The Determination of Particle Size and Electric Charge Distribution in Cigarette Smoke

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Introduction:

This paper reports our findings concerning the distribution of electric charge and particle size in cigarette smoke. The work was undertaken because of the scarcity of information on electrical properties and because of the wide diversity of opinion in the literature concerning size distribution.

The few studies of the particle size distribution of cigarette smoke appearing in the literature have each used different methods of measurement. Warner, using a cascade impactor indicated that the number mean diameter was around 0.3 micron. Sano studied the settling of individual particles and gave the number mean diameter as about 0.6 micron. Langer and Fisher using dark field microscopy reported a number mean diameter of about 0.6 micron. Keith and Derrick using the "conifuge" reported a number mean diameter of 0.2 micron.

The study of the electrical properties of cigarette smoke has received even less attention than has size distribution. Wells and Gerke made some use of the elcetric charge to measure the size of tobacco smoke but did not attempt to determine its electric charge distribution. Dalla Valle made brief mention of the electric charge distribution in cigarette smoke in a report concerning the agglomeration of aerosols. Sano reported the charge distribution of aged smoke but made no mention of the mechanism of its charging.

In this investigation a modification of Millikan's oil drop experiment was used to determine the electric charge on the smoke particles. The particle size distribution was determined by three different methods: (a) the cascade impactor, (b) gravity settling of individual par-

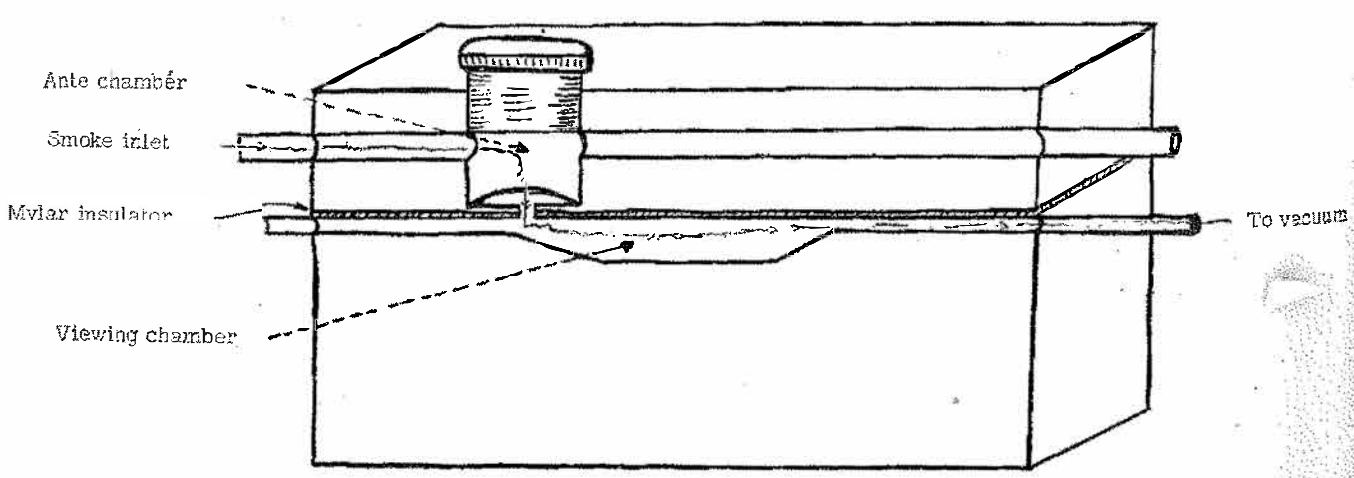

Figure 1. Side view of gravity settling chamber.

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ticles, and (c) the "Goetz Aerosol Spectrometer."

Experimental Procedure

Electric Charge Determination. The experimental work to determine electric charge was carried out by using an air-tight brass chamber consisting of an antechamber and an observation chamber (**Figure 1**). The smoke was introduced into the antechamber and drawn through a small hole into the observation chamber by means of a pump. When the smoke was in the observation chamber the flow of air was stopped and the particles were allowed to settle under the influence of gravity. The particles of smoke in the observation chamber were illuminated by a beam of light through a window in one side of the chamber. The light scattered by the particles was observed with a microscope (40X), through a window in the opposite side of the chamber (**Figure 2**). The upper half of the chamber was insulated from the lower half of the chamber by a thin sheet of Mylar. A variable, reversible potential was applied across the chamber (the upper and lower halves of the chamber are 3 mm. apart), putting a charge on the chamber in such a manner that the particle under observation reversed the direction of movement it had under the influence of gravity. The velocity of the upward movement, which was due to the electric field, was measured. The rate of fall due to gravity was also measured. To determine the electric charge on the particle, the rate of fall due to gravity and velocity due to the electric field are substituted into Millikan's equation.

