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THE MAGNIFICATION FACTOR FOR SODIUM CHLORIDE LIESEGANG CIRCLES ESTABLISHED WITH AN AEROSOL CENTRIFUGE

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Abstract—Sodium chloride particles deposited on a gelatin film containing silver nitrate form in a humid environment clearly visible dark brown reaction spots (Liesegang circles) after development in u.v.-light. The size of these reaction spots depends on the mass of NaCl in the particles. To establish the spot size vs particle size relation, particles produced by nebulising NaCl-solutions and sea water were sampled in an aerosol centrifuge. The location of deposition yields the aerodynamic diameter of the particle and the spot size is measured microscopically. In this way the spot size vs aerodynamic diameter relation is established experimentally in the so far unexplored aerodynamic diameter range between 0.5 and 2.0 μm .

INTRODUCTION

Giant sea salt nuclei (i.e. particulates between the sizes of 1 and 10 μm) are of great importance in the formation of clouds and fogs in maritime regions. These NaCl-nuclei, being the most active and in great abundance, are the most investigated despite the recently stressed importance of sulfate nuclei above the ocean (Hobbs, 1971; Georgii and Gravenhorst, 1972).

Different techniques have been developed over the last two decades for the measurements of concentration and size distribution of NaCl-nuclei. Spot test methods, developed by Liesegang in 1896, have been successfully used in atmospheric chemistry by Seely (1952, 1955), Fedele and Vittori (1953) Vittori (1954) and by Rau (1956). Several researchers (e.g. Lodge and Tufts, 1956) have shown that spot test techniques can yield quantitative and reproducible results despite the complex nature of nuclei and the great variability of chemical reactions in the atmosphere.

One of the simplest and most suitable methods for field measurements is the gelatin technique. It is based on the capturing of salt particles on a glass slide covered with a sensitized gelatin film, inserted into a cascade impactor. The precipitate diffuses into the gelatin and produces a circular spot around the original salt particle. This ring (usually brown) can then be measured under a microscope. It has a larger diameter than the particle itself and the main task of many investigations was to determine experimentally the ratio of the size of the circular spot (Liesegang circle) to that of the particle. This ratio was found to vary between 4 and 9, depending on the nature of the particle and the preparation of the gelatin (Vittori, 1955; Rau, 1956, Metnieks, 1958; Podzimek, 1959).

Several methods have been used to determine the magnification factor. The "isopiestic" method described by Woodcock and Gifford (1949), and applied later by Metnieks (1958), Toba (1966), and others, is based on the sampling of NaCl-aerosol on slides. One half of each slide is coated with a gelatin sensitized in AgNO_3 solution while the other half is left uncoated. Placing the slides in a box with a transparent lid and with controlled humidity, one can compare under a microscope the size of the Liesegang circles with the size of particles which are dissolved at a certain relative humidity.

Another method frequently applied by investigators (e.g. Rau, 1956; Podzimek, 1959) uses the sedimentation rate of particles in a tube for determining their sizes which are then compared with the sizes of the spots left by the same particles in the sensitized

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gelatin layer. Both methods have basic weaknesses. There is a difficulty in defining the point of transition between a solid and a liquid particle in the sedimentation method. Also when this method is employed, it is hard to maintain thermal stability and controlled humidity which are both essential for accurate measurements. On the other hand, the actual size of the deposited particle in the "isopiestic" method is crucial to obtain accurate ratios. There is very little data on magnification factors for particle sizes of less than $1\ \mu\text{m}$ and, in general, the spread of values around the true particle dia. of $1\ \mu\text{m}$ was very high.

Also, besides these reasons, it seemed to be useful to have magnification factors related to the aerodynamic diameter of particles (i.e. the diameter of a sphere of density $1.0\ \text{g cm}^{-3}$ which has the same sedimentation velocity as the particle in question). This paper presents an attempt to examine the magnification factor of NaCl-particles comparing the sizes of their Liesegang circles with their aerodynamic sizes measured in a centrifuge.

