Concentration and Size Distribution Measurements of Atmospheric Aerosols and a Test of the Theory of Self-Preserving Size Distributions[1]

WILLIAM E. CLARK[2] AND KENNETH T. WHITBY

University of Minnesota, Minneapolis

(Manuscript received 13 January 1967, in revised form 19 June 1967)

ABSTRACT

The concentration and size distribution of particles from 0.001 to 3 μ in radius dispersed in the urban atmosphere was measured with a continuous-sampling sizing system composed of a nuclei counter, an electrical particle-counter, and an optical counter. Atmospheric aerosol size distribution measurements made by previous investigators are reviewed and compared with the new information. The diurnal variation of size distribution was measured for four 24-hr periods, and concentration variations are shown to be related to local particulate source and meteorological conditions.

The self-preserving size distribution theory of Friedlander is reviewed and tested with 58 size distributions measured under a variety of conditions. The experimental data are consistent with the theory for particles of radii greater than about 0.05 μ, and the size distribution function, dN/dr, is found to be equal to $0.05\phi r^{-4}$ for the size range 0.05–3 μ, where N is the number of particles cm^{-3}, r the particle radius, and ϕ the particle volume per unit volume of aerosol. A good approximation to the size distribution of atmospheric aerosol for particles greater than 0.05 μ is shown to result from determining ϕ from the weight of high-volume filter samples and the particle density.

1. Introduction

The concentration and size distribution of particles dispersed in the atmosphere are important parameters in the study and control of our environment. Atmospheric particles range in size from the radius of a cluster of large gas molecules, on the order of 5Å, to radii as large as from ten to hundreds of microns, depending on the stillness of the air. Because of the difficulties involved in making simultaneous measurements over the broad range of particle sizes present, there have been only a few investigations of the complete size distribution of atmospheric aerosols. However, with recent advances in the techniques of aerosol measurement, the complete size distribution may now be measured *in situ* with a particle counting system composed of continuous sampling instruments. One of the purposes of this study was to demonstrate that such a system could be effectively used to monitor atmospheric aerosols, and to show how concentration changes in various size increments were related to local weather and source conditions.

A second objective was to use the data obtained to test the theory of self-preserving aerosol size distribution. Previously determined atmospheric size distributions, although few in number, are very similar in shape. Friedlander (1961, 1965) has proposed the theory of self-preserving size distributions, which helps to explain why atmospheric size distributions are similar. He proposed that the similarities can be explained by the existence of certain solutions to the kinetic equation which describes the relationship between the particle size distribution and time. Experimental results have indicated that the size distribution over a particular range of sizes follows the relation

$$dN/dr = C\phi r^{-4},$$

where N is the number of particles cm^{-3}, r the particle radius, C a constant, and ϕ the volume of particles per unit volume of aerosol. A substantial number of size distributions were measured in this study under a variety of weather and source conditions. The size distribution measurements of previous investigators were compared with this new information and the theory of self-preserving size distributions was tested for particles of radius from 0.001 to 3.0 μ.

2. Review of previous work

Junge (1955, 1963) determined from impactor samples and direct optical microscope counts that the size distribution function, dN/dr, was proportional to r^{-4} for particles of radii greater than 0.5 μ. Aitken nuclei counts indicated that the relationship might apply for particles down to a radius of about 0.1 μ. Junge theoretically determined the ratio of charged nuclei to all nuclei for the case of ionization equilibrium so that the

[1] This work was supported in part by U. S. Public Health Service Research Grant No. AP 00136-05.

[2] Present affiliation: Battelle Memorial Institute, Columbus, Ohio.

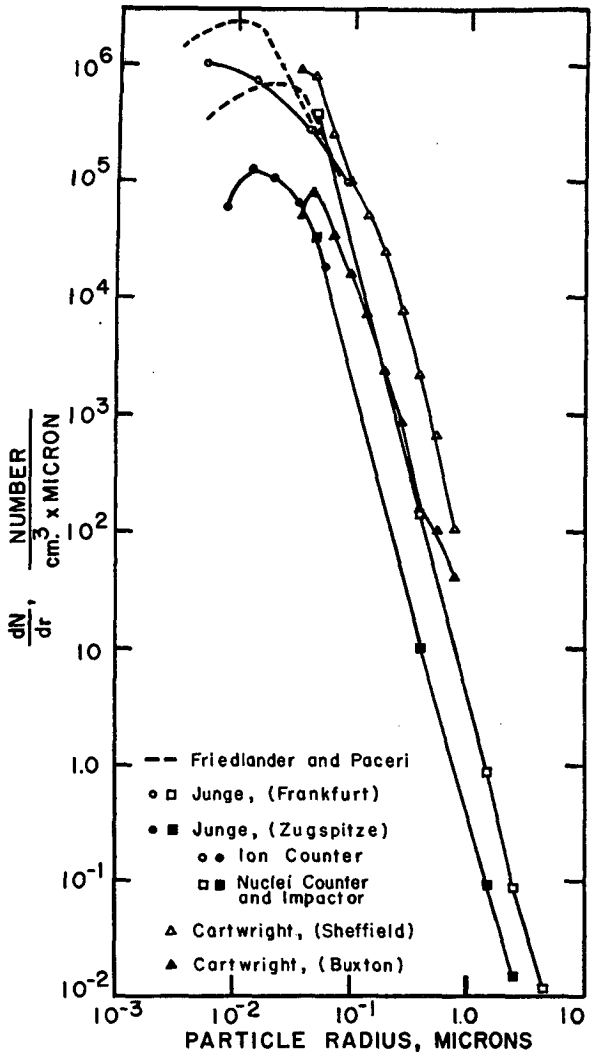

FIG. 1. Previously determined atmospheric aerosol size distributions.

size distribution of particles between 0.003 and 0.1 μ in radius could be determined from ion mobility measurements. The distributions shown in Fig. 1 represent the averages of from 11 to 25 individual measurements. The Frankfurt ion mobility measurements were previously determined by Israel (1941). Junge converted the data to a size distribution and later supplemented the information with nuclei counts and optical microscope measurements of impactor samples. The ion measurements, nuclei counts, and impactor samples used in determining the size distribution on the Zugspitze Mountain were taken simultaneously.

Cartwright *et al.* (1956) collected samples of atmospheric aerosols with a thermal precipitator. The size distribution of particles from approximately 0.03–0.9 μ in radius was determined with an electron microscope. Fig. 1 shows the size distribution near Buxton, England, a country atmosphere, and in Sheffield, England, an industrial city atmosphere.

Previous measurements of the size distribution of atmospheric aerosol have been reviewed by Friedlander and Paceri (1965). It is reported that Twomey and Severynse (1963) determined the size distribution of the atmospheric aerosol using diffusion batteries and a condensation nuclei counter. The data closely followed that of Junge with the exception that an apparent second mode in the size distribution was observed at a radius of about 0.007 μ.

