Retarding potential and induction charge detectors in tandem for measuring the charge and mass of nanodroplets

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The determination of the mass of a nanoparticle via time-of-flight typically requires a direct measurement of its charge. This can be done with a differential retarding potential analyzer and an induction charge detector operating in tandem. The spectrometer described in this article selects a particle with a specified retarding potential from a beam and directs it to an induction charge detector where both its velocity and charge are measured. The retarding potential, velocity, and charge also yield the particle’s mass. The particle is analyzed without the need to collect it, and therefore can be employed in a subsequent experiment. The high charge sensitivity of the induction charge detector and the capability for working at low retarding potentials make the characterization of electrospayed nanodroplets possible for the first time. © 2009 American Institute of Physics. [DOI: 10.1063/1.3128730]

I. INTRODUCTION

Quadrupole and time-of-flight detectors are routinely used to quantify the mass of ions in a vacuum, even though these spectrometers only resolve charge to mass ratios. To determine the mass one must guess a combination of elementary charges and atomic composition consistent with the measured charge to mass ratio. In a typical quadrupole this strategy works for ions with mass and charge of up to 50 kDa and 15 e, but fails for more complex, highly charged particles such as electrospayed viruses and nanodroplets. For example, an electrospayed nanodroplet may have a diameter of 50 nm, a mass of 60 000 kDa, and a charge of 230 e. In this case, the direct determination of the charge is unavoidable. This can be done with a differential retarding potential analyzer (RPA) and an induction charge detector (ICD) operating in tandem. This spectrometer measures the particle’s acceleration voltage, time-of-flight, and charge. These values are combined to yield the particle’s charge to mass ratio and mass. In the case of a droplet the diameter can also be found from its mass and the liquid density. An ICD resolves the charge and time-of-flight of a particle moving in a vacuum. The sensing components of an ICD are one or several tubular electrodes placed along the particle’s path. The charge is inferred by monitoring the potential induced on the electrodes by the passing particle. The ICD design with a single tube was pioneered by Shelton et al., who used it to characterize charged dust particles. Hendricks and collaborators employed a similar detector to size electrospayed droplets. More recently, Gamero-Castaño developed an ICD with multiple sensing stages with the goal of lowering the charge detection limit. The present design is an evolution of the latter, customized for the nanodroplets produced by an electrospay source operating in a vacuum. The following sections describe this new detector and presents a characterization of electrospayed droplets, some having diameters below 100 nm.

II. DETECTOR DESCRIPTION

Figure 1 shows a sketch of the detector: a charged droplet enters an electrostatic mirror through a small orifice (0.35 mm inner diameter, 13.1 mm long), where its trajectory is deflected by a planar and homogeneous electric field. The particle exits the mirror through a second orifice (0.35 mm inner diameter, 13.1 mm long) when its retarding potential coincides with the potential difference between the plates. The exit orifice is aligned with seven tubular electrodes. The particle induces electric potentials on four of the tubes (D1–D4) as it traverses them. The potential differences between consecutives tubes are amplified by a factor of 100, generating the signals A1 and A2 from which the particle’s charge and time-of-flight are inferred. A1 and A2 are each a one-period rectangular wave, with a peak-to-peak voltage \( V_{\text{PP}} \) proportional to the particle’s charge \( q \)

\[
V_{\text{PP}} = \frac{2}{C} q. \tag{1}
\]

\( C \) is the effective capacitance of a sensing electrode, which is determined via calibration with droplets of known charge. The time-of-flight \( t_F \) is the residence time inside the electrodes, or extent of the potential induction. The particle’s charge to mass ratio \( \xi \) is obtained from conservation of mechanical energy in an electrostatic field, the definition of the retarding potential \( V_{\text{RP}} \), the time-of-flight, and the length of the detector \( L_F \)

\[
\frac{1}{2} m v(x)^2 + q V(x) = \text{constant} = q V_{\text{RP}}, \tag{2}
\]

\[
\xi = \frac{1}{2 V_{\text{RP}}} \left( \frac{L_F}{t_F} \right)^2, \tag{3}
\]

while the ratio between \( q \) and \( \xi \) yields the mass \( m \).
When the particle is a liquid drop of known density $\rho$, its diameter is obtained from
\[
D = \left( \frac{6m}{\pi\rho} \right)^{1/3}.
\]

