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MONODISPERSE AEROSOLS

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I. INTRODUCTION

Almost all the properties of aerosols depend to a marked extent on the particle dimensions, and the establishment of these relationships is the chief aim of many aerosol studies. Since all real aerosols are more or less polydisperse, it is necessary, in the experimental study of these relationships, that the quantity to be determined in a polydisperse aerosol with a mean particle radius $\bar{r}$ coincides with the corresponding quantity in a monodisperse aerosol with the same particle radius. The error thus introduced increases with increase in the polydispersity of the aerosol, so that in the last twenty years there has been an ever-increasing tendency in aerosol studies to use aerosols which are as far as possible monodisperse.

In one extremely important case, however, namely in the study of various processes of aerosol deposition, for example in filters, breathing apparatus, etc., it is also possible to use polydisperse aerosols. In this case the total concentration of particles and their distribution with respect to dimensions in the original aerosol and in the aerosol which has passed through the filter or been deposited on it are determined, and the efficiency of the filter for all the particle dimensions of the aerosol is calculated. The precise determination of the total concentration of particles and their distribution with respect to dimensions, even within a fairly narrow range of the latter, is a complex and extremely tedious task, however. This method can thus be recommended only for preliminary measurements, and for accurate studies it is best in most cases to work with an aerosol with the maximum degree of monodispersity attainable by modern methods of preparation. Such aerosols may be described as "practically monodisperse", and it is to these that we shall be referring in the present review.

The degree of monodispersity is conveniently characterised by the magnitude of the coefficient of variation α, i.e. the ratio of the standard deviation of the particle radii σ to the mean radius $\bar{r}$:

$$\alpha = \frac{\sigma}{\bar{r}} = \left[\frac{\sum_i^N (r_i - \bar{r})^2}{N}\right]^{1/2} \Big/ \bar{r}. \qquad (1)$$

Since the distribution of particles with respect to dimensions in aerosols usually deviates appreciably from the normal gaussian distribution and approximates to a logarithmic-normal distribution, the degree of monodispersity, at values of α which are not too small, is conveniently expressed by the value of the logarithm of the geometric mean square deviation:

$$\sigma_g = \left[\frac{\sum_i^N \left(\ln \frac{r_i}{r_g}\right)^2}{N}\right]^{1/2}, \qquad (2)$$

where $r_g = \left[\prod_i^N (r_i)\right]^{1/N}$ is the geometric mean radius of the particles. For low values of α, when $\bar{r} \simeq r_g$, $\ln(r_i/r_g) \simeq (r_i - r_g)/r_g$ and

$$\sigma_g \simeq \left\{\frac{\sum_i^N [(r_i - r_g)/r_g]^2}{N}\right\}^{1/2} \simeq \alpha. \qquad (3)$$

Fig. 1 gives the logarithmic-normal distribution curves for $\sigma_g = 0.1$ and 0.2, and also the normal distribution curves for $\alpha = 0.1$ and 0.2. The choice of criterion for "practical monodispersity" is of course arbitrary. The present review deals with aerosols with $\alpha \leqslant 0.2$ or $\sigma_g \leqslant 0.2$. Not all authors have calculated α for the aerosols which they have prepared. Sometimes only the distribution curves or histograms are given, and in some cases only the range of radii containing a certain percentage of the particles. In these cases we calculated α with the accuracy assumed for the data given in the work cited.

Here mention must be made of the methods used to determine the degree of monodispersity of aerosols. The most reliable methods naturally involve the direct determination of the dimensions of a large number of individual particles by means of an optical or electron microscope, ultra-microscope (from the rate of sedimentation of the particles), photoelectric counter, or other methods, followed by statistical treatment of the results of the measurements. Unfortunately, these methods are not always applicable, particularly for aerosols from volatile liquids, whose particles undergo appreciable volatilisation during the removal of the specimens and the actual measurements. It is extremely difficult to eliminate evaporation. Moreover, in the measurement of liquid droplets by means of an optical microscope, it is necessary to make allowance for their spreading over the support, and only preliminary studies of the measurement of droplets with the electron microscope have been made. The measurement of the rate of sedimentation of particles or the rate of movement in an electric field by means of the ultra-microscope is possible[1] only for a particle radius greater than 0.15 μm, and the errors in the determination of the dimensions of individual particles, associated with brownian movement, lead unavoidably to high values of α.

Another method for estimating the monodispersity of aerosols, which has been widely employed, is the optical method based on the fact that the scattering of white light in more or less monodisperse systems of spherical particles produces spectral colours which are purer the higher the degree of monodispersity. If the observer looks through the aerosol towards the light beam, he sees, surrounding the light source, a "halo" consisting of coloured rings whose angular diameter is simply related to the particle dimensions and the length of the corresponding light

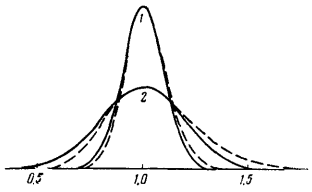


Fig. 1. Normal (solid line) and logarithmic-normal (broken line) distribution curves.

waves. The "halo" method is applicable at $\bar{r} > 1$ μm and is used in the study of fogs formed by the adiabatic expansion of air containing the vapour of water or other volatile liquid and also in the study of natural clouds and fogs. In the latter case the sun or moon is the light source.

When $\bar{r} < 1$ μm, the aerosol is introduced into a vertically-arranged cylindrical vessel with transparent walls and a narrow beam of white light is passed in a direction perpendicular to the axis of the cylinder. In the case of an aerosol which is monodisperse and has a sufficiently high concentration, spectral colours, which show a periodic variation with change in the angle of observation, are visible in the vessel. These diffraction spectra, which were first observed in monodisperse sols of sulphur by Ray[2] and were studied in detail by La Mer and coworkers[3-5], have been called "higher-order Tyndall spectra". A horizontal viewing-tube, focussed on the axis of the vessel and capable of rotating around it, is used to measure θ, the angle of deviation of the red rays, for which α is obtained with the highest accuracy. The spectra are made more distinct by using a polaroid plate, which transmits only the component of the scattered light polarised in a vertical plane. The number of spectra increases with increase in the particle dimensions and is approximately equal to the particle radius in tenths of a micrometer. By means of special tables calculated on the basis of the Mie theory, it is possible to determine $\bar{r}$ from the values of θ corresponding to spectra of different orders; the position of the spectra depends comparatively little on the refractive index of the particles. This method is applicable for the approximate range $0.15\ \mu m < \bar{r} < 1.2\ \mu m$. The measurement of θ becomes impossible at lower values of $\bar{r}$, since the spectrum becomes indistinct, and becomes impossible at higher values of $\bar{r}$, because the spectra of different orders are crowded together[6]. The instrument used has been named the Owl.

It is impossible to give a precise answer to the main problem — at what degree of monodispersity do distinct Tyndall spectra appear? It first of all follows from the theory of the phenomenon that with increase in the degree of monodispersity the spectra should appear not immediately but gradually, so that different observers may disagree on the question of whether the spectra are present or absent. Moreover, the clarity of the spectra is influenced by a number of factors: the optical density of the system[7], the mean dimensions of the particles and their refractive index, the conditions of the observation — the thickness of the illuminating beam[8], stray light in the instrument, the shading in the laboratory, the unique features of the observer's vision, etc. The use of a polaroid plate has a marked effect on the clarity of the spectra. For a given value of σ and $\bar{r}$, the possibility of observing the spectra also depends on the nature of the distribution curve, since the scattering of the light increases rapidly with increase in the particle dimensions. By using the ultramicroscope method to study the distribution with respect to dimensions for droplets of various non-volatile liquids in fogs produced in a Sinclair–La Mer generator (see below) with $\bar{r} = 0.3$–0.9 μm, Kitani[9-11] established that determination of θ for the red band is possible only for $\sigma \leqslant 0.12$ μm. According to Berner[12], who determined the dimensions of droplets in dioctyl phthalate fogs in the same range of values of $\bar{r}$ using Goetz's Aerosoloscope[13], the first red band can be observed at $\sigma \leqslant 0.14$ μm and the whole spectrum only at $\sigma \geqslant 0.10$ μm. From the data given by Goyer and Pidgeon[14], it follows that in an aqueous fog with $\bar{r} = 0.45$ μm, Tyndall spectra appear only at $\sigma \leqslant 0.09$ μm. In other papers the limiting value of σ was not determined, but the quoted values of σ at which the Tyndall spectra were or were not observed agree with the above data, with the following two exceptions.

