Aerosol Size Distributions by Multiple Filter Measurements

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ABSTRACT

Using Nuclepore filters at a sequence of flow rates, to discriminate according to particle size, and a suitable mathematical inversion procedure, particle size distributions have been obtained for surface atmospheric aerosol samples. Measurements in relatively unpolluted air at Robertson, N.S.W., Australia, yield a fairly reproducible size distribution, with a maximum always close to 10^{-6} cm radius; measurements in more polluted air at The University of Arizona have led to very similar size distributions.

1. Introduction

The size distribution of a heterogeneous aerosol can be estimated indirectly from a count of the number of particles surviving various degrees of filtration. Different degrees of filtration can be obtained by varying the flow rate and/or the length of a tube, duct or similar filtering element (which, by the precision of its dimensions, allows the efficiency of removal for various sized particles to be calculated with confidence).

In the past, such experiments have involved rather bulky and often expensive "filters." Twomey (1965) has described the use of 100 m of stainless steel tubing as a filter, while the use of "diffusion batteries" has been described by several authors (Pollak, 1959; Füchs *et al.*, 1962).

The introduction of Nuclepore[2] filters has greatly changed the picture. These filters provide a well-defined pore geometry in a conventional filter disk, and their filtration properties, calculated from physical theory, have been verified by experiment (Spurny *et al.*, 1969).

In another paper (Twomey, 1975), a theoretical discussion was given of the estimation of particle size distribution from measurements of relative particle numbers transmitted through different combinations of filters and flow rates (changing the flow rate changes the filter transmission versus size curve and, in effect, makes it a different filter). It was shown that an experimentally practicable set of measurements could provide effective size separation over the range 10^{-7}–10^{-4} cm (i.e., 0.001–1 μm) radius, and that stable inversion of measurements was feasible using an iterative numerical procedure which was discussed in detail.

The present paper will describe experimental realization of the measurements visualized in the previous paper. Size distributions obtained by the numerical inversion method will be presented. These distributions extend down to and below 10^{-6} cm (0.01 μm) radius and therefore include the region below 0.1 μm, for which very few data exist.

2. Method

A large volume ($\sim$0.2 m^3) of outside air is drawn into an aluminized Mylar bag contained inside a rigid barrel, so that the air outside the bag can be pressurized or partly evacuated to permit the sample air to be sucked in or pushed out without itself being passed through any pumps or blowers. Large-diameter tubing and short lengths are used to allow the sampling to be completed in under a minute.

The sample air is then pushed through a set of four or five Nuclepore filters at four or five flow rates in the range 1–10 liters per minute, and the emerging particle concentration is measured with a Pollak photoelectric nucleus counter. Frequent observations are also made of the particle concentration in the sample air as the measurements progress, to determine the rate of decay of particle concentration in the stored sample itself.

Since the filters were used in transmission, it was obviously vital that no leakage of air occur around the filter pads, and it proved necessary to make special filter holders to hold the Nuclepores in a way which allowed no leakage whatever. (The filters are only 10 μm thick, and holding them securely is not a trivial problem. Our experience did not indicate that commercial filter holders were adequate.) The design of the filter holders is shown schematically in Fig. 1, in which it will be seen that the filters are clamped between a pair of O-rings. The two halves of the

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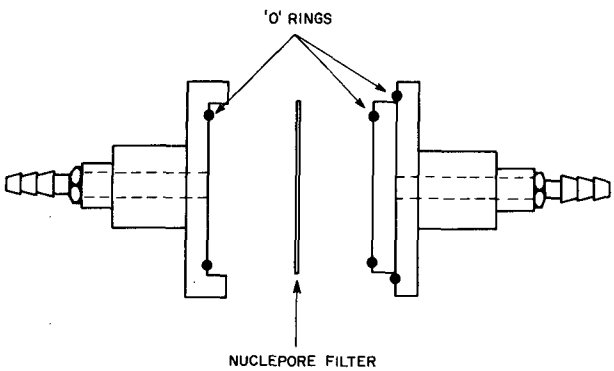

FIG. 1. Method of holding the Nuclepore filters.

holders are pushed together by an external spring-loaded plunger, which operates along the central axis of the holders. More obvious methods, such as screws around the outer circumference of the holders, were found to be less reliable. The holders were, in turn, held in a special rack with an overhead bar carrying the plungers, which clamped each filter holder together when the bar was secured in position.

