Factors Affecting Ice Nucleus Concentration Measurements with a Static Vapor-Diffusion Chamber

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ABSTRACT

This paper presents some findings and recommendations for obtaining more reliable information from ice nucleus concentration measurements with the membrane filter technique commonly in use. Variables related to chamber design, filter preparation and crystal counting are discussed.

1. Introduction

The filter method represents a popular means of measuring ice nuclei (IN) concentrations. However, the number of IN activated at a prescribed temperature and humidity can be crucially affected by the design and operation of the diffusion chamber in which the particles are detected. In addition, the type of filters used and their preparation also can influence the results. This paper presents an analysis of certain variables that affect IN measurements with a static vapor-diffusion chamber and amplifies on or adds to certain filter method variables previously addressed (Bigg *et al.*, 1963; Mossop and Thorndike, 1966; Stevenson, 1968; Lala and Jiusto, 1972; Gagin, 1973; Huffman and Vali, 1973; Langer and Rodgers, 1975). Some preliminary IN supersaturation spectra data are presented, as they also appear dependent on chamber operation. Most measurements described were made at Albany, N.Y., with selected comparisons from the 1975 International Ice Nucleus Measurements Workshop at Laramie, Wyo.

2. Equipment and operation

The SUNY static vapor-diffusion chamber used to process membrane filters represents an improved version of that described by Lala (1972). Basically the chamber, as shown in Fig. 1, is operated within any cold box of suitable size and low temperature capability. Both the bottom filter plate and upper ice surface (3.2 mm thick) are independently temperature regulated by means of heater wire. Thus, temperature control of the respective surfaces is achieved by heating rather than by thermoelectric cooling. Temperature gradients across the chamber are less than 0.1°C and the error in the temperature difference between the upper and lower surfaces is less than 0.03°C. Four filters can be processed simultaneously, and after 45–60 min, the developed crystals can be observed from above with a long working-distance microscope and vertical illumination. A distinctive feature of the chamber is the ease of altering the distance between the upper ice surface and the filters. This is accomplished by interchanging the separator rings which support the top ice plate above the filters.

All of the filter results described apply to natural IN concentrations, with the filters being typically exposed to 100 ℓ of ambient air at a flow rate of 6.25 ℓ min^{-1}. The filters used in this study were plain white and ungridded, the majority of which were 0.45 μm pore-size Millipore filters (HAWP). Other filters tested were Sartorius hydrophobic of pore sizes 0.45 μm (SM 13306) and 0.05 μm (SM 13310); 0.22 μm pore size Millipores (GSWP); hydrophobic Millipore fluoropores of pore size 0.5 μm (FHLP); and non-wettable, 0.45 μm pore size Millipores (HATF), i.e., filters without the standard Millipore wetting agent.

Several sealant materials, customarily used to seal the bottom pores of filters prior to processing, were tested for spurious crystal development: laboratory grade petroleum jelly (Petrolatum, manufactured by VWR Scientific Company); commercial grade petroleum jelly (Vaseline brand); STP oil (STP Corporation of Fort Lauderdale, Fla.); and paraffin ("Tissue-Prep," Fisher Scientific Company). In preparing a filter, 0.5 cm^3 of, say, petroleum jelly is melted and cooled on a thin (1 mm) aluminum disc. The filter is placed on top of the petroleum jelly layer, which is then reheated until a slight color change of the filter is noted. The discs with filters are then put in the chamber, and a reverse temperature gradient is applied (bottom plate warmer than the top ice surface). This serves to evaporate any droplets which fall on a filter during loading in this type of "open" cold-box system. After

