

The Effect of Vapor Depletion on Ice Nucleus Measurements with Membrane Filters

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(Manuscript received 13 February 1973, in revised form 4 May 1973)

ABSTRACT

The depletion of water vapor during humidification of filter samples, which introduces complications in the determination of ice nucleus concentrations, is considered in detail. A complete solution of the problem appears beyond reach because of the dependence of the depletion effect on the activation spectrum of nuclei; these spectra cannot be determined independently.

Measurements showed that depletion by activated nuclei is more important than by hygroscopic particles. A simple "area-of-effect" model was found to fit the observations relatively well. A generalized correction factor was derived with which the true concentrations of nuclei can be found from measured concentrations.

1. Introduction

Ice nucleus measurements by means of membrane filters have provided, in the years since the method was introduced (Bigg *et al.*, 1961), some very useful information and also prompted further thinking and experimenting on the basic nature of atmospheric ice nuclei. One of the basic attractions of the filter technique is the opportunity to collect samples by simple means and to evaluate the samples in the laboratory under proper control. Another inherent advantage of the technique arises from the fact that the aerosol sample is confined to the small surface and volume of the filter and this in turn permits the temperature and humidity conditions at which ice nucleates to be controlled more readily and thus, at least in principle, more accurately. Typically, the filter bearing the sample is cooled to some temperature below 0°C by bringing it in contact with a cold reservoir (plate). Water vapor is then supplied to the filter by diffusion or by forced circulation from a source consisting of ice at some temperature slightly warmer than the temperature of the filter. This arrangement allows nucleating activity to be determined for independently controllable temperature and humidity conditions.

It was early recognized (Bigg *et al.*, 1963) that when using the filter technique, the apparent concentrations of ice nuclei decreased as the sample volumes increased. This observation brought to light a problem of the filter technique: the particles which were widely spaced in the air are in close proximity of one another on the filter surface and therefore compete for the available water vapor. Mossop and Thorndike (1966) were able to account for the "volume effect" by assuming that

around each hygroscopic particle on the filter there is an area depleted of water vapor in which no ice nuclei can become activated. Lala and Jiusto (1972) computed the vapor density field in a typical diffusion chamber and found that with the usual numbers of vapor sinks (hygroscopic particles and ice crystals) on the filter surface the actual saturation ratios reached are far smaller than the values expected for no-sink conditions. It is the purpose of this paper to further examine the problem of vapor depletion and to present a semi-empirical method, an extension of Mossop and Thorndike's treatment, for circumventing the problem.

2. The problem due to vapor sinks

Were it not for the presence of vapor sinks on the filter all particles could be considered to be at identical temperatures and vapor saturation ratios. Because hygroscopic particles and previously nucleated ice crystals take up some of the vapor, the vapor field over the surface takes on a complex three-dimensional pattern. The problem is to estimate what vapor density exists in the vicinity of potential ice nuclei. Clearly, the actual vapor density will be different for each particle so that it will be possible only to consider some sort of statistical average. Nonetheless, for the sake of visualizing the processes at the filter surface, it is worthwhile to consider the distribution of the vapor field.

Let two particles, A and B, be located on the filter surface with a space x between them and let these particles be subject to a vapor field which, at the temperature of the filter surface, corresponds to saturation ratio S_0 with respect to ice. If the particle at A becomes a sink for water vapor, a nucleated ice crystal for example, then the vapor field around it becomes

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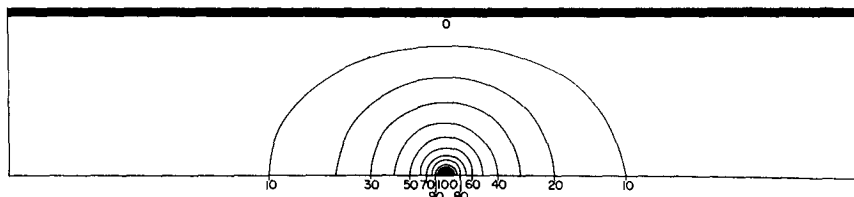


FIG. 1. Plot of the vapor density field in two dimensions between a flat ice surface and a small "vapor sink." The numbers refer to relative values.

modified in a manner similar to the field depicted in Fig. 1. This figure shows the equipotential lines for the two-dimensional field between a point and a line electrode. The vapor density prevailing at particle B could be determined from Fig. 1, depending on its distance from A.