La Mer's report[5] that the spectra disappear when equal volumes of two monodisperse hydrosols of sulphur with $\bar{r} = 0.467$ μm and 0.476 μm are mixed is undoubtedly based on some major error, since mixing in this way can lead to an increase in σ of only 0.004 μm. In actual fact, according to Maron and Elder's observations[7], the Tyndall spectra are preserved when monodisperse latexes of polystyrene with $\bar{r} = 0.164$ μm and 0.196 μm are mixed, although in this case the calculated value of σ increases by 0.016 μm. An analogous result was obtained by Petro[15], by mixing monodisperse hydrosols of sulphur with $\bar{r} = 0.310$ μm and 0.385 μm.

According to Martius[16], who prepared condensation aerosols of dioctyl phthalate with $\bar{r} = 0.34$–0.67 μm, Tyndall spectra are observed in these aerosols only at $\sigma \leqslant 0.003$–0.006 μm. Such monodisperse aerosols cannot, however, be prepared by a condensation method, and this result is due to the elementary error which Martius made in making allowance for the influence of brownian movement on the scatter of the particle-radius values found by the ultramicroscope method.

Thus the appearance of Tyndall spectra is related to the value of not the relative (α) but the absolute (σ) standard deviation. This is apparently due to the fact that the increase in monodispersity with increase in $\bar{r}$ at constant σ is compensated by the simultaneous crowding together of the spectra of different orders.

The qualitative method of estimating monodispersity from the Tyndall spectra can also be developed quantitatively. The most accurate method is the "polarisation ratio" method, based on the measurement of the ratio k of the intensities of the components of the light scattered by the aerosol and polarised in horizontal (parallel to the plane of scattering) and vertical planes. Here it is possible to illuminate the aerosol with monochromatic light of constant wavelength λ and measure k as a function of the angle θ of scattering (Kerker *et al.*[17-19]), or to carry out the measurements at constant θ (usually 90°) and varying values of λ (Heller *et al.*[20,21]). This gives sinusoidal curves, which become flatter (the maximum and minimum values of k approach) with increase in the polydispersity. For a given distribution of the particles with respect to dimensions, for example the logarithmic-normal law, these curves are calculated on the basis of the Mie theory, by means of computers, for different values of $\bar{r}_g$ and σ_g, and the results are compared with the experimental curves. The distribution parameters can be determined in this way with sufficient accuracy. For a constant value of the product $r_g \sigma_g$, close to the value of σ given by formula (3), the nature of the curves changes little with increase in σ_g.[17] This agrees with the above condition for the production of the Tyndall spectra.

To enable the Tyndall-spectra method to be applied to particles with $\bar{r} < 0.2$ μm, La Mer[5,22,23] suggested that the particle size be increased by using solvent vapour which is in equilibrium with a solution of the aerosol material in the same solvent. The increase in size is determined by the concentration of the solution. The same concentration is also rapidly established in the aerosol droplets (if the Kelvin effect is neglected, see below). In this way La Mer was able to increase the particle size by a factor of 5–10

and to obtain Tyndall spectra in aerosols with an initial value of $\bar{r} \geq 0.02$ μm. In this "cultivation" of the aerosols, the value of α, as a first approximation, should not change, but because of the Kelvin effect, it is necessary, in order to maintain equilibrium, that the concentration in the finer droplets be slightly greater than that in the larger droplets, i.e. the latter grow more than the former, so that α should increase slightly during "cultivation"[24]. At the same time the value of $\sigma = \alpha\bar{r}$ increases considerably during the "cultivation", and this possibly explains La Mer's observation[25] that the sulphuric acid fogs with $\bar{r} \geq 0.20$ μm, obtained in his generator, give Tyndall spectra, whereas highly-dispersed fogs with $\bar{r} < 0.1$ μm do not give these spectra on "cultivation".

II. PREPARATION OF MONODISPERSE AEROSOLS BY CONDENSATION METHODS

A number of conditions must be observed in order to obtain monodisperse aerosols by condensation methods. Since the monodispersity decreases on coalescence, it is necessary to eliminate coalescence as far as possible during the preparation of monodisperse aerosols. From this it follows that the concentration given by the count (the number of particles in unit volume) of the aerosols generated should not be too high, or else they should be diluted considerably immediately after their formation. The maximum permissible concentration naturally depends on the time for which the aerosol being studied should remain unchanged under the conditions of the experiment. Since the aerosol coalescence constant under normal conditions has values of about 3×10^{-10} cm^3 s^{-1}, we find that if the count concentration is to be decreased by not more than 5% after an experimental time t, the concentration should not exceed 1.7×10^8 cm^{-3} for $t = 1$ s, 0.85×10^7 cm^{-3} for $t = 20$ s, and 3×10^5 cm^{-3} for $t = 10$ min.

The question of the conditions of formation of monodisperse "primary", i.e. non-coalesced, aerosols during the bulk condensation of a vapour is more complex. In this case it is obviously necessary that formation of all the aerosol particles should take place under exactly identical conditions, and in particular that the supersaturation be the same throughout the whole volume in which the condensation is taking place. This condition can be realised in practice only by producing the supersaturation by the adiabatic expansion of a vapour–gas mixture in a sufficiently large chamber, in which it is possible to neglect the decrease in supersaturation close to the walls, or by a homogeneous gaseous chemical reaction. In ordinary methods of generating condensation aerosols — by cooling a gas–vapour mixture in a heat exchanger or by mixing it with a cold gas — variations in the degree of supersaturation at different points in the gas stream and hence fluctuations in the size of the particles formed are unavoidable.

In spontaneous condensation of vapour, another unfavourable factor is introduced — the nuclei are not formed simultaneously, even when the supersaturation is constant throughout the volume. According to the general theory of new-phase formation, the rate of spontaneous formation of nuclei increases extremely rapidly with increase in supersaturation. Thus if the supersaturation were created instantaneously, the rate of production of new nuclei would decrease extremely rapidly as the supersaturation was eliminated, i.e. all the particles would have approximately the same age. Under real conditions, however, the supersaturation is produced at a finite rate and continues to increase for some time after the start of formation of the nuclei, passing through a maximum. The slower the increase in supersaturation, the less distinct this maximum, and the longer the time interval within which new nuclei may be produced. Thus spontaneous condensation generally leads to the formation of more or less polydisperse aerosols.

As in the case of colloidal solutions, aerosols with a much higher monodispersity are obtained by the "nucleus" method, i.e. by condensation on prepared (extraneous) condensation nuclei, which may be gaseous ions or highly dispersed aerosols of non-volatile substances. If these nuclei exhibit more or less identical activities, i.e. if the condensation of vapour on these nuclei begins at approximately the same supersaturation, an aerosol with an extremely high monodispersity should be formed.

In addition to the above factors which do not favour monodispersity in the formation of aerosols by condensation, there is a factor which effectively increases the monodispersity, namely the equalisation of particle dimensions during condensation growth. The rate of growth (increase in dimensions) of particles with a radius much less than the mean free path of the vapour molecules l is independent of r, whereas when $r \gg l$ the rate of growth[26] is inversely proportional to r. Thus in the initial stage of the growth of nuclei of different ages the absolute difference in their dimensions remains constant, and later even begins to decrease. As a result, the relative difference in the size of the particles decreases appreciably as they grow. From this it follows, *inter alia*, that the degree of monodispersity of condensation aerosols should, generally speaking, increase with increase in the particle dimensions, as is observed experimentally. In this discussion we have neglected the increase in vapour pressure above very fine particles, but in the initial stage of the growth of the particles the supersaturation is usually fairly high, so that this factor is of no significance.

1. Preparation of Monodisperse Aerosols by the Adiabatic Expansion of a Vapour–Gas Mixture

From the above it follows that the most favourable conditions for the formation of monodisperse aerosols are achieved by condensing a vapour on prepared nuclei or by adiabatic expansion of a vapour–gas mixture. Unfortunately, this method has up to the present been used only to prepare fogs of volatile liquids, chiefly water, and the determination of the degree of monodispersity of the resulting fogs by direct measurement of the droplets is extremely difficult. For this purpose, only the optical methods described above can be used.

