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## **Ion induced nucleation based-generator of strictly singly charged (solid - liquid) polydisperse particles up to 1 $\mu\text{m}$ .**

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**In memory of A. Renoux.**

**Keywords:** generator, ion induced nucleation, singly charged particles, evaporation condensation.

### **Abstract:**

Calibration of optical counters, condensation particle counters, electrical impactors, filtration efficiency measurement, heterogeneous condensation (and many other laboratory applications in aerosol science and technology) are widely used with singly charged particles classified by a differential mobility analyzer with particles smaller than 1  $\mu\text{m}$ . Nevertheless the method presents an ambiguity because of the presence of multi charged large particles of the same mobility than singly ones. This ambiguity results in uncertainty in the concentration regarded as a reference. The present paper reports a generation method of strictly singly (positive and negative) charged liquid and solid particles up to 1  $\mu\text{m}$ .

This paper reports a particle generation-method based on ion-induced nucleation of singly charged atmospheric ions. The method uses evaporation and controlled condensation of liquids or solid on seed particles or ions. The ions grow and form wide continuum polydisperse distributions of positive or negative liquid/solid polydisperse particles up to 1 micron. The ions produced with a corona or radioactive or soft X ray or UV source in filtered dry stream air are used as seed nucleus in controlled condensation of vapor from solid or liquid compounds. The final formed droplets or spheres around the ions keep the positive or negative initial charge of the ions.

Vapors from low melting point solids or high boiling point and low vapor pressure liquids are used in this vaporizer-condenser generator. The paper focuses on particles with diameters up to 1  $\mu\text{m}$  dedicated to classical differential mobility analyzers (DMA). The results with larger particles produced with the same generator design using heterogeneous condensation of vapors on sub 10 nm singly charged particles from melting NiCr (Kanthal) wires in air will be published in a second paper (manuscript in preparation). A companion paper on the saturation ratio profiles modeling with Comsol and comparison theory-experiments is in preparation.

### **1\*/ Introduction:**

Liquid or solid aerosol particles (monodisperse or polydisperse) in the super and submicronic diameter range are needed in laboratories for filtration efficiency measurement, calibration of instruments, deposition-losses measurements in tubes or on surfaces, coating, evaporation/condensation studies, inhalation studies, charge states measurements and many others. Atomization/nebulization and evaporation-condensation are the most used simple and robust cheap methods of particles generation for laboratory applications. Atomization / electrospray of solutions (or suspensions) produces particles from 1 nm to 500 nm mostly. Evaporation-condensation of pure compound at high temperatures in an oven or from hot melting material (glowing wires, spark electrodes, lasers) produces particles from 1 to 30 nm single spheres non agglomerates particles.

Large particles (up to 10  $\mu\text{m}$ ) are produced by controlled condensation of liquid or low melting point solid compounds upon nuclei. Sinclair and Lamer (1949) have introduced the controlled condensation method in their well-known generator. Others have made investigations and improvements of the Sinclair-Lamer method to produce quasi monodisperse particles up to 7  $\mu\text{m}$  (Muir & Davis 1967; Swift 1967, Okada et al. 1969; Prodi (1972); Nicolaon et al. (1970); Liu and Lee (1975)) The other solution to produce monodisperse particles is to classify with a differential mobility analyzer particles produced by polydisperse distributions sources (Liu and Pui (1974)).

The differential mobility analyzer (DMA) is used to select particles in a narrow size range from existing polydisperse aerosol sources. The DMA is attractive and unique classifier-generator to study size dependency properties for many aerosol applications.

The main problem of the DMA as a classifier-generator especially for particles larger than 0.1  $\mu\text{m}$  is the presence of multi charged particles mixed with the singly charged ones. Indeed most of the polydisperse aerosol sources

produce singly charged particles mixed with multi charged ones. Neutralizers (mostly radioactive or soft X ray based) are used to bring the polydisperse generated aerosol population to a steady charge state with low concentration of multi charged particles.

The DMA classifies particles according to electrical mobility which depends on the size and charge of the particles. Particles of a given mobility can include singly, doubly and triply charged particles of different diameters. At the Boltzman charge equilibrium (for example) after the 'neutralizer' upstream of the DMA a non-negligible population of doubly and even triply charged particles are mixed with the singly charged ones depending on the size (Liu and Pui 1974).

Efforts have been devoted by several teams to solve this problem. Romay-Novas and Pui (1988) have discussed a method to improve the monodispersity by using a single stage impactor downstream of the DMA to remove the larger multi charged particles of the same mobility. The cut-off of the impactor needs to be adjusted to the geometric mean diameter of the singly and doubly charged particles.

