An Experimental Study of the Detection of Ice Nuclei on Membrane Filters and Other Substrata

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ABSTRACT

An experimental study was made of a membrane filter technique for the detection of ice nuclei in which air of controlled humidity flows across the cooled membrane as opposed to the usual static thermal diffusion procedure. This is necessary to overcome water vapor losses to various sinks on the sample substrate; the procedure also makes it possible to observe the nucleation process directedly by microscope. However, for very small nuclei such as AgI, even this flow system is not able to activate the nuclei. This is overcome by letting a puff of supersaturated air pass over the deposited aerosol, which should be on a water-repellent substrate, to promote vapor flow to the ice and condensation nuclei, rather than onto the substrate. At temperatures warmer than $-12^\circ$C, the puff procedure is not necessary since the water vapor pressure is sufficient to keep up with the vapor sinks. Following the above procedures, consistent results are obtained for AgI, kaolin, soil particles and pollution aerosols in both laboratory and field applications in the $-5$ to $-20^\circ$C range.

1. Introduction

The NCAR membrane development chamber is designed to study the following problems: detection of ice nuclei on membrane filters and in residues from rain, snow and hail samples; freezing of droplets; nucleation by particles too large to stay suspended in a cloud chamber; and time-delay effects in nucleation. This requires a device that allows the activation process to be observed microscopically while providing an adequate supply of moisture (achieved with a flow system) to control the saturation in the developing chamber. This paper gives the results of an investigation to show the effect of all the variables involved: supersaturation, substrate condition, nucleus density, associated particles, and nucleus type and size. The data are analyzed for the nucleation processes involved. Results of applying the technique in the field are given.

2. Description of development chamber and its operation

a. Development chamber

This device is in principle a thermal gradient chamber (Gagin and Aroyo, 1969; Stevenson, 1968) to simulate cloud conditions under which ice nuclei would be expected to act. The temperature of the ice surface and sample can be accurately regulated independently, thus varying degrees of ice or water saturation can be theoretically produced at the sample surface. The major problem is that the flux of water vapor is low at temperatures below $0^\circ$C because the vapor pressure of ice or water is, at best, a few millimeters of mercury, and the rate of loss to the vapor sinks on the sample surfaces can be stronger than the source. Therefore, the actual saturation will be reduced by an unknown amount from the theoretical estimate (Lala and Jiusto, 1972). To provide a stronger source of water vapor flux we use a flow system, in which air is first humidified by passing it through a bed of small ice cubes. It is then blown over the sample to provide a continuous supply of fresh water vapor to the sample.

Fig. 1 shows the schematics of the chamber while Fig. 2 gives a photographic layout. Air at 4 liter min$^{-1}$ is first dried to a dew point of $-50^\circ$C, and then filtered and precooled before entering the ice humidifier. Drying of the air prevents the formation of frost crystals that could be entrained. Freecooling is necessary so warm air does not impinge on the ice and melt it at the entrance, and to make sure that temperature and vapor equilbria are reached at the end of the humidifier. Equilibria conditions were verified by measuring how much lower the temperature of the sample substrate had to be, compared to the humidifier temperature, to produce condensation on the substrate. This temperature difference was in close accordance with the theory (see below). A perforated plate at the humidifier entrance

1 This research was performed as part of the National Hail Research Experiment, managed by the National Center for Atmospheric Research and sponsored by the Weather Modification Program, Research Applications Directorate, National Science Foundation.
spreads the airflow evenly into the ice bed. In the humidifier, the air is saturated at the vapor pressure of the ice, which is cooled by the base plate whose temperature is controlled by the expansion valve of the freon cooling system. A nozzle then aims the air at the sample, which is placed on a thermoelectrically-cooled block. To avoid any vapor sinks, the block is surrounded by iced surfaces at the same temperature as the incoming air. The optimum velocity, experimentally determined, of the air leaving the jet is about 1 m s⁻¹. The flow velocity is high enough that surrounding surfaces do not influence the sample, yet not so high that the membrane surface warms up, i.e., that an unduly high temperature gradient develops from the cooling block to the surface of the sample. At the same time, enough moisture must be supplied to the sample to keep up with the vapor sinks: growing ice crystals, cloud condensation nuclei, and water vapor absorption by the substrate. To accurately achieve a desired water supersaturation (ss) presents additional problems because of these losses.

