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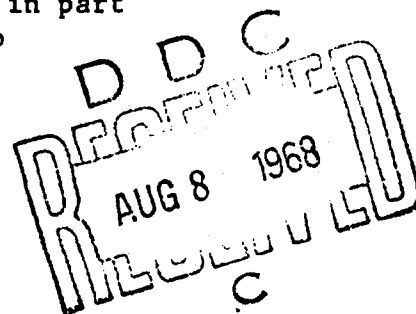21701.

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EFFECTS OF ARTIFICIAL AEROSOLS.
METHODS OF SYNTHESIS AND ANALYSIS OF
SUBMICRON AEROSOLS

Introduction

Our knowledge of the morphology of submicron-aerosols is highly
limited the moment the particles no longer present the features of
homogeneous units in proper phase relationship, which appears seldom to
be the case. A large part of air colloids which are produced both in
nature and in large cities are apparently heterogeneous and are able to
change their composition by contact, for example, with physiological tis-
sue surfaces, when suspended in air. If, then, as a result of this
contact one component of the particle substance (or the whole) is brought
in contact with the surface and reabsorbed there, then even very small
mass concentrations can bring about serious synergetic irritation (1).
In carrying out such investigations, it is always important to know
whether for any given (chemically indicated)concentration of an irritant,
it is dispersed molecularly, i.e., as gas components, or entirely or
partially as particles of the same order of size as found in colloids.
The chief difficulties in such investigations lie in the fact that the
usual methods of chemical indication (presence and concentration) do not
indicate the micromorphological condition of the irritant, while
physical separation out of the colloidal component for the purpose of
special analysis does not give any guarantee that gas traces attached
loosely to the particle are not reabsorbed, since most methods of sepa-
ration (filtration, impingement, thermal and electrostatic precipita-
tion) drastically change the state of equilibrium between particle and
gas. It is probable, then, that these very same loosely bonded irritant
traces show the most powerful synergism due to their ability to become
quickly transferred to the tissue surface on contact, and the experi-
mental data available also points to this conclusion.
    The basic difficulty pointed to above, therefore, seems to be
an example of the classic paradox, according to which the act of taking
observations basically changes the observed system, thereby rendering
measurements false unless suitable precautionary measurement rules are
used to limit or avoid uncertainty.

It is, therefore, necessary in systematic investigation of the constitution of particles to develop a method which will enable one to manufacture such air-colloidal systems synthetically and to carry out measurements over a widely varying range of conditions and measure their behavior on contact with surfaces. It is, therefore, necessary to continue to produce a well-defined gas-particle system in the form of a continuous stream which is known in respect to substance, distribution of particle sizes and concentration and which can be readily reproduced. The gas traces to be investigated are then fed into this system and determination is made of their accumulation on the basis of the change in particle size. If one succeeds in quantitatively controlling the constant stream of trace component, thereby controlling its concentration in the aerosol stream, one can then determine the mass of the accumulated traces by the increase in particle diameter of the aerosol and thereby bring it in direct relation with the indicated concentration.

The method, therefore, uses in principle a continuous straight length of cylindrical glass tube, 6 cm. in diameter. This tube is made up of a number of tubular pieces joined together with air-tight connections. The constructional design can be varied over a wide range according to the purpose for which it is to be used and is represented schematically in Figure 1.
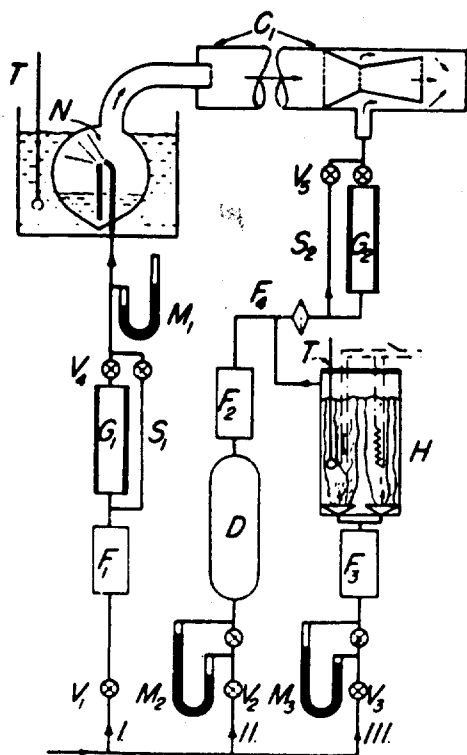

Figure 1, Part 1.

