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Paul C. Yue

Josef Podzimek

Missouri University of Science and Technology

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Potential Use of Chemical Spot Test Method for Submicron Aerosol Sizing

Paul C. Yue* and Josef Podzimek

Graduate Center for Cloud Physics Research, University of Missouri-Rolla, Rolla, Missouri 65401

A submicron particle, which is too small to be observed in an optical microscope, may form an observable spot on a chemically prepared substrate of the collector. The size of the spot or "Liesegang circle" is related to the aerodynamic diameter of the particle through a magnification factor. This paper presents the experimental results of the study of this factor using sodium chloride aerosol in the size range of 0.5 to 2 μm which has not previously been studied. We calibrated a cylindrical centrifuge with known sized latex particles. A relationship between the aerodynamic diameter and the deposition length is established. From this calibration one can obtain the aerodynamic diameter of particles of the same geometrical size but of different densities. This provides the needed parameter for calculating the magnification factor.

Introduction

For identifying chloride particles in the atmosphere several investigators used the specific reaction of chloride ions with silver nitrate or mercurous fluorosilicate contained in a gelatin layer since the early fifties (e.g., Seely, 1952; Pidgeon, 1954). The diffusing outer ions (from deposited particles) react with the inner ions (in the sensitized gelatin layer) and form a circular spot of water-insoluble silver chloride (or other precipitate) which, after being exposed to short-wave radiation (ultraviolet), has a brown-reddish color. Similar techniques were suggested later for identifying sulfate, nitrate, ammonium, and other ions contained in atmospheric particulates. The spots were evaluated with an optical microscope, and useful information about particle nature, concentration, and size distribution has been obtained.

Since the time of the first observation of this phenomenon by Liesegang in 1896, several theories have been forwarded to explain the periodic precipitation ring formation such as the supersaturation theory by Wilhelm Ostwald, adsorption theory by Bradford, coagulation theory by Dhar, and diffusion theory by Wolfgang Ostwald. Attempts have been made to describe the precipitation ring formation by wave mechanical models. A useful survey on the older investigations of the periodic precipitation was published by Stern (1954). Reviewing all theories, one observes that each theory has its strong point. However, none of the laboratory experimental studies has assigned a universal validity to any specific theory (e.g., Lurie, 1966). Common to all theories is a critical solubility product, supersaturation, or a similar quantity. Also, one concludes that diffusion can play a decisive role in ring formation because it acts rapidly over much longer distance than adsorption. The spacing of rings, usually observed if "dry" chloride particle radius is larger than 1 μm , is a very important parameter which indicates the rate of penetration and precipitation of diffusing agents. The magnitude of the ring spacing, and the total ring diameter as well, might be influenced by the gelatinous medium, temperature, and environmental humidity. Surprisingly, these factors are not included in most of the theoretical models. Also, there are few systematic studies of the influence of the humidity and temperature on the magnification factor (ratio between the circle diameter and diameter of a "dry spherical" particle), although they might have cardinal importance for the application of this technique in environmental studies and cloud physics (e.g., Podzimek, 1959).

The aim of this study is to contribute to the investigation of the limits of applicability of Liesegang circle technique for sizing of chloride particles in "dry" submicron size range and to establish a reliable magnification factor.

Standardization of Sampling Procedures

During several years of application of Liesegang circle technique for chloride particle identification the following standard technique for sampling slide preparation was developed and applied during field and laboratory measurements: A 10% reagent grade silver nitrate solution in distilled water was added to a hydrosol of 8% laboratory grade gelatin (hot filtered) in a volume ratio of 1:20. The warm sensitized gelatin was immediately used for coating the preheated impactor slides or special plastic foils. After drying, the foils were inserted into an aerosol centrifuge. Coated slides for field work were dried in vertical position in a dark room and inserted into containers which protected them against contamination and light. No dyes or glycerin were added to the gelatin as was recommended by several investigators. Our test results showed some irregularities in the circle formation which might be due to the presence of these substances. The thickness of the dried gelatin layer was between 50 and 100 μm .

