On the Optimality Assessment of Nanoparticle Size Spectrometry and Its Association to the Entropy Concept

A. Shaygani, R. Saifi, M. S. Saidi, M. Sani

Abstract**—**Particle size distribution, the most important characteristics of aerosols, is obtained through electrical characterization techniques. The dynamics of charged nanoparticles under the influence of electric field in Electrical Mobility Spectrometer (EMS) reveals the size distribution of these particles. The accuracy of this measurement is influenced by flow conditions, geometry, electric field and particle charging process, therefore by the transfer function (transfer matrix) of the instrument. In this work, a wire-cylinder corona charger was designed and the combined field-diffusion charging process of injected poly-disperse aerosol particles was numerically simulated as a prerequisite for the study of a multichannel EMS. The result, a cloud of particles with no uniform charge distribution, was introduced to the EMS. The flow pattern and electric field in the EMS were simulated using Computational Fluid Dynamics (CFD) to obtain particle trajectories in the device and therefore to calculate the reported signal by each electrometer. According to the output signals (resulted from bombardment of particles and transferring their charges as currents), we proposed a modification to the size of detecting rings (which are connected to electrometers) in order to evaluate particle size distributions more accurately. Based on the capability of the system to transfer information contents about size distribution of the injected particles, we proposed a benchmark for the assessment of optimality of the design. This method applies the concept of Von Neumann entropy and borrows the definition of entropy from information theory (Shannon entropy) to measure optimality. Entropy, according to the Shannon entropy, is the "average amount of information contained in an event, sample or character extracted from a data stream". Evaluating the responses (signals) which were obtained via various configurations of detecting rings, the best configuration which gave the best predictions about the size distributions of injected particles, was the modified configuration. It was also the one that had the maximum amount of entropy. A reasonable consistency was also observed between the accuracy of the predictions and the entropy content of each configuration. In this method, entropy is extracted from the transfer matrix of the instrument for each configuration. Ultimately, various clouds of particles were introduced to the simulations and predicted size distributions were compared to the exact size distributions.

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I. Introduction

AEROSOL technology is underlying a variety of fields such as nanotechnology, pollution monitoring, air quality measurements, combustion and engine exhaust analysis, inhalation toxicology, medical treatments, filtering, and powder coating [1]. To all mentioned applications, measurement capabilities are crucial. Among the methods proposed for the analysis and classification of nanoparticles, the method which is based on electrical mobility, is the most prevalent and widely used one. The method has been in use in many instruments for classifying nanoparticles since 1965 when Whitby and Clark offered the first practical analyzer known as Whitby Aerosol Analyzer [2] based on electrical mobility. Electrical mobility is the ability of charged particles to move through a medium in response to an electric field that is pulling them. In order to classify aerosols based on electrical mobility, sufficient amount of charge must be induced on each individual particle. Passing them through electric field, their dynamics and motions which depend on external forces applied on the particles reveal the size distribution. These forces include drag, gravitational, Brownian and electrical forces.

There are several mechanisms by which particles gain the required charge [3]. Among all charging mechanisms, charging by ion collisions has the ability to produce considerable and sufficient number of charged particles. When charging mechanism occurs due to random collisions of ions and particles in the absence of very strong electric field, the process is called diffusion charging. This is the result of Brownian motion. In the presence of strong electric field, charging by unipolar ions is called field charging [4]. The field and diffusion charging mechanisms require high concentrations of ions and the only method which could be applied to generate ions at high enough concentration is corona discharge. Corona chargers are widely used in commercial aerosol classification instruments such as Electrical Mobility Spectrometer, and Electrical Aerosol Spectrometer [5].

Schematic layout of an EMS is shown in Fig. 1. Aerosol which contains charged nanoparticles passes through the short column of EMS, made of two cylindrical electrodes. An electric field is created by maintaining the inner electrode at a high voltage (with the polarity opposite to the corona voltage) whereas the outer electrode is grounded. A set of electrode rings are laid along the outer chassis. They are separated from each other by allowing a gap in between. Each electrode is connected to an electrometer. When charged particles are trapped to the electrode rings due to the influence of electric field between the two cylindrical electrodes, the electrical currents are delivered to electrometers to indicate the size distribution.