In the adiabatic expansion of moist atmospheric air containing a large quantity of condensation nuclei with widely differing activities, an extremely polydisperse fog is formed. If, however, this fog is allowed to disappear, partly by deposition of the droplets and partly by evaporation, the largest and most active (hygroscopic) nuclei will be removed, the total number of nuclei will be reduced considerably, and when the expansion is repeated a fog with a larger particle size and hence a higher monodispersity is formed. After several expansions, the purity of the halo colours indicates that extremely monodisperse fogs are produced[27].

2. Preparation of Monodisperse Condensation Aerosols in Generators of the Heat-Exchange Type

The nucleus method for preparing monodisperse aerosols from high-boiling substances was first applied by Sinclair and La Mer [28-31]. The generator which they designed in 1941 rapidly received extensive acceptance in aerosol studies. In this generator (Fig. 2) the liquid is placed in the vaporiser (A) — a 2 litre Pyrex flask placed in an air thermostat. Filtered air or nitrogen enters the vaporiser at a rate of not more than 4 litre min^{-1}, partly through a generator of condensation nuclei (B) and partly through a tube immersed in the liquid. The gas containing the vapour of the liquid, spray, and condensation nuclei passes through two narrow nozzles into a superheater (C) — a similar but empty flask placed in another thermostat at a slightly higher temperature. In the superheater the spray is vaporised, the contents of the flask are mixed, and the gas mixture passes into a condenser (D), 50 cm long and 2 cm in diameter, with air jacket, where the gas is slowly cooled and the vapour condenses, partly on the walls and partly in the space within the condenser, forming an aerosol. On leaving the condenser, the aerosol is diluted in the mixing vessel (E) with 10–100 times its volume of filtered air, to prevent coalescence.

Let us consider what happens in the condenser of the generator. In the vapour–gas mixture entering the condenser, the vapour is unsaturated, so that in the lower section of the condenser, only gradual cooling of the gas takes place under conditions of laminar flow, since the temperature of the gas near the axis of the condenser is higher than that at the walls. At a certain height, the dew point is reached at the walls and the vapour begins to condense there; the concentration of the vapour at the walls becomes less than that at the axis. In the absence of condensation nuclei (or when the rate of flow is too low), it is frequently found that almost all the vapour condenses on the walls, since the supersaturation is insufficient for spontaneous condensation in space. With an increase in the concentration of nuclei n, the ratio of the quantity of vapour condensed in space to that on the walls increases. Thus although the mean volume v of the resulting droplets decreases, the product nv increases. The dimensions of the droplets subsequently increase with increase in the concentration of vapour (at constant n), i.e. with increase in the temperature of the vaporiser. This makes it possible to control the particle size within certain limits. The temperature of the superheater has comparatively little influence on $\bar{r}$, however.

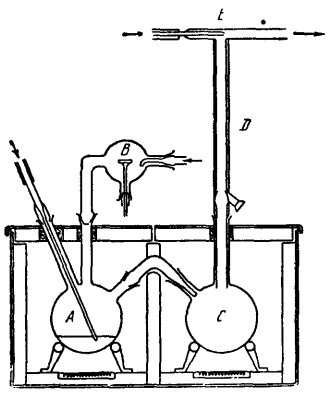


Fig. 2. Sinclair–La Mer generator.

To obtain aerosols with a low degree of dispersion corresponding to $\bar{r} > 1-2$ μm, a low concentration of nuclei and a high concentration of vapour are thus required. Since increase in temperature in the vaporising liquid may lead to its decomposition, it is recommended that the degree of vapour saturation of the gas be increased by bubbling the gas through a porous plate and by decreasing the rate of flow of gas through the nucleus generator [32-34]. Moreover, in the preparation of large droplets it is necessary to increase the duration of their growth, i.e. to use a longer condenser and to direct it not upwards but downwards, so that the rapidly-settling large droplets can leave the condenser. In this way it was possible to obtain monodisperse fogs of tetralin with $\bar{r}$ up to 27 μm. [33] On the other hand, La Mer used the generator to prepare an aerosol with $\bar{r} = 0.006$ μm; [35] but he was able to verify the monodispersity (by "cultivation") only for $\bar{r} > 0.02$ μm.

To obtain monodisperse aerosols with mean particle dimensions which do not change with time, a number of conditions must be satisfied in the Sinclair–La Mer generator. The temperature of the vaporiser should be constant to within 0.2 deg, otherwise, as we have seen above, the dimensions of the aerosol particles will change continuously. Because of the high heat capacity of the generator, the establishment of constant operating conditions requires about 6 h.

The purity of the vaporising liquid is extremely important — volatile impurities are particularly undesirable, since the dimensions of the particles decrease continuously as these are removed from the liquid. Since the liquid undergoes prolonged heating in the generator, it gradually decomposes, particularly when air is passed through; the walls of the vaporiser and superheater become covered with a deposit of decomposition products and the aerosol is no longer monodisperse [24]. It is therefore necessary to change the liquid and wash the generator at intervals. The decomposition is inhibited considerably in an inert gas atmosphere.

Thus the monodispersity of aerosols, generally speaking, increases with increase in $\bar{r}$, but it sometimes decreases sharply when a definite value of $\bar{r}$ has been reached [36]. This is probably due to the fact that spontaneous condensation of the vapour begins when the concentration of nuclei becomes too low. The same is observed when the vapour–gas mixture is cooled too rapidly in the condenser, for example when the flow rate in the condenser is too high [31].

It is also extremely important to have a constant concentration of condensation nuclei. Thus in the usual method of generating the nuclei, by the sublimation of sodium chloride or other substances, it is necessary to maintain the sublimation temperature and the rate of gas flow through the generator constant, since this affects the conditions of both the volatilisation and the condensation.

In agreement with theory, almost all authors report that aerosols obtained in the absence of nuclei are polydisperse (except for sulphuric acid aerosols, see below). The observations of Matijevich *et al.* [37] that in the production of AgCl aerosols the introduction of AgCl nuclei has no influence on the polydispersity of the aerosols ($\alpha = 0.20$–0.25) are simply explained by the fact that these nuclei

were able to volatilise before condensation of the vapour on the nuclei had begun.

In most cases the nuclei are provided by highly-dispersed sodium chloride aerosols obtained by sublimation of the salt or, less frequently, by atomisation of dilute NaCl solutions followed by drying of the resulting fog [35,38]. Sometimes other salts, for example AgCl, [39] or metals [10] are sublimed; in the latter case a spark or arc discharge between metallic electrodes is frequently used [10,35,36]. In one method widely employed — sublimation of NaCl deposited on the surface of a nichrome wire which is made incandescent — allowance must be made for the fact that the salt recrystallises with the passage of time, so that the rate of its volatilisation and hence the concentration and dimensions of the nuclei decrease considerably [40]. It is therefore necessary either to "condition" the NaCl deposit for a prolonged period or to sublime the salt under conditions where the gas is saturated with its vapour [41].

Polydisperse aerosols containing large particles should not be used to provide nuclei. The use of an AgCl aerosol of this type gave polydisperse linolenic acid fogs [39], but when aerosols containing no large AgCl particles were used the monodispersity of the fogs increased considerably. Particularly unfavourable conditions are created when the condensation nuclei dissolve in the droplets of the fog being generated, decreasing the vapour pressure above the droplets. Petro [15] prepared a fog from aqueous NaCl solution by passing the NaCl aerosol through the vaporiser of a Sinclair–La Mer generator filled with water at room temperature. Since the walls of the condenser were very wet with water, the growth of the solution droplets took place in an atmosphere saturated with water vapour. Thus in the case of polydisperse NaCl aerosols containing large particles, a fairly polydisperse fog was obtained, but when an NaCl aerosol in which the radii of all the particles were less than 0.1 μm was used, it was possible to obtain fogs which gave Tyndall spectra.

It has not been possible to find condensation nuclei for all vapours. Thus mercury vapour does not condense on the nuclei usually employed [42]. Some gases, for example NO_2, bring about the condensation of mercury vapour, but monodisperse aerosols are not obtained in this way. Indigo vapour shows analogous behaviour [43].

On the other hand, H_2SO_4 vapour obtained from the 98–99% acid not only does not require the presence of nuclei for condensation but even condenses spontaneously in the presence of condensation nuclei [25]. The spontaneous condensation of these vapours makes it possible to obtain aerosols with $\overline{r}$ = 0.1–0.4 μm, giving Tyndall spectra [25,44].

