PHYSICAL CHARACTERIZATION OF EXPERIMENTAL CYLINDRICAL-SHAPED AEROSOL OF TRIMETHYLXANTHINE, WITH SCANNING ELECTRON MICROSCOPY, USEFUL AS REFERENCE AIRBORNE PARTICLES FOR ATMOSPHERIC AND ENVIRONMENTAL STUDIES

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ABSTRACT
As part of a closure experiment scheme, involving optical measurements of aerosol for comparison purposes of its radiative properties, a method for the generation of monodisperse crystalline 'fibers' made up of a highly scattering substance to visible light was applied. To simulate artificially these particles, trimethylxanthine powder (caffeine) of high purity was used for the generation of experimental samples of cylindrical-shaped aerosol with a Monodisperse Aerosol Generator (MAGE), which is an advanced condensation-type generator. The samples were characterized microphysically by applying scanning electron microscopy (SEM) with a Cambridge S360 instrument. This characterization consisted of SEM analysis of aerosol shape and dimensions in order to determine the size average and the degree of monodispersity of the samples. This study included an estimation of the fiber's aspect ratio and therefore a numerical evaluation of the aerodynamic diameter based on the theoretical expressions given by Cox [32] for the motion of a fluid over a fiber. The results showed that the geometrically analyzed samples, representing the caffeine fibrous aerosol population generated from the MAGE, were good to account for the uniform representation of the fiber's diameter (1.21/1.35 GSD) but, to a lesser extent, relatively acceptable to represent uniformly its length (1.44/1.48 GSD). The evaluation of the aspect ratio of the fibers indicated that they were clearly well elongated crystals. These results were compared with those obtained by other authors. It is concluded that SEM aerosol examination can be applied, in combination with an optical measurement system, to obtain experimentally the radiative properties of standard airborne particles of different shapes, sizes and substances for atmospheric and environmental studies related to radiative forcing (climate changes) and air quality.

Keywords: Caffeine; aerosol; cylindrical-shaped; dimensions; average-size.

CARACTERIZACIÓN FÍSICA CON MICROSCOPÍA ELECTRÓNICA DE BARRIDO DE AEROSOLES EXPERIMENTALES DE TRIMETILXANTINA DE FORMA CILÍNDRICA, ÚTILES COMO PARTÍCULAS SUSPENDIDAS DE REFERENCIA EN ESTUDIOS ATMOSFÉRICOS Y AMBIENTALES

RESUMEN
Como parte de un esquema de experimento cerrado, que involucra mediciones ópticas de aerosoles para fines de comparación de sus propiedades radiativas, se aplicó un método para la generación de fibras cristalinas monodispersivas hechas de una sustancia altamente dispersora de luz visible. Para simular artificialmente estas partículas, se usó polvo de trimetilxantina de alta pureza en la generación de muestras experimentales de aerosoles de forma cilíndrica con un Generador de Aerosol Monodispersivo (MAGE), generador tipo de condensación avanzado. Las muestras fueron caracterizadas microfísicamente aplicando microscopía electrónica de barrido (SEM) con un instrumento Cambridge S360. Esta caracterización comprendió un análisis de la forma y dimensiones del aerosol para determinar su tamaño promedio y grado de monodispersidad de las muestras. Este estudio incluyó una estimación del cociente aspecto de las fibras que permitió una evaluación numérica del diámetro aerodinámico vía expresiones teóricas de Cox [32]. Los resultados revelaron que las muestras geométricamente analizadas, representativas de la población de aerosoles fibrosos de cafeína generadas por el MAGE, fueron buenas en cuanto a la uniformidad del diámetro de la fibra (DSG 1.21/1.35) pero, a hasta cierto punto, relativamente aceptables para representar uniformemente su longitud (DSG 1.44/1.48). La evaluación del cociente-aspecto indicó que las mismas fueron claramente cristales bien alongados. Estos resultados fueron comparados con aquellos obtenidos por otros autores. Se concluye que el examen SEM de aerosoles puede ser aplicado, combinado con un sistema de medición óptico, para obtener experimentalmente las propiedades radiativas de partículas suspendidas de referencia, de diferentes formas, tamaños y substancias para estudios atmosféricos y ambientales relacionados con forzamientos radiativos (cambio climáticos) y calidad del aire.

Palabras claves: Cafeína; aerosol; cilíndricos; dimensiones, tamaño-promedio.

INTRODUCTION

Although natural particulate matter, under normal conditions is a minor component of the air (e.g. ~ 200 particles cm^{-3} of dust for clean air), it plays, along with traces of gas, an important role in determining the physical and chemical phenomena observed in the earth's atmosphere. It is also recognized that, under abnormal conditions (e.g.~800 particles cm^{-3} of dust for polluted air), this particulate matter may cause appreciable short-term transitory changes in some physical and chemical aspects of the atmosphere thereby altering and affecting visibility, cloudiness, sky brightness, radiation balance, air quality, etc [1] - [3]. However, since the beginning of the industrial era the earth's atmosphere has been subjected to an additional and different trauma: the introduction of new sources of anthropogenic aerosol [4]. In this respect, the aerosol atmospheric system, formed by natural and anthropogenic particulate matter [5] - [8], influences our atmosphere and the environment as shown in Fig. 1.

In particular, the investigations to estimate the impact of atmospheric aerosol on climate change, through the forcing they can produce, were made initially, between 1969 and 1981, by theoretical models which necessarily, due to a lack of knowledge, made various assumptions about aerosol properties and their internal and external structures and interactions. None of those works published during this period of time took into account a realistic chemical composition of the aerosol or the atmospheric physical-chemical process producing the aerosol and that take place inside them. Therefore the modeling of the impact of atmospheric aerosol on climate change was made without a proper account on the estimation of aerosol radiative forcing.