In our investigation, as already pointed out above, we determined the temperature differences between the ice and sample necessary to achieve water saturation by noting the onset of condensation (not to be confused with the onset of haze, which can be seen only on a metal surface as a bluish tinge, while condensation is obvious under a microscope using grazing illumination on any substrate by the appearance of droplets). With an air velocity of 1 m s⁻¹, this took place at the theoretical temperature difference for liquid water condensation. This difference was measured with a microprobe surface-temperature sensor, which also showed that the sample surface warmed up as much as 0.2°C higher than the sample support block. Also, the air reached complete temperature equilibrium in the ice bed. The temperature difference (between sample and humidifier) is controlled automatically to less than 1/10th of a degree (°C); no overshoot is experienced in cooling the sample. The sample is illuminated by light parallel to the sample surface, which makes small ice crystals easily visible, even on a white membrane;

**Fig. 1.** Schematic diagram of NCAR membrane development chamber.

**Fig. 2.** Photographic view of humidifier and sample handling system.
condensing water drops can also be seen. The above procedure will be known as condensation development in this paper.

An alternate method of humidification, called cloud development in this paper, was developed empirically to detect AgI. This method provides a much stronger source of water vapor. It is in some respects similar to the transient, high-ss achieved in an expansion chamber ice nucleus counter. Our procedure uses the cloud generator shown in Fig. 1. It has a net volume of about 230 cm³ of moist air (saturated at 40°C) from which 150 cm³ are suddenly released by an equal volume of dry, filtered air in 1 s. With the air flow off and the sample slightly below water saturation, six bursts are injected 5 s apart into the 350 cm³ developing chamber through eight 5 mm holes in the chamber door. Moisture condenses very uniformly, directly on the surface in the form of numerous very small drops. The ss produced was not measured. A temperature evaluation showed that the temperature of the air in the chamber momentarily rises 0.5°C as indicated by a 1 s response thermocouple. The principal argument for this method is that a strong supply of water vapor temporarily exists for nucleation right at the membrane surface and all nuclei have a chance to act, i.e., before ice and growing drops prevent attainment of any water supersaturation in their vicinity.

b. Sample preparation

Membrane filters are mounted on a 5½ cm diameter, 2 mm thick brass disc on a 1 mm thick Vaseline layer which is first melted and allowed to cool prior to mounting in order to provide a smooth surface. For the condensation development, the assembly is then heated to 55°C until the Vaseline is just short of the membrane top surface to prevent water vapor losses to the membrane. Ideally, scratching the surface should not show any evidence of Vaseline. We have observed microscopically that clay particles soak up Vaseline; AgI particles tend to float on it. For the cloud development, partial Vaseline penetration only is desirable to avoid nucleation by impurities in the Vaseline. Concerning heat transfer, even if the membrane is only partially penetrated by Vaseline, no temperature difference larger than 0.2°C exists between the brass and the top surface of the membrane. Also, sharper definition of the ice crystals results if the Vaseline only partially penetrates the membrane, otherwise the crystals tend to grow more along the surface and are not as easily resolved. The sample plate is brought into good thermal contact with the sample block using a light-grade silicone lube. A hygroscopic material such as glycerine should not be used, since it acts as a vapor sink. A small piece of polished, wettability nickel-chrome foil is often added to easily detect the onset of condensation.

Table 1. Example of background counts from membrane filters that were not subject to any handling.

