NASA CONTRACTOR REPORT

NASA CR-2079

PROJECT FOG DROPS

Part II: Laboratory Investigations

by W. C. Kocmond, E. J. Mack, U. Katz, and R. J. Pilie

Prepared by
CORNELL AERONAUTICAL LABORATORY
Buffalo, N.Y. 14221
for George C. Marshall Space Flight Center

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C. • JULY 1972

1. Report No. CR 2079	2. Government Accession No.	3. Recipient's Catalog No.
4. Title and Subtitle: PROJECT FOG DROPS PART II:* LABORATORY INVESTIGATIONS		5. Report Date: July 1972 6. Performing Organization Code: 126-61-13-01-10
7. Author(s): W. C. Kocmond, E. J. Mack, U. Katz, and R. J. Pilie		8. Performing Organization Report No.: RM-3005-M-6 10. Work Unit No.
9. Performing Organization Name and Address: Cornell Aeronautical Laboratory, Buffalo, New York 14221		11. Contract or Grant No.: NASW-2126 13. Type of Report and Period Covered: CONTRACTOR REPORT
12. Sponsoring Agency Name and Address: NASA, Washington, D. C.		14. Sponsoring Agency Code

15. Supplementary Notes

* Part I is PROJECT FOG DROPS, Investigations of Warm Fog Properties

16. Abstract

Photochemical reactions were produced in a 600 m^3 cloud chamber by irradiating the chamber air with a 5000 watt Hg arc source. Measurements of the total nucleus concentration and cloud condensation nuclei (CCN) were acquired for several conditions representing both high normal and severe pollution levels for the Los Angeles Basin as well as clean filtered air. The data show that in filtered air (free of particles) there is a large photochemically induced increase in the total particle content within a few minutes after starting the lamp. The concentration of CCN, however, remains near zero, until sufficient coagulation and condensation occurs on the smaller Aitken particles. The addition of gaseous pollutants (SO , NO_x, CH) to filtered air results in large increases in the photochemical production of both the cloud and Aitken nucleus concentration. When unfiltered noonday country air containing appreciable numbers of nuclei was introduced into the chamber and exposed to the Hg arc source, no increase in particle concentration was observed. Mechanisms responsible for the observed behavior in particle concentration are discussed. In a series of separate laboratory experiments, fogs were generated under controlled, reproducible conditions in the cloud chamber and seeded with aerosols of various compounds which form monomolecular surface films at air-water interfaces. Visibility characteristics and droplet data were obtained for both seeded and control fogs. Cetyl alcohol stabilized fogs significantly by retarding droplet evaporation. This observation was substantiated by measurements of visibility, drop size, drop concentration, and the liquid water content of the fogs. Oleyl alcohol, a nonlinear molecule, formed fluid surface films on the droplets but did not retard evaporation or alter fog visibility.

The data suggest that droplet growth on treated nuclei can be retarded but that under the controlled conditions of these experiments, fog formation was not significantly altered by the chemical seeding. It is concluded that additional experiments designed to limit natural fog formation with evaporation retardants are not warranted.

17. Key Words (Suggested by Author(s))	18. Distribution Statement

19. Security Classif. (of this report)	20. Security Classif. (of this page)	21. No. of Pages	22. Price*
Unclassified	Unclassified	39	$3.00

* For sale by the National Technical Information Service, Springfield, Virginia 22151

TABLE OF CONTENTS

LIST OF FIGURES

INTRODUCTION

This portion of the final report encompasses two principal areas of research:

(1) a preliminary investigation of the photochemical production of cloud and Aitken nuclei; and

(2) a study of the influence of monomolecular surface films on laboratory fog formation and persistence. The latter study is a continuation of earlier experiments in which it was shown that evaporation retardants could have a substantial effect on fog behavior. In early tests, laboratory fogs were effectively stabilized by seeding with cetyl alcohol; however, it was not determined if natural cloud nuclei could be prevented from producing droplets and forming fog. Our most recent experiments suggest that droplet growth on treated nuclei can indeed be retarded but that under the controlled conditions of the laboratory, fog formation is not significantly altered. A complete summary of the investigation is presented in this report, together with recommendations relative to any further consideration of the concept for field use.

As a part of the photochemical aerosol study, we have briefly examined the effects of some common pollutants on laboratory fog behavior and studied the influence of particle concentration on fog droplet size. From previous studies of our own as well as numerous other investigators, it has been found that many forms of pollution contribute to the total nucleus concentration in the atmosphere. It is not clear, however, what net effect these changes have on the cloud nucleus population* or, more important, how they influence cloud and fog behavior. It is frequently argued that widespread increases in the cloud nucleus content of the atmosphere could lead to smaller drop

*Cloud nuclei represent a relatively small fraction of the total number of particles in the atmosphere and are defined as those nuclei which promote droplet growth at slight supersaturation characteristic of natural clouds and fog; i.e., less than 1% supersaturation.

sizes in clouds and greater colloidal stability. Under these conditions, coalescence of droplets would be limited and warm clouds, at least, would be reluctant to precipitate.

Our measurements of nuclei (Kocmond and Mack, 1972) upwind and downwind of Buffalo, New York have shown that significant increases over background levels of both the total nucleus concentration and of cloud nuclei occur immediately downwind of pollution sources and also that a secondary maximum in cloud nucleus concentration usually occurs about 10 to 15 miles farther downwind of the city. It is the secondary increase in cloud nucleus concentration that has prompted us to investigate some of the aspects of photochemical air pollution. Apparently, the interaction of gaseous constituents with water vapor in the atmosphere and photochemical reactions are primarily responsible for the observed secondary increase in cloud nuclei. Attempts in the field to relate these changes in cloud nucleus concentration to differences in cloud droplet size and concentration were not successful because of the limited data that were acquired. The far more controllable environment of the laboratory, however, is ideal for studying photochemical aerosol production and the influence of pollutants on laboratory fog behavior. Results of these initial studies are reported here.

TECHNICAL DISCUSSION

- The Influence of Particle Concentration on Fog Droplet Size

It is a widely-accepted fact that droplet sizes in clouds and fog bear an inverse relationship to the cloud nucleus concentration of the environment. Thus, clouds forming in clean maritime atmospheres with relatively few nuclei possess larger but fewer droplets than clouds and fogs which form in continental regions where the nucleus concentration is substantially greater. It is frequently argued that large increases in the number of cloud nuclei, due to photochemical reactions or atmospheric pollutants, could lead to an undesirable modification of natural clouds. It is of some importance, therefore, to understand how changes in the population of nuclei alter the characteristics of clouds and fog.

The influence of particle concentration on droplet sizes in laboratory fog can be easily demonstrated. A good example is provided by the data shown in Figure 1. In the figure, average drop-size distributions are shown for a variety of laboratory fogs formed in the 600 m^3 CAL cloud chamber. The manner in which laboratory fogs are produced has been described elsewhere (see e.g., Kocmond and Jiusto, 1968). Very briefly, however, the cloud chamber consists of a cylindrical chamber, 30 feet in diameter and 30 feet high, that can be pressurized or evacuated at controlled rates. Consequently, nearly adiabatic expansions can be produced and, under appropriate initial humidity conditions, fog forms.

The figure shows drop-size distributions for fogs formed in environments having widely different condensation nucleus concentrations. All fogs were produced in an identical manner; however, in each case prior to forming fog, the total nucleus concentration was adjusted to the desired value by filtering the chamber air through a series of absolute filters. Average particle concentrations of 400 cm^{-3}, 2500 cm^{-3}, 19,000 cm^{-3}, and 62,000 cm^{-3} were used in the experiments. The differences in fog characteristics are shown in the figure.

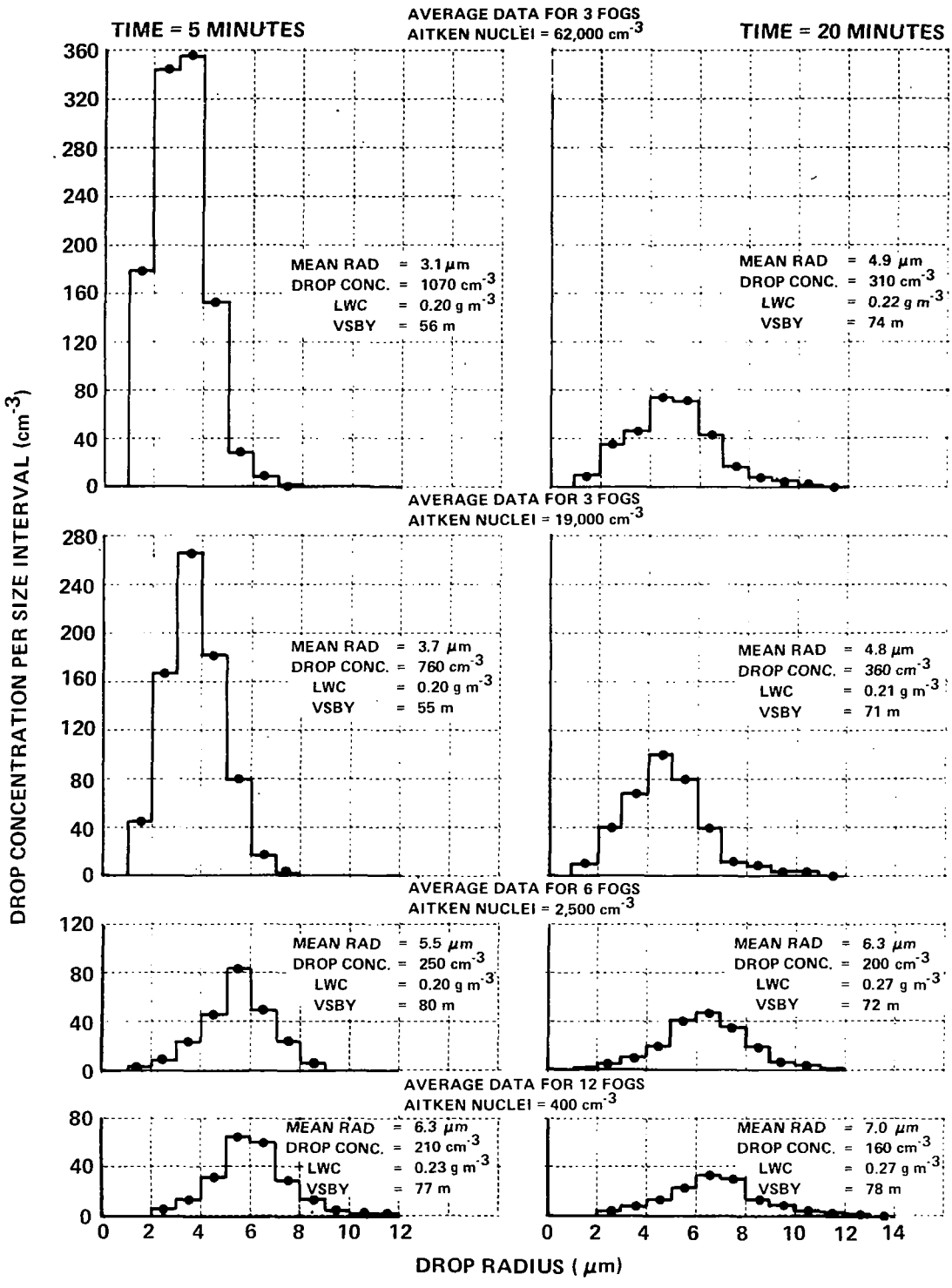

Figure 1 COMPARISON OF AVERAGE DROP-SIZE DISTRIBUTION IN LABORATORY FOG AT 5 MINUTES AND 20 MINUTES AFTER START OF FOG FORMATION IN ATMOSPHERES OF VARYING NUCLEI CONCENTRATIONS

Note that fogs formed in very clean air (400 nuclei cm^{-3}) contained the fewest droplets but largest sizes, a condition that would be expected to occur, for example, in a maritime environment. On the other hand, fogs formed in the polluted air (62,000 nuclei cm^{-3}--typical of urban areas) were found to possess much higher concentrations of droplets and they were smaller. In comparing fog characteristics at t = 5 minutes (i.e., 5 minutes after the start of the fog forming expansion), it is interesting to note that for the same fog liquid water content, average visibility in the polluted fogs was lower than in fogs formed in relatively clean air. As shown in the figure, the differences are also large at later times in the life cycle of the fogs, i.e., t = 20 minutes.

