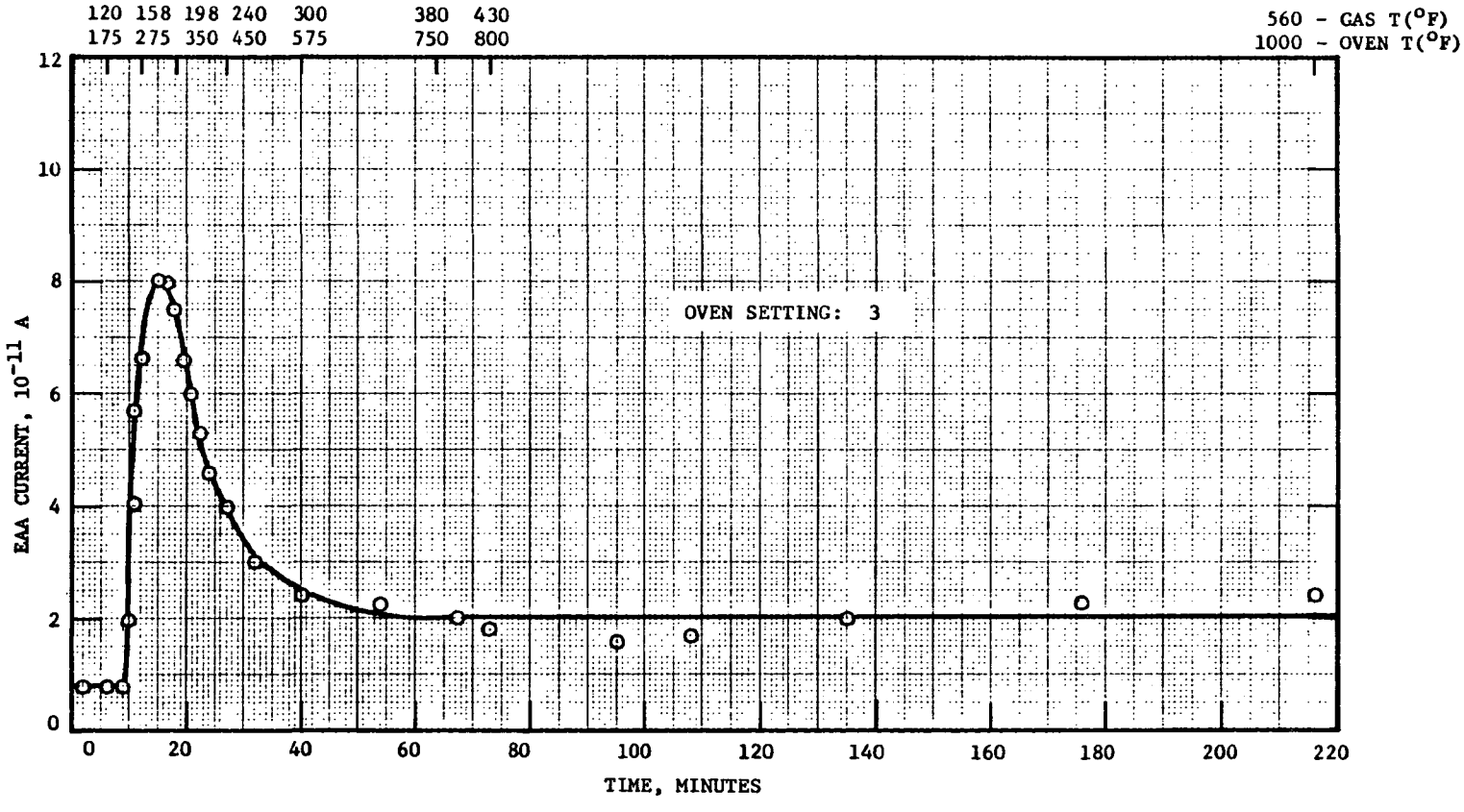

Figure 7. Variation of total EAA current with time during warm-up for a furnace temperature setting of "3".

for the system to stabilize before any size distribution measurement was made.

4) A furnace temperature setting of "lo" was adequate to completely vaporize the sulfuric acid droplets. At this setting, the furnace reached a steady operating temperature of 400°F (204°C) and the gas, 220°F (104°C).

UNIFORMITY OF THE AEROSOL IN THE EXPOSURE CHAMBER

The exposure chamber was probed at 27 different locations in order to obtain an accurate picture of the uniformity of aerosol distribution within the chamber. Figure 8 shows the nine probe locations on each of three horizontal planes, and the location of these planes within the chamber. For each experiment, the aerosol was sampled at the indicated probe locations with the EAA, and the total EAA current was recorded. Table 3 lists the results for several dilution and chamber air flows. The data include the average EAA current and the standard deviation of current in each plane, as well as the average current and the standard deviation for the entire 27 probe locations. As one would expect, increasing the chamber flow generally resulted in more uniform aerosol distributions. For instance, at a chamber flow of 132 lpm, the standard deviation of the total EAA current was only 6.2% of the average EAA current. This indicates that the exact probe location in the chamber is not critical for determining the aerosol concentration, since the aerosol distribution within the chamber is quite uniform.

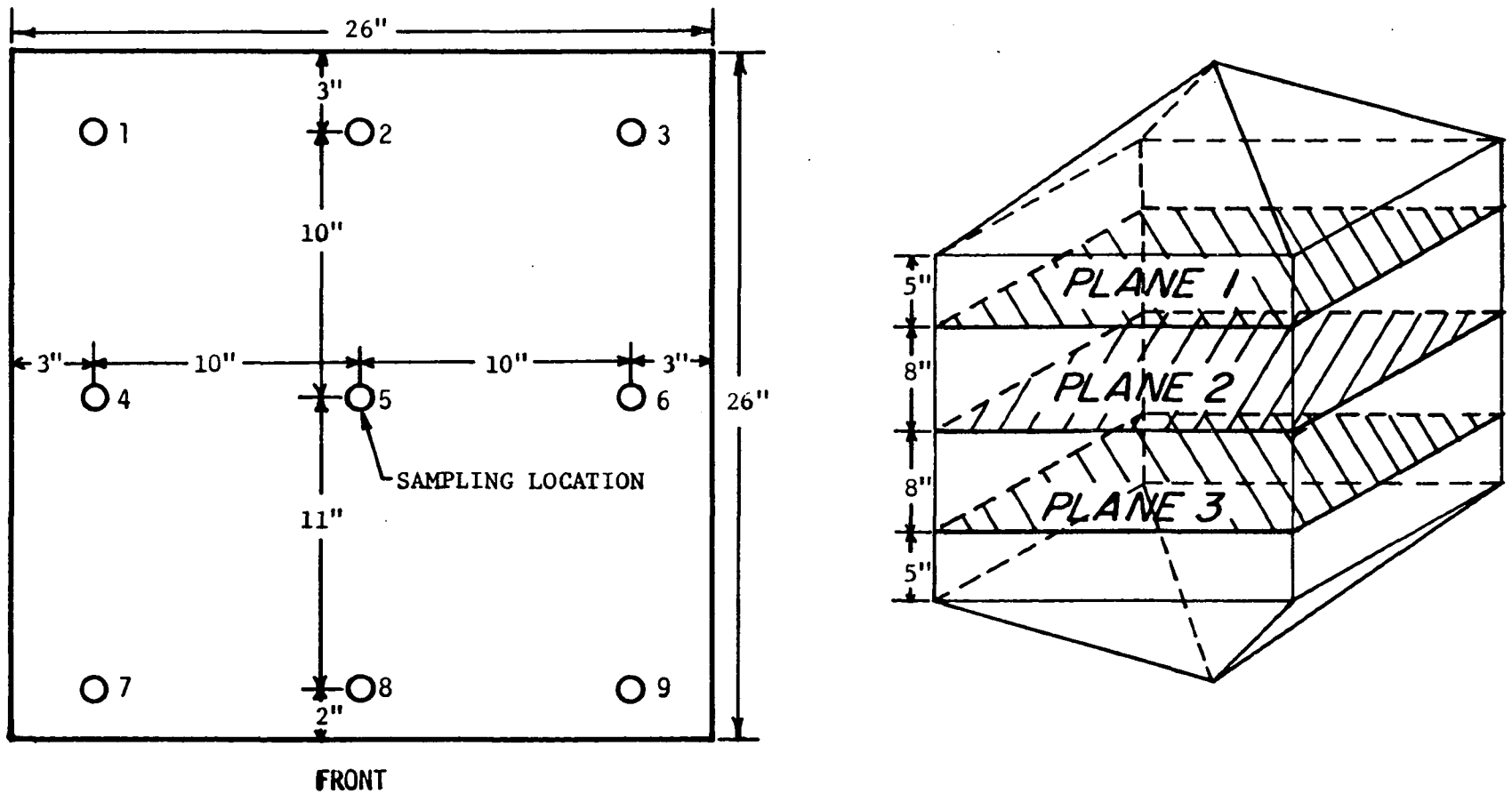

Figure 8. Location of sampling probe on a horizontal plane within the exposure chamber.

TABLE 3. VARIATION OF AEROSOL CONCENTRATION WITHIN EXPOSURE CHAMBER

Sampling Point	Q_1= 10 lpm Q_2= 132 lpm I, 10^{-11} A		Q_1= 28 lpm Q_2= 132 lpm I, 10^{-11} A		Q_1= 10 lpm Q_2= 44 lpm I, 10^{-11} A		Q_1= 28 lpm Q_2= 44 lpm I, 10^{-11} A	
1-1*	2.40		4.00		3.95		4.45	
1-2	2.31		3.89		3.50		4.23	
1-3	2.35		4.20		3.15		4.00	
1-4	2.32	$\bar{I}$=2.44	3.85	$\bar{I}$=4.14	3.50	$\bar{I}$=3.57	4.48	$\bar{I}$=4.49
1-5	2.26	σ=0.16	3.92	σ=0.23	3.27	σ=0.33	4.13	σ=0.33
1-6	2.37	$\sigma/\bar{I}$=0.066	4.10	$\sigma/\bar{I}$=0.056	3.61	$\sigma/\bar{I}$=0.092	4.79	$\sigma/\bar{I}$=0.073
1-7	2.60		4.40		3.28		4.40	
1-8	2.58		4.48		3.63		4.92	
1-9	2.77		4.40		4.27		5.02	
2-1	2.05		4.20		3.00		3.60	
2-2	2.29		3.87		2.82		3.45	
2-3	2.35		3.83		2.85		3.60	
2-4	2.45	$\bar{I}$=2.37	3.64	$\bar{I}$=3.90	2.61	$\bar{I}$=2.81	3.61	$\bar{I}$=3.49
2-5	2.27	σ=0.17	3.53	σ=0.30	2.61	σ=0.18	3.22	σ=0.12
2-6	2.34	$\sigma/\bar{I}$=0.072	3.51	$\sigma/\bar{I}$=0.077	2.50	$\sigma/\bar{I}$=0.064	3.58	$\sigma/\bar{I}$=0.034
2-7	2.35		4.00		2.90		3.38	
2-8	2.49		4.00		2.94		3.47	
2-9	2.72		4.50		3.06		3.48	
3-1	2.36		3.84		2.61		3.35	
3-2	2.40		3.80		2.75		3.30	
3-3	2.45		3.92		2.78		3.33	
3-4	2.38	$\bar{I}$=2.43	3.60	$\bar{I}$=3.76	2.48	$\bar{I}$=2.66	3.40	$\bar{I}$=3.35
3-5	2.38	σ=0.10	3.50	σ=0.30	2.58	σ=0.13	3.20	σ=0.11
3-6	2.41	$\sigma/\bar{I}$=0.041	3.55	$\sigma/\bar{I}$=0.080	2.55	$\sigma/\bar{I}$=0.049	3.41	$\sigma/\bar{I}$=0.033
3-7	2.30		3.80		2.64		3.27	
3-8	2.50		3.38		2.62		3.26	
3-9	2.65		4.45		2.94		3.61	
Overall:		$\bar{I}$=2.41 σ=0.15 $\sigma/\bar{I}$=0.062		$\bar{I}$=3.93 σ=0.32 $\sigma/\bar{I}$=0.081		$\bar{I}$=3.01 σ=0.46 $\sigma/\bar{I}$=0.153		$\bar{I}$=3.78 σ=0.55 $\sigma/\bar{I}$=0.146

Q_1 = primary dilution air flow

Q_2 = total chamber air flow

* The first digit indicates the plane location and the second digit, the location of the probe on that plane. Thus, 2-5 indicates plane 2 and probe location 5 (see Figure 8).