Exposed slides or foils coated by sensitized gelatin were processed by first illuminating them by UV lamp (Pen-ray quartz lamp, Ultra Violet Products, Inc.) for 15 min. The formation of the circle was not influenced markedly by deviating as much as 5 min from the recommended illumination time. However, a substantial difference in circle formation was found while storing the exposed slides (before the illumination) at different relative humidity.

Standardization of Sampling Procedures

Sampling and storing of salt aerosols at low relative humidity yielded cubically shaped crystals without the typical diffusional halos. After the illumination of the samples and subsequent humidification, the crystals were still apparent and the halos, if any, were smaller with the undissolved part of the crystal at the center. These findings led us to carry out an orientational qualitative study of sample preparation and storing. The results are summarized in Table I.

The table represents the result of NaCl Liesegang circle formation in a gelatin layer (50-100 μm thick) sensitized with AgNO_3 . The concentration of AgNO_3 solution varied from 2 to 20% by weight and that of pure gelatin solution was 1 to 20%. All the other steps corresponded to the standard procedures.

Table I. NaCl Liesegang Circle Formation in a Gelatin Layer

AgNO ₃ (%)	from nebulizer				through drifttube				through humidifier			
	2	5	10	20	2	5	10	20	2	5	10	20
1	-	-	-	-	-	-	-	-	-	-	-	-
3	-	-	-	+	-	-	-	+	-	-	+	+
8	-	-	-	-	-	-	-	-	-	-	+	+
20	-	-	-	-	-	-	-	-	-	-	-	-
DRY												
1	-	+	+	+	-	+	+	+	+	+	-	+
3	-	+	+	+	-	+	+	+	-	-	+	+
8	+	+	+	+	+	+	+	+	-	-	+	+
20	-	-	-	-	-	-	-	-	-	-	-	-
WET												
1	-	+	+	+	-	+	+	+	+	+	-	+
3	-	+	+	+	-	+	+	+	-	-	+	+
8	+	+	+	+	+	+	+	+	-	-	+	+
20	-	-	-	-	-	-	-	-	-	-	-	-

NaCl aerosol was generated by passing nitrogen gas at 6 L/min through a DeVilbiss nebulizer (Model 40) containing a 6% sodium chloride solution (by weight) for about 10 min. From the generator the aerosol was either vented directly into a humidifying tube or through a heated drift-tube with a water vapor absorbing substance (silica gel) before entering the storage bag which was partially filled with nitrogen gas. The size distribution of the salt particles was monitored by a laser cavity spectrometer. The aerosol was stored for half an hour after ending its generation to allow it to stabilize at a concentration of several hundreds of particles per cubic centimeter. After this time the size distribution remained essentially constant throughout the sampling period in a UNICO cascade impactor. For the purpose of our study, the slides were stored over a water absorbing substance or over a surface of distilled water at least for 3 h.

In Table I, the dry stored samples (the first four runs) yielded very few positive results in Liesegang circle observation with an optical microscope (at a magnification of 640 \times). On the other hand, the wet stored aerosol sample showed nicely formed circles almost in all combinations of concentration of AgNO₃ and gelatin (except with the 20% gelatin concentration case).

In conclusion, we can say that the gelatin concentration between 1 and 8% by weight seems to be the most suitable for Liesegang circle formation. Concentration of AgNO₃ between 5 and 20% by weight (which is mixed with gelatin solution at a ratio of 1 to 20) does provide good circle formation in gelatin. The storage of the samples in a humid environment plays a more important role in obtaining a reproducible result than the state in which the sodium chloride containing aerosol was sampled. Therefore, with high storage relative humidity, the circles so formed enable one to estimate the amount of diffusing substance (Cl ions) except for very large NaCl particles which penetrate through the gelatin layer.

The dependence of circle formation on temperature was not studied during this series of experiments because one of the authors (Podzimek, 1959) thoroughly investigated this relationship 20 years ago. In his study the main criterion was the shifting of the modal radius of the spot diameter distribution curve during the temperature increase from +2 °C to 21 and 60 °C, respectively. These increases in temperature caused an increase in circle diameter of 22% and 10%, respectively, while sampling at 15 and 25 °C caused only insignificant difference in the position of the modal radius.