For this reason, it was suggested for the first time in 1986 that modeling of the atmospheric radiative forcing by aerosol should be made separately prior to being applied to climate response modeling [9]; hence, the most convenient pathway to achieve this is through step-by-step like that presented in Fig. 2, where closure experiments plays a crucial role between the modeling and verification o validation of the radiative forcing [10].

Closure Experiments

Accordingly a closure experiment is that in which a component of a complex hypothesis is tested, by focused comparison of measured and modeled quantities from an over-determined data set. For example, a closure experiment is a validated procedure to affront both fundamental and practical problems arising when one is trying to obtain reliable laboratory measurements of extensive and intensive optical constants and radiative parameters.

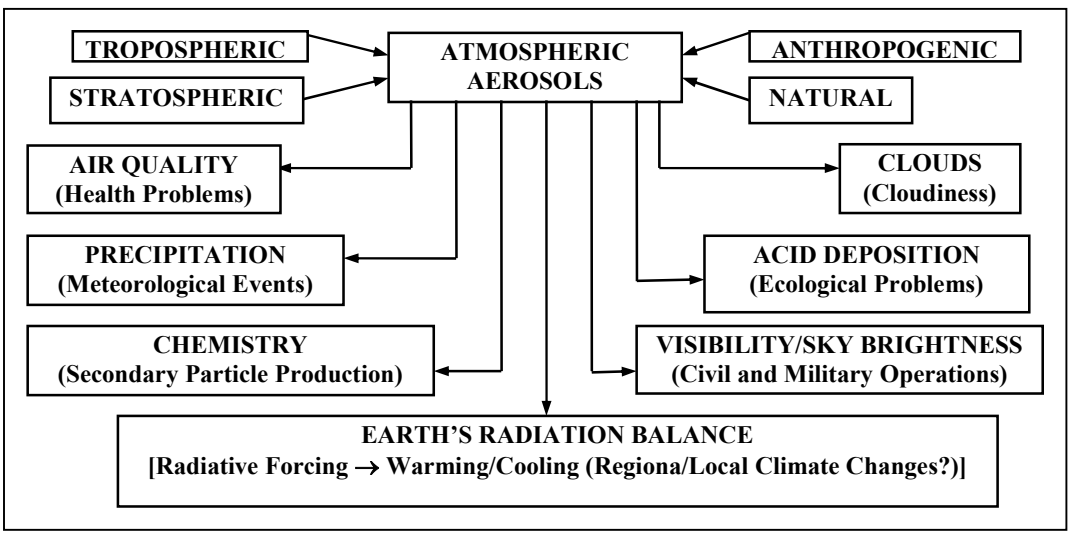

Fig. 1. Schematic representation of different influences on the environment due to atmospheric aerosol.

In this case, measured variables are compared with those obtained by applying a particular theoretical model. The agreement found between them is an indication of the degree of uncertainty contributed by the assumptions made in the model and the limitations of the measurements. This procedure has been used by several authors to investigate the aerosol physical properties. It is now being recommended in connection with the assessment of direct radiative forcing by anthropogenic and natural aerosol in the atmosphere [11] - [12], in which accurate values of the optical constants is necessary.

Among the types of activities connected to closure experiments, within an overall program to quantify aerosol radiative forcing, are laboratory analysis, experimental simulations and process studies [13]. In considering these particular activities, many aspects can be investigated [13]. For example, what is the influence of aerosol composition and its shape on the optical and radiative properties of the aerosol?

This question can be answered under the general scheme of a specific laboratory closure experiment like the one outlined in Fig. 3, in which some specific objectives can be pursued: (1) To investigate both the objectives can be pursued one outlined in Fig. 3 in which some specific experimentally and theoretically the influence of relative humidity (*RH*) on the optical properties of hygroscopic and hydrophobic aerosol particles; (2) to measure the optical properties of pure and homogenous as well as inhomogeneous aerosols and compare them with that obtained from theory; (3) to determine the influence of particle shape and orientation of these aerosols related to the direction of a light source (like a laser beam) irradiating them which, in turn, allow to decide the applicability of Mie theory to particular shapes and conditions. In pursuing point two, an aerosol optical measurement system (e.g. a cell-reciprocal integrating-nephelometer [14] - [15]) can be used. As part of this laboratory closure experiment a particle experimental characterization is included (Fig. 3). In this, before introducing the experimental particles into the optical measurement system, a generation procedure has to be achieved along with a SEM analysis in order to identify particle shape, dimensions and statistical size distribution of a particular aerosol.

