Ice nucleus measurement with a continuous flow chamber

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SUMMARY

A continuous flow vapour diffusion chamber has been designed and constructed so that ice nuclei can be activated over ranges of temperature and supersaturation similar to those found in natural clouds. A conventional filter-processing chamber was also built for carrying out comparative measurements. Simultaneous use of the two chambers under similar conditions of temperature and supersaturation has shown that the filter method leads to an underestimate of the concentration of ice nuclei in an air sample. The ratio of the two simultaneous measurements is strongly dependent on the concentration of Aitken nuclei in the air sample and is also dependent on the chamber supersaturation. Some tentative evidence of the presence of condensation–freezing nuclei active above water saturation is presented.

1. INTRODUCTION

Ice nucleus concentrations measured with the filter method often fall well below the observed concentrations of ice crystals in clouds. A recent review is given by Pruppacher and Klett (1978). Although the concentration discrepancy can sometimes be accounted for by an ice multiplication process, there are many cases where the filter method has proved inadequate. For example, in the case of cold winter-time orographic clouds reported by Cooper and Saunders (1980) the conditions did not fulfill the requirements of the Hallett–Mossop (1974) multiplication process but ice crystal and nucleus concentrations differed by two to three orders of magnitude. The major problem with the filter method, in which a filter is subjected to a supersaturation in a static diffusion chamber in order to activate the ice nuclei trapped on its surface, is that the large number of hygroscopic particles trapped together with the ice nuclei compete for the available water vapour and thus deplete the vapour supply. For this reason it is unlikely that conditions of water supersaturation can be achieved over a filter surface. This leads to two problems: (i) the number of crystals activated provides an underestimate of the true nucleus concentration; (ii) only deposition nuclei are activated. There were strong indications from ice crystal concentration measurements in the orographic clouds mentioned above that condensation–freezing nuclei were active in the cloud edges where water saturation was achieved. Such nuclei would not be activated by the filter method. The present work describes an attempt to overcome the limitations of the filter method with a processing chamber that simulates atmospheric conditions experienced by ice nuclei, both above and below water saturation. A continuous flow chamber was designed and constructed to provide a temperature- and supersaturation-controlled environment through which an air sample may be drawn in which ice nuclei may be activated and grow into ice crystals. In order to compare the continuous flow technique with the conventional filter method, a static diffusion filter processor was also built and both devices were used together.

2. THE STATIC DIFFUSION CHAMBER

The use of membrane filters to study ice nucleus concentrations has become widespread since its introduction by Bigg et al. (1961). Ice nuclei caught on the filters are activated and grow to visible size in a chamber in which the filter is cooled to cloud temperature and supersaturation is provided by a local heated ice surface. The nuclei activated are deposition (sorption or sublimation) nuclei. This technique is convenient because filter samples can be gathered and processed later without degradation of the

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nuclei (Stevenson 1968). Bigg (1963) pointed out that the nucleus concentration detected decreased with increase in volume sampled. This volume effect has been studied by Mossop and Thorndike (1966), Gagin and Aroyo (1969), Lala and Jiusto (1972), Huffman and Vali (1973), Ohtake and Jayaweera (1974), Zamurs et al. (1977) and others and has been attributed to vapour depletion on the filter surface around growing ice nuclei and hygroscopic particles. Stevenson (1968) and Alkezweeny (1970) found no volume effect, while Goldsmith et al. (1976), who used the Stevenson method of vapour diffusion from a distant source, found evidence of an effect down to volumes of only 200 ml. Lala and Jiusto (1972), Zamurs et al. (1977) and Vali (1975) noted that the separation between filter and ice surface influences the number of nuclei detected, with an extrapolated zero separation giving the largest count. Various schemes have been proposed to overcome these problems – Huffman and Vali (1973), Zamurs et al. (1977) and King (1978) – although without complete success because the correction factors depend on the aerosol composition. At the Ice Nucleation Workshop (Vali 1975) two static diffusion chambers agreed to within a factor of three for similarly processed filter samples. The workshop confirmed that the activation of ice nuclei is strongly dependent on supersaturation, in agreement with Huffman (1973), who found that the nucleus concentration $N_i$ follows the relation $N_i = AS_i^b$, where $A$ and $B$ are constants and $S_i$ is the supersaturation with respect to ice (in per cent). At the workshop, this relationship was found to be valid between $-12$ and $-20 \, ^\circ\mathrm{C}$ for values of $S_i$ in the range 8 to 22%. The value of $B$ varied between 3 and 10 depending on the particular aerosol.

