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ENGINEERING EXPERIMENT STATION
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PROGRESS REPORT NO. 1

PROJECT NO. B-174

INTERACTION OF SUBMICRON SMOG PARTICLES AND VAPORS

By

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This report covers the progress made on this project since its initiation and covers the period October 1, 1958, through June 15, 1960.

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I. SUMMARY

Using a radial ion counter, the rate of growth of aerosols particulates commonly found in polluted atmospheres is being studied. Preliminary measurements have been made on the exhaust from a small four-cycle gasoline engine and artificial "smogs" produced by the reaction of an unsaturated hydrocarbon with nitrogen dioxide and sulfur dioxide in the presence of ultraviolet radiation. The ion counter has also been used to study the uptake of organic vapors by organic particulates, e.g. the adsorption of benzene on stearic acid.

The radial ion counter provides a means of obtaining a continuous mobility distribution of charged aerosols in the size range 0.01 to 0.10 micron radius. The mobility distribution is related to a particulate size distribution by techniques specially developed for ion counters.

II. STATEMENT OF PROGRESS

A. Description of Equipment

A schematic diagram of the apparatus is shown in Figure 1. Essentially it consists of (1) the radial ion counter with its attached electrical equipment, (2) air-cleaning, pressure-regulating, and flow-measuring equipment, (3) particulate generator, (4) devices for sharpening the aerosol size distribution, (5) chambers for controlling humidity, and (6) a chamber for aging the aerosol and radiating it with ultraviolet light.

1. Radial Ion Counter

During the period covered by this report all equipment necessary to obtain a size distribution for small aerosols was constructed. The major item is the radial ion counter shown in Figure 2. Figure 3 is an engineering drawing of the ion counter. The counter consists of two circular, stainless steel electrodes 40 cm in diameter enclosed in a grounded electrostatic shield. The top electrode is suspended from the electrostatic shield by four stainless steel rods inserted through cylindrical teflon insulators mounted above the electrostatic shield. The teflon insulators are heated approximately 5° C above the other parts of the counter to prevent condensation on the teflon. Cooling fins are provided just below the insulators to prevent the heaters from disturbing the temperature maintained in the ion counter. The bottom plate is mechanically fixed to the electrostatic shield but insulated electrically from it by a 1/4-inch-thick teflon sheet. Four-centimeter-diameter teflon discs were press-fitted in the center of the top and bottom electrodes to ensure that laminar flow is fully developed before reaching the electrodes. An entrance one centimeter in diameter was provided in the center of the bottom electrode. The distance between the two electrodes was adjusted by raising the top electrode, initially at rest on the bottom electrode, the desired distance. By use of an optical micrometer, this distance was accurately measured outside the electrostatic shield by observing the stainless steel supports protruding through the electrostatic shield. The top electrode is connected to ground through a micro-microammeter, model 410, manufactured by Keithley Instruments Inc., Cleveland 6, Ohio. The bottom electrode was connected to a Keithley, Model 240, regulated variable high voltage supply. This supply provides voltages from 0 to 1000 in 1/10-volt increments with an accuracy