Until recently, the Sinclair–La Mer generator was used to obtain monodisperse aerosols only from organic substances, sulphur, and sulphuric acid. Recently, Movillat [36] used a slightly modified generator to prepare a cadmium aerosol with $\overline{r}$ = 0.28 μm and $\alpha < 0.17$.

A considerably simplified generator is used in Kerker's laboratory [17,45]. The substance to be volatilised is placed in a boat in a long tubular furnace through which helium is passed. The gas, saturated with the vapour of the substance, leaves the furnace and passes through a tube, which apparently acts as an air condenser, into the chamber for examination. Since condensation nuclei are not used, aerosols with a fairly high polydispersity are obtained.

Rapaport and Weinstock [46] developed a fundamentally different design of heat-exchange generator (Fig. 3).

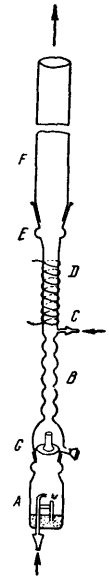


Fig.3. Rapaport and Weinstock's generator.

Filtered air passes at a rate of ~ 4 litre min^{-1} into a pneumatic atomiser (A), which gives an extremely polydisperse fog. Large particles are deposited on the walls of the vaporiser, which acts as a screen. When the fog is passed through the column (B), further deposition of the large droplets takes place, and only droplets with $\overline{r} \leqslant$ $\leqslant$ 1 μm remain in the fog. Where necessary, the fog is diluted with air supplied through the side arm (C). The fog then passes into the volatiliser (D) (2.0 cm in diameter and 25 cm long), heated with a nichrome spiral, and the temperature is raised to a value at which all the drops volatilise. This is verified by the absence of a Tyndall cone at the point E. The gas–vapour mixture then enters the condenser (F) (2.5 cm in diameter and 120 cm long), where the vapour condenses on the nuclei which remain after volatilisation of the droplets and consist of the non-volatile impurities present in the liquid. The liquid which has not volatilised flows downwards over the walls into the ring (G) and leaves the generator.

This generator gives the same degree of monodispersity as the Sinclair–La Mer apparatus, but it has a number of important advantages: steady-state operating conditions are attained in times of the order of 10 min instead of several hours; the cost of the generator is much lower; decomposition of the substance has no effect, since the spent liquid is removed and fresh liquid is supplied continuously to the generator; and the quantity of liquid used is very small.

Another characteristic feature of this generator is that the temperature of the vaporiser need not be strictly constant, since under the condition that volatilisation of the primary drops is complete the concentration of the vapour is independent of temperature. Moreover, since the concentrations of both the vapour and the condensation nuclei are proportional to the concentration of primary drops, change in the latter again has no significant effect on the

particle dimensions of the aerosol generated. In order to decrease $\bar{r}$, air is introduced as diluent through the side arm (*C*), but this permits a change in $\bar{r}$ only within comparatively narrow limits.

As shown by Lassen[47], it is possible, by varying the distance from the atomiser to a special screen, to alter considerably the dimensions and number of primary droplets and hence $\bar{r}$. In this way Lassen was able to change $\bar{r}$ in a dioctyl phthalate aerosol from 0.15 μm to 0.7 μm at constant vaporiser temperature and constant rate of flow of air.

According to Berner's experiments[12], the purity of the liquid used is of considerable importance in the production of monodisperse aerosols in a Rapaport–Weinstock generator. Very pure liquids or liquids appreciably contaminated with high-boiling impurities give fogs with a greater polydispersity than those given by liquids with a low concentration of these impurities: in the first case, the nuclei remaining after the evaporation of the primary droplets are so fine that their growth requires a high supersaturation, at which spontaneous condensation is possible; in the second case, large polydisperse nuclei are formed.

Martius' generator[48], which is intermediate between the two assemblies described above, consists of a glass tube, 30 mm in diameter and 2 m long, arranged at an angle of 30° to the horizontal. The lower half of the tube is heated with a nichrome spiral and the upper part is fitted with a jacket and acts as condenser. Dry filtered air is passed into the tube at a rate of 0.3–3 litre min^{-1}. In the centre of the heated section of the tube there is a side arm containing a syringe, which is operated from a servo-motor and passes the fog-forming liquid to the lower wall of the tube at a controlled rate within the range 10^{-3}–10^{-2} ml × × min^{-1}. The air–vapour mixture is then superheated and passes to the condenser, in the jacket of which water at a controlled temperature is circulated (for dioctyl phthalate a temperature of 17° is recommended).

In this generator the products of the thermal decomposition of the liquid being vaporised are not removed from the heated zone. It is thus hardly possible to maintain steady-state generating conditions over more or less prolonged periods. Martius does not mention this, and the data which he gives[16] do not indicate the monodispersity of the fog generated.

The generator of Fuks and Sutugin[49] is a modification of Kogan and Burnasheva's mixer-generator[50] (see below). The gas containing the condensation nuclei, before being mixed with the hot gas containing the vapour of the liquid, is heated to the temperature of the hot gas, after which the mixture is passed to the condenser. In the ultramicroscope study of dibutyl phthalate fogs with $\bar{r}$ = 0.61–1.3 μm and α = 0.02–0.12, obtained in this generator, it was found that the distribution of the droplets with respect to dimensions approximates more or less satisfactorily to the normal distribution. It was later found that, with decrease in the concentration of nuclei n, the mean radius of the particles increases only to a certain limit and then remains constant. Thus, at a vaporiser temperature of 95° and a flow rate of gas equal to 2.8 litre min^{-1}, the maximum value of $\bar{r}$ is 0.9 μm (at $n = 1.5 \times 10^3$ cm^{-3}). Calculation showed that for this value of n, only ~ 2% of the total vapour condensed on the nuclei, while the rest condensed on the walls of the condenser. Thus under these conditions, the supersaturation of the vapour inside the condenser is determined almost entirely by the rate of condensation of the vapour on the walls and is independent of the concentration of nuclei.

3. Preparation of Monodisperse Condensation Aerosols in Generators of the Mixer Type

A generator of the mixer type was designed by Kogan and Burnasheva[50]. Filtered gas passes at a rate of ~ 1 litre min^{-1} through a vaporiser (*A*) (Fig. 4), which is placed in a thermostat and is filled with large-pore silica gel impregnated with the liquid to be evaporated; the gas then passes in a narrow stream into the conical nozzle (*B*) of the mixer. Cold gas containing condensation nuclei passes at a rate of ~ 4 litre min^{-1} through the tube (*C*) and a narrow annular gap (whose width can be varied) into the same nozzle. The degree of supersaturation in the mixture depends on the nature of the liquid, the velocity of the two gas streams, the temperature of the mixer, the concentration of nuclei, and the width of the annular gap; it is controlled in such a way that the supersaturation is not so high that spontaneous condensation begins, or so low that all the vapour condenses on the walls of the mixer. For liquids with a high boiling point (dioctyl sebacate), it was possible to use gaseous ions as condensation nuclei. In this generator the mean dimensions of the particles cease to depend on the concentration of nuclei n at high values of n, of the order of 10^4 cm^{-3}, probably because the ratio of the quantities of vapour condensing on the nuclei and on the walls is even lower than that in heat-exchange generators. At a higher concentration of nuclei ($n > 10^6$ cm^{-3}) the volume of the particles is approximately inversely proportional to n. The methods used to vary $\bar{r}$ are the same as those for the Sinclair–La Mer generator. The degree of monodispersity and the shape of the curves giving the distribution of the particles with respect to dimensions in the aerosols obtained in this generator and in the Fuks–Sutugin generator are approximately the same.

Fig. 5 shows a typical distribution of droplets with respect to dimensions (on a probability graph) in dibutyl phthalate fogs which we prepared in a Kogan–Burnasheva generator[49]. The distribution approximates to the normal distribution given by the straight line.

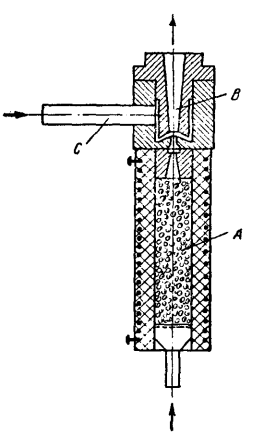


Fig. 4. Kogan and Burnasheva's generator.