SECTION 6

PERFORMANCE OF THE AEROSOL GENERATING SYSTEM

As a result of the preliminary experiments described above, the following operating conditions were adopted as the standard for the aerosol generating system:

Atomizer pressure: 35 psig (241 kPa)

Furnace temperature: Control set to "lo" giving a steady state furnace temperature of 400°F (204°C) and a gas temperature of 220°F (104°C)

Chamber air flow: 350 liters per minute*

The system was then evaluated under these conditions.

The experiments to evaluate system performance were carried out using an auxiliary blower, rather than with the exhaust blower on the chamber, since the latter was found to have inadequate capacity to draw the needed chamber flow through the absolute filter at the chamber intake, as shown in Figure 4. During these experiments, two filters were used, one at the inlet to the chamber, as shown in Figure 4, and the other at the chamber outlet and upstream of the exhaust blower. This arrangement insured that there would be no leakage of the sulfuric acid aerosol into the laboratory room, the whole system being under vacuum.

In each experiment, the chamber flow was always turned on prior to the atomizer flow. When both flows were on, the furnace would be switched on and set to the "lo" setting, or if the heating process was to be speeded up, the dial would be set to "high" for a couple of minutes and the furnace temperature closely watched. When a temperature of 400°F (204°C) was reached, the temperature control was then returned to "lo". Usually half an hour

* In these experiments, a Variac was used to vary the blower speed. It was difficult to set the chamber flow exactly to 330 lpm. All the experiments were consequently made with the chamber flow at 350 lpm.

was allowed after the furnace had reached a steady temperature and before any measurements were made.

MASS CONCENTRATION

Four different methods were used to measure the aerosol mass concentration in the exposure chamber.

The aerosol was collected by drawing a sample flow of at least 1 m^3 through a 1.0 μm pore Fluoropore filter (Millipore Corp., Bedford, MA 01730). This was achieved by timing a flow of 14 lpm through a critical orifice for a minimum of 71 minutes. The filter was weighted before and after the experiment, and the mass concentration of the aerosol was deduced. An electronic microbalance (Model AD-1, Perkin Elmer Corp., Main Ave., Norwalk, CT 06856) was used for this purpose. The filters were subsequently analyzed by wet chemical methods at EPA to give the SO_4^{--} concentration. Previous experiments (Liu and Kuhlmey, 1977) have shown that the efficiency of the Fluoropore filter is in excess of 99.9%.

A quartz-crystal mass monitor (QCMM) (Model 3500 Piezobalance, TSI Inc., P. O. Box 3394, St. Paul, MN 55165) was used simultaneously during the experiments. The instrument measures the aerosol mass concentration by sensing the change in vibrational frequency of a quartz crystal as particles are deposited onto its surface by a small electrostatic precipitator. The sampling period of the instrument is 24 seconds for high mass concentrations or 120 seconds for low concentrations. Several readings were taken for each run and averaged to give a representative concentration.

The fourth method used was the Electrical Aerosol Analyzer, or EAA. This instrument measures the size distribution of the aerosol in the 0.0032 to 1.0 μm diameter range by charging the particles and measuring the resulting particle mobilities. The operating principle of the instrument has been described by Liu and Pui (1975) and Liu et al. (1976), who also presented the basic calibration data for the instrument. However, in order to convert the instrument readings into a size distribution, a "data reduction scheme" must be used. In the present case, the "simplex minimization" technique described by Liu and Kapadia (1977) was used. From the measured size distribution, the aerosol volume was calculated. The mass concentration was then calculated by

multiplying the aerosol volume concentration by 1.35 g/cm^3, which is the density of sulfuric acid droplets at 45% relative humidity.

The EAA measurement was made by drawing all the required 50 lpm flow from the exposure chamber. Except for the case of the 0.1 N solution, all EAA samplings required a dilution. This diluter is shown in Figure 9, and the flow of aerosol to the diluter was monitored by a linear flowmeter in order to obtain the dilution ratio (130 to 1 dilution was used in these experiments).

The experiments were performed with 0.1 N and 1.0 N H_2SO_4 solutions. Table 4 shows a comparison of the measured aerosol mass by filter weighing and by SO_4^{--} analysis. The agreement between the two methods is seen to be satisfactory -- the mean difference is about 13%, and the maximum difference, 29%.

The discrepancy between the two methods of measurement for samples A and C may have been due in part to the partial neutralization of the collected H_2SO_4 by ammonia in the laboratory air. Neutralization of H_2SO_4 on the filter would not affect the measured SO_4^{--} mass by chemical analysis. However, if the collected H_2SO_4 particles had been partially neutralized by ammonium at the time of weighing of the filter, the particle mass would be reduced. The calculated SO_4^{--} mass would then also be lower, since it was calculated assuming no neutralization had taken place. This may have been an important factor contributing to the discrepancy between measurement methods for samples A and C, since the total collected mass for these samples was quite small (about 0.1 of that for samples D, E, and F).

In Table 5, the aerosol mass concentrations measured by the several techniques described above are summarized and compared. Again, there is good agreement among the four independent measurement techniques. In view of the differences in the operating principles involved, the agreement may indeed be considered as excellent.

The experimental results obtained above are summarized and plotted in Figure 10, showing the aerosol concentration in the exposure chamber as a function of the normality of the H_2SO_4 solution in the atomizer. Also shown in Figure 10 are the results obtained by the EAA for several intermediate

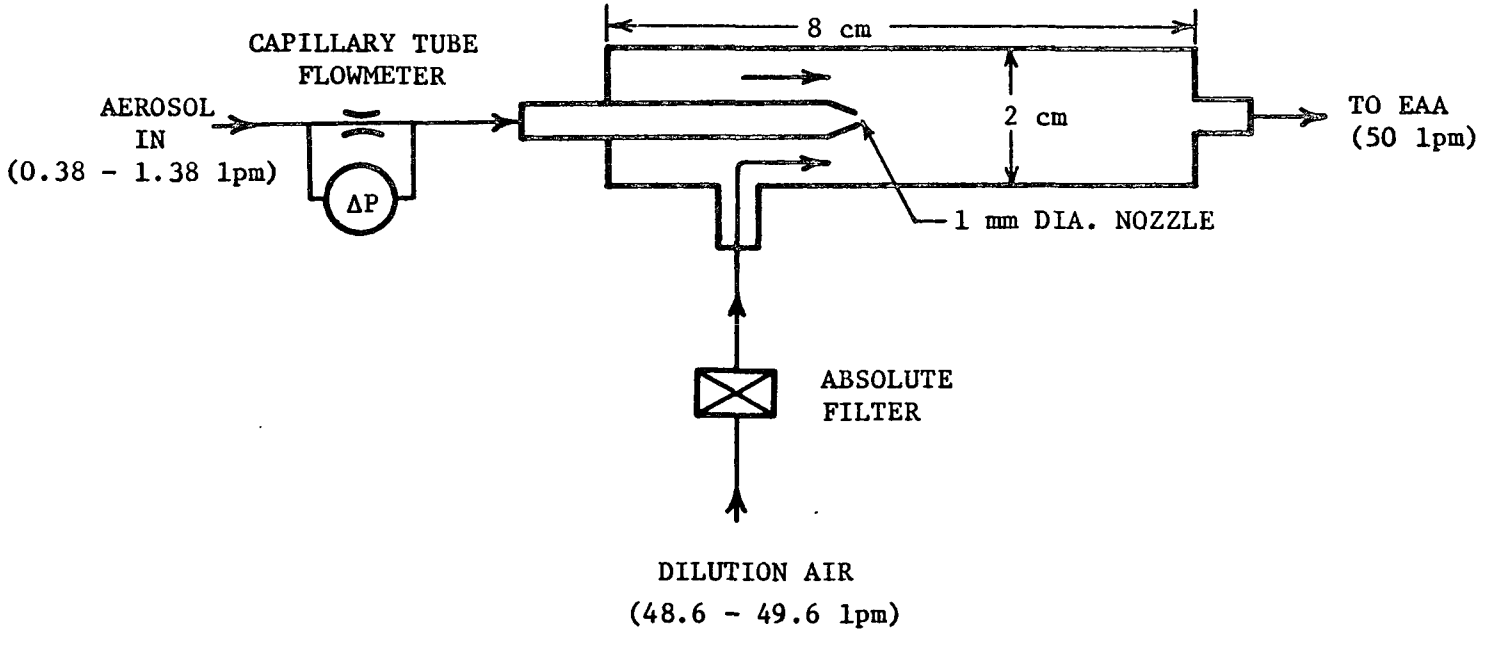

Figure 9. Schematic diagram of aerosol diluter.

TABLE 4. COMPARISON OF AEROSOL MASS MEASUREMENT BY WEIGHING AND BY SO_4^{--} ANALYSIS

Sample	H_2SO_4 Conc.	Primary Dilution Air, lpm	Sample Volume, m^3	Aerosol Mass, mg	SO_4^{--} Mass by Aerosol* Mass, M_1, mg	SO_4^{--} Mass Measured, M_2, mg	Ratio M_1/M_2
A	0.1 N	10	1.0	0.24	0.106	0.121	0.88
B	0.1 N	20	1.24	0.34	0.150	0.148	1.01
C	0.1 N	30	1.06	0.25	0.110	0.154	0.71
D	1.0 N	10	1.35	4.41	1.945	1.66	1.17
E	1.0 N	20	1.48	4.87	2.148	1.97	1.09
F	1.0 N	30	1.44	4.92	2.170	1.98	1.10

* The values given are obtained by multiplying the measured aerosol mass by the factor

$$\left(\frac{96}{98}\right)(0.45) = 0.441$$

where 96 and 98 are respectively the molecular weights of SO_4^{--} and H_2SO_4, and 0.45 is the equilibrium mass concentration of H_2SO_4 in the solution droplet at an R.H. of 45%.

