Development of a sorter device to purify nanocristals

J. Perri, A. Bragas, O. Martinez, G. Artana

Abstract— **We show in this work the ability of an electrostatic sorter device with droplets produced by lateral excitation of an aqueous jet. In the system all droplets are electrified and in droplet flight it is sensed the droplet that contains the desired nanocristal. Deflecting pulses imposed to the droplets of small duration enable a good separation of this droplet from the train.**

I. Introduction

There has been an increasing interest on the use of quantum dots as quantisation tags in biological assays as a substitute of organic fluorophores or radiaoactive labelling. These nanoparticles offer advantages over conventional dye molecules in that they have tunable fluorescence signature, narrow emission spectra, brighter emission and good phtostability [Penn 2003]. In general emission of these particles is determined by its shape and size. Upon photoexcitation they can emit from the ultraviolet to the infrared and smaller particles tend to emit short wavelength radiation meanwhile larger particles emit on the longer wavelength range. One of the most important disadvantages is that when chemically synthetized a relative spread distribution of nanocristals sizes is found. This has as a consequence that emissions with less defined wavelength are obtained. It is in consequence of interest to try to classify the samples of nanocrystals obtaining monodisperse distributions ensembles.

In a project that involved different laboratories from the University of Buenos Aires we have proposed to develop a device to produce populations of nanocrystallites (NC) with controlled size dispersion, based on the optical detection of the photoluminescence of single NC. The peak value of the single particle photoluminescence spectrum is intimately related to the size of the NC and, hence, a spectrum classification is equivalent to a particle size sorting.

The device comprises a droplet generator apparatus to produce droplets containing one NC in average, starting from a solution of colloidal chemically synthesized NC. This apparatus classifies electrically charged droplets by applying a deflecting voltage, controlled by the measured optical signal.

One of the particularities of the device is that to reduce the problems of conventional cell sorters [Petersen 2003] a detection is proposed with droplets in flight. The sensing is proposed through high sensitive light detectors with low dark noise and using a set of filters chosen properly to achieve the desired size dispersion.

The objective of this work is to report results on the sorter performance to generate and separate droplets with the requirements and limitations associated to the detection system proposed.

II. Experimental setup

Droplet Generator System: Droplets were generated from an aqueous liquid jet emanating from a removable stainless steel capillar (length 10mm, inner diameter: 190μm) with blunt tip. The liquid flowed from a pressurized reservoir at constant flowrate monitored with a flowmeter with a regulating valve.

In order to obtain monosized droplets, the aqueous liquid jet was perturbed cyclically with lateral movements produced by a piezoelectric. A function generator with an amplifier and a narrow passband filter were connected in serie to the piezoelectric to excite the jets in a frequency of 100-2000 Hz.

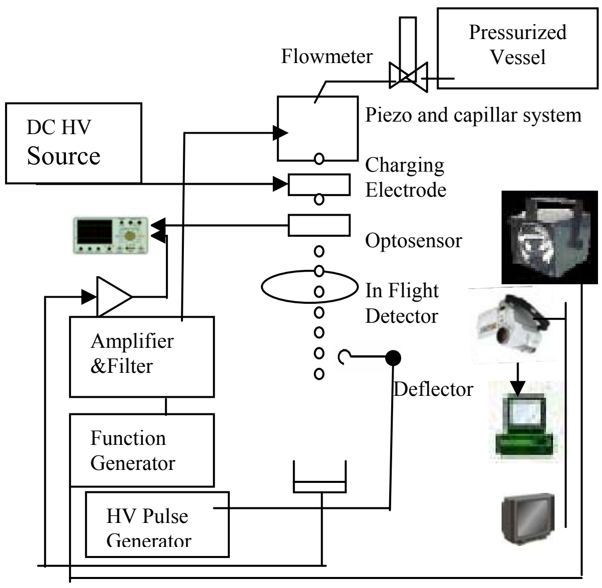

Figure 1:Schematic of the Sorter device

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The droplet generation operation was monitored with two optical devices. Each one was a whole built in emitter and receptor in the infrared range. The device was placed in order that the droplets traversing the beam produced a signal that enabled its detection. Phase difference between signals enabled also to monitor the constancy in the flow rate. A stroboscope lamp enabled the visualization and freezing of the train of droplets and image recording was produced with a digital video camera and frame grabber system.