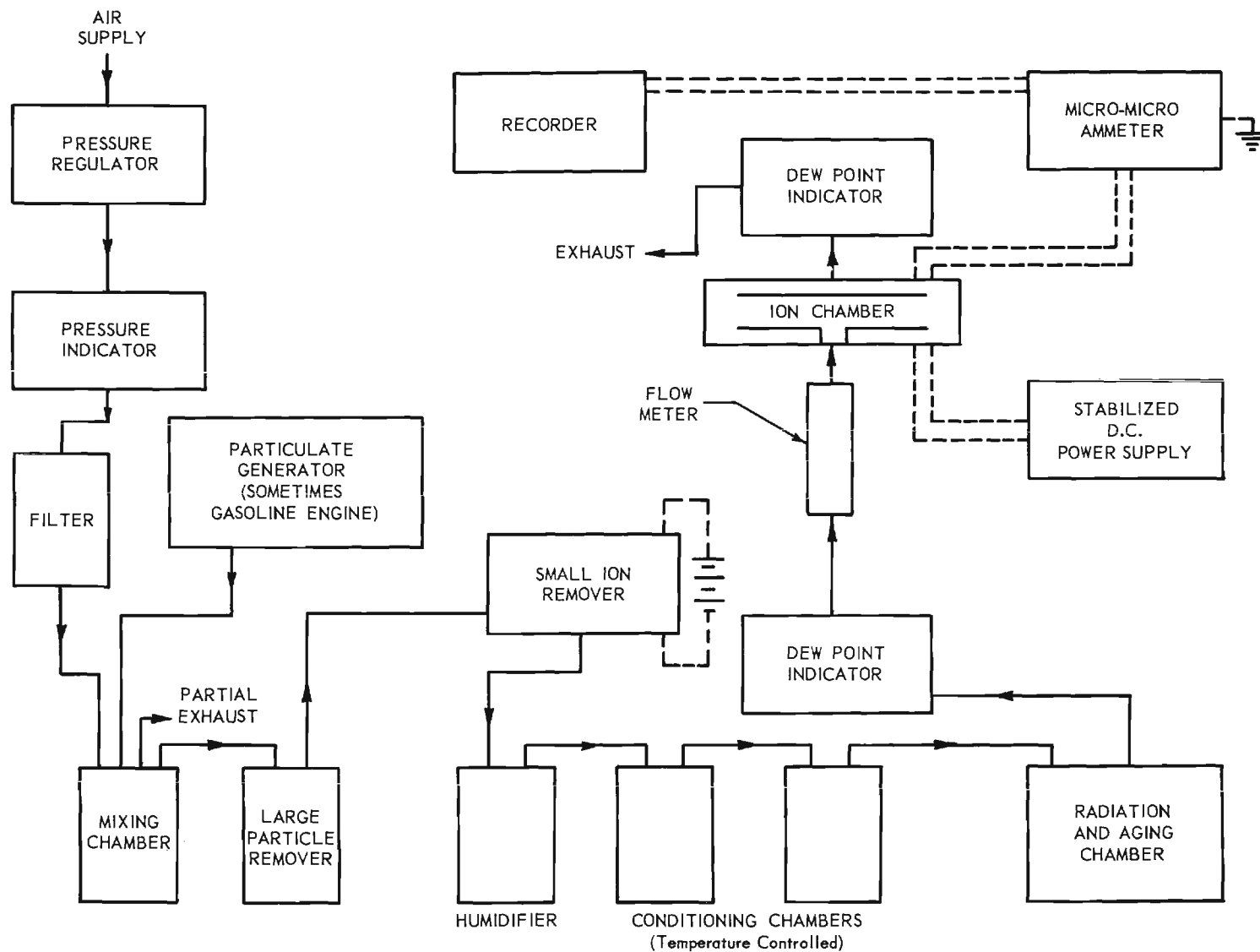


Figure 1. Schematic Diagram of Ion Counter and Related Equipment.



Figure 2. Ion Counter and Related Equipment.