Aerosol generator with device for immediate rarification of the aerosol using a variable addition of pure air having defined and adjustable humidity.

The aerosol generator (on the left) is the first unit of the apparatus. It can be used to provide immediate rarefaction of the aerosol by means of a variable addition of pure air of defined and variable humidity, thereby decreasing the variation in the spectrum of particle sizes due to coagulation and premature fall-out during the further course of the stream.

A stream of air under pressure supplies the apparatus at three tap connections (I, II, III), which makes it possible to control the supply to each arm of the stream through needle valves (V_1, V_2, V_3), which can be measured by flow meters (M_1, M_2, M_3). Filtration through membrane filters (F_1, F_2, F_3) also takes place separately for each arm. The first arm (I) supplies a compressed air atomizer (A), which is preferably kept at a constant temperature (T) in a water bath to thoroughly compensate for changes in the aerosol formation caused by temperature changes (heat of vaporization). After being filtered (F_1) the air can be made to flow either directly through (S_1) or, if so desired, partially through tube (G_1), which makes it possible to enrich the stream of air with additional gaseous substances (for example, traces of olefines, etc.), which could affect the formation of the aerosol in the atomizer.

The streams through arms (II) and (III) are used to rarify the atomized aerosol; stream (II) runs through the receiver (D) in the line, while (III) runs through (H), bubbling through the chamber filled with distilled water and carbon filter elements (to achieve a high moisture content), being filtered through (F_3). Streams (II) and (III) unite at (F_4) where they are filtered again. With proper setting of (M_2) and (M_3) the behavior of the stream and along with it the relative humidity of this secondary stream of air can be varied over a wide range (10% to almost 100%), which plays a very important part in the manufacture of hygroscopic aerosols.
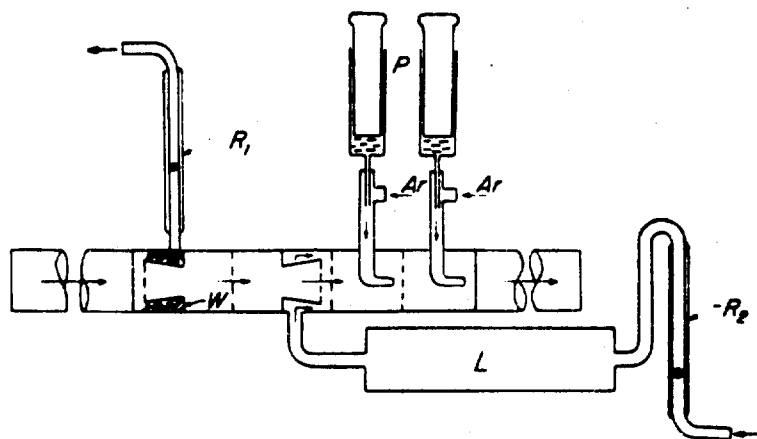

Figure 1, Part 2. Unit for varying the concentration of aerosol in the main tube and device for constant injection of trace components of gaseous reaction partners in very low concentrations.

The (C_2) unit (see Figure 1, Part 2) first of all makes it possible to partially decrease the concentration of the aerosol by drawing off given velocities through a radial ring (W_1) of glass wool, using flow meter (R_1). The material drawn up through (R_1) is replaced in the next jet by an equal quantity of pure air, having the same velocity of flow (R_2), which passes through filter (S) before entering the main tube.

This way of varying the concentration is required because it is impossible to change it in the atomizer by varying the air pressure, since, of necessity, so doing would disturb the distribution of particle sizes. This method keeps it the same and merely brings about a measurable rarification of the aerosol components in the mainstream.