Electrification system: In our device the meniscus was always electrified and in consequence all droplets produced by the breakup of the jet were electrically charged. The electrification system consisted on a cylindrical electrode coaxial with the jet (electrode inner diameter 1.5 mm, outer diameter 2mm, length 8mm) stressed with a d.c. high voltage. The liquid jet was grounded in a position quite close to the capillary exit. The electrode was disposed in such a way that the breakup region of the jet occured at the interior of it.

The charge to mass ratio of the droplets was evaluated with the use of a current-voltage amplifier (gain 10MVA/400kHz). The current measured divided by the flowrate enabled the determination of the mean charge to mass ratio. Being the system quite stable this value was expected to be quite close to the value of individual droplet charge-mass ratio.

Deflection system: Downstream the classifier sensor a deflector was placed at close proximity of the axis of the train of droplets. The device consisted in an horizontal bended wire of 1mm diameter. A high voltage pulse generator (1200 V, rise time 100μs) enabling different time delays was used to electrically stress this deflector and deviate the selected droplets. The determination of the angle of deflection was undertaken from suitable image analysis treatment of the recorded images of the deflected trains compared with non deflected trains.

III. Results

Droplet production regimes and As a consequence of jet excitation with lateral vibrations the jet rupture may give rise to different regime [Bassani 1988].

-*The normal break up regime:* in this regime the droplet production rate occurs at the frequency of excitation producing monosized droplets

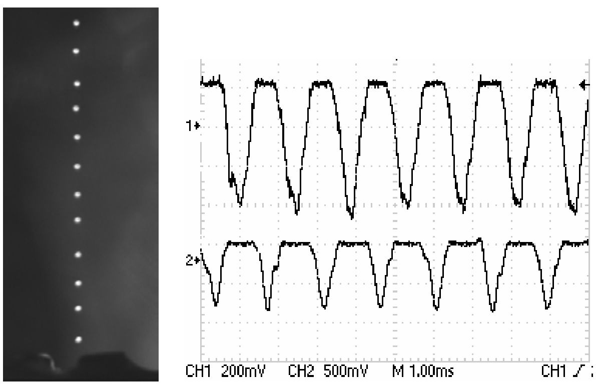

Figure 2 Normal breaking and signal detected with optosensors. Flowrate 4ml/min, f=700Hz

As in the normal breaking regime one droplet is generated from each cycle an immediate determination of droplet radius may be obtained from the continuity equation

$$r_d = \left(\frac{3a^2 V_j}{4\,f} \right)^{1/3}$$

where a is capillary radius, V_j mean jet velocity, and f is the excitation frequency.

-*The merging droplet regime* that produce a number of drop per second greater than expected for the excitation frequency. Subsequent merging of the smaller droplets mask this mechanism as far away from the capillary tip monodisperse droplets are again observed [Bassani 1988]