Other evidence of the effects of particle concentration on fog drop sizes can be found from the photomicrographs of droplet impressions shown in Figure 2. In this case, drop samples (gelatin replicas) were taken in two laboratory fogs formed in the identical manner but in environments containing a high and low concentration of cloud nuclei. Note that the impressions of fog droplets shown in the top of the figure, i.e., laboratory radiation or inland fog, are substantially smaller than those in the simulated coastal fog. Even though the same fog forming procedure was used in both instances, the much higher concentration of cloud nuclei in the radiation fog resulted in greater competition for available water and hence a fog composed of very small droplets.

- Effects of Pollution on Fog Behavior

Additional experiments were performed to determine the effect of common pollutants on fog microstructure. In these experiments, various amounts of automobile exhaust were introduced into the chamber prior to forming fog. The purpose of these tests was to determine if increased particulate loading of the atmosphere would result in fogs of lower visibility and greater resistivity to seeding. Results of three experiments in which fogs were seeded with 5 grams of carefully-sized NaCl nuclei are shown in Figure 3. The figure shows traces of visibility as a function of time and also time histories of the total particle concentration during the experiments.

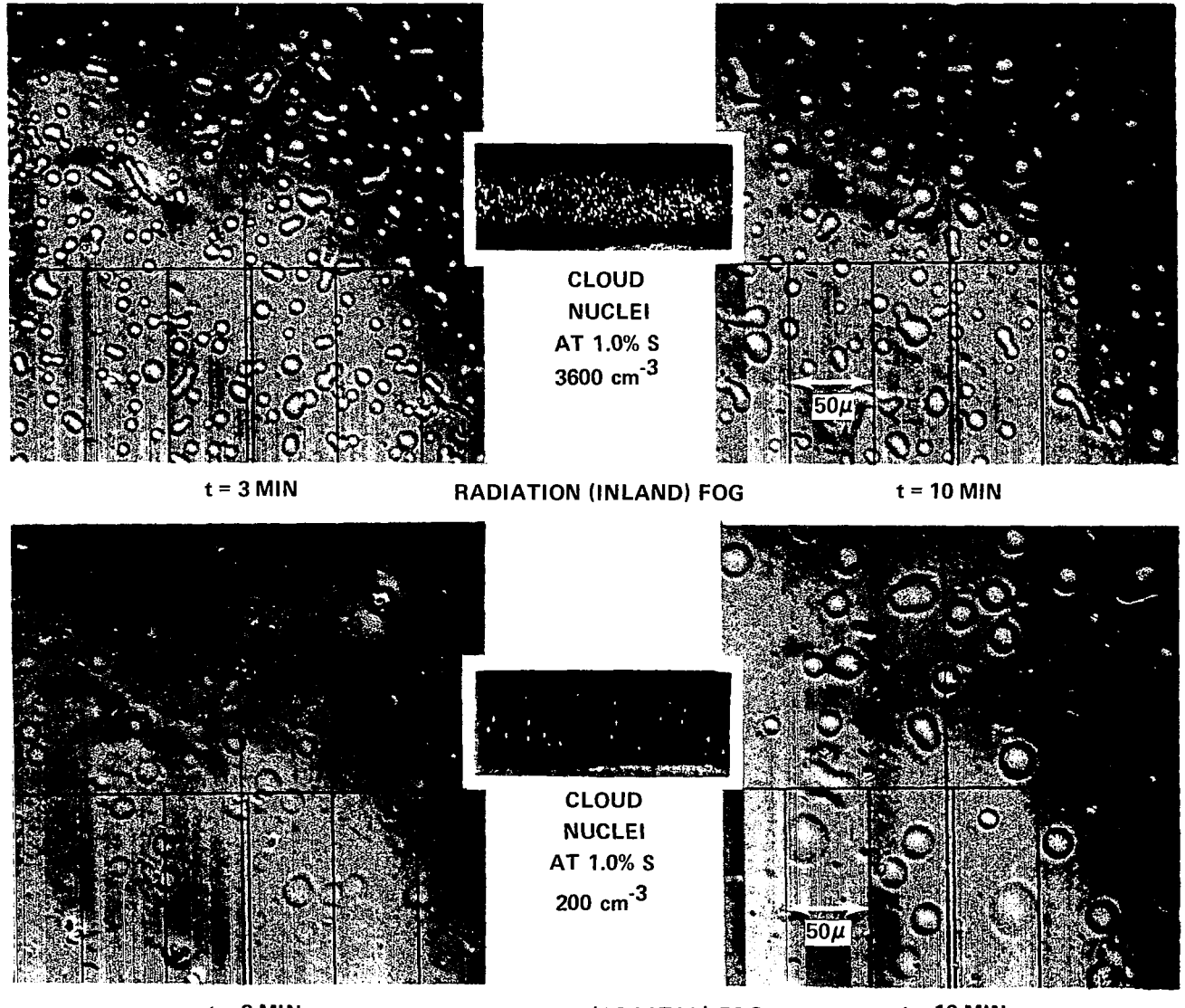

Figure 2 DROPLET REPLICAS FROM TWO FOG TYPES CAL FOG CHAMBER

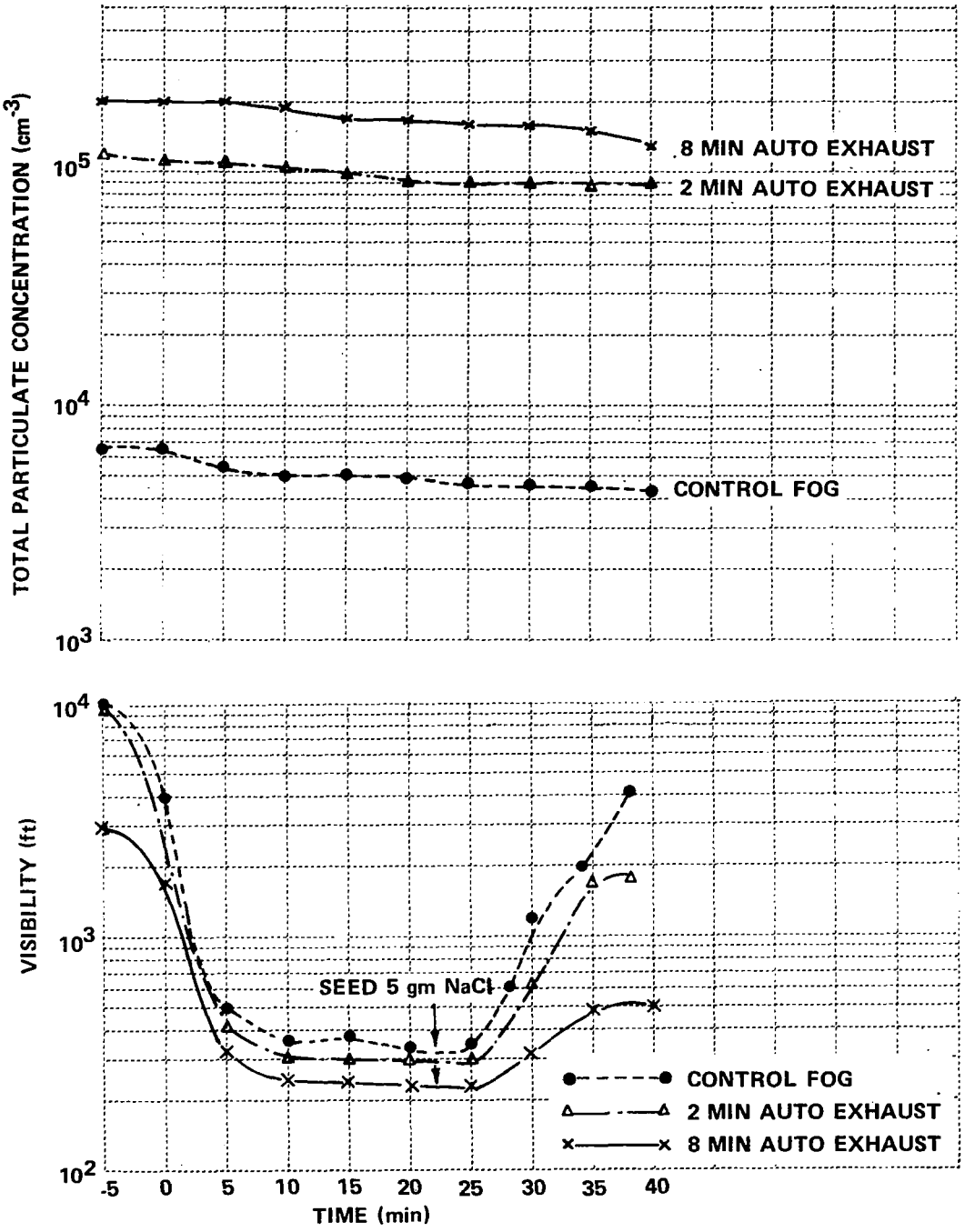

Figure 3 **TOTAL PARTICULATE CONTENT AND VISIBILITY AS FUNCTIONS OF TIME IN THREE FOG EXPERIMENTS**

After introducing nuclei into the chamber, fog was formed by producing a rather sudden expansion of the nearly-saturated chamber air. Fog density was maintained by initiating a slow secondary expansion 6 minutes after the start of the fog forming process. In the control experiment, fog was formed on the natural nuclei that exist in the rural atmosphere. Within 15 minutes after seeding, visibility improved from approximately 400 feet to 4000 feet. The polluted case behaved quite differently; after admitting auto exhaust into the chamber and forming fog, seeding produced only a modest increase in visibility. In the most polluted case (particle concentration of 5×10^5 nuclei cm^{-3}), visibility improved from 250 ft to only 500 feet after seeding.

It is not clear from these tests whether the greater stability of the polluted fogs was due to (1) the increased numbers of hygroscopic nuclei (admitted with the auto exhaust) which effectively compete for the available water vapor or (2) the presence of oil vapors which could have coated the existing fog droplets with a monomolecular surface film and retarded evaporation. It is likely that both mechanisms were responsible for the observed results; but in order to define the dominant influence, additional tests will be required.

These results suggest that natural fogs formed in environments heavily polluted with automobile exhaust are likely to be stable and difficult to modify. The implication is that warm fog modification schemes employing hygroscopic materials may be impractical at airports in the vicinity of large cities. Additional laboratory experiments designed to test the consequences of various levels and types of pollution on fog modification are recommended.