<table>
<thead>
<tr>
<th>Filter type and pore size</th>
<th>Nominal supersaturation* (%)</th>
<th>Condensation: -20°C</th>
<th>Condensation: -14°C</th>
<th>Cloud***</th>
</tr>
</thead>
<tbody>
<tr>
<td>Millipore, 0.8 μm</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Millipore, 0.22 μm</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Aquapel, 0.22 μm</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Sartorius, 0.2 μm</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Millipore, 0.8 μm</td>
<td>1</td>
<td>0</td>
<td>4</td>
<td>0</td>
</tr>
<tr>
<td>Millipore, 0.22 μm</td>
<td>1</td>
<td>0</td>
<td>32</td>
<td>0</td>
</tr>
<tr>
<td>Aquapel, 0.22 μm</td>
<td>1</td>
<td>0</td>
<td>4</td>
<td>0</td>
</tr>
<tr>
<td>Sartorius, 0.2 μm</td>
<td>1</td>
<td>0</td>
<td>144</td>
<td>0</td>
</tr>
<tr>
<td>Millipore, 0.8 μm</td>
<td>3</td>
<td>0</td>
<td>4</td>
<td>0</td>
</tr>
<tr>
<td>Millipore, 0.22 μm</td>
<td>3</td>
<td>0</td>
<td>36</td>
<td>0</td>
</tr>
<tr>
<td>Aquapel, 0.22 μm</td>
<td>3</td>
<td>0</td>
<td>12</td>
<td>0</td>
</tr>
<tr>
<td>Sartorius, 0.2 μm</td>
<td>3</td>
<td>0</td>
<td>52</td>
<td>0</td>
</tr>
<tr>
<td>Millipore, 0.8 μm</td>
<td>5</td>
<td>0</td>
<td>4</td>
<td>0</td>
</tr>
<tr>
<td>Millipore, 0.22 μm</td>
<td>5</td>
<td>0</td>
<td>20</td>
<td>0</td>
</tr>
<tr>
<td>Aquapel, 0.22 μm</td>
<td>5</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Sartorius, 0.2 μm</td>
<td>5</td>
<td>0</td>
<td>140</td>
<td>0</td>
</tr>
</tbody>
</table>

* With respect to water. ** Average area exposed for a 47 mm filter. *** Cloud applied as soon as final temperature was reached for 0% ss case and after 15 min for the others.

The air flow must be on when the sample is put in place to avoid penetration of room air moisture into the chamber.

Ice from a hail slice (or snowflakes) is first warmed (in the chamber) several degrees (with respect to the airflow) to sublime the ice in order to study the residue for nucleation activity. These samples are usually placed on a clean Vaseline-treated membrane filter. Aerosol samples collected on hydrophobic metal foil or membranes from electrostatic precipitators or impactor samples, can be directly mounted on the sample plate to test for the presence of ice nuclei. A highly polished brass plate with a silicone resin® coating makes a very good substrate for impactors.

For any substrate it is important to test periodically for background counts, i.e., for the number of nuclei found when no sample has been collected on it. Filters must be handled under dust-free conditions, preferably in a clean bench. Table 1 shows background counts for four filters of each kind (which will be described later) used in this study for typical supersaturations and the cloud development. Only at −20°C are problems encountered and those only with the cloud method, if it is applied after first developing at some supersaturation with the condensation method. Background counts can vary considerably with different batches of filters and results as good as those in Table 1 are not usually feasible in practice because the filters are subject to contamination while being mounted and transported. Also, these data apply to our particular development system only. The background counts for the silicone resin treated metal surfaces are subject to more varia-

®SR-516 silicone contact adhesive (General Electric, Silicone Products Dept., Waterford, N. Y. 12188) diluted about 90% with toluene.
tion. The surface must be well cleaned and polished and then one can expect at $-20^\circ$C about 1 count cm$^{-2}$ for development at 3% ss and up to 3 with the cloud. At warmer temperatures the metal substrate has no background problems.

3. Detection of various types of AgI ice nuclei on membranes

a. Experimental results from tests with AgI

AgI samples were derived from different sources: a thermal generator for relatively pure AgI particles (Langer, 1973a), a typical AgI flare composition, a Skyfire AgI-NH$_4$I generator, and AgI powder (Langer, 1973a). Small pieces of flare material were ignited by heating in the same system as for the thermal AgI. Characteristics of the various AgI aerosols are given in Table 2.