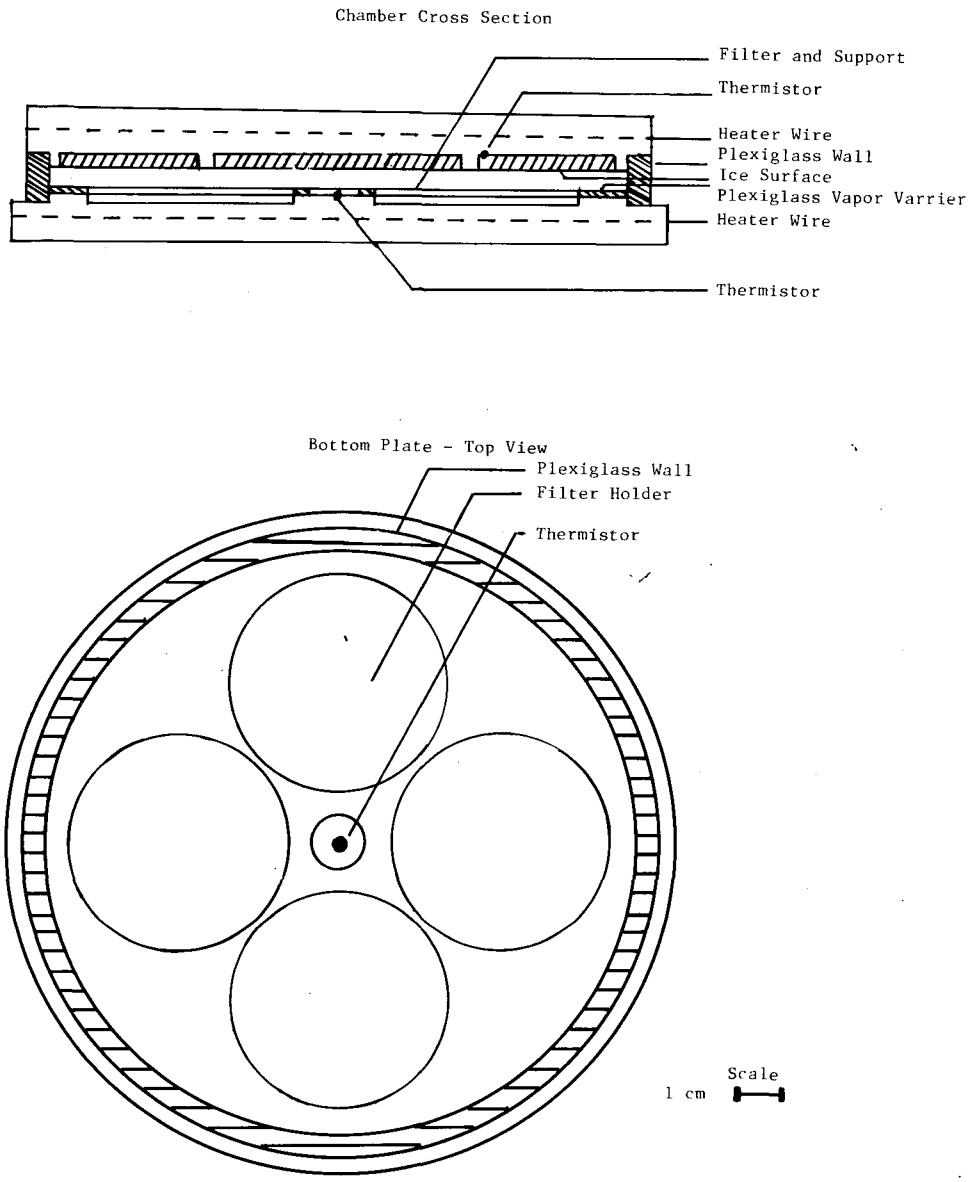

FIG. 1. SUNY ice nucleus chamber (static vapor diffusion type).

several minutes, the bottom plate is cooled to the operating temperature and then the top plate is warmed to establish the required temperature gradient and humidity at which the filters are then processed.