3. Accuracy

The Pollak counter used was a faithful reproduction of Pollak's 1957 design. Since it has not been calibrated against a standard, Pollak's calibration data had to be used to convert extinction readings to number concentration. It is difficult to estimate what error might be introduced by such a procedure. Pollak (1959) published a figure showing the frequency of differences in reading between identical pairs of counters during the development of his instrument. He quoted a figure of not more than 3% in nucleus concentration, but considerably less in some ranges of concentration, in 72% of all comparisons. Such comparisons would not, of course, give any idea of the magnitude of possible errors in Pollak's calibration tables. Emmanuel and Squires (1969) have published comparisons of photographic counts with the counts given by Pollak's tables, showing differences at low concentrations of up to 30%. These measurements were made in Boulder, Colo., at an elevation quite different from that (at Dublin) where Pollak's calibration was derived. On the other hand, Pollak used artificial nuclei from heated platinum wire, and there must be some question when one uses his calibration data on heterogeneous (in particle size and composition) natural aerosol. The reproducibility of individual readings with the counter used in the present work was extremely high, being typically 0.2 division in the extinction reading (full scale 100 divisions), which is equivalent to better than 1% in concentration for all but the lowest concentrations of particles.

In early experiments, we adopted the manufacturer's data for the filter material but found, in some instances, rather large differences from measured characteristics. We thereafter measured the filter pore size, pore density (per unit area) and pore length (filter thickness), a somewhat tedious procedure, which also posed a problem in representation since the fluctuations of measured quantities seemed to contain a systematic as well as a random component. Pore density was the most variable parameter, and this unfortunately is also the most important. The accuracy with which the various averages were determined was estimated to be about 5% (resulting primarily from fluctuations in the measured quantities in different parts of the filter or from filter to filter). Flow rate was measured to an accuracy of better than 2%.

4. Experimental results and their reduction

The raw measurements consisted of a set of Pollak counter readings, the corresponding filter parameters, and the volumetric flow rate A computer program then calculated the filter transmission $K_i(x)$ as a function of the size x (log radius was used as the measure of size) and then iteratively calculated a size distribution $f(x)$ by the procedure discussed in detail by Twomey (1975), thus arriving at a numerical estimate of the solution to

$$\int K_i(x) f(x) dx = g_i + \epsilon_i, \quad i = 1, 2, \ldots, N, \qquad (1)$$

where g_i are the measured particle concentrations and ϵ_i the errors therein. It is, of course, not possible to give values for $\epsilon, \epsilon_2, \ldots, \epsilon_N$, but the rms error, $|\epsilon| \leqslant (\sum \epsilon_i^2)^{\frac{1}{2}}$, can be estimated for the experimental conditions. It should be emphasized that the ϵ_i contain not just errors in g_i but also errors originating on the left side of Eq. (1), such as errors in the flow rate or the filter dimensions.

As the iteration proceeds, one can at any time take the current estimate of $f(x)$, calculate $\int K_i(x) f(x) dx$ using that estimate, and thereby arrive at an error or discrepancy, which can be called $\delta_i^{(m)}$. The rms value of $\boldsymbol{\delta}^{(m)}$, i.e., $\{\sum_i [\delta_i^{(m)}]^2\}^{\frac{1}{2}}$, which we shall denote by $|\delta|$, conveniently measures the progress of the iteration toward an acceptable solution. If $|\delta|$ is very much larger than $|\epsilon|$, a large amount of the variance of the g_i is still unaccounted for. If $|\delta|$ is smaller than $|\epsilon|$, we are doing the impossible—in fact, we are inverting the error noise itself, and, in such a situation, disaster in the shape of instability of the solution, manifested by large and capricious oscillations, is inevitable. However, the algorithm discriminates strongly against high frequencies, and in none of the tests which we have applied has instability been experienced. In artificial situations where the solution $f(x)$ is postulated and g_i calculated therefrom and the error terms deliberately introduced, so that

$f(x)$ and the ϵ_i are known, $|\delta|$ is found to decrease asymptotically toward $|\epsilon|$, but even after several hundred iteration cycles, $|\delta|$ in the real situation was still much larger than the estimated experimental error.