The sections of tube which follow are used for constant injection of traces of gaseous reaction partners in highly rarified form (see below). One unit of this kind is connected into the main tube for each component to be added. Each unit consists of a glass jet coaxial with the main tube and prenetrating into the main tube through the latter's side wall. The upper end of each unit has a vertical opening and a horizontal branch with open end. The vertical branch serves as an air-tight container for a thin glass capillary which is fed by a glass injection piston (50-100 ml). The capillary tube is designed so that the gas-filled spray under the weight of the injection piston forces 1 to 2 ml/minute into the main tube. In order to avoid unevenness in the rate of speed at which the piston moves downward caused by friction with the glass wall, the piston is kept spinning rapidly against an impeller wheel (not shown) acted upon by a tangential stream of air, the impeller being attached to the upper end of the piston. This method makes it possible to have a constant speed of flow of the gas content out of the capillary tube within approximately 2%, during a test period of about 30 minutes.

The horizontal branch is used to supply a neutral gas (Argon), which reduces the strength of the flow from the capillary by 100 to 1000 times. Either Argon or pure nitrogen is used as a rarifying medium and the velocity of this stream of gas is correspondingly adjusted. This precautionary measure prevents premature reaction between the trace component and the walls on the one hand and, on the other hand, favors rapid homogeneous mixing in the main tube. Ozone or oxides of nitrogen (NO or NO_2) were used as oxidizing trace components, while unsaturated hydro-carbons were used in the second unit as photochemical reaction partners for the former. In order to achieve the necessary degree of rarifica-tion (10^{-4} to 10^{-7}) the reaction components were previously mixed in a ratio of 1 : 10 to 1: 100 with argon in the piston injector chamber.

Unit (C_3) makes it possible to subject the stream in the main tube to isothermic lighting by means of twelve mercury-vapor fluorescent lamps (f) arranged symmetrically around the tube (see Figure 1, Part 3).
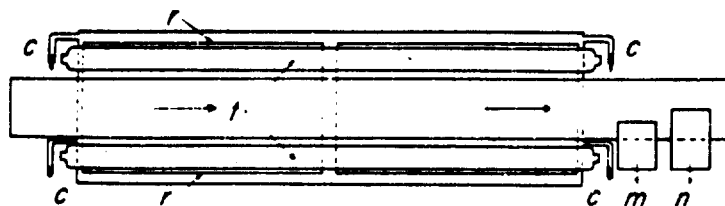
Figure 1, Part 3.   Device for isothermic lighting of the
main tube, using 12 mercury-vapor
fluorescent lamps. (Temperature varia-
tions of the aerosol stream less than
1° D.)

Each lamp emits on a wave length of 160 cm radiation in the range between
3200 and 4500 angstroms, i.e., in an area of the spectrum which
corresponds to the short-wave portion of solar radiation in the atmos-
phere at ground level. Thus photochemical reactions in the lower layer
of the atmosphere can be artificially produced in the aerosol stream.
In order to prevent heating by such intensive radiation (1,200 watts),
the fluorescent lamps lay embedded in a coolant liquid which flowed
inside the outer tube, and this coolant circulated around the inner main
tube so that in spite of an intensity of radiation of about 40,000
lumens per liter, which in this range of the spectrum represents six to
ten times that of the sun, the heating of the aerosol stream did not
exceed 1° C. In the same way photochemical reaction products are brought
into being in nature, too, under practically isothermic conditions. A
set of seven transformers allows one to vary the radiation intensity
symmetrically between from two to twelve lamps, so the effect of the
radiation intensity on the reaction product and on its power to accumu-
late on the aerosols and the accompanying change in the spectrum of
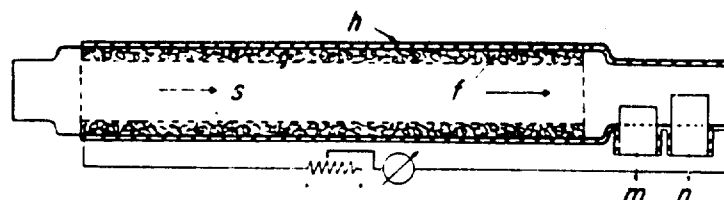particle sizes can be measured.