- Photochemical Aerosol Experiments

In view of the demonstrated effects of pollution on laboratory fog behavior and the importance of photochemical reactions in producing particulates and smog, there is a need to know more about the mechanisms involved in the photochemical production of aerosols. Numerous investigators have performed studies of the photochemical aspects of air pollution. Notable reviews of the literature have been made by Wilson et al. (1969), Bufalini (1971), and Altschuler and Bufalini (1971) who have published results

from significant previous investigations. To date, however, most of the research has concentrated on the chemistry of the reactions with lesser concern for the formation and growth of the aerosols. In a typical experiment, individual pollutants are introduced into a reaction vessel of some type and irradiated with light of the appropriate wavelengths. Irradiation experiments are conducted under either dynamic or static conditions. In the former case, the reactant mixture is continuously introduced into the chamber, while the reacting mixture is removed at an equivalent flow rate. In static experiments, such as the ones reported here, a specified mixture of reactants is introduced into the chamber and irradiated with simulated sunlight. Measurements of aerosol production are normally monitored with such devices as light scattering photometers, aerosol spectrometers, integrating nephelometers, or total condensation nucleus counters. There are no known instances where a thermal diffusion cloud chamber has been used as a sensitive indicator of the conversion of gaseous constituents into photochemical aerosols.

In the present study, measurements of both the total nucleus concentration (Aitken nuclei) and of cloud and haze nuclei were made in order to study the relative activity of the aerosols in terms of contributing to actual cloud or fog formation. The GE small particle counter and the CAL thermal diffusion chamber were used for making these measurements. The thermal diffusion chamber is described in Appendix A. By observing the concentration of particles which promote droplet growth at slight supersaturations and comparing these data with the total nuclei concentration, one can deduce a considerable amount of information in terms of the evolution of particle sizes in photochemical aerosols.

Most photochemical and photosensitized reactions in the atmosphere are considered as originating from photons having wavelengths between 3000 and 4000 Å. The shorter wavelength cutoff results from the absorption characteristics of the upper atmosphere (ozone in particular) and the longer wavelength cutoff is due to minimum energy requirements for dissociating typical atmospheric molecules. For our preliminary experiments, we installed an intense mercury arc light source (5000 watts) in the large

aerosol chamber to study and control most variables of photochemically-induced aerosols. In the experiments, the 3000 Å cutoff was produced by a pyrex filter around the lamp.

Results of one experiment are shown in Figure 4. In this experiment, air within the chamber was first filtered until the total particle content was less than 200 cm^{-3}. (Normally, clean country air contains several thousand nuclei cm^{-3}.) Measurements of cloud nuclei at 3.0% and 1.0% supersaturation (S) indicated concentrations of less than 10 cm^{-3}. No attempt was made in these initial experiments to filter trace gaseous constituents out of the atmosphere.

After allowing conditions to equilibrate within the chamber, the Hg arc lamp was started; and, as expected, a large photochemically-induced increase in the number of Aitken nuclei was observed. The particle sizes were known to be very small (probably <0.01 μm) because no increase in cloud nuclei was observed for about 40 minutes after starting the lamp. Within 50 minutes, however, the coagulation rate of the small particles exceeded the production rate and the total nucleus concentration began to fall. As coagulation proceeded, larger, and hence more favorable, condensation nuclei were produced; and the number of particles active at 3.0% S began to increase. During the performance period of this experiment, the particles did not become large enough to cause an appreciable increase in the cloud nucleus count at 1.0% S. We suspect that such an increase would have occurred if the experiment had been prolonged.

Studies conducted by the University of Minnesota (Husar and Whitby, to be published) suggest that a smog chamber-produced aerosol goes through four periods of evolution:

(1) a brief and hard-to-detect period of homogeneous nucleation; it is during this period that the first observable increases are seen in the total nucleus concentration;

(2) a somewhat longer period of mixed homogeneous nucleation and condensation on existing particles; the number of particles increases during this period until a maximum concentration is achieved;

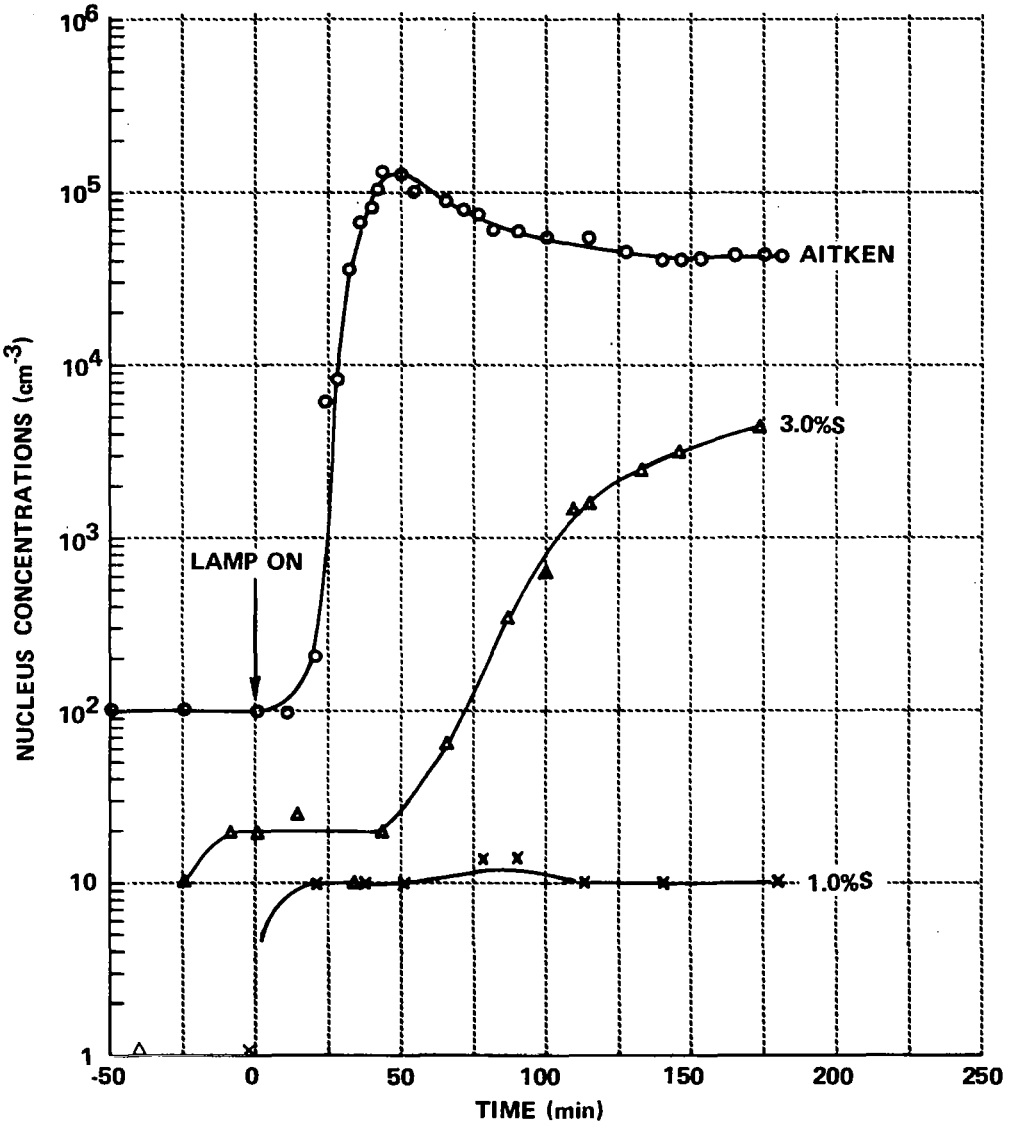

Figure 4 **PHOTOCHEMICAL PRODUCTION OF CONDENSATION NUCLEI IN FILTERED AIR**

(3) a longer period during which few or no new nuclei are produced, and the number declines primarily as a result of coagulation; during this period, the cloud nucleus concentration is at a peak because of the production, through coagulation, of larger particulates;

(4) a long period during which removal mechanisms such as sedimentation and inertia are dominant and account for a steady decrease in the large particle concentration.

In reality, there is considerable overlap in these phases; and it is, therefore, not always possible to determine the exact mechanisms responsible for the evolution of the aerosol size distribution. Our studies of aerosol behavior in the cloud chamber, however, are consistent with these phases of aerosol production and provide some additional basis for interpretation of smog chamber results.

In another experiment (Figure 5), the production of a photochemical aerosol was examined in a polluted atmosphere. Again, the air within the chamber was filtered until the total nucleus content was less than 200 cm^{-3}. A combination of gaseous constituents representing high normal pollution levels for the Los Angeles Basin were then introduced into the test chamber and thoroughly mixed. Note the substantial increase in both cloud (1%, 0.3%, and 0.1% supersaturation) and Aitken nuclei after introducing the gases into the chamber. A far more significant increase was noted, however, after irradiating the atmosphere with the Hg arc lamp.

For example, the total particle content increased by several orders of magnitude to approximately 1.2×10^6 nuclei cm^{-3} after starting the lamp. Similarly, the cloud nucleus concentration increased; more than 6×10^3 cloud nuclei cm^{-3} were observed after irradiating the polluted atmosphere where formerly there were less than 10 cm^{-3}. Coagulation of many of the smaller nuclei accounted for the steady decrease in the Aitken count and partly accounted for the slow rise in cloud nuclei. Additional condensation onto existing particles also accounted for the increase in the cloud nucleus concentration. It is interesting to note the large increase in the number of haze nuclei (particles that are about 1.0 μm diameter near 100% relative humidity) after introducing the pollutants and starting the lamp.

