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Measurement methods for size and charge distributions of electrosprayed water droplets

Abstract. *The electrospraying of water and waterborne solutions (e.g. waterborne coatings and pesticides) is thoroughly investigated because of considerable gain in environment protection. The droplet size and charge distributions of water aerosol droplets are of key importance in many applications of the process in industry and in medical treatments. The measurement of the distributions of size and charge of electrosprayed water droplets using laser-based measurement techniques is a nonintrusive and technologically advanced solution.*

Streszczenie. *Elektrostatyczne rozpylanie wody stanowi ważne zagadnienie z uwagi na zastosowania roztworów wodnych z udziałem substancji oddziaływujących na środowisko naturalne. Pomiar rozkładu wielkości kropelek oraz ich ładunków ma duże znaczenie w wielu procesach technologicznych i w zabiegach medycznych. (**Metody pomiaru rozkładów wielkości i ładunku kropelek wody rozpylanej elektrostatycznie**).*

Keywords: electrospraying of water, droplet size and charge distributions, droplet size and charge measurement methods.
Słowa kluczowe: elektrostatyczne rozpylanie wody, rozkład wielkości i ładunków kropelek, metody pomiaru wielkości i ładunku kropelek.

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Introduction

Electrospraying, also called electro-hydrodynamic spraying (or electro-hydrodynamic atomisation, EHDA), is a method that relies on breaking up a liquid jet into fine droplets by means of electrostatic forces. The size of the droplets obtained by this method ranges from a few nanometers to hundreds micrometers [1], depending on the parameters of the process of electrospraying. Several modes of operating an electrospray are distinguished; among them, in recent years the cone-jet mode has focused many research efforts [2], because it allows to obtain droplets with a narrow size distribution, practically monodispersed high quality spray.

Although first experiments with electrospraying of liquids were described by Nollet in 1745, first mathematically supported research was made by Lord Rayleigh in the last quarter of XIXth century. In the 1878-1882 period, Rayleigh studied the Coulombic fission of an electrically charged droplet which occurs when the electrostatical forces of repulsion exerted by the charges exceed the maximum theoretical value of the total charge on the droplet surface, called the Rayleigh limit.

In the first quarter of XXth century, Zeleny established experimentally and gave scientific description of several modes of electrospraying [3]. After the World War II, industrial applications of electrospraying emerged, and more detailed investigations were continued. Many researches contributed to better understanding the electrospray phenomenon; among them, most influential works were performed by Kelly (electrostatic atomisation of fuels) and Taylor (e.g. cone-jet mode is based on the Taylor cone theory). The investigations have produced knowledge about parameters which influence the electrospraying process: flow rates, operating voltage ranges, geometric arrangement of the electric fields, electrical and rheological properties of the electrosprayed liquids.

The scientific interest was focused on electrospraying method of liquid atomization because of its advantages. Firstly, droplet size and charge can be controlled by adjusting the flow rate and the voltage applied, resulting in fairly uniform droplets even in the submicron range (not possible to produce by most of purely hydrodynamic methods). Secondly, the trajectories of the motion of electrically charged droplets can be easy controlled by electrostatic forces in a tailored electric field (thus, the deposition efficiency is higher than for an uncharged spray). Thirdly, if the droplets are unipolarly charged (e.g., positively only), strong mutual Coulomb repulsion (as the droplets can be charged up closely to the Rayleigh limit) causes spatial self-dispersing effect, which do not allow droplet agglomeration or coagulation; no chance for droplet clustering which can occur at purely hydrodynamic spraying. The last but not least advantage is that very little energy is required to create charged droplets electrostatically [4].