TABLE 5. COMPARISON OF AEROSOL MASS CONCENTRATION MEASUREMENT BY SEVERAL DIFFERENT TECHNIQUES*

H_2SO_4 Concentration	0.1 N			1.0 N		
Primary Dilution Air, lpm	10	20	30	10	20	30
	Aerosol Mass Concentration ($H_2SO_4 + H_2O$), mg/m^3					
Filter Weighing	.24	.27	.24	3.26	3.29	3.42
SO_4^{--} Analysis**	.27	.27	.33	2.79	3.02	3.12
QCMM	.16	.25	.24	2.75	3.00	3.00
EAA***	.25	.30	.27	2.73	3.00	2.65

* Measured at 45% relative humidity.

** Obtained by multiplying the measured SO_4^{--} concentration by (1/0.45)(98/96) = 2.27, where 0.45 is the mass concentration of H_2SO_4 in the solution droplet at 45% R.H., 98 is the molecular weight of H_2SO_4, and 96, that of SO_4^{--}.

*** Obtained by multiplying the measurement aerosol volume concentration by 1.35 g/cm^3, the density of the sulfuric acid droplet at 45% R.H.

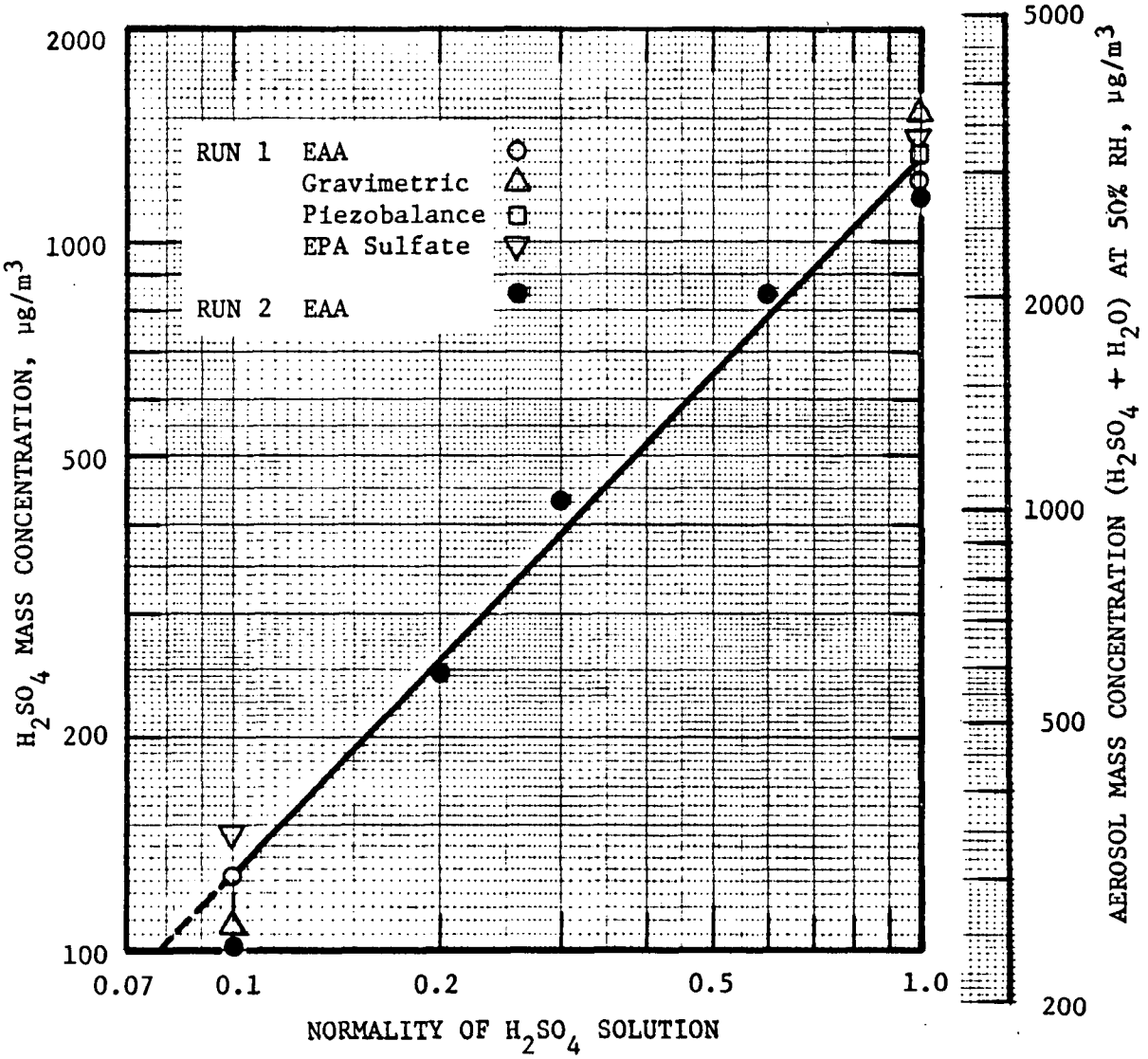

Figure 10. H_2SO_4 and aerosol mass concentration in exposure chamber as a function of solution normality.

solution normalities. These additional EAA measurements are described in more detail in the next section.

It is interesting to note in Figure 10 that the aerosol mass concentration is proportional to the solution normality, and that over the normality range of 0.1 N to 1.0 N, the H_2SO_4 mass concentration in the chamber varied from 0.13 to 1.3 mg/m^3.

SIZE DISTRIBUTION

The aerosol size distribution was measured by the EAA for various sulfuric acid concentrations and for primary dilution airflow of 10, 20, and 30 lpm. The data were reduced by means of the "Simplex Minimization" technique of Liu and Kapadia (1977). The results are summarized in Table 6, and a few selected size distribution curves are plotted and compared in Figures 11 and 12. More complete size distribution data are given in Tables A1 to A4 in Appendix A.

Although the aerosol volume concentration is not greatly affected by primary dilution airflow, the particle size is seen to decrease with increasing dilution airflow. This is to be expected, since the aerosol volume concentration is determined primarily by the atomizer output, which was unchanged in these experiments. The smaller particle size obtained at the higher primary dilution airflows was apparently the result of the more rapid mixing of the vapor with the dilution air. With more rapid mixing, a greater number of small particles are produced, resulting in a reduction in the overall size distribution of the aerosol. In all cases, the σ_g of the aerosol was not greatly affected, the σ_g being in the range from 1.5 to 2.0 with an average of about 1.7.

Experience with the aerosol generator shows that the generator has good operational stability when the primary dilution air was kept above 20 lpm. The result in Table 6 shows that the measured size distribution of the aerosol was quite stable when primary dilution airflows of 20 and 30 lpm were used, whereas at a primary dilution airflow of 10 lpm, less stable results were obtained. Consequently, 30 lpm has been chosen as the standard operating flowrate for the primary dilution air. In Figure 13, the variation of

TABLE 6. SUMMARY OF AEROSOL SIZE DISTRIBUTION PARAMETERS FOR VARIOUS GENERATOR OPERATING CONDITIONS

Solution Normality	0.1 N			0.2 N			0.3 N			0.6 N			1.0 N		
Primary Dilution (lpm)	10	20	30	10	20	30	10	20	30	10	20	30	10	20	30
VMD* (1)†	.14	.056	.041				.077	.058	.056				.088	.082	.082
VMD (2)†	.082		.038	.077	.051	.049	.083	.058	.072	.093	.080	.081	.16	.11	.089
σ_g (1)	1.9	1.7	1.5				1.7	1.6	1.7				1.5	1.5	1.7
σ_g (2)	1.8		1.6	1.7	1.6	1.7	1.7	1.6	1.8	1.6	1.7	1.8	2.0	1.8	1.7
V_t‡ (1)	189	226	204				823	680	622				2060	2264	2000
V_t (2)	215		167	424	425	408	787	640	718	1530	1430	1400	1830	2077	1910

* VMD = geometrical volume mean diameter, μm

† (1) and (2) refer to the first and second runs, respectively

‡ V_t, total volume in $\mu m^3/m^3$

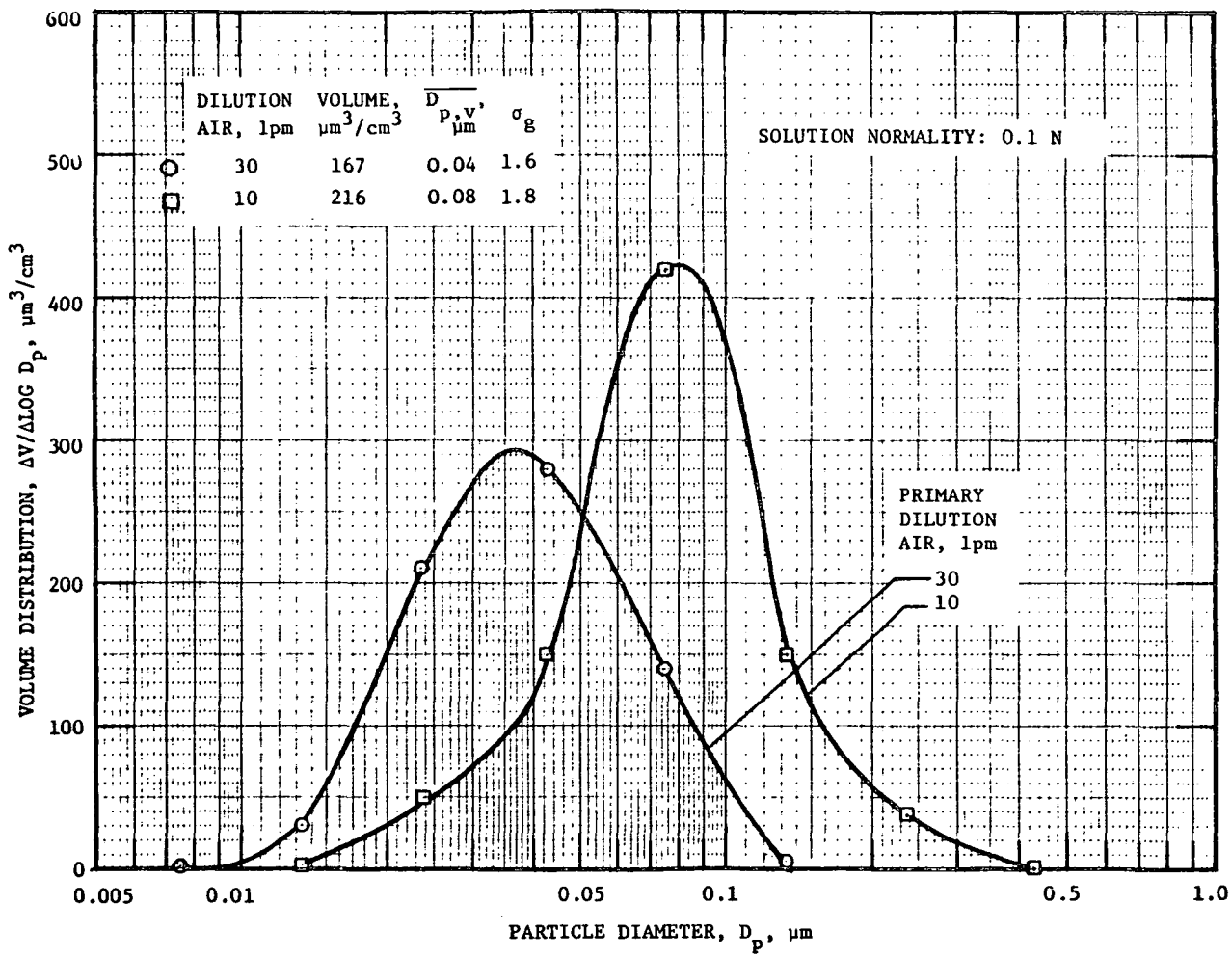

Figure 11. Aerosol size distribution for 0.1N H_2SO_4 solution.