Preparation of sensitized gelatin sheets

The sensitized gelatin sheets were widely used to detect aerosols particularly after 1954 due to Fedele and Vittori (1953) and later Rau (1956) who also described the preparation of the layers. The NaCl-particles were usually deposited on a gelatin film, which contained AgNO_3 . By diffusion of the ions in the gelatin and by photo-chemical reaction a AgCl-Liesegang circle is formed, with a dark brownish-red color. If the mass of the dry NaCl-nucleus is greater than 10^{-12}g the circular spot may be easily seen using an optical microscope. However, if its mass is less than this it is usually impossible to see. By adding some materials to the gelatin film, Vittori (1954) was able to increase the sensitivity of the method to particles of 10^{-15}g .

In spite of some objections to the use of AgNO_3 in preparing the layers sensitized for chloride particulates (Durbin, 1959), most of the experimenters used it in preparation on microscope slides (with a 5–10% gelatin solution). Some time before exposing the slides they are dipped in a 5% AgNO_3 solution and dried before inserting them into a cascade impactor. The foils (such as used in a xerox machine for making transparencies) were prepared in a similar way. However, sometimes in this experiment the foil surface was not entirely covered with an homogeneous sheet of gelatin. Because the investigation under the optical microscope showed that the gelatin layers were thicker than $5.0\ \mu\text{m}$, and because none of the radii of the Liesegang circles exceeded this thickness during the calibration, no corrections for the limited thickness of the gelatin layer were applied on the spot diameter conversion. The experience gained during the studies to be described differ on this point from the results of the NaCl-aerosol detection by Ueno and Sano (1971). They applied much thinner layers of polyvinyl alcohol (0.32–0.37 μm). Due to this major difference (in layer composition and thickness) the ratio between the spot diameter and dry salt particle and the semi-empirical formula describing the dependence of the magnification factor on the size of the chloride particle in this paper and in Ueno's study cannot be compared.

The chemicals used in preparing the 5% AgNO_3 solution in which the foils (with gelatin layer) were dipped for 20 sec were: AgNO_3 with chloride content less than 0.0005% and the granular gelatin prepared by hot filtering of a 8% solution. Because of the photosensitivity of the sensitized gelatin foils, they were stored in darkness until being exposed in the Aerosol Centrifuge.

The experiments with the aerosol centrifuge

The Aerosol Centrifuge (AC) is described in detail elsewhere (Berner and Reichelt, 1969; Abed *et al.*, 1976). Its operating principle is the following: air is sucked through a system of slits and channels in a rotating centrifuge head (Fig. 1) and cleaned of all particles. Finally a clean air stream is established in a vertical cylindrical gap. The outer wall is lined on its inside with a removable foil. A narrow horizontal slit in the inner cylinder is supplied with the aerosol to be investigated at the axis of rotation.

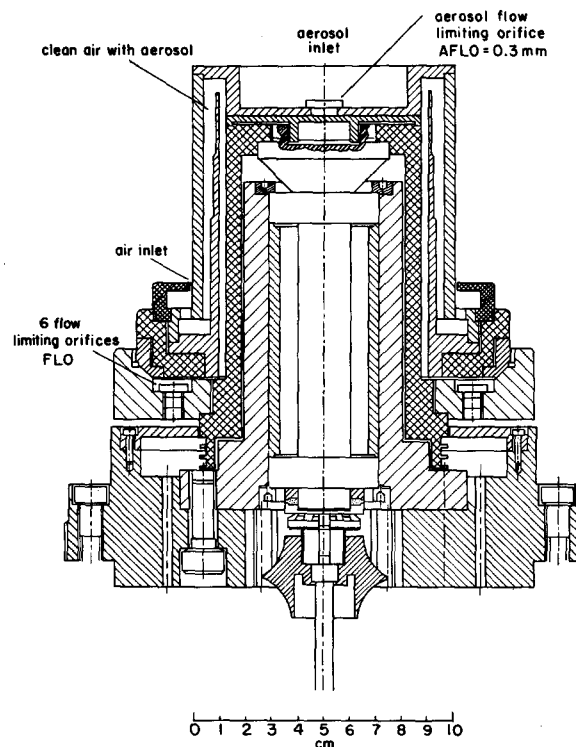


Fig. 1. Head of the aerosol centrifuge, cross section.