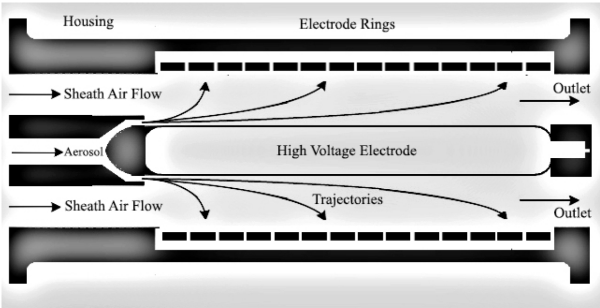

Fig. 1 Schematic Layout of the EMS

Since the charging process is an uncertain phenomenon resulted from random collisions and Brownian motions, the induced charge on particles with the same diameter is not uniform. Having a nonuniform charge distribution on the same-sized particles causes them to land along the passage due to the difference in their mobilites and so spreads the reported signals (currents) over the set of electrometers. On the other hand, particles with different size may trap on the same place due to their nonuniform charge distributions and causing them to be identified by the same electrometer. Therefore the reported signal could not differentiate between large particles having more charges and smaller ones having less. This makes impossible to measure size distribution without post-processing the signals.

In this study, a wire-cylinder corona charger is simulated and numerical results of space charge density and electric field were applied to simulate the field-diffusion charging process of aerosols passing through the charger. Then the charged particles were fed into the CFD simulation of EMS. Modeling steady state fluid flow considering Brownian motion and neglecting gravitational effect, particle trajectories were estimated in the spectrometer. The gravitational force is negligible for submicron particles. The electrical currents delivered to electrometers were measured by tracing the particles and assuming all the charges induced on trapped particles were transferred (as currents) to electrode rings. According to the output signals, a modification was applied to the size of the rings, in order to evaluate particle size distributions more accurately.

We redefined the accuracy of the measured data by a system as *capability of the system to capture and transfer information contents about the quantity under the measurement* (here, the particle size distribution). Therefore, the more accurate the size distribution is, the more information can be transferred by the transfer function (transfer matrix) of the system (EMS instrument). The process of finding the optimal design is somehow reverse to the procedure used to reduce the dimensionality of large data sets common in image processing for compression. In the image compression techniques, application of singular value decomposition (SVD) is prevalent. It is to find largest singular values and eliminate the others to re-express the compressed image with more dominant singular values. Reducing the capacity, dropping the image quality is inevitable. In the evaluation of the optimal design, by contrast, estimating the entropy after calculating SVD of the transfer matrix, the most informative transfer matrix (having higher entropy) must be of the optimal design.

Utilizing the benchmark proposed for the assessment of optimality of the EMS design, six EMS configurations (including the modified design) were checked and we found that the modified design also had the most informative transfer matrix and higher entropy. Correspondingly, few clouds of particles were introduced to the simulations and measured size distributions were compared to the actual size distributions.

II. Simulation of the Charger and Particle Charging Process

Corona occurs when a high potential difference is applied between at least two electrodes with various radii of curvatures including dielectric insulator in-between. The electrode with the sharp edges or smaller radius of curvature is called corona electrode. The blunt electrode with much larger radius of curvature is usually grounded [6]. Conservation of electric charge (current continuity) or charge transport equation combined with basic postulates of electrostatics [7] describes the mathematical model of corona discharge phenomenon. Hence, the coupled equations describing single species corona discharge, decoupled from fluid flow equations, were solved to describe ion production in the aerosol charger of this study. Finding space charge density and electric field, charge distribution on particles in the diameter range from 50 nm to 500 nm were obtained (assuming the combined Field-diffusion charging mechanism) for further simulations.