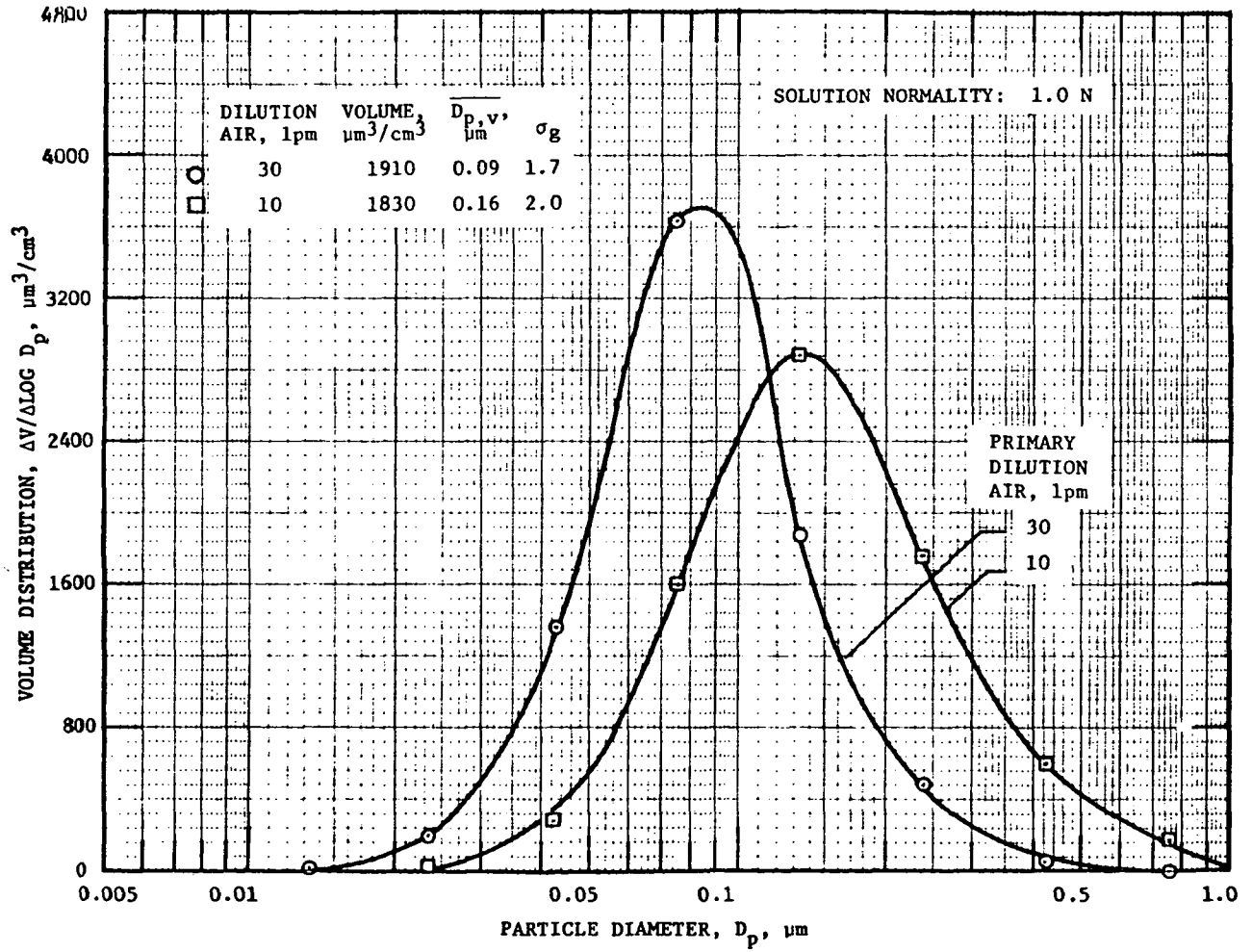

Figure 12. Aerosol size distribution for 1.0N H_2SO_4 solution.

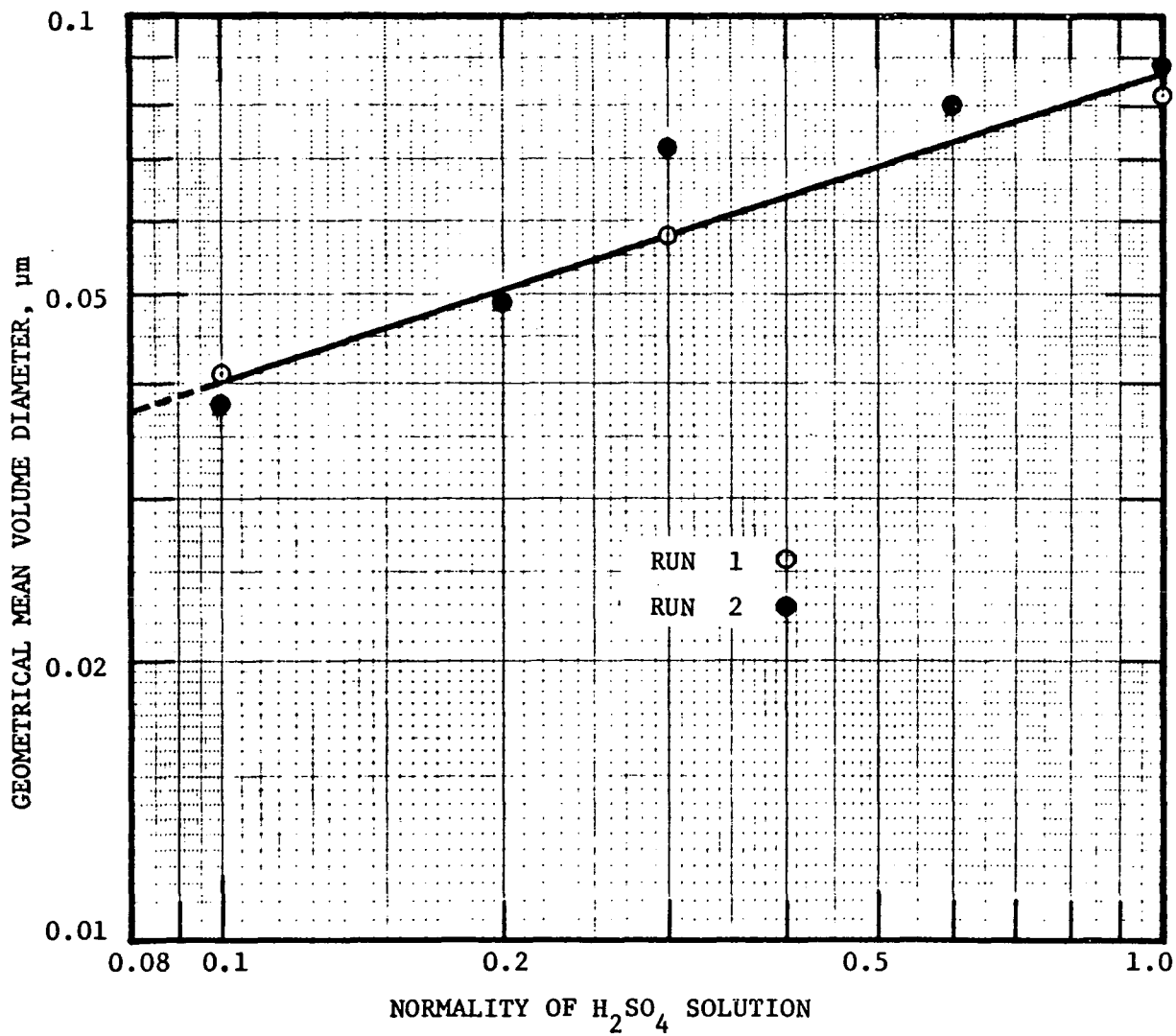

Figure 13. Aerosol particle size as a function of solution normality for primary dilution airflow of 30 lpm.

the geometrical mean volume diameter of the aerosol with solution normality is shown for a primary dilution airflow of 30 lpm.

COAGULATION CHAMBER

The result of the above-described studies shows that the aerosol generator is capable of generating sulfuric acid aerosols in the 0.04 to 0.087 μm diameter range when sulfuric acid solutions in the 0.1 N to 1.0 N range is used. Although larger particles can be produced by means of more concentrated solutions, it was decided to investigate the use of a coagulation chamber for increasing the size of particles produced.

The experiment was performed with 1.0 N solution in the atomizer. The size distribution of the aerosol was measured with and without the optional 20 liter coagulation chamber shown in Figure 4. It was found that the geometrical mean volume diameter increased from 0.087 μm when no coagulation chamber was used, to 0.130 μm when a 20 liter chamber is inserted into the system. It was found that the measured aerosol volume concentration remained essentially unchanged, indicating that there was negligible aerosol loss in the coagulation chamber.

To determine the aerosol particle diameter for other coagulation chamber volumes, we note that for a coagulation-limited aerosol, the number concentration, N, is inversely proportional to the coagulation time, t, according to Equation (5). Since $t \propto V'$, we have

$$N \propto (1/V') \tag{9}$$

where V' is the total effective coagulation volume in the system. In addition, the aerosol mass concentration is given by

$$m = (\pi D_p^3/6)(N)(\rho) \tag{10}$$

If there is no loss of aerosol mass during coagulation, we have, according to Equation (10), $D_p \propto N^{-1/3}$, and with Equation (9),

$$D_p \propto (V')^{1/3} \tag{11}$$

The total effective coagulation chamber volume in the system is the sum of

the coagulation chamber volume, V_o, in the absence of a coagulation chamber, and the volume, V, of the coagulation chamber, or

$$V' = V + V_o \tag{12}$$

By means of Equations (11) and (12), we have

$$D_p \propto (V + V_o)^{1/3} \tag{13}$$

Using the experimental result,

$$\begin{aligned} D_p &= 0.087\ \mu m \quad \text{for } V = 0 \\ D_p &= 0.13\ \mu m \quad \text{for } V = 20 \text{ liters} \end{aligned} \tag{14}$$

and treating V_o in Equation (13) as an empirically adjustable parameter, we have

$$D_p = \left(\frac{V + 8.55}{8.55}\right)^{1/3}(0.087),\ \mu m \tag{15}$$

which can be used as an interpolation or extrapolation formula to estimate the aerosol particle size for various coagulation chamber volumes. The result of the calculation is shown in Table B2 in Appendix B. The result shows that with a 30 liter coagulation chamber, particles as large as 0.144 μm can be obtained using a 1.0 N solution in the atomizer.

SECTION 7

FINAL REMARKS

The aerosol generator described in this report may be considered as a developmental prototype. Although it performed satisfactorily during the evaluating phase of the program, we believe certain improvements can and should be made. In addition, certain precautions need to be taken in order to insure proper operation of the generator. These are described below.