3. Experimental results on system variables

a. Filter preparation and processing

Laboratory grade petroleum jelly proved to be the preferred sealant because of generally lower associated background counts, i.e., approximately 15 at −20°C and calculated water saturation. Vaseline is an acceptable alternate, as well as STP (based on other tests at the Wyoming Workshop), provided the latter is not used in an "open" system. In addition, petroleum jelly hardens after application, whereas oils such as STP remain in the liquid state. Petroleum jelly can also be prevented from flooding through the filters with relative ease. This may be a consideration since all the sealants tested promote spurious growth of ice crystals on the respective substance alone (no filters) comparable to the above filter background count.

A method for reprocessing the same filters has been occasionally used. After counting the crystals, they are sublimated by warming the filters for 15 min. Thereafter, the normal processing procedure is repeated at the same or a higher relative humidity. Spyers-Duran (1975) activated nine filters twice after an intermediate drying period in a desicator; counts during the second processing agreed quite well with those of the first

with some 83% correspondence between crystal sites. We have reprocessed filters up to four times at the same or monotonically increasing humidities to obtain concentration-supersaturation spectra. A final processing can be made at the original temperature-humidity condition to serve as a reliability check, or comparisons made with other filters from the same sampling. Agreement in crystal counts averaged within 20–30% (128 filters tested in sets of four), with a tendency for increased concentrations after reprocessing. Photographs revealed that respective crystal locations do not always correspond, as was also noted by Spyers-Duran. One factor, we feel, is that the sublimation residue from crystals (or evaporating droplets) is changed by the incorporation of the adjacent aerosol material into the residue, thereby leading to new crystal growth, or perhaps in some cases retardation. However, the overall IN concentration agreement is considered sufficiently good such that reprocessing offers a means of obtaining maximum information from a given set of filters.

b. Chamber height effect

Relatively little attention has been paid to the effect of chamber height (ΔZ) on peak filter humidity achieved and corresponding IN counts in a static diffusion chamber. It was shown theoretically (Lala and Jiusto, 1972) that this variable was highly significant. In short, as ΔZ was decreased, the effective filter humidity reached progressively higher values.

Experiments were run to evaluate theoretical predictions at computed saturation conditions (nominal RH = 100%) and at temperatures of −15 and −20°C. From data obtained in Laramie, Wyo., as well as Albany, N.Y., the trend was confirmed, with IN concentration being an exponential function of height over the range investigated (Fig. 2). Thus, $N \approx N_0 \times e^{-1.7\Delta Z}$, where N_0 is the limiting concentration value as ΔZ approaches zero. For $\Delta Z = 0.25$ and 0.5 cm,