The scientific and industrial applications of electrospraying can be roughly categorized into small-output and large-output processes. The first category comprises ink-jet printing, micro- or nanopattering in electronics (non-contact alternative to photholitography), fuel injection, microparticle manufacturing for drug delivery, thin film deposition, micromachining, nanoparticle sprays (esp. in electrospray ionisation for mass spectrometry of highly charged biological macromolecules (e.g. proteins), ingredients dosage in the cosmetic and food industries. To the second category belong e.g. fire extinguishing, wet scrubbers (precipitation of dust or smoke), agriculture sprays crop protection (pesticides), spray coating and painting, or ceramic films fabrication. There are also projects intended to apply electrosprayed water droplets in renewable energy systems [4].

The knowledge of distribution characteristics of droplet size, charge and velocity is necessary for designing electrospray systems, and for validating models used in computational simulations [5]. In recent years, the submicron range is an area of growing interest to many industries (e.g. pharmaceutical aerosols); in consequence, direct and accurate measurements in the submicron diameters are becoming more essential for studies on quantitative characteristics of electrosprays [6].

This article proposes a brief comparison of a few measurement methods for size and charge distributions, mainly of water-based electrosprays.

Conceptual and measurement considerations of size and charge distributions

Although the instrumentation has much common in the field of aerosol science, the research on sprays is a subfield of aerosol investigations, and the measurement of a solid particle population differs from such measurement of a spray of droplets. In general, the terms “aerosol” and “particle” are in use even if the article concerns a spray and droplets. Strictly speaking, by droplets often are meant small liquid particles of a near-spherical shape, and the diameter lower than 500 µm.

The behaviour (in aerosol) of both solid particles and droplets depends on their size, charge, velocity, shape, and mass; for measurement purposes the optical, electrical and rheological properties of the dispersed phase are also essential. However, droplets are prone to take spherical shape spontaneously (for minimizing its surface energy), and their diameter conveys information of the mass. On the other side, droplet's spherical shape can be easily disturbed by factors like electric field. Droplets can be intruded by small solid particles or ions which can penetrate to their centre.

The electrostatic charge magnitude and polarity are independent parameters that appear even during non-electrical hydrodynamic spraying as inherently bipolar charging (which can even cause explosions, e.g. on tankers). The amount of charge on a droplet cannot evaporate with liquid molecules. That means approaching the Rayleigh limit [7]:

$$q_R = 8\pi\sqrt{\varepsilon_0 \sigma r^3} , \tag{1}$$

where ε_0 is the electrical permittivity of free space, σ is the surface tension (which depends on the two media on both sides of the surface), and r is the radius of the droplet (after simple rearrangement, the formula for the maximum number n_R of elemental charges e on the droplet can be obtained [8]). Then the droplet disintegrates (on several possible ways) and both the size and charge distributions change progressively. This formula was derived by Rayleigh for the case of a single charged droplet. In aerosols, within the cloud of charged droplets which acts on each other, the fissions occur at droplet charge levels below the Rayleigh limit value [9].

The instrumentation for measuring the electrical mobility of charged droplets μ_d evolved from the devices for measurement of the mobility of ions. The electrical mobility μ_d is expressed as the ratio of the droplet drift velocity and the magnitude of the electric field [10]:

$$\mu_d = \frac{\upsilon_d}{E} = \frac{neC_c}{6\pi\eta r} , \tag{2}$$

where E is the electric field, υ_d is the drift velocity of the droplet, η is the air viscosity, n is the number of elemental charges hold by the droplet, and C_c is the Cunningham slip correction factor.

Measurement methods for size and charge distributions of droplets

Since the size and charge distributions are time-dependent, there is a strong demand to measure them simultaneously. The methods combine sizing with the static or dynamic methods for measuring droplet charge (or its electrical mobility) distribution. As the droplet size distributions were characterized elsewhere [11], this section is focused on droplet charge distribution measurement, but simultaneously with sizing. The expectations towards the size and charge distribution measuring systems include: high data rate of analysed droplets, nonintrusive interaction with spray, real-time measurement, no ambiguity of polarity sign indication, small dimensions, stability and robustness.

