THE GENERATION AND PROPERTIES OF SOLID MONODISPERSE AEROSOLS OF STEARIC ACID AND CARNAUBA WAX

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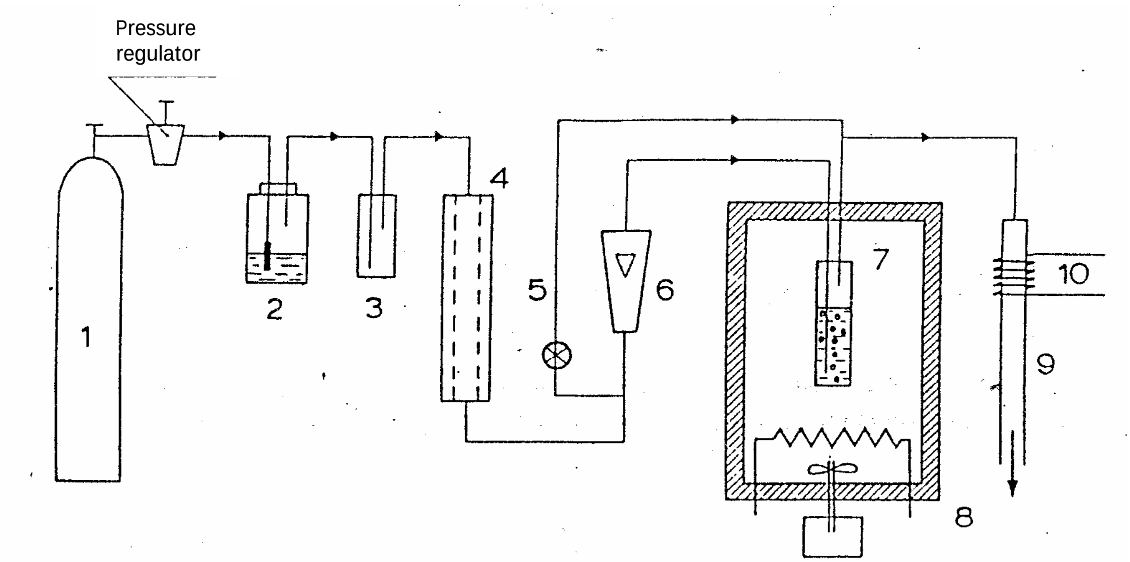
ABSTRACT

A monodisperse aerosol generator (MAGE) was used to generate calibration or monodisperse aerosols containing stearic acid and carnauba wax. Some of the factors affecting the size of aerosol particles generated with the MAGE were determined. The factors include: temperature of operation of the MAGE, type and purity of coating material used. The reproducibility of aerosol particles and stability of the aerosol generated were evaluated. The performance characteristics of the MAGE over an extended period of time of operation were also established. The calibration aerosols generated with the MAGE can be used *in situ* for studies of aerosol deposition measurement equipment.

Keywords: Generation, Calibration aerosols, Monodisperse aerosol generator, Performance characteristics