A main contributor to the error was evidently the loss of nuclei by diffusion to the walls of the containing vessel during a complete experiment. Each experiment lasted 20 min or so, and, in that time, the total concentration of nuclei in the bag fell to about two-thirds its initial value in a typical experiment (Fig. 2). Furthermore, the loss is size-dependent, since small particles diffuse to the walls more rapidly than large particles.

Theoretical calculations of diffusion loss for containers with volumes of the order of several hundred liters indicate a very small loss in times of the order of tens of minutes, but such calculations envisage stationary air within the container. The air, in fact, moves in convection currents, and even quite small convection speeds of the order of millimeters per second can appreciably influence the loss to the walls. It is well known that the loss of particles or other diffusing substance to the walls of a container large enough to permit convection is better approximated by postulating a well-mixed interior region within which concentration is constant and a diffusion boundary layer across which diffusive transport dominates, i.e., one considers the concentration N to be uniform everywhere except in a boundary layer near the walls, across which the diffusive flux $D\nabla N$ transports the particles to the walls. Assuming a boundary layer of uniform thickness h and complete retention of particles on the walls ($N=0$ at the wall, for a wall area A), the rate of change of N is easily found to be

$$\frac{1}{N}\frac{dN}{dt}=\frac{A}{hV}D,$$

if the volume of the boundary layer region can be neglected in comparison to the total volume V. This simple boundary layer model, therefore, leads to a time decay of the form

$$N=N_0e^{-\eta Dt},$$

where η depends on the geometry and on the thickness of the boundary layer.

Inserting the expression just derived into Eq. (1) to account for diffusion losses to the walls, we have

$$g_i=\int_0^\infty K_i(x)\exp[-\eta t_i D(x)]f(x)dx. \qquad (2)$$

If η were known, this could be written again in the same form as Eq. (1), since the time t_i at which the ith measurement occurred and the diffusion coefficient of a particle of given size are known quantities. In that event, one need only define a modified kernel

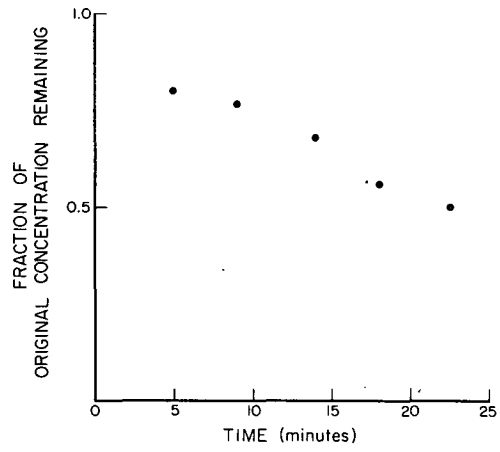

FIG. 2. Decay of particle concentration with time, while stored in a 150 liter bag.

$K_i'(x)$ into which the exponential factor was incorporated, and the inversion process would otherwise be unaffected.

There is, however, very little *a priori* knowledge of the intensity of the convection currents in the storage bag, and there seems to be no simple way to get a value for η.

In a sense, η is just another unknown, in addition to the unknown tabular values $f(x_1), f(x_2), \ldots, f(x_N)$ which represent the solution, and had it entered linearly into the basic Eq. (2), it could probably have been handled in that way. However, it enters nonlinearly, and there is no obvious way to restore the linearity by redefining variables, etc. We therefore had to resort to a time-consuming and pedestrian method for getting η. A sequence of values of η was selected, and for each value in turn an iterative inversion was made out to m cycles. The discrepancy $|\delta^{(m)}|$ after m iteration cycles was then plotted against η, giving a graph such as that of Fig. 3. Since the minimum discrepancy occurred with values for η of about 2 cm^{-2}, this value was adopted for η and used for further iterations, etc. (Using the formula relating η to the geometry and the thickness of the diffusion boundary layer, a value of η around 2 corresponds to a boundary layer thickness around $\frac{1}{2}$ mm.)