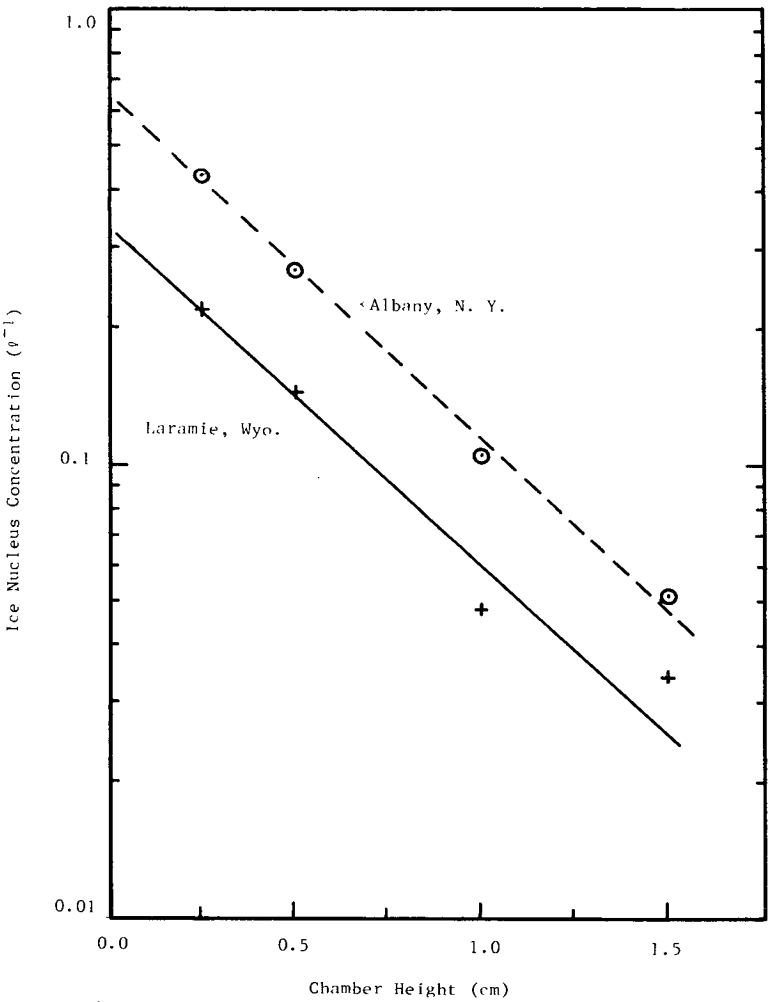

Fig. 2. Ice nuclei concentrations vs chamber height [$T = -20$°C; RH = 100%; $V = 394\ \ell$ (Wyo.), 100 ℓ (N. Y.)].

$N_0 \approx 1.5\,N$ and $N_0 \approx 2.3\,N$, respectively. It is evident that 1) chamber height should be as shallow as possible and 2) an IN concentration correction scheme involving extrapolation of ΔZ to 0 appears appropriate. When so done, filter concentration values approach those made with current and historical cloud formation apparatus (Jiusto *et al.*, 1976).

c. Volume effect

The well-known volume effect whereby crystal concentrations decrease with increasing volume was evident at all four chamber heights tested (0.25–1.5 cm). In general, over the range of volumes from 100 to 800 ℓ the concentration of ice nuclei was reduced by a factor of approximately 5–6. In terms of the customary $N \propto V^{-k}$, relation between concentration and volume a mean k value for Albany is 0.9 with a range of 0.7 to 1.1 ($\sigma = 0.1$) and no systematic variations with chamber height.

Based on limited measurements at the Wyoming Workshop, a k value of 0.86 was obtained. The similarity between results in Albany, and Laramie, suggests that the volume effect might be less dependent on air mass type than previously thought. Indeed, the Albany data, which exhibited only a modest k range, were obtained under significantly differing air mass characteristics. It appears that there are sufficient condensation nuclei even in relatively clean continental airmasses to produce a significant and rather uniform volume effect.

The volume effect was still evident at low volumes ($<100\,\ell$), as was also noted by Ohtake and Jayaweera (1974). The measured concentrations at 50 and 25 ℓ were still increasing from that at larger volumes. We believe that at such small volumes, with fewer IN and aerosol sinks, a higher filter humidity results and the background effect progressively becomes more significant. For standardization and a statistically acceptable number of crystals on a filter, a 100 ℓ sample volume is recommended.

d. Filter types and pore sizes

Experiments were performed to ascertain any difference in ice crystal counts between filters of different types and pore sizes. Millipore fluoropore filters (hydrophobic teflon) were compared to standard cellulose acetate filters of the same pore size (0.45 μm). Based on an average of 16 exposed filters (fluoropore: $N = 1.03\,\ell^{-1}$, $\sigma = 0.30$; standard Millipore: $N = 0.57\,\ell^{-1}$, $\sigma = 0.37$), the fluoropore filters showed a factor of 2 higher ice crystal concentrations. Similarly at the Wyoming Workshop, concentration measurements with Sartorius hydrophobic filters exceeded standard Millipore filters by a factor of approximately 3. Thus hydrophobic filters are superior to regular cellulose filters. They give lower background counts, have more consistent concentrations and yield higher exposed counts. This last factor is due to the hydrophobic nature of the filter which apparently reduces its capability as a sink for water vapor.