The aerosol flows outward under the action of the centrifugal force and finally meets at a right angle the clean air stream upon which it is superimposed as a thin sheet. The particulates are carried downstream with the clean air stream as they migrate under the action of centrifugal force to the outer wall and are finally deposited on the removable foil cover. All particles enter at the same vertical position and are carried downstream with the same velocity. However, their drift velocity to the outer wall differs according to their aerodynamic diameter. Hence the time taken for downstream motion depends on the aerodynamic diameter and the location of deposition (deposition length L) is a measure of it.

The resolution of the centrifuge is high as particles which differ in their aerodynamic diameters by as little as 1% will be deposited at different locations. If a monodispersed aerosol is fed to the centrifuge all its particles are deposited at practically the same distance from the entrance slit. If the foil is taken out and developed on a plate, the deposits of monodispersed aerosols appear as straight lines across the rectangular foil parallel to its longer side. The line is a direct image of the entrance slit: its width depends on the entrance slit width, the monodispersity of the aerosol used, and on the instrument performance. A measure of the line width is the standard deviation of the area concentration of particles vs deposition length curve. The influence of the entrance slit width and the instrument performance on this standard deviation is so small that it only needs consideration if the monodispersities of spray dried latex aerosols are investigated. The calibration curve for latex particles is shown in Fig. 2. The aerodynamic diameter of the spray dried latex particles of the calibrating aerosol were calculated assuming a density of 1.05 g cm^{-3} .

The assessment of the magnification factor

Sodium chloride aerosols were produced by drying the spray of sea water (surface samples from the Gulf of Mexico near the shore of Padre Island) and of NaCl-solution (6 and 1% by weight). Nebulization was done in a De Vilbiss 40 glass nebulizer with the dilution hole plugged. The flow rate through the nebulizer was kept at 5.0 l/min and the gas containing aerosol was mixed in a turbulent flow with 10 l/min clean

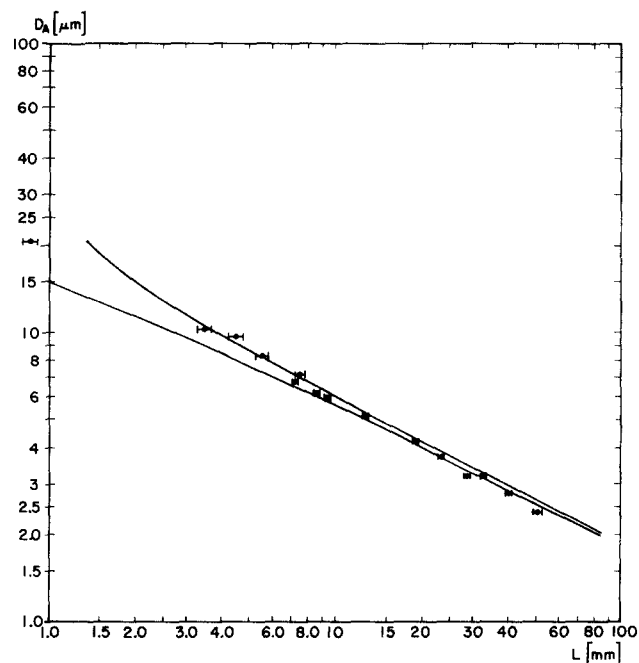


Fig. 2. Calibration curve. AC operating conditions 4000 rpm, 6 flow limiting orifices, dia., 1.02 mm.

dry dilution gas. The gas used for dilution was filtered nitrogen. Then the diluted aerosol was fed into a cylindrical mixing chamber (a glass tube of i.d. 9.0 cm and length 71.0 cm mounted horizontally) through an end plate. After passing through the mixing chamber the aerosol was drawn via an open "T" to the Aerosol Centrifuge (AC) inlet tube. The use of an open "T" tube insured that the excess aerosol would leave the "T" and that the atmospheric pressure was maintained at the entrance tube of the AC. This was an absolute necessity to ensure sampling under controlled conditions in the AC. The foil used in the AC was a gelatin covered plastic sheet such as used in an overhead projector (Xerox 3R 163) cut to fit in the AC. The gelatin was sensitized by AgNO_3 using the procedure which has been described in the previous paragraphs.