Friedlander (1965) and Friedlander and Pasceri (1965) have measured the atmospheric size distribution in Baltimore, Md. Particles of radius greater than 0.4 μ, collected with a four-stage impactor, were sized with an electron microscope. It was found that the slope of the size distribution function, dN/dr, for outdoor samples varied somewhat over the range of 0.1–20 μ. The size distribution function for an indoor sample, however, was closely proportional to r^{-4}. Two indoor runs were also made to sample large particles. It was found that the size distribution function remained proportional to r^{-4} up to a radius of 70 μ. Particles of radius less than 0.1 μ were sized with an electron microscope after being collected by Brownian diffusion to an electron microscope grid placed at the center of a rotating disk. The disk was operated indoors at a speed at 2000 rpm over two time periods of 13 and 25 hr. The results are shown in Fig. 1. The distribution of higher concentration occurred when the axis of the disk was vertical and the distribution of lower concentration occurred when the disk axis was horizontal.

The size distribution measurements by Junge on the Zugspitz Mountain represent the only outdoor aerosol study over a broad size range in which measurements were taken simultaneously for all sizes. Thus, at the beginning of this study there were relatively few complete data on the entire size range of urban aerosols.

3. Experimental equipment

An electrical particle counter, a condensation nuclei counter, and an optical counter were used to size the particles dispersed in the atmosphere from 0.001 to 3μ in radius. The electrical particle counter, developed by the Particle Technology Laboratory of the University of Minnesota, is a continuous sampling instrument capable of determining aerosol concentration and size distribution over a range of radii from 0.0075 to 0.5 μ. A complete description of the counter and theory of its operation have been presented by Whitby (Whitby *et al.*, 1964; Whitby and Clark, 1966). The aerosol was continuously drawn into a diffusion charger at a flow rate of 1 ft^3 min^{-1}, where the particles were charged negatively in such a manner that electrical mobility was a decreasing function of particle size. The charged particles were distributed in a thin annular cross section

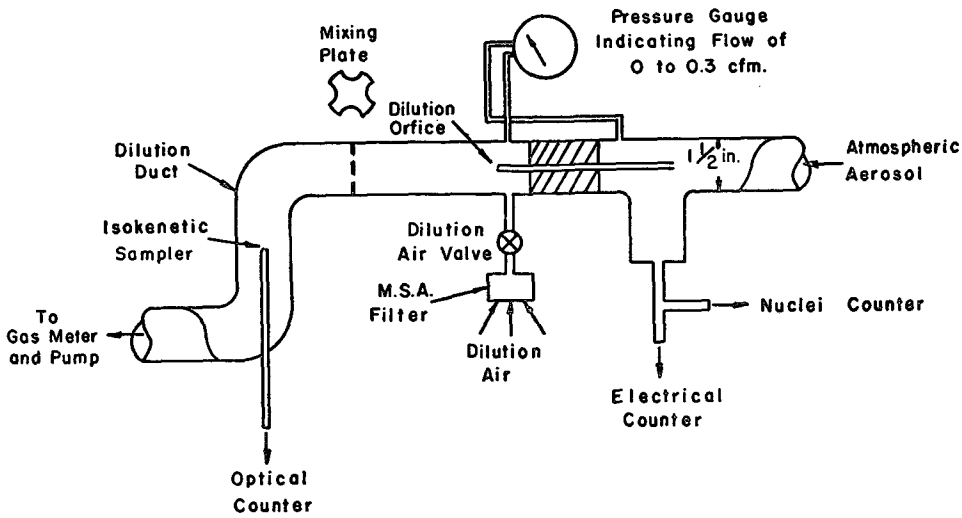

FIG. 2. Schematic representation of the distribution and dilution system.

in a cylindrical electric precipitating field. For each value of electric field strength, there corresponded a unique value of mobility such that all particles with a greater mobility were collected, while those with a lesser mobility bypassed the electric field and were collected by a filter paper stretched across a porous metal disk. The current from the collection disk was measured with a sensitive electrometer. For each incremental increase in the electric field strength, there resulted an incremental decrease in the measured current. Given the charge per particle, the concentration in each of the following radius increments, in microns, was determined: 0.0075–0.015, 0.015–0.03, 0.03–0.05, 0.05–0.15, 0.15–0.3 and 0.3–0.5.

A General Electric condensation nuclei counter was used to measure the total concentration of particles greater than approximately 0.001 μ in radius. The counter has been described in detail by Skala (1963). It samples at a rate of 100 cm^3 sec^{-1} and has a response time of from 1–2 sec and a concentration range of from $10–10^7$ particles cm^{-3}. The counter was operated at an under-pressure expansion of eight inches of mercury. For this condition condensation occurs on particles of 0.001 μ in radius and larger. The absolute accuracy of concentration measured over the total range is somewhat uncertain since there is no "standard" which shows less variation on a stable aerosol than this counter. However, considering interchecks between various standards, it is thought that the present calibration is within 10% of absolute value over the range from 1000 to 75,000 particles cm^{-3}. Above 100,000 particles cm^{-3}, the standards become less reliable due to diffusion and coagulation losses. The nuclei count of the urban atmosphere fluctuated extensively, and for some time periods the range of fluctuation was as great as $\pm 80\%$ of the average value. An average value was chosen for each period of interest from a strip chart record. The concentration between 0.001–0.0075 μ was determined by subtracting the number greater than 0.0075 μ, as found by the electrical and optical counters, from the nuclei count.

A Royco PC-200 optical particle counter was used to measure the upper size range. The application and theory of the instrument have been discussed by Zinky (1962). The atmospheric aerosol was sampled at a flow rate of 150 cm^3 min^{-1} and the counter was allowed to count for 0.3 min for each of 15 size increments. For this operating condition, the counter is able to count up to 2250 particles per 0.3 min with an estimated 10% coincidence loss. It was found that a sufficient number of particles just below the lower size limit of the Royco counter caused the whole indicated size distribution to be shifted upward in size from the actual distribution. To minimize the coincidence loss and the effect of particles smaller than the range of the Royco, the indicated count was kept below 1500 particles per 0.3 min by means of a dilution system. The concentration was determined for the following radius intervals in microns: 0.15–0.3, 0.3–0.5, 0.5–0.75, 0.75–1.5 and 1.5–3.0. A very small concentration of larger particles does exist in the atmosphere, but because a dilution system was used, it was believed that the few particles counted with a radius greater than 3 μ were not representative enough to be included in the data.

The system used to distribute the atmospheric aerosol to the various instruments and to dilute the aerosol for the optical counter is shown schematically in Fig. 2. The system operated as follows: The aerosol was sampled through a 1-inch diameter pipe which extended $4\frac{1}{2}$ ft from the side of a building. A flow rate of from zero to 0.3 ft^3 min^{-1} through the dilution orifice was controlled by the dilution air valve which also adjusted the flow of air through the dilution air filter.

