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CONTINUOUS MEASUREMENT OF
SULFUR IN SUBMICROMETRIC AEROSOLS

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ABSTRACT

A method is described for measuring continuously the total sulfur in submicrometric aerosols suspended in air containing sulfur dioxide. The aerocolloid is passed through a tube coated internally with lead dioxide. The gaseous sulfur dioxide diffuses to the surface of the tube and reacts irreversibly to form lead sulfate. The aerosol is not significantly removed in the tube. The total sulfur in the aerosol is determined by a hydrogen-air flame photometric detector.

A sulfur balance has been demonstrated for the sulfur dioxide-ozone-olefin reaction system, which produces aerosols containing sulfur.

CONTENTS

Abstract	iii
I Introduction	1
II Summary	3
III Conclusions	3
IV Recommendations	4
V Experimental	5
VI Results and Discussion	7
References	15

SECTION I

INTRODUCTION

For the study of sulfur dioxide reaction systems, the estimation of sulfur in aerosols, such as sulfuric acid droplets, may be made by taking the difference between the responses of a sulfur flame photometric detector (FPD) analyzer to filtered and unfiltered sample air (1). The filtered air yields only a response for sulfur dioxide, but the unfiltered air yields a response for sulfur dioxide plus aerosol sulfur. Presumably, the difference in responses is an estimate of the aerosol sulfur concentration. An appreciation of the difficulties encountered by employing this method can be gained by examining its application to the measurement of sulfuric acid in the aerosol phase in the presence of sulfur dioxide at concentrations likely to be encountered in power plant plumes and laboratory chamber experiments. For example, if the sulfur dioxide concentration is $2660 \mu\text{g}/\text{m}^3$ (1 ppm), and the sulfate concentration is $150 \mu\text{g}/\text{m}^3$ ($100 \mu\text{g}/\text{m}^3$ or 0.038 ppm expressed as equivalent to sulfur dioxide), the difference in the linearized FPD responses between the unfiltered and filtered sample air would be about 3.7%. For most laboratory and atmospheric measurements, such a low signal-to-noise ratio is not acceptable. If a FPD sulfur analyzer is to be employed, the signal-to-noise ratio for measuring aerosol phase sulfur can be increased only by selectively decreasing the concentration of sulfur dioxide (and other gases present that contain sulfur).

The difference in diffusivities is a physical parameter that may be conveniently exploited in separating gases from aerosols with diameters greater than about $0.01 \mu\text{m}$. The diffusion coefficient of sulfur dioxide is $0.13 \text{ cm}^2/\text{sec}$ (2), whereas the diffusion coefficients of 0.01 to $1 \mu\text{m}$ diameter aerosols range from 5.2×10^{-4} to $2.7 \times 10^{-7} \text{ cm}^2/\text{sec}$. If a dilute mixture of sulfur dioxide and sulfuric acid aerosol flows laminarily through a tube whose wall is a perfect sink for sulfur dioxide, at the exit the concentration of each species (gases and aerosols) being depleted by diffusion to the wall is given by the Gormley-Kennedy (3) equation:

$$C_i = C_{oi} \{0.819 \exp(-3.657 M_i) + 0.097 \exp(-22.3 M_i) + 0.033 \exp(-57 M_i)\}$$

where i = the diffusing species

C_i = the exiting concentration

C_{oi} = the entering concentration

$M_i = \pi D_i L/Q$

D_i = the diffusion coefficient of species i

L = the length of the tube

Q = the volume flow rate

The use of a "diffusion denuder" for selectively removing sulfur dioxide in the presence of sulfuric acid has been mentioned previously by Crider et al (4), but operational parameters and performance were not reported. These workers showed that cupric ion intensifies the sulfur chemiluminescence. Fish and Durham (2) have shown that the removal of sulfur dioxide by a diffusion denuder coated with lead dioxide can be described by the Gormley-Kennedy equation.

SECTION II

SUMMARY

A sulfur dioxide "diffusion-denuder" was used to measure continuously the concentration of sulfur in the aerosol phase for the sulfur dioxide-ozone-propylene-water vapor reaction system.

The disappearance of sulfur dioxide was quantitatively matched by the appearance of sulfur in the aerosol phase.

SECTION III

CONCLUSIONS

I It appears that for the reaction conditions studied, the sulfur dioxide diffusion denuder permitted direct observation of aerosol sulfur concentration. For the three cases observed, the sum of the sulfur FPD response for sulfur dioxide concentration and the sulfur FPD response for the aerosol sulfur concentration was approximately constant ($\sigma \leq 3\%$) over the duration of the reaction period, demonstrating that a sulfur balance has been made. This behavior indicates that the depletion of sulfur dioxide occurred by conversion to aerosols, probably in the form of sulfuric acid.