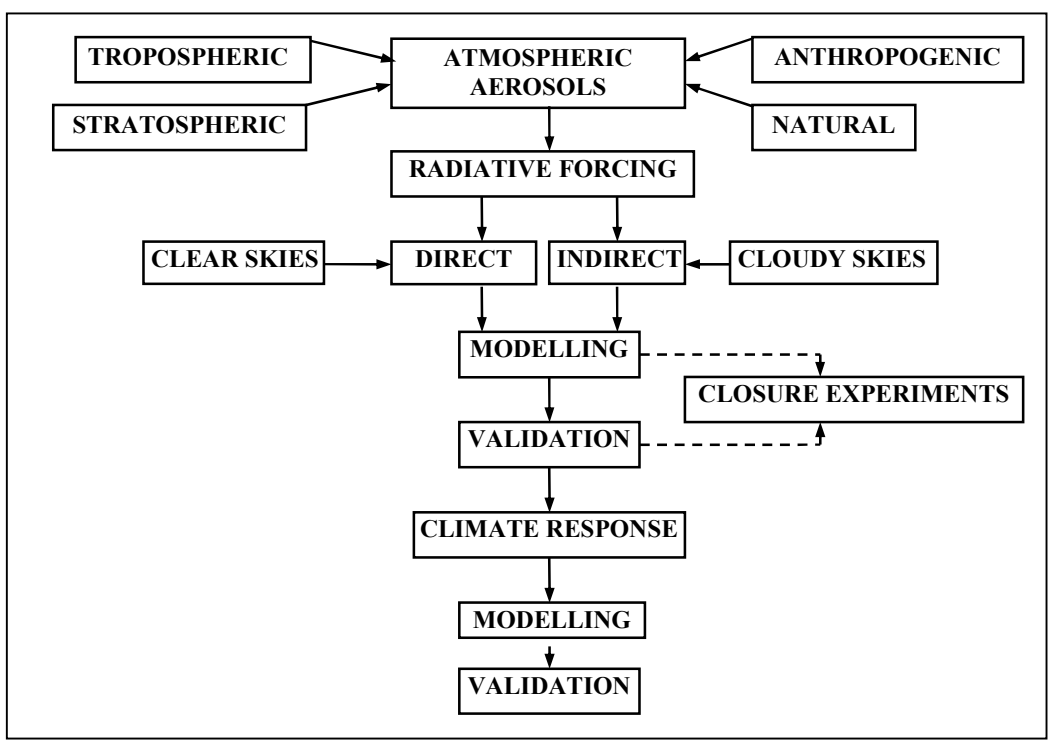

Fig. 2. Schematic pathway of the main investigation steps and its relations in atmospheric aerosol influences studies.

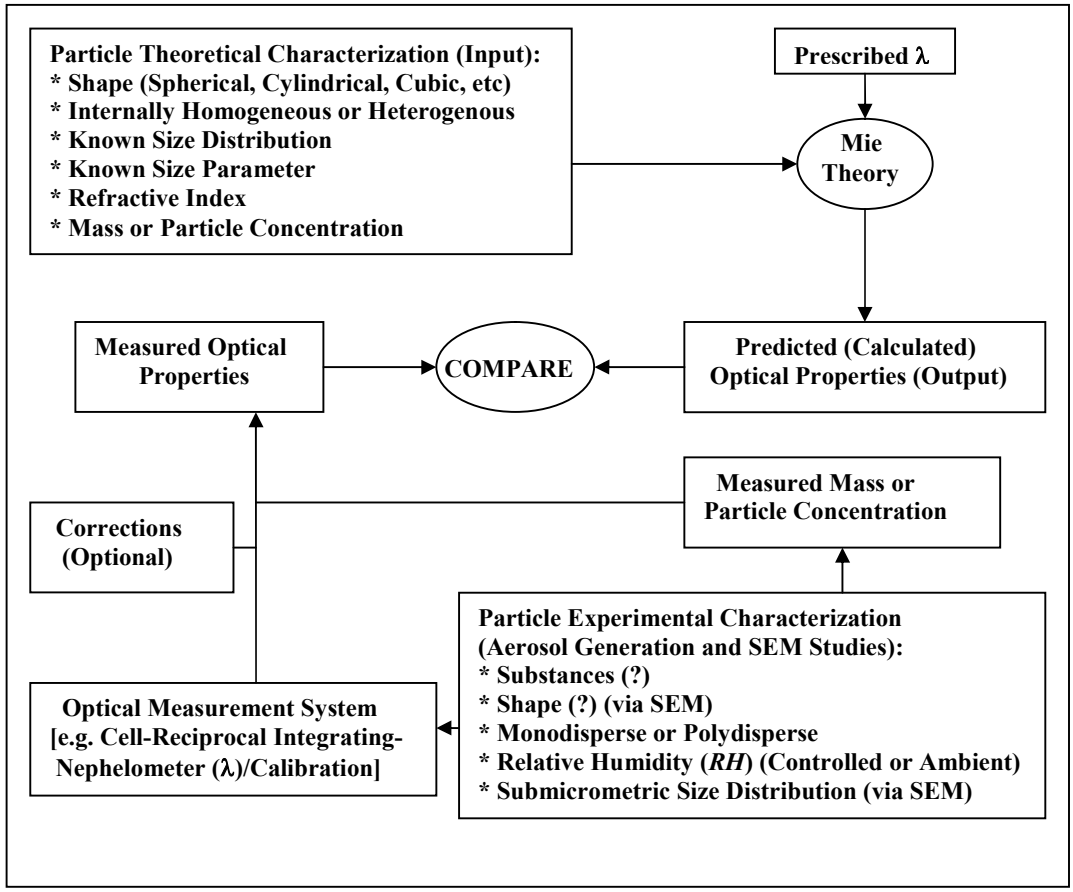

Fig. 3. Conceptual depiction of a general laboratory closure experiment to investigate the influence of aerosol composition and shape on the optical and radiative properties of a particular aerosol. λ referes to wavelength. Note the role played by the scanning electron microscopy (SEM) technique in determining the particle experimental characterization.

Specific Objectives

A particular case refers to the experimental generation and microphysical characterization, via SEM, of monodispersive cylindrical-shaped or fibrous-aerosol made up of substances having a high scattering of visible light. This is with the subsequent intention of knowing their measured radiative properties and comparing them with those estimated from the theory [16]. It can be emphasized that these properties, on the other hand, are fundamental in the estimation of radiative forcing associated with climate change response models (Fig. 2).