5. Size distributions obtained

Using the procedure just described to correct for diffusion loss to the walls, experimental measurements made at Robertson, N.S.W., in late 1972 have been inverted to obtain size spectra primarily for clean continental or modified maritime air masses. Typical size spectra are shown in Fig. 4 and some individual spectra in Fig. 5. Most of the size spectra obtained showed the same shape as the one illustrated in Fig. 4. The maximum of the spectrum always occurred close to 10^{-6} cm radius, and the spectrum fell off steeply for smaller sizes.

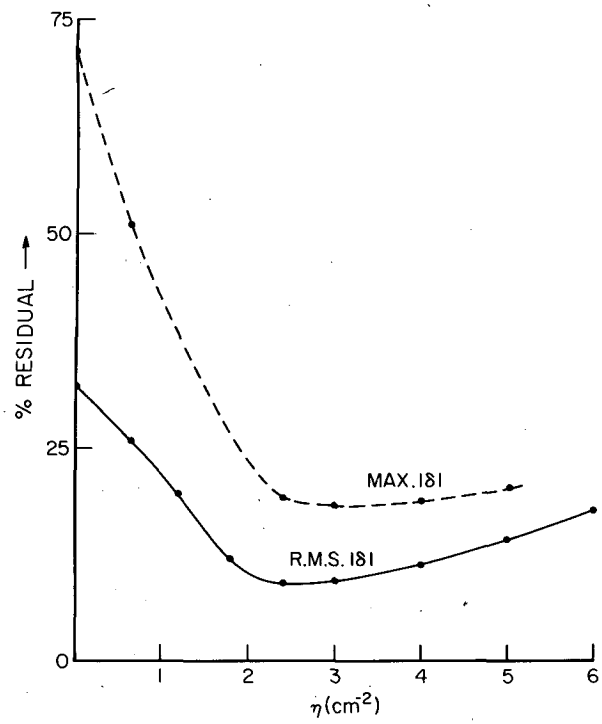

FIG. 3. Curve of rms residual variance after 20 cycles of iteration (320 iterative steps) as a function of the value assumed for the diffusion loss parameter η.

It will be seen that the slope of the size distribution from 10^{-6} cm radius up was fairly close to the r^{-3} dependence of the Junge distribution; but the slope tends to be smaller than the Junge slope between 10^{-6} and 5×10^{-6} cm and larger beyond 5×10^{-6} cm, i.e., there is an elbow in the size distribution around 5×10^{-6} cm. This again was found in most of the experimental spectra, and, although it does not appear very prominent in the figure, the logarithmic ordinate scale is largely responsible. In fact, the elbow cannot be deleted without increasing the rms discrepancy several times; furthermore, when a distribution with the elbow smoothed out was subjected to further iterative adjustment, the elbow was found to return. One is therefore inclined to believe that it is real and not an artificial by-product of the numerical procedure.

Some years ago, Friedlander (1960) pointed out that dimensional analysis predicted a specific slope for steady-state size distributions, if one could define either a subrange of sizes wherein diffusive coagulation only was effective in moving material from smaller to larger sizes or a subrange in which diffusive coagulation was negligible and material moved through the subrange because of gravitational sedimentation of the particles. For the diffusive subrange, $n(r)$ was predicted to follow an $r^{-5/2}$ law; and for the sedimentation subrange, an $r^{-19/4}$ law was predicted. It is of interest to note that these slopes (which become $r^{-3/2}$ and $r^{-15/4}$ when log radius rather than radius is used as a measure of size) are quite close to the slopes prevailing on either side of the elbow in the size distribution (Fig. 4). It is, of course, questionable whether steady-state conditions ever prevail in the atmospheric aerosol, and even if they do, there is no assurance that separable subranges exist. Furthermore, it is hard to see how gravitational sedimentation could be important for particles of the order of 0.1 μm in radius (Stokes falling speed ~1 μm s^{-1}). However, the close agreement of the slopes of the experimental size distribution with those predicted by Friedlander is interesting.

6. Position of the maximum

The size spectra obtained indicate that, at least in the air masses sampled, a Junge law describes the distribution fairly well down to near 10^{-6} cm radius; but the increase in number per log radius interval ceases quite abruptly below about 10^{-6} cm and falls off quickly with further decrease in size. No tendency was observed for a further appreciable increase at smaller sizes, and a second maximum, such as that tentatively suggested by Junge and Jaenicke (1971), was not found.