1) Due to its availability in our Laboratory, Tygon tubing was used throughout as the connecting tubeing in the generator. For long-term operation, a more chemically inert tubing such as Teflon should be used. It is recommended that the existing tubing be replaced with Teflon for long-term operation of the generator and in any new generator to be constructed following the basic design reported here.

2) To avoid neutralizing the generated sulfuric aerosol particles by NH_3, which may be present in the compressed air line or in the supply air for the main chamber air flow, it is recommended that these airstreams be purified by passing through an absorbent material with high affinity for NH_3.

3) Although the generator has been found to be quite stable during its operation over a period of several days, its true long-term stability needs to be established. It is recommended that during the operation of the generator in the actual animal exposure experiments, the performance of the generator be monitored closely in order to obtain some practical working experience to determine how frequently the generating system needs to be cleaned and serviced.

REFERENCES

Fuchs, N. A. 1964. The Mechanics of Aerosols. MacMillan Company, New York. 408 pp.

Liu, B. Y. H., and A. Kapadia. 1977. A Computer Data Reduction Program for the Electrical Aerosol Analyzer. Publication Number 325, Particle Technology Laboratory, Department of Mechanical Engineering, University of Minnesota, Minneapolis, MN 55455. 26 pp.

Liu, B. Y. H., and G. A. Kuhlmey. 1977. Efficiency of Air Sampling Filter Media. In: X-Ray Fluorescence Analysis of Environmental Samples, T. G. Dzubay, ed. Ann Arbor Science, Ann Arbor, MI. pp. 107-119.

Liu, B. Y. H., and K. W. Lee. 1975. An Aerosol Generator of High Stability. Am. Ind. Hyg. Assoc. J., 36:861-865.

Liu, B. Y. H., and D. Y. H. Pui. 1975. On the Performance of the Electrical Aerosol Analyzer. J. Aerosol Sci., 6:249-264.

Liu, B. Y. H., D. Y. H. Pui, and A. Kapadia. 1976. Electrical Aerosol Analyzer: History, Principle and Data Reduction. Presented at the Aerosol Measurement Workshop, University of Florida, Gainesville, FL, March 24-26, 1976. To be published in the Proceedings of the Workshop.

Liu, B. Y. H., D. Y. H. Pui, and Y. Kousaka. 1977. Properties of H_2SO_4-H_2O Solution Droplets. Particle Technology Laboratory, University of Minnesota, Minneapolis, MN 55455.

Maugh, T. H., II. 1977. Sulfuric Acid from Cars: A Problem that Never Materialized. Science, 198:280-284.

Perry, R. H., and C. H. Chilton, eds. 1973. Chemical Engineers' Handbook, 5th Edition. McGraw-Hill Book Company, New York.

Sabinina, L. and L. Terpugow. 1935. Die Oberflachenspannung des Systems Schwefelsaure-Wasser. Z. Phys. Chem., A173:237-241.

Whitby, K. T., D. B. Kittelson, B. K. Cantrell, N. J. Barsic, and D. F. Dolan. 1976. Aerosol Size Distributions and Concentrations Measured during the General Motors Proving Grounds Sulfate Study. Presented before the Division of Environmental Chemistry, American Chemical Society, San Francisco, CA, August, 1976.

Wilson, W. E., L. L. Spiller, T. G. Ellestad, P. J. Lamothe, T. G. Dzubay, R. K. Stevens, E. S. Macias, R. A. Fletcher, J. D. Husar, R. B. Husar, K. T. Whitby, D. B. Kittelson, and B. K. Cantrell. 1977. General Motors Sulfate Dispersion Experiment: Summary of EPA Measurements. J. Air Pollut. Control Assoc., 27:46-51.

APPENDIX A

DETAILED SIZE DISTRIBUTION DATA OBTAINED BY EAA

TABLE A1. SIZE DISTRIBUTION MEASUREMENT BY EAA*

Date of Experiment: July 11 (0.1 N) and July 14 (1.0 N), 1977

Solution Normality	0.1 N						1.0 N					
Primary Dilution Air, lpm	10		20		30		10		20		30	
	ΔI	$\frac{\Delta V}{\Delta \log D_p}$	ΔI	$\frac{\Delta V}{\Delta \log D_p}$	ΔI	$\frac{\Delta V}{\Delta \log D_p}$	ΔI	$\frac{\Delta V}{\Delta \log D_p}$	ΔI	$\frac{\Delta V}{\Delta \log D_p}$	ΔI	$\frac{\Delta V}{\Delta \log D_p}$
Channel, D_p, μm												
.0100 - .0178	.3	.64	6.0	12.8	10	21.2	0	0	0	0	.05	.104
.0178 - .0316	2.4	8.2	27	114.8	45	204.8	.2	.35	.35	.76	.60	2.07
.0316 - .0562	1.7	43.8	11	300	13	343	.3	7.6	.42	11.2	.45	12.28
.0562 - .100	4.3	195.7	11.2	382	10.1	222.8	.7	35.9	.82	40	.70	30.68
.100 - .178	2.45	263.7	2.34	79.2	1.6	12.7	.255	18.2	.265	16	.215	13.96
.178 - .316	.61	173	.32	14	.2	.64	.035	1.96	.035	1.72	.027	2.64
.316 - .562	.14	53.7	.07	.68	.04	--	.007	.048	.007	.04	.005	.20
.562 - 1.00	.04	8.4	.02	.036	.01	--	.003	--	.003	--	.003	.016
> 1.00	.06	--	.05	--	.05	--	0	0	0	--	0	0
Measured Aerosol Volume, $\mu m^3/cm^3$	186.8		225.8		201.4		16.0		17.5		15.49	
Dilution	No		No		No		129:1		129:1		129:1	
Aerosol Volume in Chamber, $\mu m^3/cm^3$	186.8		225.8		201.4		2064		2258		1998	
Geometric Mean Volume Diameter, μm	.14		.056		.041		.088		.082		.082	
σ_g	1.9		1.7		1.5		1.5		1.5		1.7	

* ΔI, 10^{-11}A; $\frac{\Delta V}{\Delta \log D_p}$, $\frac{\mu m^3}{cm^3}$.

TABLE A2. SIZE DISTRIBUTION MEASUREMENT BY EAA* (10 LPM PRIMARY DILUTION AIR)

Date of Experiment: July 21, 1977

	Solution Normality									
	0.1 N		0.2 N		0.3 N		0.6 N		1.0 N	
	ΔI	$\frac{\Delta V}{\Delta \log D_p}$	ΔI	$\frac{\Delta V}{\Delta \log D_p}$	ΔI	$\frac{\Delta V}{\Delta \log D_p}$	ΔI	$\frac{\Delta V}{\Delta \log D_p}$	ΔI	$\frac{\Delta V}{\Delta \log D_p}$
Channel, D_p, μm										
.0100 - .0178	3.0	6.4	2.0	4.0	.1	.22	.05	.1	.1	.2
.0178 - .0316	13	52	23	84	.9	3.3	.9	3	.4	1
.0316 - .0562	7.3	197	15	412	.7	19	1	27	.3	8
.0562 - .100	10.2	420	20.7	868	.99	43	1.83	86	.99	45
.100 - .178	2.14	147	4.5	272	.258	17	.55	43	.7	80
.178 - .316	.25	36	.54	52	.036	4	.086	11	.154	49
.316 - .562	.04	4.4	.13	4	.009	.6	.018	1	.033	16
.562 - 1.00	.01	.4	.03	--	.003	--	.008	--	.012	4
> 1.00	.06	--	.08	--	.004	--	.008	--	.011	--
Measured Aerosol Volume, $\mu m^3/cm^3$	215.4		424		21.9		42.5		50.8	
Dilution	No		No		36:1		36:1		36:1	
Aerosol Volume in Chamber, $\mu m^3/cm^3$	215.4		424		787		1530		1830	
Geometric Mean Volume Diameter, μm	.082		.077		.083		.093		.16	
σ_g	1.84		1.7		1.72		1.64		1.97	

* ΔI, 10^{-11}A; $\frac{\Delta V}{\Delta \log D_p}$, $\frac{\mu m^3}{cm^3}$.

TABLE A3. SIZE DISTRIBUTION MEASUREMENT BY EAA* (20 LPM PRIMARY DILUTION AIR)

Date of Experiment: July 21, 1977

	Solution Normality									
	0.1 N		0.2 N		0.3 N		0.6 N		1.0 N	
	ΔI	$\frac{\Delta V}{\Delta \log D_p}$	ΔI	$\frac{\Delta V}{\Delta \log D_p}$	ΔI	$\frac{\Delta V}{\Delta \log D_p}$	ΔI	$\frac{\Delta V}{\Delta \log D_p}$	ΔI	$\frac{\Delta V}{\Delta \log D_p}$
Channel, D_p, μm										
.0100 - .0178			11	24	.22	.4	0	0	.2	.4
.0178 - .0316			54	232	1.74	7	1.9	7	1.1	3.8
.0316 - .0562			25	688	.88	25	1.3	36	.9	24
.0562 - .100			21.7	672	.92	32	1.83	79	2.17	98
.100 - .178			3.6	76	.195	6	.47	30	.76	72
.178 - .316			.45	8	.032	.8	.073	7	.123	27
.316 - .562			.09	--	.006	--	.015	.6	.026	6
.562 - 1.00			.03	--	.003	--	.005	--	.009	.7
> 1.00			.09	--	.004	--	.007	--	.012	--
Measured Aerosol Volume, $\mu m^3/cm^3$			425		17.8		39.7		57.7	
Dilution			No		36:1		36:1		36:1	
Aerosol Volume in Chamber, $\mu m^3/cm^3$			425		640		1430		2077	
Geometric Mean Volume Diameter, μm			.051		.058		.08		.11	
σ_g			1.61		1.6		1.67		1.82	

* ΔI, $10^{-11}A$; $\frac{\Delta V}{\Delta \log D_p}$, $\frac{\mu m^3}{cm^3}$.

TABLE A4. SIZE DISTRIBUTION MEASUREMENT BY EAA* (30 LPM PRIMARY DILUTION AIR)

Date of Experiment: July 21, 1977

	Solution Normality									
	0.1 N		0.2 N		0.3 N		0.6 N		1.0 N	
	ΔI	$\frac{\Delta V}{\Delta \log D_p}$	ΔI	$\frac{\Delta V}{\Delta \log D_p}$	ΔI	$\frac{\Delta V}{\Delta \log D_p}$	ΔI	$\frac{\Delta V}{\Delta \log D_p}$	ΔI	$\frac{\Delta V}{\Delta \log D_p}$
Channel, D_p, μm										
.0100 - .0178	14	30	22	48	.2	.4	.2	.4	.1	.2
.0178 - .0316	45	209	69	304	2.08	9	2.4	9	1.7	6
.0316 - .0562	11	280	22	588	.83	22	1.2	33	1.4	38
.0562 - .100	7	139	20	600	.86	34	1.74	72	2.25	101
.100 - .178	.83	5.6	3.3	80	.185	11	.465	31	.7	52
.178 - .316	.09	.3	.5	14	.03	3	.065	8	.105	13
.316 - .562	.02	--	.08	--	.077	.4	.016	1	.022	1
.562 - 1.00	.01	--	.03	--	.003	--	.005	.1	.011	.1
> 1.00	.05	--	.09	--	.005	--	.009	--	.012	--
Measured Aerosol Volume, $\mu m^3/cm^3$	167		408		20		39		53	
Dilution	No		No		36:1		36:1		36:1	
Aerosol Volume in Chamber, $\mu m^3/cm^3$	167		408		718		1400		1910	
Geometric Mean Volume Diameter, μm	.038		.049		.072		.081		.089	
σ_g	1.56		1.68		1.82		1.77		1.70	

* ΔI, 10^{-11}A; $\frac{\Delta V}{\Delta \log D_p}$, $\frac{\mu m^3}{cm^3}$.