III. Fluid Flow Simulation in the EMS, Particle Dynamics and Trajectories

Aerosol transport inside the analyzer (EMS) depends on the flow characteristics and applied electric field. A cloud of poly-disperse particles would trap on each electrode ring, depending on the applied voltage, aerosol flow rate and the charge carried by particles in all diameters. Once particle charge distributions for all diameters were obtained by simulation of the charger, fluid flow field inside the EMS was studied using computational fluid dynamics to simulate the flow pattern, electric field and particle trajectories in the device numerically. This gives the signals reported by each electrometer by which size distribution of the injected particles can be predicted. To describe behavior of the fluid flow inside the device Navier-Stokes equation and Continuity equation were solved numerically. Since the fluid is usually at low temperatures and almost at atmospheric pressures, furthermore its velocity is extremely below the speed of sound, the flow was assumed to be incompressible, steady and laminar. For the prediction of particle motions and tracking aerosol particles in steady state condition, particle tracking was performed using Lagrangian approach. In this case the drag force, the electric field force and the effect of Brownian motion needed to be considered [8].

For the fluid flow simulation in the EMS, diameters of the inner and outer electrodes was 20 mm and 50 mm respectively, outer diameter of the aerosol inlet was 24 mm and the active length of the sensing passage was 180 mm from the entrance of the aerosol, where the electrode rings were arranged along the passage. It is illustrated as the red rectangle in Fig. 2. The aerosol flow rate at the entrance was set to be 1 lpm and sheath air flow rate was 10 lpm. The electric field inside the EMS was calculated separately for the estimation of particle trajectories. The inner electrode was set to 2kV and the outer electrode (cylinder) was grounded. As an example, Fig. 2 shows trajectories for 50 nm, 200 nm and 500 nm particles (released from aerosol inlet and trapped to the above rings); highlighted according to their fractions with respect to the amount of charge they carry.

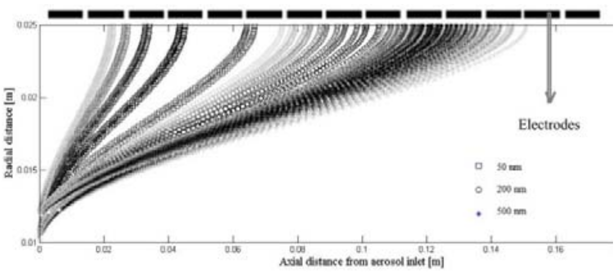

Fig. 2 Trajectories for 50 nm, 200 nm, and 500 nm particles, highlighted according to their fractions with respect to charge

IV. Calibration of the Instrument and Obtaining Transfer Matrix

For the calibration of the instrument, a poly-disperse (in size) calibrating aerosol was considered and the size distribution was discretized into J (e.g., 41) mono disperse classes of diameter d_j and treat each class independently. For each size class charge distribution was computed. After simulating the EMS instrument and tracing particles, calibrating response for each size class d_j is recorded as a vector I_j^c. Since the particles in size class d_j have different charges they may hit different electrometers. Therefore for a device with K electrometers, the signal I_j^c is a vector of length K containing responses of all electrometers to the calibrating concentration for size d_j. Gathering I_j^c in a matrix called transfer matrix F, we have:

$$F = [I_1^c \quad \cdots \quad I_J^c] = \begin{bmatrix} i_{11}^c & \cdots & i_{1J}^c \\ \vdots & \ddots & \vdots \\ i_{K1}^c & \cdots & i_{KJ}^c \end{bmatrix} \qquad (1)$$

There is a linear relationship between the reported currents and the concentrations (in each class d_j). Since the number of charges transferred to the electrode is magnified with the same factor as the number of particles, for any other concentrations of poly-disperse particles, knowing F, size distribution function can be obtained by solving an under-determined system of equations from the data reported by set of electrometers as vector I. Solving the following system of equations to find A (matrix of unknown size distribution parameters), size distribution function will be obtained based on the size distribution of calibrating aerosol.