INTRODUCTION

An important aspect of aerosol technology is the production of test aerosols with which to calibrate instruments used to simulate behaviour on inhalation. These test aerosols are usually monodisperse or practically so. A monodisperse aerosol is defined as one having a particle size distribution with a geometric standard deviation (GSD) less than 1.25 (Fuchs and Sutugin, 1966). The more widely used modern monodisperse aerosol generators are based on three mechanisms: spinning disc, vibrating orifice and controlled condensation. The spinning disc generators are based on the formation of uniform liquid filaments around the lip of a fast rotating disc. These filaments break up into a main drop at the outer end of the filament and into several smaller "satellite" droplets. Air circulation around the "satellite" droplets extracts them on the basis of their smaller inertia leaving only the main monodisperse drops. A large variety of materials can be made into aerosols by this method. Size control is achieved by controlling rotational speed, suspension or solution concentration and feed flow rate. Reproducibility is a problem with spinning disc generators and, often, an independent measurement of aerosol particle size may have to be carried out. Vibrating orifice generators eject a liquid filament under pressure from a calibrated orifice. Superimposition of an appropriate disturbance, like an ultrasonic field, breaks up the filament regularly, producing monodisperse droplets (Fulwyler and Raabe, 1970; Berglund and Lin, 1973; Tu, 1982). Particle coagulation, high particle electrostatic charges and particle size drift due to clogging of orifices are some problems associated with vibrating orifice generators. The condensation aerosol generators are all derived from the LaMer-Sinclair (Sinclair and LaMer, 1949) generator in which a uniform and constant mixture of condensation nuclei is produced and combined with vapours of the desired material in an inert gas. If the cooling is slow, under controlled conditions, each nucleus takes up, by condensation, a constant mass of condensate and uniform liquid or solid particles are formed (at room temperature). Examples of such aerosol generators are the Prodi generator (Prodi, 1972), the falling film generator (JJicolaon *et al.,* 1970), the Tu single stage generator (JJicolaon *et al.,* 1970), the Kogan-Burnasheva generator (Kogan and Burnasheva, 1960) and the Rapaport and Weinstock generator (Rapaport and Weinstock, 1955). A comprehensive investigation into aerosol formation by homogeneous and heterogeneous nucleation using a laminar continuous flow aerosol generator was presented by Nguyen and others (see Tu, 1982). A review of the condenser conditions for practical monodispersity of many examples of these aerosol generators using dimensionless heat and mass transfer groups was given by JJicolaon *et al.* (1970). The objective of this study was generation and characterization of solid, monodisperse aerosol particles suitable for calibrating devices used in deposition experiments.



Key: *1= CP nitrogen, 2 = collision generator, 3 = mist arrestor, 4 = diffusion drier, 5 = bypass line, 6 = bubbler line, 7 = bubbler, 8 = forced air circulation thermostat, 9 = reheater, 10 = heating tape*

Figure 1: MAGE a modified Sinclair-LaMer generator, with a forced air circulation thermostat and bypass - which allows rapid size adjustments during aerosol generation

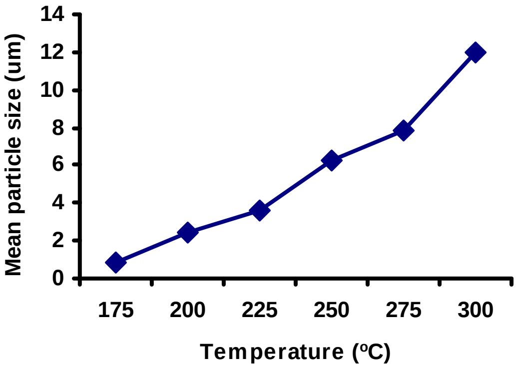


Figure 2: Effect of temperature on aerosol particle size

Monodisperse aerosol particles in the size range 1 - 12 μm, of high concentration output rates, are required for this purpose.

MATERIALS AND METHODS

Aerosol Generator: The MAGE is custom built equipment and its performance characteristics have not been fully ascertained. There is no published information on the factors affecting the performance of the MAGE outside the claims of the manufacturers. The successful generation of aerosols in our laboratory at King's College, London was the primary objective of this work. This success, after years of effort, necessitated the determination and validation of some of the important factors affecting the performance of the MAGE. MAGE is a modified Sinclair-LaMer Generator, with a forced air circulation thermostat and bypass - which allows rapid size adjustments.

Essentially, a dilute solution or colloidal suspension is atomized by pressurised compressed, forcibly recirculated air as a working fluid and a Proportional-Integral, Proportional-Derivative temperature control unit, with an overall stability within ± 0.5°C. At the outlet of the bubbler, the vapours condense on the nuclei, producing an aerosol with a narrow size distribution. A reheater, as the final stage, repeats the evaporation-condensation cycle producing better size distribution control. A by-pass around the bubbler allows the vapour flow rate to be decreased without affecting the nuclei flow rate; thus, at constant temperature, a fine and rapid size adjustment is possible, when the whole stream is again processed through the reheater.

The performance of the generator can be estimated by appropriate assessment of the ensuing aerosol particles. The system takes about 1 hour to warm up from a cold start, but if the oven is left on, the time taken for a useful, stable aerosol to be produced is about 30 minutes after the nebulizer is turned on. After equilibrium has taken place, diameter stabilisation takes less than 1 minute. The generator can be operated with only slight adjustments to give solid stearic acid particles for over 3 hours. The length of time MAGE generates aerosols is temperature-dependent. The higher the temperature setting, the shorter the performance time.