The analog of the ensemble methods of sizing, is the static method of collecting the charge in a cumulative way using the Faraday cage and en electrometer; thus the accumulated charge can be related to the mass of water droplets. This technique estimates the average charge-to-mass ratio [12]. Similar approach is applied in the electrical low pressure impactor (ELPI): only net charge levels of aerosols can be obtained [13]. The ensamble sizing diffraction techniques are recommanded by the ISO 13320:2009 Standard for droplets ranging from 0.1 μm to 3 mm with possible extending down to 0.02 μm with special instrumentation [14]. The accuracy of 1% can be obtained for transparent homogeneous droplets of spherical shape [15].

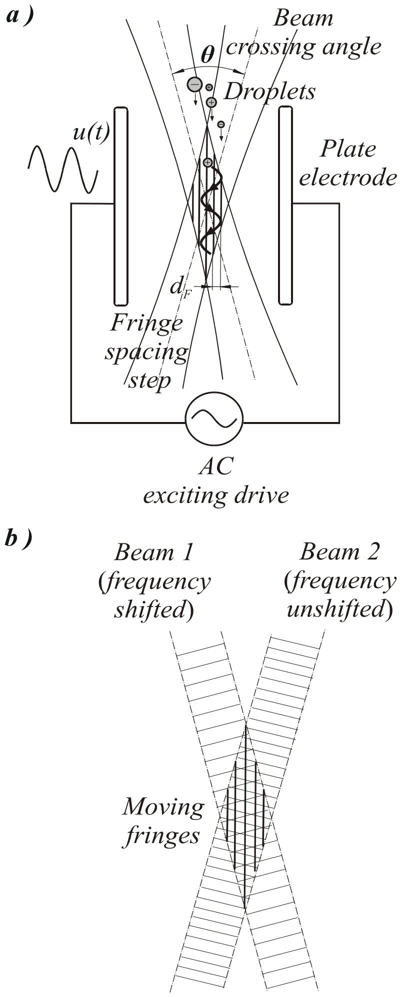

Fig.1. a) single droplet size and velocity (i.e. electrical mobility) LDV-based measurement arrangement, b) schematic of interference pattern forming

The single droplet simultaneous measurement of size and charge is performed using the laser-based interferometric methods which employ the Doppler effect (sometimes can be combined with shadowgraphy [9]). In that case, the device must ensure that the size and charge are measured on the same droplet. The charge is measured with techniques evolved from Millikan method, which assumes constant velocity of the droplet. The time required for a droplet to attain the same speed as the surrounding air is called “the relaxation time” and for water droplets 5 μm in diameter is about 0.1 ms [16].

A group of simultaneous measurement methods evolved from the Laser Doppler Velocimetry (LDV) technique [17]. The original application was oriented on toner particle size and charge distribution, but the same concept is valid for electrosprayed droplets (Fig.1). The oscillating electric field (of exciting frequency f_e , $\omega=2\pi f_e$) exerts an electrostatic force on the droplet which starts to oscillate with the same frequency. The phase lag φ_e of the droplet's oscillation with respect to the exciting field, caused by the inertia of the droplet, corresponds to the droplet size (its aerodynamic diameter), whereas the amplitude of the oscillations depends upon the charge q on the droplet and the electric field E (τ is the aerodynamic relaxation time of the droplet):

$$\varphi_e = \operatorname{arc\,tg} \omega\tau , \tag{3}$$

$$q = \frac{d_a \upsilon_d}{E} \frac{3\pi\eta}{C_c} \sqrt{1 + (\omega\tau)^2} . \tag{4}$$

The aerodynamic diameter d_a is expressed as:

$$d_a = \sqrt{\frac{18\eta\tau}{\rho_0 C_c}} , \tag{5}$$

where ρ_0 is 1 g/cm^2. The (equivalent) aerodynamic diameter is the diameter of a unity density spherical droplet having the same settling (or: sedimentation) velocity as a given droplet. On this parameter depends the trajectory of a droplet of significant inertia in a flow field [10].