$$\begin{bmatrix} i_{11}^c & \cdots & i_{1J}^c \\ \vdots & \ddots & \vdots \\ i_{K1}^c & \cdots & i_{KJ}^c \end{bmatrix} . \begin{bmatrix} a_1 \\ \vdots \\ a_J \end{bmatrix} = \begin{bmatrix} i_1 \\ \vdots \\ i_J \end{bmatrix} \rightarrow F.A = I \qquad (2)$$

V. Post-processing the EMS Signals for Size Distribution Deciphering

As described in previous section, having F, size distribution of injected aerosol can be predicted by solving the under-determined system of (2) for A. In this case, the problem is to seek a solution A that minimizes the energy of the error and has a minimum norm that is a constrained optimization problem of Nonnegative Linear Least Square Method (NLLS) with a cost function as:

$$Cost = \|I - F.A\|_2^2 + \lambda \|D.A\|_2^2 \qquad (3)$$

The second order difference of A is presented in the second term. Minimizing the second term guarantees a smooth size distribution. Here, λ is a positive real number as regularization factor and D is a sparse matrix defined as:

$$D = \begin{bmatrix} 1 & -2 & 1 & 0 & \cdots & 0 \\ 0 & \ddots & \ddots & \ddots & \ddots & 0 \\ 0 & \cdots & 0 & 1 & -2 & 1 \end{bmatrix}_{J-2\times J} \qquad (4)$$

Taking the derivative of the cost function with respect to A, setting it to zero, plugging into (2) and performing some manipulations and simplifications gives:

$$A_{est} = (F^T F + \lambda D^T D)^{-1} F^T I \qquad (5)$$

Therefore, size distribution will be obtained by the above equation.

VI. Electrical Optimization of the EMS

As described earlier, charging process is an uncertain phenomenon followed from random collisions and Brownian motions. Having a nonuniform charge distribution causes particles to land along the passage due to the difference in their mobilites. This spreads the reported signals (currents) throughout the set of electrometers. There are regions along the EMS cylindrical passage (and on the electrode rings) that targeted by charged particles the most. Concentrating the rings in the most targeted areas increases the accuracy of the measurements and sensitivity of the device, by capturing more information about the size distribution in these regions. To find the most targeted areas along the EMS passage, thousands of particles were charged and then their trajectories were estimated in the spectrometer to obtain regions with higher delivered currents by the trapped charged particles. Altering the length of the rings by concentrating them in the regions where particles target the most in order to receive almost equal currents from those released particles, optimizes the of EMS. This obviously changes the transfer matrix F of the instrument. According to the previous sections, size distribution measurement ends up by solving an under-determined system of equations. Having a higher ranked matrix in this system reduces dimension of the null-space and lowers the uncertainties of the answer. This provides a more accurate answer to the system. Optimizing the length of the rings by the proposed method increased the rank of the transfer matrix F to the maximum possible value which is equal to the number of electrometers or rows K in matrix F. After finding particle trajectories and calculating the currents transferred by charged particles to electrometers, length of the electrode rings was altered to concentrate them in the most targeted regions and to capture currents more accurately. The following figure illustrates the length of 14 electrode rings for two configurations, the first one, an EMS with equal-sized rings and the later, an EMS with optimized-length rings.

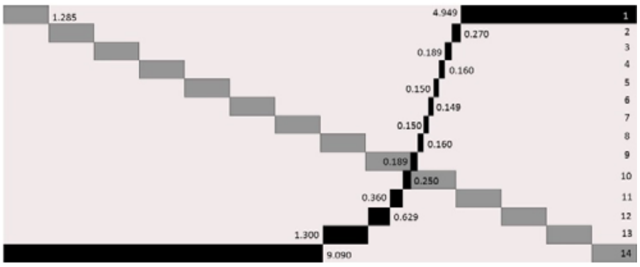

Fig. 3 Comparison of the lengths of 14 electrode rings of the first (Grey) and the optimized (Black) EMS in (mm)