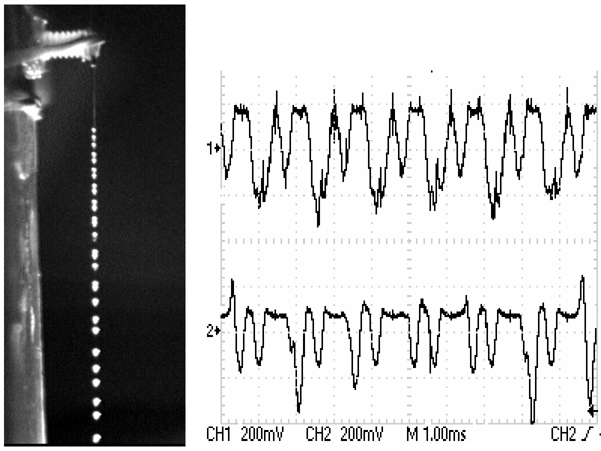

Figure 3 The merging droplet regime. 5ml/min, f=700Hz

-*The branching liquid jet regime* [Basani 1988, Lin 1991, 1994] with the development of two or more monodisperse file of drops. This mechanism has been associated to the excitation with frequencies in the resonance frequency of the capillar (in our case first modes are at 625Hz , 3920Hz).

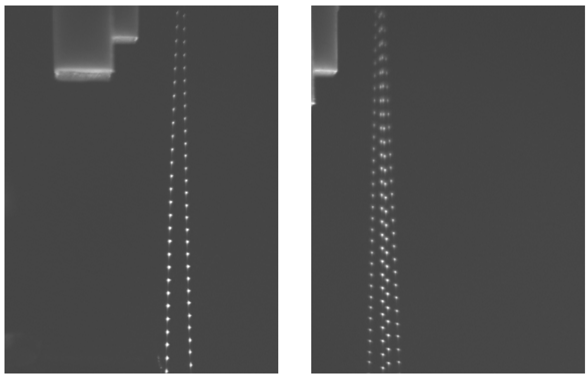

Figure 4 Branching of the jet a)in two files, b)in 4 files

The presence of any one of these regimes can be easily determined by visual inspection or through the opto-device. The peak of the spectrum frequencies of the signals produced by the shadow of the flying droplets in the case of anomalous breaking largely deviates from the frequency of excitation of the piezoelectric.

Range of frequencies of droplet generation : For axial perturbation of the jets the acceptable range of frequencies to generate monodisperse droplets is in general governed by two extremes lower limit is associated to wavelengths slightly in excess of the jet circumference (as predicted by linear theory) and the other associated to random vibration interference and [Bailey 1988]

$$6a < \frac{V_j}{f} < 14a$$

For the lateral vibration of the capillar imposed the range of excitation of the electrified jet in our case this range was modified and fore instance for a voltage of the charging electrode (V_{ch}) of 166 Volts the range extended to $7{,}1a < \frac{V_j}{f} < 31a$. In general it was also observed that electrification of the jet, even slight, enabled a more easy establishment of the normal breakup regime.

Droplet spacing: Droplet separation can be determined if the velocity of the droplets are known with $d_d = \frac{V_d}{f}$ where V_d represents the droplet velocity. If the droplet train is aligned in an horizontal axis for non charged liquid droplets the velocity of the droplets may be estimated with

$$V_d = V_j\left(1-\left(\frac{V_c}{V_j}\right)^2\right)$$

where V_c is the capillary velocity expressed as $V_C = \left(\frac{2\,\sigma}{\rho\, a}\right)^{1/2}$ with σ the surface tension and ρ liquid mass density. This expression can be considered as the initial velocity of droplets issued from the capillary in a vertical axis. Downstream it has to be corrected to take into account for gravitational, aerodynamic and electric forces effects. The figure represents the spacing between droplets for different heights measured from the nozzle. In figure 5 a fitting with a simple theoretical expression (dashed line) that neglects the last two effects indicating that aerodynamic and electric forces does not produce considerable modifications on the droplet spacing.