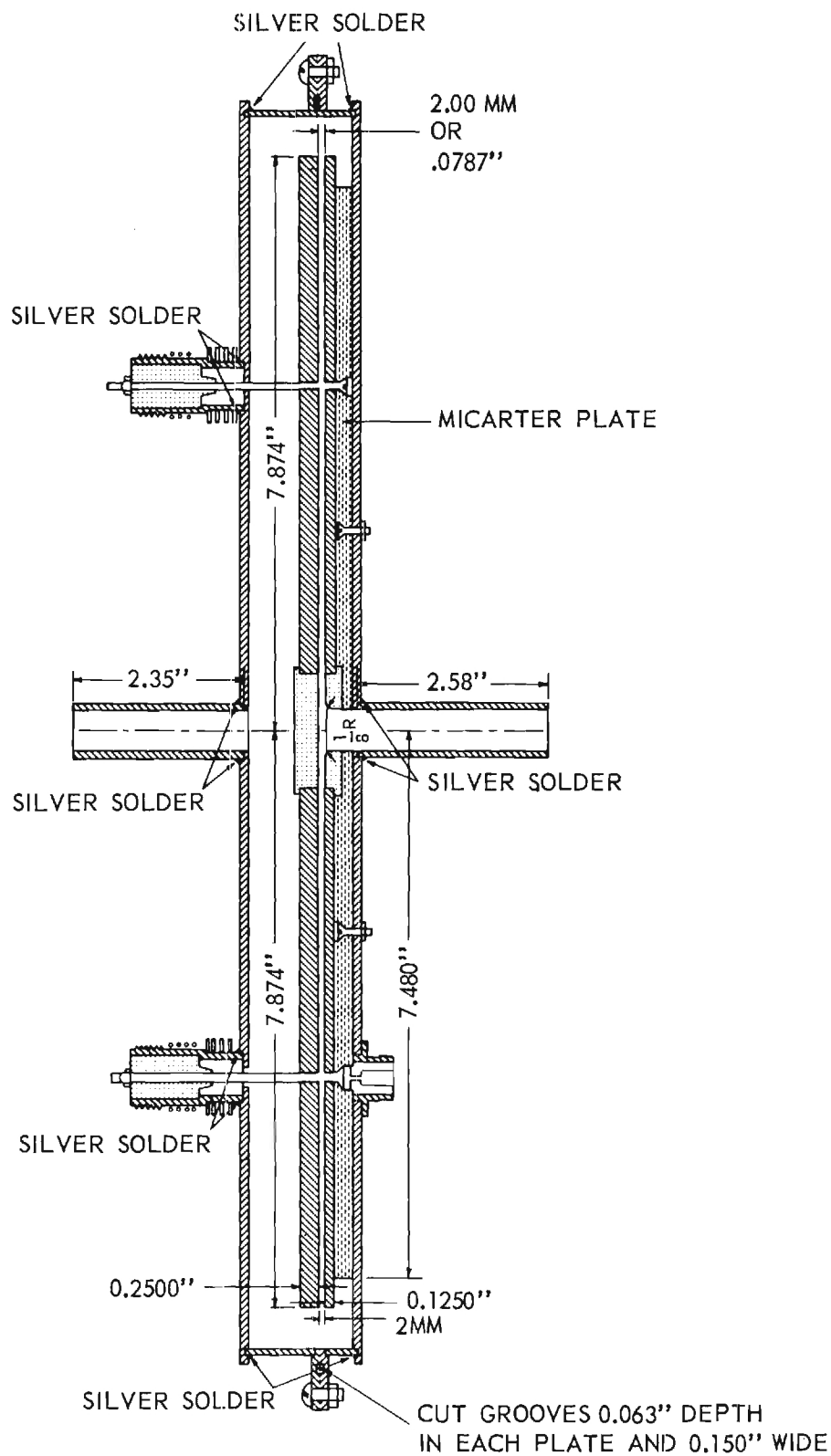


Figure 3. Ion Counter.

of plus or minus one per cent or one tenth of a volt. All connectors and shielded, teflon-insulated cables.

The grounded electrostatic shield surrounding the two electrodes was constructed of 1/8-inch stainless steel sheet and designed to permit ready access for cleaning of the electrodes. The aerosol enters through the bottom of the shield, passes radially outward between the electrodes, and exhausts through an opening in the top of the shield. The output from the micro-microammeter is recorded on a recorder, type 5-72150, manufactured by E. H. Sargent and Company, Chicago 30, Illinois.

2. Air-Cleaning, Pressure-Regulating, and Flow-Measuring Equipment

Air is taken directly from a compressed air line at approximately 90 pounds per square inch and reduced to 20 pounds per square inch with a pressure regulator. The air passes from the regulator to a surge tank and filter. From here it passes through a second pressure regulator where the pressure is reduced to the desired level. Rotameters, manufactured by the Fisher and Porter Co., Hatboro, Pennsylvania, were used to measure the rates of flow throughout the system.

3. Particulate Generators

Various particulate generators have been employed: (1) a four-cycle engine, model 60102, manufactured by Briggs and Stratton Corporation, Milwaukee 1, Wisconsin, equipped with a glass-wool-packed muffler, (2) a DeVilbiss No. 180 atomizer for soluble materials, (3) a small oxygen-natural gas burner for carbon particles, and (4) an irradiation chamber for generating artificial "smog".

4. Devices for Sharpening the Aerosol Distribution

a. Small Ion Remover. A small ion (i.e., diameters below 0.01 micron) remover constructed similarly to the radial ion counter described previously, is included to remove very small ions if desired. Voltage is supplied to the electrodes by dry cell batteries.

b. Large Ion Remover. Two types of large ion (i.e., diameters approximately 0.2 microns and larger) removers have been used. These are (1) a 3-inch-diameter vertical column filled to a depth of 30 inches with water and (2) filtering media such as glass wool.

5. Chambers for Controlling Humidities

Desired aerosol stream humidities are obtained by passing the aerosols over solutions of lithium chloride contained in flasks surrounded by temperature-controlled water baths.

6. Chambers for Aging and Irradiating with Ultraviolet Light

A chamber having a volume of 300 liters for irradiating and aging the aerosols was constructed of plywood and four 15-watt ultraviolet lamps were installed in it. The box was lined with aluminum foil. A sealed fan was mounted on the inside to permit uniform mixing. A plexiglas inspection port was provided for observation of aerosol growth. When generating artificial "smog" the chamber served also as a batch-type generator.

B. Operation of Equipment

An aerosol, generated by one of the means listed under section A3 was passed through the various conditioning parts of the system until it reached the ion counter. In the ion counter the aerosol was subjected to various known potential differences and the current resulting from the migration of ions to the top electrode was indicated by the micro-microammeter and recorded. A typical recording of the ion current is shown in Figure 4. Either the positive or negative ions may be measured by reversing the polarity of the applied voltage and reversing the scale direction on both the micro-microammeter and the recorder. The method of obtaining a size distribution from a current-versus-voltage curve is described in detail in the appendix.

To obtain a suitable aerosol for analysis from the gasoline engine, a small quantity of exhaust gas was diluted with a large quantity of air and passed through the humidity chambers to adjust the aerosol to a certain predetermined humidity. The aerosol was then passed into the aging chamber where it was irradiated with ultraviolet light. The average time of a particle in the irradiation chamber was, of course, a function of the flow rate and easily calculated.

The synthetic "smog" was generated by introducing predetermined quantities of nitrogen dioxide, sulfur dioxide, and 1-pentene into the irradiation chamber. The resulting aerosol is sampled continuously by displacing the aerosol and carrier gases from the chamber by introducing air into a plastic bag inside the chamber.