VII. The Von Neumann Entropy and its Associations to the Optimal Design

The Von Neumann entropy, in statistical quantum mechanics, is the extension of classical entropy concepts such as Gibbs entropy and Shannon entropy to the field of quantum mechanics. Considering a system described by a density matrix ρ, the von Neumann entropy (H) of the system is defined by [9], [10]:

$$H = -tr(\rho \ln \rho) = -\sum_j^n \varphi_j \ln \varphi_j \tag{6}$$

where tr denotes the trace and the density matrix ρ is a positive semi-definite operator, which can be written in terms of its n orthonormal eigenvectors V_j and scalars φ_j as:

$$\rho = \sum_j^n \varphi_j \left|V_j\right\rangle\left\langle V_j\right| \ , \sum \varphi_j = 1, \varphi_j > 0 \tag{7}$$

We borrowed the definition of entropy from information theory to apply it for the assessment of optimality of the EMS design. Entropy according to the Shannon entropy, is the average amount of information contained in an event, sample or character extracted from a data stream [11]. By this definition, the density matrix ρ was considered as the modified matrix of singular values of F. The singular value decomposition (SVD) of a matrix F is in the form:

$$F = USV^T \tag{8}$$

where the columns of U are left singular vectors of F or orthonormal eigenvectors of FF^T, the columns of V are right singular vectors of F or orthonormal eigenvectors of F^TF and S is a diagonal matrix contained n singular values of F or square roots of eigenvalues (λ_i) of F^TF in descending order. Therefore we defined ρ as:

$$\rho = \frac{S}{\sum_1^n \sqrt{\lambda_i}} = \begin{bmatrix} \sqrt{\lambda_1}/\sum\sqrt{\lambda_i} & \cdots & 0 \\ \vdots & \ddots & \vdots \\ 0 & \cdots & \sqrt{\lambda_n}/\sum\sqrt{\lambda_i} \end{bmatrix} \tag{9}$$

Consequently, entropy as information content of a matrix F can be estimated by applying (9) into (6) as:

$$H_F = -tr(\rho \ln \rho) = -\sum_{j=1}^n \frac{\sqrt{\lambda_j}}{\sum\sqrt{\lambda_i}} \ln \frac{\sqrt{\lambda_j}}{\sum\sqrt{\lambda_i}} \tag{10}$$

This gives a benchmark for assessment of the optimality of the EMS design. By the above definition, an optimal design provides more accurate size distribution prediction which is identical to the fact that its transfer matrix F contains more information or has higher entropy $H_{(F)}$.

VIII. Results and Discussions

The accuracy of the estimated size distribution depends directly on the transfer matrix which indeed depends on the geometry and other specifications such as charging process. In other words, the more accurate size obtained by a transfer matrix with higher rank. This means that the transfer matrix is more informative, or it transfers more information about the size distribution. To compare the two configurations in transferring information about size, for both cases transfer matrices were calculated after particle trajectories. The square roots of eigenvalues of the covariance of the transfer matrices (F^TF) were used as a benchmark for informativeness of the two configurations. As is shown in Fig. 4, the first nine principal components (eigenvectors) account for almost 100% of the variance in the first geometry and 80% of the variance in the optimized one. This means that only nine electrometers are informative in the first geometry and the five others transfer almost no information about the size distribution. Furthermore, only five electrometers in the first configuration account for the majority of the information (more than 80% of the variance) compared to the nine electrometers in the optimized one. For the EMS used in this study with 14 electrometers and 451 diameter classes from 50 nm to 500 nm, the transfer matrix F was a 14×451 dimensional matrix. The transfer matrix obtained for the optimized EMS was a 14 ranked matrix. The transfer matrix obtained for the first configuration was an 11 ranked matrix (contained 3 linear dependent rows) whereas 2 other rows of the matrix where very close to linear dependency (singular values on the order of 10^{-10}).