The following performance characteristics of the MAGE were established and validated: effect of coating material type on aerosol particle size, effect of purity of coating material on aerosol particle size, effect of aerosol particle size on Malvern

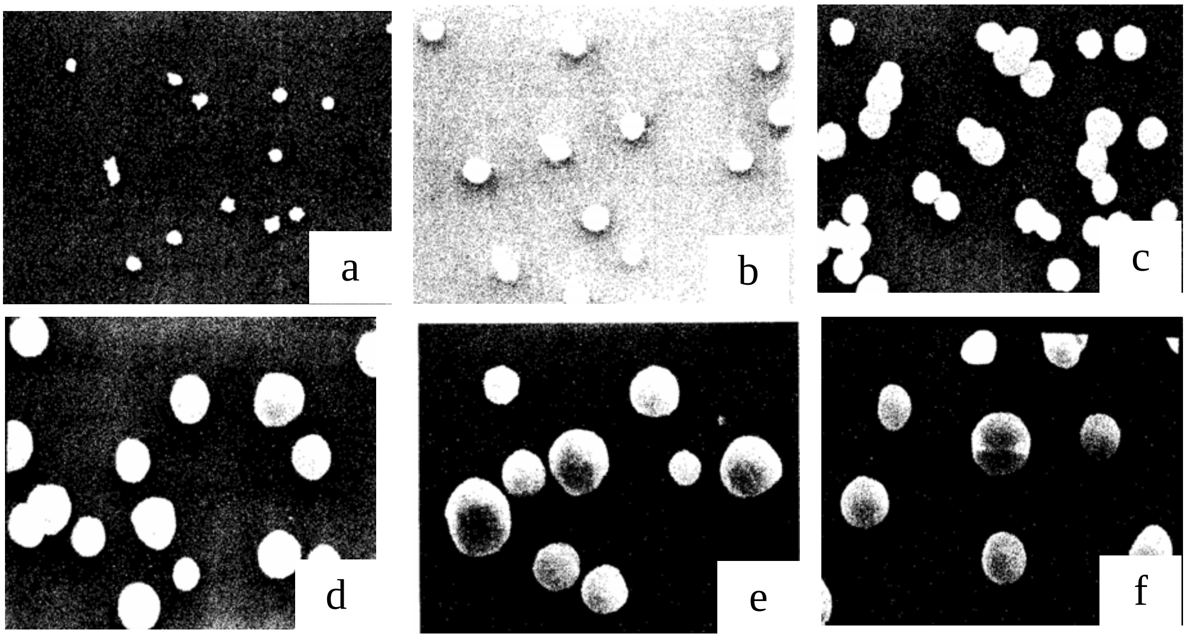


Figure 3: Scanning electron micrograph of stearic acid aerosols generated with MAGE showing the effect of temperature on aerosol particles size. Aerosol in the micrographs have the same magnification and were generated at a) 174, b) 200, c) 225, d) 250, e) 275 and f) 300 °C

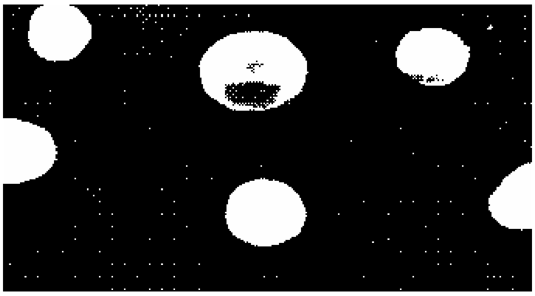


Figure 4: Scanning electron micrograph of stearic acid aerosols generated at 300 °C

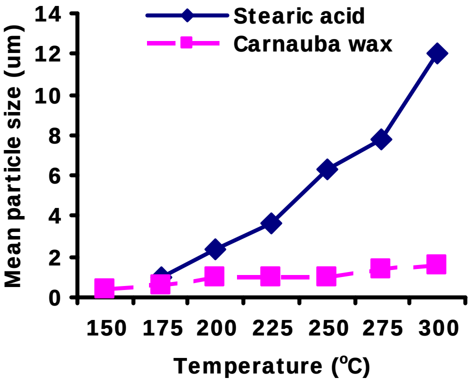


Figure 5: Effect of coating material type on aerosol particle size

analysis mode, reproducibility of the properties of aerosol particles generated, effect of carrier gas flow rate on aerosol properties, the stability of the aerosols generated from the MAGE, effect of by-pass flow control of the MAGE on aerosol properties and the performance characteristics of the MAGE over an extended period of time.