APPENDIX B

OPERATING INSTRUCTIONS

INTRODUCTION

The sulfuric acid aerosol generator described in this manual has been developed at the Particle Technology Laboratory, University of Minnesota. The generator was designed for the Environmental Protection Agency for use with its 0.33 m^3 animal exposure chamber. It was tested with the chamber at the University of Minnesota and shipped to EPA together with the test chamber.

This manual covers the operating instructions for the aerosol generator only. More detailed information concerning the generator is given in the main body of this report.

UNPACKING AND SETUP

As the schematic diagram of the system in the next section shows, there are three main parts to the generator: (1) an atomizer sub-assembly, (2) a flow control panel, and (3) an evaporator-mixer unit. The atomizer sub-assembly, the flow control panel, and the evaporator-mixer are placed within the test chamber during shipment, whereas the furnace for the evaporator is shipped separately in its own container.

Following the receipt of the shipment at EPA, carefully unpack and remove the contents from the test chamber. Carefully unwrap the atomizer sub-assembly, the flow control panel, and the evaporator-mixer. The evaporator-mixer is made of pyrex glass (see Figure B1). Be careful not to break it. Two units are supplied, one to be used in the generator, and the other as a spare. A detailed drawing of the evaporator-mixer is shown in Figure B6.

Set up the system as follows:

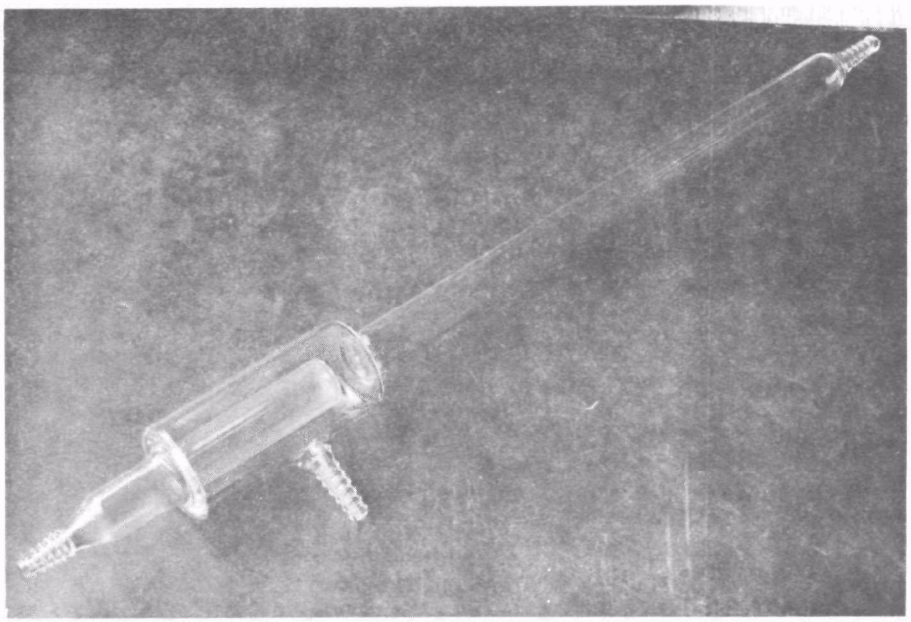

Figure B1. Photograph of evaporator-mixer.

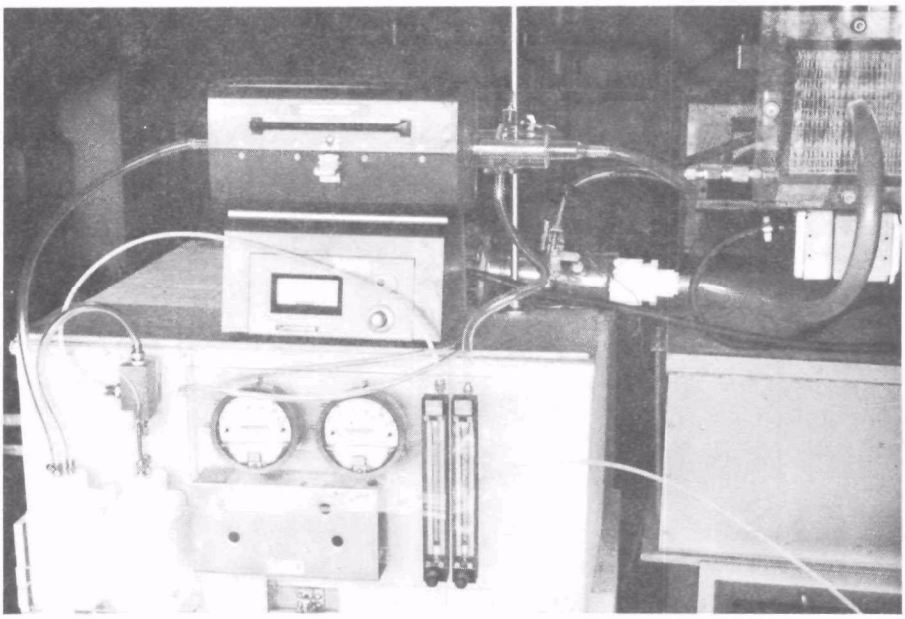

Figure B2. Photograph of sulfuric acid aerosol generator installed on the exposure chamber.

1. Mount the atomizer sub-assembly on the front of the test chamber near the upper left-hand corner as in Figure B2. The acrylic back panel of the atomizer sub-assembly is fastened to the front of the test chamber with eight screws.

2. Mount the flow control panel on the front of the test chamber above the chamber door as in Figure B2. The panel is fastened to the stainless steel bracket - the original mounting bracket for the Magnehelic pressure gauge - with four screws.

3. Set up the furnace on top of the test chamber on the piece of plywood supplied. Set up the metal stand and clamp, and install the evaporator-mixer in the furnace as shown in Figure B2. Adjust the evaporator-mixer so that the evaporator is inserted all the way into the furnace.

4. Make the following interconnections with tubings supplied:

   a) Connect the outlet of the atomizer-flow rotameter to the compressed air inlet of the atomizer with the 1/4" nylon tubing and Swagelok fitting.

   b) Connect the outlet of the settling chamber to the inlet of the evaporator with the 5/16" i.d. Tygon tubing supplied.

   c) Connect the outlet of the primary dilution air rotameter to the side-inlet on the mixing nozzle with the 5/16" i.d. Tygon tubing supplied.

   d) Connect the outlet of the mixing nozzle to the aerosol inlet of the test chamber with the 1/2" i.d. Tygon tubing supplied.

   e) Connect the Magnehelic gauge to the orifice meter with the 3/16" i.d. Tygon tubing supplied.

The completed system should appear as in Figure B2. Compare the connections you have made with those shown in the photograph.

OPERATING PRINCIPLES AND CHARACTERISTICS OF THE SULFURIC ACID AEROSOL GENERATOR

This section provides a brief description of the operating principles and characteristics of the aerosol generator. A schematic diagram of the system is shown in Figure 4.

Dry, filtered and regulated compressed air at 35 psig (241 kPa) is supplied to the atomizer via a 0 - 9 lpm rotameter. In the atomizer, the H_2SO_4 solution is atomized to form a polydisperse spray. The spray is then introduced into a one-liter settling chamber to remove the large drops and to allow any accumulated liquid on the connecting tubing to settle. The spray then enters the evaporating tube, which is heated externally by the tube furnace. In the evaporating tube, the droplets are vaporized. The vapor is then injected into the mixing nozzle where it encounters the primary dilution air supplied to the nozzle via the 0 - 30 lpm rotameter. The rapid mixing of the vapor and the primary dilution air causes a fine H_2SO_4 aerosol to be formed. This aerosol is then introduced into the chamber inlet where it is further diluted by the chamber air flow just upstream of the orifice flowmeter. This diluted aerosol is used in the test chamber.

Under normal operating conditions, the temperature control on the tube furnace is set to "lo". At this setting, the furnace will reach a steady operating temperature of 350 - 400°F according to the front-panel meter on the furnace. The actual gas temperature at the exit of the evaporator will be approximately 220°F.

Under a given set of operating conditions, e.g., for a fixed furnace temperature and fixed primary and secondary dilution air flows, the size and the concentration of the sulfuric acid aerosol produced by the generator are determined by the concentration of the H_2SO_4 solution used in the atomizer. This is the primary means by which the aerosol size and concentration are varied. Table B1 shows the characteristics of the aerosol produced by the generator for various H_2SO_4 solution concentrations. Normally, H_2SO_4 solutions in the 0.1 N to 1 N concentration range are used. This results in an H_2SO_4 mass concentration of 130 to 1,300 $\mu g/m^3$. The corresponding particle size range is from 0.04 to 0.87 μm diameter.

TABLE B1. CHARACTERISTICS OF AEROSOL PRODUCED BY THE SULFURIC ACID AEROSOL GENERATOR

Primary dilution air flow = 30 lpm (see Note 1)
Chamber air flow = 350 lpm
Relative Humidity = 45% (see Note 2)

	Measured Values	H_2SO_4 Solution Normality				
		0.1	0.2	0.3	0.6	1.0
Run 1	Filter: Mass Conc., $\mu g/m^3$	240				3420
	TSI Piezobalance: Mass Conc., $\mu g/m^3$	240				3000
	EAA: Volume Conc., $\mu m^3/cm^3$	204				2000
	D_p (volume median dia.), μm	0.041		0.056		0.082
	σ_g	1.5		1.7		1.7
	EPA sulfate: $\mu g/m^3$ of sulfate	145				1375
Run 2	EAA: Volume Conc., $\mu m^3/cm^3$	167	408	718	1400	1910
	D_p (volume median dia.), μm	0.038	0.049	0.072	.081	0.089
	σ_g	1.6	1.7	1.8	1.8	1.7
	Calculated Mass Concentration of H_2SO_4, $\mu g/m^3$					
Run 1	Filter } (see Note 3)	108				1540
	TSI Piezobalance	108				1350
	EAA (see Note 4)	128				1220
	EPA Sulfate (see Note 5)	148				1400
Run 2	EAA (see Note 4)	101	248	437	851	1160

(continued)

TABLE B1 (continued)

Notes

Note 1 Due to flow instability, the experiments were run with a mean chamber flow of 350 lpm rather than the standard chamber flow of 330 lpm. It is expected that reducing the chamber flow from 350 to 330 lpm will have a negligible effect on the measured aerosol characteristics.

Note 2 The relative humidity varied between 42 and 48% during these experiments, with a mean of 45%. At a 45% relative humidity, the droplet will have an equilibrium concentration of 0.45 g of H_2SO_4 per gram of solution and a solution density of 1.35 g/cc.