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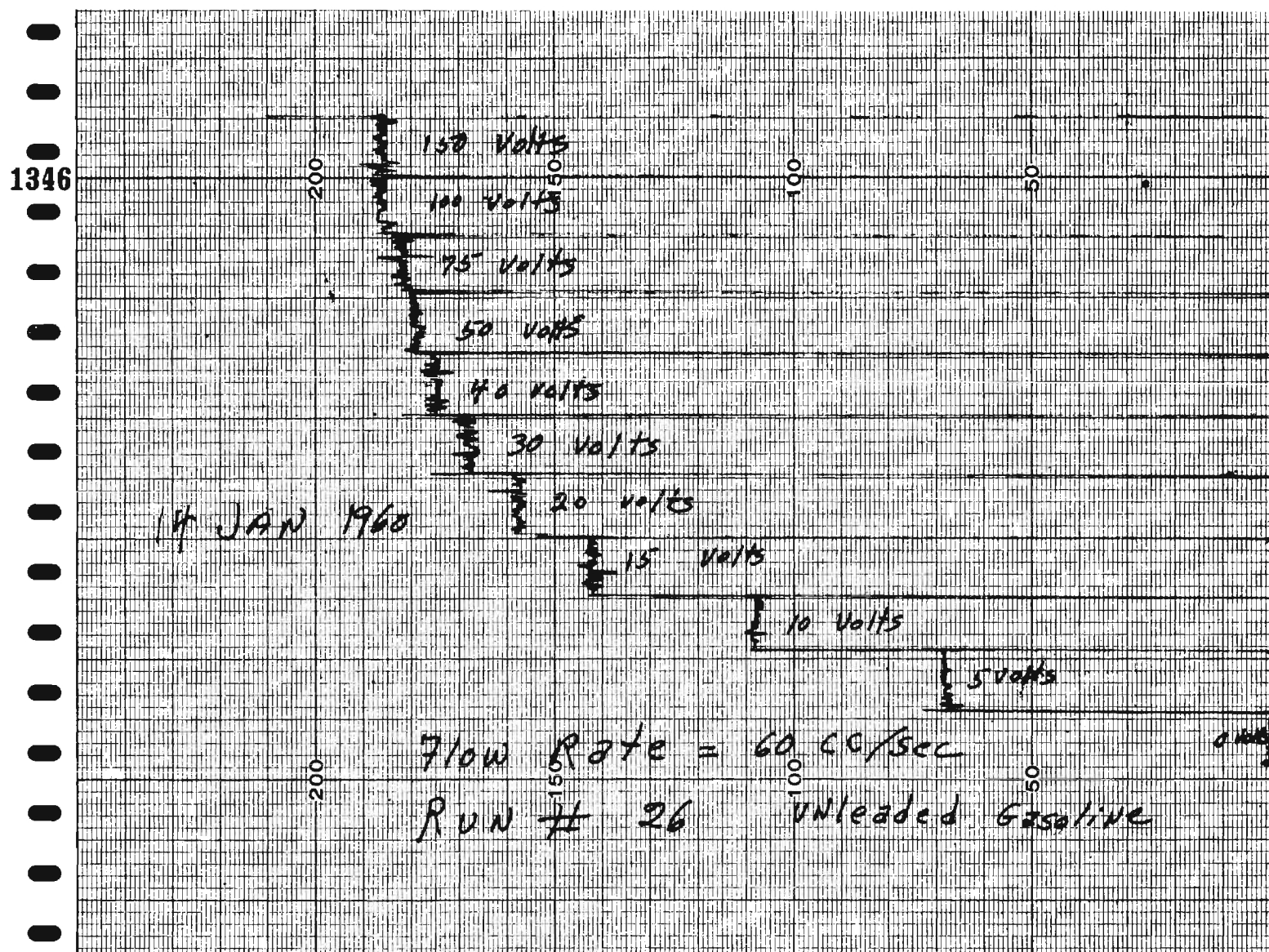


Figure 4. Typical Recording of Voltage Versus Ion Current.

C. Results

1. Solid Particulates

Carbon particles were generated by several means in an attempt to obtain a steady distribution of particles in the size range and quantity desired. The most satisfactory method of obtaining carbon particles in a continuous flow was by simply burning a small oxygen-natural gas burner inside the system and sharpening the resulting aerosol by passing it through the large ion remover and the small ion remover. The resulting distribution did not show any change in size upon being exposed to gasoline vapors of varying concentrations. The undesirable feature of this aerosol is that the carbon particles produced contain certain adsorbed impurities.

Various other solid particulates that were soluble were generated in a DeVilbiss atomizer. Sodium chloride was used to compare the size distribution obtained in the ion counter with electron micrographs. The distributions obtained compared very closely with the electron micrographs obtained from thermal precipitation of the generated sodium chloride aerosol.

Stearic acid and paraffin aerosols were produced by atomizing solutions in benzene. The resulting aerosols were not suitable for studying in the ion chamber, because of the small number of ions that were charged. The primary reason for studying an aerosols of this type was to determine if sufficient size change would result from exposing the dried particles to organic vapors in which they normally dissolve. Because of the difficulty in charging, these particles were deemed undesirable for further study.