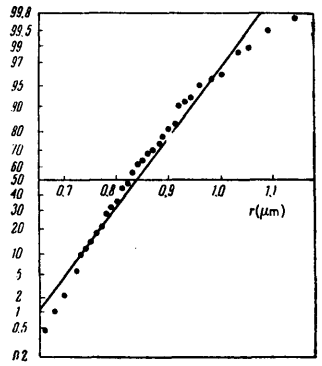


Fig.5. Distribution of particles with respect to dimensions in dibutyl phthalate fog.

In some cases, mixer-generators give fairly monodisperse aerosols even without extraneous condensation nuclei, for example from sulphuric acid (see above). In some cases atmospheric condensation nuclei appear to have been used, although no reference was made to these. Nuclei of this type are probably responsible for the production of dioctyl phthalate aerosols with $\overline{r}$ = 0.1–0.2 μm, giving Tyndall spectra, in mixer-generators [51,52].

4. Formation of Monodisperse Condensation Aerosols as a Result of a Chemical Process

There are very few data on this subject. An extremely promising method involves the preparation of monodisperse aerosols by photochemical or radiochemical gas reactions. When nitrogen containing methyl acrylate or methyl methacrylate vapour but no condensation nuclei was passed through a quartz tube illuminated with ultraviolet light, polymer aerosols with $\overline{r}$ = 0.05–1 μm, giving Tyndall spectra, were obtained [53]. When sufficiently fine condensation nuclei were introduced, it was possible in this way to obtain an aerosol with an extremely high monodispersity, since in this case it is possible to achieve constant supersaturation of the polymer vapour throughout the whole period of growth of the particles.

Fogs of aqueous ammonium chloride solution, with $\overline{r}$ = 0.15–0.40 μm and $\alpha \simeq 0.10$, were prepared by mixing NH_3 and HCl, in a long vertical tube, with air which had been saturated with water vapour and freed from gaseous-ion condensation nuclei [54].

In concluding this section we would point out that the particles of condensation aerosols obtained at low temperatures, at which no thermoelectronic emission takes place, are uncharged or very weakly charged (as a result of capture of atmospheric ions).

III. PREPARATION OF MONODISPERSE AEROSOLS BY DISPERSION METHODS

The extremely varied dispersion methods for preparing monodisperse aerosols can be divided into three groups: (1) atomisation of liquids; (2) atomisation of monodisperse suspensions; and (3) atomisation of monodisperse powders.

1. Preparation of Monodisperse Aerosols by Atomising Liquids

The mechanical atomisation of liquids in jets, nozzles, etc. is used in many branches of technology and generally produces extremely polydisperse fogs. The mechanism of atomisation in all cases involves the action of hydraulic pressure or centrifugal or aerodynamic forces which draw the liquid out into a fine stream or film [55] which then breaks down to form droplets under the influence of surface tension. The finer the liquid stream or film, the smaller the resulting droplets, but the degree of polydispersity is always high.

On the other hand, it is known that, when a liquid is drawn slowly from a capillary tip, drops with constant dimensions are formed, although these are accompanied by very fine droplets or satellites. The latter are formed from the fine thread of liquid joining the droplet to the rest of the liquid before the actual rupture. The radius r of the main drops is determined from the condition that the force of gravity on the drop G and the capillary force H are equal at the moment when the neck of the drop begins to narrow

$$G = \frac{4}{3}\pi r^3 \gamma g = H = 2\pi\rho s k, \qquad (4)$$

where s is the surface tension, γ the density of the liquid, ρ the radius of the neck when it begins to narrow, approximately equal to the radius of the capillary from which the liquid is flowing, and k is a numerical constant of the order of unity. It can readily be shown that only droplets of the order of 1 mm can be obtained in this way, even from very fine capillaries.

To obtain finer droplets, it is necessary to increase considerably the force causing the drop to break away. Lane [56] suggested that this be done by blowing a fine stream of air downwards against the capillary (syringe needle with an internal diameter of 0.45 mm). When the needle was placed exactly along the axis of a short tube (diameter 2.5 mm) through which the air was blown, it was possible to obtain water droplets with values of r in the range 0.15–0.50 mm, depending on the velocity of the air and the rate of supply of liquid V. The value of α decreased from 0.012 to 0.005 with increase in $\overline{r}$, i.e. the degree of monodispersity was very high. Finer droplets could be obtained by using finer needles or by placing wires inside the needles, and by decreasing V.

Other workers [57], unlike Lane, did not allow the liquid to flow spontaneously [under the action of gravity (Ed. of Translation)] into the needle but forced the liquid into the needle by means of a micro-plunger. In spite of this, the degree of monodispersity was slightly lower than that obtained by Lane: the value of α varied in the range 0.11–0.05 for values of $\overline{r}$ in the range 22–220 μm.

Lane's generator has a very low output. When an attempt was made to increase the output by means of a battery of 169 needles with an internal diameter of 0.22 mm, the degree of monodispersity decreased sharply, the decrease being greater, the smaller the droplets [58]. For $\overline{r}$ = 0.45 mm, α = 0.22. The reason for the polydispersity was the small difference between the internal and

external diameters of the needles, the latter determining the flow-rate profile in the surrounding stream; moreover, the drops obtained in the middle of the battery were larger than those obtained at the edges. The output of the battery was 200 g of water per minute for $\overline{r}$ = 0.5 mm and 20 g per minute for $\overline{r}$ = 0.1 mm. The monodispersity of the fog generated in the battery could probably be increased considerably if it were constructed with greater precision.

Much finer droplets can be obtained by centrifugal force in the so-called disc atomisers consisting of a horizontal disc rotating around a vertical axis passing through its centre. The liquid supplied to the disc flows to the tapered edge of the disc. At a high flow rate of liquid the latter forms a thick ring on the edge of the disc from which streams or films are drawn out to give a polydisperse fog.

Walton and Prewett[59] discovered, however, that when the flow rate of liquid is sufficiently low, so that it forms a very thin layer on the surface of the disc and a narrow ring at the edges, individual droplets are torn from the latter. If the liquid is supplied to the exact centre of the disc and its surface is effectively wetted by the liquid, the thickness of the ring is constant over the whole perimeter and droplets with equal dimensions are formed (together with much finer satellite droplets).

From the theory of the breaking away of drops from a wall which they are wetting, it follows that in this case the quantity ρ in Eqn. (4) should be replaced by a quantity close to the radius $\overline{r}$ of the actual drop. Further replacement of g by $\omega^2 D/2$, where ω is the angular velocity of the disc and D its diameter, and of r by $d/2$, where d is the diameter of the drops, gives

$$d\omega (D\gamma/s)^{1/2} = C. \qquad (5)$$

The value of the constant C is $\sqrt{12} = 3.47$.

In Walton and Prewett's experiments at low rates of rotation the values of C were in fact close to 3.47 for organic liquids which effectively wetted the surface of the disc; the value was slightly lower for water, which did not wet the disc effectively. At very high values of ω, equal to several hundred rev s^{-1}, the liquid is unable to acquire the tangential velocity of the disc, the drop dimensions are greater than the theoretical, and the values of C reach 5.

Water droplets with $\overline{r}$ = 0.1–1.5 mm were obtained on a disc rotating at 10–50 rev s^{-1}, and droplets of non-volatile liquids with $\overline{r}$ down to 8 μm were obtained at 1500 rev s^{-1}. Methyl salicylate droplets with $\overline{r}$ = 0.9 mm were obtained with a disc diameter of 4 cm and a velocity of 15 rev s^{-1}. At a flow rate of liquid $V \leq 0.4$ ml s^{-1}, the mass of the main droplets is greater by several orders of magnitude than the mass of the satellite droplets, but increase in V leads to an increase in both the relative number and dimensions of the satellite droplets, and at V = 2.8 ml s^{-1} an obviously polydisperse fog is formed. The greater the rate of rotation and the smaller the diameter of the disc, the smaller should be the value of V necessary to obtain a monodisperse fog. Since the droplets fly further from the disc the greater their dimensions, it is possible, when the satellite droplets are much smaller than the main droplets, to separate the two by surrounding the disc with a jacket sectioned to allow the passage of the main droplets.

In May's experiments[60], the flow rate of liquid was very low ($\leq$ 1 ml min^{-1}) and more attention was paid to the application of the liquid exactly in the centre of the disc and to the determination of the degree of monodispersity of the fog generated. For dibutyl phthalate fog with $\overline{r}$ = 32 μm, α = 0.014, and for a water fog with $\overline{r}$ = 22 μm, α = 0.031, i.e. in the second case the monodispersity was slightly lower, in agreement with what was said above. The value of α changes little with the mean dimensions of the droplets, but increases appreciably as $\overline{r}$ approaches the height of the irregularities on the disc surface. It is therefore recommended that the disc be polished and treated with wetting agents to improve its wettability with water.