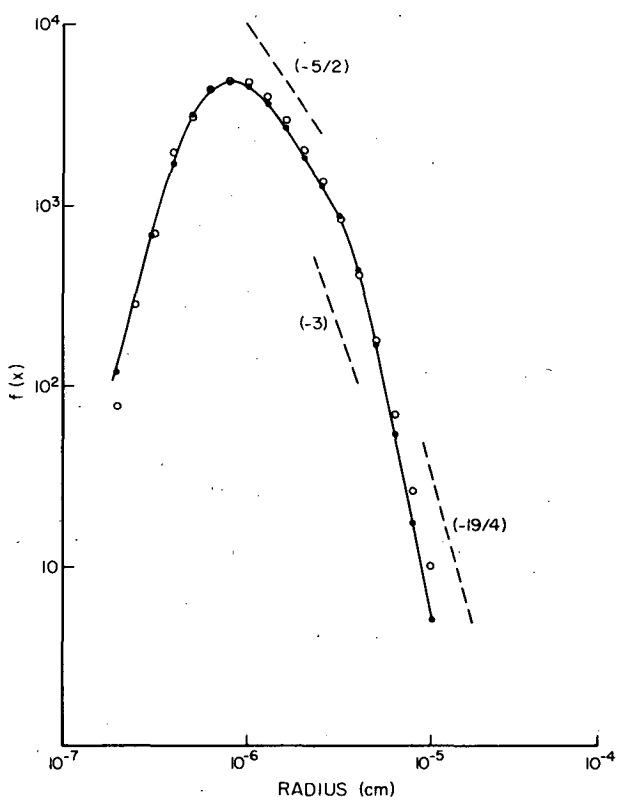

FIG. 4. Typical size distribution obtained by inversion of the multiple filter measurements in relatively clean (Aitken count $\sim10^4$ cm^{-3}) rural air. Slopes for Junge's r^{-3} distribution and Friedlander's inertial and diffusive subranges are shown for reference.

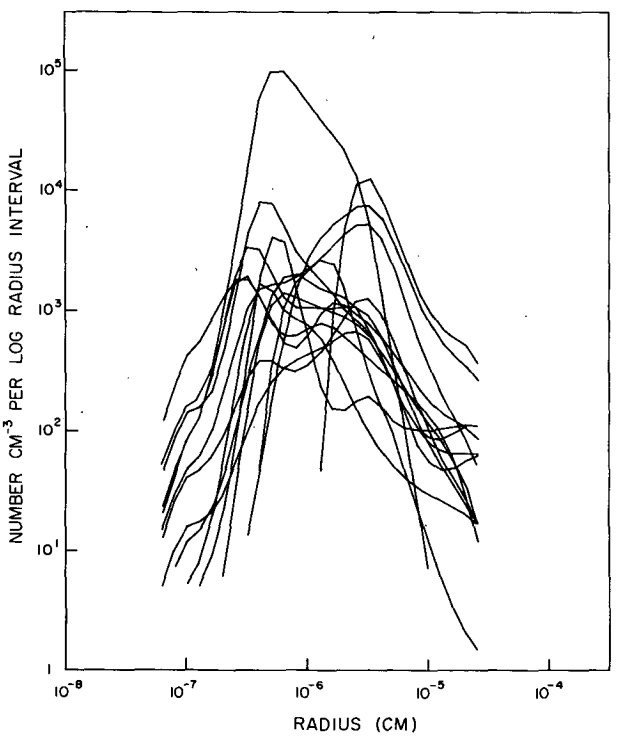

FIG. 5. A representative set of size distribution curves for relatively clean rural air at Robertson, N.S.W.

An inspection of the filter characteristics [which were given in a previous paper (Twomey, 1975)] shows that the size interval between 10^{-7} and 10^{-6} cm is well resolved—in the sense that the filters used show wide variations in transmission in this size region—and failure to observe a second maximum in this region cannot be attributed to inability of the technique to observe such a feature. Numerical tests with computed filter data for a hypothetical bimodal distribution confirmed that a second maximum in this size region was reconstructed well by the inversion procedure.