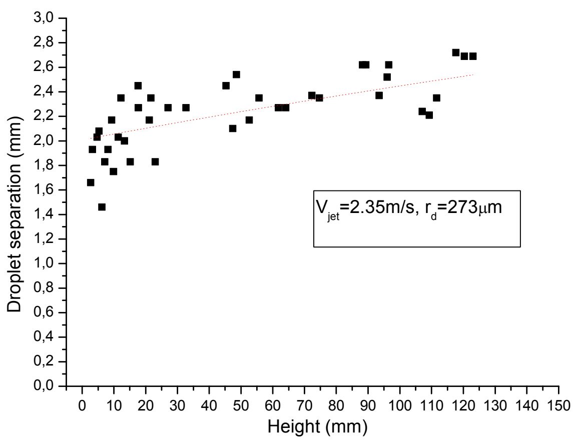

Figure 5 Droplet separation as a function of the height to the nozzle. In dashed line separation produced by gravitational effect with Droplet Velocity at the nozzle exit V_d=2m/s

Taking into account mass conservation and neglecting aerodynamic and electric effects it can also be easily deduced that droplet spacing is linked to r_d through

$$d = \frac{4}{3}\sqrt{\frac{2gh}{V_j^{\,2}} + \left(1-\left(\frac{V_j}{V_d}\right)^2\right)^2}\;\frac{r_d^{\,3}}{a^2}$$

where h is the height form the capillary tip. The fitting of experimental data with this expression can be observed in figure 6 and is rather satisfactory.

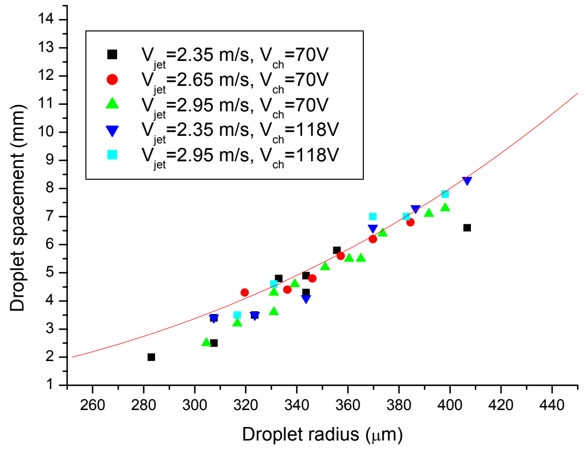

Figure 6.: Droplet separation as a function of droplet radius for different jet velocities and droplet electrification. Height from the nozzle 140 mm

Mean charge to mass ratio: Different works have analyzed the charge of droplets when a jet is electrified by induction [see for instance Atten 1992]. In our case the time required for electric potential diffusion results much shorter than the characteristic time of convection. It is expected in consequence that charge separation is fully achieved in the breakup region of the jet. The experimental results concerning charge to mass ratio for a fixed voltage are represented on figure7 and present slight variations with frequency of excitation and jet velocity.

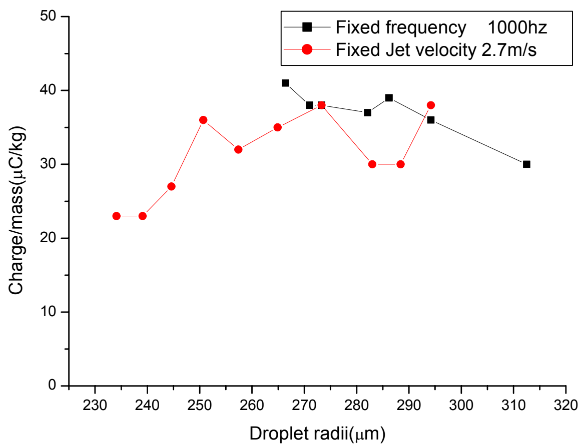

Figure 7 Charge mass ratio for a fixed V_{ch}=166 V

Considering the normal breakup regime the Rayleigh limit for droplet charging $\frac{q_R}{m} = \frac{6}{\rho}\left(\frac{\varepsilon_0 \sigma}{r_d^{\ 3}}\right)^{1/2}$ it can be observed that in our cases this ratio is about 25 times much lesser.

Deflection angle: The electric force that produces deflection and imposes a lateral velocity to the train of droplets is a function of the time duration of the pulse and of its intensity. If time duration of the pulse is very large an important number of droplets will receive a similar deflection producing a large number of droplet with similar trajectories. (see figure 8 and table I) that determines an angle of deflection.