Condensate Materials: Common solid organic materials of great purity were investigated with the requirements of low melting points and low vapour diffusion coefficients. Two solid condensate materials were chosen, stearic acid and carnauba wax, with specific gravities of 0.847 and 0.997 respectively. After several studies showing excellent monodispersity, it became obvious that carnauba wax was unsuitable for use, because at the highest operating temperatures, a maximum particle diameter of only 2 μm was attainable. Stearic acid is readily available in very pure form and is non-toxic. It has a low thermal conductivity and needs to be chilled quickly in droplet form or the particles will grow into non-spherical crystalline structures. The air in the system was found to be adequate to solidify the particles into spheres, suitable for calibration experiments. When stearic acid aerosol particles were sampled onto microscope slides, the spheres began to crystallise into non-spherical particles after 12 hours or longer at room temperature. The aerosol particles should therefore always be used within 12 hours of generation and in these studies, they were used immediately.

Vapour-Nuclei Generation: The nebulizer of the MAGE conforms to the classic six-jet Collision nebulizer (British Standard 1984).

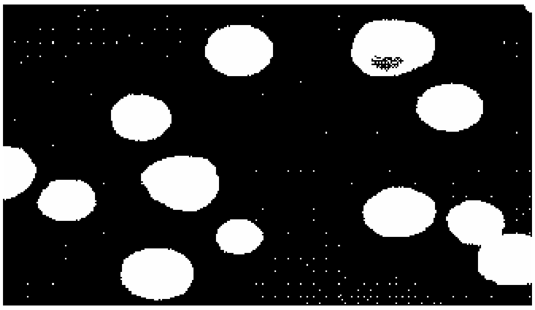


Figure 6: Scanning electron micrograph of stearic acid aerosols generated at 250 °C

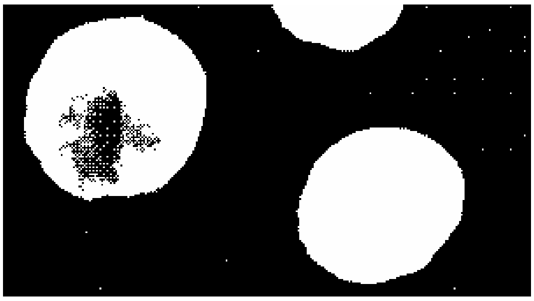


Figure 7: Scanning electron micrograph of stearic acid aerosols generated at 300 °C

Figure 8: Scanning electron micrograph of stearic acid aerosols generated at 275 °C

Its glass and metal design allows it to withstand high temperatures. The nuclei are produced by atomization of a very dilute solution of NaCl in water by means of the collision atomizer, using pressurised compressed nitrogen. The droplets are dried and the condensation nuclei are sent to the bubbler filled with stearic acid (see Figure 1). The particles are produced at a high concentration, are practically neutral and start from sizes as low as 0.1 μm.

Aerosol Sizing Methods: The aerosols were measured by two different methods, using a commercial Malvern Series 2600 Particle Sizer (Malvern Instruments Limited, Malvern, Worcestershire, England) and scanning electron microscopy (SEM). No detailed comparison of these two methods of size measurement was made in these experiments and data reported are those obtained with the Malvern Series Particle Sizer. The aerosols were characterised by determining volume mean diameter with associated GSD. The Malvern Particle Sizer is capable of several modes of particle size analysis. The log-normal distribution has proved useful in many types of particle size analysis problems, including the sizing of aerosols. 'The log-normal distribution particle size analysis mode was used in this work. The particle size results given by the Malvern were accepted when obscuration was between 10 – 30 % and the log difference in the analysed set of data was below 5.