Stokes' equation was used to calculate the diameter of the particles:

$$d = \sqrt{\frac{18\, n\, u}{(P-P')g}}$$

where d = diameter of the particle
n = viscosity of air
u = velocity of fall due to gravity
g = acceleration due to gravity
P = density of the particle
P' = density of air

Since the experimental procedure had only limited accuracy, Cunningham's correction to Stokes' equation was not applied. Drozen and LaMer point out that there is disagreement in the literature as to the necessity of applying Cunningham's correction.

When the diameter had been calculated, the mass of the particle was

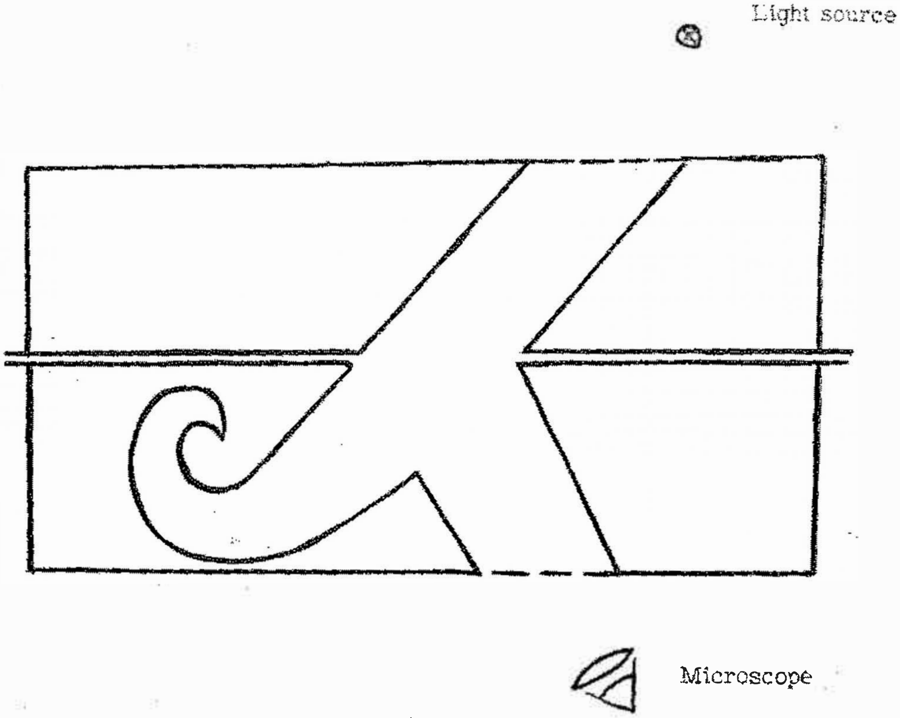

Figure 2. Top view of gravity settling chamber.

calculated from this diameter, and Millikan's equation was used to determine the charge on the particle.

$$q = \frac{Mg\,(V_1 + V_2)}{FV_1}$$

q = charge on the droplet
M = mass of droplet
g = acceleration due to gravity
F = electric field strength
V_1 = velocity down (gravity fall)
V_2 = velocity up (under influence of electric field)

The number of electronic charges per particle was determined by dividing the total charge on the particle by the charge of the electron.

$q/e = c$
c = number of electronic charges/particle
e = electron charge
q = charge on the particle

The smoke sample for the electrical measurements was obtained by taking a 35 ml. puff with a large syringe and was introduced directly into the antechamber. Two minutes after the start of the sampling puff all smoke was expelled from the chamber and a fresh puff was taken. This procedure insured that the smoke under observation was not more than two minutes old.

The effect of aging on the electric charge distribution was measured by collecting the smoke in a three-liter flask. The smoke was transferred from the flask to the gravity settling chamber and measurements were made over a period of thirty to forty-five minutes, depending upon how long a usable sample remained in the three liter flask. One hundred particles were observed for each determination of electrical charge distribution.