The centrifuge was run for 30 min at operating conditions as indicated and NaCl particles were collected on the sensitized foil. After this was accomplished, dried latex aerosol of known size was deposited in the AC on the same foil (Fig. 3). Then the foil was taken out and several strips of approx. 7 mm width were cut for evaluation under a microscope. The strips were mounted on a standard microscope slide and placed in a plastic box above a water surface for several hours. Then the samples were "developed" using u.v.-light for approx. 10 min at a distance of 2 cm.* Evaluation was done in the Zeiss standard RA Research microscope with Epiplan HD $80 \times$ n.a. 0.95 and with the eyepiece C8X, equipped with a semi-automatic 35 mm camera. The spot sizes were compared with a Zeiss object micrometer (with mark distances of 10 μm) and the final evaluation was made either while projecting the film on a screen or on the enlarged photographic prints. The measured distances of deposited particles (their halos) from the foil edge, the deposition length, gives the aerodynamic diameter of the particle corresponding the Liesegang circle (Fig. 4).

There are two different types of errors while evaluating the samples and calculating the magnification factor: (1) The error in defining the aerodynamic diameter (2) The error in measuring the size of the Liesegang circle.

The aerodynamic dia. (D_A) was derived from a length measurement on the microscope stage micrometer. The error of the length measurements is approx. ± 0.1 mm, however, the positioning of the foil is good for only ± 0.5 mm. This error has a different influence for different deposition lengths and limits the largest particle size analyzed to about

* From the lamp (Penray[®] quartz lamp, Ultra Violet Products, San Gabriel).