RESULTS AND DISCUSSION

Effect of MAGE Temperature on the Particle Size of Aerosols Generated: The manufacturer's claim is that the particle size of aerosols generated with the MAGE depends on the temperature of operation of the MAGE. The MAGE was therefore operated at different temperatures and the particle sizes of aerosols issuing from the equipment at these temperatures were characterized. The results obtained are shown in Figure 2. It can be seen that particle size of aerosols generated increased with increase in the temperature at which the MAGE was operated. The scanning electron micrographs (SEMs) of stearic acid aerosols generated at different temperatures are shown in Figures 3 and 4. It can be seen that the higher the temperature of operation of the MAGE, the larger the particle size achieved. The higher temperatures result in higher vapour concentrations at the outlet of the bubbler and a greater amount of material to each condensation nucleus. A size range 1 - 12 μm was achieved within the operational temperatures possible with the MAGE. This result is however specific for stearic acid.

Effect of Aerosol Material Type on Aerosol Particle Size: Two aerosol materials, carnauba wax and stearic acid were investigated for use in the calibration experiments. Figure 5 shows the particle size data obtained with carnauba wax and stearic acid. Carnauba wax gave excellent monodisperse aerosol particles but the particle size obtained at the highest MAGE operational temperature was inadequate. A maximum 2 μm particle diameter was obtained. The type of aerosol material was therefore shown to influence the resultant aerosol particle size. Several other materials are capable of being used in the generation of solid aerosol particles. Such materials include di-2-ethylhexyl sebacate (DBS) and triphenyl phosphate. The shape and surface characteristics of the aerosol particles were ascertained by scanning electron microscopy. Figures 6, 7 and 8 are the micrographs for stearic acid and carnauba wax microspheres, respectively.

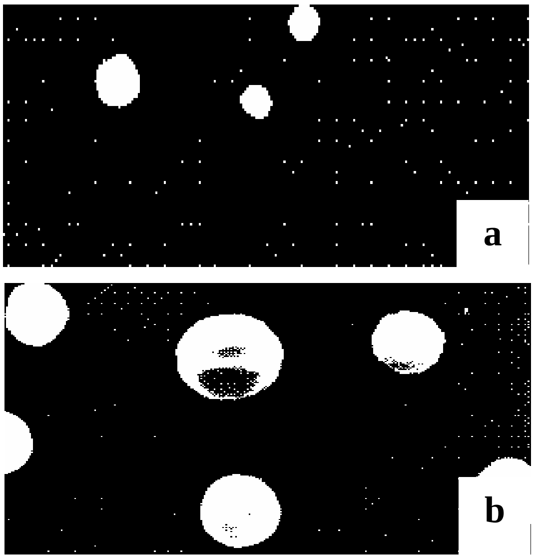


Figure 9: Effect of type of aerosol material on aerosol particle size. Scanning electron micrographs are for a, carnauba wax and b, stearic acid generated at 300 °C

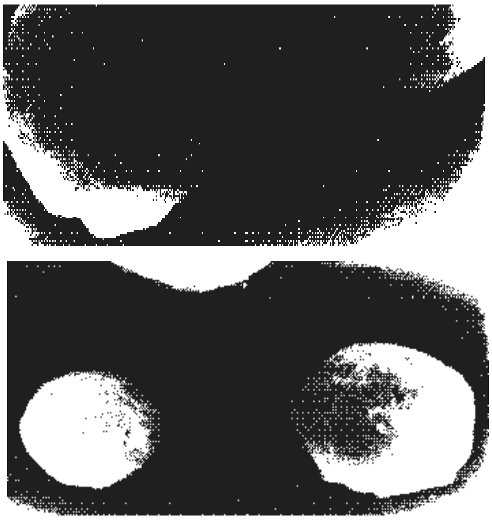


Figure 10: Effect of purity of coating materials on particle size of aerosols generated at 300 oC. Scanning electron micrographs at the top are for 99 % purity stearic acid and those below are for 90 % purity stearic acid