The chamber built for the present work, Fig. 1, followed the design of Gagin and Aroyo (1969) and Jiusto and Lala (1976) in which four 47 mm diameter filters could be processed simultaneously. Filters of pore size 0.45 $\mu \text{m}$ were used, which trap most particles of the size of ice nuclei on their surface (Roddy 1978). The sample time was 20 minutes during which four filters were exposed simultaneously achieving a sample volume of 1001 per filter. Activated ice nuclei grew to visible size in 45 min after which the top plate was replaced with a transparent plastic cover while the crystals were counted with the aid of a magnifying glass and a light beam to illuminate those crystals which grew at various angles to the filter surface.

![Side View](image)

**Figure 1.** The static diffusion chamber.

The chamber height of 0.7 cm was chosen after preliminary experiments with various wall heights showed that the nuclei detected increased with smaller chamber heights, in agreement with other workers. The commonly used value is 1 cm (Bigg 1971; Huffman 1973), while Zamurs et al. (1977) used four thicknesses from 1.5 to 0.25 cm. An excessive chamber height causes air currents to be set up which distort the uniform vapour diffusion field. Elliott (1971) calculated that chamber aspect ratios greater than five to one are required to minimize this circulation; the present chamber has a ratio of 20 : 1.

Preliminary experiments were performed to check that the chamber behaved in the same manner as other chambers and therefore could be compared fairly with the data from the continuous flow chamber. Several types of blank filter were processed at $-16\, ^\circ\mathrm{C}$
and 16% supersaturation with respect to ice. It was found that Hydrophobic Sartorius 13306 filters had the lowest background count, 2.3 ± 1.1, and so were used in the main experiments; a correction was applied to the data.

The volume effect was investigated by sampling volumes between 50 and 10001; the samples of over 5001 generated visible colouring of the filter by dust. The filters were processed at −15.5°C and $S_i = 15\%$; the detected nucleus concentration, $N_i$, plotted against sample volume, $V$, is shown in Fig. 2, where the power curve $N_i \propto V^{-k}$ gives values for $k$ of 0.63 and 0.67 for two sets of filters gathered on different occasions. Figure 2 shows that the volume effect in the present chamber is similar to that in other chambers of similar design.

![Figure 2](image)

Figure 2. The SDC volume effect. A, Mossop and-Thornbke (1966); B, Huffman and Vali (1973); C, present study.

3. DEVELOPMENT OF THE CONTINUOUS FLOW CHAMBER

The chamber constructed for these studies is similar in concept to the continuous flow chamber, CFC, developed by Hudson and Squires (1973) for the study of cloud condensation nuclei and is similar in design to that built for ice nucleus studies by Cooper, Vali and Rogers (1976, private communication). These chambers draw sample air, sandwiched by clean, dry, filtered air, between two horizontal temperature-controlled plates. For ice-nucleus studies the plates are ice coated and a supersaturation is obtained in the chamber when the top plate is warmer than the lower plate. The design is such that nuclei experience only a very narrow range of supersaturation as they flow through close to the mid-plane between the plates.