A rigorous analytical solution for the vapor field around a vapor sink in the three-dimensional geometry of a diffusion chamber (plane ice surface vapor source) cannot readily be obtained; but a close approximation is available in the potential field of a small sphere at the center of a large spherical shell. (For the two-dimensional case shown in Fig. 1 it was determined that replacing the line source by a semi-circle decreased the distance along the surface to the 10% line by 30% and to the 50% line by 5%.) The results of calculations for the spherically symmetric system are shown in Fig. 2. Based on these results, it would be predicted that for a crystal of 100 μm radius in a chamber of 1-cm plate separation the vapor density is restored to 90% of the undepleted value outside a circle of 1 mm radius centered on the crystal. Thus, if the undepleted saturation ratio is S_0 and the saturation ratio over the ice crystal unity, then a particle located 1 mm away from the ice crystal would see a saturation ratio equal $1 + 0.9(S_0 - 1)$. Similar results for other proportions can be taken from Fig. 2.

The above discussion refers to a steady-state situation. In practice, the saturation ratio can only be brought gradually toward the desired value. The diffusion of vapor from the source to the filter can

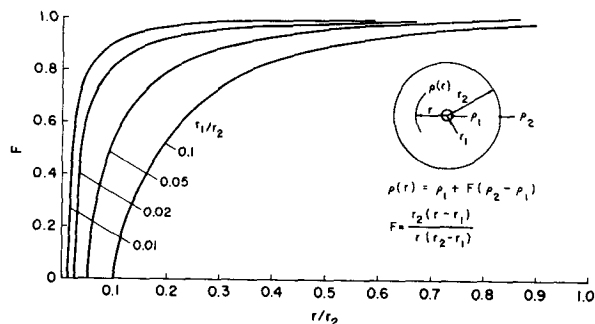


FIG. 2. Variation of the vapor density between a small sphere and a large spherical shell. Symbols are defined in the insert. The quantity F is the fractional change of vapor density for some radius r compared to the total vapor density differential.

occur only at finite rates and this leads to an additional time-dependent factor. The nucleation process itself is time-dependent but this will have to be excluded from the discussion for the moment. Since soluble particles will begin to take on water even at low saturation ratios and since the nucleation of some ice crystals can occur, at least in principle, at any saturation ratio greater than unity, the numbers of vapor sinks can be expected to be continually increasing as the saturation ratio is increased. The resulting variation of the vapor density at the filter surface as a function of time can be discussed with the aid of Figs. 3 and 4.

Fig. 3a depicts qualitatively the trend that the saturation ratio at the filter surface would follow in the absence of sinks. Fig. 3b shows the saturation ratios at the particles A and B under the assumption that ice is nucleated on A when the saturation ratio reaches some value S_A^* . Following nucleation, S_A remains unity while S_B takes on the value $S_A + R(x)[S_0(t) - S_A]$,