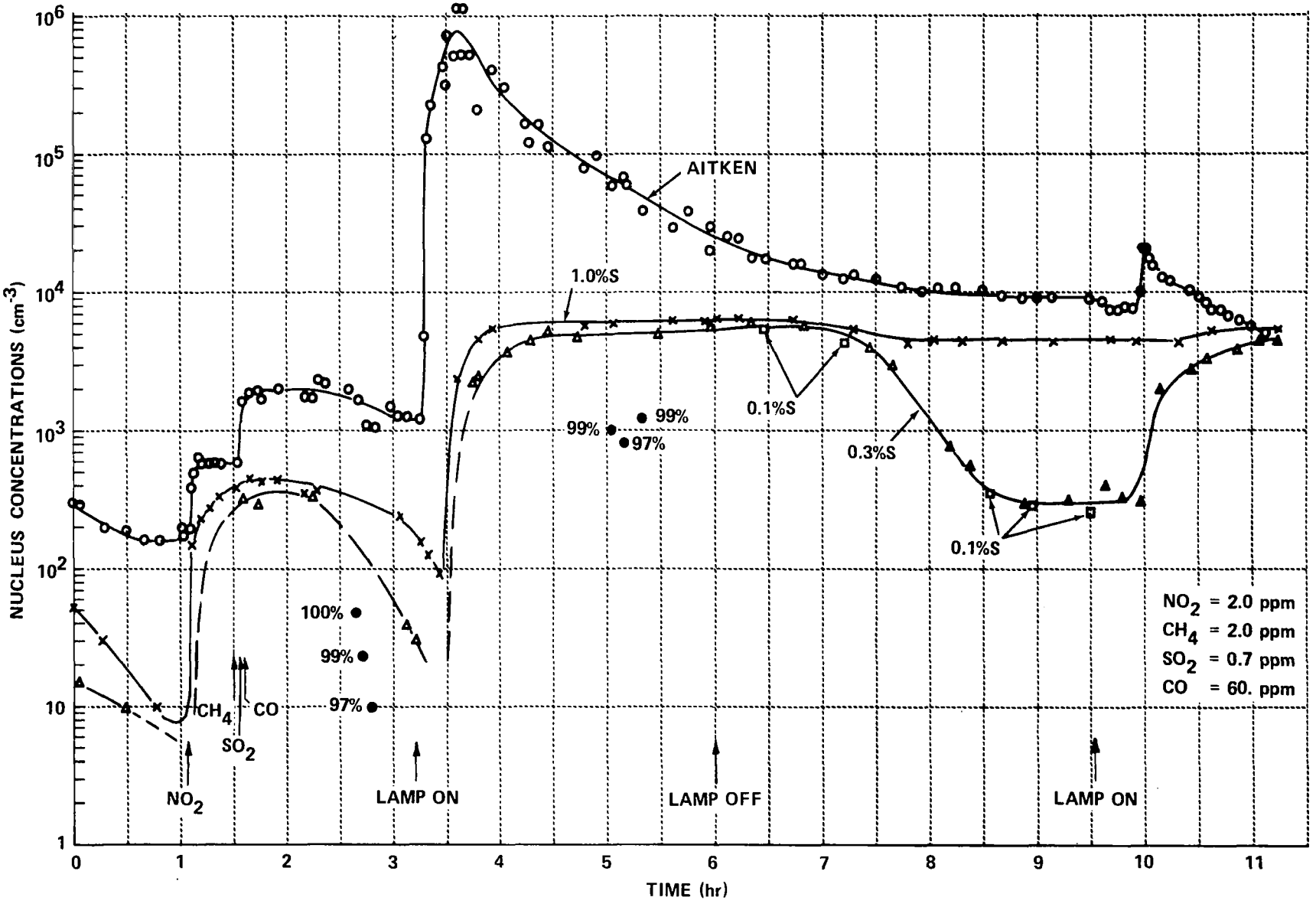

Figure 5 PHOTOCHEMICAL PRODUCTION OF CONDENSATION NUCLEI - HIGH NORMAL LOS ANGELES POLLUTION LEVELS IN PREFILTERED AIR

After the lamp was turned off, it was possible to observe the decay in particle concentration with time, including the sudden and rather rapid decrease in large particles. It is not yet known whether the changes in the cloud nucleus concentration at this stage were due to physical or surface chemical effects; we are presently considering the design of experiments to examine this problem. Part of the loss, of course, can be accounted for through removal mechanisms such as sedimentation and impaction on obstacles. When the lamp was again turned on, the total number of large particles that were generated approached the former high concentrations of several thousand cm^{-3}. It is obvious from this experiment that the effects of gaseous contaminants on photochemical particle production and coagulation were enormous, and, as an extension of this, that irradiation of pollutants in the real atmosphere can lead to sizable increases in the number of effective condensation nuclei.

We have also performed a third type of experiment in which no attempt was made to prefilter the air. It is of some importance to know, for example, if the vast number of natural nuclei in the atmosphere can serve as effective sinks and accommodate any additional photochemical reaction products that are produced. The results of one experiment designed to study that problem are shown in Figure 6.

In this experiment, outside country air containing normal levels of trace gaseous vapors and natural condensation nuclei was introduced directly into the chamber. The mercury arc was then started and particle concentration was monitored.

In this case, no increase in either cloud or Aitken nuclei was observed after starting the lamp. Evidently, there were sufficient natural nuclei in the sample to serve as sinks and promote coagulation of particles at a rate equal to the rate at which they were being produced, or to serve as nuclei on which the reaction products could condense. Hence, there continued to be a slow decrease in the total particle concentration after irradiating the air sample.

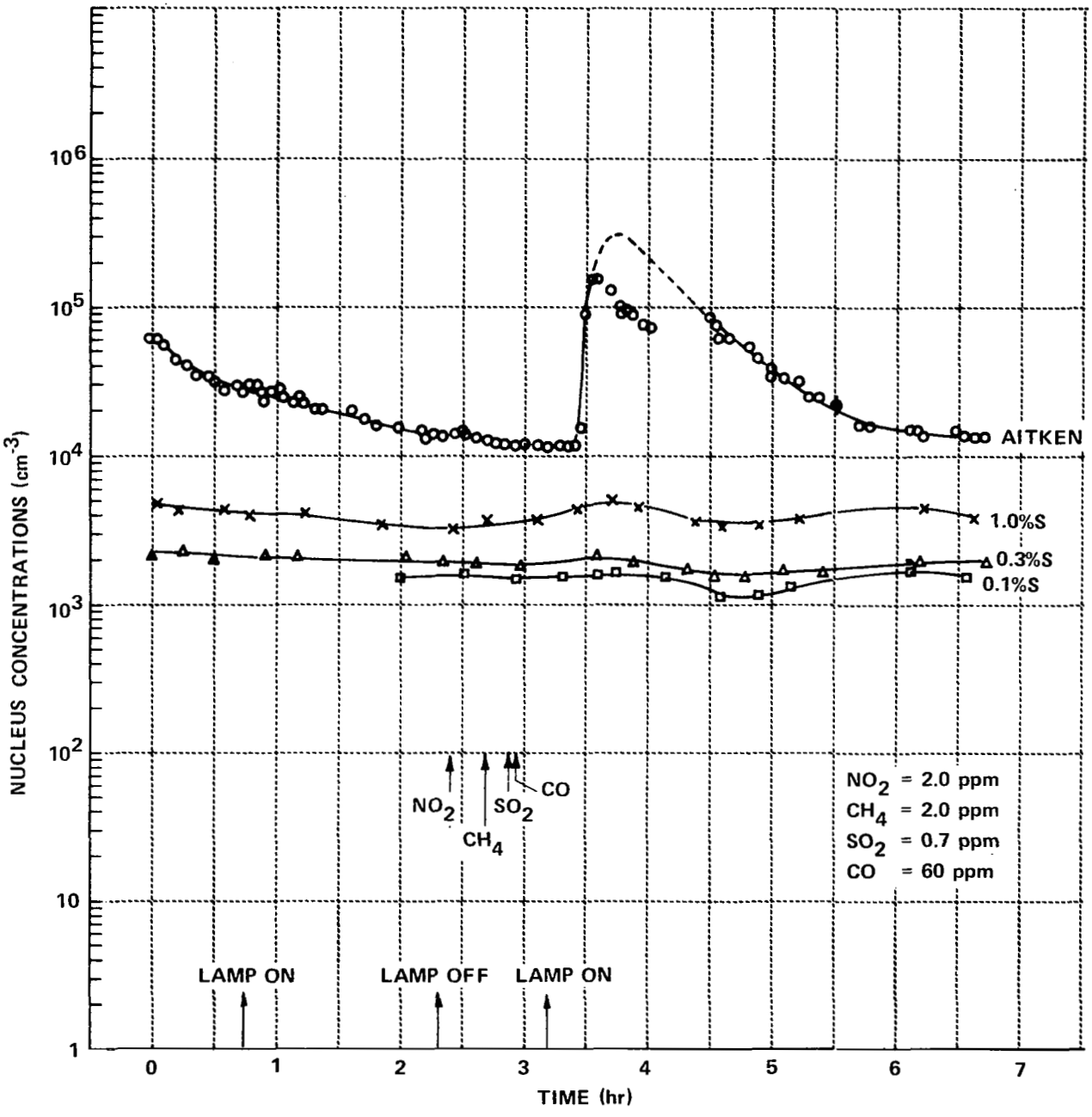

Figure 6 PHOTOCHEMICAL PRODUCTION OF CONDENSATION NUCLEI - HIGH NORMAL LOS ANGELES POLLUTION LEVELS IN UNFILTERED AIR

After turning the lamp off and introducing additional pollutants and then restarting the lamp, a marked increase in the Aitken count was observed. Only a slight increase in the cloud nucleus population was noted in this instance, probably because there were already several thousand cloud nuclei cm^{-3} acting as sinks at the time the lamp was started.

In reality, at cloud base, there are fewer nuclei present than was the case in this experiment and hence sudden increases in gaseous atmospheric pollutants can lead to very large increases in both cloud and Aitken nuclei. This was demonstrated in earlier experiments, typified by the results shown in Figure 4.

We expect to conduct additional experiments of this type during the coming year; in particular, we will examine the effects of photochemically-produced aerosols on the microphysical features (drop size, drop concentration, liquid water content) of laboratory fogs. Results of these experiments should improve our understanding of the fate of photochemical reaction products in atmospheric processes.

MODIFICATION OF LABORATORY FOG WITH MONOMOLECULAR SURFACE FILMS*

• Introduction

There has been considerable research into the influence of monomolecular films on droplet evaporation. Particularly relevant contributions have been made by Bradley (1955), Eisner et al. (1960), Jiusto (1964), Derjaguin et al. (1966), and Garrett (1971). These researchers have shown that a variety of film-forming materials with linear molecular configurations can effectively suppress droplet evaporation, although Garrett (1971) has suggested that some of the literature claims of retardation effectiveness can be ascribed to evaporation measurements of the film-forming organic material itself rather than that of the water droplet.

Jiusto (1964) went on to show, with the aid of a chemical gradient diffusion chamber, that droplet growth rates could be appreciably retarded by treatment with monolayers of straight-chain fatty alcohols. He considered the hypothesis that visibility in natural fogs might be improved if a percentage of the natural nuclei in the atmosphere could be deactivated prior to fog formation. The resultant fog might then consist of fewer, larger droplets with improved visibility characteristics. Initial laboratory experiments suggested that the deliquescence rate of sodium chloride crystals coated with octadecanol and hexadecanol could be retarded. Later, in additional laboratory tests, Pilié (1966) showed that condensation on individual sodium chloride nuclei could be retarded at high humidities but could not be prevented from occurring.

More recently, field experiments were performed in Australia (Bigg et al., 1969), which were designed to inhibit fog formation by seeding with long-chain alcohols. The results suggested that the alcohol smoke was

*This paper was submitted to the Journal of Geophysical Research in January 1972 for publication at a later date. Much of the work reported here was done in cooperation with William D. Garrett of the Naval Research Laboratory, Washington, D. C.

effective in preventing fog; however, the authors concluded that there was no certain evidence that the observed results would not have happened naturally.

It was the purpose of this laboratory investigation to determine the influence of evaporation retardants on fog formation and persistence. Comparative laboratory tests were also run in which fogs were seeded with a chemical whose molecular structure was nonlinear.

- Experimental Procedure

Experiments were conducted in the 600 m^3 CAL cloud chamber. The procedure for evaluating the effects of surface active agents on laboratory fog was as follows: after forming fog in the cloud chamber, controlled amounts of cetyl alcohol (1-hexadecanol) vapor were introduced into the chamber. The vapor, upon entering the chamber and contacting the cool environment, immediately condensed to form tiny particles having a size range of 0.5 to 1 μm. The cetyl alcohol haze was allowed to reside in the fog for periods ranging from a few minutes to nearly a half hour during which time the fog droplets became coated with monomolecular films of the surface active agent. (From coagulation theory (Fuchs, 1964), it was possible to estimate the number of 0.5 μm cetyl alcohol particles that were scavenged by 10 μm radius fog droplets in the cloud chamber. Taking a typical value of droplet concentration of 6×10^2 cm^{-3} and a cetyl alcohol concentration of 10^4 cm^{-3}, calculations suggest that slightly more than 200 particles cm^{-3} were scavenged by the fog droplets within 10 minutes. Recent laboratory experiments conducted at CAL indicate much higher scavenging efficiencies than this, perhaps by as much as a factor of ten. Data presented in this paper support these findings.)