Particles $<10^{-6}$ cm radius are quite mobile and readily lost by diffusion to walls and coagulation. Any appreciable loss of such particles during the sample intake operation is unlikely, since the air flow is so high and the sample tubing only a few inches long. Losses in connecting tubing (which was of stainless steel) during passage of the air from the storage bag to the filters and thence to the counter can be estimated. The tubing run was less than 2 m (total), and the maximum flow rate used was 133 cm^3 s^{-1}, so that the ratio l/q (length of tube divided by volume flow rate) at that flow was less than 2 cm^{-2} s, while at the minimum flow rate (15 cm^3 s^{-1}), it was still only about 60 cm^{-2} s. Particles with diffusion coefficients of the order of 10^{-2} cm^2 s^{-1} (10^{-7} cm radius) would be transmitted almost unchanged ($\sim$75%) at the higher flow rates at which the coarser filters transmit down to those small sizes. A considerable fraction would be removed at the minimum flow rate, but none of the filters transmit 10^{-7} cm radius particles at the lowest flow rate anyway. It seems unlikely that such losses can be invoked to explain the relative absence of particles much below 10^{-6} cm radius.

To minimize coagulation losses, the observations at high flow rates (where the smallest particles could penetrate the filters and be counted) were made first and were completed within a few minutes. Coagulation of 10^{-7} cm particles with the larger particles could be appreciable but not overwhelming in a few minutes and can hardly have been sufficient to cause the inferred distribution to be greatly distorted. For the distribution of Fig. 4, the coagulation rates for various small sizes of particles were calculated using Füchs' values for the coagulation coefficient $K(r_1, r_2)$. The fractional rate of removal by coagulation of particles with radius r_1 is given by

$$\int_0^\infty K(r_1,r_2)n(r_2)dr_2.$$

Calculation of this integral gives the values shown in Table 1.

TABLE 1. Fractional rate of particle removal by coagulation.

Radius (cm)	Fractional coagulation rate (s^{-1})	Characteristic time (h)
10^{-7}	1.3×10^{-4}	2.1
2×10^{-7}	1.07×10^{-4}	2.6
3×10^{-7}	3.6×10^{-5}	7.7

Thus even at 10^{-7} cm coagulation does not grossly alter the size spectrum in times of the order of $\frac{1}{2}$ h. It should be noted that the sequence of measurements was arranged so that those filters which transmitted appreciably down to the smallest sizes were used first.

The procedure used to derive the quantity η would also tend to correct for coagulative losses. Certainly, diffusion of smaller particles to the surface of larger particles (the mechanism of Brownian coagulation) is represented by the same fundamental equation as diffusion to the walls, differing only in the boundary conditions. However, solutions to diffusion problems lead to relationships containing more than just one exponential, of the kind

$$\frac{n}{n_0}=a_1\exp(-b_1Dt)+a_2\exp(-b_2Dt)+\cdots,$$

where the quantities a_i and b_i depend on the boundary conditions. If two processes of diffusion loss are going

on simultaneously, the second being described by

$$\frac{n}{n_0}=\alpha_1 \exp(-\beta_1 Dt)+\alpha_2 \exp(-\beta_2 Dt)+\cdots,$$

then if only the first term of each expression is significant (i.e., when appreciable decay has been produced by each process), one can combine the two mechanisms into a single exponential term

$$\frac{n}{n_0}=\alpha_1 a_1 \exp[-(b_1+\beta_1)Dt].$$

Otherwise the combined effects give more complicated expressions. For this reason, and also because of the fact that coagulation changes the size distribution and hence the boundary conditions, one cannot claim that both diffusive losses could exactly be corrected for by the inclusion of a single factor $e^{-\eta Dt}$, in which η is assumed constant in time. One should also point out that the experimentally determined decay curves were not very similar to exponentials or to the concave upward curves (on a log number versus time plot) which would be realized by a heterogeneous aerosol when each size interval therein exhibited exponential decay.