Boshoff[61], working with a large disc (D = 35 cm) at 2.7–27 rev s^{-1}, found that monodisperse fogs with $\overline{r}$ = = 0.35–1.15 mm are formed only at $6 < V < 22$ ml s^{-1}. The existence of the lower limit for V is undoubtedly due to rupture of the layer of liquid when it becomes very fine (the actual thickness is not stated) on the surface of the disc. Ryley[62], working at D = 5 cm, V = 0.4–0.8 ml s^{-1} and a velocity of 1000 rev s^{-1}, obtained water droplets with $\overline{r}$ = 11 μm, but no data on the degree of monodispersity are given. Monodisperse fogs can also be obtained on conical dishes with tapered edges, rotating about a horizontal axis[55].

The output of disc atomisers is higher than that of other monodisperse-fog generators; a slight inconvenience associated with their use is that the drops fly in all directions.

The mechanism of operation of a generator with a vibrating capillary, proposed by Dimmock[63], is not quite clear. A glass tube is drawn out at one end to form a 20 cm long capillary with an external diameter of 0.6 mm. A piece of steel needle from a syringe is fixed to the capillary at a distance of 2–5 cm from its base. An electromagnet supplied with alternating current is used to vibrate the capillary and the liquid fed to the latter is atomised to give drops of identical dimensions. The dimensions of the capillary are chosen in such a way that it is brought into resonance with the forced vibrations. From the diagram published in the paper, it is evident that the liquid is thrown not from the tip of the capillary, as stated in the text, but from the side opening, and individual droplets are torn away. Since 100 drops per second were torn from the capillary, the frequency ν of the vibrations was evidently 50 c s^{-1}. The maximum acceleration of the capillary tip is $(2\pi\nu)^2 a$, where a is the amplitude of the vibrations, with an order of magnitude in any case not more than 1 cm. Thus according to Eqn. (4), only water drops with $\overline{r}$ = 0.5 mm could be obtained in these experiments. In actual fact, Dimmock obtained drops with $\overline{r}$ = 5–150 μm, and this is extremely difficult to explain. All other workers[64-66] working with a generator of this type obtained drops with $\overline{r} \geq 150$ μm. Ryley[62] pointed out that a quite different mechanism of drop formation is possible. By using a syringe needle with an internal diameter of 0.14–0.61 mm and a tip polished at right angles to the axis, and by making this needle vibrate at a frequency of 200–3000 c s^{-1}, Ryley obtained a fine sinusoidal stream of liquid, which broke down to form droplets at a certain distance from the capillary. In order to obtain a monodisperse fog with $\overline{r}$ = = 0.15–0.68 mm, the stream had to be broken down into fragments with a length equal to the total period of the sinusoid λ. In agreement with Rayleigh's theory, breakdown in this way is favoured when the ratio of λ to the thickness of the stream has the value 4.5 or a multiple of this figure. In this case the volume of the drops formed is directly proportional to the linear velocity of the stream. The capillary may be vibrated extremely simply by directing over it a narrow stream of compressed air[67].

In Mason's laboratory[68] needles with an internal diameter of 0.1 mm and a frequency of vibration equal to 1000 c s^{-1} were used to obtain water drops with $\overline{r}$ = 15 μm.

In the same laboratory use was made of the phenomenon of reflection of water droplets falling on the surface of water at a definite velocity and at a definite angle. When an electric potential is applied to the vibrating needle, the drops which are torn away are charged, and lose some of their mass when reflected from water, the quantity lost being greater, the higher the potential. Thus the drops leaving the water are identical and smaller than the primary drops; moreover, their dimensions can be controlled within certain limits. When the potential is sufficiently high, the drops falling on the water surface are completely absorbed, but by applying an additional pulsating voltage to the needle it is possible to vary at will the frequency of formation of the secondary droplets and the distance between them, and this is very convenient in certain studies [69].

In the work cited transverse vibrations of the capillary were used; analogous results are obtained with longitudinal vibrations. If pressure pulsations are applied to a liquid in a vessel with a narrow side-tube, large drops with a high degree of monodispersity are ejected from the tube [66], and in this case, unlike the case of the vibrating-capillary generators, no satellite droplets are formed. Drops with $\overline{r}$ = 1–4 mm were prepared in this way; with increase in $\overline{r}$, α decreased from 0.005 to 0.002.

A similar method is based on the following principle. When a point is rapidly immersed in a liquid and then removed, a connection is formed between the point and the liquid surface and is drawn into a fine thread. This thread breaks away first from the liquid and then from the point, and forms a drop which flies in the direction of movement of the point. This process is repeated periodically by using a vibrating point. The size of the drops is determined by the nature of the liquid, the shape and dimensions of the point, the frequency and amplitude of the vibrations, the wettability of the point, and, more particularly, the depth of its immersion in the liquid. It is extremely convenient to work with a liquid which flows slowly from a capillary. In this case the depth of immersion of the point and the dimensions of the droplets generated increase with increase in the dimensions of the drop hanging from the capillary. As a result, the rates of flow and atomisation (ml s^{-1}) are equalised automatically and the dimensions of the droplets are determined only by the flow rate. Drops with $\overline{r}$ = 25–200 μm can be obtained in this way, at 100 vibrations s^{-1}. [70,71]

In Wolf's experiments [72] the point (a rod with a diameter of 10–50 μm) was immersed not in a hanging drop but in the meniscus of a liquid filling a horizontal slit cut in a piece of porous glass, through which the liquid was passed. At a frequency of 120 c s^{-1}, drops of water and aqueous solutions with $\overline{r}$ = 5–100 μm, and drops of molten wax and paraffin with $\overline{r}$ = 2–20 μm, were obtained. In the latter case the rod was immersed vertically in the free surface of a melt, held accurately at a constant level.

The vibrating rod may be replaced by a 3 mm broad, 0.5 mm thick plate with a tapered end, cut from a safety razor blade and rotating at 10–20 rev s^{-1}. [73] Drops with $\overline{r}$ = 40–350 μm were obtained in this way from aqueous solutions and Diesel fuel flowing from a capillary. To obtain monodisperse drops, it is important that the capillary and blade be effectively wet by the liquid. In contrast to the work with a vibrating point, where the monodispersity was estimated visually from photomicrographs of the droplets, the work cited gave numerical data: α = 0.012–0.22 for $\overline{r}$ = 50–60 μm.

The electrostatic atomisation of liquids, now used for painting manufactured articles, depends on the repulsion forces between the electric charges on the liquid surface. These forces decrease the surface tension of the liquid, and when they are sufficiently high the surface of the liquid becomes unstable. In small protuberances formed randomly on the surface, the charge density increases, the repulsion forces become greater than the surface tension, and the raised section is drawn out into a thread, rupture of which produces a drop.

In accordance with the foregoing, the immersion of an electrode into a vessel containing a liquid flowing through a capillary, and the application of a voltage of constant sign and increasing magnitude to the electrode lead to a decrease in the surface tension, and the dimensions of the droplets decrease, in accordance with Eqn. (4), while the frequency of their formation increases. In this way it is possible to obtain several hundred drops (accompanied by satellite drops) of identical dimensions per second, with $\overline{r}$ varying from 50 μm to several hundred μm. [74,75]

At a certain critical voltage the nature of the process changes sharply; in addition to a stream of comparatively large drops, a broad beam of highly-dispersed fog giving Tyndall spectra begins to be formed. At the critical voltage, the above-mentioned process of liquid-thread formation evidently begins. It cannot yet be stated with certainty why the threads give a monodisperse fog.

In most work using this method glass apparatus was employed, and it was found that a highly-dispersed fog can be obtained only when the sign of the voltage applied to the electrode is positive and when the conductivity of the liquid lies between 10^{-13} Ω^{-1} cm^{-1} and 10^{-5}–10^{-6} Ω^{-1} cm^{-1}. Distilled water, alcohol, and other polar liquids lie in this range [76]. When the conductivity is very low (non-polar liquids) the charges evidently accumulate too slowly on the liquid surface. When the conductivity is high (electrolyte solutions), atomisation is apparently accompanied by a corona discharge from the regions of the surface with high curvature, and this prevents the formation of threads.