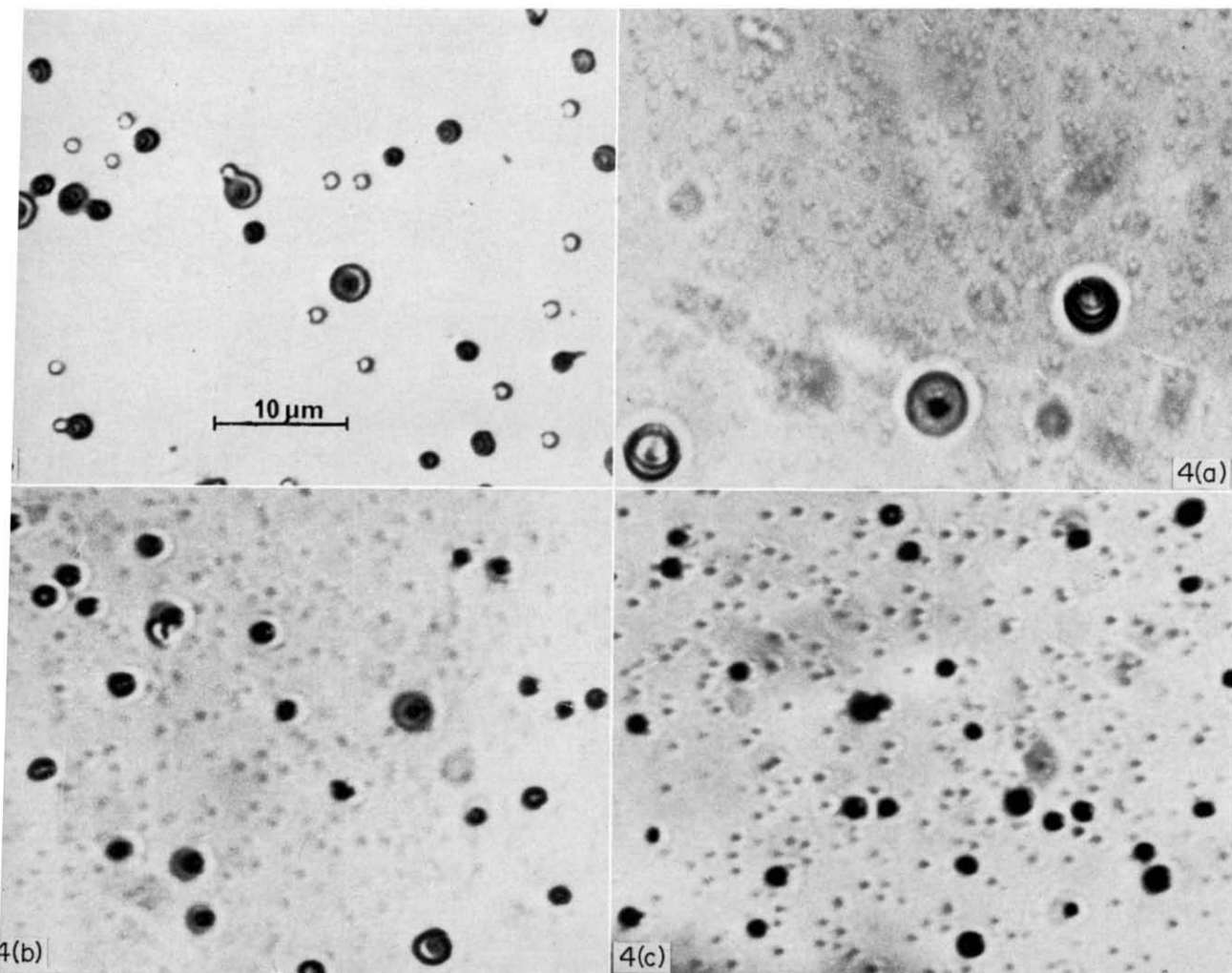


Fig. 3. Photograph of the deposited latex-particles among the Liesegang circles of NaCl particles. 2400 × magn.

Fig. 4. Sequence of pictures showing the dependence of spot size change on the distance from the edge of the foil (a) at a distance of 6.4 mm from the edge; (b) 7.1 mm; (c) 7.6 mm; (d) 9.6 mm, (e) 11.6 mm; (f) 15.6 mm. 2400 × magn.

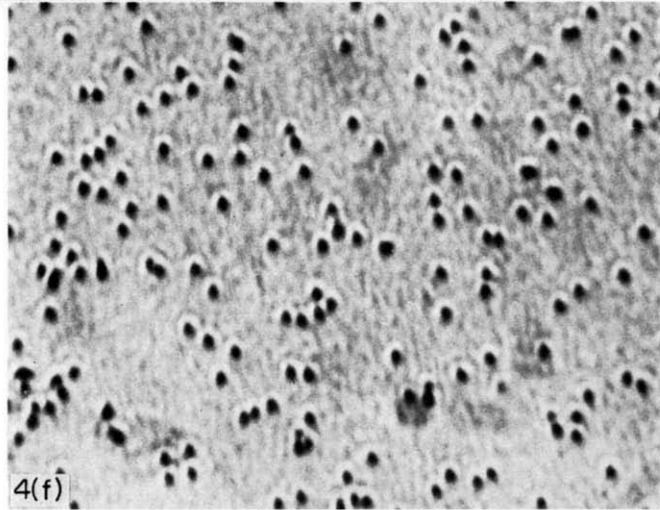
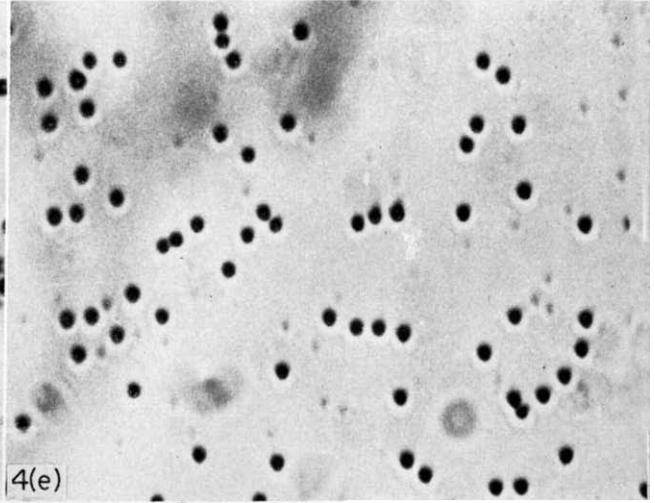
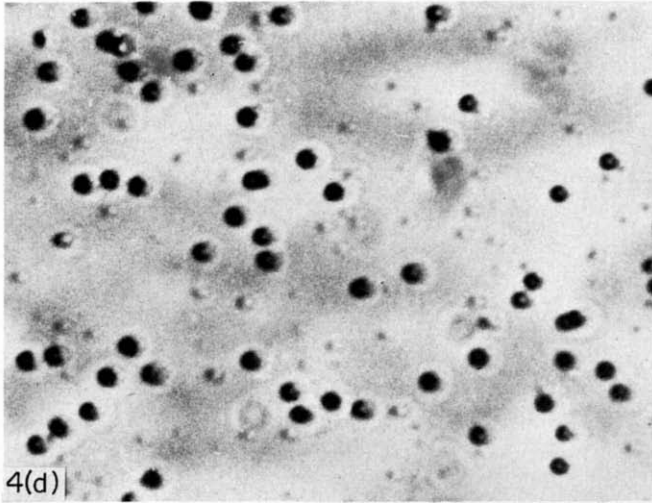