Fig. 3 compares thermal AgI and flare material. Each membrane was cut into four equal pieces so that a piece of the same sample was used at each temperature to compare against other membrane types and AgI materials. In that manner four different membrane quarters could be developed together at a particular temperature and ss. The erratic AgI vs temperature variation for the condensation development is typical and may be due to condensation sites not related to the AgI sample that compete for the moisture. Fig. 3 also presents the data for similar sets of quarters developed by the cloud technique. The ice crystals formed almost at once. The counts are much more consistent and an order of magnitude higher than before, and are within 58 and 67% of an NCAR ice nucleus counter (Langer, 1973a) monitoring the same aerosol. The NCAR counter has been in close agreement with the CSU isothermal chamber (Langer, 1973a) which operates at a low ss and is considered the best system for evaluating AgI generators. The shape of the membrane temperature-spectra curve for the flare particles from the cloud is flatter than a typical acetone generator curve from the CSU facility as shown in Fig. 3. This is typical for flares compared to acetone generators.

The shape of the membrane temperature-spectra curve suggests mutual interference of ice nuclei, because the curve is not as steep as the CSU curve when a higher number of ice nuclei are potentially available at lower temperatures. Fig. 4 shows a photo of four AgI samples of varying concentrations. The decreases of crystal size with an increase of nucleus concentration is obvious. The water-deprived region around an ice crystal, which can grow uninhibited to 100 μm in 5 min at a nominal 2% ss, can be seen in Fig. 5; it extends to four crystal diameters. The problem of interference is therefore greater when the crystals do not appear at the same time and is therefore less severe for cloud development. There the ice crystals develop at the same time and a stronger supply of moisture exists. From experience: an upper limit of 100 ice nuclei cm$^{-2}$ is recommended to avoid interference when using the cloud method.

Fig. 6 shows the temperature spectra from membrane filter (Millipore 0.22 μm) samples taken during the operation of an AgI-NH$_4$I generator. The curve for AgI-NH$_4$I at 1% ss for the condensation process shows a poor response, but the relative shape of the cloud development curve is in good agreement with the CSU calibration of this type of generator. At $-20^\circ$C the cloud membrane counts are within 20–50% of those obtained by the NCAR counter, depending on the type of membrane used for the AgI-NH$_4$I samples. The 0.22 μm membranes give the highest counts.

Fig. 7 shows temperature spectra for powdered AgI particles in the 0.5 to 3 μm range (deposited by settling

<table>
<thead>
<tr>
<th>Material</th>
<th>Size range (μm)</th>
<th>Median diameter by count (μm)</th>
<th>Form of particles*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal AgI</td>
<td>0.01–0.08</td>
<td>0.06</td>
<td>Small chains of 2–10 particles</td>
</tr>
<tr>
<td>Flare AgI</td>
<td>0.05–1.0</td>
<td>0.1</td>
<td>Chains of up to 100 particles</td>
</tr>
<tr>
<td>AgI-NH$_4$I solution</td>
<td>0.01–0.07</td>
<td>0.03</td>
<td>Single particles</td>
</tr>
<tr>
<td>AgI powder</td>
<td>0.1–3.0</td>
<td>0.5</td>
<td>Single particles</td>
</tr>
</tbody>
</table>

* Not necessarily all AgI particles.
Fig. 4. Ice crystals nucleated by varying concentrations of AgI flare particles on membrane filters.

Fig. 5. The effect of water depletion on the area surrounding a growing ice crystal.

Fig. 6. Temperature spectra for AgI nuclei from the AgI-NH$_4$I complex using cloud and condensation development at different supersaturations.

Fig. 7. Temperature spectra and absolute efficiency of powered AgI for cloud and condensation development.
in still air on 0.22 μm Millipore filters). The percentage of particles nucleating is shown, giving temperature vs the absolute efficiency of nucleation, which reaches nearly 100% at −20°C for cloud development. The response at 3% ss by condensation development is not as strong and the curve is flatter, but the response is consistent. It was observed that at −6, −11 and −15°C a delay of 6, 2 and ½ min, respectively, was encountered before ice crystals appeared by condensation development. With the cloud they appeared at once; evidently all the active sites were supplied with sufficient water vapor to act immediately. Also, these larger particles nucleated more efficiently at the warmer temperatures than the samples discussed previously. The cloud development curve is of the expected shape. Fig. 7 shows another important effect that was also noted for other nuclei, namely, at the warmer temperatures the curves for the cloud development and condensation process approach each other. This points to the fact that for the condensation development method the vapor supply to the nuclei on a membrane surface becomes inadequate at lower temperatures. That is, the vapor pressure of the ice in the humidifier decreases, while the demand for water vapor increases as the number of ice crystals increases. Finally, during these tests and those with the other AgI particles, it was found that nucleation by vapor deposition at or at less than water saturation was slight compared to the numbers of nuclei activated above water saturation by the condensation and cloud methods.