SECTION IV

RECOMMENDATIONS

1. The sulfur dioxide "diffusion-denuder" should be used to measure submicron aerosol sulfur (sulfate) continuously in smog chamber experiments. Caution should be exercised in using this technique for aerosols that contain metal cations, which may modify the chemiluminescence in the FPD.
2. The sensitivity of the sulfur FPD ($\sim 10 \mu\text{g}/\text{m}^3$) needs to be improved in order to allow the sulfur dioxide "diffusion-denuder" technique to be used for continuous submicron aerosol sulfate concentration ($\sim 5 \mu\text{g}/\text{m}^3$) measurements in urban atmospheres.
3. Development work should begin to develop techniques for using "diffusion-denuders" to remove reactive gases (sulfur dioxide, ammonia, ozone, nitrogen dioxide, hydrocarbons, etc.) before they contact filters in aerosol samplers. The "diffusion-denuder" technique offers a means of reducing to an insignificant level gaseous chemical reactions with the filter sample.

SECTION V

EXPERIMENTAL

For this study, diffusion denuders were constructed from tubes 8 mm in diameter and 20 cm long. The inside wall of a diffusion denuder was made a perfect sink for sulfur dioxide by coating it with lead dioxide. The lead dioxide coating was applied by introducing a thick slurry of lead dioxide mixed with isopropyl alcohol into the tube. The tube was held horizontally and rotated about its axis, and warm air was passed through the tube until the lead dioxide coating was dry. The lead dioxide coating may also be prepared as described by Durham *et al* (5).

In sampling the air mixture given as an example in the Introduction, for which $[SO_2] = 2660 \mu\text{g}/\text{m}^3$ and $[S_a] = 100 \mu\text{g}/\text{m}^3$ (expressed as equivalent to SO_2), the diffusion denuder at a flow rate of $3.33 \text{ cm}^3/\text{sec}$ will reduce $[SO_2]$ to $0.24 \mu\text{g}/\text{m}^3$. If the size of the aerosol is between $0.01 \mu\text{m}$ and $1 \mu\text{m}$, the decrease in $[S_a]$ by diffusion to the wall in the denuder is on the order of 2% or less. The ratio $[S_a]/[SO_2]$ at the entrance of the diffusion denuder is 0.038, but is 410 at the exit. For this set of conditions, the ratio has been increased by a factor of about 10^4 , mainly by a reduction in the sulfur dioxide concentration. Aerosol smaller than $0.01 \mu\text{m}$ may be depleted by diffusion to the tube wall, and aerosol larger than $1 \mu\text{m}$ may be depleted by sedimentation and impaction.

The dark gas phase reaction of propylene, ozone and sulfur dioxide to produce aerosol was employed in an attempt to obtain a sulfur balance for reactants and products. The experimental system has been described in detail by McNelis (6). The reaction took place in a 400-liter bag constructed from Dupont "Tedlar" PVF film. The surface-to-volume ratio was approximately 7.8 m^{-1} . The "Tedlar" bag was covered with an aluminized polyester bag, which served as an optical filter to prevent ultraviolet radiation from entering the reactor. During the experiments, continuous measurements were made of the ozone concentration. Propylene concentration measurements were made approximately at 10-minute intervals. The sulfur dioxide concentration measurement was made continuously with a sulfur FPD analyzer that had a Teflon filter (pore size: $0.45 \mu\text{m}$) inserted in its Teflon sample inlet line. The production of submicron aerosol containing sulfur (S_a) was monitored continuously by using a sulfur FPD analyzer that had only a diffusion-denuder tube inserted in its sample inlet line. The sample line with diffusion-denuder tube was attached to the bottom of the bag and operated in the vertical position. The sulfur analyzer was modified such that the exit line from the diffusion-denuder was connected directly to the air inlet of the hydrogen flame

burner of the flame photometric detector. Bypassing the valves and rotometer in the air-flow control section of the analyzer is necessary because the loss of aerosol at these points would be significant. In order to make this direct connection, a 180 degree bend in the sampling line was required, which may introduce turbulence in the sampling line and result in aerosol deposition. However, this loss is not as great as that for the aerosol sample passing through the air-flow control section of the analyzer. The optimum configuration would have been to mount the sulfur analyzer above the reactor and aspirate the sample through a vertical line (containing the diffusion-denuder tube) with no bends. Laboratory space considerations precluded the use of such a configuration for this investigation. Aerosol size distributions were made during the reaction by using an electrical mobility analyzer. The commercially-available instruments used in these experiments are listed in Table I.

TABLE I. COMMERCIAL INSTRUMENTS USED IN THESE EXPERIMENTS.