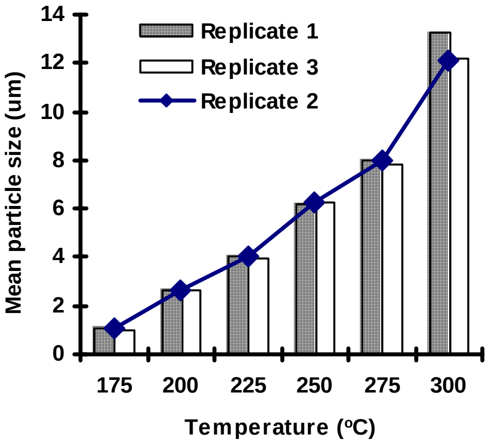


Figure 11: Reproducibility of the characteristics of aerosols generated

The particles are spherical and fairly ideal. Instruments used for the particle size analysis of aerosols encounter both ideal and non-ideal particles in practice. Both classes of aerosol particles are used in their calibration. It is important therefore to determine the aerodynamic properties of such particles prior to use.

Effect of Purity of Aerosol Material: The effect of purity of stearic acid on particle size was determined by selecting two different grades of 90 % and 99 % purity for study. There was little difference in the particle size range of the particles produced from the different grades of stearic acid. SEMs of aerosols produced from 90 % purity stearic acid at 300 ^{o}C are shown in Figure 9. SEMs of aerosols generated with 99 % purity stearic acid at 300 ^{O}C are shown in Figure 10. It is possible that impurities alter the vapour pressure of the stearic acid and induce the larger particle size of the aerosol particles at higher temperatures. It was thought desirable to use high purity grades of stearic acid, since crystallisation, which occurs on the storage of stearic acid particles, is likely to be less of a problem. The sample of stearic acid used in this work was therefore 99 % pure.

Reproducibility of Properties of Aerosol Particles Generated by MAGE: Particles were generated at the same temperatures on three separate occasions. Other variables, such as concentration of NaCl solution, by-pass control, sampling regimen and particle size analysis mode, were maintained constant. Figure 11 shows the results obtained and on the basis of which, it was concluded that the particle sizes of the generated aerosol particles were reproducible. The stability of the aerosol particles issuing from the MAGE was determined over a 3 hour period when the MAGE operational temperature was below 250 °C.

Particle size analyses were performed at 60 minutes intervals. Over the three hours of the experiment, the particle size remained constant. In calibration experiments, the generation of data from a single calibration point seldom lasts 1 hour or more; hence, it can be concluded that the reproducibility of the aerosols generated by MAGE is sufficient for the purposes of the experimentation.