Thus, this work presents experimental results, obtained under the scheme described above, for the specific case of cylindrical-circular-shaped aerosol generated from polyform crystals of trimethylxantine (best known as caffeine) which is a substance with a high purity and guarantees a high scattering to visible light (Fig. 4).

Additionally, an aerosol like this is relatively reproducible in the laboratory [17] - [18]. Although caffeine is not normally present in the atmosphere, experimentally simulates very well a change in shape of an aerosol made up of a highly scattering substance[1]. At present it continues being used in other aerosol studies; for example, this chemical was recently used to generate particles which were subsequently used to develop and

[1] In a separate investigation [15], this was performed for the classical spherical shape, generated and characterized, via SEM, aerosol of pure ammonium sulfate which is a substance present as an atmospheric real component of polluted air [4] and also is a highly scattering substance.

characterize a single particle mass spectrometer aimed to carry out organic aerosol studies [19].

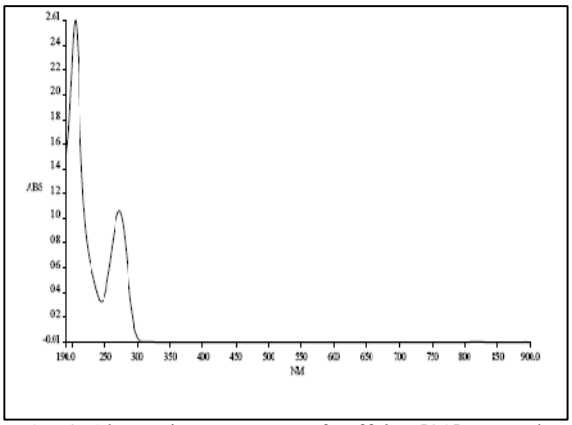

Fig. 4. Absorption spectrum of caffeine [20]. Note the absence of absorption in the visible or shortwave range.

AEROSOL GENERATION PROCEDURE

The most general classification of aerosol according to shape is that which divides them in regular and irregular particles. Irregular shapes are associated with chain aggregates and fractal clusters such as those found in smoke and fume. Regular shapes are commonly found in mists, fog and haze. The generation of aerosol of different shapes in the laboratory follows different procedures and techniques. Some shapes are more difficult to produce than others. For regular patterns, a variety of aerosol geometries have already been obtained experimentally, spherical particles being the most common one and easiest to generate. Due to their simple geometries, regular shapes have been and still are basic reference particle shapes to make exploratory studies in aerosol optical properties. In particular, the spherical shape is commonly used due to the fact that the mathematical theory describing their optical properties is well known and less complicated. Other regular shapes, however, with different symmetries, like prisms, cubes and flakes, have already begun to be used in theoretical and experimental comparisons [21] - [22].

A reference aerosol shape of atmospheric and environmental interest (air quality) is the cylindrical shape which is found in many artificial and natural airborne aerosol species. Among these are asbestos and mineral fibers. Organic fibers, such as wood and other cellulosic materials, are widely present in the environment, both from commercially produced materials as well as natural sources. From an aerosol behavior point of view, a variety of materials can be considered as fibers. The term "fiber" is applied to a diversity of particles having an elongated shape, i.e., one particle dimension significantly greater than the other. Baron [23] reviews the generation of cylindrical and fiber aerosol and other aspects related to the measurements of these, and state that fibers are more difficult to generate than compact particles because of their tendency to intertwine when in contact with each other (Fig. 8).

In this investigation the interest is focused on caffeine fibers because they constitute an important experimental reference aerosol of this shape and also, on the other hand, are relatively easy to reproduce in the laboratory.

Generation of Cylindrical-Shaped Aerosol

The generation of monodisperse aerosol fibres of caffeine, circular-cylindrical-shaped, has experimentally been studied by other authors [17]-[18]. To generate this type of aerosol in the laboratory, caffeine crystals at 99% purity produced by Aldrich-Chemie (Steinheim, Germany), were used following the method applied by the referred authors. The physical properties of these crystals are given in Table 1 [24]-[25].

As aerosol generator, a MAGE was used which is a condensation-type generator. It is claimed to be capable of producing highly monodisperse particles with a geometric standard deviation (GSD) close to 1.1, in that size ranged between about 0.2 to 8 μm geometric diameter [26].

In the MAGE a stream of nuclei is exposed to the vapor of a low-volatile liquid at an elevated temperature, and the controlled heterogeneous condensation of the vapor onto the nuclei results in the formation of the product aerosol. To describe briefly how the MAGE works, readers are referred to the schematic diagram in Fig. 5 that shows the gas flow path.

Table 1. Physical properties of pure caffeine crystals [24]-[25].

Chemical formula	$C_8H_{10}N_4O_2$ (1, 3, 7 trimethylxanthine)
Composition	C 49%; H 5.19%; N 28.85 %; O 16.48%
Molecular weight	194.19
Density (ρ)	1.23 g cm^3
Sublimation point	Between 180-200 ºC
Melting point	238 ºC* (anhydrous caffeine, at atmospheric pressure)
Description	A fine white crystalline powder
Crystals	Long, colorless and very fine hexagonal prims, needles, stubby prisms and rods, depending on temperature condition to form.
Optical properties	Bi-refrigents (-0.272), 1.707 perpendicular to length and 1.435 parallel to length (i.e. lenght fast)
Toxicity information	Suspected teratogen. Use gloves and approved dust mask. Wash thoroughly after contact.

(*) Bucknell [25] gives 236 ºC for the melting point.