<u>Parameter</u>	<u>Instruments</u>
Propylene	Tracer, Inc., Model MT150 Gas Chromatograph; Poropak Q column
Ozone	Meloy Laboratories, Inc., Model OA350 Ozone Analyzer
Sulfur dioxide	Meloy Laboratories, Inc., Model SA 185-2 Flame Photometric Detector Sulfur Analyzer (with Teflon particulate filter)
Sulfur in aerosol (S_a)	Meloy Laboratories, Inc., Model SA 185-2 Flame Photometric Detector Sulfur Analyzer (air sample line modified; see text)

SECTION VI

RESULTS AND DISCUSSION

The performance of the diffusion-denuder was tested for three different mixtures of ozone, propylene and sulfur dioxide. The relative humidity was 16% and the temperature was 31°C for these mixtures. The initial reactant concentrations for Run A were: $[\text{SO}_2] = 1700 \mu\text{g}/\text{m}^3$ (0.5 ppm), $[\text{C}_3\text{H}_6] = 8000 \mu\text{g}/\text{m}^3$ (4 ppm), and $[\text{O}_3] = 2000 \mu\text{g}/\text{m}^3$ (1 ppm). In Figure 1, the disappearance curves for the reactants and the appearance curve for aerosol sulfur $[\text{S}_a]$ are plotted. Although the aerosol sulfur is probably sulfuric acid, $[\text{S}_a]$ is plotted in the figures in gravimetric units equivalent to SO_2 . It can be seen in Figure 1 that the $[\text{SO}_2]$ depletion rate is approximately matched by an increase in $[\text{S}_a]$. Since the concentrations of SO_2 and S_a are in compatible units, the sum $[\text{SO}_2] + [\text{S}_a]$ should be constant if a sulfur balance has been made. For Run A, the initial sulfur dioxide concentration was $1700 \mu\text{g}/\text{m}^3$. During the 60 minutes of reaction that were monitored, the average of the sum of $[\text{SO}_2] + [\text{S}_a]$ was $1670 \mu\text{g}/\text{m}^3$, with a standard deviation (σ) of 2%.

Particle size distributions were made during the reaction period and were converted to volume distributions, which are shown in Figure 2. These data indicate that generally the aerosol volume below $0.07 \mu\text{m}$ was not significant during the reaction period, especially after the first 7 minutes. Size distributions were not obtained for diameters greater than $1 \mu\text{m}$; thus, it is not known what the volume fraction was that had diameter greater than $1 \mu\text{m}$. From the small variation ($\sigma = 2\%$) of the sum of the sulfur dioxide and aerosol sulfur concentrations during the reaction period, it appears that loss of aerosol sulfur in the sampling line was small. Most likely, the fractional aerosol volume with diameter greater than about $2 \mu\text{m}$ was insignificant. The small variation in $[\text{SO}_2] + [\text{S}_a]$ could reasonably be due to deficiencies in the performance characteristics of the sulfur FPD, such as a 95% response time of about 10 minutes to a change of a factor of 10 in the sulfur concentration.

The initial reactant concentrations for Run B were: $[\text{SO}_2] = 1660 \mu\text{g}/\text{m}^3$; $[\text{O}_3] = 3000 \mu\text{g}/\text{m}^3$; and $[\text{C}_3\text{H}_6] = 8200 \mu\text{g}/\text{m}^3$. The decrease in reactant concentrations and the appearance of the reactant product S_a for Run B are plotted in Figure 3. This reaction mixture had the same concentration of sulfur dioxide as for Run A, but had about 50% more ozone and 30% more propylene. Inadvertently, the concentration of S_a was not recorded for the first 24 minutes of the reaction, but for the periods for which data were recorded, the behavior exhibited