Recently a method for charging normally uncharged particles by subjecting them to a highly charged atmosphere has been described^{*}. A device to accomplish this charging has been constructed. Preliminary results show that it works very satisfactorily. This phase of the investigation is being reactivated and should now produce interesting results.

2. Gasoline Exhaust

The aerosol distributions obtained from the dilution of the exhaust from a small four-cycle engine are indicated in Table I, and a typical electron

^{*}Dr. K. T. Whitby, Private Communication, University of Minnesota.

TABLE I
TYPICAL SIZE DISTRIBUTIONS OBTAINED FROM GASOLINE ENGINE EXHAUST

Per Cent Less Than Indicated Size	Particle Radius			
	Regular Gasoline			Unleaded Gasoline
	Distribution 1 ^a (Microns)	Distribution 2 ^b (Microns)	Distribution 3 ^c (Microns)	Distribution 4 ^a (Microns)
20	0.043	0.054	0.056	0.038
30	0.050	0.062	0.067	0.041
40	0.056	0.069	0.081	0.044
50	0.060	0.079	0.097	0.047
60	0.064	0.091	0.114	0.050
70	0.068	0.105	0.140	0.053
80	0.072	0.123	0.172	0.056
90	0.080	-----	-----	0.059

^a Aerosol was taken direct from engine exhaust without aging.

^b Aerosol was passed through aging chamber without irradiation. Average time in chamber was one hour.

^c Aerosol was passed through aging chamber with irradiation. Average time in chamber was one hour.

micrograph of the aerosol is shown in Figure 5. The results indicate the rapid formation of "smog" produced from gasoline engine exhaust. The number of variables to be controlled i.e., constant engine speed, temperature, fuel type, fuel mixture, air intake temperature and humidity, etc. make it extremely difficult to obtain reproducible results and to specify the conditions for a given set of results.

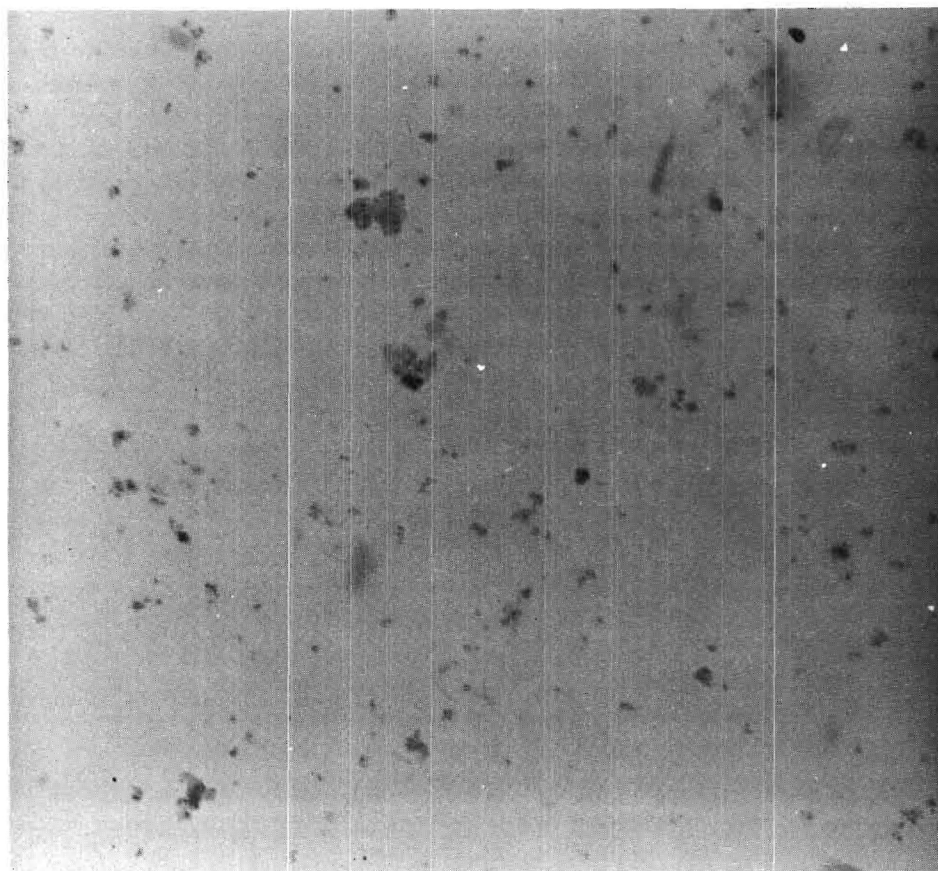


Figure 5. Electron Micrograph of Particulate Matter from Gasoline (Unleaded) Engine Exhaust. (1 Millimeter = 1 Micron)

III. FUTURE WORK

Because of difficulty in working with the gasoline engine "smog" aerosols, it seems desirable at this stage to concentrate future work on using the ion counter technique with synthetic aerosols. These synthetic aerosols, described by Schuck and Doyle¹, have been found to be very similar to those formed from automobile exhaust upon exposure to sunlight. The effects of small particulate aerosols, e.g. carbon, sodium chloride, and other solids normally found in atmospheres, will be determined if possible. The use of carbon particles will be dependent on developing suitable means of production. In the event the ion counter can be used to give rates of aerosol growth as a function of humidity, intensity of irradiation, concentration of gasoline, and concentration of nitrogen dioxide, the method could then be used for the much more complicated and expensive problem of studying the rates of growth of natural aerosols using automobile exhaust. The simpler approach is proposed at present because of the expensive instrumentation required in studying actual smogs.