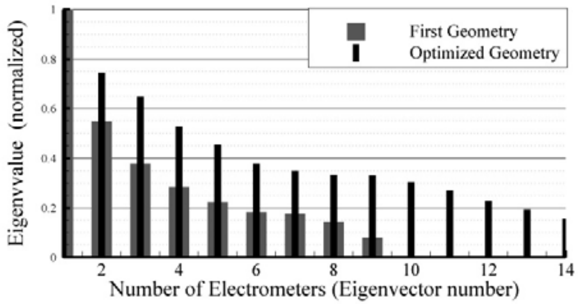

Fig. 4 Comparison of the first and the optimized configurations in sorted square roots of eigenvalues (eigenspectrum) of the corresponded ($F^{T}F$)

The amount of information latent in transfer matrices for six configurations (including the two, mentioned in Fig. 3) calculated using (10) are depicted in Fig 5. The information content (entropy) obtained for the optimized configuration was higher compared to the others as expected. We observed that those configurations having more concentrated detectors in the regions with more electron bombardments (from trapped particles) had higher entropies and vice-versa.

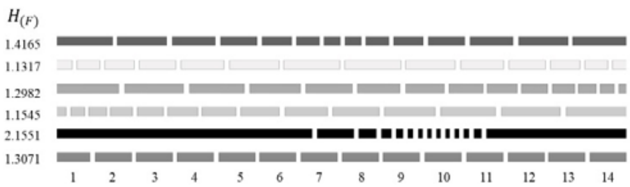

Fig. 5 Six configurations of electrode rings colored by entropy content $H_{(F)}$

Using the data obtained from electrical mobility spectrometer, several clouds of particles with different size distribution functions were passed through the corona charger and then classified using the EMS with the two configurations (Optimized configuration and the first one which had a set of equal-sized rings). The results are shown in Fig. 6. It indicated that the first geometry failed to predict distributions accurately, whereas Estimation of size distribution with the optimized EMS was close to the actual size distributions.

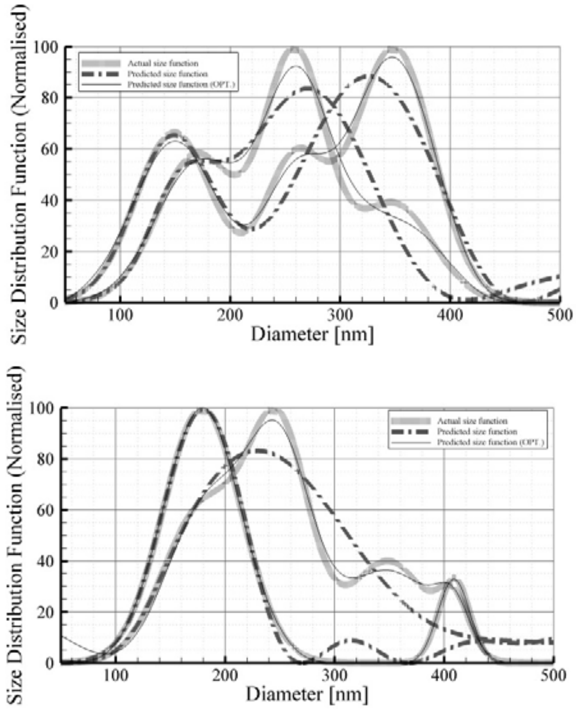

Fig. 6 Six Size distributions predicted using the two EMS configurations applying NLLS

IX. Conclusions

A method is reported in this study to optimize the EMS instrument by concentrating the detecting electrodes in the most targeted regions along the aerosol pathway to capture signals more accurately and measure size distribution of particles more precisely. Also the association of the optimal design with the definition of Von Neumann entropy and Shannon entropy was investigated. We found that the optimal configuration transfer higher rates of information about the size distribution of aerosol particles and therefore has higher entropy. Finally, some clouds of particles were charged and then EMS data were simulated and translated into their size distributions. The results showed that the measurements using the optimal design of EMS were close to the actual size distributions. The measurements using the first EMS completely failed to predict size distributions correctly in some cases.

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