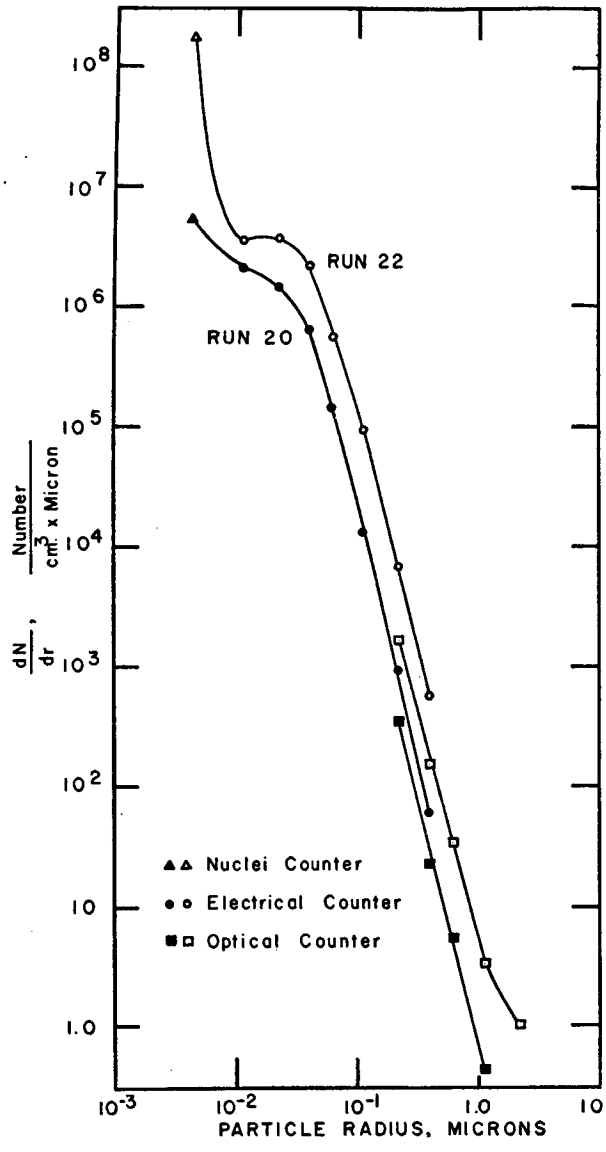

FIG. 3. Two size distributions of atmospheric aerosol measured at the University of Minnesota for 0400 (Run 20) and 0800 (Run 22).

4. Results and discussion

Atmospheric size distributions. The size distribution of the atmospheric aerosol at the University of Minnesota, Minneapolis, was measured 58 times. The data, time, weather condition, total concentration and size distribution are tabulated for each run by Clark (1966). Two distributions which are representative in shape and range of all the distributions are shown in Fig. 3. Run 20 was recorded at 0400 local time, 25 January 1966. Run 22 was measured 4 hr later during a time of heavy traffic and a temperature inversion. In some instances, the magnitude of the distribution function, dN/dr, measured by the optical counter was less than the magnitude measured by the electrical counter in the overlapping size range of radii $<0.5\ \mu$. Whitby and Vomela (1965) have reported that optical counters calibrated with polystyrene latex aerosols, such as the Royco, underestimate the size of absorbing aerosols by factors of from 2 to 5. Filter samples of urban aerosol show a large number of opaque particles which are assumed to be rich in carbon and products of the combustion of carbonaceous fuels. It is thought that the concentration of optically absorbing particles was great enough during some time periods to have caused the shift in indicated size as shown in Fig. 3. The agreement between the optical counter and an extension of the electrical counter data was better for particles of radii $>0.5\ \mu$

The size distributions for radii $>0.0075\ \mu$ were similar to those determined by previous investigators, as shown in Fig. 1. The distribution function was approximately proportional to r^{-4} for particles $>\sim 0.05\ \mu$. Below this size, the magnitude and shape of the distribution function was highly dependent on local source and weather conditions. Higher concentrations of particles in the range of radii from 0.001 to 0.0075 μ were measured in this study than previously reported. While only one data point could be plotted for the distribution curve in this range, each size distribution measured indicated a mode in this region. Previous measurements, except for the Frankfurt determination, indicated that the distribution function was a maximum in the region between 0.01–0.05 μ and then decreased for smaller radii. It is thought that this difference resulted from the fact that particles were counted to a radius of 0.001 μ in this study, while the lower sizing limit for Junge's and Friedlander's data was 0.003 μ.

The diurnal variation of size distribution. The atmospheric aerosol was measured at 2-hr intervals on four different days from a north second-story window of the Mechanical Engineering building on the University of Minnesota campus. The area directly below the sampling probe was a parking lot which was blocked off during this study because of construction. The temperature, relative humidity, wind speed and direction were obtained from the Weather Bureau station, approximately 6 mi south of the point of sampling. Vertical weather data were obtained from a television tower located approximately 1 mi east of the sampling location. At this facility the temperature was recorded at heights of 70, 170, 300 and 500 ft. The diurnal variations of size distribution are shown in Figs. 4 through 7. The four days monitored are characterized as follows:

Saturday, 22 January 1966 was a clear, cold day with a sunrise at 0743 and a sunset at 1707. The temperature increased from −8F at 0800 to 3F at 1400, and then decreased to −8F by midnight. The wind was from the northwest and ranged from 4–10 mph.

Tuesday, 25 January 1966 was also clear and cold, the sun rising at 0741 and setting at 1711. The temperature increased from −8F at 0600 to 12F at 1400 and then decreased to −6F at 0200 the morning of 26 January. A calm was recorded at 0400 and winds

from the southwest, southeast and south from 2–7 mph prevailed the remainder of the day.

Wednesday, 23 February 1966 was clear and somewhat warmer than the days monitored in January. Sunrise was at 0702 and sunset at 1752. The temperature increased from 6F at 0600 to 26F at 1600, decreased to 15F at 2000, and remained steady until 0200 the morning of 24 February. The wind was predominantly from the south and ranged from 2–9 mph.

Friday, 4 March 1966 was, for the most part, an overcast and windy day with the sun shining through a cloudy sky only between 0800 and 0900. The temperature decreased from a high of 33F at 0400 to a low of 26F at 0200 the morning of 5 March. Winds ranged from 9–18 mph and varied from the southwest, south, southeast, northeast and north as the day progressed.