As a first step, a collison atomizer or nebulizer is used to generate nuclei from an aqueous solution containing high purity sodium chloride (NaCl).

This atomizer is operated by a flow of filtered high-purity nitrogen at an applied pressure of 2.5 bar gauge and at the flow rate of 210 liters per hour. The droplets leaving the atomizer section are dried by passing them through a vertical tube containing silica gel desiccant. Then the gas flow is split into two parts: one flow going into the bubbler and the other one by-passing it. The bubbler is inside an oven which heats the substance to be aerosolized. The oven is set above the sublimation point of the substance to produce a vapor in the bubbler which is blown out by the nitrogen. In the re-heater section of the MAGE, the two nitrogen flows are mixed. There the vapor condenses onto the condensation nuclei, forming a monodisperse aerosol. In the MAGE, the particle size depends on the condensation nuclei concentration and the vapor density. The vapor concentration can be controlled by means of either the bubbler flow rate, or the oven temperature. More details on how to operate the MAGE to produce monodisperse aerosol, can be found in [17] - [18] and [26] - [27]. In this work a commercial version of the MAGE, manufactured by Lavoro e Ambiente (Bologna, Italy) was used during its operation in the laboratory of the Aerosol Research Group of the University of Essex (Colchester, England).

The collision nebulizer was filled with a certain quantity of weak dilute NaCl solution (i.e. 0.002% w/v) in order to produce condensation nuclei and evaporation. A known amount of caffeine was put into bubbler of the MAGE which was heated above its melting point, at 250 ºC, and then cooled at 200 ºC allowing a solid mass to form in the bottom of the bubbler. This ensured that nitrogen would not disperse this powder when it passes through the generator. Care had to be taken to avoid overfilling the bubbler with caffeine, blocking the bubbler tube perforation, and so, preventing the passage of nitrogen. Total nitrogen flow through the generator was set to 3.50 l min^{-1} by using the gas regulator in the supply line. However, this flow rate produced a very low flow maximum rate in the bubbler so that condensation of caffeine crystals in the output bubbler pipe was produced. In this manner, the caffeine aerosol generation was blocked in approximately three minutes as was found by Vaughan [17]. To overcome this problem, the gas regulator was removed from the supply line and the bubbler flow rate was set to 100 l min^{-1}. In addition, the re-heater section was also by-passed to abridge the aerosol output before condensation occurs. By controlling the oven temperature, between 200 – 240 ºC, different sizes of caffeine fibers were obtained.

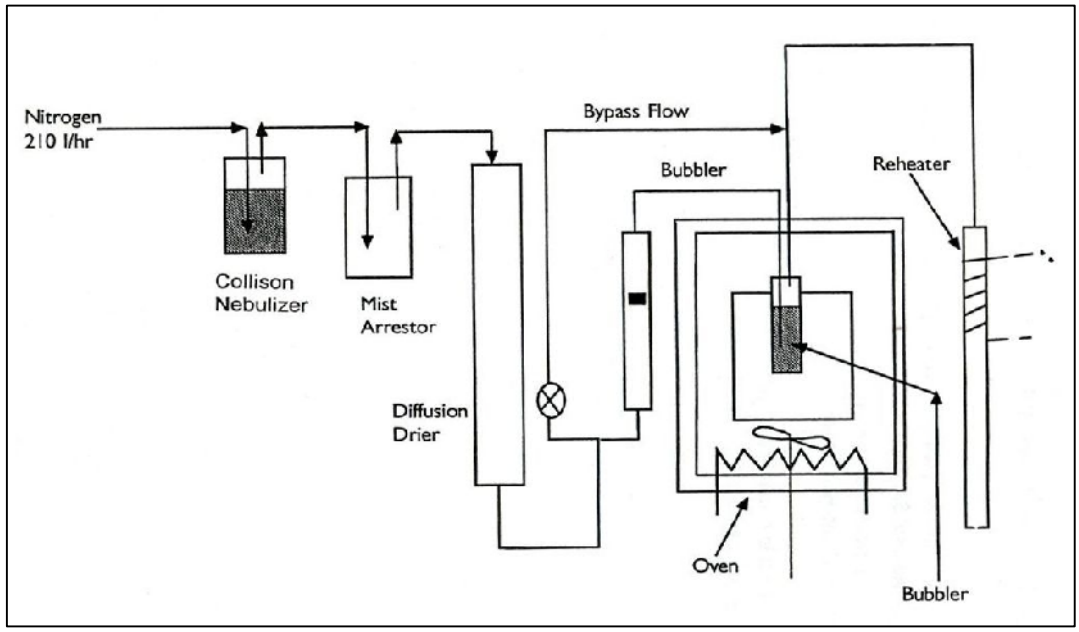

Fig. 5. Schematic diagram showing the gas flow path through different sections of the MAGE(reproduced from [18]).

Sampling

Samples of caffeine aerosol were collected by impaction by holding a SEM aluminum stub, covered by a filter, close to the generator output. The filters used to obtain the samples were porous-membrane types. The stubs were covered either by a Matricel porous-membrane filter (0.45 μm pore size) or by a Nucleopore porous-membrane filter (0.40 μm pore size). Particles were captured by the surface filter provided by its structure, principally by Brownian motion and inertial impaction mechanisms. In general, the pressure drop and particle collection efficiency are very high, even for particles significantly smaller than the characteristic pore size [28]. The aim of this sampling is, of course, to obtain specimens that represent the population to be studied. Aerosol obtained directly from the generator must not be considered, *a priori*, as exactly the same after passing through the transportation system including the drier or even within the optical measurement system. The original population can be affected and altered by sampling efficiency, internal losses, and sensor response of the optical system, and/or data processing [29].