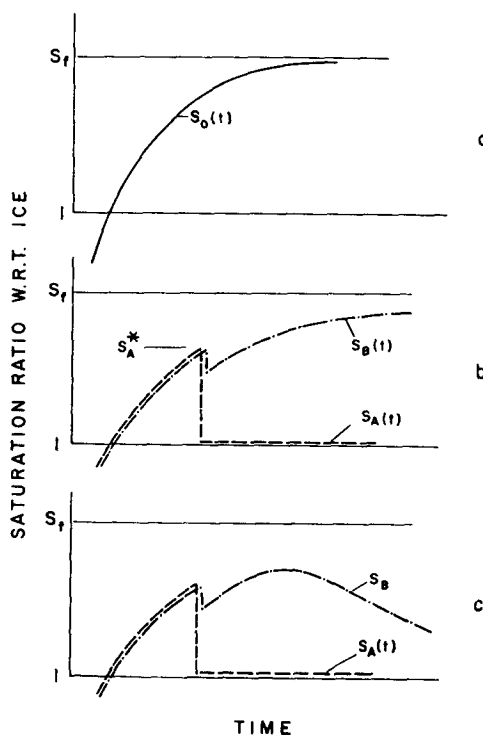


FIG. 3. Variations of saturation ratio with time in the vicinity of an ice crystal vapor sink. See text for description.

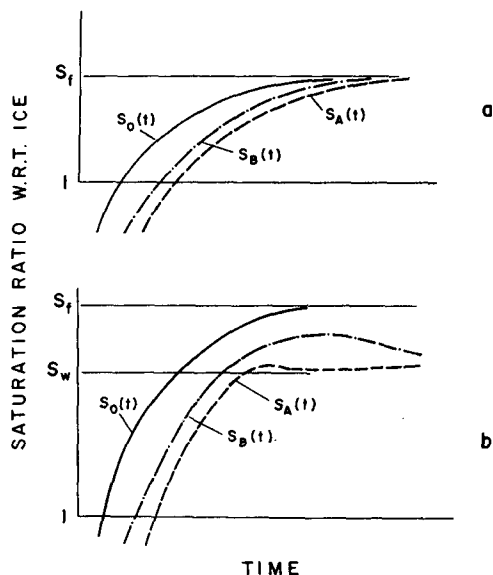


FIG. 4. Variation of saturation ratio with time in the vicinity of an hygroscopic particle. See text for detailed description.

where $R(x)$ is defined as the function describing the fractional recovery of the saturation ratio as a function of distance x from the sink (in analogy with F given in Fig. 2). For an isolated sink, $R(x)$ is independent of time. The final and highest saturation ratio achieved at B would be $S_A + R(x)[S_f - S_A]$, where S_f is the final value of the saturation ratio without sinks. If the ice crystal at A is considered to grow following nucleation, then x and hence $R(x)$ diminish with time so that S_B takes some form similar to that shown in Fig. 3c. This curve exhibits a peak which corresponds to the maximum saturation ratio that can occur at B; nucleation at B will thus be possible if the nucleus is capable of activation at some saturation ratio below the maximum value reached. Strictly speaking, the time available for nucleation under the peak should also be considered.

If instead of an ice nucleus, the particle at A is taken to be a soluble condensation nucleus, the variations of S_A and S_B become similar to that shown in Fig. 4a. The saturation ratio over A lags behind the ambient value as the solution droplet grows toward its equilibrium size. Provided that $S_f < S_w$ (S_w denoting saturation with respect to water), S_A and S_B both reach the equilibrium value S_f and, in effect, no detrimental consequences arise from the take-up of vapor by A. If, on the other hand, $S_f > S_w$ then the situation changes to that shown by Fig. 4b which is closely similar to Fig. 3c, except that S_A after nucleation is at a higher value for the soluble nucleus and thus the effect on S_B is less noticeable. There will be a peak in S_B sometime after the saturation ratio at A settles down to its value S_w ; beyond the peak, S_B will decrease because of the growth of the water droplet at A.

The qualitative analyses given above cannot be made quantitative at this time, not only because of the

complexity of the problem but because the numbers of ice crystals nucleated during the humidification process depend on the activity spectrum of the sample and this spectrum is precisely what one desires to obtain from the measurements. To a lesser degree, the numbers of condensation nuclei that become vapor sinks is also an unknown but this can at least be determined by an independent measurement—a measurement of the CCN spectrum. The best hope for obtaining a solution to the problem would seem to be in the prospect that the slope of the ice nucleus activation spectrum may turn out to be a relatively conservative quantity. In this case a solution could be obtained to provide a correction factor to the results of a measurement performed at some temperature and saturation ratio.