b. Effect of filter pore size on AgI nuclei counts

An important variable is the membrane filter pore size, when dealing with submicron nuclei. Tests with Millipore 0.8 μm membrane filters yielded an 80% lower activity for the AgI nuclei than did Millipore 0.22 μm membranes. Nucleopore 0.4 μm membrane filters were also tested (by the cloud method mounted without Vaseline on a silicone treated metal surface) because of their unique uniformity in pore size. They presented a different response for smaller (0.02–0.1 μm) particles of AgI and phloroglucinol, respectively. The latter were atomized from an ethyl alcohol solution and the response was about the same on the Nucleopores as on the 0.22 μm membranes. For the AgI, only about one-tenth as many nuclei were detected on the Nucleopores as on the membranes. The collection process for the much smaller AgI particles leads to deposition along the pore periphery and in the pores (Roddy, 1971; Spurny et al., 1971) and may lead to agglomeration of particles.

c. Mode of nucleation of AgI

For AgI detection it is evident that the condensation procedure is only effective for larger particles. But it cannot be concluded that small AgI particles are inactive under natural conditions where the ss is low, only that the standard membrane technique fails for those small nuclei because they require a certain amount of ss to nucleate. For example, pure AgI particles of modal size 0.05 μm require a 0.5% ss as determined experimentally by Jiusto and Kochmond (1968). Lala and Jiusto (1972) point out it is unlikely that even water saturation can be reached on a membrane surface in a static thermal gradient system. They suggest that an airflow system should help; our results support this, but we still show a problem of insufficient moisture supply until the cloud development method is applied. One conclusion is that the AgI particles under natural conditions are reasonably active cloud condensation nuclei, given some time to age in the atmosphere (Alkezweeneey and Radke, 1973), and nucleate ice by the condensation-freezing process. However, Mahata and Alofs (1974) dispute any CCN activity by AgI. Or, as reported by Katz and Filié (1974), AgI nucleates by vapor deposition at or above water saturation. Another possibility is that AgI particles nucleate principally by direct contact (Farung, 1973; Sax and Goldsmith, 1972) with water droplets, which could be the case in our cloud procedure, i.e., drops form by condensation on the substrate and then touch AgI particles. But other studies (Langer, 1973a; Medaliev and Sulakvelidze, 1965) indicate that this contact process is not effective. Because of these divergent views the following tests were made.

With an electrostatic precipitator, submicron AgI particles were deposited at room temperature simultaneously on a piece of hydrophobic membrane, a hydrophobic metal surface (highly polished, thoroughly cleaned brass, treated with silicone resin), and a hydrophilic metal surface (polished brass, detergent and solvent washed, distilled water rinse). These samples were then removed and developed at −20°C by the cloud technique. If the nuclei were active by contact with drops, which remained on the plate for over 5 min, the nucleation rate should be reduced on a hydrophobic surface, because fewer drops form and the chances of a drop touching AgI particles are reduced. On the other hand, if the nuclei act by condensation-freezing or vapor deposition, activity should increase in view of the fact that these processes would now favor the AgI particles because interference from the substrate is reduced. On the hydrophilic metal, surface droplet condensation was very dense but no ice crystals formed. On an adjacent area that was hydrophobic (treated with silicone resin), an excellent response to AgI was noted. This indicates that water vapor condenses or deposits on small AgI particles when there is not an excess of other active condensation sites. Thus,

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6 See footnote 3.
condensation-freezing or deposition predominates. The hydrophobic membrane also behaved like the hydrophobic metal surface. On the hydrophilic metal surface, condensation easily takes place on the metal itself, i.e., no measurable ss is required for condensation; this is not the case for the AgI nuclei, which remained inactive. But, many of the AgI nuclei should have nucleated regardless on the hydrophilic metal foil, if they act by contact, when they were touched by growing water drops, which surely must have been the case since the drops were very numerous. That not one froze indicates that the AgI did not act efficiently by contact, at least on a substrate.