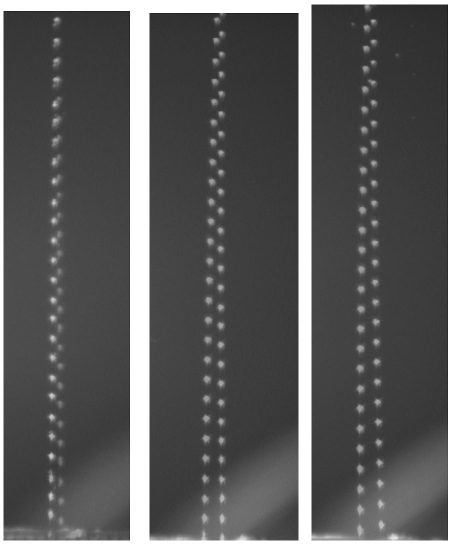

Figure 8: Flowrate 5 ml/min, Frequency 1300 Hz Pulse duration: 1 second-Deflection Voltage: 1kV
a) Charging Voltage: 118 Volt Angle 0,82,
b) Charging Voltage: 166 Volt Angle 1,38°
c) Charging Voltage :214 Volt Angle 1,58°.

	Angle (°)		
Frequency (HZ)	*4,0 ml/min*	*4,5 ml/min*	*5,0 ml/min*
400	0.54	1,00	0.49
500	1.27	1,10	0.64
600	1,51	1,26	1.05
1000	1.56	1,30	1.65

TABLE I Angle of deflection Charging Voltage V_{Ch}=166V Deflecting Voltage 1kV-Pulse duration 1s

When the droplet duration is short enough, only a small fraction of the train of droplets is deflected and droplets trajectories result quite different enabling a better separation process. (See figure 9 and Table II). The deflection here is no longer uniform and only one or two droplets attain maximum deflection by a suitable tuning of the delay of the pulse. The difference produced in droplet trajectories as a consequence of the deflecting pulse enables the recovery of the desired droplet at a distance of about 75 cm from the nozzle exit. This distance however can be shortened by the use of additional plate electrodes placed.

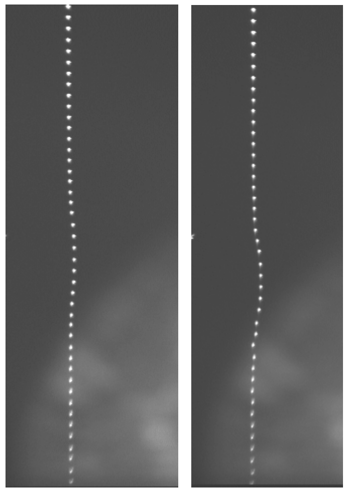

Figure 9 : Flowrate 4,6 ml/min, Frecuency 1400 Hz, Deflecting Pulse 1KV with a duration of 1ms. a) Charging Voltage 166V b) Charging Voltage 261V

Charging Voltage (V)	Angle of Deflection	Number of deflected droplets	Number of deflected droplets
	Pulse duration 1s	Pulse duration 0.01s	Pulse duration 0.001s
70		16	
118	0.82	17	
166	1.22	15	9
214	1.53	17	9
261		16	10

Table II: Deflecting Voltage 1KV
Droplet diameter 256 μm

IV. Conclusion

We have shown in this work the ability of an electrostatic sorter device with droplets produced by lateral excitation of an aqueous jet. In the system all droplets are electrified and in droplet flight it is sensed the droplet that contains the desired nanocristal. Deflecting pulses imposed to the droplets of small duration enable a good separation of this droplet from the train

The development of this kind of sorter to purify quantum dots from in flight droplets is still in a proof phase. We have designed a generation and classifier system that suitable separates droplets at the desired frequency of operation. The coupling of this system with a detecting system is at present subject of research of our groups.

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