Fig. 4. (d-f).

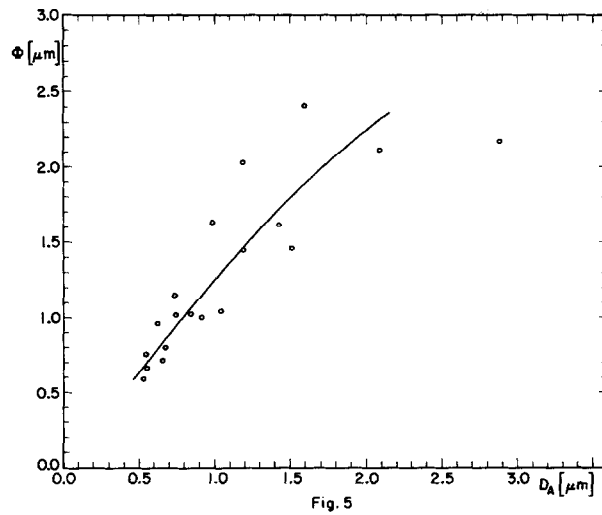


Fig. 5. Spot size vs aerodynamic diameter [$\phi = f(D_A)$] for particles produced by spray-drying NaCl solution, 1% by weight.

2 μm aerodynamic dia. corresponding to a deposition length of 0.85 mm. At this length, however, particles were found with diameters between 1.4 and 3.2 μm , which corresponds to a rather large uncertainty of $\Delta D = 1.8 \mu\text{m}$ in defining the aerodynamic dia. Fortunately ΔD narrows already to 0.05 μm for the particle dia. of 0.5 μm .

Particles of identical size will be deposited in the AC not at one deposition length but in a narrow band of finite width. This also contributes to some uncertainties in the value of aerodynamic diameter. The estimated limits of uncertainties (\pm S.D.) are plotted in Fig. 2 together with the errors caused by inaccurate foil positioning.