The possibility that AgI would nucleate by contact in the airborne state was investigated by placing 2–3 mm diameter water drops mounted on a lightly Vaseline treated membrane into the developing chamber with the air at ice saturation at −15°C. Two cubic centimeters of AgI nuclei in approximately −40°C dew point air (10⁴ nuclei cm⁻³, as determined with an NCAR counter at −20°C) were injected with a syringe. The nuclei were in the 0.01–0.1 μm range. After about 10 s the first drop froze and others followed during the next 30 s, but 20–50% remained unfrozen. After a few minutes all activity ceased, the nuclei having diffused to the walls. Most of the drops were frozen by ice crystals that drifted in from an adjacent drop that was freezing. These crystals were clearly seen to form in the air next to a freezing drop, i.e., from the moisture that was released as a drop warmed to near 0°C during freezing. [Rosinski and Kerrigan (1972) have treated this process mathematically.] The crystals settled out around the freezing drop. Significantly, in the several runs made, the fraction of unfrozen drops was inversely proportional to the number of original drops (from 4 to 50 drops were used, spaced uniformly on a clean 47 mm hydrophobic membrane filter). This is inconsistent with nucleation by contact, since the probability of nucleus contact with any given drop does not depend on the number of drops. However, the probability of contact of a drop with a floating crystal is dependent on the spacing of drops. As seen in the undisturbed air in the chamber, the crystals settled within 1 cm of the drop whose freezing created them. The crystal effect does not suggest contact nucleation as taking place. Subsequent cloud development of the membrane filter revealed an active ice nucleus density of 2×10⁹ cm⁻³, between as well as near drops. Therefore, each drop was contacted by at least 100 nuclei. It is concluded that the freezing was initiated by a rarer nucleus that became active by vapor deposition near a drop where the saturation with respect to water is nearly 100%. This set off the ice crystal effect described above.

These findings are consistent with the conclusion by Medaliev and Sulakevildze (1965) that large drops are not efficiently nucleated by contact with small AgI particles. That is, the nuclei do not become active until −13°C or below. Also, small drops in the 1–10 μm range are not effectively nucleated by 0.02 μm diameter AgI particles by contact above −18°C according to research at the British Meteorological Office (Klaar, 1973). We obtained similar results with small drops in the 5–100 μm range using our above technique of placing the droplets on a Vaseline treated membrane and injecting submicron AgI smoke particles.

4. Detection of natural nuclei on membranes

Tests with kaolin, a clay material found in many soils, are given in Fig. 8 to show the response of a homogeneous particle population of a natural material. The particles (deposited by settling in still air on 0.22 μm Millipore filters) are in the 1–10 μm range. The difference between condensation development and the cloud is much less than for AgI. Also, the changes in activity vs temperature parallel each other for the two methods of development. Note that at the warmer temperatures the difference between two developing methods becomes smaller, a trend noted before (see the data for the larger AgI powder particles in Fig. 7). It indicates that the increased water flux at the warmer temperatures for condensation development is better able to keep up with the extraneous vapor sinks on the membrane. It is evident that the membrane method using the conventional condensation procedure is effective for these larger particles.

Fig. 9 gives data from samples of outside air collected during a strong inversion that filled the Denver–Boulder
area of Colorado with smog that reached the NCAR laboratory. Three NCAR ice nucleus counters were operating at $-20$, $-17$ and $-14^\circ$C respectively and showed very high ice nucleus counts for this location. These counts were quite stable for a period of several hours. Simultaneous samples of 10, 30, 47 and 74 liters were taken on three sets of four membrane filters, each set of a different filter type.\footnote{The Sartorius membrane filters (Catalog no. 11307) are available from Science Essentials Co., Box 6100, Anaheim, Calif. 92806.} (see Fig. 9). The deposit area of a 47 mm diameter membrane filter is 15 cm$^2$. The data are rather variable but some definite trends can be noted. The NCAR counter becomes less responsive at warmer temperatures compared to the membranes developed by the cloud procedure. (The data from the condensation process show little response to the nuclei, indicating that the nuclei are quite small and need a definite supersaturation to become active). The response of the Millipore type membrane is interesting, as it shows high activity even at $-14^\circ$C. It is surmised that the condensation nuclei ($\sim 10^4$ cm$^{-3}$) collected along with the ice nuclei (probably the larger lead particles) interfered less. Possibly, they penetrated further into this membrane. The volume effect (the failure of counts to be proportional to volume) becomes quite noticeable with samples greater than 250 liters (not shown in figure), that is, there is no further increase in count with increases in the sample volume. As the sample volume increases the response becomes less variable; at this point the condensation nuclei are starting to mask the ice nuclei.