When a metal capillary — a syringe needle connected to a voltage source, with tip polished at right angles [77,78] — is used and an earthed metallic plate is set up parallel to the needle at a short distance from it, the atomisation becomes much easier; fairly highly-dispersed fogs of any liquid, including non-polar liquids and dilute electrolyte solutions, could be obtained, irrespective of the sign of the potential. The dimensions of the droplets decreased with increase in the voltage, and drops with $\overline{r}$ = 1 μm could be obtained.

Unfortunately, there are very few data on the degree of monodispersity of the fogs obtained by means of an electric field: it is known only that in highly-dispersed fogs obtained in this way, Tyndall spectra are observed, and there are no data for larger drops. The drops have high charges, with the same sign as the electrode, and in a number of cases this limits their application.

Mention must be made of some less important methods. When air is bubbled from narrow capillaries through distilled water or sea water, a polydisperse fogs forms from the bursting bubbles, but segregation of the droplets according to size takes place in the ascending current of air and collection of the droplets at a definite height makes it possible to obtain monodisperse drops with $\overline{r}$ = 1–250 μm. [79]

Ultrasonic atomisation appears to give fogs with fairly high polydispersity [80].

2. Preparation of Monodisperse Aerosols by Atomising Suspensions

When non-aggregated monodisperse suspensions in water or other volatile solvent are atomised under conditions where not more than one particle is present in each drop, drying of the resulting fog should obviously produce monodisperse aerosols. This method of generating aerosols was first used by microbiologists, who prepared bacterial aerosols in this way. The atomisation of suspensions acquired practical importance as a method for generating monodisperse aerosols with the introduction of monodisperse polystyrene latexes with accurately spherical particle shape, developed by the Dow company. In these latexes, α is equal to ~ 0.09 at $\overline{r} = 0.044$ μm, ~ 0.04 at $\overline{r} = 0.07$–0.09 μm, 0.015–0.023 at $\overline{r} = 0.13$–0.28 μm, and ~ 0.012 at $\overline{r} = 0.4$–0.6 μm.[81]

The latexes contain $\sim 7\%$ of polymer and before atomisation are diluted extensively with distilled water. The resulting fog is dried by mixing with dry filtered air. In the first experiments on the preparation of monodisperse aerosols with $\overline{r} = 0.17$–0.49 μm by this method it was found that the degree of monodispersity is much lower than that of the latexes themselves[82], and in most cases α varied from 0.11 to 0.16 (the dimensions of the particles were determined with a photoelectric counter). This phenomenon may be due to the presence of more than one particle in the drops, leading to the formation of twins, etc., when the drops are dried, and to the presence of the water-soluble non-volatile emulsifier in the latexes ($\sim 30\%$ of the weight of polymer). Thanks to the emulsifier, the latex particles do not aggregate even on extensive dilution of the suspension, but with complete removal of the emulsifier, coagulation of the suspensions is unavoidable. The probability that the drop contains more than one particle depends on the concentration of the suspension and on the dimensions of the drops and particles. If it is assumed that a concentration of 5% of twins in the aerosol is permissible (in this case the number of triplets, etc. will be negligible), we find from Poisson's formula that, for the mean drop radius of ~ 1 μm attainable in practice by means of special atomisers, the concentration of the suspension should not exceed 1% for a particle radius $\overline{r} = 0.5$ μm, $\sim 0.1\%$ for $\overline{r} = 0.25$ μm, and $\sim 0.01\%$ for $\overline{r} = 0.1$ μm. These conditions have obtained in most work.

The greatest difficulty is due to the presence of emulsifiers in the suspension; we have already seen that its complete elimination is impossible. The emulsifier is apparently extremely hygroscopic, and when the above method is used to dry drops containing polymer particles, a coating of concentrated emulsifier solution is deposited on the particles; when drops containing no particles are evaporated, "blanks" of the same solution are left. Moreover, it follows from Poisson's formula that when the number of twins is low, the number of "blanks" should be much greater than the number of droplets with polymer particles.

This was observed particularly clearly in work by Langer and Lieberman[83]. In the atomisation of a suspension prepared by tenfold dilution of a latex with $\overline{r} = 0.407$ μm, into a chamber containing air with a moisture content of 4%, study of the resulting aerosol by means of a photoelectric counter showed that the concentration of particles was 25 times the calculated value, because of the presence of the "blanks". The radius of the "blanks" varied from the limit of sensitivity of the counter ($\overline{r} \simeq 0.25$ μm) to 1.5 μm, the mean radius of the aerosol particles was 0.7 μm, and the value of α was 0.39.

When the fog was heated to 165°, the number of particles recorded by the counter decreased by a factor of 10–100; the radius of most of the completely dried "blanks" was evidently less than 0.25 μm and was not recorded by the counter. The maximum particle radius decreased to approximately 0.5 μm, approaching the true radius of the polymeric granules. An analogous effect was observed for hundredfold dilution of the latex: in the aerosol dried at room temperature, $\overline{r}$ decreased to 0.55 μm and α to 0.22; the number of "blanks" recorded decreased considerably, because of their smaller size.

It must be emphasised that in the microscopic measurement of the particles the emulsifier solution, which effectively wets the support, flows over the latter in a very thin film and cannot be seen. Thus the authors who studied these aerosols only by the microscope method concluded that the aerosols had a high monodispersity[84,85]. However, the presence of a large number of "blanks" could also be detected under the microscope in the deposit from an aerosol with $\overline{r} = 0.407$ μm, obtained in an electrostatic sorter, in which the particle dimensions are determined from their position in the deposit[86]. In other work[87] with an aerosol prepared from the same latex and deposited in a centrifugal sorter (conifuge) in which the particle dimensions are determined in analogous fashion, the value found for $\overline{r}$ corresponded to the dimensions of the particles in the latex, and the influence of the emulsifier was revealed only in the increase in the value of α from ~ 0.012 to 0.11. In the second case the degree of dilution was probably greater and the drop dimensions smaller, than in the first case.

Aerosols have also been prepared by atomising extremely highly monodisperse AgI suspensions[88]. Since coagulation took place during purification of the suspensions from the salts present, the monodispersity of the aerosols was probably low.

A monodisperse aerosol with very fine particles was prepared by atomising suspensions, thoroughly freed from all impurities, of *E. coli* bacteriophage T3 with $\overline{r} = 17.5$ mμ and $\alpha = 0.07$. Electron-microscope study of the suspension and the aerosol prepared from it showed that the particle distribution with respect to dimensions was the same in each[89].

3. Preparation of Monodisperse Aerosols by Atomising Powders

The chief disadvantage of the above method for generating monodisperse aerosols, associated with the presence of dissolved substances in the suspensions, is obviously eliminated in the atomisation of dry monodisperse powders, but in this case other difficulties arise. Powders with $\overline{r} > 5$ μm are comparatively readily atomised by compressed air, with the formation of aerosols containing completely disaggregated particles, but with decrease in the particle size the atomisation becomes more difficult and for powders with $\overline{r} < 0.5$ μm, complete atomisation has not yet been achieved. Important factors, in addition to particle size, are the shape, elastic properties, and moisture content of the particles. Lamellar or acicular particles are more difficult to atomise than spherical particles. Powders of hard materials are more readily atomised than those from soft materials. Increase in the moisture content of the particles leads to a sharp decrease in the ease of atomisation, but powders which have been

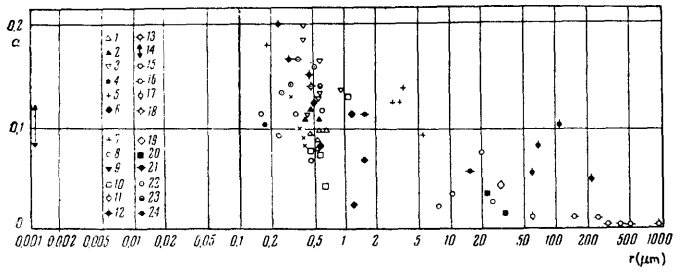


Fig. 6. Characteristics of monodisperse aerosols prepared by different methods, from published data.
Condensation method: aerosols from:
1) dioctyl phthalate[46]; 2) dioctyl phthalate[120]; 3) dioctyl phthalate[10,11]; 4) dioctyl phthalate[138]; 5) dioctyl phthalate[119]; 6) dibutyl phthalate[49]; 7) glycerol[125]; 8) tetralin[33]; 9) stearic acid[36]; 10) stearic acid[143]; 11) linolenic acid[39]; 12) linoleric acid[19]; 13) sodium chloride[45]; 14) sodium chloride[41]; 15) cadmium[36].
Atomisation of liquids:
16) blow capillary, water[56]; 17) rotating blade, mineral oil[73]; 18) pulsating pressure, water[66]; 19) rotating disc, water[126]; 20) dibutyl phthalate[60]; 21) electrostatic atomisation, butyl benzoate[78].
Atomisation of suspensions:
22) latex[82]; 23) spores of *B. globulis*[144].
Atomisation of powders:
24) lycopodium[105].

over-dried are also difficult to atomise, because of the high triboelectric charges.