The CFC consists of two flat aluminium plates (120 cm × 30 cm) separated by vertical perspex side walls (Fig. 3). Chilled methanol solution is pumped from coolers having ±0.03°C temperature control through cooling courses inside the plates. The outer walls and sides of the chamber are insulated with 10 cm thick polystyrene sheets. Unique to the design of this chamber are the hinges along its length which permit the inside plate surfaces to be exposed and lie flat. The ice layers are made by pouring water onto the
plates, which are then frozen and polished before the chamber is closed. Rubber gaskets lubricated with silicone grease between the side wall and the plates are compressed tightly by clamps which pull the plates together to make the chamber airtight. Thermocouples, embedded in the ice, were calibrated to ±0.03°C by means of a platinum resistance thermometer to provide accurate values of the supersaturation. A cooled extension to the bottom plate supports a shallow tray holding supercooled sugar solution used to detect the ice crystals. An alternative unit connects the end of the chamber directly to a Royco optical particle counter in parallel with the pump. The air sample is drawn into the chamber through a row of fine jets mid-way between the plates. The sample air flows between layers of dried and filtered air. Smoke tests verified that the sample remains in a thin layer during its passage through the CFC for the flow rates used in the experiments. The Reynolds number for the maximum flow rate used, 151min⁻¹, was only 224 confirming that flow through the chamber is laminar.

The supersaturation in the chamber is determined by assuming a linear temperature and vapour pressure gradient between the plates (Katz and Mirabel 1975). The saturation vapour pressure, $e_{ix}$, determined from the Clausius–Clapeyron equation for the appropriate temperature at any point distant $x$ from the bottom plate, is less than the actual value, hence the saturation ratio with respect to ice, $s_i$, is given by

$$s_i = \frac{x(e_{iT} - e_{iB})/d + e_{iB}}{e_{ix}}$$

where $d$ is the plate separation and $e_{iT}$ and $e_{iB}$ are the vapour pressures at the top and bottom plates respectively. For water saturation, $s_w$ is obtained by replacing $e_{ix}$ with $e_{wx}$ in the above equation. The steady-state, parabolic profiles of $s_i$ and $s_w$ across the chamber show that, typically, their peak values are about 0.5 mm below the mid-plane.

When an air sample is introduced between the plates of the CFC it takes time for the velocity profile, equilibrium vapour pressure and temperature profiles in the chamber to be set up. The parabolic velocity profile for this chamber is set up in about 2 cm (Brown and Schowengerdt 1979). Carslaw and Jaeger (1951) give non-steady-state solutions for vapour and thermal diffusion which have been solved for the supersaturations and air velocities used in the present experiments. At a mid-plane temperature of −15°C and at 1000 mb with an ice layer separation of 7 mm, time constants for vapour diffusion and
thermal diffusion are 0.26 s and 0.30 s, respectively. Because vapour diffusion occurs faster than thermal diffusion and the incoming sample air is at the environmental humidity, high transient supersaturations can occur before the air reaches temperature and vapour equilibrium. This undesirable effect has been eliminated by leaving the top surface free of ice for 15 cm from the entrance. Thus, a sample of air at +20 °C with a velocity of 10 cm s\(^{-1}\) experiences a temperature gradient which brings it down to 99.9% of its final value in eight time-constants, which corresponds to 24 cm from the entrance. For sample air at 60% r.h. with plate temperatures of -10 and -20 °C the sample loses vapour to the cold ice plate during the first 15 cm (about 5.8 time-constants) and then experiences a vapour pressure gradient when the top ice layer starts. A further four time-constants bring the air to vapour equilibrium at about 26 cm from the entrance. Thus vapour equilibrium occurs after temperature equilibrium so that the only supersaturation experienced occurs when the sample vapour pressure builds up to its predetermined final value between the ice layers. Calculations show that growing particles use up a negligible amount of vapour and so there is no problem due to vapour depletion in this chamber.

The dimensions of the CFC are controlled by the requirement of a high aspect ratio to limit convection-driven circulation (Elliott 1971); thus a ratio of 30:1 was chosen, which also provides a sufficiently large sample volume at the flow rate used. The length of the chamber is controlled by the crystal growth rate, the vertical fall velocity and the velocity through the chamber so that crystals grow to a detectable size, about 10 μm, by the time they reach the end of the chamber, whereupon they fall out onto the supercooled sugar solution. A total chamber length of 120 cm was determined to accommodate both the ice-free region required for temperature equilibrium and the region required for vapour equilibrium followed by ice crystal growth.