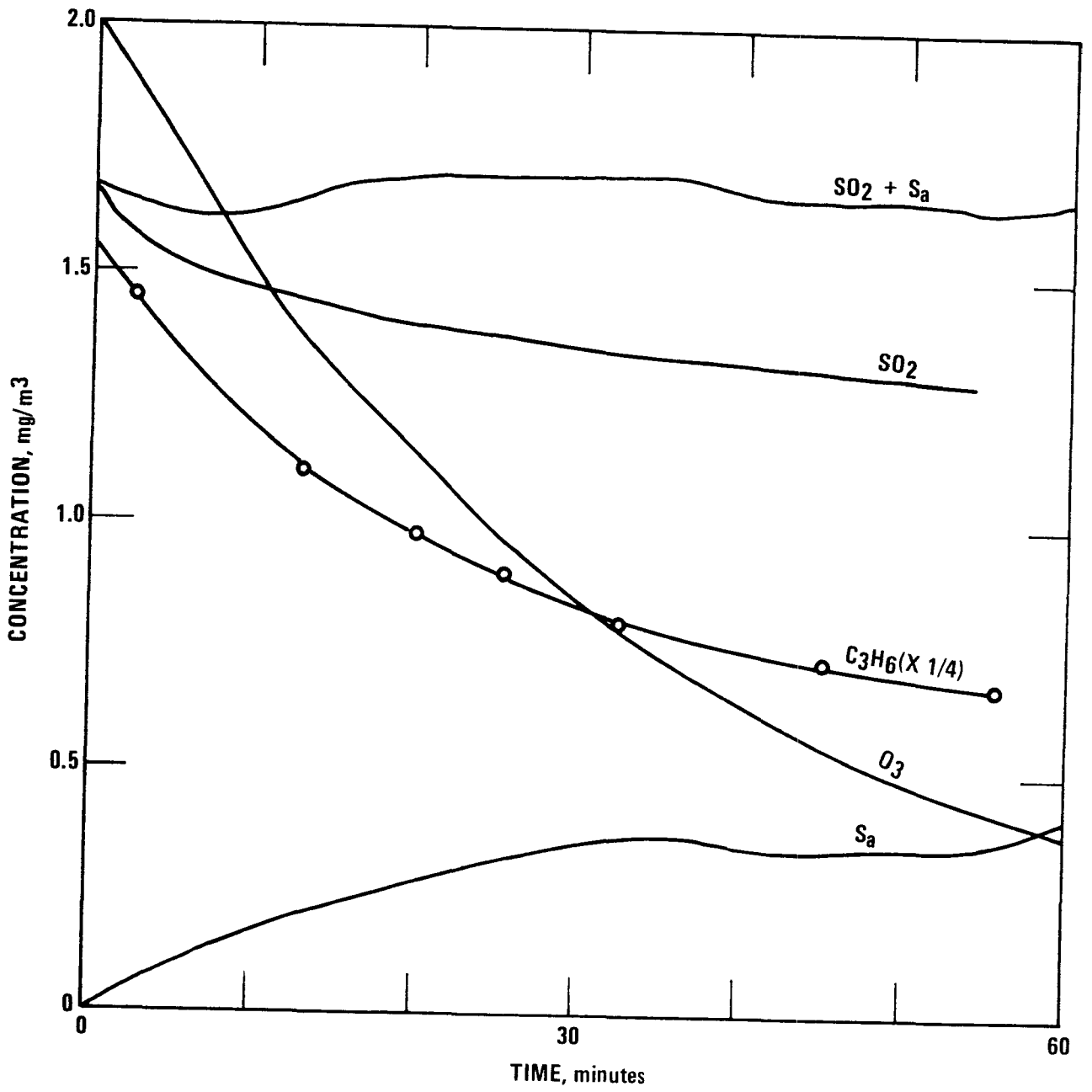


Figure 1. Variation of concentration with time for Run A.