The retarding potential of the particle is required to compute $\xi$ and $m$ from the ICD signal. I am particularly interested in the characterization of electrosprayed nanodroplets. The droplets in an electrospray beam exhibit a distribution of retarding potentials with a standard deviation of the order of 100 V. In previous work with micron-sized droplets, I avoided measuring the retarding potential of individual droplets by working at large acceleration potentials (say 2000 V). In this case, the average retarding potential of the beam differs little from that of individual droplets, and a simpler characterization of the cumulative retarding potential distribution of the beam suffices. Unfortunately, I cannot make use of this simplification to characterize electrosprayed nanodroplets with the ICD in Ref. 4: the high charge to mass ratios of nanodroplets combined with acceleration voltages of a few kilovolts induce large velocities, and the amplifiers cannot reproduce the fast droplet waves. The present design overcomes this problem by using the differential RPA as an initial stage: droplets with a low and accurately known retardation potential can be selected and directed to the ICD.

Upon solving the equation of motion of a droplet traversing the RPA, its retarding potential is written in terms of the mirror’s potential $V_M$ and geometrical parameters
\[
V_{RP} = \frac{(L_M + \delta_{in} - \delta_{out})V_M}{2S_M \sin(2\alpha)}.
\]

$L_M$ is the distance between the centers of the entrance and exit orifices at the inner face of the grounded mirror plate, $L = 25.4 \pm 0.025$ mm. $S_M$ is the spacing between the mirror plates $S_M = 12.7 \pm 0.025$ mm. $\delta_{in}$ and $\delta_{out}$ are the offsets of the particle trajectory with respect to the orifice centers; $\delta_{in}$ and $\delta_{out}$ are bounded by the radii of the orifices (0.17 mm). $\alpha$ is the angle of incidence of the particle with the grounded plate and is constrained by the length and diameter of the orifices, $\alpha = 45 \pm 1.5$ deg. The measurement of $V_M$ is accurate within 1%. From these values it follows that $V_{RP}$ is equal to $V_M$, with an estimated uncertainty of the order of 1% (the uncertainty associated with $V_M$ dominates all other error sources).

### III. DETECTOR EVALUATION

Figure 2(a) illustrates the charge calibration of the sensing electrodes D1–D2, using positively charged droplets of liquid propylene carbonate. For this task the passage of D3 is blocked with a conducting rod and the electrode connected to ground through a 1%, 100 MΩ resistor. A droplet selected by the mirror flies through D1 and D2, generating a one-period rectangular wave with $V_{PP} = 0.645$ V (trace A1). The droplet then impacts on D3 and generates a potential peak (trace A2). The peak decays exponentially due to the effective capacitance of D3 in parallel with the 100 MΩ resistor. The time constant of the exponential is obtained from the curve $RC3 = 0.225$ ms and the capacitance from the time constant and the known resistance, $C3 = 2.25 \times 10^{-12}$ F. To the first order, the charge of the droplet is the product of the potential peak times $C3$, divided by the gain of the amplifier ($V_P = 0.284$ V, gain = 100, $q = 6.37 \times 10^{-15}$ C); a more accurate value is obtained by taking into account the finite rise time of the potential peak, $q = 6.59 \times 10^{-15}$ C. Finally, knowledge of the charge makes it possible to calibrate the peak-to-peak voltage of the A1 trace, $q(V_{PP})$. The resulting calibration factor is $1.02 \times 10^{-14}$ C/$V_{PP}$. This procedure was repeated with 89 droplets. The linear regression of the $\{q, V_{PP}\}$ data, shown in Fig. 2(b), yields a calibration factor of $1.04 \times 10^{-14}$ C/$V_{PP}$, and a value of 0.974 for the coefficient of regression $R^2$.

Figure 3 displays the two ICD signals generated by a
negatively charged nanodroplet with the following characteristics: \( D=114 \ \text{nm}, \ \rho=1.18 \times 10^{-18} \ \text{kg}, \ \gamma=-1.32 \times 10^{-16} \ \text{C} \) (825 elementary charges). The retina potential is \(-394 \ \text{V} \). The density of the droplet is 1520 \( \text{kg m}^{-3} \) (EMIIm ionic liquid).\(^7\) The usefulness of having a second trace when the droplet signal is comparable to the background noise is apparent. Since the second droplet wave must be identical to the first one with a lag of \( 3\tau/2 \) (\( \tau \) is the time-of-flight inside the D1–D2 electrode pair), a simple comparison of the two traces is sufficient to eliminate false droplet counts. The good correlation between A1 and A2 when a droplet flies through is shown by plotting \( (A1+A2)/2 \), after advancing the second signal by 87 \( \mu\text{s} \). The combination of the two traces produces a droplet wave very similar to that of A1. The lag time that maximizes the correlation is used to define the time-of-flight (the path of flight is then the length occupied by three sensing tubes, \( L_f=25.92 \ \text{mm} \), and the average of the two signals to compute \( V_{pp} \) (averaging attenuates the background noise).