The stability of the circle images in the exposed gelatin sheet was very good. After the diffusion (in humid atmosphere for several minutes) and illumination processes,

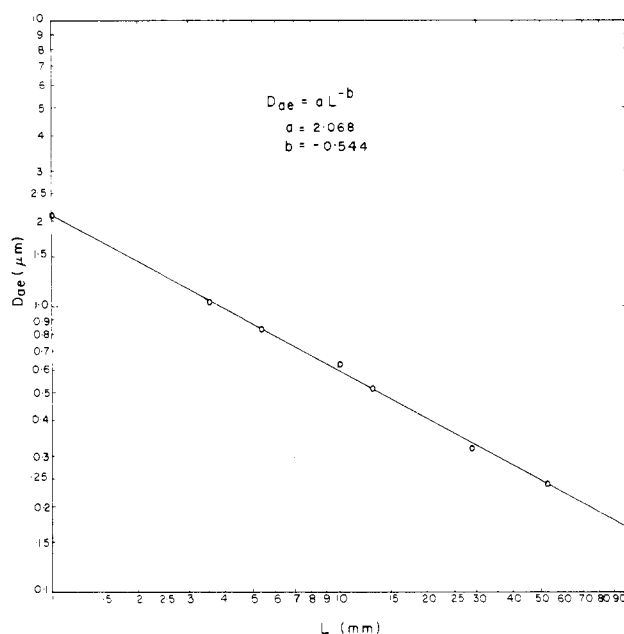


Figure 1. Calibration curve for the cylindrical aerosol centrifuge.

the slides were stored in a dry environment and reevaluated after several months. No substantial changes in the size distribution were found, although the transparent gelatin layer became darker.

Magnification Factor of Liesegang Circles

The knowledge of relating the circular spot size in the sensitized gelatin layer to the particle volume equivalent diameter is critical for the application of the spot test technique to particle sizing. Several methods have been used for determining the magnification factor of chloride particles such as direct comparison of the size of salt crystals or solution droplets deposited on a slide smeared with silicone grease with the halos left in the sensitized gelatin layer by the same salt aerosol (e.g., Pidgeon, 1954; Metnieks, 1958) or direct comparison of the salt crystal equivalent diameter calculated from the settling velocity of aerosol in a drift tube with the spot diameter (e.g., Rau, 1956; Podzimek, 1959). The magnification factors calculated by the use of these methods varied between 5.0 and 9.0 depending on the individual techniques and environmental conditions. Considerably lower values of the magnification factor (around 2.7) were found by Durbin (1959) and by Ueno and Sano (1971). The latter authors used a polyvinyl alcohol coating of the substrate, however.

This study reports on the determination of the magnification factor related to the aerodynamic diameter of NaCl particulates in submicron size range. The aerodynamic diameter seems to be a more useful parameter than the geometric one. It reflects the particle behavior during aerosol sampling by inertial deposition without requiring the information about the particle shape and density. A similar approach has been used by Preining et al. (1976), who established the calibration curve for the aerosol centrifuge

$$D_{ae} = aL^{-b}$$

where D_{ae} is the aerodynamic diameter of latex particles of known size, L is the distance between the aerosol entrance slit and the position of a particle on the foil in a cylindrical centrifuge, and a and b are constants to be determined from the experiment (see Figure 1).

Two series of experiments were performed in order to check the potential effect of environmental humidity on

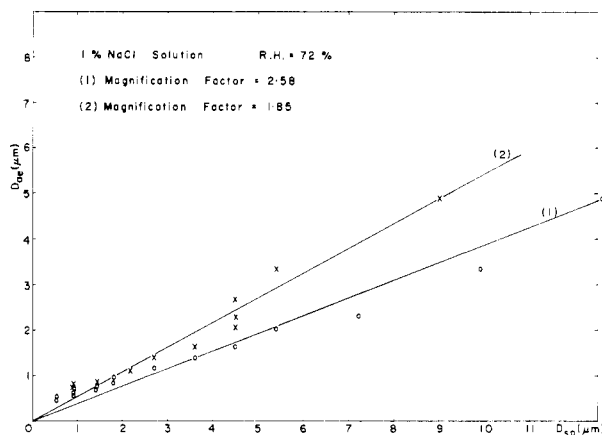


Figure 2. Magnification factor for NaCl droplets from 1% solution sampling at R.H. = 72%.