Size Determination. The cascade impactor used for determination of particle size was essentially the same as that described by Pilcher *et al.* except that its flow rate was set at 1.05 liter/min. and that special precautions were taken to make the internal volume of the impactor as small as possible to minimize the residence time of the smoke. **Figure 3** is a schematic diagram of the im-

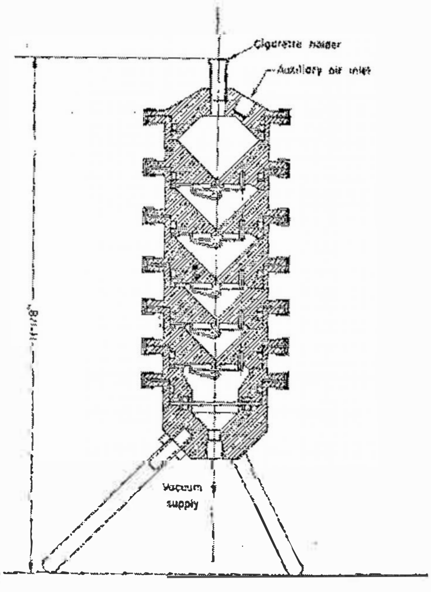

Figure 3. Assembly drawing of new stainless steel cascade impactor.

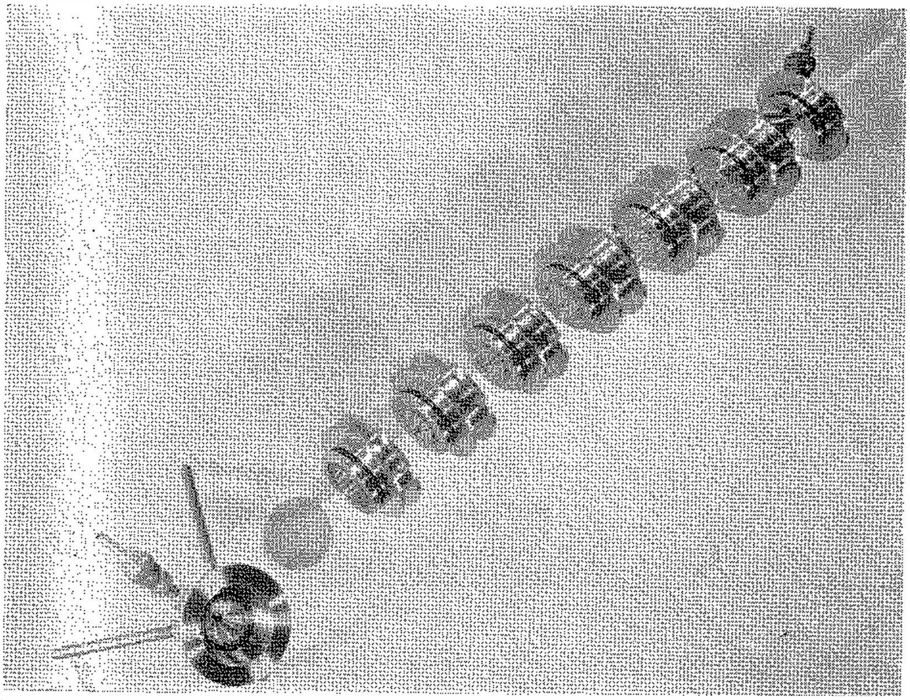

Figure 4. Photograph of new cigarette smoke cascade impactor.

pactor and **Figure 4** is a photograph showing the details of construction. Polystyrene latex spheres, puff ball spores, and Bacillus globigi spores were used to calibrate the impactor.

A sampling system was designed to allow smoking of cigarettes under standard conditions which would maintain a constant flow of air through the impactor. **Figure 5** is a schematic drawing of the system. The cycle is timed by a one-rpm synchronous motor which operates a micro switch that opens a solenoid valve for 58 seconds and closes it for two seconds. While the valve is open, filtered air at atmospheric pressure is introduced into one arm of the inlet tee at a flow rate equal to that of the impactor. When the valve is closed, all air which enters the impactor must pass through the cigarette in the other arm of the tee.

The apparatus shown in **Figure 6** was used to study the effect of dilution on the size distribution of cigarette smoke. Air at a rate of 17.5 ml. per second was introduced continuously to the cigarette-holding section and vented through a bleed valve. During each 60 second period of operation the bleed valve was open for 58 seconds with no flow through the cigarette and closed for two seconds during which time 35 ml. of air passed through the cigarette. The diluting air enters the main body of the diluter tangentally.