The analyses given by Lala and Jiusto (1972) consisted of a solution of the diffusional vapor field in a filter processing chamber by assuming all points in a given horizontal plane to have the same vapor density. This reduction of the problem to one dimension then permitted a calculation of the average saturation ratio over the filter surface with preassigned numbers of condensation nuclei and ice crystals serving as vapor sinks. As Figs. 1 and 2 demonstrate, the areas on the filter surface affected by the vapor sinks is relatively limited; portions of the filter area can be exposed to saturation ratios considerably in excess of the average value. For this reason, and because of the difficulty in assigning *a priori* values for the numbers of vapor sinks, the conclusions drawn by Lala and Jiusto need to be qualified.

Mossop and Thorndike (1966) assumed that a “deactivation area” of fixed size exists around each vapor sink. As Figs. 3 and 4 indicate, this assumption is an oversimplification. Nonetheless, for a processing chamber of given dimensions, employing fixed rates of humidification, and for relatively similar aerosols, it does not appear unrealistic to define such a deactivated area. This area cannot be predicted without a complete solution of the problem but an empirical determination of the area may be possible. The results presented in the following section bear out this suggestion.

The magnitude of the vapor depletion problem is clearly dependent on the experimental arrangement used. For example, the forced air circulation utilized by Langer (1971) could be expected to be considerably less sensitive to vapor depletion effects than the diffusion chambers used by Alkezweeny (1971), Bigg (1971) and Gagin (1971). The data given in the following sections all refer to results obtained by means of a diffusion chamber; the sensitivity of the results to the particular chamber geometry cannot be well assessed without further investigations.

3. Measured volume effect

Experiments were conducted using samples of outdoor air and samples of artificial aerosols. The natural air

samples were obtained in the vicinity of Laramie, and represent very moderately polluted air. The artificial aerosols were thermally generated silver iodide. Sampling was conducted using sets of four filters drawing air from a common manifold with different rates of flow. The filters were 37-mm diameter Millipore type HA cellulose ester filters in plastic holders. The flow rates were varied by adding various backup filters to the primary filter; the flow rate could be varied over a factor of about 4 by this method. All filters in a set were exposed for the same period of time and were subsequently also processed at identical conditions. The outdoor air samples contained very low concentrations of ice nuclei and therefore very large volumes (several thousand liters) were sampled. The artificial aerosols, on the other hand, have provided much higher ice nucleus concentrations and the sample volumes were correspondingly reduced to a few liters.

Sixteen sets of filters were obtained for outdoor air and four sets for silver iodide aerosols. In all cases it was found that the indicated ice nucleus concentrations (the observed numbers of crystals on the filter divided by the sample volume) decreased as the sample volume increased. This is as to be expected from the vapor depletion effect. For the samples of natural air both hygroscopic particles and ice crystals serve as vapor sinks, for the silver iodide samples the numbers of hygroscopic particles on the filter is negligibly small so that the depletion effect is primarily by ice crystals. The present observations are in agreement with those of Mossop and Thorndike (1966) for outdoor air but differ for the artificial aerosols. They stated that kaolin nuclei exhibited no volume effect unless hygroscopic particles were also added to the filter. However, this conclusion was based on experiments in which the numbers of nuclei on the filters were too low for the depletion effect to be readily detectable (Mossop, 1973, private communication). In any system where the depletion effect by hygroscopic particles is noticeable, one might expect that ice crystals would lead to an even more pronounced effect due to the greater vapor pressure drop at the ice crystal compared to that at a water droplet (cf. Figs. 3c and 4b).