Figure 1, Part 4.   Device to bring the aerosol to
correspond to physical conditions
which reign during inhalation. (Body
temperature, stirring with saturated
water vapor, 30 seconds duration).

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The vertical tube connections (m and n, Figure 1, Part 4) are for connection to the aerosol spectrometer as described later.

Units (C_4) enables one to find the change in distribution of particle sizes in the aerosol, when the latter is raised for about 30 seconds to body temperature and is brought near to saturation with H_2O, i.e., when it is exposed to the physical conditions which accompany inhalation. (C_4) consists of a glass tube, the inner wall of which is coated with a layer of felt (f) about 1 cm thick. The inner surface of the layer of felt is formed by a cylinder made of fine-meshed wire netting (s) and the outer wall of the tube is warmed to body temperature by a spiral electric heating element (h) extending evenly along its entire length (approximately 1.3 meters). Although the geometry and dimensions of this unit are far different from those of the respiratory passages, the time during which the stream remains in them is long enough to achieve a comparable condition heat and humidity, so that on taking samples at (m) and (n) from unit (C_4), the spectrum of particle-size distributions should be seen to approach the conditions in the deeper respiratory passages.

The connecting up of C_1, C_2, C_3 and C_4, one to another enables one to synthesize aerosol systems over a wide range of variations under constant dynamic conditions and to test changes in particle size or the distribution of masses caused by the passage through each section of the main tube.

The distribution of particle sizes according to number or mass in kinetic particle diameter (d) according to Stokes, was determined by the aerosol spectrometer over the range of 0.03 to 3 microns, inclusive. As has been described elsewhere (2, 3) in complete detail, the separation of the particles out of a laminar, continuous stream of air took place radially in a centrifugal field ($\sim$30,000 G) under almost isothermic and isobaric conditions on the inner surface of a conical rotor (Figure 2), which drew in the air test through the inlet tube (m) at a rate of 2 to 7 liters per minute, depending on the test conditions. The rotor was cooled by a coaxially arranged casing through which a coolant flowed. The rotor temperature was measured through the soldered joints (9) of a thermopile, whose respective soldered joints were held at the temperature of the stream in the main tube by a stream drawn in through connecting tube (n). Thus the temperature of the rotor caused by air friction (speed $\gg$ 24,000 rpm) was measurable to $0.2°$ C. It is possible, by controlling the temperature of the coolant liquid (using a refrigerator) to compensate for this difference. By so doing changes in the distribution of particle sizes due to condensation or evaporation of the particles during separation are avoided. Evaluation of the distribution of particle sizes (see below) of the aerosol precipitate should, therefore, approach correspondence with that of the suspended in air condition.
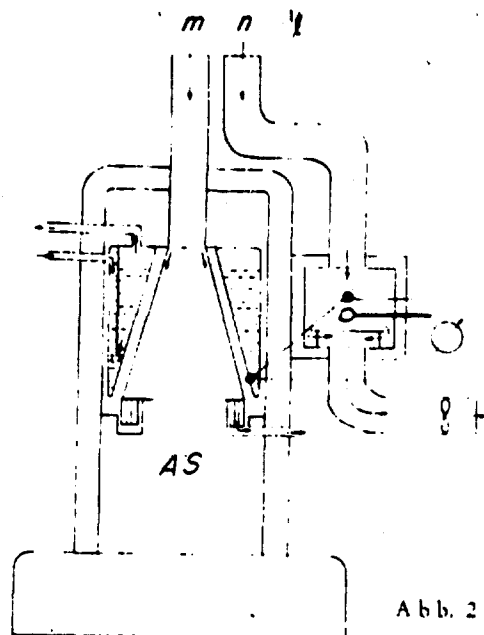
Figure 2. Aerosol spectrometer

Under these conditions the farthest point of fall-out or pre-cipitation of a particle on the wall of the main tube is given, even through its path in flight in a radial direction crosswise to the laminar stream, which is determined in turn by the "kinetic particle-diameter" (d) in accordance with the Stokes-Cunningham law of falling bodies. Thus (d) is defined in accordance with the geometrical position of the particle in the fall-out, independent of changes which the particles may have undergone after striking against the wall, as long as they are still identifiable as such, i.e., are still susceptible to being counted. The quantitative relationship between (d) and the point of fall-out is defined by calibration against mono- and multidisperse polystyrene aerosols. In respect to details and the analytical methods, reference must be made to the pertinent literature on the subject.