The ability of the atmosphere to disperse and dilute particulate matter depends on the degree of atmospheric turbulence present. Turbulence is characterized by wind variability in speed and direction and is dependent on the stability of the atmosphere. The notation "I" in Figs. 4–7 indicates that the size distribution was measured during a period in which temperature increased with height, and the designation 170 or 300 refers to the height in feet at which each inversion began. The notation "S" denotes times for which there was no

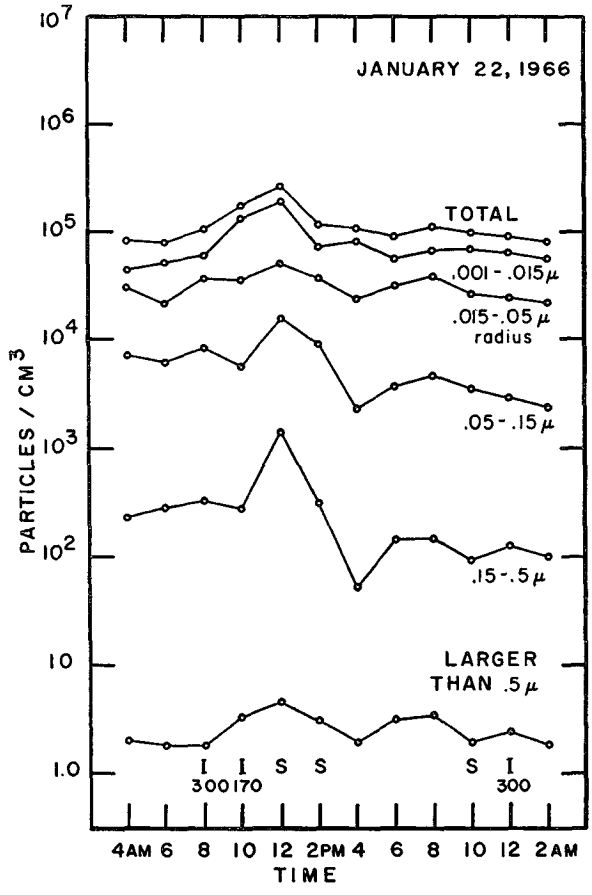

FIG. 4. Diurnal size distribution variation for 22 January 1966.

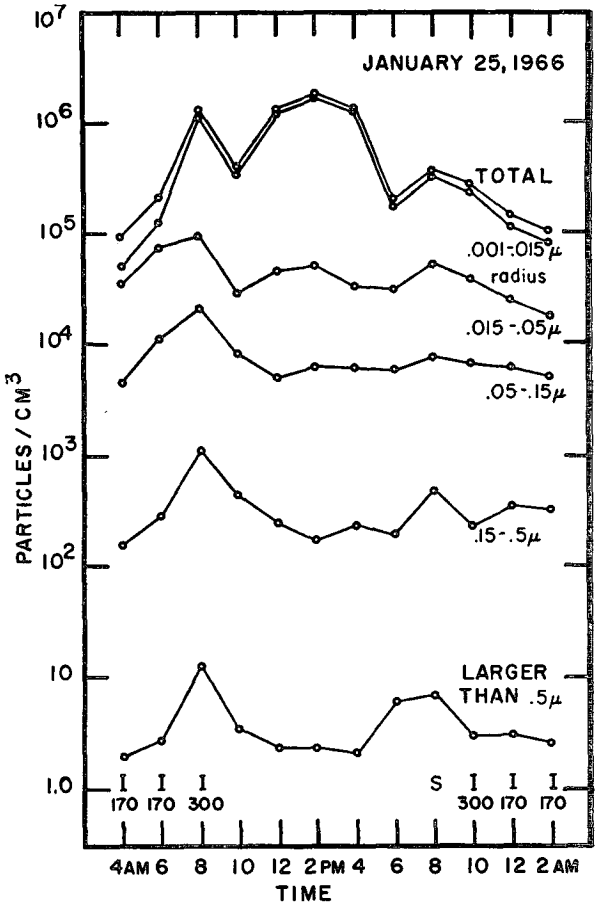

FIG. 5. Diurnal size distribution variation for 25 January 1966.

change in temperature with height from 300–500 ft, indicating the height of a relatively stable layer.

Although the four days monitored constitute a limited amount of data, several observations can be made concerning the diurnal variations. Particles having a radius of 0.001–0.015 μ constituted the majority of the total concentration as indicated by the nuclei counter. The diurnal variation depended to a large extent on the combination of the strength of particulate sources and on the degree of natural ventilation available. On the three weekdays sampled, the concentration of particles >0.05 μ increased to a maximum at 0800, decreased and remained steady through the afternoon, built up to a smaller peak in the evening, and then decreased. This is a well-known weekday concentration variation which has previously been determined by measuring the optical density of soiled spots on filter paper as described by Hemeon (1953) and Summers (1961).

Although high levels of source activity continued through the afternoon, the concentration of particles >0.05 μ decreased as the atmosphere became less stable. The evening concentration peaks occurred during periods of reduced natural ventilation, but were not as

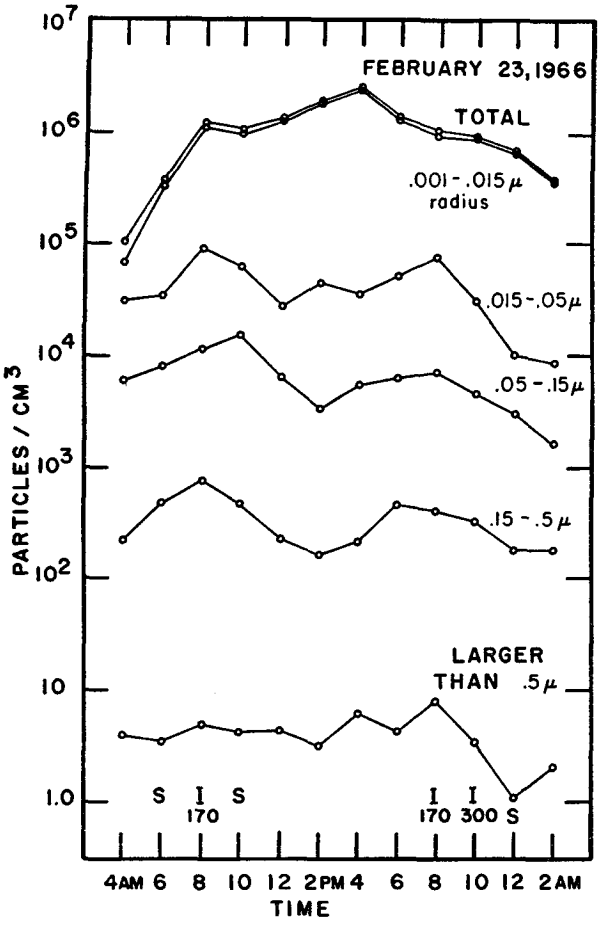

FIG. 6. Diurnal size distribution variation for 23 February 1966.

extreme because there were fewer sources of particles in effect such as vehicles, industrial processes, and photochemical reactions. On 4 March there were no periods of low-level inversions or relatively stable lapse rates, and the wind was high in speed and variable in direction. The concentration of particles $>0.05\ \mu$ was consequently lower, and the morning and evening peaks less extreme. On Saturday, 22 January, in the absence of normal traffic and industrial sources, the concentration in all size ranges was less than on the clear weekdays sampled.