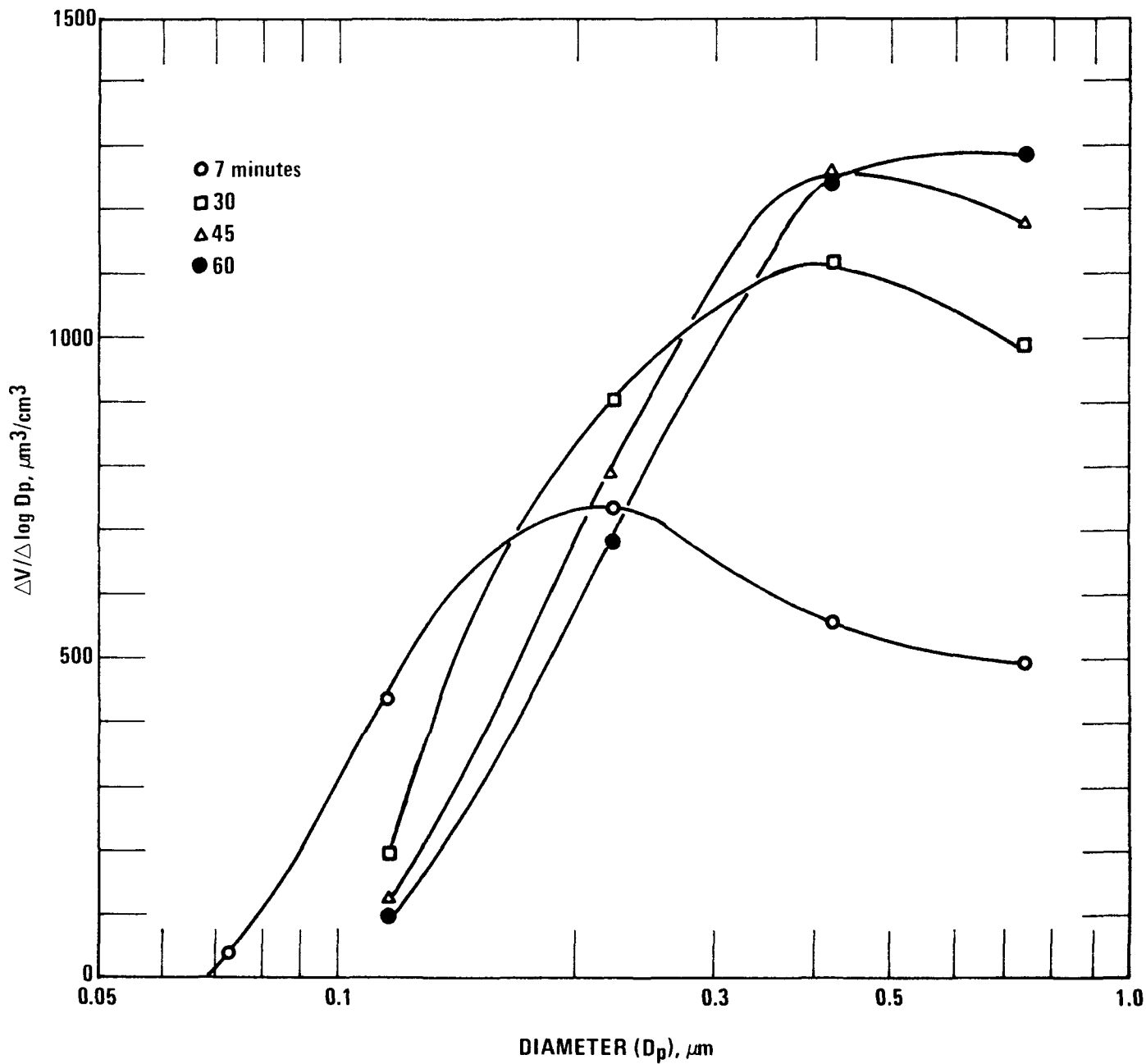


Figure 2. Development of the volume distribution with time for Run A.

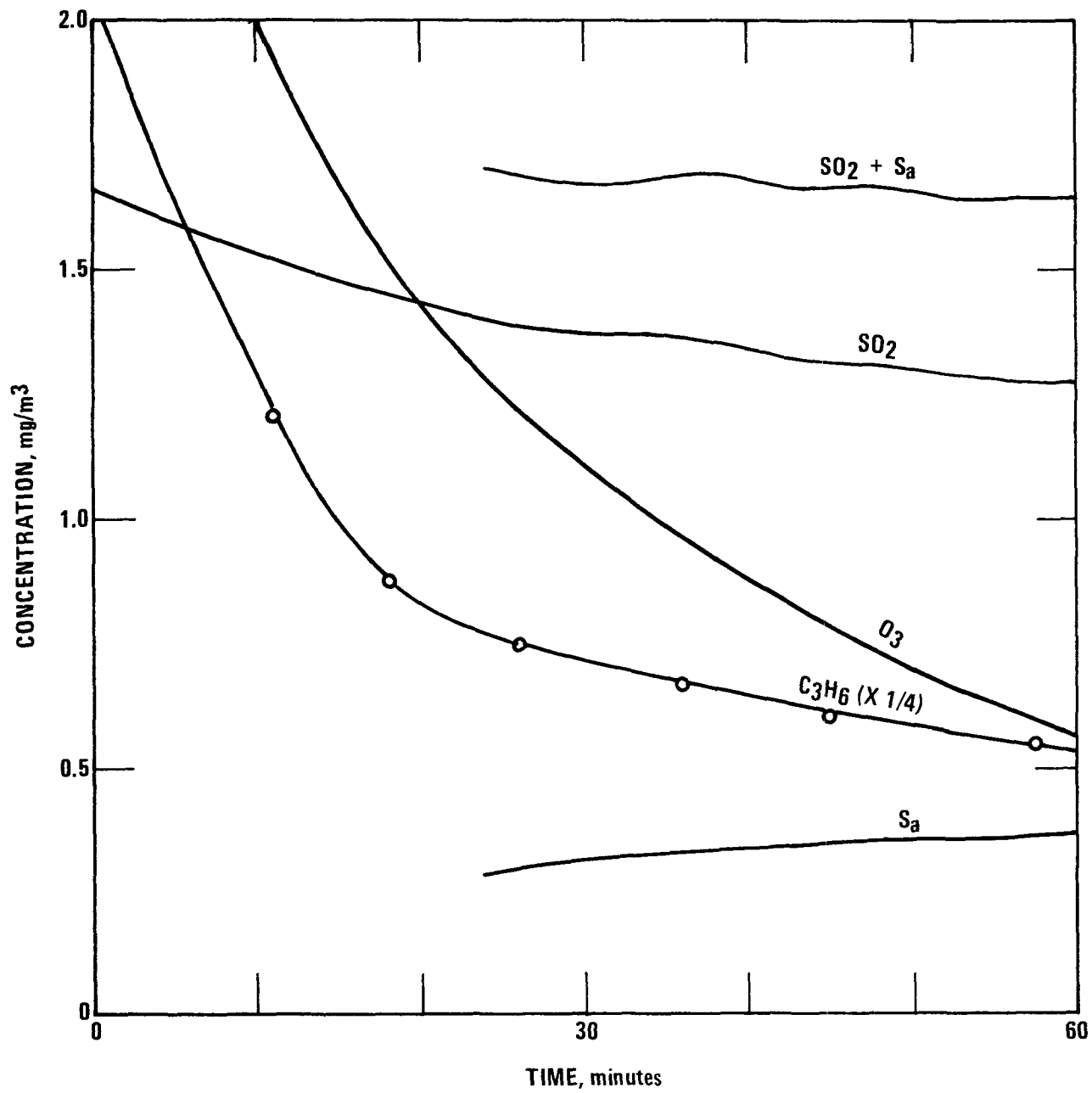


Figure 3. Variation of concentration with time for Run B.