The rate of fall due to gravity of the smoke particles, as observed in the gravity settling chamber, was used to calculate the Stokes' diameter of the individual smoke particles. A particle size distribution of cigarette smoke was found from the calculated Stokes' diameters. The size was plotted on log-probability paper against percentage of the mass of particles less than maximum size, the result being a straight line with the

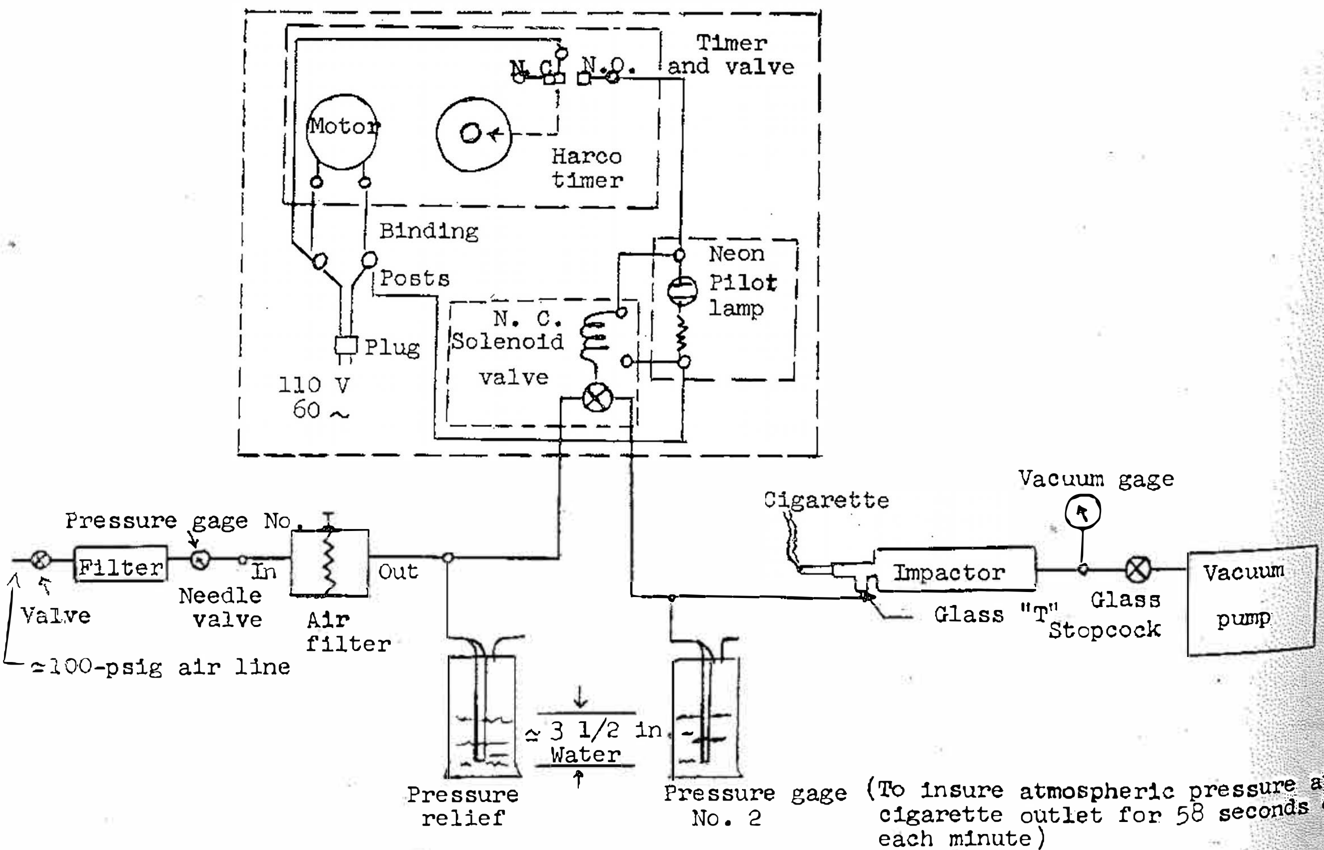

Figure 5. Cigarette smoke sampling system.