The estimation of the diameter of electrosprayed nano-droplets is an important problem in our research. It is known that the charge of larger electrosprayed droplets is typically between 1 and 0.5 of the Rayleigh stability limit \( q_R \), or maximum charge that a droplet can have without undergoing a Coulombic explosion.\(^4\) These limits place upper and lower bounds on the diameter

\[
(72 \gamma^{2} \rho^2 \varepsilon^2)^{1/3} < D < (288 \gamma^{2} \rho^2 \varepsilon^2)^{1/3},
\]

\( \rho, \gamma, \) and \( \varepsilon_0 \) are the density and surface tension of the electrosprayed liquid, and the permittivity of the vacuum. The 50\% limit is an approximation that has been demonstrated for micron-sized electrospray droplets,\(^9\) but there is not a similar confirmation for nanodroplets. To eliminate this uncertainty, I have studied with the present detector electrosprays of the ionic liquid EMIIm \( (\rho=1520 \ \text{kg m}^{-3}, \ \gamma =0.0349 \ \text{N/m})\)\(^2\) and propylene carbonate \( (\rho=1200 \ \text{kg m}^{-3}, \ \gamma=0.0419 \ \text{N/m})\)\(^3\). Figure 4(a) shows the diameter limits for EMIIm droplets, together with measurements of 35 negatively charged droplets, while Fig. 4(b) shows similar data for propylene carbonate (57 positive droplets). Note that the experimental data confirms the validity of Eq. (7). The average ratio between the charge of an EMIIm droplet and its Rayleigh limit is \( \langle q/q_R \rangle=0.679 \). Although the spread of \( q/q_R \) in Fig. 4 is important (roughly between 0.5 and 1), a similar \( \langle q/q_R \rangle=0.678 \) is obtained for propylene carbonate.

Depending on the residence time and vapor pressure of the droplet, liquid evaporation may jeopardize the characterization of its retarding potential, mass, and diameter. For a drop in free-molecule conditions and constant temperature the rate of change in diameter due to evaporation is given by\(^10\)

\[
\frac{dD}{dt} = \frac{2m^{1/2} p_v (T)}{\rho (2\pi k_B T)^{1/2}}.
\]

The molecular mass of propylene carbonate is \( m =102.09 \ \text{amu} \). Using the Antoine equation and tabulated coefficients, its vapor pressure is estimated to be \( p_v=2.9 \ \text{Pa} \) at \( T=293 \ \text{K} \).\(^11\) The diameter of a propylene carbonate droplet then diminishes at a rate of 12.4 \( \mu\text{m/s} \). The typical velocity of the droplets in Fig. 4(b) is 395 \( \text{m/s} \) \((\xi=40 \ \text{C/kg}, \ V_{pp} =1955 \ \text{V})\). The path of flight between the electrospray source and the exit of the ICD is approximately 0.15 m. Thus, the residence time associated with the experiment is of the order of \( 4 \times 10^{-4} \ \text{s} \), and the reduction in diameter is 4.9 nm. This value is small compared to the diameters in Fig. 4(b), and therefore evaporation introduces a small uncertainty in the characterization of these droplets. The very low vapor pressures of ionic liquids in general, and EMIIm in particular, are largely unmeasurable. Furthermore, the residence times of EMIIm nanodroplets are much smaller than those of propylene carbonate drops. Therefore, the evaporation of EMIIm can also be neglected.

IV. CONCLUSIONS

This article has shown that the charge and mass of electrified nanoparticles can be independently determined with an ICD and an electrostatic mirror operating in tandem. In particular, electrosprayed droplets with diameters as small as 100 nm have been fully characterized. To the best of my knowledge, this is the first time that either the charge or the diameter of individual electrosprayed droplets has been measured in this size range. This measuring technique features two additional qualities: it is nondestructive, making it possible to conduct research with the particle after its characterization; and because the measurement is carried out in a vacuum, the velocities of the particles can be very high, and the residence times in the experimental apparatus small. This is important to avoid significant evaporation from liquid droplets, and the associated error in the determination of the

FIG. 4. Diameter limits and individual droplet measurements for (a) EMIIm ionic liquid and (b) propylene carbonate.
mass and diameter. Note that the much larger residence times inside aerosol instruments, operating at or near atmospheric pressure, makes it difficult to characterize the size of liquid nanodroplets with finite vapor pressure.