The chamber was then repressurized to cause adiabatic heating and droplet evaporation (forced dissipation). In this way, we hypothesized, the surface layers on evaporating treated droplets would coat the natural condensation nuclei with cetyl alcohol. After several minutes, a slow expansion was produced in order to re-form the fog on treated nuclei. The visibility

characteristics of the treated fog were compared with control fogs produced in an identical manner but without seeding. As a final step in the evaluation, the natural fog was allowed to dissipate naturally.

By following the above procedure, artificial fog formation and dissipation could be studied; and in so doing, the overall effect of treating nuclei with evaporation retardants could be examined. Visibility was recorded continuously during the experiments and fog microphysics data were obtained at various times during the life cycle of the fogs.

- Results of Fog Chamber Experiments

In Figure 7, visibility curves are shown for a control fog and a fog seeded with 0.9 gm of cetyl alcohol. It is apparent from the figure that after seeding and then repressurizing the chamber (i.e., fog dissipation at t = 12 minutes) evaporation of the treated droplets was greatly retarded. Note from the data that several minutes after the start of the fog reformation expansion (t = 15 minutes) that visibility in the treated fog continued to improve slowly, indicating that evaporation of treated droplets had not been arrested and, as a corollary, that sufficient supersaturation had not been achieved to produce droplet growth. It is probable that the relative humidity was slightly depressed in the seeded case at this time, since much of the water within the chamber was still in the liquid phase as droplets. Once adequate cooling occurred and supersaturation increased, growth proceeded on the droplets and fog intensified (e.g., t = 20 minutes). At t = 40 minutes, the expansion was terminated and the fog was allowed to dissipate naturally. The resulting stabilization of the fog against dissipation is evident from the data shown in the figure.

Drop-size distributions for the control and seeded fogs are shown in Figure 8 for several times (specifically, t = 5, 25, 40, and 50 minutes) during the experiments. At t = 5 minutes, prior to seeding, the shape of the distributions are nearly identical as are the average drop radii. Differences in the concentration of droplets observed at this time are not highly significant. At t = 25 minutes, i.e., after seeding, repressurization and initiation of the secondary fog forming expansion, the distributions of the seeded and control

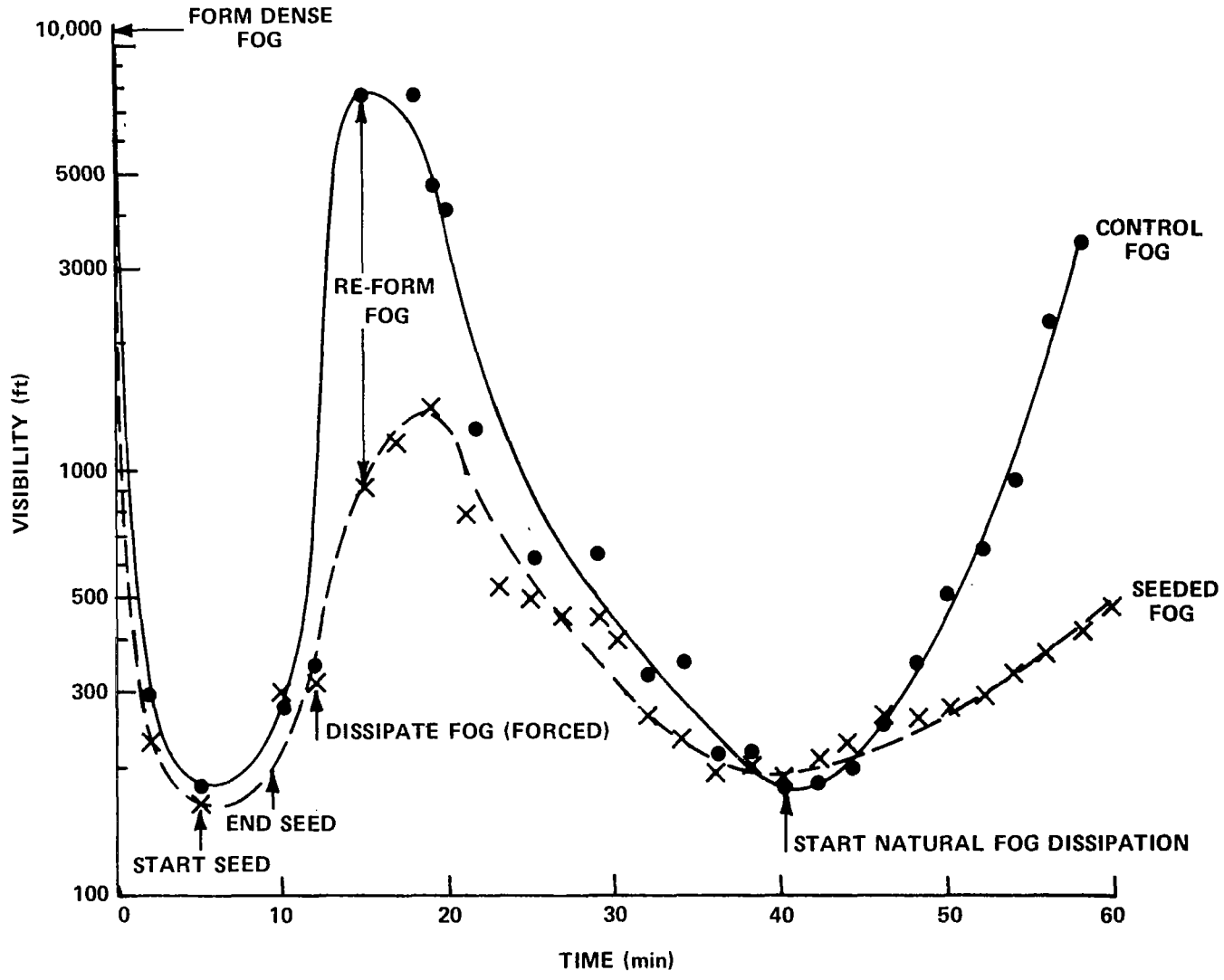

Figure 7 VISIBILITY AS A FUNCTION OF TIME FOR A CONTROL FOG AND A FOG SEEDED WITH 0.9 gms CETYL ALCOHOL

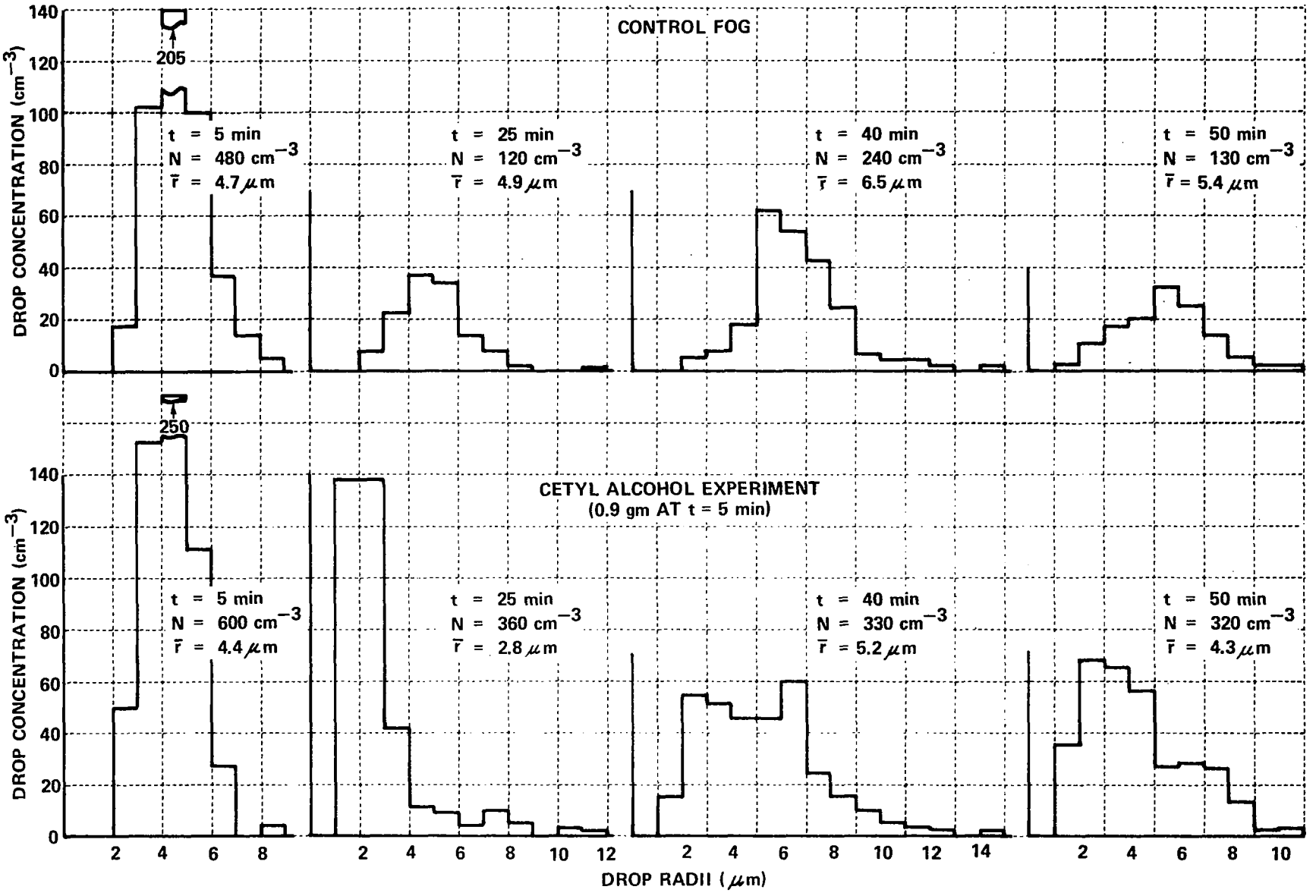

Figure 8 COMPARISON OF DROP SIZE DISTRIBUTIONS FOR A CONTROL FOG AND A FOG SEEDED WITH 0.9 gms CETYL ALCOHOL

fogs were much different in both shape and drop concentration. The seeded fog at this time was comprised of high concentrations of very small droplets, suggesting that growth on treated droplets remaining in the chamber from the initial fog was substantially retarded. As a result of these factors, visibility in the seeded fog was actually worse than in the control fog at this time.

At t = 40 minutes, the distributions were similar and the visibilities were nearly the same. The seeded fog drop distribution is skewed somewhat toward smaller sizes again, indicating retarded growth; however, the differences between the distributions are not great.

At t = 50 minutes, approximately 10 minutes after the expansion was stopped and fog was allowed to dissipate naturally, the differences in visibility, drop size, and drop concentration were large. The effective manner in which the cetyl alcohol stabilized the fog is obvious from a comparison of the number of droplets and the shape of the distribution. Somewhat later, i.e., t = 60 minutes, the visibility data in Figure 7 show even greater differences, again attesting to the stabilization effect of the cetyl alcohol.

It might reasonably be argued at this point that residual haze in the form of high concentrations of cetyl alcohol particles could restrict the visibility to the values shown and that treated fog droplets may not have been responsible for the observed low visibility. In order to help determine if this were true and to study the influence of a monolayer-forming chemical which does not retard evaporation, a second experiment was run, using 0.9 gm of oleyl alcohol (9-octadecen-1-ol, cis isomer), a non-linear surface active compound. Oleyl alcohol is nearly identical to cetyl alcohol in composition but does not inhibit evaporation since the structure of the oleyl alcohol molecule prevents close molecular packing at the air-water interface (Garrett, 1971).