A second phase of the future work will be to examine the growth behavior of aerosols of organic solids in the presence of varying concentration of solvent vapors. The availability of the ion generator to charge these aerosols promises to make this phase of the investigation compatible with the ion counter technique.

Respectfully submitted:

Clyde Orr, Jr.
Project Director

Approved: _____

✓ Wyatt C. Whitley, Chief
Chemical Sciences Division _____

¹E. A. Schuck and G. J. Doyle, "Photooxidation of Hydrocarbons in Mixtures Containing Oxides of Nitrogen and Sulfur Dioxide," Report No. 29, Air Pollution Foundation, San Marino, California, October, 1959.

IV. APPENDIX

A. Interpretation of Data from Radial Ion Counter

For very slow laminar flow between the circular plates of the ion counter the velocity profile of the air flow in cylindrical coordinates is

$$\bar{V}_r = \frac{b^2 \Delta P}{2 R \mu \ln R_2/R_1} [1 - (Z/b)^2], \quad (1)$$

where \bar{V}_r = radial velocity,
 R = distance from the center of the circular plates,
 $2b$ = distance between the two plates,
 R_1 = inner radius,
 R_2 = outer radius,
 ΔP = pressure drop from the inner radius to the outer radius,
 μ = viscosity of the air,
 and Z = displacement along the vertical axis measured with the origin halfway between the plates.

Since the flow rate, F , can be expressed as

$$F = \int_{-b}^{+b} \bar{V}_r (2 \pi R) dZ, \quad (2)$$

integration yields

$$F = \frac{4}{3} \frac{\pi b^3 \Delta P}{\mu \ln R_2/R_1}. \quad (3)$$

Equation 3 may then be substituted into equation 1 to give the velocity profile as a function of F , Z , and R . The resulting equation is

$$\bar{V}_r = \frac{3 F}{8 b \pi R} [1 - (Z/b)^2]. \quad (4)$$

If a distribution of ions with a single discrete mobility, ω_i , is considered,

$$\omega_i = \bar{V}_Z / E, \quad (5)$$

where \bar{V}_Z is the velocity in the Z direction and E is the field strength. The field strength between parallel plates is

$$E = V/2 b, \quad (6)$$

where V is the applied potential difference between the plates. Substituting equation 6 into equation 5, the mobility of each ion is

$$\omega_i = \frac{2 b \bar{V}_Z}{V} . \quad (7)$$

The Z coordinate of an ion with mobility ω_i entering the chamber at R_1 and Z_0 is given at time, t , after entering as

$$Z = Z_0 + \bar{V}_Z t . \quad (8)$$

Substituting this into equation 4 yields

$$V_r = \frac{dR}{dt} = \frac{3 F}{8 b \pi R} \left[1 - \left(\frac{Z_0 + \bar{V}_Z t}{b} \right)^2 \right] , \quad (9)$$

which may be integrated for a particular flow rate and voltage to obtain

$$\int_{R_1}^R R dR = \frac{3 F}{8 b \pi} \int_0^t \left[1 - \left(\frac{Z_0 + \bar{V}_Z t}{b} \right)^2 \right] dt . \quad (10)$$

A particle initially at Z_0 will reach the upper plate and be collected at a time t_f given by

$$t_f = \frac{b - Z_0}{\bar{V}_Z} . \quad (11)$$

Integration of equation 10 and substitution of equation 11 results in

$$\frac{R_c^2 - R_1^2}{2} = \frac{F}{8 b \pi \bar{V}_Z} \left[\frac{Z_0^3}{b^2} + 2 b - 3 Z_0 \right] . \quad (12)$$

The above equation gives the radius R_c at which an ion initially at Z_0 will be collected. By setting R_c equal to R_2 the equation may be rearranged to give

$$\bar{V}_Z = \frac{F}{4 b^3 \pi} \frac{[Z_0^3 - 3 b^2 Z_0 + 2 b^3]}{[R_2^2 - R_1^2]} , \quad (13)$$

and substitution of \bar{V}_Z from equation 7 gives

$$V_0 = \frac{F [Z_0^3 - 3 b^2 Z_0 + 2 b^3]}{2 \pi b^2 \omega_i [R_2^2 - R_1^2]} \quad (14)$$

The above equation gives the minimum voltage, V_0 , required to collect an ion of mobility ω_i entering the chamber of Z_0 . All ions with $Z > Z_0$ will also be collected. The number of ions entering the chamber at R_1 with $Z > Z_0$ is

$$N_i = 2 \pi R_1 N_1 \int_{Z_0}^b \bar{V}_r dZ, \quad (15)$$

where N_1 is the number of ions of mobility ω_i per cubic centimeter.