Gagin (1973) reported a factor of 1.5–3 concentration difference between 0.05 and 0.45 μm pore sizes of *regular* (nonhydrophobic) Sartorius filters. Yet measurements in Albany with 24 filters of each pore size of Sartorius hydrophobic filters exposed to 100 ℓ of ambient air resulted in no great difference in respective crystal numbers. On the 0.05 μm filters the average number of crystals was 41.3 ($\sigma = 14.8$) versus 32.7 ice crystals ($\sigma = 9.5$) on the 0.45 μm filters. The approximately 26% higher counts with 0.05 μm filters was partially due to higher background counts on these filters (18.9 crystals versus 8.5 crystals on 10 pairs of blank filters tested). Therefore, the 0.45 μm filters commonly in use appear adequate, and considering cost and pressure drop factors, may be preferable. (In addition, no significant difference in crystal counts was observed between 0.22 and 0.45 μm standard Millipore filters, nor between standard Millipore filters with and without a wetting agent.)

e. Blank filters

At -15°C blank filter counts have typically been found to average between 0 and 5 ice crystals (Bigg *et al.*, 1963; Stevenson, 1968), while at -20°C the value of approximately 10 ice crystals per blank filter has been reported (Bigg, 1973). Similarly with the SUNY diffusion chamber, at -15°C and 100% relative humidity about 5 crystals are noted, and at -20°C, 15–20 ice crystals.

It is well known that condensation nuclei influence IN activation on exposed filters, and the same is true for blank filters. A blank filter attains a higher peak filter relative humidity than one with representative concentrations (10^6–10^7 cm^{-2}) of aerosol present. Thus, a blank filter that is free of condensation nuclei will, when processed, allow activation of IN that otherwise would not occur in the presence of aerosol sinks. It is not readily apparent if and how a background correction should be made except for disregarding exposed filters with obvious contamination patches.

f. Measurement reliability

As is now known, the relative humidity in a static vapor diffusion chamber is not constant but reaches a peak and declines. The value of the peak relative humidity is a function of instrument cooling rate, time, and the number of condensation and ice nuclei on the filters. The relative humidity achieved generally does not reach its stated value due to the competition for water vapor by the various sinks. Methods of correcting for vapor depletion effects have been suggested here and elsewhere (Huffman and Vali, 1973; Jiusto *et al.*, 1976).

TABLE 1. Supersaturation spectra values* ($T = 20°C$ and $V = 100\ \ell$ in all cases).

Relative humidity (%)	S_i (%)	IN concentrations (ℓ^{-1}) per set of four filters											
		1	2	3	4	5	6	7	8	9	10	11	12
91	10	0.065	0.038	0.098	0.082	0.090	0.050	0.100	0.043	0.113	0.045	0.065	0.080
95	15.4	0.115	0.055	0.115	0.085	0.188	0.152	0.163	0.103	0.170	0.078	0.108	0.115
100	21.5	0.142	0.122	0.405	0.298	0.590	0.455	0.805	0.593	0.883	0.570	1.010	0.383
105	27.6	0.648	0.370	0.935	0.773	1.130	0.945	1.853	1.053	1.848	0.985	1.715	1.413
110	33.6	0.752	0.410	1.870	0.845	1.550	1.440	2.435	1.605	2.475	1.508	3.120	1.545
α		2.12	2.16	2.56	2.23	2.48	2.85	2.90	3.19	2.82	3.17	3.47	2.75
$\gamma(10^{-4})$		3.86	2.04	1.81	3.42	2.67	0.691	0.967	0.247	1.32	2.42	0.164	1.04
ΔZ (cm)		0.25	0.50	0.25	0.50	0.25	0.50	0.25	0.50	0.25	0.50	0.25	0.50
Air type*		clean		urban		urban		clean		clean		urban	
Date		8/28/75		10/1/75 am		10/1/75 pm		4/28/76		4/28/76		5/6/76	

* Clean air is defined by visibilities greater than 25–30 mi; urban air by visibilities between 3 and 20 mi.