It is obvious from the resulting visibility data (Figure 9) that an organic haze was not responsible for restricting visibility. Note, for example, that after seeding (t = 5 minutes) and forcing fog dissipation (t = 12 minutes) the treated fog droplets completely evaporated and visibility returned to a value equal to that observed in the control fog. In fact, the

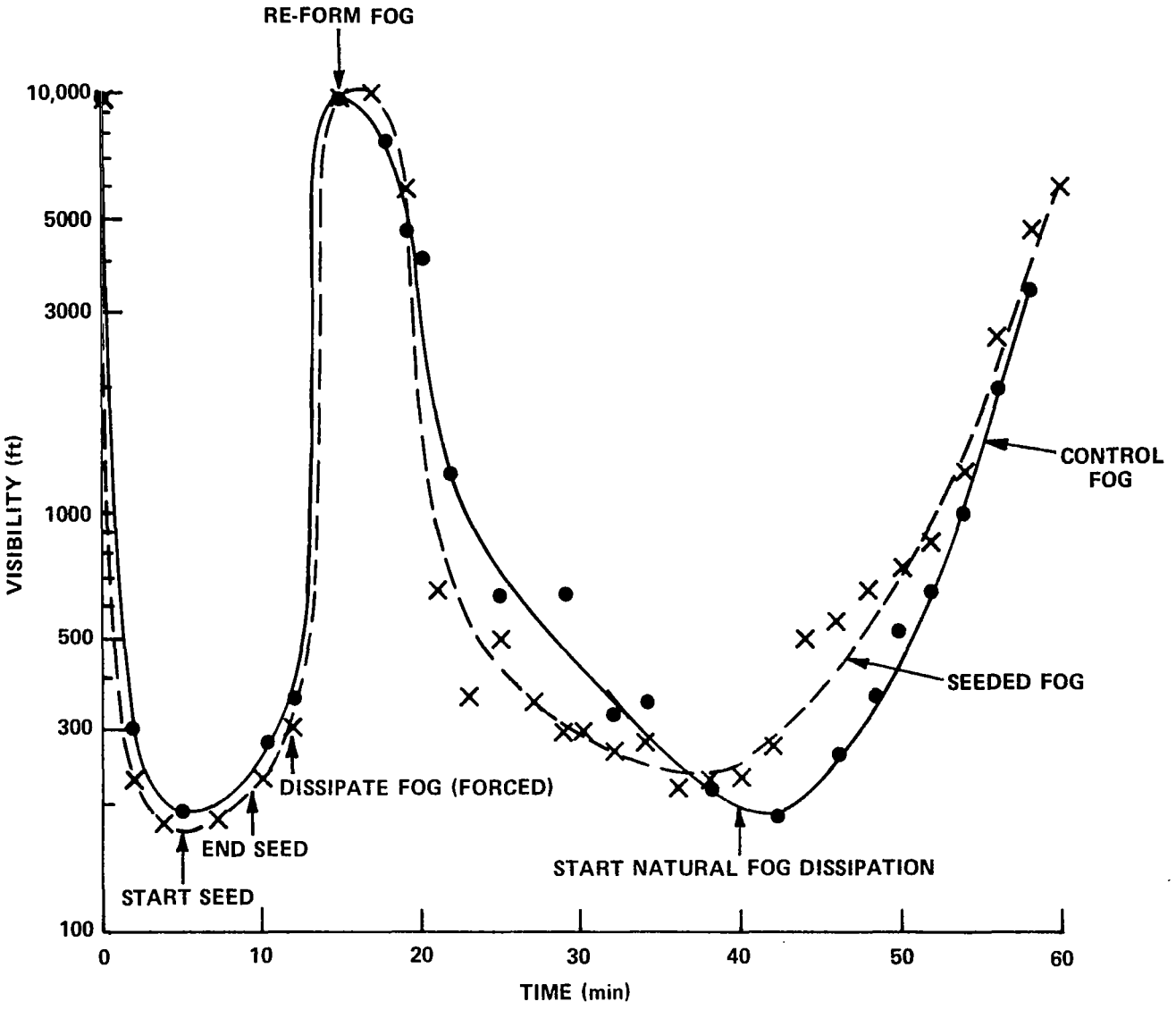

Figure 9 VISIBILITY AS A FUNCTION OF TIME FOR A CONTROL FOG AND A FOG SEEDED WITH 0.9 gms OLEYL ALCOHOL

entire sequence of events shown in this figure for the seeded and control fogs were very similar. One can only conclude, therefore, that seeding with an equivalent amount of oleyl alcohol produced no significant changes in the visibility characteristics of the laboratory fog and that scattering of light by the high concentrations of cetyl alcohol particles in the previous experiment were not in themselves responsible for the low visibility that was observed.

Additional seeding experiments were performed in which cetyl alcohol was allowed to come in contact with the fog droplets for appreciably longer times (up to 50 minutes) before causing complete fog dissipation and subsequent reformation. The purpose of these experiments was to increase the probability of coating the fog droplets with cetyl alcohol before attempting to cause droplet growth on treated nuclei. The results of these experiments showed essentially the same trend in events; that is, substantial retardation of droplet evaporation but relatively little influence on the fog formation process.

The visibility data shown in Figure 10 bear this out. In this experiment, the effective manner in which droplet evaporation was retarded is obvious from the persistent nature of the initial, treated fog. Later, after allowing nearly an hour for complete droplet evaporation, a fog forming expansion was reinitiated in both the control and seeded fog. As in the previous example, very little influence was observed in the formation of fog as a result of seeding.

The drop-size spectra shown in Figure 11 provide additional insight into the mechanisms responsible for the observed differences in visibilities in this experiment. At t = 5 minutes, shortly after producing fog, the drop-size spectra and concentrations were nearly identical in the two fogs. At t = 16 minutes, 7 minutes after the completion of seeding and 2 minutes after attempting to cause fog dissipation, the drop data were vastly different. Whereas rapid dissipation was occurring in the control fog, large numbers of treated droplets remained in the seeded fog and visibility was still low. Drop spectra taken much later in the experiment after reforming fog (i.e., t = 57, 60, and 67 minutes) are largely alike and show only minor differences, thus