Integration of equation 15 yields

$$N_i = \frac{N_1 F}{4 b^3} [2 b^3 - 3 b^2 Z_0 + Z_0^3]. \quad (16)$$

If each ion is assumed to carry one electronic charge e , then $N_i e = I$ the ion current. In order to obtain the number of ions collected per second as a function of voltage, equation 16 and equation 14 may be combined to eliminate Z_0 .

However, more important is the relation expressing the change with voltage in ions collected per second. Since

$$\frac{dN_i}{dV} = \frac{dN_i}{dZ_0} \cdot \frac{dZ_0}{dV}, \quad (17)$$

differentiating equations 14 and 16 results in

$$\frac{dN_i}{dV} = \frac{\pi N_1 \omega_i [R_2^2 - R_1^2]}{2 b}, \quad (18)$$

which yields the important result that for a discrete mobility the change in the number collected with voltage is a straight line relationship until, of course, all ions are collected.

The preceding results, although derived for a single mobility ω_i , are valid for each mobility in a mobility distribution.

Using the above equations, a typical ion-current-versus-voltage curve as shown in Figure 6 may be analyzed under certain conditions to obtain a size frequency curve. Equation 14 may be solved for a voltage V_0 which will remove all ions of mobility ω_0 . Replacing Z_0 by $-b$,

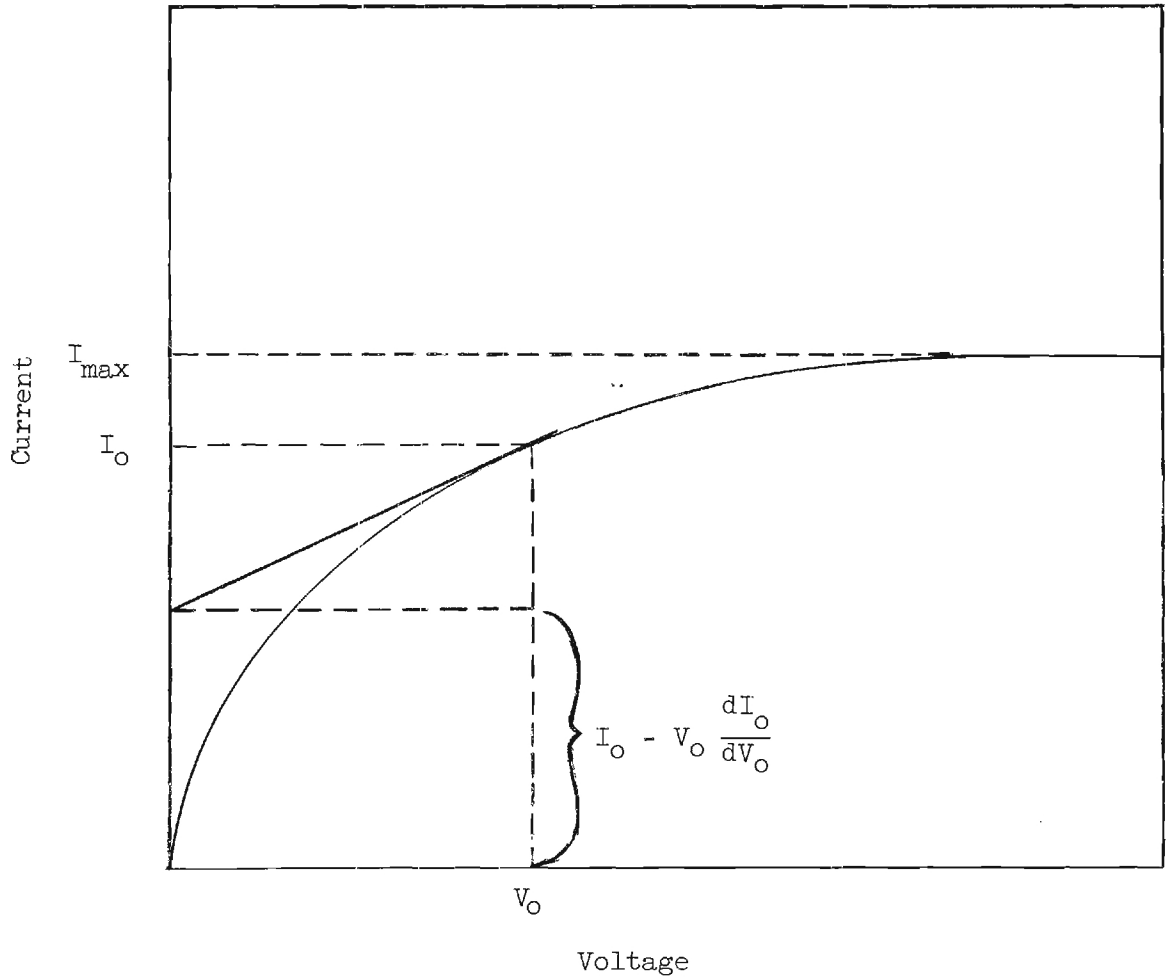


Figure 6. Typical Current-Versus-Voltage Curve.

$$V_O = \frac{2 F b}{\pi \omega_O [R_2^2 - R_1^2]} \quad (19)$$

Furthermore for an applied voltage of V_O , all ions with $\omega > \omega_O$ will be collected and also since $d\omega_1/dV$ is constant the fraction ω/ω_O of those ions with $\omega < \omega_O$ will be collected.