The number of particles from 0.001 to 0.015 μ in radius appeared to depend on the degree of photochemical activity present as well as on source and natural ventilation conditions. On the clear weekdays, Figs. 5 and 6, the concentration of these very small particles increased to a second peak in the afternoon, while the concentration of particles $>0.05\ \mu$ decreased to a minimum. Because the coagulation rate for particles of this size is very high, the instantaneous concentration is more dependent on their production. It is reasonable to assume that since their life is relatively short, the concentration of these small particles is not affected as much by the degree of natural ventilation available. On the cloudy day, 4 March, the sky was completely overcast from 0900 throughout the day and there was no large-scale increase in concentration of the small particles. It is thought that the photochemical effect on the clear weekdays was quite dependent on the normal traffic flow and on industrial sources, because the concentration of the very small particles varied in somewhat the same manner as those $>0.05\ \mu$ on the clear Saturday monitored.

By measuring the distribution at shorter time intervals than the 2-hr increments used in this analysis, the continuous change in concentration for various size intervals could be determined. Coupled with accurate weather data recorded at the point of sampling, and incorporating a knowledge of local particulate source characteristics, the system would be a valuable tool in air pollution research.

A test of the theory of self-preserving size distributions. Previously measured atmospheric size distributions and the distributions determined in this study are very similar in shape, even though they were measured using a variety of methods and under a variety of conditions. This is particularly true for particles of radii $>0.05\ \mu$. Friedlander has proposed that similarities in size distributions can be explained by the existence of certain

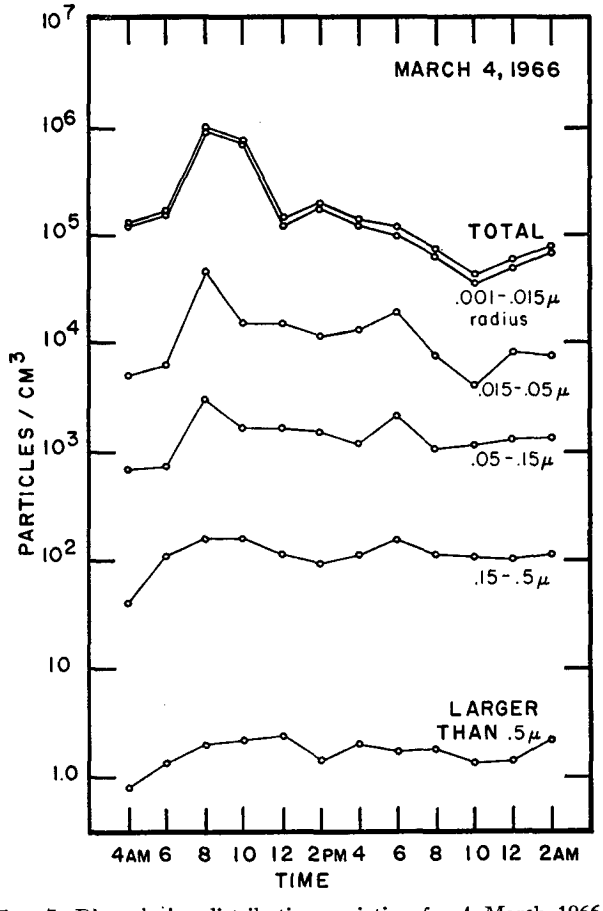

FIG. 7. Diurnal size distribution variation for 4 March 1966.

special solutions to equations which describe the rate of change of particle size distribution with time. The special solutions are termed "self-preserving" because they do not vary in shape with time. Equations which describe the rate of change of particle size distribution with time must take into account the initial distribution of size, and the decay processes of coagulation and sedimentation. Friedlander (1961) has shown that such an expression for atmospheric aerosol is a partial integro-differential equation which could be solved if initial conditions and boundary conditions were known. For the urban atmosphere, this information cannot be specified, and the equation cannot be solved. Friedlander has suggested the use of a similarity transformation to change the partial integro-differential equation to that of a total differential equation and reduce the number of independent variables.

The basic assumption for the transformation is that the size distribution function, $n(r)=dN/dr$, can be given by

$$n(r)=g(t)\Psi(r/r_0(t)), \tag{1}$$

where $n(r)$, $g(t)$ and $r_0(t)$ are time dependent and Ψ is a dimensionless distribution function which is independent of time and dependent only on the dimensionless radius, $r/r_0(t)$. The total number of particles N_t, per cm^3, is given by

$$N_t=\int_0^\infty n(r)dr, \tag{2}$$

and the total particulate volume ϕ per unit volume of aerosol by

$$\phi=\int_0^\infty (4/3)\pi r^3 n(r)dr. \tag{3}$$

For an aerosol isolated from particulate sources and for which the only process of decay is by coagulation, ϕ is a constant. Although the atmospheric aerosol is continually influenced by particulate sources and the process of sedimentation, Friedlander (1961) has suggested that quasi-stationary states exist for the middle range of the size spectrum in which the particulate matter formed by the process of coagulation is equal to the rate at which matter is lost by sedimentation. For this equilibrium range, the value of ϕ may be assumed constant over short time intervals. By substituting Eq. (1) into (2) and (3), the time dependent parameters $g(t)$ and $r_0(t)$ are given by

$$g(t)=\frac{N_t}{r_0(t)}\left[\int_0^\infty \Psi d(r/r_0(t))\right]^{-1}, \tag{4}$$

$$r_0(t)=\left[\frac{3\phi\int_0^\infty \Psi d(r/r_0(t))}{4\pi N_t\int_0^\infty (r/r_0(t))^3\Psi d(r/r_0(t))}\right]^{\frac{1}{3}}. \tag{5}$$

For any one size distribution, the expressions

$$\int_0^\infty \Psi d(r/r_0(t)) \quad \text{and} \quad \tfrac{4}{3}\pi\int_0^\infty (r/r_0(t))^3\Psi d(r/r_0(t))$$

are dimensionless constants. By substituting Eqs. (4) and (5) into (1), the self-preserving form of the size-distribution function can be given by

$$n(r)=\frac{N_t^{\frac{4}{3}}}{\phi^{\frac{1}{3}}}\Psi_r[r(N_t/\phi)^{\frac{1}{3}}]=\frac{N_t^{\frac{4}{3}}}{\phi^{\frac{1}{3}}}\Psi_r(\eta_r), \tag{6}$$

where Ψ_r is a dimensionless size-distribution function different from Ψ and dependent only on $\eta_r=r(N_t/\phi)^{1/3}$.