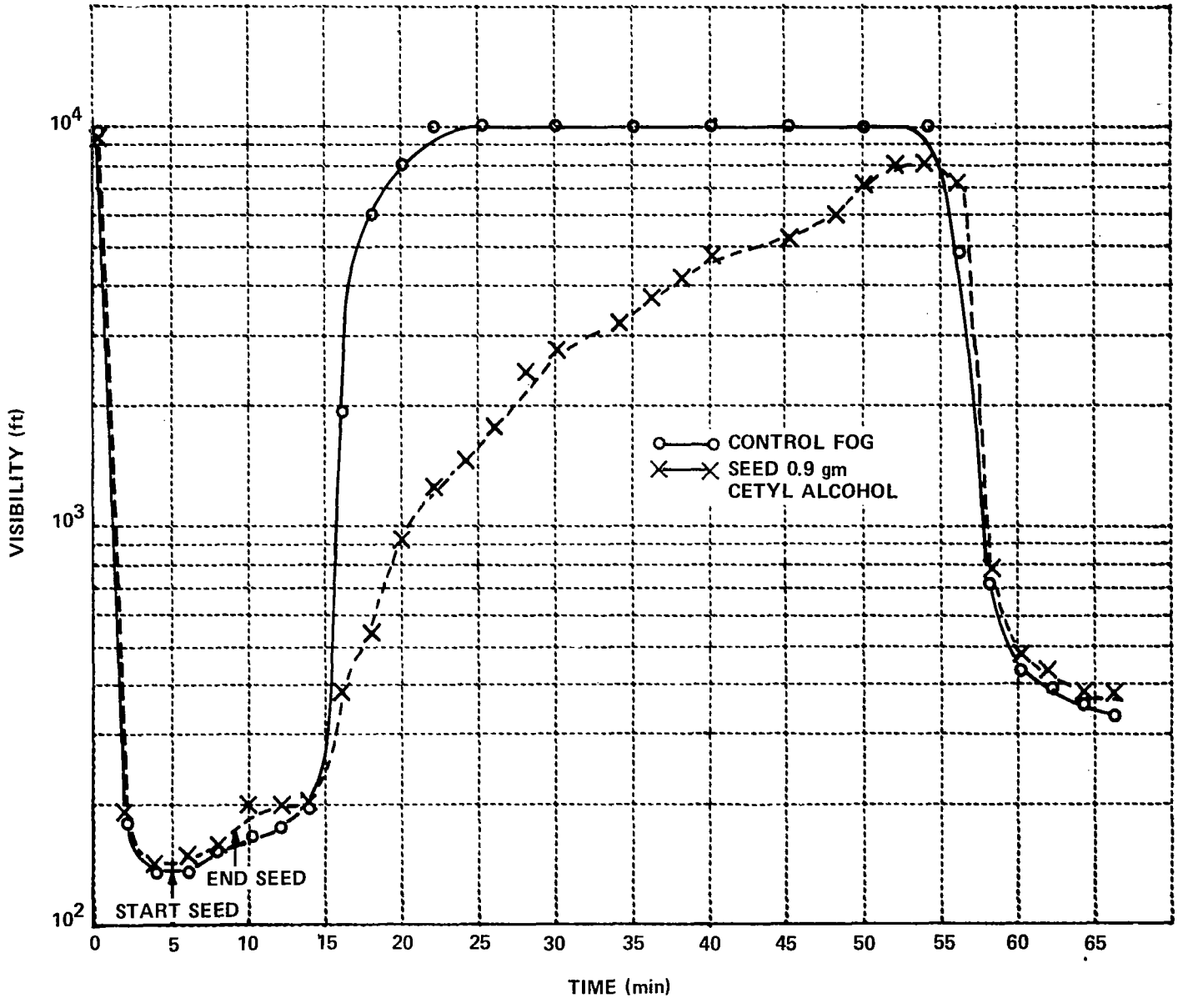

Figure 10 VISIBILITY AS A FUNCTION OF TIME FOR A CONTROL FOG AND A FOG SEEDED WITH 0.9 gms CETYL ALCOHOL

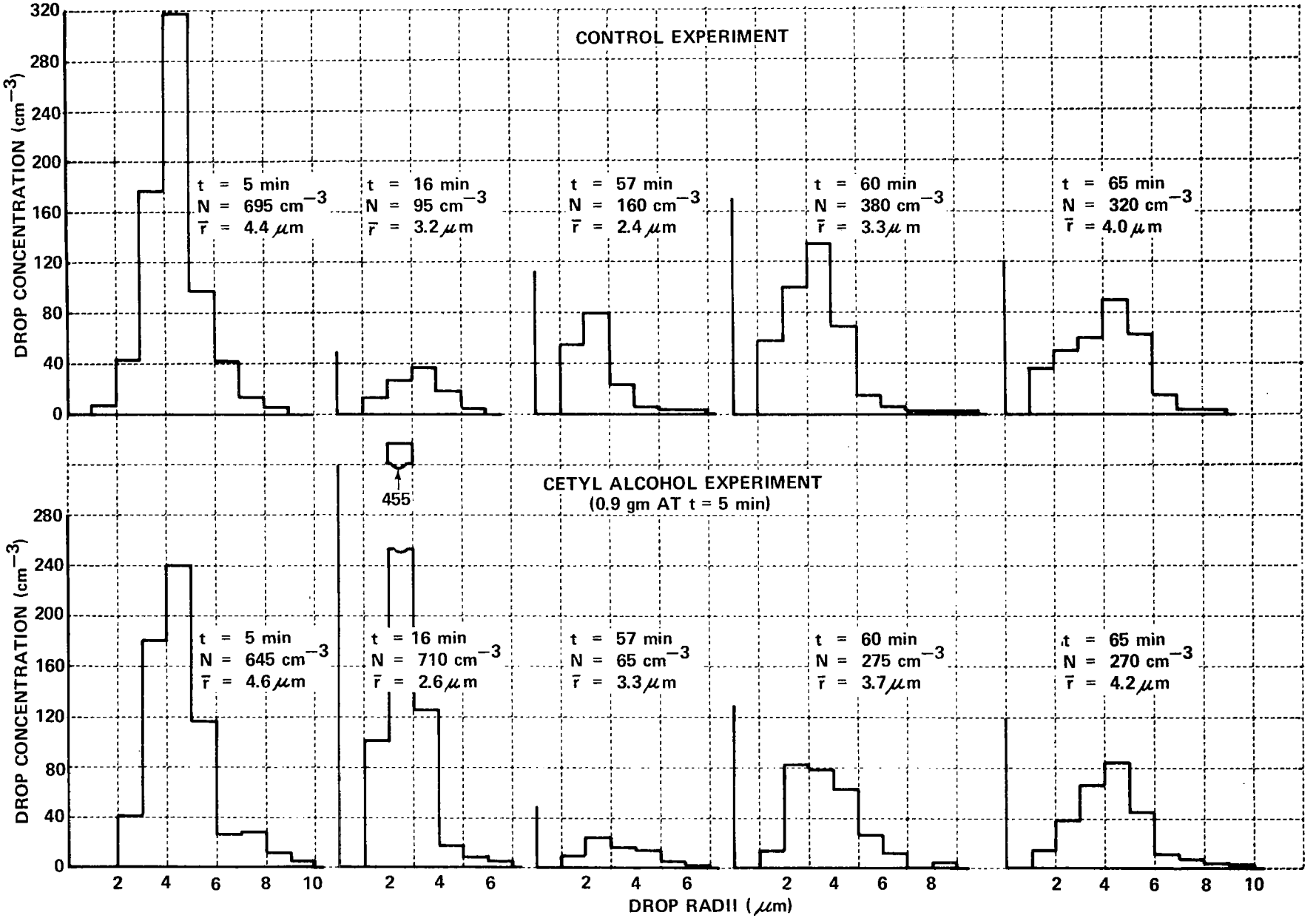

Figure 11 COMPARISON OF DROP SIZE DISTRIBUTIONS AT VARIOUS TIMES FOR A CONTROL FOG AND A FOG SEEDED WITH 0.9 gm CETYL ALCOHOL

attesting to the small influence of cetyl alcohol seeding on fog formation. Variations in the droplet concentration between the control and seeded fog at t = 57 minutes are thought to be the result of the rapidly changing conditions in both fogs at the time these data were taken.

A final set of tests of the possible influence of cetyl alcohol on fog formation was performed by "preseeding" the chamber atmosphere with prescribed amounts of the cetyl alcohol vapor before forming fog. After allowing the cetyl alcohol to equilibrate with the natural aerosol for 30 minutes, fog was formed on the natural and treated nuclei in the chamber. Results were compared with a control fog produced in the same manner but without seeding. Visibility data from a representative experiment of this type (Figure 12) show that the overall influence of cetyl alcohol seeding on fog density was small. Initially, visibility was greater in the treated fog but after about 10 minutes, the two fogs were essentially the same. Later, after fog was fully-developed, visibility in the seeded case degraded to somewhat lower levels than in the control fog.

In spite of the similarities in visibility between the two fogs, the drop-size spectra reveal some important differences (Figure 13). At t = 3 minutes, shortly after initiating the fog forming expansion, the seeded fog was comprised of substantially fewer and smaller droplets than the control situation. This, of course, would be expected if droplet growth were being retarded on the treated nuclei. By t = 6 minutes, the drop concentration was about the same in both fogs although the sizes were still somewhat smaller in the seeded case. By t = 15 minutes, the seeded fog had more than twice as many droplets as the control fog; visibility was therefore quite poor. Finally, by t = 25 minutes, sufficient growth and sedimentation of droplets had occurred in the control fog so that visibility was improved; retardation of droplet growth in the seeded fog produced a more stable fog whose visibility characteristics were unchanging or slowly degrading. The net result of seeding in this experiment, therefore, was to retard fog formation somewhat but ultimately to produce a fog of lower visibility than in the control case.

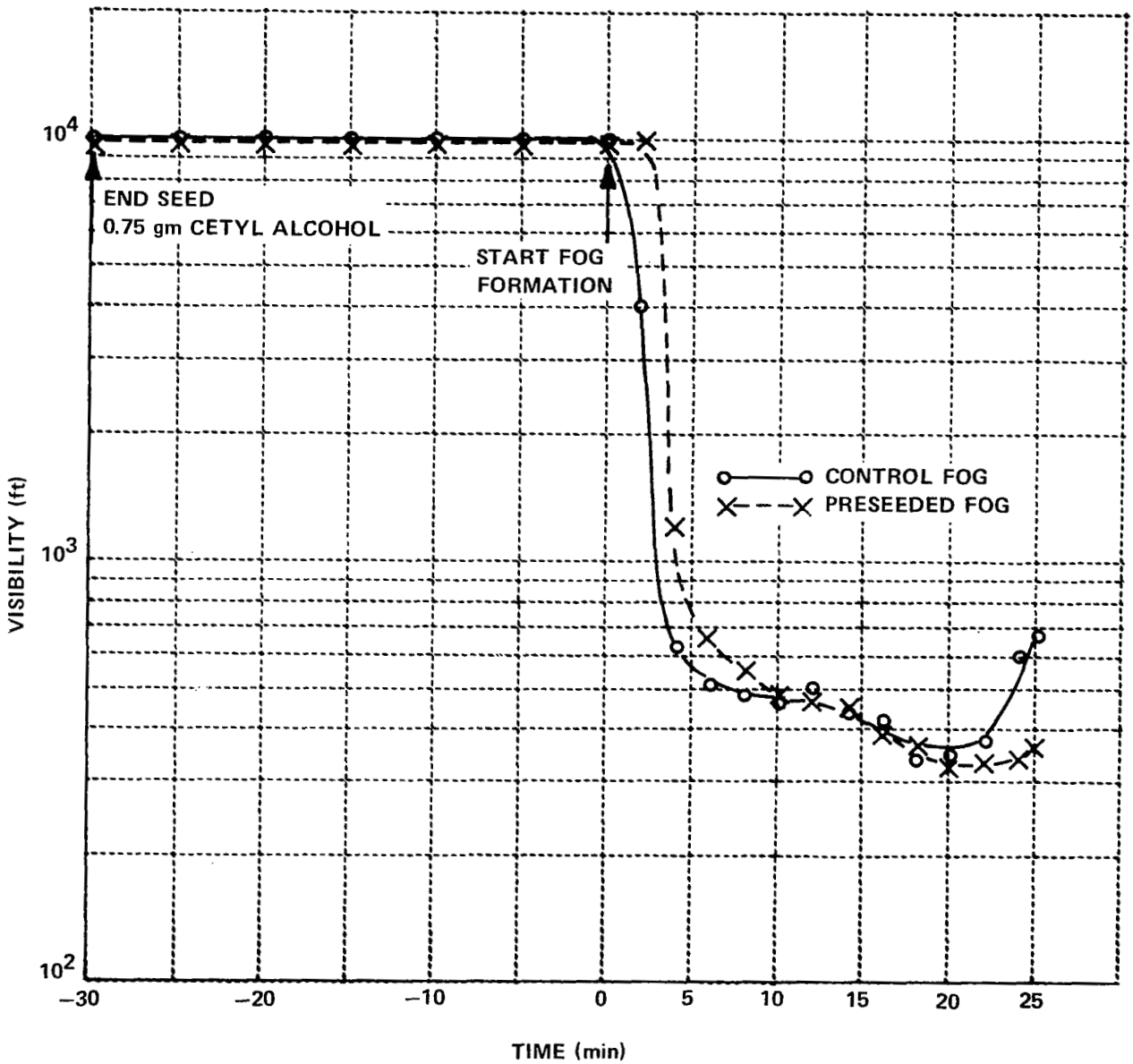

Figure 12 VISIBILITY AS A FUNCTION OF TIME FOR A LABORATORY CETYL ALCOHOL PRESEEDING EXPERIMENT

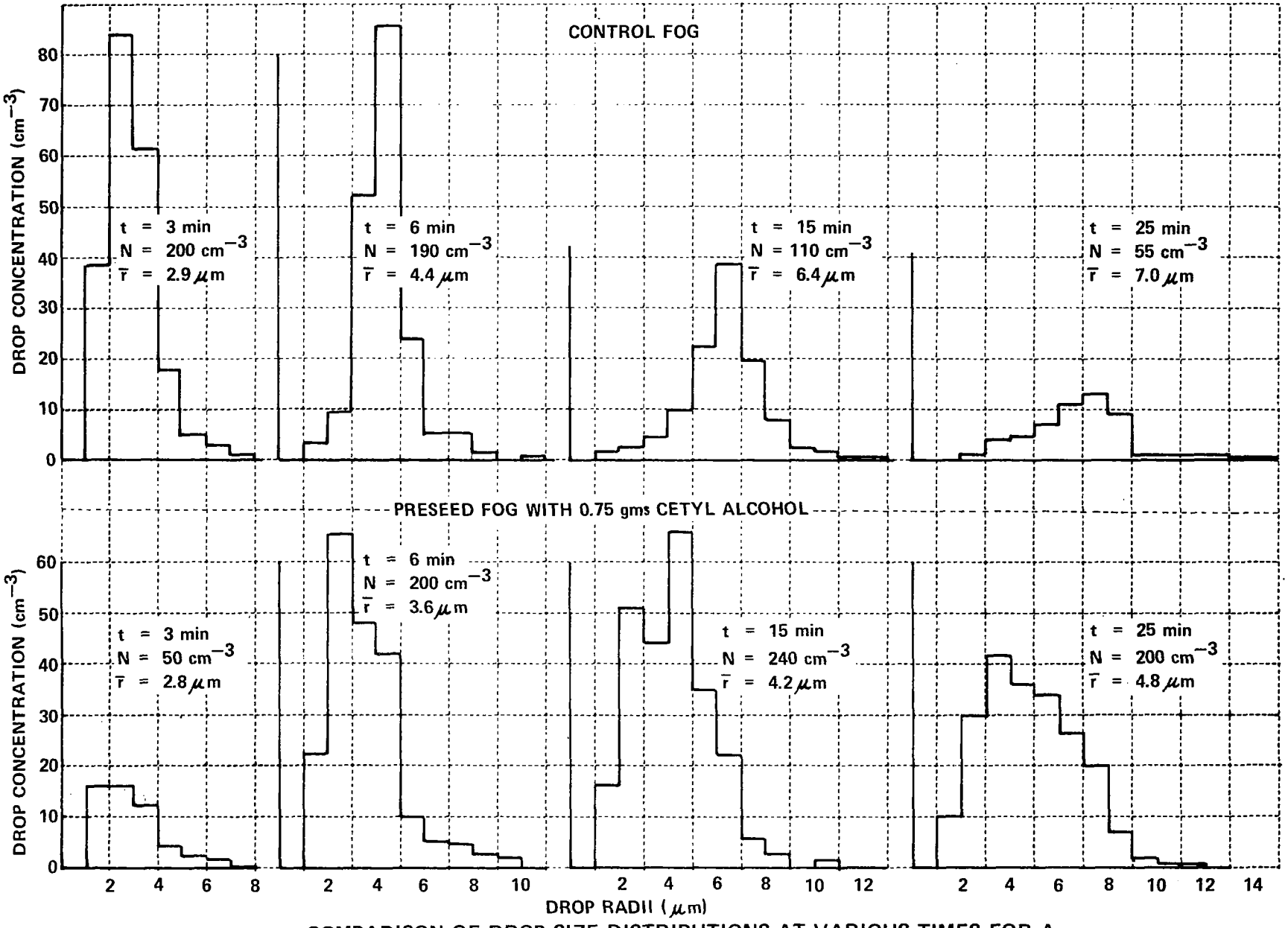

Figure 13 COMPARISON OF DROP SIZE DISTRIBUTIONS AT VARIOUS TIMES FOR A CONTROL FOG AND A CETYL ALCOHOL PRESEEDING EXPERIMENT

• Conclusions

These data show that laboratory fog dissipation can be greatly retarded by seeding with controlled amounts of evaporation retardants such as cetyl alcohol. The data also suggest that droplet growth and laboratory fog formation can be slightly retarded but that under the conditions of these experiments, dense fog could not be prevented from occurring. It is concluded, therefore, that further attempts to modify natural fog formation, with the intent of producing a fog of less severe visibility characteristics, are not warranted.