The only conclusion which can safely be drawn is that the present observations give no indication of a second maximum below the prevalent maximum near 10^{-6} cm radius. The shape of the aerosol distribution below 10^{-6} cm may be an important guide toward understanding the mechanisms of formation of aerosol particles. Some results, especially those of the Minnesota group [Particle Technology Laboratory, University of Minnesota, Minneapolis (Whitby *et al.*, 1972)], indicate large numbers of particles below 10^{-6} cm, while the present results indicate relatively few. It seems most desirable that these disagreements be resolved. If contact of particles results in coagulation on all or most occasions, sizable numbers of particles around 10^{-7} cm radius can occur only if the particles are of very recent origin. In this study, obviously polluted situations were avoided, and it is possible that the absence of very small particles in these results simply indicates the absence of a local source or of recent production.

The curve of Fig. 3 shows that, even when the optimum value of η was used, there remained a residual variance $(\sum_i \delta_i^2)^{\frac{1}{2}}$ of about 9–10% rms. When idealized data (i.e., computed for a hypothetical distribution) were used, the residual at an equal number of iterations was always less than 1%. Since the actual readings and conversion to particle concentration were quite precise, the failure of the iterative procedure to reduce the unexplained variance below 9% indicates that the total error from all sources is of this order. If the errors are random, numerical tests indicate that the solution will not be systematically distorted, but systematic errors could produce significant distortions in the solution. Further work is needed on this aspect of the question, but the stability of the solutions toward large changes in the initial first-guess distribution provides some assurance that the solutions obtained are close to reality. This is shown by the circles plotted in Fig. 4, which were obtained with a totally different initial distribution ($dN/d\ln r \propto r^{-3}$ down to below 10^{-7} cm), yet follow the solid curve (initial distribution, $dN/d\ln r$ constant across the entire passband of the filters) very closely indeed.

7. Conclusions

The multiple filter method appears to be a useful technique for studying aerosol size distributions. Its main drawback is the relatively long time taken to complete the necessary observations.

The results obtained in relatively unpolluted air at Robertson, New South Wales, suggests a stable size distribution, the distribution function showing a maximum which was always close to 10^{-6} cm radius. Above this, the distribution fell off, first relatively slowly, but more steeply approaching 10^{-5} cm and thereafter. A steep falling off (approximately as r^4) was inferred on the small-size side of the maximum.

Results obtained at The University of Arizona during 1974 (spring and summer) gave distributions quite similar to those found for Robertson (see Fig. 6)

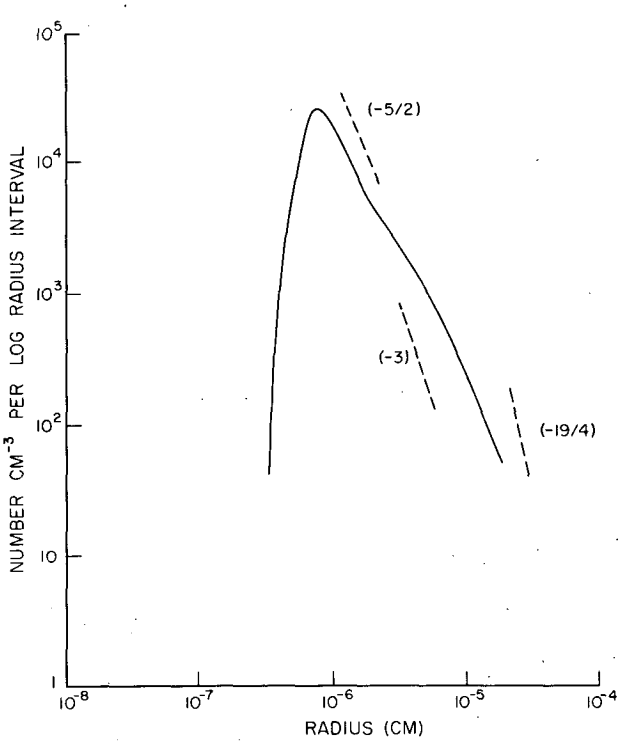

FIG. 6. Typical averaged size distribution for relatively clean continental air at Tucson (probably containing some local pollution).

and show essentially the same features, the position of the maximum being identical. It should be emphasized that the Robertson site is a rural one, whereas the Arizona measurements were obtained from a fifth-floor location on the campus. A more detailed discussion of the results, hopefully including Arizona samples less liable to local pollution, will be given at a later date.

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