Elutriation under the influence of gravity or in a centrifuge can be used to obtain powders with any degree of monodispersity, but the method is time-consuming. The well-fractionated glass powders consisting of spherical particles, supplied by some Non-Soviet firms, are very convenient. Powders with extremely high monodispersity are also found in nature. Thus in lycoperdon spores $\bar{r}$ = = 2.09 μm and α = 0.08;[90] in maize-rust spores $\bar{r}$ = 3.9 μm and α = 0.038;[91] and in clover pollen $\bar{r}$ = 26 μm and α = = 0.04.[92] Because of its availability, lycopodium spores with $\bar{r}$ = 15 μm and α = 0.10 have been most widely used[93].

In concluding this section we would point out that in all aerosols obtained by dispersion methods, with the exception of fogs formed by non-polar liquids, the particles have fairly high charges of either sign. In some studies this property is extremely undesirable.

Fig. 6 gives data on the particle size and degree of monodispersity of aerosols obtained by condensation and dispersion methods.

IV. APPLICATIONS OF MONODISPERSE AEROSOLS

The titles of most papers describing the use of monodisperse aerosols for different purposes do not mention the application. In many cases the application is mentioned only in a few lines in the text of a paper. Moreover, monodisperse aerosols are used in the solution of an extremely varied range of problems, and the appropriate papers may be found in specialised journals of the widest range. All this makes a search of the literature on this subject extremely difficult, and cannot but be reflected in the completeness with which it is covered in a review.

Monodisperse aerosols have been used in the study of various optical properties of aerosols (condensation aerosols[24,31,39,94-96] prepared from latexes[85,97] or lycopodium[98]); the absorption of sound in aerosols (lycoperdon[99]); the vibrations of particles in a sonic field (condensation[100]); deposition of aerosols on obstacles from a stream (condensation[101-103], latex[104], and lycopodium[105]), on the walls of tubes from a turbulent stream (lycopodium[106]), in impactors (condensation[101], lycopodium[107], and latex[142]), in thermal precipitators (condensation[108], disc atomiser[109]), in electrostatic precipitators (latex[84]), and in breathing apparatus (condensation[110], atomisation of bacterial suspensions[111]); methods for sampling aerosols (condensation[112], fractionated powders[113]); diffusion deposition during flow in narrow channels (condensation[114]); sedimentation and diffusion in a cell (condensation[115]); filtration of aerosols through fibrous filters (condensation[24,31,115-122], latex[123], bacterial and virus suspensions[124,144]) and granular filters (condensation[121]); the efficiency of collisions between drops and solid walls (condensation[125], vibration atomiser[70]), liquid surfaces, and one another (vibration[64,65] and disc[126] atomisers); the charges of particles in condensation aerosols during their formation[127] and during charging by an ion beam[119,128]; the elution of aerosols by rain (lycopodium[129]); the dependence of the efficiency of insecticides and herbicides on drop dimensions (condensation[32], disc atomiser[130,131]); the supercooling of droplets[132] and their vapour pressure (condensation[38]); the ice-forming power of AgI particles (atomisation of a suspension[88]); the movement of coarse dust in tubes (glass spheres[133]); the activation of aerosols by radioactive gases (condensation[134], latex[134]); the chemical reaction of aerosols with gases (condensation[44]); and the lubrication of ball bearings with oil fogs (disc atomiser[135]). They have also been used to verify Stokes' law (lycoperdon[90]) and Kelvin's law (condensation[22,23]), to prepare monodisperse emulsions (condensation[136], electrostatic atomisation[78]); for the calibration of instruments used for the dispersion analysis of aerosols — photometers (latex[137]), photographic[138], photoelectric (condensation[139]), and thermoelectric (vibration atomiser[67]) counters (sorters), and electrostatic (condensation[128]) and centrifugal (condensation[140], latex[87,141]) sorters.

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THE PRESENT STATE OF THE ANALYTICAL CHEMISTRY OF TECHNETIUM

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I. INTRODUCTION

Interesting properties of technetium have been discovered in recent years. Unlike its nearest analogue, the perrhenate ion, the pertechnate ion exhibits exceptional anti-corrosion properties[1], greatly superior to those of CrO_4^{2-} ions. For example, iron which has been immersed in ammonium pertechnate solution with a technetium concentration of only 5 $\mu g\ ml^{-1}$ undergoes no rusting over a period of several years. This reveals promising possible applications of technetium compounds as effective inhibitors of the corrosion of iron and steel. These compounds may prove particularly useful for preventing the corrosion of homogeneous boiling reactors[2], certain submarine parts, etc.

Metallic technetium and its alloys (for example an alloy containing 50% Tc and 50% Mo) are superconductors at low temperature[3,4] and can be used to replace super-purity niobium in inertial control systems in rocket technology[2], as memory elements in electronic machines[5,6], and in thermonuclear-synthesis assemblies for the production of magnetic fields of high intensity[6]. Many fundamental properties of this element have not been studied, since large quantities are not available. When larger quantities are produced, new properties of technetium and extensive possibilities for its use in industry may be revealed.

Thus the problems of preparing large (kilogramme) quantities of technetium and separating it from the neighbouring elements rhenium, molybdenum, and ruthenium are now of pressing importance. It is therefore of interest to examine the latest achievements in the analytical chemistry of technetium, since recent reviews on the chemistry of technetium[6-12] devote little space to this topic, and there are no special reviews on the subject.

II. METHODS OF ISOLATING AND CONCENTRATING TECHNETIUM

A large number of technetium isotopes with mass numbers from 92 to 107 and half-lives from several seconds to 2×10^6 years are now known. The most important isotopes of technetium, their radioactive characteristics, and methods of preparation are given in Table 1.[13]

Four of the isotopes given in Table 1: ^{95m}Tc, ^{96}Tc, ^{97m}Tc, and ^{99m}Tc, are used as tracer atoms in the study of the chemical properties of technetium. The most readily available for this purpose is the nuclear isomer ^{99m}Tc, which is formed with high specific activity from molybdenum irradiated with neutrons. The other three isotopes: ^{97}Tc, ^{98}Tc, and ^{99}Tc are long-lived, with half-lives $>10^5$ years, and can be used for the study of the chemistry of technetium in ponderable quantities. The last of these isotopes is the most readily available, since it is formed by the fission of uranium and plutonium nuclei or by the prolonged irradiation of molybdenum in a reactor.

TABLE 1. Most important isotopes of technetium.

Isotope	Half-life	Decay type	Energy of radiation, MeV		Method of preparation
^{95m}Tc	60 days	e.c. ~96% i.t. ~3% β^+ ~0.4%	β^+ γ	0.4 0.201	$^{95}Mo(p,n)^{95m}Tc$
^{96}Tc	4.2 days	e.c	γ	0.77–0.84	$^{96}Mo(p,n)^{96}Tc$
^{97m}Tc	91 days	i.t.	γ	0.096	$^{97}Mo(p,n)^{97m}Tc$
^{97}Tc	2.6×10^6 years	e.c.	γ		$^{97}Mo(d,2n)^{97}Tc$ $^{97m}Tc \rightarrow {}^{97}Tc$
^{98}Tc	1.5×10^6 years	β^-	β^- γ	0.30 0.66; 0.75	$^{98}Mo(p,n)^{98}Tc$
^{99m}Tc	6.04 h	i.t.	γ	0.14	$^{98}Mo(n,\gamma)^{99}Mo \xrightarrow{\beta} {}^{99m}Tc$
^{99}Tc	2.12×10^5 years	β^-, no γ	β^-	0.296	fission products from uranium and plutonium; daughter ^{99m}Tc