Fig. 5 shows two typical examples of the variation of measured ice nucleus concentrations as functions of sample volume. The curves fitted to the measured points in this figure are based on the model to be presented in the next section. As the figure demonstrates the measured concentration decreases nearly exponentially with increasing volumes. The range of volumes for which measurements could be obtained for any given sample was only a factor of 4. For very small volumes insufficient numbers of crystals appear to be significant and for much higher sample volumes an excessive density of crystals on the filter makes evaluation difficult. Even this relatively small range in sample volumes was found sufficient to exhibit the depletion effect

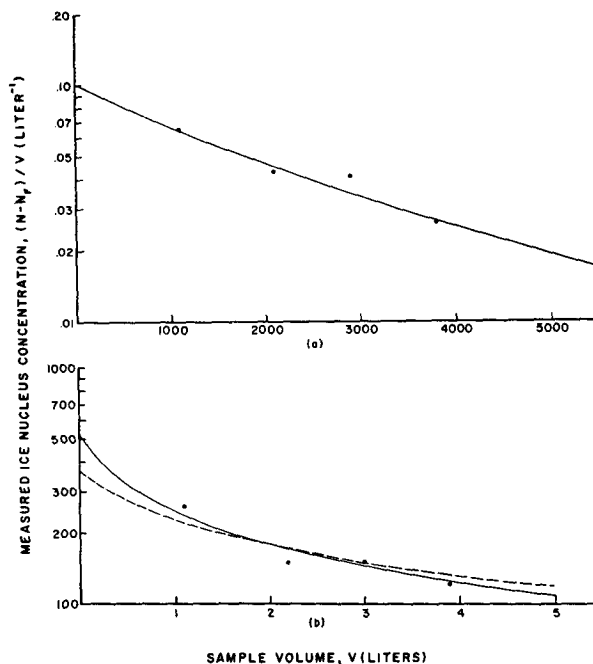


FIG. 5. Examples of the observed dependence of ice nucleus concentrations on sample volume for outdoor air, a., and for silver iodide aerosol, b. Curves are based on model described in text.

With sets of measurements like those in Fig. 5 the true concentration of ice nuclei can be found by extrapolating the measured data to zero sample volume. However, the question of what scheme of extrapolation is justified needs to be examined. The model described in the next section provides one answer to this question based on arguments similar to those given by Mossop and Thorndike (1966).

4. The "area-of-effect" model

For the purposes of this model it is assumed that there exists some effective radius r_1 around each activated ice crystal and a radius r_2 around each hygroscopic particle within which further ice nucleation is prevented from taking place due to the depression of the saturation ratio. These effective radii are taken as average values and as such are not related to individual particle sizes. Thus, the presence of each vapor sink reduces the area on which ice nuclei can be detected by a fraction $(1 - \pi r_i^2 / A_0)$, where A_0 is the total area of the filter surface. Taking into account possible overlap between depleted areas, assuming the vapor sinks to be randomly located on the filter, and neglecting complications at the edges of the filters, the un-depleted area for a filter with N ice crystals and M hygroscopic particles can be written as

$$A_{N+M} = A_0 \left(1 - \frac{\pi r_1^2}{A_0} \right)^N \left(1 - \frac{\pi r_2^2}{A_0} \right)^M \quad (1)$$

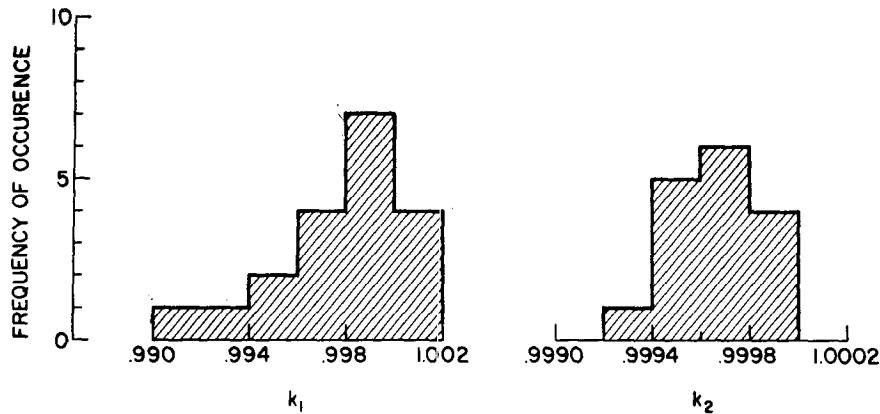


FIG. 6. Frequency distributions of the parameters k_1 and k_2 .