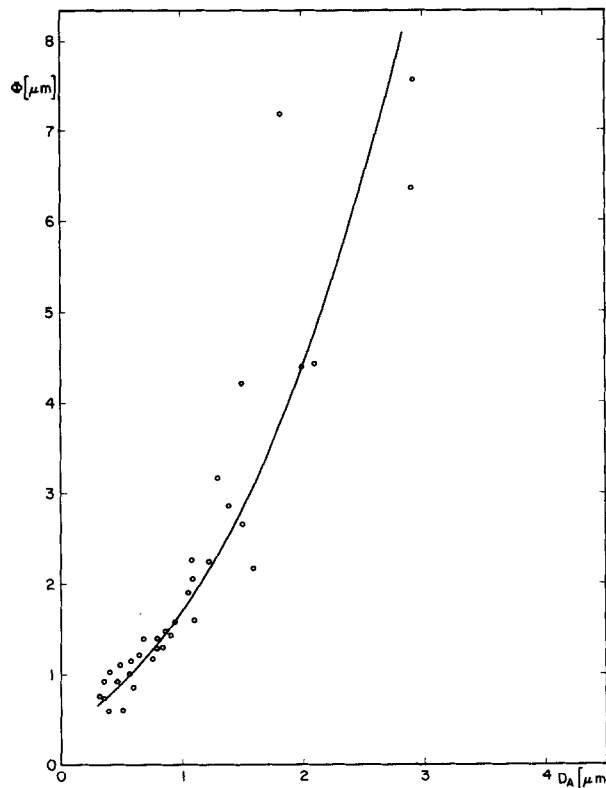


Fig. 6. Spot size vs aerodynamic diameter for particles produced by spray-drying NaCl solution, 6% by weight.

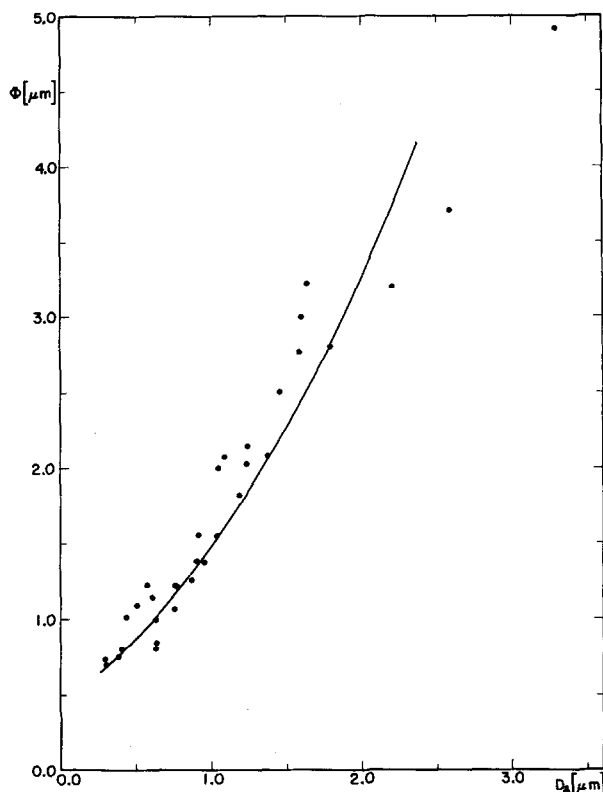


Fig. 7. Spot size vs aerodynamic dia. for particles produced by spray-drying sea water.

The error in measuring the spot size is determined by the error in magnification and by the optical image of the spots on the gelatin sheet. For spot diameters below $1\ \mu\text{m}$ the image is often distorted by light diffraction and focusing of the microscope becomes a tedious task, especially when the foil is covered by an uneven coat of gelatin. This makes even estimates of the spot sizes below $0.5\ \mu\text{m}$ impossible. The diffraction might be the cause of bending of the curve ϕ (spot size) = $f(D_A)$ around $\phi = 0.6\ \mu\text{m}$ (Figs. 5–7). A rough idea can be obtained about the accuracy of the spot evaluation by calculating the standard deviation of the spot sizes evaluated from one frame (corresponding to a certain location on the foil strip, the variation of the deposition length across the frame is only $0.12\ \text{mm}$) as given in Table 1.

These calculated standard deviations cannot be used for smaller than $1.0\ \mu\text{m}$; however, they might be representative for the salt nuclei samples.

Results of the magnification factor measurement

The magnification factor was established for NaCl nuclei generated in the way described in the previous paragraph. The curves $\phi = f(D_A)$ are plotted for the 1 and 6% NaCl- solution in Figs. 5 and 6 and for sea water in Fig. 7. Disregarding large dispersion of points for nuclei larger than $2.0\ \mu\text{m}$ and smaller than $0.5\ \mu\text{m}$ we can deduce some general conclusions from the diagrams.

There is a considerable difference between the very small concentrations of NaCl in water (1%) and the concentration in sea water. There is apparently no substantial difference between sea water (approx. 3.0%) and the NaCl solution of 6%.