Friedlander (1961) has shown that when the self-preserving form is substituted into the equation describing the rate of change of the size-distribution function with time for atmospheric aerosol, a total integro-differential equation for Ψ_r results with η_r as an independent parameter. This indicates that the self-preserving form, Eq. (6), is a particular solution to the equation. Swift and Friedlander (1964) have shown that the self-preserving form is a solution to the equation describing the decay process of coagulation by Brownian motion, and have tested the theory experimentally using several dilute hydrosols with various coagulation rates. It was found that for initially unimodal distributions, the dimensionless size-distribution function Ψ tended to preserve its shape as the hydrosols coagulated with time, thus substantiating the theory of self-preservation. It was also found that when two heterodisperse hydrosols were mixed, the dimensionless distribution function tended to approach the same shape as that found with initially unimodal distributions.

Hidy (1965) performed numerical coagulation experiments with a computer. An equation expressing the change in size distribution with time for Brownian-motion coagulation was solved for several size spectrums having initially one discreet size, and two size spectrums having initially two discrete sizes and four discrete sizes. The values of λ/r ranged from 0 to 10 for the initial spectrums of one discreet size, where λ is the mean free path and r is the particle radius. It was found that the dimensionless size-distribution function approached a self-preserving form which was independent of the initial distribution after sufficiently long coagulation times. Hidy found that varying the value of λ/r up to a value of 1 shifted the maximum value of the dimensionless size-distribution function but did not affect the upper end of the curve for values of η greater than 0.15. The form of the dimensionless size-distribution function was consistent with the experimental results of Swift and Friedlander.

To substantiate the self-preservation theory, the 58 atmospheric size distributions measured in this study were plotted in the dimensionless coordinates Ψ_r vs. η_r. Since Ψ_r depends only on η_r, the experimental data

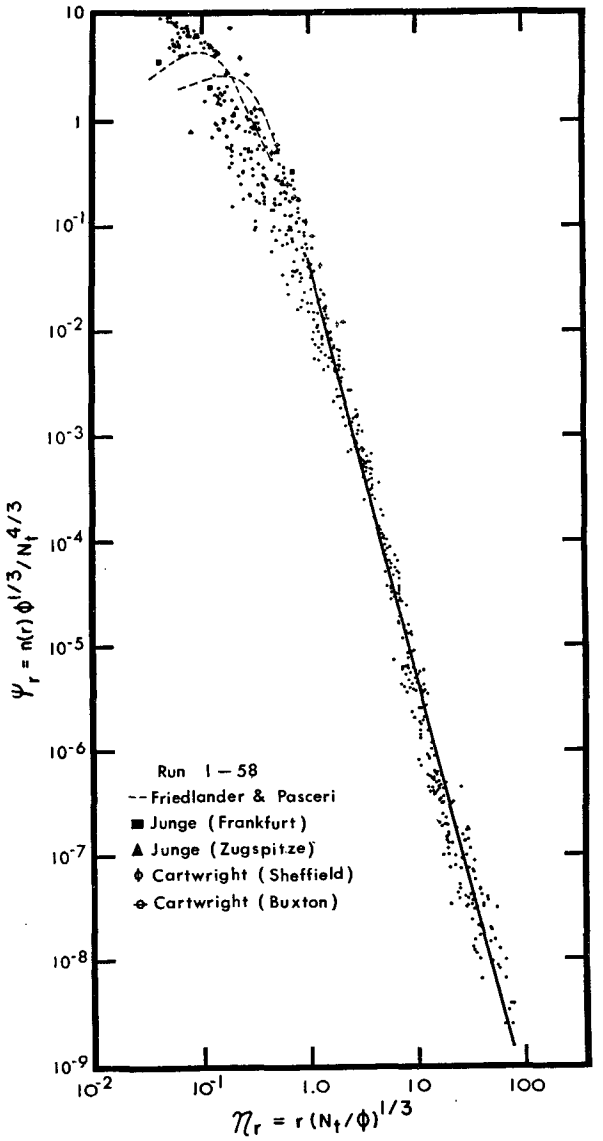

FIG. 8. Test of the theory of self-preserving size distributions.

should fall on a single curve. The total particle concentration N_t was taken to be the nuclei counter indication. The particle volume ϕ, per unit volume of aerosol, was approximated for each distribution with summation given by

$$\phi = \sum_{0.001}^{3} (4/3)\pi r_i^3 N_i, \qquad (7)$$

where r_i is the midpoint of each radius increment in which the original data was measured, and N_i is the particle concentration in each radius increment. The value of the size distribution function corresponding to each radius r_i was found by

$$n(r) = N_i/\Delta r_i,$$

TABLE 1. Values for N_t and ϕ for the size distributions of Fig. 8.

Investigator	N_t (particles cm^{-3})	ϕ (μ^3 cm^{-3})
Friedlander	3.5×10^4	80.0
Friedlander	6.0×10^4	80.0
Junge (Zugspitze)	6.8×10^3	6.9
Junge (Frankfurt)	4.12×10^4	76.7
Cartwright (Buxton)	3.15×10^3	55.0
Cartwright (Sheffield)	4.18×10^4	356.0
This study (minimum values)	4.25×10^4	10.4
This study (maximum values)	2.58×10^6	251.0

where Δr_i is the size of each radius increment. The data of this study and that of previous investigators as presented by Paceri and Friedlander (1965) are shown in Fig. 8. Table 1 shows the range of ϕ and N_t for each investigation. The total concentration, for most runs

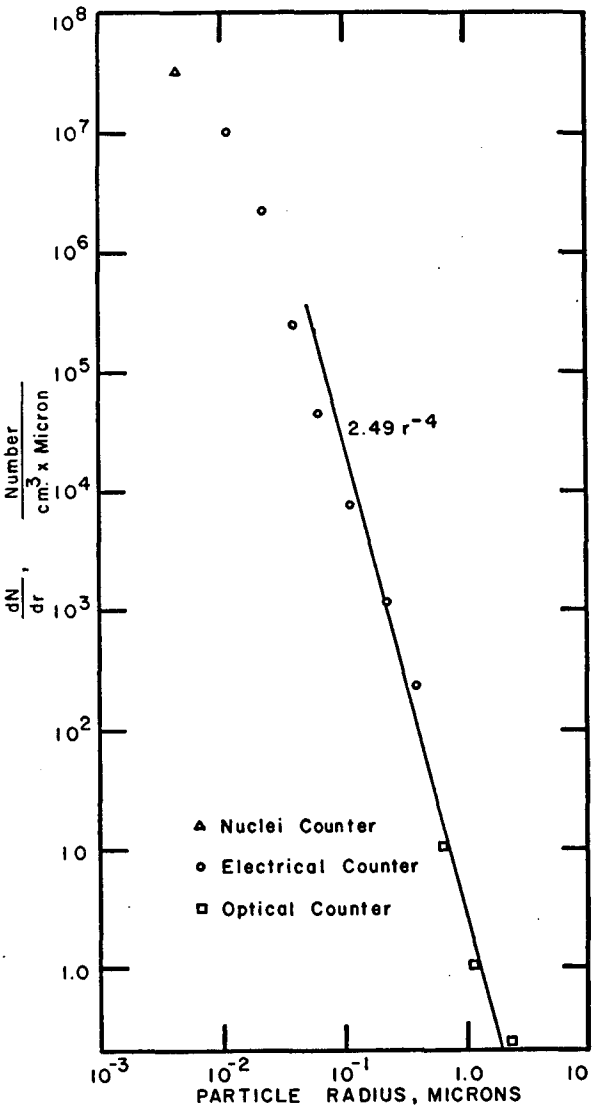

FIG. 9. Particle size distribution for Run A$_8$

TABLE 2. Values of Ψ_r and η_r for maximum and minimum values of N_t and ϕ.