Now, the number of observed ice crystals (activated nuclei) N is related to the total number of nuclei N_0 on the filter surface by

$$\frac{N}{A_{N+M}} = \frac{N_0}{A_0} \quad (2)$$

If the sampled volume was V , and C and c denote the concentrations of ice nuclei and of hygroscopic particles in the sampled air (so that $N_0 = CV$ and $M = cV$), then (1) and (2) can be rewritten as

$$C = \frac{N}{V} k_1^{-N} k_2^{-V}, \quad (3a)$$

where

$$k_1 = \left(1 - \frac{\pi r_1^2}{A_0}\right), \quad k_2 = \left(1 - \frac{\pi r_2^2}{A_0}\right)^c. \quad (3b)$$

With the above, C can be determined from the observed ice crystal count N , for given V and A_0 , if k_1 and k_2 are known. It should be noted that k_2 depends on the concentration c of hygroscopic particles which is an independent property of the air which was sampled.

It is known that a small number of crystals form even on unused filters. This background count, N_F , can be taken into account by writing (3) as

$$C = \frac{N - N_F}{V} k_1^{-N} k_2^{-V}; \quad (4)$$

that is, by subtracting N_F from N in the pre-exponential factor but not in the exponent. The reason for this is that all crystals contribute equally to the depletion factor.

For comparison with experimental data it is convenient to take the logarithm of (4) to obtain

$$\ln \frac{N - N_F}{V} = \ln C + N \ln k_1 + V \ln k_2. \quad (5)$$

As (5) shows, the left-hand side of the equation plotted as a function of V should yield a curve whose shape depends on C , k_1 and k_2 . With sets of points, for which N , N_F and V are known, the unknowns (C , k_1 , k_2) can be determined by a multi-parameter, least-square fitting of (5) to the data. The background count, N_F , has been determined independently for various combinations of temperatures and saturation ratios and the results used in evaluating (5). The least-square analysis was applied to the 20 sets of measurements, examples of which are shown in Fig. 5. Even though C was different for each set of filters, the values of k_1 and k_2 showed fairly good consistency. The average values for these two parameters are found to be $k_1 = 0.998$ and $k_2 = 0.9997$ with the standard deviations in these values being 0.002 and 0.0002, respectively. The frequency distributions of the k_1 and k_2 values are given in Fig. 6. It was not possible to obtain an accurate value for k_2 for the silver iodide samples because the last term in (5) was negligible for the large concentrations of nuclei present. In Fig. 5a the line of best fit is shown for k values which for this set of data happen to be coincident with the average values given above. In Fig. 5b the full line shows the curve of best fit ($k_1 = 0.997$ and $k_2 = 1$), while the dashed curve was obtained by using the average values of k_1 and k_2 and allowing C to be variable.

The data discussed above were obtained by processing each set of filters at a particular temperature and saturation ratio. Temperatures between -12 and -20°C were utilized and the vapor source was adjusted to temperatures giving undepleted saturation ratios of 98–102% with respect to water. Derived k_1 and k_2 values were examined to see if a dependence on processing conditions could be detected; from the limited data available it appears that there is no dominant dependence of these parameters on the processing conditions. This is somewhat contrary to expectations since the numbers of hygroscopic particles activated and the area of effect around each vapor sink could be expected to depend on the saturation ratios utilized. The range

of variation of processing conditions was perhaps too small to detect the expected trend.

