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A generic electrospray classification

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One of the major unknown factors when working with electrosprays is the precise spraying mode that is obtained when operating an electrospray. However, as the spraying mode determines to a significant extent the properties of the obtained particles, knowing the spraying mode is crucial for many applications. Currently the spraying modes presented in the literature are defined based on optical observations of the liquid meniscus. In a laboratory set-up this approach works fine but in many other situations such an approach is not feasible. For this reason a different approach is developed which uses measurements of the current through an electrospray system to determine the spraying mode of the system. These measurements are relatively simple and can be implemented cost effectively. Although not all spraying modes can be distinguished using this approach, the spraying modes used in most applications can be identified.

1. Introduction

Due to its extraordinary properties the number of applications using ElectroHydroDynamic Atomisation (EHDA) has increased dramatically during the last few decades. EHDA, sometimes called electrospraying, is among many other things applied in crop spraying (Geerse, 2003), the creation of emulsions (Abu-Ali & Barringer, 2005), the creation of thin films (Jaworek, 2007) and the production of particles with a very specific size and/or composition (Borra et al., 1997, 1998; Camelot, 1999; Ciach, 2006; DePaoli et al., 2003; Enayati et al., 2011; Yurteri et al., 2010). The technique is also widely used as a soft but an efficient ionisation technique in mass spectrometry set-ups (Cech & Enke, 2001; Dülcks & Juraschek, 1999; Wei et al., 2002). The wide variety in applications together with their rather different requirements illustrates the versatility of the technique. For correct operation of all applications it is however crucial that the electrospraying happens in a well-defined way.

It is well known that the behaviour of an electrospray depends strongly on the electric field it experiences, the material properties of the used liquid, the electrode geometry and other boundary conditions. In the literature a number of classifications have been proposed to distinguish between the various spray situations (Cloupeau & Prunet-Foch, 1990, 1994; Grace & Marijnissen, 1994; Jaworek & Krupa, 1999; Juraschek & Röllgen, 1998). These classifications are mainly based on visual observations of the liquid meniscus. Together with a mapping of the effect of experimental conditions like the applied liquid flow rate and the applied electric field, these classifications are helpful in getting the wanted electrospray behaviour. However, when using those classifications, it remains necessary to check whether a certain spraying "mode" was obtained.

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Nomenclature

C_{BC}	transferred charge during the development time of a pulse, C
C_{DE}	transferred charge during the relaxation time of a pulse, C
$\overline{C_R}$	average charge development–relaxation ratio, –
d_{cap}	outer diameter of a capillary, m
$d_{cap,in}$	inner diameter of a capillary, m
G	amplifier gain, –
$\bar{I}$	mean current, A
$\bar{I}_{min.}$	minimum $\bar{I}$, A
K_l	bulk liquid conductivity, S m^{-1}
$N_{ep,i}$	number of extrema in pulse i, –
$\overline{N_{extr.,p}}$	average number of extrema per pulse, –
p	total number of pulses in the signal, –
P_{DC}	normalised DC-power, –
P_{DLCS}	offset of the linear regression of the DC-corrected and re-normalised cumulative power spectrum density, –
$R_{meas.}$	measurement resistance, Ω
RSD	relative standard deviation, –
t_{BC}	development time of a pulse, s
t_{DE}	relaxation time of a pulse, s
$\overline{T_R}$	average development–relaxation ratio, –
ΔV	potential difference, V
t	time, s
ε	permittivity, C^2 N^{-1} m^{-2}
σ	standard deviation, –
τ_e	electrical relaxation time, s

For real-life and/or up-scaled applications, this often becomes unpractical and/or expensive so a different approach is needed.

It was found that for the geometries and liquid flow rates often used in mass spectrometry set-ups, the current through the system and the behaviour of the liquid meniscus are correlated (Cech & Enke, 2001; Juraschek & Röllgen, 1998; Marginean et al., 2007; Wei et al., 2002). A similar observation was made for unforced nano-electrosprays (Alexander, 2008; Alexander et al., 2006; Paine et al., 2007). These correlations seem to be specific for a given liquid and configuration. It should also be noted that both a mass spectrometry and an unforced nano-electrospray set-up employ a relatively small nozzle (typically $\lesssim$200 μm) and relatively low flow rates (typically $\lesssim$0.1 mL h^{-1}). The effect of larger nozzle diameters and/or higher flow rates on the correlation remains to be investigated.

Here it is attempted to find a general mapping between the properties of the current through the system and the spraying mode that is independent of the material properties of the liquid, the electrode geometry and other experimental conditions. To accomplish this, it is assumed that a change in the liquid meniscus is "directly" reflected as a change in the current through the system and that a change in the current reflects a change in the liquid meniscus. As a result analysing the current characteristics is a (indirect) way to analyse the behaviour of the meniscus that may be used to classify the various spraying modes. The assumed relation between the meniscus and the current through the system has already been shown to be valid for systems with a small nozzle diameter and relatively low flow rates (Alexander et al., 2006; Juraschek & Röllgen, 1998; Marginean et al., 2007). For systems with larger nozzles and higher flow rates the amount of (semiconducting) liquid close to the nozzle will be significantly larger in many cases. For this type of systems the validity of the assumption has not been shown yet. However, the electrical relaxation time, τ_e, defined as

$$\tau_e = \frac{\varepsilon}{K_l} \tag{1}$$

with ε being the permittivity of the liquid and K_l being the bulk liquid conductivity, is rather small for most liquids used in electrospraying. Together with the limited amount of liquid per spray system, it can be expected that even for the larger systems changes in the liquid meniscus are "directly" reflected in the currents through the system, especially when the currents are measured close to the liquid meniscus. Experimental validation is however still needed.

2. Experimental set-up and techniques

The experimental set-up used in this study is shown schematically in Fig. 1. In the experiments a syringe pump (Harvard, PHD2000) was used to pump liquid through a nozzle at flow rates in the range of 0.1–10 mL h^{-1}. A number of different nozzles were used, all with outer diameters $\geqq$0.71 mm. In order to ensure that the currents were measured close to the liquid meniscus, all nozzles were made of conducting (metallic) materials and the current measurements were performed at the nozzle. At some distance from the nozzle a conducting collector plate was located onto which the created droplets deposited. In some experiments a ring electrode was placed between the nozzle and the collector plate. An electric field was created by applying a high electric potential to either the collector or the ring electrode. When a ring electrode was used, the collector was kept at ground potential. Figure 2 gives an schematic overview of the various nozzle–ring–plate combinations that were used. The main difference between the "needle type" (Type I and II) and the "nozzle type" (Type III and IV) nozzles is the ratio of the inner and the outer diameter of the nozzle. For the needle type nozzles the inner diameter, $d_{cap,in}$, is comparable to the outer diameter, d_{cap}, whereas the nozzle type nozzles have an inner diameter of 0.2 mm which is significantly smaller than d_{cap} for the nozzles used in the current experiments. This leads to rather different situations close to the nozzle tip for both generic types. Together with the extra ring electrode used in a number of configurations, it is clear