by the reactants and aerosol sulfur product is similar to that of Run A. The aerosol volume distribution, shown in Figure 4, is not as wide as that of Run A. A mode exists at about 0.4 μm , and it appears that most of the aerosol volume was below 1 μm . For Run C, the initial reactant concentrations were: $[\text{SO}_2] = 830 \mu\text{g}/\text{m}^3$; $[\text{O}_3] = 2000 \mu\text{g}/\text{m}^3$; and $[\text{C}_3\text{H}_6] = 5280 \mu\text{g}/\text{m}^3$. This mixture had the same initial concentration of ozone as Run A, but 50% less sulfur dioxide and 20% less propylene. The behavior exhibited by the reactants and aerosol sulfur product S_a for Run C is shown in Figure 5 and is also similar to that of Run A. The aerosol volume distributions for Run C, shown in Figure 6, are shifted toward smaller sizes with respect to those of Run A. The distributions for Run C indicate that the aerosol volume is insignificant below 0.05 μm . After the reaction time of 30 minutes, a mode appeared at about 0.3 μm , and due to the small change in the sum $[\text{SO}_2] + [S_a]$, it is unlikely that significant aerosol volume existed for aerosol with diameters greater than several micrometers. For Runs B and C, the consumption of sulfur dioxide is matched by the appearance of aerosol sulfur, similar to the observation for Run A, within the expected performance limitations of the sulfur FPD. The sums $[\text{SO}_2] + [S_a]$ for Runs B and C are plotted in Figures 3 and 5, respectively. The standard deviation of $[\text{SO}_2] + [S_a]$ for Run B is 2% and for Run C is 3%. The initial values for the sulfur dioxide concentration, average values for $[\text{SO}_2] + [S_a]$, and standard deviations for the three Runs are summarized in Table II.

TABLE II. COMPARISON OF AVERAGE VALUE OF $[\text{SO}_2] + [S_a]$ WITH INITIAL VALUE OF $[\text{SO}_2]$.

	<u>Initial $[\text{SO}_2]$, $\mu\text{g}/\text{m}^3$</u>	<u>Average of $[\text{SO}_2] + [S_a]$</u>	<u>Standard Deviation, %</u>
Run A	1660	1670	2
Run B	1660	1670	2
Run C	830	810	3