50 per cent point indicating the mass mean diameter. The settling rates of 500-1000 smoke particles were observed for these determinations.

The "Goetz Aerosol Spectrometer" was also used to determine the size distribution of cigarette smoke. This instrument subjected the smoke aerosol to a strong centrifugal force while the aerosol was flowing in a helical channel. This separated the particles according to size because the smaller particles traveled further than the larger particles in the channel before being deposited on the collection plate. The number of particles that had been deposited at various distances was determined by microscopic count. The size distribution was determined from a plot of the number of particles versus the distance along the channel at which the count was made. The aerosol spectrometer was calibrated by using polystyrene latex spheres of known size.

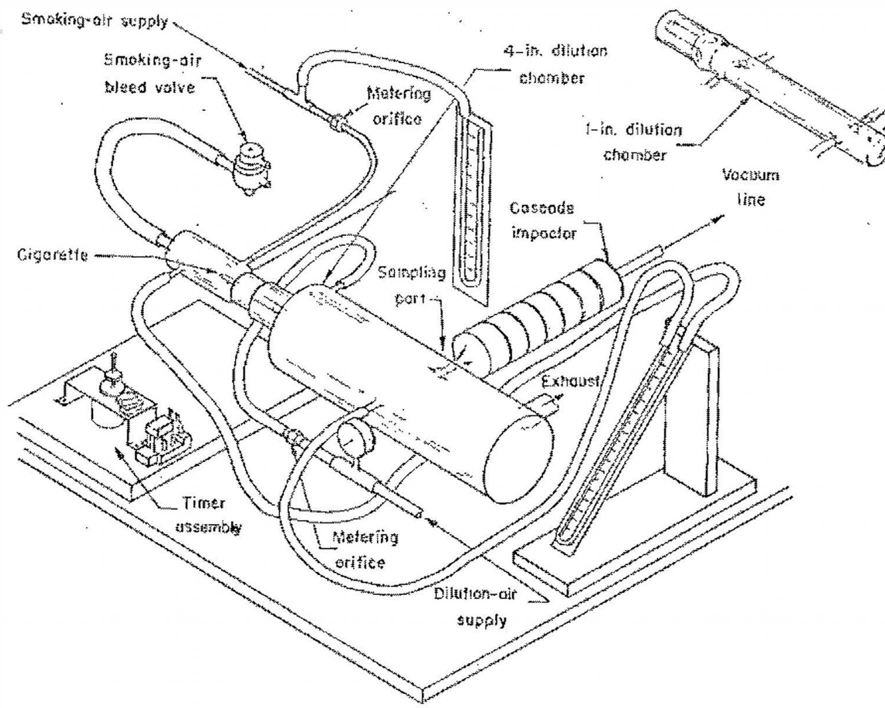

Figure 6. Cigarette-smoke dilution apparatus.

Results and Discussion

Positive, negative, and neutral particles were observed in the gravity settling chamber when the smoke was exposed to an electric field. The electrical properties of smoke from several brands of cigarettes are summarized in **Table 1**. The charge on the smoke particles was measured at different applied voltages 0.278, 0.388, 0.444, 0.555 and 1.11 stat volts/cm. It was found that 0.388 stat volts/cm was the lowest voltage that could be applied and still have a strong effect on the particles. There were many particles that were unaffected by the electric field even at the highest voltages; these particles carried no electric charge. **Figure** 8 shows that the distribution of charges is fairly symmetrical, indicating that the smoke aerosol as a whole is electrically neutral. The majority of the charged particles carried from one to ten charges per particle; only 2-5 per cent of the charged particles had more than 20 charges per particle. The average number of charges per particle was 4-9. Aerosols generated by a relatively mild process, such as condensation from a super-saturated vapor in which there is little possibility of acquiring an electric charge by any means other than collision with atmospheric ions, carry very few electronic charges per particle. More violent generation processes such as spraying or high temperature combustion produce aerosols which carry many more elementary charges per particle than does tobacco smoke. The distribution of charges in cigarette smoke approximated that of the more violent burning process. However, the average number of charges per particle in the tobacco smoke