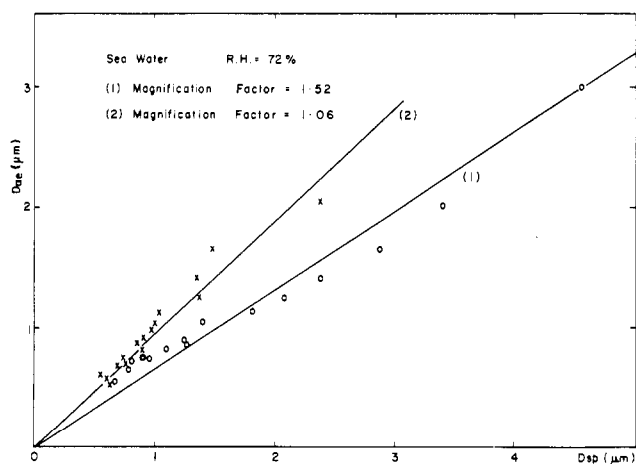


Figure 3. Magnification factor for NaCl droplets from sea water sampling at R.H. = 72%.

the magnification factor: sampling at relative humidity 72% or lower, and experiments at relative humidity 82% or higher. For the latter case we expected salt solution droplet deposition. The droplets (from 1% and 6% NaCl solution and sea water from the Gulf of Mexico) were generated by a De Vilbiss (No. 40) nebulizer and injected into an air flow of controlled humidity. They entered into a cylindrical centrifuge and deposited, according to their inertial mass and the applied centrifugal acceleration, at different distances from the centrifuge inlet slit. Two strips were cut from the exposed plastic foil coated with sensitized gelatin and one of them was placed over distilled water in a Petri dish for 30 min. The other strip was kept over a water absorbing substance. All the following steps including sample illumination and evaluation in an optical microscope were identical with standard procedures.

Sampling at low relative humidity (R.H. = 72% referring to Figures 2, 3, and 4) yielded two curves (approximated by lines) of the functional dependence of the spot diameter D_{sp} in the sensitized gelatin layer on the particle aerodynamic diameter D_{ae} . Both have distinct different slopes. That of the strip which was placed over distilled water (designated by \times in the figure) indicates higher magnification factor in comparison to the sample stored in dry environment (points marked by \circ in the figure). Larger difference in slopes corresponding to wet and dry sample storage is found for higher salt concentration in drops. If one assumes that the salt solution drop size distribution is originally the same, the experiments show that most of the salt particles produced by spraying of 6% NaCl solution and sea water are "dry" crystals. The fact that de-

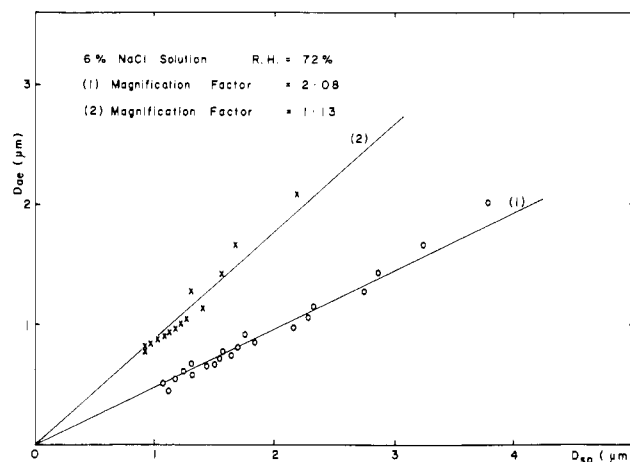


Figure 4. Magnification factor for NaCl droplets from 6% solution sampling at R.H. = 72%.

position at low humidity and storage in dry environment still gives a magnification factor greater than one (1.13 and 1.06) reveals that the particles are not completely "dry". This conclusion is supported by microscopical examination which usually shows a small halo around well-formed salt crystals. Placing the sample strips over distilled water supports the circle formation due to the absorption of water vapor, but the diffusion of Cl ions is not completed after exposing the samples to water vapor for an hour.