This method, therefore, makes it possible to quantitatvely determine from the change in distribution of particle sizes of a physically and chemically defined aerosol whether and to what extent added gaseous trace components or their reaction products can accumu-late on the particles tested, i.e., what relationship exists between the molecularly dispersed and the colloidal phase portions of such sub-stances.

Mention is made in the following of the quantitative relation-ships resulting from this arrangement:

a. The concentration of aerosols in the stream of the main tube, calculated in terms of mass (grams/ml), neglecting (C_2) (Figure 1)

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is given by the (M'_a) produced in (C_1) and the volume of **air** (F_1) added there, plus the (F_2) taken up in (C_2) and the further added volume (F_3) as:

$$M_a = M'_a (F_1 - F_2) / (F_1 - F_2 + F_3) \qquad (1)$$

    b. The concentration, in terms of volume (ml/ml air) of the gaseous trace elements added to (C_2) is defined as follows:

    If (V_p) signifies the content in volume of the piston injector, (V_g) the volume of gas traces fed in, (F_p) the volume pouring from the capillary (see above) per unit time, (F_v) the stream of argon or nitrogen added to it, then the concentration by volume is given by:

$$C_g = \frac{V_g \cdot F_p}{V_p (F_v + F_1 - F_2 + F_3)} \qquad (2)$$

The amounts required from the individual added flows to create a given value of (C_g) are thus, in any case, easy to calculate, so that the only requirement which must be fulfilled is that the total amount of material in the stream in the main tube must be considerably greater than that which is drawn up by the aerosol spectrometer.

    c. The total volume (V_c) of a condensate on the aerosol particles of previously known size (d_o), whose kinetic diameter has become enlarged to (d), can be found by the following simple consideration:

$$V_c = 0.52 \ N \ (d^3 - d^3_o) \quad \text{oder: } d/d_o = \left[\frac{1.92 \ V_c}{N \cdot d^3_o} \right] + 1 \qquad (3)$$

where (N) is the number of particles per ml. This is only valid when (N) remains constant, which means that no new particles are formed as a result of the reaction. This relationship shows that the effect (i.e.: d/d_o) for a given value of (V_c) becomes greater as values of (N) and (d_o) decrease, so that for $(V_c = \text{constant})$ the decrease in (M_a) to (M'_a) in equation (1) must give an increase in (d), which as a first approximation appears to be inversely proportional to the cube root of (N) and which can be predicted from equations (1) and (3). As a result of this one is able to.check against the results quantitatively, and systematic discrepancies in results (for example, as a result of the Kelvin-effect) can be ascertained.

Test Results

The method described above was evaluated by testing it on photo-oxidation of hydrocarbons containing olefines in the presence of (10^{-5}) of NO_2 (Haagen-Smit Reaction) (4, 5). To test equation (3), monodisperse Polystyrene-Latex emulsions were used, whereupon both (N) and (d_o) were varied. Figure 3 is a photographic reproduction of three aerosol spectra, the upper having a diameter (d_o = 0.57 microns), the lower (d_o = 0.28 microns), for equal trace concentrations (C_g), flow rates in the main tube, temperatures and relative humidities.