Table 1. Electrical properties of smoke

Brand of Cigarette	Age of Smoke	Electric Field Strength (Stat volts/cm)		% of the Number of Particles Carrying Each Charge			Total Number of Elementary Charges	Total Mass of All Particles	Total Number of Particles	Total Charge (Electrons per Gram of Smoke)
			+	—	neutral	+	—			
I	2 Min.	.388	49.1	33.2	17.5	263	151	33.77X10^{-12} gm.	114	12.2X10^{12}
F	2	.388	30.0	28.0	42.0	254	186	126.12X10^{-12}	101	3.5X10^{12}
E	2	.388	36.2	20.6	43.1	208	159	106.56X10^{-12}	102	3.4X10^{12}
C	2	.444	37.2	19.5	43.4	296	209	159.94X10^{-12}	114	3.2X10^{12}
G	2	.444	33.6	29.2	37.2	408	284	120.92X10^{-12}	113	5.7X10^{12}
H	2	.444	30.0	27.0	43.[illegible]	287	280	115.[illegible]X10^{-12}	100	4.9X10^{12}
J	2	.444	42.1	34.6	23.4	408	308	70.08X10^{-12}	107	10.2X10^{12}
A	30-45	.388	38.1	48.8	13.0	454	503	100.15X10^{-12}	131	9.6X10^{12}
D	30-45	.388	44.6	51.7	3.4	478	568	72.93X10^{-12}	116	14.3X10^{12}
C	30-45	.388	38.6	37.7	23.7	337	307	54.08X10^{-12}	114	11.9X10^{12}
B	30-45	.388	36.2	45.7	18.1	316	502	85.76X10^{-12}	113	9.5X10^{12}
Cigar	2	.444	35.8	26.6	37.6	466	241	128.85X10^{-12}	109	5.5X10^{12}
Pipe	2	.444	55.9	44.1	...	347	256	61.95X10^{-12}	93	9.7X10^{12}

was not as great as the average number of charges per particle in the aerosol produced by the more violent burning process.

As seen in **Table 1** the smoke that has aged 30 to 45 minutes has fewer neutral particles than the smoke that has aged only two minutes. Also the total number of elementary charges and total number of charges per gram of smoke increases as the smoke ages. Smoke aged 30 to 45 minutes has more highly charged particles **(Table 2)** than does the smoke aged only two minutes. Two mechanisms by which the particles could increase their charge while aging are: (a) collision with atmospheric ions, and (b) coagulation of smaller charged and neutral particles. Evidence points strongly to charging by collision with atmospheric ions as the principle cause of the increase. Coagulation of the smaller charged particles and neutral particles probably accounts for some of the increase in charge.

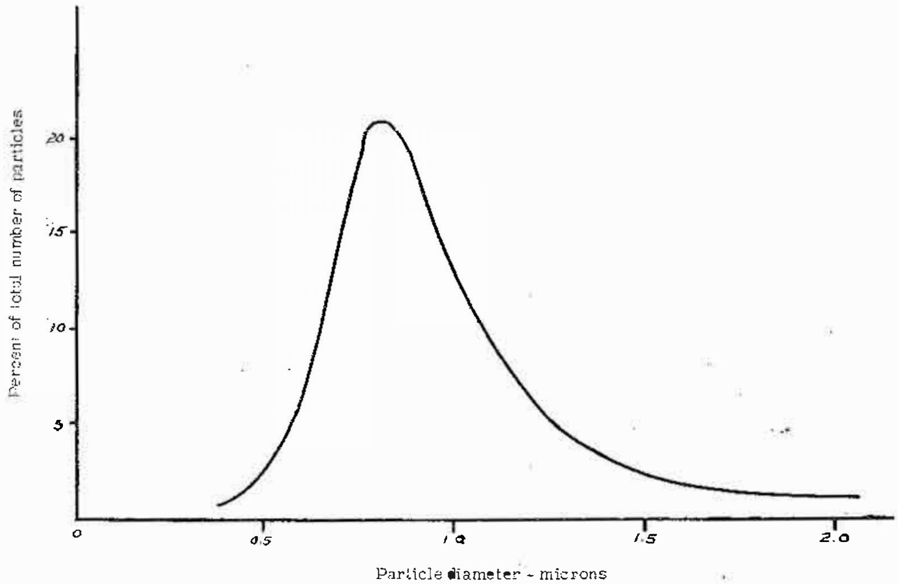

Figure 7. A typical size distribution curve of cigarette smoke particles.