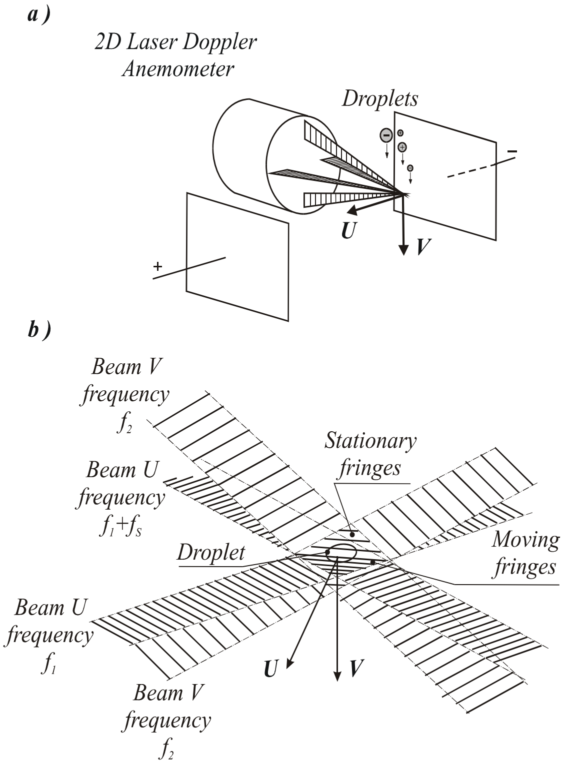

Fig.2. a) single droplet size and velocity (i.e. electrical mobility) PDA-based measurement arrangement, b) schematic of forming of interference patterns

In order to generate moving fringes inside the measurement volume, a diode laser beam is divided in two equal interfering beams; one of the beams is frequency-shifted through a modulator (e.g. Bragg cell). The light scattered on the droplets passing the fringe region, is collected by the receiving optical-electronic system. The fringe separation d_F is expressed as:

$$d_F = \frac{\lambda}{2\sin\frac{\theta}{2}} , \tag{6}$$

where θ is the angle between the interfering beams.

Using an additional acoustic field, parallel to the electric field and synchronous in phase, the polarity of the charge can be determined. The acoustic waves are highly susceptible to temperature [10] which can be a cause of errors. On the other side, the electric wave does not act on uncharged droplets. For low charged droplets the measurement accuracy is poor; the measurement range is from 20 to 10000 elementary charges. Except the low-charge limit, a low-size limit is imposed on those measurements because of using scattered light signal to localize the droplets [10].

For measuring single droplet's both size and charge, the 2D Phase Doppler Anemometry (2D PDA) technique can be applied [16]. Two pairs of laser light beams intersect in one small measurement volume. Two interference patterns in two mutually perpendicular planes are formed with different spacing. The vertical stationary fringe pattern allows for measuring the phase difference in the scattered light, and the receiving optical-electronic system determines the droplet diameter linearly corresponding to the phase shift.

The horizontally moving fringe pattern allows the passing droplet to scatter light at a Doppler frequency f_D proportional to its velocity component υ_U normal to the fringes, and to the frequency shift f_S introduced to one of the beams for resolving the ambiguity of velocity direction. The formula for f_D is written as:

$$f_D = f_S + \frac{2\upsilon_U}{\lambda} \sin\frac{\theta}{2} . \tag{7}$$

This method allows measuring the size and velocity of up to 1000 droplets per second with an accuracy of 0.5 %. The equations describing the phase shift are rather cumbersome [6]; however, that shift depends only on the angles of the measurement geometry, the wavelength of the applied laser, and on the refractive index of the droplets. The measurement accuracy is related to the accuracies of determining these parameters, which are either geometrical or physical properties. Providing that these values are known accurately, no calibration is required for that instrumentation. One of sources of error is the nonspherical shape of some droplets. To avoid this error, the postprocessing software compares phase shift difference from two pairs of detectors, and if the difference exceeds 10 % threshold value, that reading is discarded [6]. For correct measurements, the flow inside the measurement cell must be laminar. The maximum number of droplets that enter the measurement volume per second is limited by the risk of coincidence error as well as the additional error introduced by the space charge of unipolar highly charged droplets.