The discrepancy between the expected magnification factor 1.00 for "dry" crystals and the measured ones can be partly explained by the polycrystalline structure of salt particles during the evaporation of solution droplets and salt crystallization. Assuming that the volume equivalent diameters, D_e , of two salt particles are the same but their densities differ, the ratio of the corresponding aerodynamic diameter D_{ae} will be

$$\frac{D_{ae1}}{D_{ae2}} = \frac{D_{e1} \left(\frac{\chi C_{ae2}}{\sigma_{ae2} C_{e2}} \right)^{1/2}}{D_{e2} \left(\frac{\chi C_{ae1}}{\sigma_{ae1} C_{e1}} \right)^{1/2}}$$

for $D_{e1} = D_{e2}$

$$\frac{D_{ae1}}{D_{ae2}} \approx \left(\frac{\sigma_{ae1}}{\sigma_{ae2}} \right)^{1/2} = \left(\frac{D_{sp1}}{D_{sp2}} \right)^{3/2}$$

The particle shape factor χ (cubes $\chi = 1.03$) and the slip correction factors (C_{ae} , C_e) were considered to be the same for both particles because their shapes are similar. The relationship between the Liesegang circle diameter, D_{sp} , and the equivalent volume diameter was obtained from equating the amount of outer ions distributed homogeneously in the diffusion hemisphere in the gelatin layer to those contained in the airborne salt particle (or solution droplet). A wrong assumption on the density of salt particles ($\sigma = 2.17 \text{ g cm}^{-3}$ instead of $\sigma = 2.00 \text{ g cm}^{-3}$) will lead to a decrease in the magnification factor of approximately 2.76%. This simple relationship holds only for the case of the complete diffusion of outer ions in the gelatin. When the steady state was reached polycrystalline structures were occasionally observed in salt aerosol generated by the spraying of salt solution. However, they were frequently observed if furnace technique (condensation aerosol) was used.

Figures 5, 6, and 7 show results of experiments performed under higher relative humidity (R.H. = 82%). In

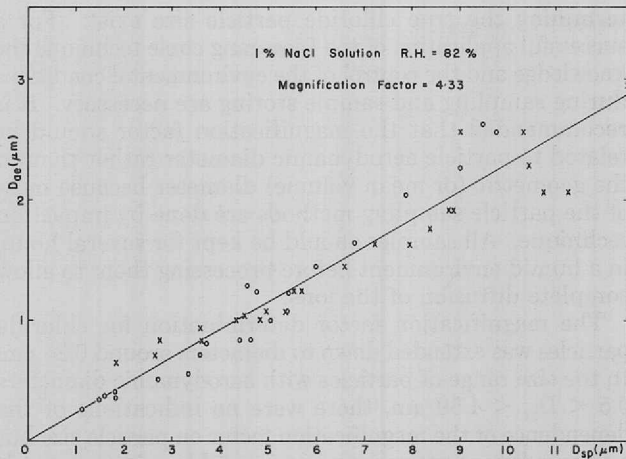


Figure 5. Magnification factor for NaCl droplets from 1% solution sampling at R.H. = 82%.

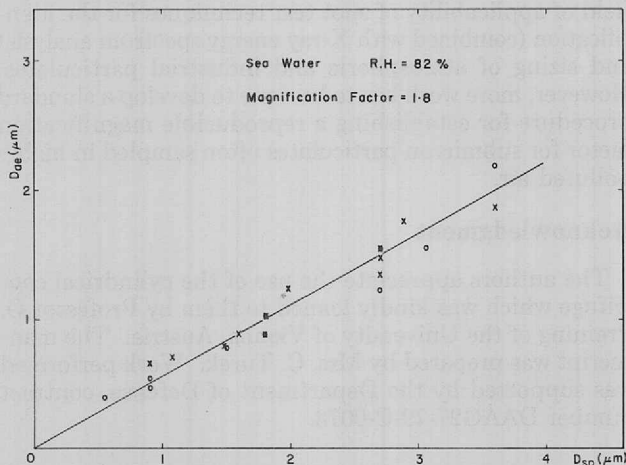


Figure 6. Magnification factor for NaCl droplets from sea water sampling at R.H. = 82%.