Modifications could occur in the aerosol while it is taken downstream, for example, to the aerosol closed cell of the optical measurement system [14] - [15], via drier and ducts which, in turn, are variable in length, diameter and curvature. Predominantly large particles are lost by impaction [30]. Possible aerosol modifications during its transportation from the generator up to the aerosol cell or chamber of the optical measurement system [14] - [15] could be a subject of further investigation. To do this, samples also should be taken at the drier outlet and at the cell outlet.

SEM PHYSICAL CHARACTERIZATION OF THE PARTICLES

In the context considered so far, the parameters to be controlled in an experiment like this are size and shape of aerosol made up of a particular substance. Both aspects are closely linked to the influence which may have problems of air pollution with direct or indirect, impact on health, climate and, in general, the quality of air. Also these aspects are very important since light scattering depends not only on the substance chosen but also on the aerosol geometry. And in this case, the scanning electron microscopy (SEM) plays a crucial and essential role as illustrated in Fig. 3.

The generation of aerosol, as outlined in the preceding section, of different shapes is the first step; then, a SEM

analysis follows. The latter provides an insight on the aerosol morphology in order to determine what kind of shape the aerosol possesses. Next a second SEM analysis is necessary to determine the size distribution which, in turn, provides knowledge of the monodispersity or polydispersity of the aerosol sample. To attain these goals laboratory aerosol generation is made at different levels of purity or internal mixture, that is to say, at a certain degree of mixing composition. Apart from pure aerosol, that can eventually be used as reference particles, many aerosols consist of internal mixtures. Among these are mixtures with water vapor, hydrocarbons or surfactants.

SEM Analysis of Aerosol Morphology (Shape)

Figure 6 shows a SEM image of caffeine aerosol generated by the MAGE apparatus. The sample scanned turned out to be similar in shape to those found by Vaughan [17] and Baldwin [18]. Vaughan called it "Christmas cracker" due to overall appearance. This type of fiber-aerosol was specifically obtained at 210 ºC with a rate of 101 l h^{-1} (bubbler flowmeter), in the nitrogen supply line. In this case the aerosol appeared to be small crystals with almost perfect straight cylinders but with hexagonal, pentagonal or tetragonal cross-section at the ends.

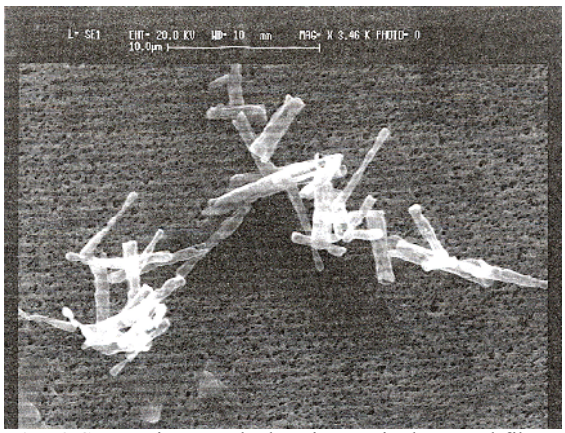

Fig. 6. SEM micrograph showing typical aerosol fibers of caffeine obtained with the MAGE. The bar represents 10.0 µm.

In addition, as confirmed by SEM examination, the crystals ends were clearly hollow regardless the size of the aerosol. Similar results were obtained by Baldwin [18].

Figure 7 shows a close-up of one of these "Christmas crackers". It is important to not the similarities between the caffeine aerosol obtained in this work and those obtained by the cited authors.

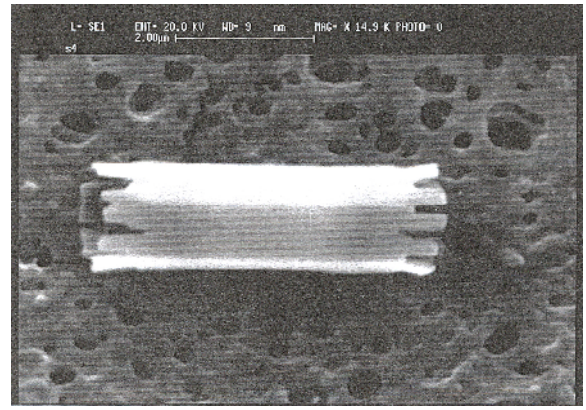

Fig. 7. SEM micrograph showing a close-up of a caffeine aerosol fiber from the MAGE. Note the shape of "Christmas cracker" of the fiber. The bar represents 2.0 µm.

Alternatively, another sample was taken by gravitational settling onto an ordinary glass slide within an aerosol cell or chamber. It was examined extensively by SEM micrographs, showing a fiber-shape but not very similar to that of "Christmas cracker" obtained previously. Figure 8 presents an image of a particular area of the general sample.

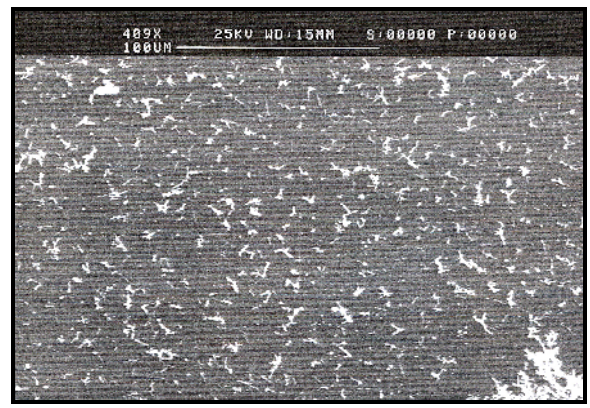

Fig. 8. SEM image of aerosol fibers of caffeine generated with the MAGE for optical measurement purposes. The bar represents 100 µm.