Note 3 Obtained by multiplying the measured aerosol mass concentration by 0.45.

Note 4 Obtained by multiplying the measured aerosol volume concentration by (1.35)(0.45) = 0.608.

Note 5 Obtained by multiplying the measured SO_4^{--} concentration by the ratio of molecular weights of H_2SO_4 and SO_4^{--} or (98/96) = 1.021.

The mass concentration of the sulfuric acid aerosol was measured with several different techniques as shown in Table B1. The techniques used include filter collection and weighing, the integration of the measured size distribution by the electrical aerosol analyzer to obtain the total aerosol volume, direct mass measurement by the quartz-crystal microbalance (TSI Model 3500 Piezobalance) and sulfate measurement by the EPA wet chemical technique. The agreement is seen to be good with the spread of data generally within ±20% from the mean. The results are also shown plotted in Figures 10 and 13, which can be used to interpolate between the measured values.

To generate sulfuric acid aerosols larger than can be obtained by the use of a 1 N solution, an optional coagulation chamber is inserted between the aerosol generator and the test chamber as shown in Figure 4. This causes the particles to coagulate and grow to a larger size. Experiments show that with a 20-liter coagulation chamber, the 0.087 μm diameter aerosol produced by a 1 N solution with a 30 lpm primary dilution air flow will grow to a size of 0.13 μm diameter with negligible reduction in mass concentration. Other chamber sizes can also be used. The corresponding particle size at the chamber can be estimated by means of Table B2.

The rate of liquid consumption by the atomizer has been measured and found to be 6.4 ml/hr when dry, filtered compressed air at 35 psig (241 kPa) was used as the atomizing air. Of this, 1.9 ml/hr, or 30%, represents an evaporative loss, and the remaining 4.5 ml/hr, or 70%, represents the actual liquid consumed by atomization. Due to evaporation, the solution in the atomizer reservoir will become more concentrated during operation. The rate of increase in solution concentration will depend upon the amount of liquid that is in the atomizer reservoir. Table B3 shows the calculated volume of liquid remaining in the atomizer reservoir and the concentration of the remaining liquid at various times for an initial liquid volume of 1,000 ml. As the table shows, although 1,000 ml will provide sufficient liquid to operate the generator continuously for six days, the increase in solution concentration due to evaporation will necessitate more frequent liquid changes. For instance, if the solution concentration in the reservoir is to be maintained within 30% of the initial concentration, the solution must be replaced

TABLE B2. AEROSOL PARTICLE SIZE AS A FUNCTION OF COAGULATION CHAMBER VOLUME

Chamber Volume, liters	Volume Mean Diameter, μm*
0	0.087 (measured)
5	0.101
10	0.113
20	0.130 (measured)
30	0.144

* Calculated by means of the interpolation formula

$$D_p = \left(\frac{V + 8.55}{8.55}\right)^{1/3} (0.087)\ \mu m$$

where V is the volume of the coagulation chamber in liters.

TABLE B3. CONSUMPTION AND CONCENTRATION OF H_2SO_4 SOLUTION BY ATOMIZER AS A FUNCTION OF TIME

Time, hr	Liquid Volume in Atomizer, ml	Ratio $\frac{H_2SO_4 \text{ Conc. at } t}{H_2SO_4 \text{ Conc. at } t = 0}$
0	1,000	1.00
16	900	1.03
31	800	1.07
47	700	1.13
63	600	1.20
78	500	1.30
94	400	1.45
109	300	1.69
125	200	2.19
141	100	3.68

whenever the liquid volume in the reservoir is down to 500 ml, or after about 78 hours of continuous operation. Other solution changing intervals can be easily determined from Table B3 when the maximum allowable concentration change is known.

OPERATING PROCEDURE

In order to operate the aerosol generator, you will need a source of regulated compressed air. The compressed air should be dried and filtered as shown in Figure 4 before it is introduced into the aerosol generator. A suitable filtered air supply unit is available commercially (Model 3074 Filtered Air Supply, TSI Inc., P. O. Box 3394, St. Paul, MN 55165).

Connect the compressed air supply to the inlet of the rotameters as shown in Figure B2. Then operate the generator as follows:

1. Set the pressure regulator on the filtered air supply unit to zero output pressure.

2. Fill the atomizer reservoir with H_2SO_4 solution of the desired concentration. Use more or less liquid in the reservoir depending upon the length of operating time needed. One full bottle (one liter) will provide sufficient liquid to operate the generator continuously for about six days, or three days if the concentration change is to be kept within 30% of its initial value (see preceding section).

3. Turn on the exhaust blower on the test chamber and adjust the flow to obtain a deflection of 0.7" H_2O on the Magnehelic gauge. This will provide a chamber air flow of 330 lpm, or one chamber volume per minute. (For other chamber air flows, refer to the calibration curve for the orifice meter given in Figure B3.)

4. With the rotameter inlet valves closed, adjust the pressure regulator to obtain an output pressure of 35 psig (241 kPa).

5. Adjust the inlet valve on the primary dilution air rotameter to obtain a full-scale reading of 150 mm. This will produce a primary dilution air flow of 30 lpm. (To obtain other dilution air flows, refer to the calibration curve in Figure B4 for the rotameter.)

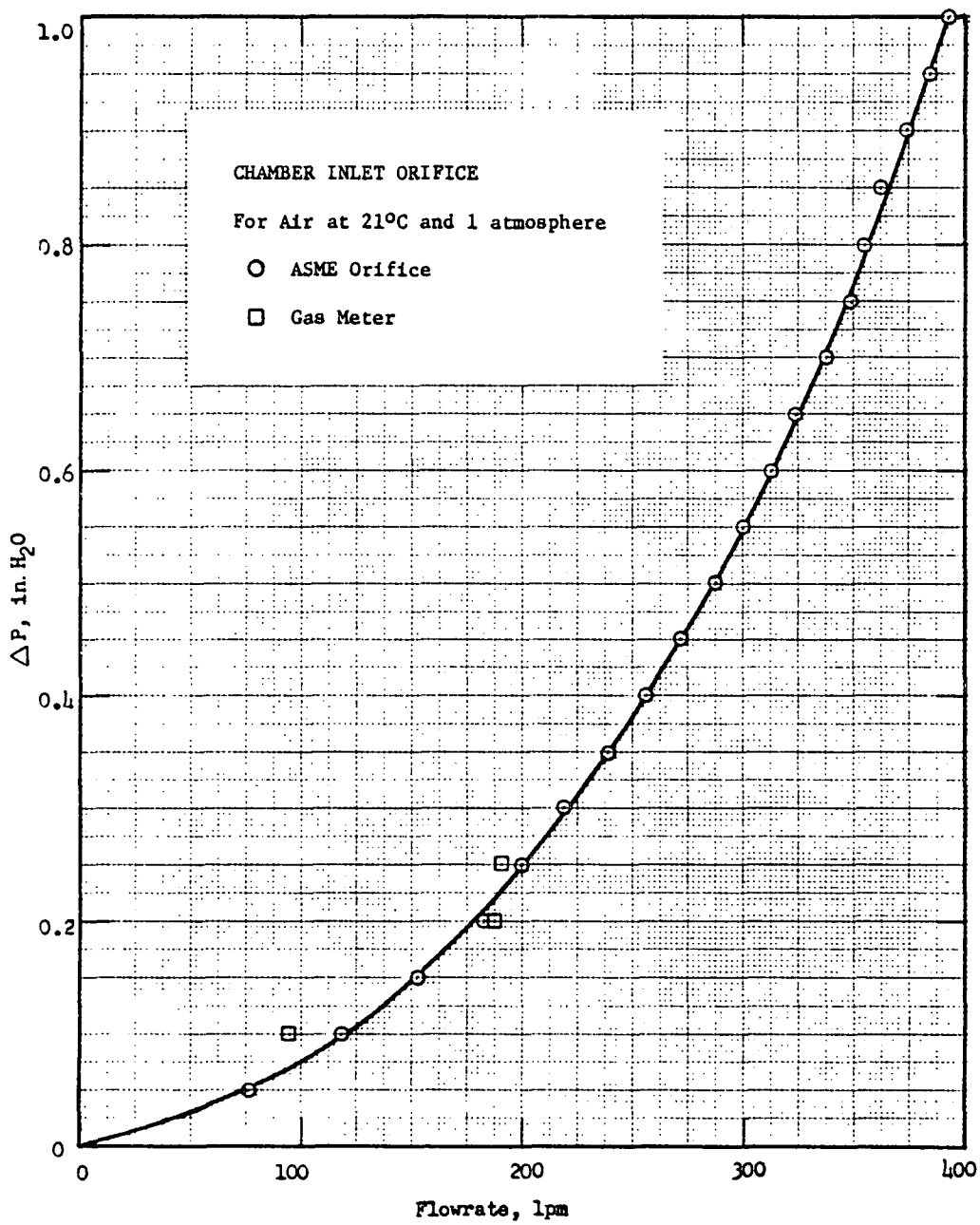

Figure B3. Calibration curve of orifice meter for total chamber flow.

6. Open the inlet valve on the atomizer flow rotameter. The rotameter should read 25 mm on the scale corresponding to an atomizer flow of 2.4 lpm. If the reading is substantially lower, the orifice in the atomizer is probably plugged. The atomizer should then be cleaned. (See Figure B5 for the rotameter calibration curve provided by the manufacturer.)

7. Turn on the furnace and set the temperature control to "lo". When starting with a cold furnace, it will take about two hours for the generator output to become steady. If the heating process is to be speeded up, the temperature control dial can be set to "high" for a couple of minutes and the furnace temperature closely watched. When a temperature of 400°F (204°C) is reached, the dial should then be returned to "lo".

8. To shut down the generator, turn off the compressed air supply and the furnace. If the aerosol generator is to be shut down temporarily for short periods, say from a few hours to overnight, the furnace may be left on its "lo" setting. Simply turn off the compressed air. When the generator is started up again with a warm furnace, it will take only one hour for the output to become steady.

NOTES ON THE OPERATION OF THE AEROSOL GENERATOR

1. Under no circumstances should the furnace be operated above a temperature of 1000°F, corresponding to a temperature control setting of "3". The pyrex evaporator will soften or melt at high temperatures.

2. When changing from a concentrated H_2SO_4 solution to a more dilute solution, the atomizer reservoir, the settling chamber, the evaporator-mixer, and all connecting tubing in contact with H_2SO_4 aerosol or vapor should be thoroughly cleaned and dried. Over a period of time, H_2SO_4 solution will accumulate at various points in the system. If the system is not cleaned, the H_2SO_4 solution may act as a desiccant, a humidifier, or as a source of H_2SO_4 vapor to change the characteristics of aerosols produced by the generator.