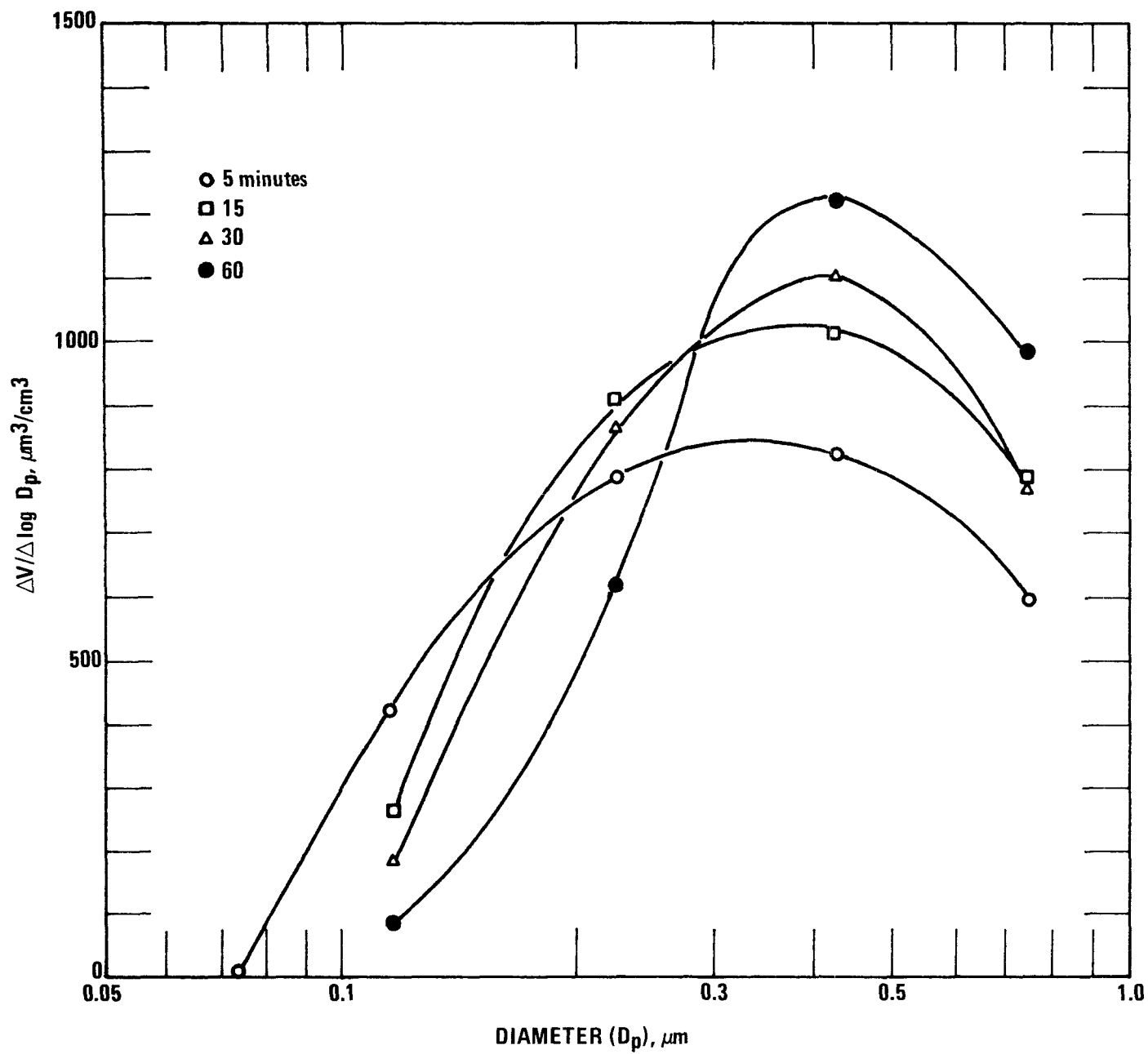


Figure 4. Development of the volume distribution with time for Run B.