It is not precisely known what percentage of the fog droplets were actually treated in these experiments. Calculations and the fact that fog dissipation was greatly retarded indicate that many of the droplets were coated with an effective monomolecular film of the chemical. Seeding of laboratory fog with oleyl alcohol, a compound with a nonlinear chemical structure, produced no important effect on the fog.

The fact that during the fog formation process growing droplets are additionally coated with residual cetyl alcohol vapors is undesirable since this condition results in a dense fog that is reluctant to dissipate naturally. This occurrence, of course, makes application of the seeding concept unattractive for airport use. Other potential applications may exist in which it is desirable to prolong the presence of fog, e.g., frost prevention.

The striking stabilization of fogs by film-forming organic chemicals suggests that inadvertent cloud and fog modifications may result from a release of man-made organic matter into the atmosphere. The scope and magnitude of such a possibility merits scientific attention.

REFERENCES

Altshuller, A. P., and Bufalini, J. J., 1971: Photochemical Aspects of Air Pollution: A Review, Env. Sci. & Tech.

Bigg, E. K., J. L. Brownscombe, and W. J. Thompson, 1969: Fog Modification with Long-Chain Alcohols, J. Appl. Meteor., 8, 75.

Bradley, R. S., 1955: The Rate of Evaporation of Micro-drops in the Presence of Insoluble Monolayers, J. Colloid Sci., 10, 571.

Bufalini, Marijon, 1971: Oxidation of Sulfur Dioxide in Polluted Atmospheres, Env. Sci. & Tech.

Derjaguin, B. V., V. A. Fedoseyev, and L. A. Rosenzweig, 1966: Investigation of the Adsorption of Cetyl Alcohol Vapor and the Effect of this Phenomenon on the Evaporation of Water Drops, J. Colloid Interface Sci., 22, 45.

Eisner, H. S., B. W. Quince, and C. Slack, 1960: The Stabilization of Water Mists by Insoluble Monolayers, Disc. Faraday Soc., 30, 86.

Fuchs, N. A., 1964: The Mechanics of Aerosols, Pergamon Press.

Garrett, W. D., 1971: Retardation of Water Drop Evaporation with Monomolecular Surface Films, J. Atmos. Sci., 28, 816.

Husar, R. B. and K. T. Whitby, 1971: On the Size Distribution of Photochemical Aerosols, Paper Submitted to the J. of Env. Sci. & Tech.

Jiusto, J. E., 1964: Investigation of Warm Fog Properties and Fog Modification Concepts, NASA Contractor Report CR-72.

Kocmond, W. C. and J. E. Jiusto, 1968: Investigation of Warm Fog Properties and Fog Modification Concepts, NASA CR-1071.

Kocmond, W. C. and E. J. Mack, 1972: The Vertical Distribution of Cloud and Aitken Nuclei Downwind of Urban Pollution Sources, J. Appl. Meteor., 11, 1.

Kocmond, W. C. et al., 1971: Investigation of Warm Fog Properties and Fog Modification Concepts, NASA CR-1731.

Pilié, R. J., 1966: Investigation of Warm Fog Properties and Fog Modification Concepts, NASA CR-368.

APPENDIX A

CORNELL AERONAUTICAL LABORATORY THERMAL DIFFUSION CHAMBER

The CAL thermal gradient diffusion chamber has been used for making measurements of cloud nuclei since about December, 1964[1-4]. The basic design of the chamber is patterned after that of Langsdorf, Wieland and also Twomey[5-7]. Photographs of the chamber in its present configuration are shown in figures 1 and 2.

In brief, the unit consists of a cylindrical plexiglass chamber with upper and lower water reservoirs, a collimated light beam to illuminate a small volume within the chamber, and a polaroid camera for photographing droplets that have formed on condensation nuclei.

During operation, water vapor diffuses from the warmer upper surface to the lower reservoir, with the chamber supersaturation being a known function of temperature difference between the two reservoirs. A series of 10 thermocouples (five on each surface) is used to measure ΔT. When the desired supersaturation has been achieved, an air sample containing nuclei to be investigated is drawn into the chamber at a continuous rate for several seconds. The air sample is allowed to reside in the supersaturated environment where, in a few seconds, droplet growth proceeds on the most active condensation nuclei. The growing droplets are illuminated by a 200 watt Osram lamp and photographed at 90° to the light beam moments before sedimentation begins (this can be easily estimated after some experience in using this instrument). Enlarged photos of droplets formed in the chamber are shown in figure 3.

The number of active nuclei can be estimated from the photographs by using a transparent overlay having dimensions of 0.5 cm x 1.0 cm.

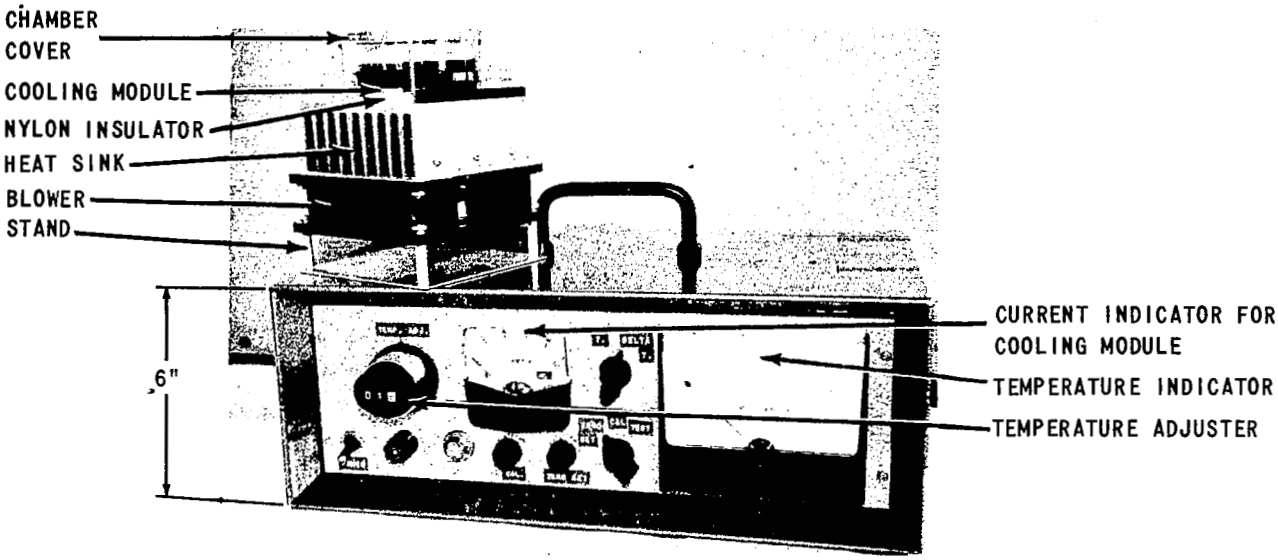

FIGURE 1 CAL THERMAL DIFFUSION CHAMBER
AND TEMPERATURE CONTROL UNIT

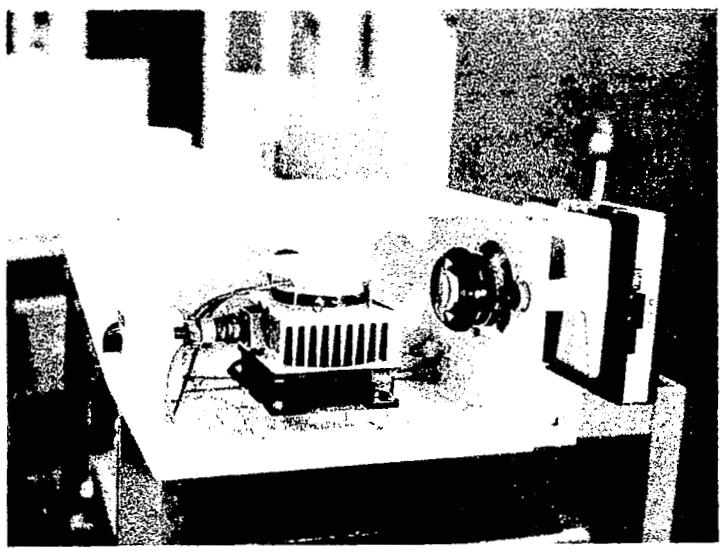

Figure 2 CHAMBER CONFIGURATION DURING OPERATION

WATER DROPLETS FORMED AT 0.3%
SUPERSATURATION 1050 DROPS/cm^3

WATER DROPLETS FORMED AT 0.9%
SUPERSATURATION 4200 DROPS/cm^3

WATER DROPLETS FORMED AT 3.0%
SUPERSATURATION 5000 DROPS/cm^3

Figure 3 ENLARGED PHOTOGRAPHS OF DROPLETS FORMED IN THERMAL DIFFUSION CHAMBER

REFERENCES

1. Kocmond, W. C. (1965) - Investigation of Warm Fog Properties and Fog Modification Concepts. Report No. RM-2788-P-9, Cornell Aeronautical Laboratory, pp 36-47.

2. Pilié, R. J. and W. C. Kocmond (1967) - Project Fog Drops, NASA Contractor Report CR-675, pp 11-22.

3. Kocmond, W. C. and J. E. Jiusto (1968) - Project Fog Drops, NASA Contractor Report CR-1071, pp 47-55.

4. Jiusto, J. E. and W. C. Kocmond (1968) - Note on Cloud Nucleus Measurements in Lannemezan, France, J. Res. Atmos., pp 101-104.

5. Langsdorf, A. (1936) - A Continuously Sensitive Cloud Chamber, Phys. Rev. 49, p 422.

6. Wieland, W (1956) - Condensation of Water Vapor on Natural Aerosol at Slight Supersaturation, Z. Agnew. Math. U. Phys. 7, pp 428-460.

7. Twomey, S. (1963) - Measurements of Natural Cloud Nuclei, J. Res. Atmos., I, 1, p 101.

NASA-Langley, 1972 — 20 M198