The distribution of ion mobilities is assumed to be continuous. The frequency curve $f(\omega)$ is defined by

$$\int_0^\infty f(\omega) d\omega = 1. \quad (20)$$

The relationship between $f(\omega)$ and the current voltage curve must next be established and finally related to ion size. For the specified voltage V_0 all ions of mobility $\omega \geq \omega_0$ are captured and produce a current

$$I_1 = I_{\max} \int_{\omega_0}^{\infty} f(\omega) d\omega, \quad (21)$$

where I_{\max} is the current obtained from the entire distribution. For ions of mobility $\omega < \omega_0$ the fraction ω/ω_0 which is collected produces a current

$$I_2 = \frac{I_{\max}}{\omega_0} \int_0^{\omega_0} \omega f(\omega) d\omega. \quad (22)$$

The total current I_0 corresponding to an applied voltage V_0 is given by

$$I_0 = I_{\max} \left[\frac{1}{\omega_0} \int_0^{\omega_0} \omega f(\omega) d\omega + \int_{\omega_0}^{\infty} f(\omega) d\omega \right]. \quad (23)$$

Differentiation of equation 23 gives

$$\frac{dI_0}{d\omega_0} = - \frac{I_{\max}}{\omega_0^2} \int_0^{\omega_0} \omega f(\omega) d\omega, \quad (24)$$

and differentiation of equation 19 gives

$$\frac{d\omega_0}{dV_0} = - \frac{F}{KV_0^2} = - \frac{K}{F} \omega_0^2, \quad (25)$$

where

$$K = \frac{\pi [R_2^2 - R_1^2]}{2b}, \quad (26)$$

which depends only on the geometry of the system. Combining equations 24 and 25 gives

$$\frac{dI_0}{d\omega_0} \cdot \frac{d\omega_0}{dV_0} = \frac{dI_0}{dV_0} = I_{\max} \frac{K}{F} \int_0^{\omega_0} \omega f(\omega) d\omega. \quad (27)$$

From equation 23

$$\int_{\omega_0}^{\infty} f(\omega) d\omega = \frac{I_0}{I_{\max}} - \frac{1}{\omega_0} \int_0^{\omega_0} \omega f(\omega) d\omega, \quad (28)$$

or, substituting equation 27,

$$\int_{\omega_0}^{\infty} f(\omega) d\omega = \frac{I_0}{I_{\max}} - \frac{F dI_0}{\omega_0 K I_{\max} dV_0}, \quad (29)$$

but from equation 19

$$\frac{F}{K\omega_0} = V_0,$$

therefore

$$\int_{\omega_0}^{\infty} f(\omega) d\omega = \frac{I_0 - V_0 \frac{dI_0}{dV_0}}{I_{\max}}. \quad (30)$$

In equation 30 the left side represents the fraction of ions with $\omega > \omega_0$. Referring to Figure 6, the right hand side of the equation is the intercept on the current axis of the tangent to the voltage-current curve divided by the maximum current. This procedure permits a mobility distribution from current-voltage curves to be constructed.

To relate mobility to particle size for small particles, Stoke's law is applied with a correction for slip. The relation is

$$\omega = \frac{e}{6\pi\mu} \left(\frac{k}{r} \right), \quad (31)$$

where μ = viscosity of air,

r = particle radius,

and e = charge on particle.

From a review of the best data available, Davies² found that the slip correction, k , for particles comparable in size to the mean free path of air molecules at room temperature was given by the expression

²C. N. Davies, Proc. Phys. Soc. 57, 259-70 (1945).

$$k = 1 + \lambda/r [A + B \exp (-Cr/\lambda)], \quad (32)$$

where λ = mean free path of air,

$$A = 0.882,$$

$$B = 0.281,$$

$$\text{and } C = 1.57.$$

For calculation purposes equation 31 is substituted into equation 30 to give

$$\int_{r_0}^{\infty} g(r) dr = \frac{I_0 - V_0 \frac{dI_0}{dV_0}}{I_{\max}}, \quad (33)$$

where the left side is now the fraction of the total number of ions of radius $r < r_0$. Thus the size distribution of the aerosol particles can be established from the current-voltage curve by simply reading tangent intercept points for the current-voltage curve and dividing by I_{\max} to give the fraction of the size distribution with $r < r_0$.