Using (3b) and the values of k_1 and k_2 given above, it is found that $r_1 = 760 \mu\text{m}$ and that $cr_2^2 = 8.6 \times 10^{-4} \text{ cm}^2 \text{ liter}^{-1}$. To a good approximation it may be assumed that the radius of water vapor depletion is proportional to the size of a hygroscopic particle. Also, the size distribution of hygroscopic particles may well be taken to follow Junge's law ($dn/dq \propto q^{-4}$), so that

$$r_2 = \alpha \bar{q} = \alpha \frac{3q_0}{2}, \tag{6}$$

where \bar{q} denotes the average size of the hygroscopic particles, q_0 the lower size limit of the hygroscopic particles, and α is a constant to be evaluated. Mossop and Thorndike (1966) determined that the depletion radius was $30 \mu\text{m}$ for NaCl particles of $1 \mu\text{m}$ mean radius; from their results we can get $\alpha = 30$ if the composition of natural hygroscopic aerosols is assumed to be similar to NaCl. Taking then the lower size limit of particles to be $0.01 \mu\text{m}$, it is found that the average depletion radius $r_2 = 0.45 \mu\text{m}$. Combining this with the value given above for cr_2^2 , one gets $c = 4.3 \times 10^5 \text{ liter}^{-1}$

$= 430 \text{ cm}^{-3}$. This is approximately equal to the numbers of particles becoming CCN at a few percent above water saturation in the air of southeastern Wyoming.

It will be found useful to define a correction factor E as the ratio of the observed ice nucleus concentration to the true ice nucleus concentration. From (4) we may write

$$C = \frac{N - N_p}{V} E, \tag{7a}$$

where

$$E = \left(1 - \frac{\pi r_1^2}{A_0}\right)^{-N/A_0} \left(1 - \frac{\pi r_2^2}{A_0}\right)^{-cV/A_0}. \tag{7b}$$

It is desirable to rewrite (7b) in a form that is independent of the size of filter employed and which would express E as a function of the areal densities of ice crystals and of hygroscopic particles. This can be achieved by recognizing that r_1 and r_2 are both small relative to the filter size. The binomial expansion can be used to put (7b) in the form