Run number	40		56		22		47	
Date	23 Feb. 1966		4 Mar. 1966		25 Jan. 1966		4 Mar. 1966	
Time	1600		1000		0800		0400	
Temperature	26		28		−7		33	
Wind (direction, mph)	S-7		NE-12		SE-3		SW-15	
Relative humidity (%)	63		78		61		82	
Pressure (inches Hg)	30.50		29.41		30.44		29.17	
$\phi(\mu^3\ cm^{-3})$	101.7		28.07		250.6		10.42	
N_t (particles cm^{-3})	2,575,000		42,500		1,300,000		128,000	
Radius (μ)	Ψ_r	η_r	Ψ_r	η_r	Ψ_r	η_r	Ψ_r	η_r
0.001 -0.0075	4.95	1.25×10^{-1}	8.56	4.88×10^{-2}	7.88	7.36×10^{-2}	5.44	9.81×10^{-2}
0.0075-0.015	1.76×10^{-1}	3.30×10^{-1}	2.76	1.29×10^{-1}	1.56×10^{-1}	1.95×10^{-1}	8.07×10^{-1}	2.60×10^{-1}
0.015 -0.03	2.26×10^{-2}	6.61×10^{-1}	4.29×10^{-1}	2.59×10^{-1}	1.62×10^{-1}	3.90×10^{-1}	8.32×10^{-2}	5.19×10^{-1}
0.03 -0.05	7.36×10^{-3}	1.18	8.94×10^{-2}	4.59×10^{-1}	9.70×10^{-2}	6.92×10^{-1}	2.33×10^{-2}	9.23×10^{-1}
0.05 -0.075	2.29×10^{-3}	1.84	7.10×10^{-2}	7.18×10^{-1}	2.49×10^{-2}	1.08	5.86×10^{-3}	1.44
0.075 -0.15	2.41×10^{-4}	3.30	6.94×10^{-3}	1.29	4.28×10^{-3}	1.95	9.98×10^{-4}	2.60
0.15 -0.3	1.64×10^{-5}	6.61	1.33×10^{-3}	2.58	3.09×10^{-4}	3.90	7.85×10^{-5}	5.19
0.3 -0.5	2.08×10^{-6}	1.18×10^{1}	1.15×10^{-4}	4.59	2.59×10^{-5}	6.92	9.11×10^{-6}	9.23
0.5 -0.75	1.89×10^{-7}	1.84×10^{1}	5.84×10^{-6}	7.18	1.52×10^{-6}	1.08×10^{1}	6.32×10^{-7}	1.44×10^{1}
0.75 -1.5	2.98×10^{-8}	3.30×10^{1}	8.58×10^{-7}	1.29×10^{1}	1.49×10^{-7}	1.95×10^{1}	9.03×10^{-8}	2.60×10^{1}
1.5 -3.0	9.70×10^{-9}	6.61×10^{1}	4.29×10^{-7}	2.58×10^{1}	4.56×10^{-8}	3.90×10^{1}	1.51×10^{-8}	5.19×10^{1}

in this study, was higher than previously measured because a broader range of particle sizes was included. Table 2 shows the weather conditions, computed values of Ψ_r and η_r for the extreme cases of maximum and minimum N_t, and maximum and minimum ϕ measured in this study.

The experimental data falls approximately along a single curve for values of η_r greater than 1.0. This value corresponds to a particle radius of approximately 0.05 μ. The deviation for values of $\eta_r<1.0$ is thought to have occurred because the size distribution of the smaller particles was more dependent on the character and strength of local sources than on the process of coagulation. The scatter in data for values of $\eta_r>\sim10$ may in part be explained by the fact that the aerosol was diluted, and there were insufficient numbers of large particles counted.

For values of $\eta_r>1.0$, the dimensionless distribution function Ψ_r varies approximately as η_r^{-4}. The agreement for data near $\eta_r=10$ may be somewhat better than shown in Fig. 8, because this is the region of transition between the electrical and optical counter data. By approximating the data of this subrange with a straight line, shown in Fig. 8 as the solid line, Ψ_r is given by

$$\Psi_r=0.05[r(N_t/\phi)^{\frac{1}{3}}]^{-4}. \quad (9)$$

Substituting this equation into Eq. (6), we have

$$n(r)=0.05\phi r^{-4}. \quad (10)$$

The size distribution of atmospheric aerosol for radii $>\sim0.05$ μ may thus be approximated if ϕ is known. Paceri and Friedlander (1965) have suggested that ϕ be determined from the weight per unit volume of aerosol W as determined by a high-volume filter sample and the particle density ρ as given by

$$\phi=W/\rho. \quad (11)$$

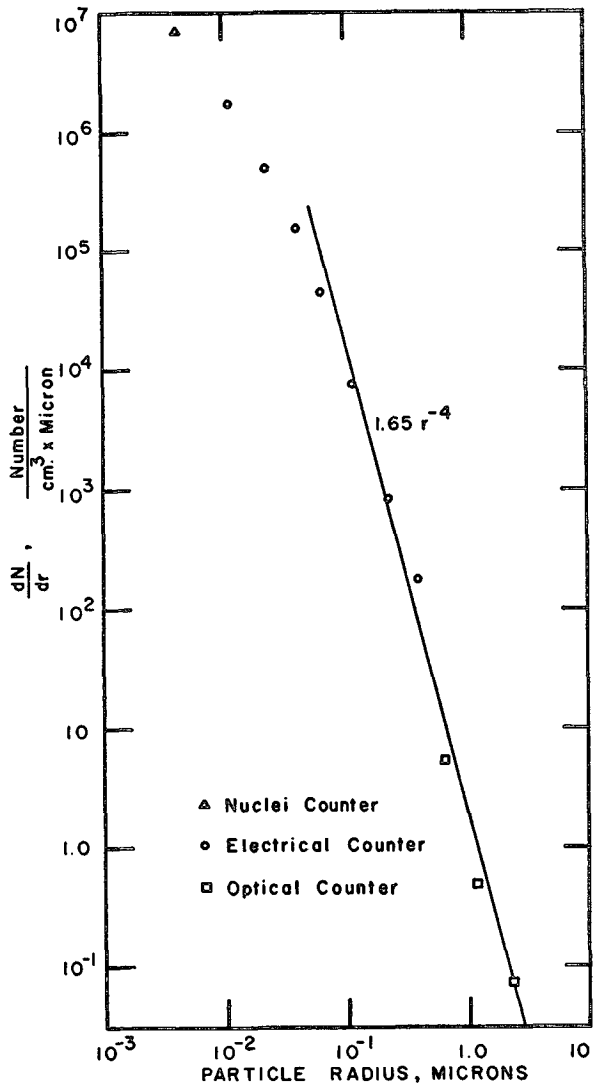

FIG. 10. Particle size distribution for Run B.