Table 2. Statistical parameters for samples of aerosol fibers of caffeine obtained from the MAGE (sample sizes = 100/160)

Parameter	Mean (μm)	Arithmetic Standard Deviation (μm)	Geometric Standard Deviation	Monodispersity
Diameter (D_f)	1.36/0.71	0.24/0.22	1.21/1.35	Good
Length	4.96/3.64	1.80/1.32	1.24/1.48	Dependable

SEM Analysis of Aerosol Dimensions (Size)

To explore the basic information contained in the cylindrical-circular samples of the caffeine aerosol population, measurements of the length and diameter were performed for each specimen. Three values of the diameter were taken across, and two values of the length along were taken on the fiber. The length average was taken based on one measurement assuming the filled part of each particle (minimum length), that is to say, excluding the hollow end parts, and another one including these parts (maximum length) (Fig. 9).

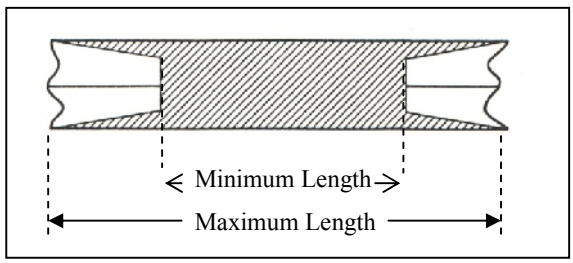

Fig. 9. Idealized section of a cylindrical-shaped aerosol of caffeine, based on SEM examination.

Then averages over these parameter values were made to represent appropriately the geometrical dimensions of each fiber. For the first sample hundred values were obtained and from this average were calculated, for the size of caffeine sample. Results of the basic statistical size information for the first caffeine aerosol sample obtained from the MAGE are shown in Table 2.

The average figures and standard deviations (SDs) are significantly close to those published by Vaughan [17] and Baldwin [18]. In reference [17] the author, employing three different MAGE samples of cylindrical-circular aerosol of caffeine, obtained mean diameters in the interval of 0.64 – 1.99 μm, SDs between 0.07 and 0.20 μm, and geometric standard deviations (GSDs) between 1.08 and 1.12. The corresponding mean lengths, SDs, and GSDs were, between 5.55 and 8.29 μm, 0.54 and 0.78 μm and, 1.09 and 1.12, respectively. In reference [18] the author, working with five different MAGE samples, at different temperatures, obtained mean diameters between 0.5366 and 1.107 μm. Some of the corresponding lengths were, for example, 1.243 μm (at 220 ºC) and 5.65 μm (at 230 ºC), with SDs of 0.41 μm and 1 μm, respectively, etc.

In comparing the results given in Table 2, it can be observed that the fibers of lager sample (160) turned out to be 52% thinner in width but 73.4% shorter in length. The monodispersity in length turned out to be not very good as in diameter; yet this latter is better in comparison.

Therefore, it can be seen that first statistical analyzed caffeine sample, representing the caffeine aerosol population from the MAGE, is good to account for the statistical representation of the fiber diameter, but to a lesser extent for its length. Therefore, it is highly recommended not only to increase the size of the sample but also the number of measurements of the maximum length, per fiber, to assess properly the statistical characteristics. It can be noted that a morphological detail of these fibers is the irregular border at their ends which impede a good determination of the maximum length.

Finally, pertaining to the evaluation of the aspect ratio, β (= maximum length/minimum length), of these fibers, a value of 3.65 and 5.13 were found (Table 3), on the average, for each sample indicating that they were

indeed distinctly elongated crystals, in accordance with Vaughan [17].

Aerodynamic Particle Size (Diameter)

The previous SEM analysis of aerosol shape and dimension yield data which can be used for additional physical characterization of the particles. Thus, an estimation of the aerodynamics particle size, via aerodynamic diameter (D_a), could be made. It can be recalled that particles of equal aerodynamic size are very important because [31]: (1) They tend to deposit in similar locations of the human respiratory system. (2) They have similar airborne lifetimes in the atmosphere and in most other aerosol system. (3) They have similar probabilities of penetrating a filter, a cyclone, and other particulate removal devices. (4) They have similar probabilities of entering into a particle sampling system. (5) They have similar probabilities of penetrating a pipe, tube, duct, or channel.

In this case, the theoretical aerodynamic diameter derived by Cox [32] for the motion of a fluid over a fiber, was applied. The formulae that this author developed for the diameter were investigated experimentally by Griffiths and Vaugham [33] and found to describe the aerodynamics diameter of a fiber correctly. The formulae are:

$$D_a^{\perp} = D_f\,[(9\rho/8\rho_o)(\ln 2\beta + 0.193)]^{1/2} \qquad (1)$$

for motion perpendicular to the fiber's major axis, and by:

$$D_a^{\parallel} = D_f\,[(9\rho/4\rho_o)(\ln 2\beta + 0.81)]^{1/2} \qquad (2)$$

for motion parallel to the fiber's major axis, where β is the fiber's aspect ratio and D_f is the average geometrical diameter (Table 2) of the aerosol sample previously estimated in the SEM analysis for the aerosol dimensions; ρ is the substance's density (Table 1) and ρ_o is unit density. With data of Table 1 and 2, each aerodynamic diameter, $D_a^{\perp}$ and $D_a^{\parallel}$, was calculated. The results are given in Table 3.