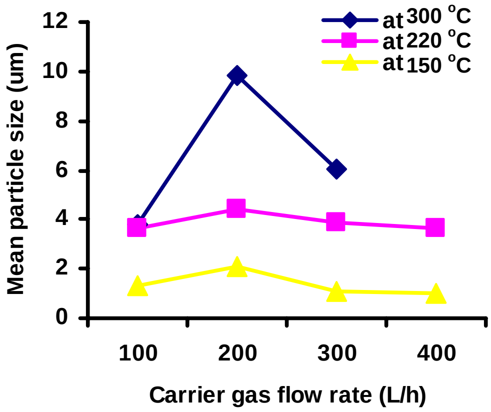


Figure 12: Effect of carrier gas flow rate on aerosol particle size

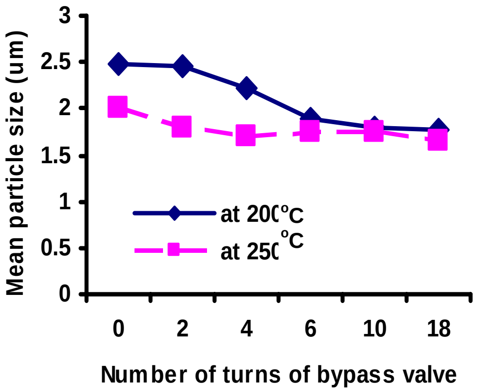


Figure 13: Effect of bypass flow control on aerosol particle size

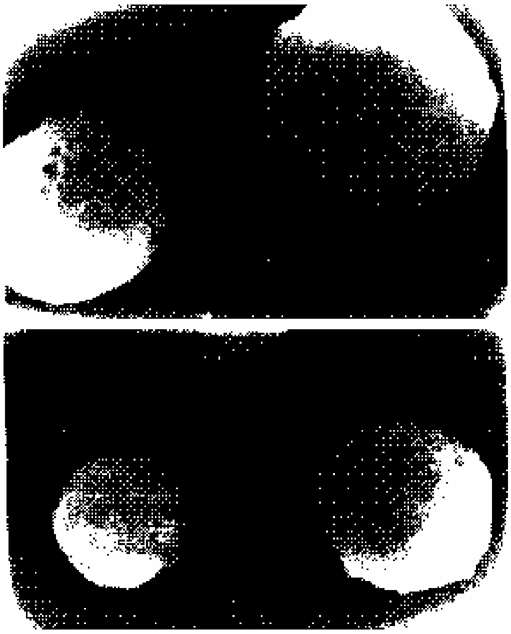


Figure 14: Typical scanning electron micrographs of stearic acid containing aerosols generated with the MAGE at 225 °C after storage for six hours on a glass slide at room temperature of 25 °C and 50 % relative humidity

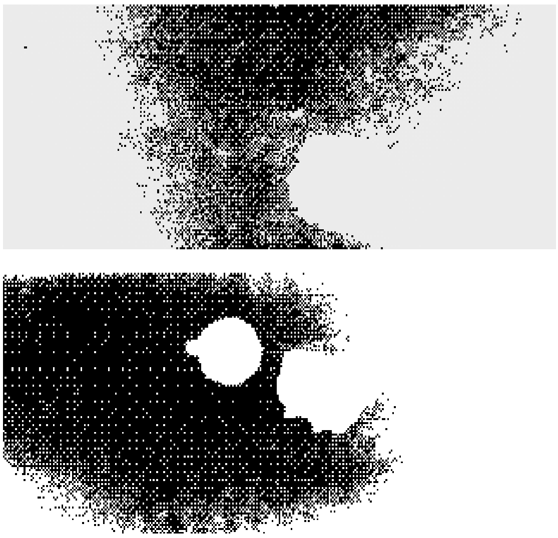


Figure 15: Typical scanning electronic micrographs showing the stability of stearic acid containing aerosols generated with the MAGE at 300 °C (above) and 174 °C (below). The aerosols were stored overnight for 12 hours on a glass slide at ambient conditions (room temperature of 25 °C and 50 % relative humidity)

Effect of Carrier Gas Flow Rate: The MAGE uses compressed nitrogen as the carrier gas. The carrier gas flow rate influences nuclei supply for condensation. Various carrier gas flow rates were used to determine their effect on aerosol particle size. In Figure 12 it can be seen that carrier gas flow rate affects particle size of aerosol generated. The carrier gas flow rate in the MAGE is accurately controlled. Any variation in the flow rate is related to temperature that can be digitally set. A by-pass flow allows a fine and prompt particle size decrease since the by-pass flow contributes to the condensation nuclei effectively decreasing the mass available to each nucleus. The effect of by-pass flow control is shown in Figure 13. At 0 setting, the by-pass flow is completely turned off. After 18 turns, the bypass flow is fully open. The effect of bypass flow control is more noticeable at higher temperatures and it is important that the flow be properly adjusted before sampling for particle size analysis. Any change from a fixed setting affects particle size thereafter.

Stability of Aerosols Generated with the MAGE: The stability of the aerosol generated with the MAGE was monitored overnight. Measurement involving calibration aerosols are usually made *in-situ* at the time of generation of the aerosols. There is need however to determine aerosol characteristics over a 24 hour period. Aerosol particles containing stearic acid were deposited on microscopic slides which were left to stand on the laboratory bench at ambient conditions (25 °C and 50 % RH) overnight. SEMs of the storage aerosol particles were obtained after 6 and 12 hours. Figure 14 shows result obtained with stearic acid aerosol generated at 225 ^{o}C. It can be seen that the aerosol particles lost their smooth surface characteristics over the 6 – 12 hours storage period. Crystallization of the stearic acid occurred from the aerosol samples deposited on the glass slides. It is normal practice to measure the particle size of aerosols as they issue from aerosol generators and use them, during calibration experiments. The aerosols are generated, characterized and used immediately without the need for storage.