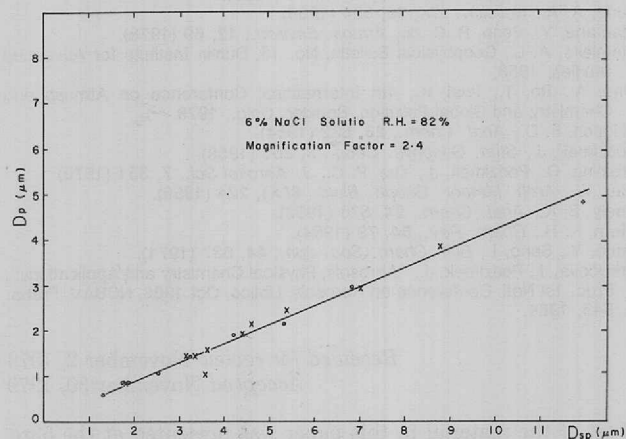


Figure 7. Magnification factor for NaCl droplets from 6% solution sampling at R.H. = 82%.

this case we see that measurements from both strips (stored in dry air and humid air) give essentially the same magnification factor. These indicate that at R.H. = 82% the particles are in aqueous form as was anticipated. The exposure of the strip to water vapor has minimal effect on the magnification factor. Hence in dry particle deposition, the environmental humidity should be a factor to be considered.

Further Development of the Technique

From the results presented in many papers on the spot test techniques one concludes that the application of the



Figure 8. SEM micrograph of 0.5- μm diameter latex particle and a Liesegang circle scanned at a zenith angle of 85°.

method is limited by the resolution of a simple optical microscope and by being obscured by other atmospheric aerosol. In clean air the particle diameter of $D_{ae} = 0.5 \mu\text{m}$ and in "polluted" atmosphere $D_{ae} \geq 1.5 \mu\text{m}$ for chloride particulates are considered as the lowest detectable sizes using either polarized or normal light. The technique can be applied for other constituents of the atmospheric aerosol. The particle detectability depends very much on the specific chemical reaction (many reactions do not lead to well developed circles—Vrkocova and Podzimek, 1964), and also, on the optical contrast of the spot in a sensitized substrate layer. Thus, the detectable size limit of sulfate particles will be larger than 1.0 μm if one uses a simple method similar to that for chlorides. In general, the sample evaluation is time consuming and automatic evaluation of submicron atmospheric particles with the aid of scanning optical instruments is almost impossible.

The resolution problem can be solved by using an electron microscope either scanning or transmission type. A special technique of sensitized substrate preparation for the detection of submicron sulfate particles was suggested and applied by Bigg et al. (1974) and by Mamane and de Pena (1978). It consists of coating a substrate (e.g., impactor plate or electron microscope screen covered with a thin film of carbon) with barium chloride and evaluating the samples at an appropriate humidity in an electron microscope. Similar technique for the detection of sulfate particles was described and applied in marine atmosphere by Ono et al. (1979).

Three years ago an attempt was made to evaluate the imprints left in the sensitized gelatin sheet by sodium chloride particles in a scanning electron microscope. The samples were processed in the same way as was described above. However, the layer was coated with gold by vacuum deposition technique before being examined at a very low angle. By superimposing latex particles of known size on the sodium chloride aerosol deposited one can infer directly the aerodynamic diameter of the "dry" sodium chloride crystal which forms the Liesegang circle. Figure 8 is an electron micrograph which shows a 0.5- μm diameter latex particle sitting on top of a Liesegang circle. It was taken with magnification of 30 000 \times and at a zenith angle of 85°. Using this technique it is possible to extend the resolution to particle size of 0.1 μm in diameter. The photograph in Figure 9 shows NaCl aerosol deposited on the electron microscope screen. The mean particle diameter is 0.08 μm , which corresponds to an aerodynamic diameter of 0.13 μm . The same aerosol was deposited on a sensitized gelatin