Table 3. Aerodynamic diameters of caffeine aerosol fibers, estimated from Cox's formulation.

SAMPLE SIZE	β	$D_a^{\perp}$ (μm)	$D_a^{\parallel}$ (μm)
100 specimens	3.65	1.23	1.28
160 specimens	5.13	2.54	2.78

Vaugham [17], for one of his sample, obtained a value of 2.09 μm for $D_a^{\perp}$.

COMPLEMENTARY CHARACTERIZATION

Once the SEM characterization has been done the aerosol, as next step, is driven from the outlet generator to a settling cell or chamber, which is part of the optical measurement system (Fig. 3). In these measurements of the aerosol mass concentration and ambient *RH* within the chamber were made. The results are presented in Fig. 10 and Fig. 11, respectively.

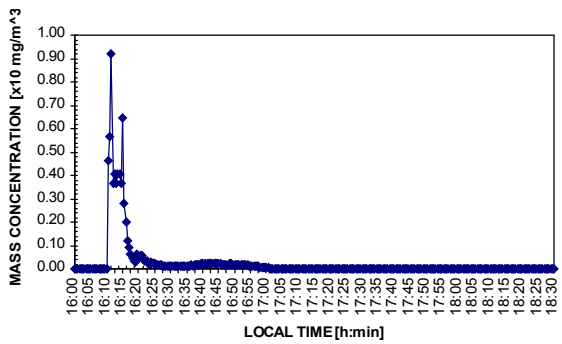

Fig. 10. Mass concentration variation of the aerosol fibers of caffeine randomly orientated. This graph indicates that the aerosol settles down almost completely in less than an hour within the cell.

It is interesting to note that this aerosol settles down very quickly in comparison with that of spherical shape made up of ammonium sulfate [15], and the strong reduction in mass concentration, in less than one hour, is different from that corresponding to an exponential decay. This has a very important implication for the estimation of the optical properties, as will be shown in a follow-up paper. The instrument used to make this measurement was an airborne particulate monitor (APM) Casella, model AMS 950IS .

The *RH* (%) within the cell is presented in Fig. 11 in order to show that the aerosol is not hygroscopic.

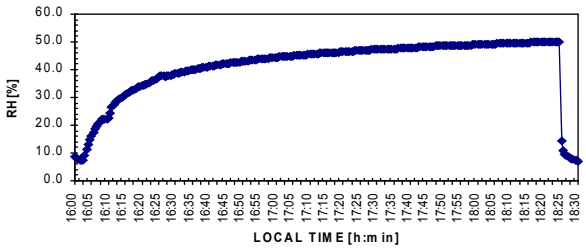

Fig. 11. Variation of the *RH* (%) within the cell just before pumping of the caffeine aerosol, and after the purge with clean and dry air.

According to this figure, after the initial purge of the cell (described elsewhere [15]) with dry clean air, to introduce the aerosol, the *RH* goes up steadily towards the ambient value until the cell is purged again. On the contrary, if the aerosol were to be hygroscopic, a reduction of the *RH* would be noticed as in the case of ammonium sulfate [15]. The *RH* was monitored with a probe VH-L type (Vaisal, Finland).

CONCLUSIONS

The aerosol SEM morphological analysis and aspects of characterization have shown that it is possible to generate cylindrical-shaped aerosol, made up of 1, 3, 7 trimethylxanthine (caffeine) with dimension in the submicrometric range. The present work has confirmed that the MAGE, under crucial conditions, is capable of producing aerosol similar to those reported by Vaugham [17] y Baldwin [18], known as "Christmas crackers".

The size statistical analysis of caffeine aerosol fibers samples reveals that it is to some extent monodispersive in diameter. However, albeit the result for the length is quite different from that expected for a monodisperse sample[2], this does not mean that the MAGE is incapable of generating monodisperse caffeine aerosol at all like those generated by other authors [17] - [18]. Simply the size of the sample chosen was not enough to determine whether or not it is monodisperse in length. However, the reliability in the accuracy of the research previously carried out by these authors, it is assumed that the MAGE is an appropriate monodisperse aerosol generator to obtain caffeine fibers which can subsequently be optically characterized to assess their radiative properties (Fig. 3).

The samples examined in this analysis were obtained under conditions of low levels of *RH*. Therefore, they can be considered as dry samples. For more realistic cases in which the aerosol contains variable content of *RH*, complicated physical processes take place that can alter the composition, shape and size distribution of the aerosol.

It is finally concluded that SEM aerosol examination can be applied, in combination with an optical measurement system, to obtain experimentally the radiative properties of standard airborne particles of different shapes, sizes and substances for further atmospheric and environmental studies related to climate changes and air quality.

In this sense, in a subsequent paper, the results of the optical characterization of these fibers will be presented, following the conceptual depiction illustrated in Fig. 3, in which an optical measurement system, based on an instrument called cell-reciprocal integrating-nephelometer [14], was used.

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[2] The definition of monodispersity suggested by Fuchs and Sutugin [34] provides a guide for an evaluation of the monodispersity level of a specific particle size distribution. If the coefficient of variation (ratio of SD to the mean) of the distribution size is less tha 0.2 (20%), the aerosol may be satisfactorily described as having "practical monodispersity". For a log-normal distribution, this is equivalent to a GSD < 1.2. Although aerosols whose GSD varying between 1.12 and 1.13 are not strictly monodisperse, they can still be useful for the assessment of aerosol behavior in situations where characteristic being studied is not highly dependent on particle size [27].

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