To obtain a representative value of ice nuclei concentration, sampling with a single filter is not always sufficient. Ice crystal counts on simultaneously sampled filters can vary significantly, such that an average of four filters will give a more reliable concentration measure. Of 222 runs (each consisting usually of four filters sampled and processed simultaneously) the average mean percentage deviation of a single filter from the set of four was 21.7% with a range from 1.4 to 68.1%. For 68 blank filter runs, the average mean percentage deviation was 40.9% with a range of 1.1 to 87.9%.

4. Supersaturation spectra

Analogous to CCN-supersaturation spectra, IN concentrations are sometimes expressed in the form $N = \gamma S_i^{\alpha}$ (Huffman, 1973; Gagin, 1973), where N is the concentration, S_i the calculated supersaturation with respect to ice, and γ and α are constants. The general validity of the approximation remains to be clearly established; at best one might expect it to be valid only if the temperature is lower (colder) than the critical threshold of activation of the particular nuclei and the nuclei are of the condensation-freezing or deposition types.

In processing filters at -12 and $-20°C$ Huffman (1973) found a slope factor α of 4.1–5.1 in winter at Laramie, Wyo., and 2.6–3.2 in summer in northeast Colorado, while summer measurements in St. Louis yielded α values of 6.8–8.3. Gagin (1973) reported similar α values of 1.59 and 1.73 for Jerusalem and Fort Collins, respectively, (processing at $T = -18°C$ and generally high S_i).

Twelve sets of Albany filters processed at a common filter temperature of $-20°C$ are shown in Table 1, each concentration value in the table representing the average of four filters. Tentative results to date, as indicated by Table 1 values, are as follows:

1) The slope factor α varied over a limited range of 2.1–3.5, with an average value of 2.7 ($\sigma = 0.4$).

2) No measurable discontinuity in ice activation was evident as nominal "water saturation" was exceeded. When comparing the lowest three humidities to the highest three, the respective average α values were 2.4 and 2.7—essentially no significant difference. This may indicate, as previously suggested, that water saturation is difficult to achieve in such chambers.

3) No trends in α for "clean" versus "urban" air were discernible, nor for the two chamber heights used.

4) The slope values were dramatically lower than those reported by Huffman in St. Louis, a region more similar in urban character to eastern New York than any of the other locations reported.

Thus few consistent trends are evident in the supersaturation spectra slope values observed to date. It seems apparent that α may vary depending on the temperature and humidity range considered, and perhaps with aerosol type.

5. Conclusions

The filter method continues to be one of the more convenient means of measuring ice nucleus concentrations. There are a number of factors to be taken into account—including chamber design, filter processing and data interpretation—in order to obtain reliable information.

The height of the static diffusion chamber is critical in determining peak filter humidity reached. Ice crystal (nucleus) counts increase exponentially as the height is decreased. Hydrophobic filters, acting as less of a vapor sink, lead to higher IN concentrations by a factor of 2–3 over customary cellulose acetate filters. For our system, 0.45 μm pore-size filters are as adequate as 0.05 μm filters in capturing natural ice nuclei. STP and laboratory-grade petroleum jelly are suitable pore

sealants, with the latter preferred in an "open" chamber system or where reprocessing of the same filters is practiced. The volume effect is unavoidable and appears relatively insensitive to chamber height, chamber type or continental airmass variations. Samples of 100 ℓ represent a reasonable standard to adopt, although the volume effect has not necessarily stabilized at that volume. Random sampling and processing variations dictate that an average of 3–4 filters be simultaneously processed for a more representative data point.

Even when adhering to painstaking processing techniques, IN concentrations obtained generally represent only relative-value measurements. By applying a simple height-correction factor, which seemingly accounts for most of the vapor sink problems, we believe that more accurate IN concentration values are obtainable. Supersaturation spectra, a convenient means of expressing IN data, require additional experimental and theoretical clarification.

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