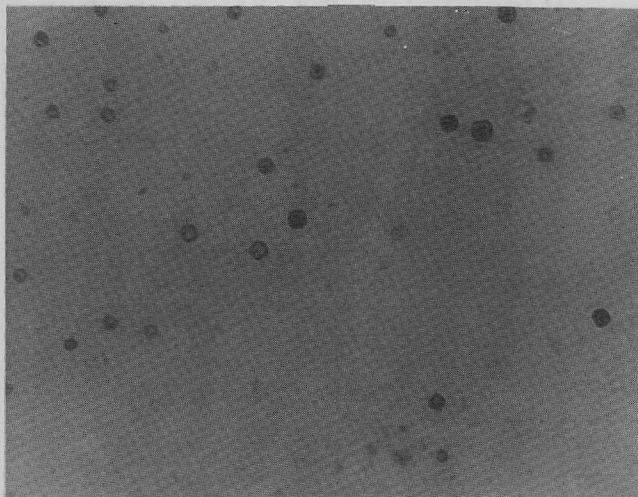


Figure 9. NaCl particle deposited on a electron microscope screen.

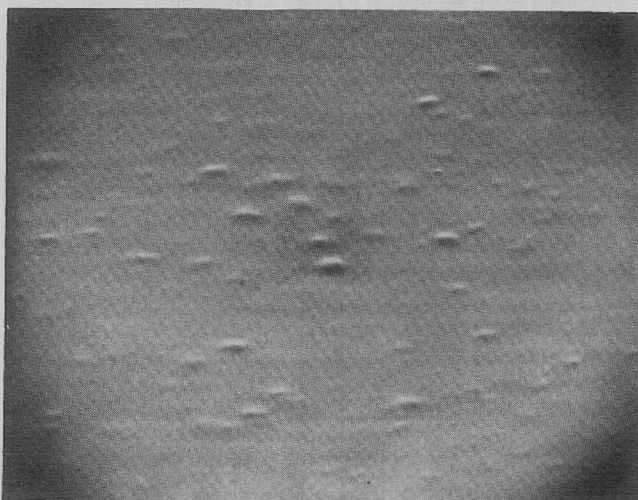


Figure 10. SEM micrograph of "processed" NaCl aerosol deposited on sensitized gelatin layer.

layer, processed, and photographed in a scanning microscope at an angle 75° (Figure 10). The Liesegang circle diameter is determined by measuring the swollen gelatin around the deposited particle; one finds the mean spot diameter $0.8 \mu\text{m}$. From the ratio of the mean spot diameter and particle aerodynamic diameter we obtained a magnification factor of 6.1. This depends very much on the viewing angle of the scanning electron microscope. This magnification factor does not differ very much from the magnification factors established for larger chloride particles if the sample was taken and kept in a humid environment.

Conclusion

The results of laboratory experiments explain why large discrepancies between the magnification factors in de-

termining the true chloride particle size exist. For a successful application of the Liesegang circle technique the knowledge and the control of the environmental conditions during sampling and sample storing are necessary. It is recommended that the magnification factor should be related to particle aerodynamic diameter rather than to the geometric (or mean volume) diameter because most of the particle sampling methods are done by impaction technique. All samples should be kept for several hours in a humid environment before processing them to allow complete diffusion of the ions.

The magnification factor determination for chloride particles was extended down to diameters around $0.25 \mu\text{m}$. In the size range of particles with aerodynamic diameters $0.5 < D_{ae} < 4.50 \mu\text{m}$, there were no indications of the dependence of the magnification factor on particle size but a strong dependence on environmental humidity and salt concentration in the solution droplet was indicated.

The use of scanning electron microscopy opens a new field of applicability of spot test techniques for the identification (combined with X-ray energy spectrum analysis) and sizing of atmospheric and industrial particulates. However, more work has to be done to develop a standard procedure for establishing a reproducible magnification factor for submicron particulates often sampled in highly polluted air.

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