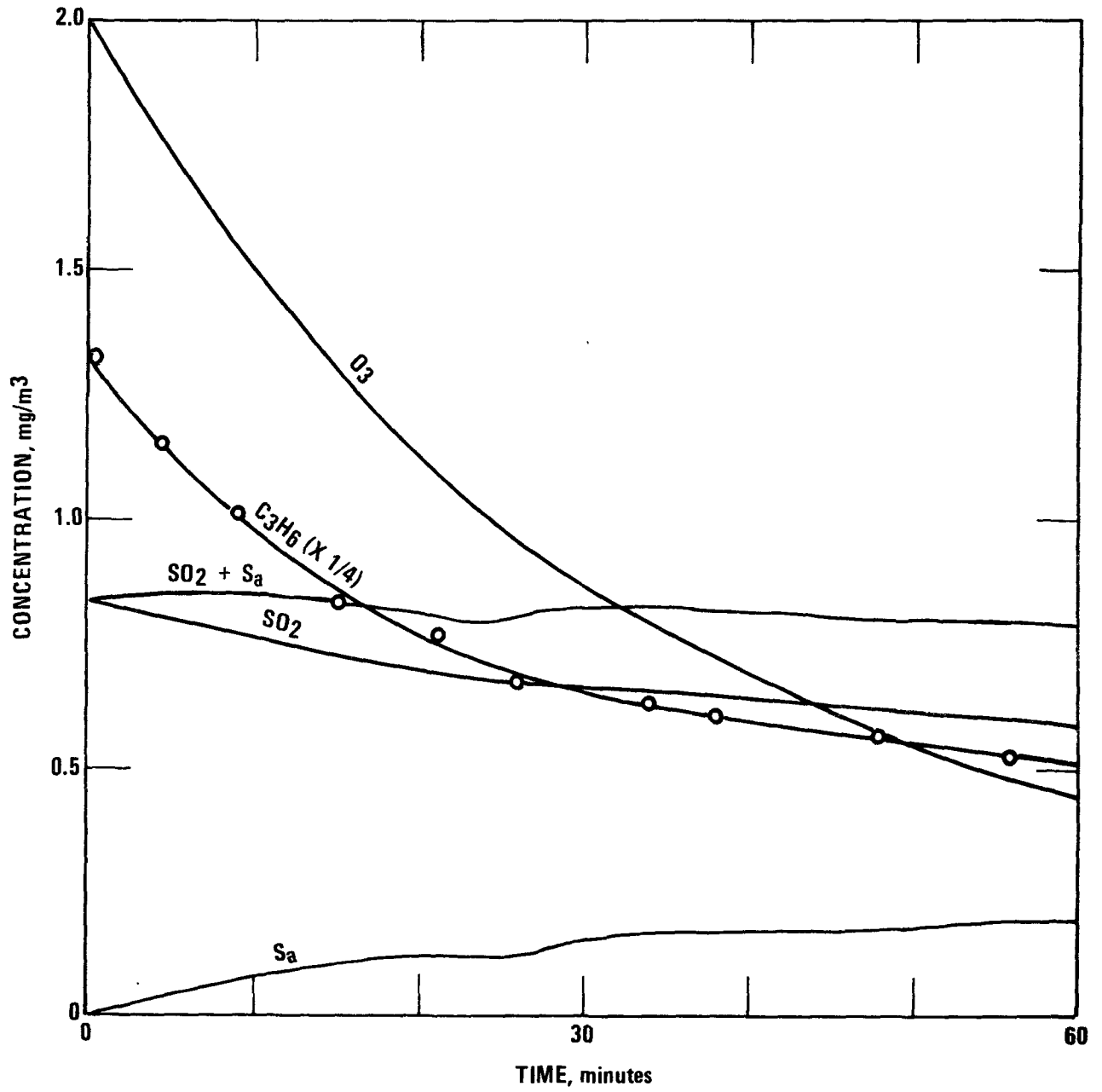


Figure 5. Variation of concentration with time for Run C.

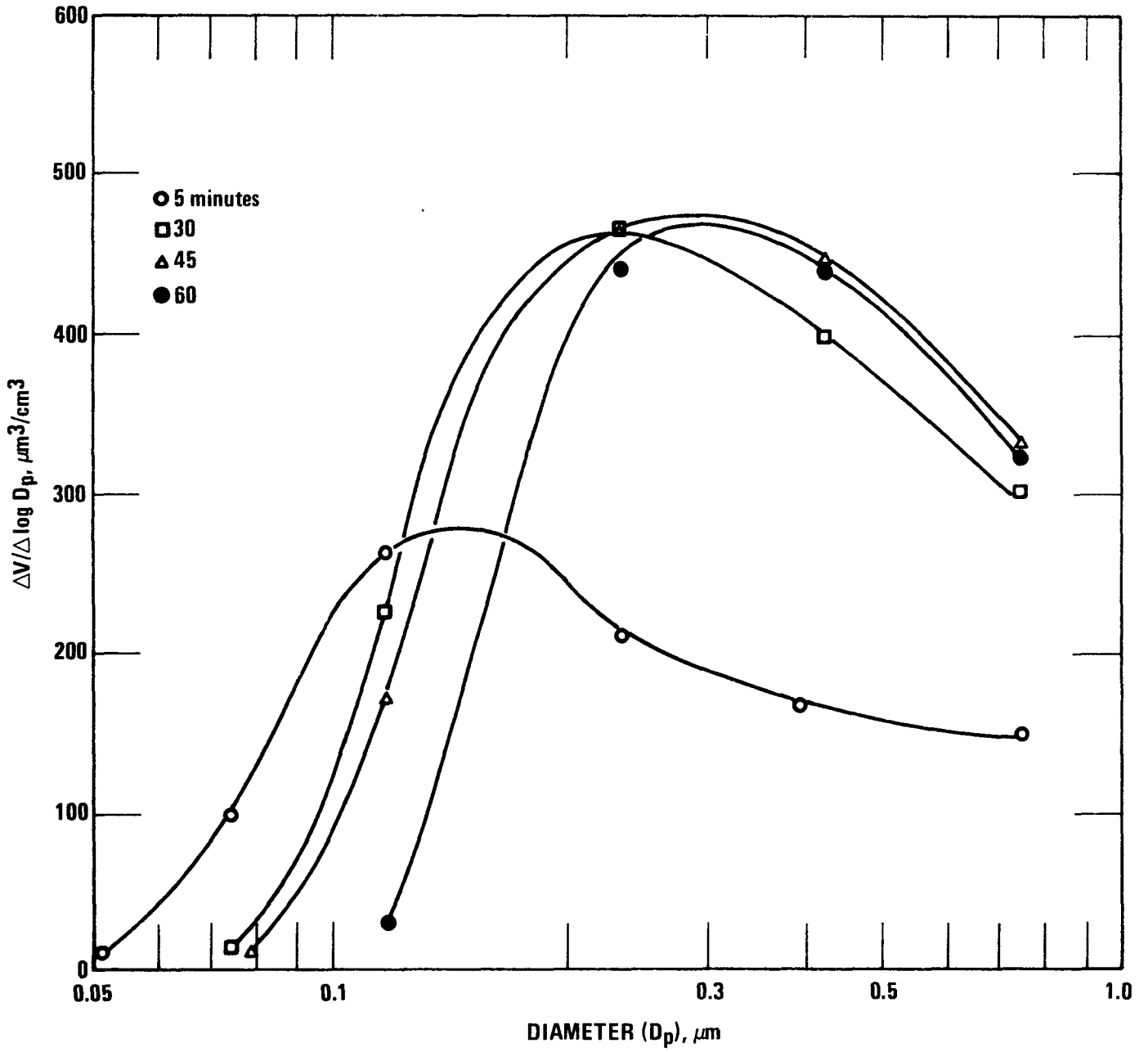


Figure 6. Development of the volume distribution with time for Run C.

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