$$E \approx (1 - \pi r_1^2)^{-N/A_0} (1 - \pi r_2^2)^{-cV/A_0}. \tag{8}$$

Values of E are plotted as isopleths in Fig. 7 according

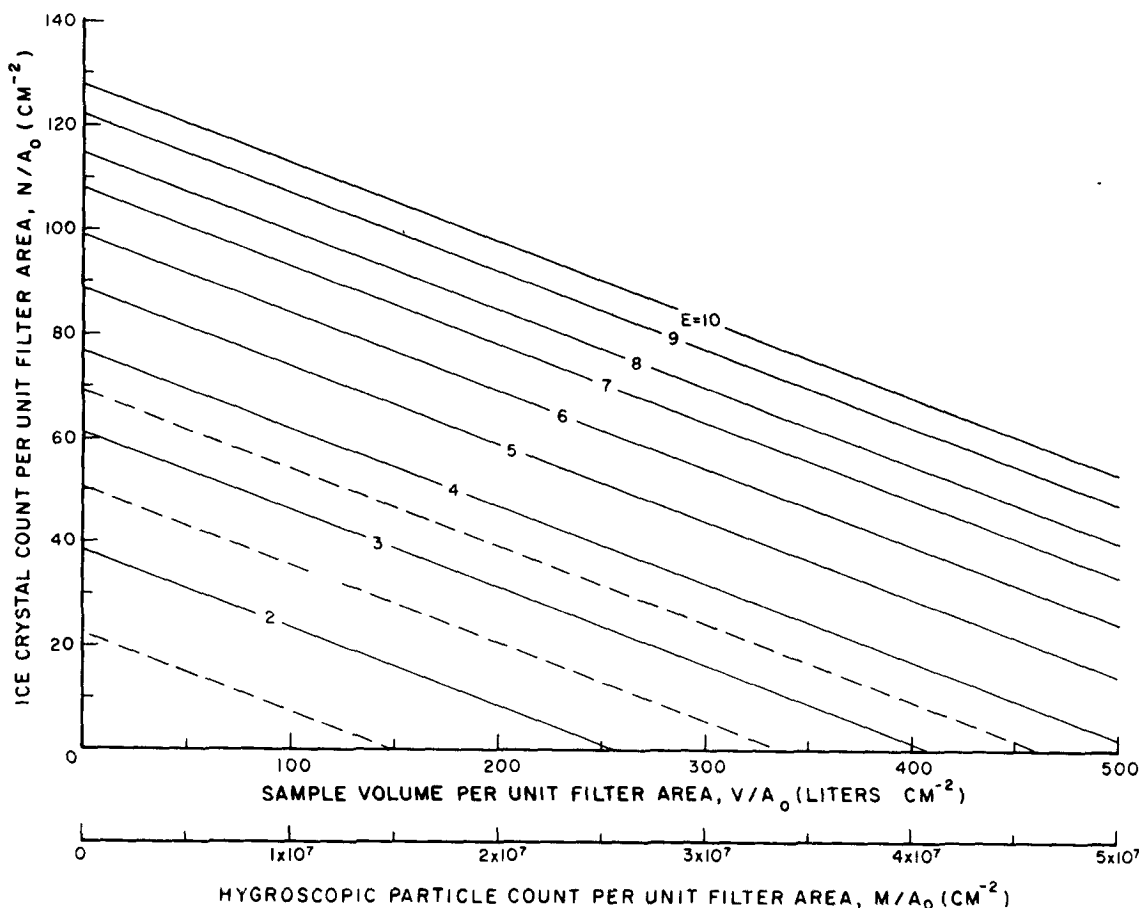


FIG. 7. Isopleths of correction factor E for different surface densities of ice crystals and of hygroscopic particles.

to (8) with the appropriate values for r_1 and r_2 . The upper abscissa is valid for $c=10^5$ liter $^{-1}$, while the lower abscissa is appropriate for any hygroscopic particle concentration. With the aid of Fig. 7 the results of a measurement using the filter technique can be corrected to obtain the true ice nucleus concentration in the sample air. In general, however, there is a difficulty in assigning the proper value to M (or c) since it is not well defined in the model what constitutes a hygroscopic vapor sink.

5. Summary

Examination of the details of the vapor depletion process, which leads to the undesirable "volume effect" in the determination of ice nucleus concentrations by the filter technique, showed that the problem should be solved by finding a description for the three-dimensional and time-dependent variation of the vapor field over the filters during humidification in a processing chamber. There is a principal difficulty in finding an analytic solution for the problem in that the activation spectrum of the particles would need to be known (as a function of temperature and saturation ratio), but no independent determination of these spectra can be made at the present. If further measurements show that the slopes of the activation spectra are relatively conservative quantities, the problem may be simplified to a point where an analytic or numerical solution becomes possible.

Measurements of the volume effect for natural and artificial aerosols indicated that the apparent concentrations of nuclei decreases with increasing concentrations of both hygroscopic particles and of the ice nuclei themselves. The observed dependence of measured nucleus concentrations on sample volume can be adequately explained on the basis of an "area-of-effect" model. It is assumed in this model that ice nucleation is precluded within a certain radius of each vapor sink due to the depression of the local vapor density. It was shown that the radius of depression is about 760 μm for activated ice nuclei and 0.5 μm for hygroscopic particles (average value for distribution of particle sizes). The relative magnitudes of these radii are in agreement with the fact that the vapor density is

depressed to a lower level over ice crystals than over hygroscopic particles.

Using the results of the above model a correction factor can be predicted. This factor can be applied to the results of any particular measurement in which the numbers of ice crystals are observed on the filter and the numbers of hygroscopic particles are estimated or measured independently. As Lala and Jiusto's (1972) work indicates, the way in which vapor depletion influences the activation of nuclei on filters is dependent on the geometry of the processing chamber used for the measurement and on the procedure used for humidification in that chamber. Thus, the correction factors found in this work may not be generally applicable; the sensitivity of the results on the techniques employed cannot be assessed without further research.

Acknowledgements. The research here reported was supported by the National Hail Research Experiment under subcontract NCAR 176-71 and by the Division of Atmospheric Water Resources Management, Bureau of Reclamation under contract 14-06-D-6801.

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