Checks with thermocouples placed at various positions on the ice surfaces showed that incoming air at +20 °C at a rate of 10 l min\(^{-1}\) increased the temperatures near the entrance by up to 0.5 °C but that 20 cm inside the chamber ice temperatures remained constant. Ice surface temperatures across the air flow direction in the region of thermal equilibrium were measured with a central thermocouple and another 1 cm from a side wall. The resulting difference in saturation was around 10% of the value at the centre of the plates.

The crystals were detected when they fell onto a bath of sugar solution; experiments showed that a solution of 60% sugar by weight at -8 °C worked well. While detecting activated ice nuclei the solution surface rapidly became covered by growing ice crystals and was unusable after about 10 minutes. An optical particle counter was also used (Royco model 225) which could be connected at the end of the chamber to draw a fraction of the air from the total air flow. This could be used with or without the sugar bath. Results showed that when both techniques were used together, the Royco, set on the range to detect particles greater than 3 μm diameter, detected more crystals than did the sugar bath. The larger crystals were falling into the sugar, but the smaller ones, possibly activated later in the CFC, were being drawn into the pump. A new manifold was built which connected the Royco and suction pump directly to the chamber with adjacent tubes so that the Royco would capture a representative volume of the activated nuclei. (The Royco flow rate of 2-8 l min\(^{-1}\) was fixed and so the air velocity through the chamber was controlled by the variable suction pump flow rate.)

The air sample was introduced into the CFC through a 20 cm long tube and tests were conducted to confirm that particle losses in this tube had no effect on the detected ice nucleus concentration, thus indicating that the nuclei were smaller than 1 μm. Before and after an experimental run, the incoming sample air was passed into the CFC through a filter in order to determine the background count. Experiments conducted above 0 °C showed, in agreement with theory (Pich 1972), that the concentration of particles larger than 3 μm passing through the CFC was negligible due to losses both in the CFC and in the tubes transporting the air sample. Thus the background count detected between runs
was attributed to crystal growth on the ice plates followed by the breaking off of crystals and fragments, which would be counted by the Royco. The background count was high before the first run due to ice 'dust' left on the plates following polishing; in subsequent runs the background was low and then rose steadily between successive runs. A scheme was employed in which data were rejected if the background count was larger than 50% of the actual count, both being sampled for the same time. As an example of the effect of this scheme, of 54 runs at various temperatures and supersaturations only 14 runs were rejected. When the background count was high enough to cause data rejection, the CFC was opened and the ice plates were re-polished. The nucleus count was corrected by subtracting the average of the preceding and following background counts.

It was verified that water saturation could be achieved in the chamber by observing a droplet cloud formed on condensation nuclei in the sample air. A laser was used to illuminate the chamber through the perspex walls and a thin layer of cloud was clearly visible mid-way between the plates. Above water saturation, the water droplets grew in the chamber in the mid-plane region but they evaporated when they fell into the subsaturated region. Confirmation that 3 μm droplets did not reach the Royco was obtained by noting the count as the supersaturation was gradually increased through water saturation; a large increase in count was not noted even when the Royco was used on the 1-4 to 3 μm range.

Preliminary experiments were carried out using the sugar bath alone as a nucleus detector. Total flow rates between 6 and 151 min⁻¹ were used, depending on the required crystal growth time for the value of S₁ applied. The sample flow rate was between 2 and 41 min⁻¹. Each experiment took 45 to 60 minutes during which time 3 to 5 runs were possible under similar chamber conditions. These values were averaged to give a measure of the variability as an 'error' of between 2% and 20% of the mean value. A series of measurements in Cumbria at an average S₁ of 14-7%, all below water saturation, detected an average nucleus concentration of 0.71⁻¹; in Manchester, with an average S₁ of 14-4%, the average was 0.91⁻¹ which increased to 1.21⁻¹ for S₁ > 1. The errors involved indicate that these differences are insignificant; however, the air samples were not the same over the period of study. Studies in Manchester with many air masses in which two or more values of S₁ were applied to samples from the same air mass, showed that the ice nucleus concentrations increased by a factor of between 2 and 8 when S₁ was increased from 12% to 20%. In one set of experiments with easterly winds accompanied by snow, no ice nuclei were detected with the CFC or with the filter method.