Figure 3. Aerosol spectra which show the photo-oxidation of hydrocarbons containing olefines in the presence of NO_2 traces. More detailed description in text

This typical example does not show any change in (d_o) in the absence of light (left row), that is, the same spectra of particle size as in the absence of the gas traces. The middle row clearly shows an enlargement (d/d_o greater than 1), when the flow in the main tube in (C_3), Figure 1 is subjected to radiation by six lamps (approximately 20,000 lumens/liter) over a period of about 40 seconds. The row on the right shows only a very slight increase in size of the particle diameter after maximum radiation for the same period by 12 lamps. The quantitative evaluation for the upper row was (d/d_o = 1.9) for six lamps and (d/d_o = 2.4) for 12 lamps, which means an increase in volume of the particles of 7 and 14 times, respectively.

The lower row gives $(d/d_o = 1.5)$ for six lamps and $(d/d_o = 2.2)$ for 12 lamps, whereupon attention should be given the fact that (N) was correspondingly greater for the smaller particles than for the larger ones in the upper row. It should be noted that the gravimetric (in centrifuge field) change in weight for individual particles was found to correspond to an order of size of 10^{-14} Gm.

Similar attempts were made to polydisperse propylene glycol aerosols colored with methylene blue. The distribution of masses, that is, their displacements according to larger or smaller (d) values were determined colorimetrically with qualitatively similar results.

Although the use of this method on the morphology of aerosols is in its infancy, the material which has been accumulated as a result of hundreds of experiments not only suggests its general applicability, but also has already given indication of the following:

a. Maximum radiation (under isothermic conditions) in pure air brings about no measurable change in the distribution as to size of particles latex, glycol or paraffin aerosols.

b. The same is also true for the present of olefines and NO_2 traces as long as they are present alone.

c. In the absence of aerosols, i.e., colloid-dispersed substances, the application of light radiation to co-existing traces of olefines and NO_2 leads to the formation of aerosols having extremely fine particle sizes. This points to the possibility of auto-nucleation.

d. Such co-existing traces of olefines and NO_2 in the presence of aerosol particles show a very intensive capability of association with them when subjected to light radiation. If their density (N) is sufficient, then no measurable quantities of auto-nucleated particles can be found. For lower values of (N) they make their appearance in increasing quantitie. This appears to satisfy theoretical considerations, since according to the theory of Gibbs, the configuration of the smallest surface energy must have preference, instead of newly forming such surfaces through direct association.

Concluding Remarks

The method of synthesis of gas-aerosol systems herein described gives promise within the framework of the spot tests made to date of making it possible to go deeper into the morphology and formation of such systems than could have been done in the past. This method enables one to investigate the effect which particulate substances have in respect to their hydrophobic or hydrophilic, as well as their hygroscopic and electrolytic properties, on their possibilities of association with gas traces. The latter appears to be important as a way of evaluating the mechanism of reabsorption upon the penetration of such substances into the respiratory passages, a process which will apparently be rendered accessible to measurement for the first time, using this method.

References

        (1) Goetz, A., "On the Nature of the Synergistic Action by
Aerosols," Int. J. Air and Water Pollution, Vol 4, 1961, pages 168-184.
"On the Physics of Airborne Colloids in the Submicron Range," Physikertag
Heidelberg (Heidelberg Session of Physicists), Chief reports, 1957,
pp. 170-184, Physik-Verlag Publishers, Mosbach (Baden), Germany, 1958.
        (2) Goetz, A. and H. J. R. Stevenson, "The Aerosol Spectrometer,
Its Theory, Construction and Application to the Analysis of Exhaust and
Atmospheric Aerosols." APCA Proceedings of the Semi-Annual Technical
Conference, San Francisco, pp. 228-267, 1957.
        (3) Preining, O., H. J. R. Stevenson and A. Goetz, "Analysis of
Aerosol Spectra," Proceedings 52nd Annual Meeting of APCA, June 1959.
        (4) Haagen-Smit, A. J. and Colleagues, "Ozone Formation in
Photochemical Oxidation of Organic Substances," Ind. Engin. Chem., Vol
45, 1953, pp. 2086-2089; Vol 48, 1956, pp. 1884-1887.
        (5) Doyle, G. J. and N. A. Renzetti, "The Formation of Aerosols
by Irradiation of Dilute Auto Exhaust," J. APCA, Vol 8, 1958, pp. 23-32.