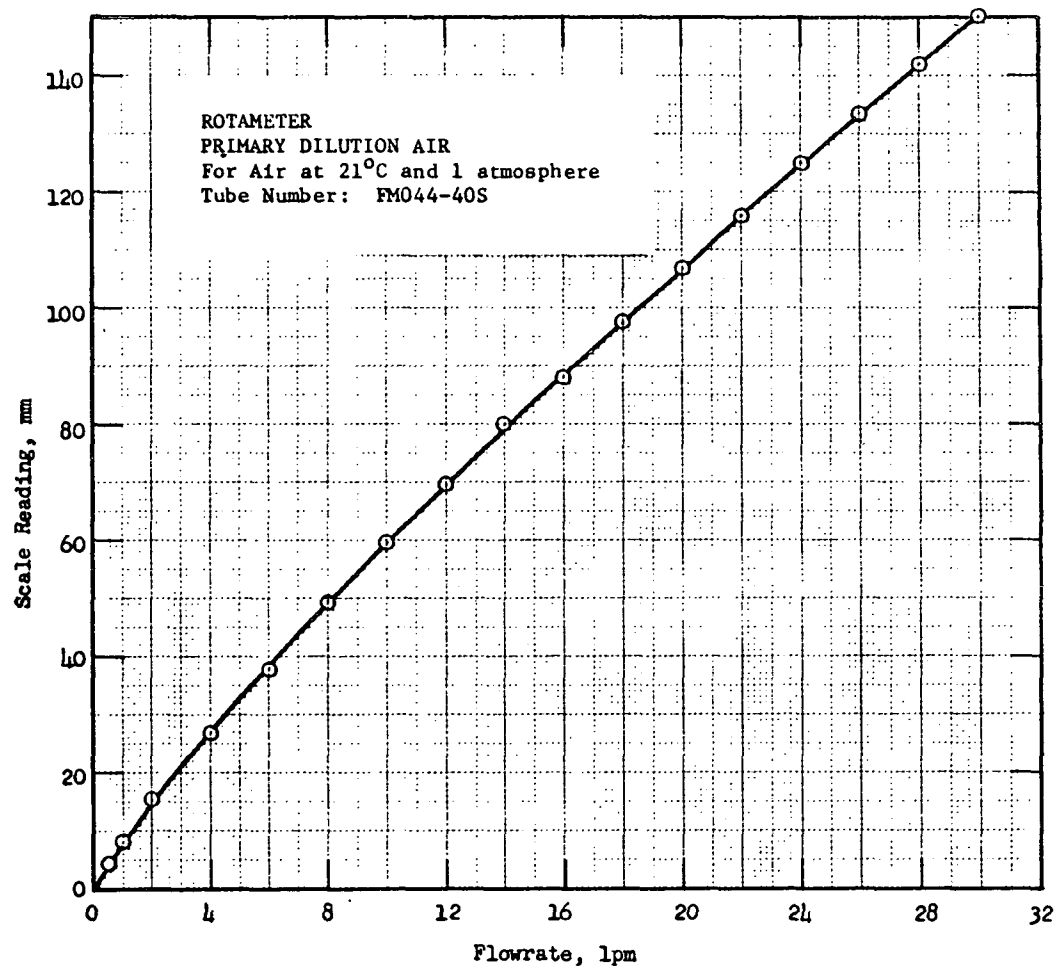

Figure B4. Calibration curve of rotameter for primary dilution flow.

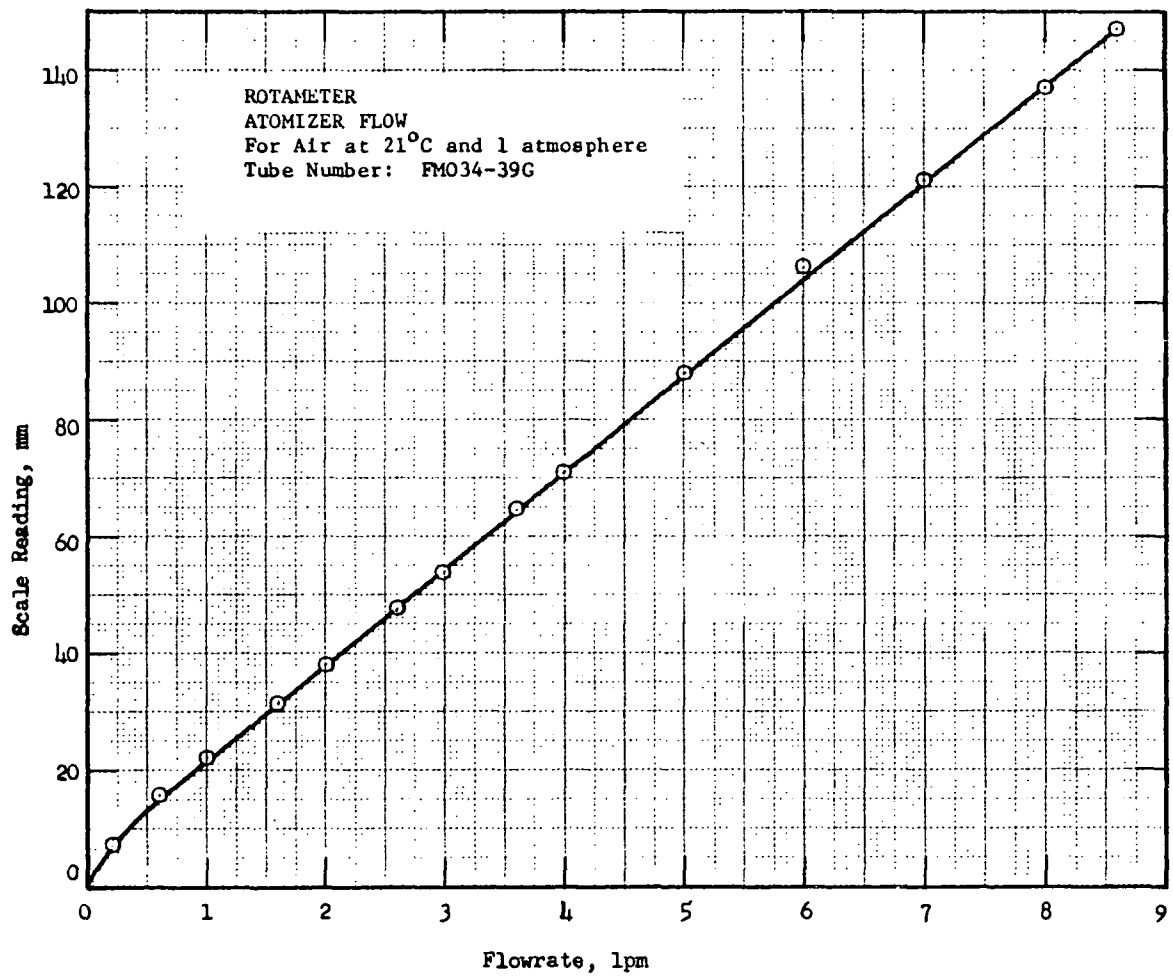

Figure B5. Calibration curve of rotameter for atomizer flow.

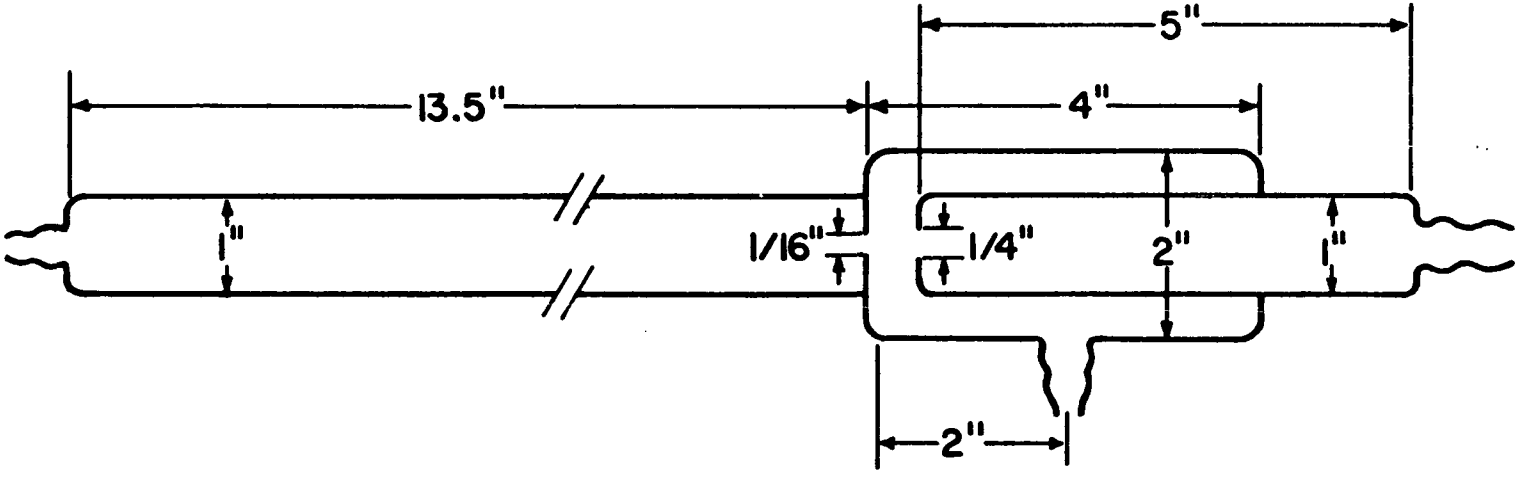

Figure B6. Dimensions of pyrex evaporator tube and mixing nozzle.

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/2-78-104	2.	3. RECIPIENT'S ACCESSION NO.
4. TITLE AND SUBTITLE GENERATION OF SULFURIC ACID AEROSOLS FOR HEALTH EFFECT STUDIES		5. REPORT DATE June 1978
		6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) B. Y. H. Liu and J. Levi		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Particle Technology Laboratory, Mechanical Engineering Department, University of Minnesota, Minneapolis, MN 55455		10. PROGRAM ELEMENT NO. 1AA601 CA-24 (FY-78)
		11. CONTRACT/GRANT NO. R-801301
12. SPONSORING AGENCY NAME AND ADDRESS Environmental Sciences Research Laboratory - RTP, NC, Office of Research and Development, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711		13. TYPE OF REPORT AND PERIOD COVERED Interim 9/76-3/78
		14. SPONSORING AGENCY CODE EPA/600/09
15. SUPPLEMENTARY NOTES		

16. ABSTRACT

A generator has been developed and constructed for producing sulfuric acid aerosols at 330 liters per minute to an animal exposure chamber of 330 liters internal volume. Sulfuric acid concentrations in the chamber range from 0.13 to 1.3 mg/m^3. Geometrical mean volume diameters of the aerosol range from 0.04 to 0.15 μm, and the geometrical standard deviation of the aerosol is about 1.6.

The generator operates by atomizing a sulfuric acid solution to form a polydisperse spray. The droplets are then vaporized in a tube-furnace and the vapor injected into filtered air at room temperature to form a high concentration of small sulfuric acid particles.

The aerosol generating system has been evaluated by means of several techniques. Particle size distribution was measured by an Electrical Aerosol Analyzer. Four independent techniques were used to measure the aerosol concentration: an Electrical Aerosol Analyzer, a Quartz-Crystal Aerosol Mass Monitor, filter collection and weighing, and chemical analysis of collected particle samples. Good agreement was found.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
* Air pollution		13B
* Aerosols		07D
* Sulfuric acid		07B
* Aerosol generators		13D
* Development		

18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC	19. SECURITY CLASS *(This Report)* UNCLASSIFIED	21. NO. OF PAGES 68
	20. SECURITY CLASS *(This page)* UNCLASSIFIED	22. PRICE

EPA Form 2220-1 (9-73)