4. Results and Discussion

A direct comparison was made between the CFC and filter techniques for the detection of natural ice nuclei. Filters were sampled after running the CFC with a mid-plane temperature of −16 °C over a range of supersaturations. The filters were later processed at the same temperature and supersaturation. The data are plotted in Figs. 4(a–f), while Table 1 shows the corresponding values of B. Each CFC spectrum was obtained within 60 minutes in order to make all measurements from the same air mass; each point has an error of between 5 and 20% and is the average of several experiments. The error bars on the filter, SDC, spectra reflect differences between the four filters processed simultaneously. An average factor, F, was determined of the ratio of nucleus concentration detected by the CFC to that detected by the filter method; at 12% S₁, F = 5 ± 2; at 15%, F = 8 ± 3; while at 18%, F = 13 ± 4. There is a clear increase in F with supersaturation.

The results of an investigation into the relationship between ice nucleus concentration detected using the two techniques at −16 °C and the Aitken particle concentration (CN) detected with a Nolan–Pollak counter are shown in Fig. 5. Figure 6 is derived from Fig. 5 and they both show that the CFC indicates an increase in ice nuclei detected with increase in the CN concentration and supersaturation whereas the filter method shows a
Figure 4. Continuous flow and static diffusion chamber data. △, CFC; ▲, SDC. The arrows mark water saturation.

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TABLE 1. COMPARISON OF THE CFC AND SDC ICE NUCLEUS–SUPERSATURATION SPECTRA (VALUES OF B FROM $N_i = AS_i^B$) FOR THE SIX CASES SHOWN IN FIG. 4.

decrease in ice nucleus count with increased CN concentration. These results highlight the dependence of $F$ on CN concentration. For example, at water saturation, when the CN concentration is $6 \times 10^7 \text{L}^{-1}$, $F = 1.4$ but for CN $= 24 \times 10^7 \text{L}^{-1}$, $F = 36$. The results are qualitatively consistent with vapour depletion at the filter surface due to competition between growing crystals and hygroscopic particles captured with the ice nuclei, a problem avoided in the CFC.
An initial objective of these studies was to look for evidence of the condensation-freezing mode of ice nucleation. Figures 4(a–f) show results obtained both below and above water saturation which indicate that the data fit the usual relationship $N_i = AS^p$. The different slopes of the CFC and filter data provide some evidence of a different mechanism of ice nuclei activation by the two methods. By replotting this data on linear
plots, the behaviour of the nuclei as water saturation is reached and exceeded can be studied. Below water saturation, the nucleation mode is that of deposition although condensation followed by freezing may occur on some mixed aerosols having both hygroscopic and insoluble components. Above water saturation there is a greater possibility of condensation followed by freezing as well as the activation of deposition nuclei. Figure 7 shows that there is evidence in some cases that the gradient increases above water saturation. It appears therefore that some of the nuclei present in these experiments may have been condensation–freezing nuclei which were activated in the CFC above water saturation.

5. CONCLUSIONS

A continuous flow technique of activating ice nuclei has been developed which overcomes some of the problems associated with the widely used filter technique. The filter method is very convenient while the continuous flow method involves bulky apparatus at the site of the air sample which will not always be possible to arrange. Comparisons between the filter and CFC results for samples from the same air mass have provided here a factor $F$ which is a function of the chamber supersaturation and the total number of aerosol particles present. The higher counts obtained with the CFC compared with the filter method suggest that such particles can also contribute to the vapour depletion problems associated with the filter method, which are manifest in the volume effect.

The values of $B$ in $N_i = A S_i^B$, obtained here with the filter method, are similar to values obtained elsewhere in the world, while the values of $B$ from the CFC are higher (Table 1). Thus there is some evidence that the CFC activates both deposition and condensation–freezing nuclei.

The major conclusion of this work is that the discrepancy between ice crystal and ice nucleus concentrations observed in some clouds is probably due to the limitations of the filter technique which can be overcome with the use of a continuous flow chamber.

ACKNOWLEDGMENTS

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