For the above samples water saturation may not be exceeded at all unless the cloud technique is used. It is clear that the smaller nuclei, below 0.1 $\mu$m, will not experience even H$_2$O saturation unless a strong source of water vapor is present. Evidently these small particles, being totally within the surface structure of the membrane, are not able to act as effective CCN compared to when they are suspended in air. Particles of this size may partially penetrate into the filter and become completely inaccessible for nucleation. Tests were made to evaluate this possibility. Equal volume samples of smog were collected at the same time on four membranes, each of a different porosity. The count by the cloud method for the 0.22 $\mu$m membrane was from 4 to 7 times more than that of the 0.45, 0.65 and 0.8 $\mu$m membranes.

Initial work samples of smoke from coal or oil fired power plants showed an interesting difference between membrane filters and the NCAR counter. The membrane samples show considerable activity, while the NCAR counter does not respond. The nuclei are apparently relatively soluble and when condensation takes place on them at temperatures above freezing in the NCAR counter, they dissolve and do not nucleate ice. With the membranes, condensation does not take
place until the final temperature is reached, so the nuclei can be detected.

Samples were also taken at ground level and a few thousand meters above ground level in a prairie grass area with some farming activity in northeast Colorado, in order to obtain air samples free of city pollution. The temperature spectra (Fig. 10) with 0.22 μm Millipores show more activity than with kaolin and again demonstrate the tendency for the counts by the condensation and cloud methods to approach each other at warmer temperatures. Also, the difference between the two methods is much less than for small AgI and smog particles. Unlike the kaolin, these dust samples are active below water saturation.

During the above tests it was noted that particles over 15 μm often seemed to have rolled off the membrane onto the filter housing during subsequent handling, and were not included in the nuclei counts. So tests were made with different size fractions above 10 μm of northeast Colorado soil particles on membranes to estimate their ice nucleating potential. Table 3 summarizes some of the results. It is obvious that the larger particles are very active. At the warm temperatures these particles had an activation period of 10 min at −6°C. The particles were oven dried before fractionation by sieves, so in the field the delay may not be as long. This points out the advantage of the membrane technique, where particles can be exposed to the desired conditions for long periods of time, whenever a delay in the activation of the ice nuclei may be significant. The question is, in what quantity do they exist in nature?

5. Application of membrane technique to field projects

It is interesting to examine the data obtained from various field projects with membrane filters in light of the above research as it may explain the discrepancies encountered and, more importantly, will help in making proper use of the membrane technique.

Various efforts have been made to sample naturally-occurring ice nuclei with membranes. In 1969, a worldwide network was operated for three months (Bigg, 1970). There was so much variability in the data that no particularly significant trends could be discerned. In 1973, initial results from several months of operating a network in the western United States (Allee, 1973) showed internal consistency of data and definite trends related to large-scale air circulation. The membrane filters were developed using the NCAR flow method with condensation development at water saturation. Another important point was that the stations were carefully selected away from local sources of ice nuclei. As pointed out earlier, small nuclei from industrial activity and automobile traffic are not detected effectively at low ss. In that respect, the results of Mossop (1972), relating ice nuclei counts from membranes to ice crystal counts in maritime cumulus clouds, are of interest. The nuclei counts were very much lower than the ice crystal counts, while Gagin (1971), running a