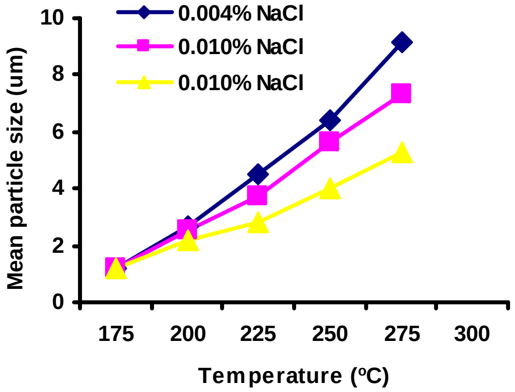


Figure 16: Effect of concentration of core material solution on aerosol size

Effect of Concentration of Core Material Solution an Aerosol Particle Size: The MAGE is a condensation aerosol generator which works by the generation of uniform and constant mixture of condensation nuclei that combine with vapours of the desired coating material (stearic acid or carnauba wax, in this study) in an inert gas atmosphere. It was desirable to assess the effect of concentration of core material solution on the particle size of aerosols generated with the MAGE since the MAGE is dedicated equipment and not much is published about the factors affecting its performance. Figure 15 shows the effect of concentration of core material solution on aerosols particle size. The concentration of core material solution does not have any effect on aerosol particle size at low temperatures (175 – 200 ^{0}C) (Figure 16). At higher temperatures (225 – 300 ^{0}C) differences are noticeable, but there is no consistent trend in these differences (Figure 16). The same concentration of core material solution was therefore used in the generation of aerosols used in our calibration studies.

Conclusion: The monodisperse aerosol generator, MAGE, a condensation aerosol generator, has been used to generate solid, monodisperse calibration aerosols of 1 - 12 µm particle size range. Stearic acid and carnauba wax were used to produce the aerosol particles which contained sodium chloride nuclei. Scanning electron microscopy was used to characterise the aerosol particles. A Malvern Series Particle Size Analyser was used for determination of aerosol size. The aerosol particles can be assayed for their NaCl content by a flame photometric method after extraction by ultrasonication or heating in aqueous solution for 2 minutes. The aerosol particles generated with the MAGE are currently being used in the calibration of the Andersen ICFM Ambient Sampler with pre-separator and other impactors.

REFERENCES

BERGLUND, R. M. and LIU, B. Y. H. (1973). Generation of monodisperse aerosol standards. *Environmental Science and Technology,* 7: 147 – 153.

FUCHS, N. A. and SUTUGIN, A. G. (1966). Generation and use of monodisperse aerosols. Pages 1 – 2. *In:* Davies, C. N. (Ed.) *Aerosol Science,* Academic Press, London.

FULWYLER, M. J. and RAABE, O. G. (1970). The ultrasonic generation of monodisperse aerosols. *Proceedings of American Industrial and Hygiene Association Conference,* Detroit, Mien. May 11 – 15, 1970.

JJICOLAON, G. D., COOKE, D. D., KERKER, M. and MATIJEVIC, E. (1970). Generator for homogenous liquid aerosol. *Journal of Colloid and Interface Science,* 34: 534 – 544.

KOGAN, Y. I. and BURNASHEVA, Z. A. (1960). Growth and measurement of condensation nuclei in a continuous stream. *Russian Journal of Physical Chemistry,* 34: 1240 – 1243.

PRODI, V. (1972). A condensation aerosol generator for solid monodisperse particles. Pages 169 – 179. *In:* MERCER, T. T. MORROW P. E. and STOBER, W. (Eds.) *Assessment of Airborne Particles.* CC Thomas, Springfield.

RAPAPORT, E. and WEINSTOCK, S. G. (1955). An aerosol generator for high concentration of 0.5 – 5 µm. *Experimentia,* 11: 363 – 365.

SINCLAIR, D. and LAMER, V. K. (1949). A device for the control of particle size in the La Mer aerosol generator. *Chemistry Reviews,* 44: 245 – 267.

TU, K. W. (1982). Aerosol generator system for monodisperse aerosols of different physicochemical properties. *Journal of Aerosol Science,* 13: 363 – 371.