The measurement method of size and charge distributions using an impaction principle is employed for evaluation of the whole population of droplets conveyed in aerosol. The operation of a conventional (single stage) impactor is based on the Stokes number of a droplet-laden gas flow from a nozzle towards an impaction plate. The small droplets pass by the impaction plate placed under the nozzle whereas larger droplets are collected on the plate. More useful is to connect several impactors with different nozzles in one cascade impactor, usually consisting of more than ten stages, which ensures more discrete ranges of droplet size. The gas velocity in successive stages rises, in order to make smaller droplets to impact the plates [18].

One of method to estimate the number of droplets collected on each stage is to charge the electrically neutral droplets at the inlet of the cascade impactor, and to measure the amount of charge on impaction plates. Such device is called ELPI (Electrical Low Pressure Impactor), and consists of a corona charger, successive isolated stages with metal impaction plates, and a multi-channel electrometer for measuring the electric current from each stage. The lowered pressure along the stages, generated by a vacuum pump at the outlet of the cascade impactor, allows enhancing the size range down to several nanometers, because of higher values of the slip coefficient C_c. In the case of electrosprayed liquids, the corona charger is switched off, and the electrometers measure the size-classified droplet charge distribution.

Each stage is characterized by its cut-off diameter, i.e. the size of particles collected with 50 % efficiency (D_{50}). The ratio of the cut-off diameters of two adjacent ranges is around 2, e.g. in the “ELPI+” 13-stage impactor the lowest range was 16.7 nm (at 43.4 mbar) whereas the highest was 9.99 µm at 1013.2 mbar (atmospheric pressure) [19].

The highest droplet collection efficiency errors occur for the largest and smallest droplets where cut-off diameters are less sharp; therefore, the tails of the distributions should be kept within the measurement range of the impactor, or estimated accordingly to knowledge of the shape of the distributions. Another source of errors can be the bouncing of the droplets from one stage to the next or from the inner walls. The accuracy depends also on the density of the droplets, which is a function of temperature. On ocasion, also a source of errors may be the partial blocking of the impactor nozzles. For bipolarly charged population of droplets, there should be two parallel impactors with a splitter of the stream of droplets into two unipolarly charged sets sized in separate impactors; that allows avoiding the error caused by the measurement of algebraic sum of the droplet charge in a single impactor.

The problem of impactor calibration requires special instruments generating calibration aerosols. More recently, such instrument called Single Charge Aerosol Reference (SCAR) was built and validated [19]. This reference generator of calibration aerosols is based on the di-octyl sebacate (DOS) droplets with average charge of one e up to 500 µm in diameter with relative uncertainty of 0.16 %. The primary droplets are very small but the charge is known very strictly; then the droplets can be enlarged to the required diameter without change in each droplet’s charge.

Conclusions

The operation rate of single droplet measuring techniques can be insufficient in the case of unstable electrospray clouds or very dense aerosols. Another limitation is the size of the droplet to be measured: in the submicron range, especially for nanodroplets (<30 nm) the optical signals are too weak to ensure good accuracy. On the other hand, very large droplets are difficult to handle with because of their high inertia, and possible very large charge levels, which in turn require traversing systems for mapping the volume of the measurement cell [6].

The evaporation effect can be reduced by inserting small solid particles inside original droplet set. During evaporation, the droplet charge should migrate intact to the solid core enveloped in the liquid layer which should evaporate without fission. The charge distribution of solid particles can reflect the onset distribution of droplet charge.

The relationships between the size and charge distributions of electrosprayed droplets is confirmed both experimentally [7, 9] and theoretically [21, 22]; the higher the applied voltage, the smaller and higher charged are the droplets. However, the size distribution exhibits rather normal shape, whereas the charge distribution tends to log-normal left skewed; the mutual relationships between the size and charge distributions need further investigation.

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