The size distribution of the atmospheric aerosol was measured five times in each of two 3-hr periods during which high-volume filter samples were obtained. An average distribution was calculated for each time period from the individual runs. A value for particle density was needed to determine ϕ, and it was decided to calculate an average density for this location from the two 3-hr runs by dividing the weight per unit volume w by the value of ϕ as calculated from the average size distributions using Eq. (7). The calculated density for Run A and B was 1.305×10^{-12} and 1.538×10^{-12} gm μ^{-3}, respectively. The average of these calculated densities is 1.421×10^{-12}, a reasonable estimate of the effective density of the atmospheric aerosol. Using this value for particle density and Eq. (11), ϕ based on the weight of the high-volume filter samples was determined and the size distribution of particles $>\sim0.05$ μ was approximated using Eq. (10). For Run A the size distribution function is given by

$$n(r)=dN/dr=2.49r^{-4}, \tag{12}$$

and for Run B

$$dN/dr=1.65r^{-4}. \tag{13}$$

The size distributions as determined by the self-preserving theory and as measured with the particle sizing system are shown in Figs. 9 and 10. The agreement is quite good considering that the measurements were taken over 3-hr periods.

5. Summary and conclusion

The concentration and size distribution of the urban atmospheric aerosol was measured with a continuous-sampling sizing system over the size range from 0.001 to 3.0 μ in radius. The size distributions were similar to previously determined measurements for radii >0.05 μ in that the size distribution function dN/dr varied as r^{-4}. The distribution function mode was a maximum in the range from 0.001 to 0.0075 μ.

The diurnal variation of size distribution was found to vary with the strength of local particulate sources and to the degree of natural ventilation available. Particles from a radius of 0.001–0.015 μ constituted the majority of the total concentration as indicated by the nuclei counter, and the concentration in this range appeared to depend on the degree of photochemical activity present as well as on source and natural ventilation conditions.

The theory of self-preserving size distributions was tested by plotting the 58 size distributions determined in this study in the dimensionless coordinates Ψ_r vs. η_r. The data fell approximately along a single curve consistent with the theory for values of $\eta_r>1.0$, or for particles of radius $>\sim0.05$ μ. This study represented quite a severe test of the theory in that a substantial number of size distributions were involved, which were recorded under a variety of weather and source conditions and which included a broad range of particle sizes.

Approximating the experimental data with a straight line, the size distribution function for radii $>\sim0.05$ μ can be given by

$$dN/dr=0.05\phi r^{-4}.$$

The above equation was further tested by measuring ϕ with a high volume sampler and comparing the calculated distribution with that measured with the particle counting system. Agreement was good for radii >0.05 μ, suggesting that useful estimates of urban aerosol size distributions could be made from high volume sampler data.

REFERENCES

Cartwright, J., G. Nagelschmidt and J. Skidmore, 1956: The study of air pollution with the electron microscope. *Quart. J. Roy. Meteor. Soc.*, **82**, 82–86.

Clark, W. E., 1966: The concentration and size distribution of atmospheric aerosol. M. S. Thesis, University of Minnesota, 64–74 pp.

Friedlander, S. K., 1961: Theoretical considerations for the particle size spectrum of the stratospheric aerosol. *J. Meteor.*, **18**, 753–759.

——, 1965: Theory of self-preserving size distributions in a coagulation dispersion. *Radioactive Fallout from Nuclear Weapons Tests*, U. S. Atomic Energy Commission, 253–259.

——, and R. E. Paceri, 1965: Measurements of the particle size distribution of the atmospheric aerosol: I. Introduction and experimental methods. *J. Atmos. Sci.*, **22**, 571–576.

Hemeon, W. C. L., 1953: Measurement of air pollution. *Instruments*, **26**, 566–570.

Hidy, G. M., 1965: On the theory of the coagulation of noninteracting particles in Brownian motion. *J. Colloid Sci.*, **20**, 123–144.

Israel, H., 1941: Ionen und Kerne; eine kritische Studie. *Beitr. Geophys.*, **57**, 261–282.

Junge, C. E., 1955: The size distribution and aging of natural aerosols as determined from electrical and optical data on the atmosphere. *J. Meteor.*, **12**, 13–25.

——, 1963: *Air Chemistry and Radioactivity*. New York, Academic Press, 117 pp.

Paceri, R. E., and S. K. Friedlander, 1965: Measurements of the particle size distribution of the atmospheric aerosol; II. Experimental results and discussion. *J. Atmos. Sci.*, **22**, 577–584.

Skala, G. F., 1963: A new instrument for the continuous measurement of condensation nuclei. *Anal. Chem.*, **35**, 702–706.

Summers, P. W., 1961: Smoke concentrations in Montreal related to local meteorological factors. Symposium: Air Over Cities, Public Health Service, Robert A. Taft Sanitary Engineering Center, SEC Tech. Rept. A62-5, 89-112.

Swift, D. L., and S. K. Friedlander, 1964: The coagulation of hydrosols by Brownian motion and laminar shear flow. *J. Colloid Sci.*, **19**, 621–647.

Twomey, S., and G. T. Severynse, 1963: Measurements of size distributions of natural aerosols. *J. Atmos. Sci.*, **20**, 392–396.

Whitby, K. T., and W. E. Clark, 1966: Electrical aerosol particle counting and size distribution measuring system for the 0.015 to 1 micron size range. *Tellus*, **18**, 573–586.

——, R. C. Jordan, and C. M. Peterson, 1964: Generation and decay of small ions. Prog. Rept. USPHS Grant No. AP-00136-03, Mech. Eng. Dept., University of Minnesota, 1–28.

——, and R. A. Vomela, 1965: Evaluation of optical particle counters. Prog. Rept. USPHS Grant No. AP-00283-01, Mech. Eng. Dept., University of Minnesota, 38 pp.

Zinky, W. R., 1962: A new tool for air pollution control. *J. Air Pollution Control Assoc.*, **12**, 578–583.