<table>
<thead>
<tr>
<th>Method of development</th>
<th>Temperature (°C)</th>
<th>Nominal ss</th>
<th>10–44</th>
<th>44–74</th>
<th>74–117</th>
<th>117–250</th>
<th>250+</th>
</tr>
</thead>
<tbody>
<tr>
<td>Condensation (low ss)</td>
<td>−6</td>
<td>2</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
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<tr>
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<td>0.6</td>
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<td>66</td>
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<tr>
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<tr>
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<td>12</td>
<td>88</td>
<td>100</td>
</tr>
<tr>
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<td>0.7</td>
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<td>100</td>
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<tr>
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<td>21</td>
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</tr>
<tr>
<td>Cloud</td>
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<td>—</td>
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<td>2.9</td>
<td>14</td>
<td>96</td>
<td>100</td>
</tr>
</tbody>
</table>
similar experiment on continental clouds, did not encounter this discrepancy. These questions again may be related to the size of the nuclei, i.e., in Mossop’s case the nuclei may have been small.

Considerable experience has been accumulated with membrane filters in detecting AgI by the cloud technique in parallel with an NCAR counter, and at times with a Bigg-Warner expansion chamber. This was done during a winter orographic cloud seeding project, with samples being taken on the ground and from an aircraft, and during a cumulus seeding project in the summer (Super and McPartland, 1973), where airborne samples only were collected. The response from the 0.22 \( \mu \text{m} \) membranes and a Bigg-Warner chamber were rather erratic under seeding conditions in the winter program (Grainger and Super, 1973); that is, the counts were lower by one order of magnitude on the average, and correlated poorly with the concentrations indicated by the NCAR counter. The latter gave counts in good agreement with the established output of the AgI ground generators (Super, 1974). Airborne membrane-filter samples taken in winter under cloudy conditions but with little precipitation gave better agreement with the NCAR counter (Super, 1972); that is, the membranes gave on the average 40% of the NCAR counter counts but with considerable scatter. It seems clear that in this case not as many of the active nuclei were removed by precipitation formation. In summer plume tracking with no precipitation (Grainger and Super, 1973), the agreement with the membranes at \(-20^\circ\text{C}\) was good. For 20 samples it averaged at a 1:1 ratio but with some scatter.

6. Overall conclusions and suggested scope of the technique

The first question is the choice of membrane filters. The 0.22 \( \mu \text{m} \) pore size is usually the best compromise from the standpoint of flow rate vs penetration by particles. Also, the membranes should have a low blank count, which was satisfactory for the membranes tested. Roddy (1971) reports better results with hydrophobic filters, with which we agree. Filters that are readily wetted by water make it impossible to detect AgI even by the cloud method, because the hygroscopic glycerine that is usually incorporated into these filters will prevent water saturation at the membrane surface.

To detect AgI efficiently, the cloud method must be used at lower temperatures (below \(-12^\circ\text{C}\) or so) because the water vapor flux is too low with the condensation method. This is also true for other nuclei of small size. Basically, ice nuclei are not very soluble and condensation on the ice nuclei is further interfered with by the substrate on which the particles rest; that is, the affinity of the substrate and other non-nucleating particles for water vapor at the lower temperatures is stronger than the flux of water vapor available and no supersaturation or not even water saturation can be achieved. This view is also confirmed by Gravenhorst et al. (1973) who found much improved development of membrane filters in a vacuum diffusion chamber which avoids the resistance of the air molecules to the transport of the water molecules.

The condensation procedure gives good results with particles \(>1 \mu\text{m} \). These particles protrude above the surface discontinuities of the substrate and so are freer of substrate interference because of their bulk. For these particles, the membrane technique is especially attractive to study delay of activation, effect of relative humidity, particle size, pre-treatment, etc. For giant particles, which cannot be held suspended for detection in mixing chambers or the NCAR counter, the membrane technique is unique.

The question of interference by other particles collected along with the nuclei also relates to nuclei size. Interference was found to be severe with the submicron nuclei in urban haze, limiting the total sample volume to 5 \( \ell \text{cm}^{-3} \) of filter surface and requiring cloud development. Away from cities, where blown dust is the main source of nuclei which are relatively large, i.e., above 1 \( \mu\text{m} \), no volume effect was noted, even when the filters were obviously discolored with sample.

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REFERENCES