Table 2. Comparison of electric charge distribution of smoke aged two minutes and smoke aged 30-45 minutes

Brand of Cigarette	Age of Smoke	Percent of Particle with 1-10 Charges	Percent of Particle with More than 10 Charges	Percent of Neutral Particles
B	2 Min.	79%	4%	18%
C	2	41	16	43
E	2	51	6	43
F	2	45	13	43
A	30-45 Min.	65	22	13
B	30-45	41	35	18
C	30-45	65	11	24
D	30-45	66	30	3

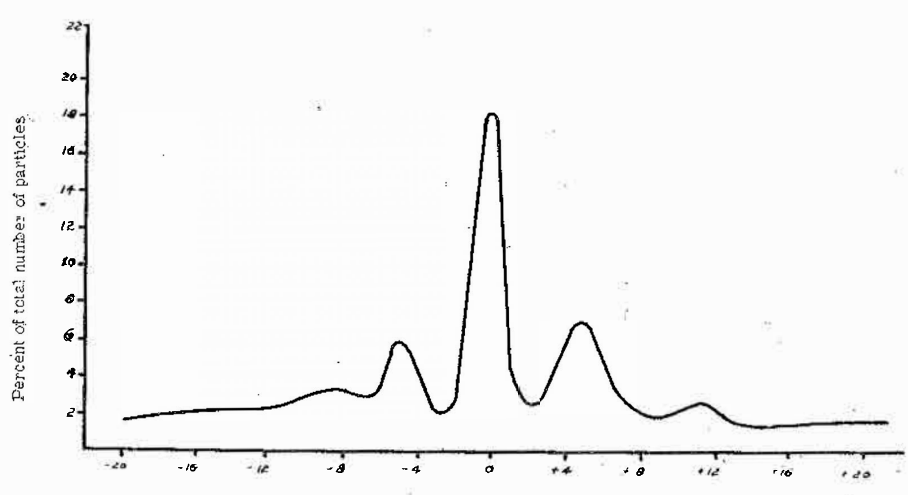

Figure 8. Charge distribution of cigarette smoke.

The size distribution of undiluted smoke from several brands of cigarettes, from pipes, and from cigars was measured with the cascade impactor, the gravity settling chamber, and the "Goetz Aerosol Spectrometer." The size distribution from all these measurements was found to be independent of the number of puffs taken, of the weight, and of resistance to draw of the cigarette. The mass mean diameters as determined with cascade impactor and the gravity settling chamber shows that the particle size distribution of filtered and unfiltered smokes differ (**Table 3**). Table 4 shows that the number mean diameters of filtered and unfiltered smoke particles differ by only .13 microns on an average, and that the mass mean diameters of filtered and unfiltered smoke particles differ by .25 microns on an average. These facts indicate that the filter of a cigarette removes the larger particles and that this removal of the larger particles has only a small effect on the number concentration.

The spread of particle sizes found in cigarette smoke is relatively narrow indicating that cigarette smoke is a nearly monodisperse aerosol (**Figure 7**). Evidence of the relative monodispersity of cigarette smoke was optained with the "Goetz Aerosol Spectrometer." For monodisperse aerosols the plot of number of particles versus distance at which the count was made is a straight line and for polydisperse aerosols this same plot is a curved line. Two such experimental plots of number versus distance resulted in straight lines and number mean diameters of 0.5 micron. Two others resulted in curved lines and number mean diameters of 0.5 microns. When these number mean diameters from the curved lines were converted to mass mean diameters, the mass mean diameters shifted to 0.6 micron and 0.9 micron respectively. This shows a relatively narrow range of particle sizes.

The effect of agglomeration on the measured mass mean diameter was determined by studying the size distribution of cigarette smoke at various dilution ratios. Smoke was diluted with clean filtered air as quickly as possible after leaving the cigarette and its size measured with the cascade impactor. The size determined (Table 5) at the highest dilution ratio is probably closest to the true size of smoke coming from the cigarette. Using the weight of material collected at each stage of the impactor and the mean size of the particles collected at each stage, the concentration was calculated to be 2 x 10^{10} particles per milliliter. This concentration is high and, therefore, the rate of agglomeration is high; however, the rate of agglomeration decreases rapidly as the concentration decreases so that after a short time the size is stable enough for reproducible measurements to be made on undiluted smoke.