The linearity of the functional relationship $\phi = f(D_A)$ seems to be maintained between the particle sizes 0.6 and $1.8\ \mu\text{m}$ for 1% solution. However, for higher salt concentrations the curves are bent upwards indicating an increased magnification factor for larger particulates.

Table 1

Mean distance from the edge (mm)	Total number of particles	Mean spot size (μm)	S.D. (μm)	Relative S.D. (%)
7.7	43	2.03	0.157	7.70
8.2	61	1.82	0.207	11.3

The value of the magnification factor for 1% solution is very close to 1.25 and for 6% solution varies between 1.6 and 2.8. For sea water the magnification factor is 1.6 for particles with $D_A = 0.6 \mu\text{m}$ and 1.7 for particles with $D_A = 2.0 \mu\text{m}$.

One can conclude from the data plotted from different runs (Figs. 6 and 7) that the reproducibility of the experiments is reasonably good.

CONCLUSION

The application of the aerosol centrifuge enabled one to relate the magnification factor of NaCl aerosol to the aerodynamic diameter which is, e.g. more convenient for the sampling techniques used for sea salt aerosol. Also, it was possible to extend the calibration to the small sizes of nuclei ($D_A < 0.6 \mu\text{m}$) which are generated by bubble bursting above the ocean surface. However, the accuracy of the measured magnification factors for the smallest NaCl-particles is limited by the difficulties in imaging the particle in an optical microscope. On the other hand, the method which has been described, is not suitable for particles larger than $D_A = 2.0 \mu\text{m}$.

At a given concentration of gelatin and AgNO_3 the magnification factor for NaCl-Liesegang circles is a function of NaCl concentration and size of particles. For very low concentrations of NaCl (1% by weight), much larger dispersion of measured points was found than in the 6% solution or the salt concentration corresponding to sea water. For a 1% solution the magnification factor was close to 1.25 and for a 6% solution it varied between 1.6 and 2.8. Chlorides from sea water yielded magnification factors between 1.6 and 1.7. However, due to the uncertainty in defining the factor for larger particles the latter value could be higher. The values of the magnification factors are lower than the factors previously used by several investigators (Rau, 1956; Metnieks, 1958; Podzimek, 1959) which varied between 4 and 9, and are much closer to the value established by Ueno and Sano (1971) for approximately the same concentration on AgNO_3 and by Durbin (1959).

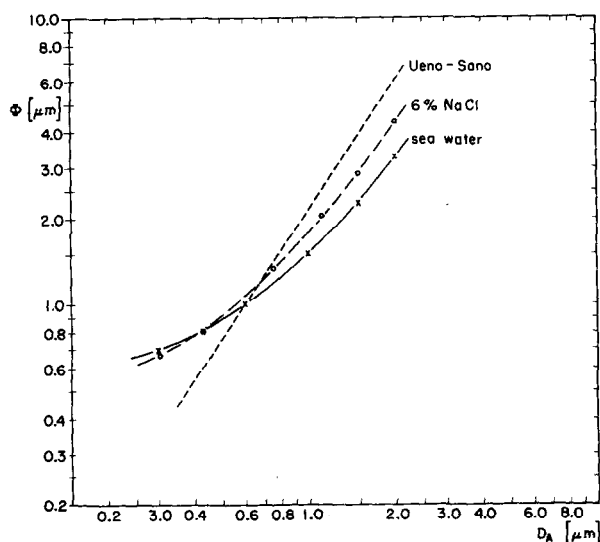


Fig. 8. Comparison of the relationships $\phi = f(D_A)$ for 6% NaCl solution and for sea water with Ueno and Sano's relation $D^3 = K\phi^2$.

The measured functional relationship between the spot size and aerodynamic diameter deviates from Ueno's relation $D^3 = K\phi^2$ (where D is the volume average diameter and K is a constant, Fig. 8). However, one has to consider that the former calibrations were made with relatively large particles for which the magnification factors become larger than those for smaller ones. Also, there is still an open question how the environmental humidity and its changes inside of the aerosol centrifuge might affect the calibration. The preliminary results show that the humidity changes do not strongly influence the size of spots, unless the relative humidity is far below the critical point for the dissolution of NaCl-crystals.

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