The cascade impactor was used to determine how the particle size of cigarette smoke changed as the smoke aged. Measurements showed that the mass mean diameter of undiluted smoke increased from 0.9 to 2.0 microns following two minutes of aging. This increase in size was due to agglomeration of the smoke particles. Agglomeration while the smoke ages accounts for the difference between the mass mean diameters normally determined with the cascade impactor and the mass mean diameters determined with the gravity settling chamber (Table 4). In the case of the gravity settling chamber, the smoke had aged from a few seconds to 45 minutes. Usually with the cascade impactor the smoke was unaged.

Table 3. Mass mean diameter of undiluted cigarette smoke

Brand	Cascade Impactor	Gravity Settling Chamber
A (nonfilter)	0.94 microns	1.33 microns
B (filter)	0.85	1.07
C (filter)	0.84	1.01
D (filter)	0.82	1.10
D (filter removed)	1.00	1.34

Table 4. Comparison of mass mean and number mean diameters of filtered and unfiltered cigarette smokes

Non-filter Brand	MMD*	NMD*	Filter Brand	MMD	NMD
A	1.33 microns	0.93 microns	B	1.07 microns	0.82 microns
D (filter removed)	1.34	1.08	C	1.01	0.81
E (filter removed)	1.38	0.90	D	1.10	0.89
			E	1.21	0.83

*MMD means mass mean diameter
MMD means number mean diameter
The diameters listed here were determined using the gravity settling chamber.

Summary and Conclusions

Tobacco smoke is a lightly charged aerosol in which the individual particles carry only a few elementary charges. The aerosol as a whole, is electrically neutral. While some of the electronic charge may be acquired from the burning process the number of electronic charges per particle found in the tobacco smoke indicates most of the charge is acquired through collision with atmospheric ions.

There are probably particles present in cigarette smoke which are too small to be observed by any of the techniques reported here or elsewhere. These small particles, which must be present at very high number concentrations, are intimately associated with the mechanism of formation of the smoke emerging from the cigarette. The measured size of smoke particles is dependent upon both the age and degree of dilution of the smoke. Thus, it is rather difficult to compare reported values for size of cigarette smoke particles unless the age and degree of dilution at the time of measurements are known.

Table 5. Variation of mass mean diameter with dilution ratio

MMD	Dilution Ratio
0.2 micron	300:1
0.5 "	45:1
0.6 "	30:1
0.64 "	22.5:1
0.92 "	undiluted

Literature Cited

Dalla Valle, J. M., Clyde Orr, Jr., and B. L. Hinkle, The aggregation of aerosols. *Brit. J. App. Phys.*, Sup. 3, 198-206 (1954)

Drozen, Vadin G. and LaMer, V. K. The Determination of the Particle Size Distribution of Aerosols by Precipitation of charged particles. *J. Coll. Sci.*, 14, 74 (1959)

Goetz, A. and Stevenson, Heber J. R. The aerosol spectrometer. APCA, Proceedings of the Semi Annual Technical Conference, San Francisco (Nov. 18-19, 1957). Air Pollution Control Association, 4400 Fifth Avenue, Pittsburgh, Pa.

Keith, C. H., and Derrick, J. C., Measurements of particle size distribution and concentration of cigarette smoke by the Conifuge. So. Eastern Regional Meeting, A.C.S., Durham, November, 1957.

Langer, G., and Fisher, M. A., Concentration and Particle size of cigarette smoke particles. *AMA Arch. Ind. Health*, 13, 372-78 (1956)

Pilcher, J. M., Mitchell, R. I., and Thomas, R. E., The cascade impactor for particle size analysis of aerosols. Proceedings 42nd Meeting Chemical Specialities Manufacturers Assoc. Inc., December, 1955, New York.

Sano, I., and Fikitan, F., and S. Sakata. Colloid Chemistry of tobacco smokes, distribution of size and charge of the particles. *J. Chem. Soc. Japan; Pure Chem. Sec.*, 74, 664-668 (1953)

Warner, B. R., Wells, R. L., and Hobbs, M. E., Size and size distribution of particles in tobacco smoke. Tobacco Chemists' Research Conference, Dec. 4-5, 1952 University of Louisville, Louisville, Kentucky.

Wells, P. V., and Gerke, R. H., An oscillation method for measuring the size of ultramicroscopic particles. *J.A.C.S.*, 41, 312-329 (1919)

Whytlaw-Gray, R., and Patterson, H. S., Smoke. Edward Arnold and Co., London, 1932.