Gupta and McMurtry (1989) developed a bipolar charger that avoids the production of multi charged particles in the 0.1 to 1  $\mu\text{m}$  diameter range. Their charger consists of a 23 cm long, 2.1 cm ID cylindrical tube internally coated with 0.09  $\mu\text{Ci}$   $^{63}\text{Ni}$  radioactive source. Zero charged particles at the inlet of the charger are exposed to low ion concentrations for short time periods. Ion concentrations and residence time must be adjusted to ensure that the particles are mostly neutral or singly charged. For example 1.09  $\mu\text{m}$  particles leaving their charger have far fewer multi charged particles (21%) whereas 72% in the classical 'neutralizer'. Vivas et al. (2008) applied pulse voltage of variable amplitude and duration to a corona charger to reduce the multi charging level similar to bipolar charger with an increase of the singly charging efficiency. Recently Chen et al. (2019) used a corona based unipolar charger where they control the  $Nt$  product to maximize the singly charged fraction of sub-micrometer particles.  $N$  is the concentration of ions per  $\text{cm}^3$ ,  $t$  is the residence time (Pui & Liu 1974). They managed to increase singly charged population of particles in the 20-200 nm versus the concentration given by a classical bipolar charger.

The other way or method is to use controlled condensation on singly charged particles produced with an atomizer or an oven. Uin et al (2009) introduced a method to produce standard large aerosols from singly charged small size nuclei for producing standard aerosols which eliminates the problems arising from the presence of the multi charged particles. They used a tube furnace ( $\sim 1050^\circ\text{C}$ ) to produce silver nucleus ( $\sim 18\text{ nm}$ ), a neutralizer and evaporator- condenser Sinclair-Lamer generator. Their Sinclair Lamer generator uses heated di octyl phtalate (DOP) between 60 and  $225^\circ\text{C}$ . The use of DOP is not encouraged anymore because of its toxicity. Because DOP causes cancer and birth effects among others its use is regulated in EU, USA and many other countries. Di ethyl octyl sebacate nowadays is used thanks to its inhalation safety.

Yli-Ojanperä et al. (2010) use mainly the same set up to develop a standard generator of singly charged particles (traceable particle number concentration standard: singly charged aerosol reference, SCAR). They use an atomizer-dryer before the oven (as suggested by Bartz et al. 1987) before a radioactive source and a differential mobility analyzer to produce small NaCl particles as condensation nucleus. They preferred the atomizer (sodium chloride) thanks to the stability of the nuclei source. Indeed the atomization method of Bartz et al. (1987) is more stable than the evaporation in a tubular oven method given by Scheibel and Porshtendorfer (1983). The aerosol selected by the DMA is then led through a saturator filled with di-octyl sebacate (DOS). A vertical descendant evaporator- condenser similar to the instrument introduced by Lee and Liu (1975) is used by the Finn team to grow the particles. They were able to produce singly charged particles up to 500 nm with an error of 0.15% of multi charged particles.

These methods are based on the use of neutralized particles which cannot ensure 100 % of singly charged particles before and after growth. To circumvent or solve this problem it's convenient to start with strictly singly charged nuclei before the evaporation-condensation process for the growth. Atmospheric ions are the solution since one can produce them bipolar in high concentrations (up to  $10^9\text{ ions/cm}^3$ ) with a home-made and cost effective corona source without any permission nor health risk. One have to keep in mind that the method produces  $\text{NO}_x$  and  $\text{O}_3$ .

Evaporation-condensation method is a well-known (documented and used) method in aerosol science and technology for different purposes. For example Suh et al. (2005); Choi & Kim (2007), used ethylene glycol in a particle size magnifier (PSM) to enhance the charge of nanoparticles.

Kogan and Burnasheva (1960) developed a kind of mixing CPC called particle size magnifier where they mixed a room temperature aerosol in a conical nozzle with a very hot vapor of dibutylphtalate. Their concept was used later by many others in different designs for turbulent CPCs or PSMs. Kogan and Burnasheva (1960) managed to

activate and enlarge sub 10 nm aerosol particles to stable droplets of around 1µm. Okuyama et al. (1987) used the evaporation condensation in his PSM to study the homogeneous nucleation of DBP.

The key idea is to combine condensational growth of nanoparticles and unipolar charging is given by the equation (1).

$$\frac{d(Dp)}{dt} = \frac{4MDv}{R\rho_p Dp} \left( \frac{P_\infty}{T} - \frac{P_d}{T} \right) \cong \frac{4MDvP_d}{R\rho_p TDp} (S - 1) \propto \frac{1}{Dp} \quad (\text{Hinds 1999}) \quad (1)$$

Where M is the molecular weight of the condensing vapor;  $\rho_p$  is the density of the liquid (or solid) working fluid; Dv the diffusion coefficient of the vapor; R the gas constant;  $P_\infty$  the partial vapor of the vapor close to the particle;  $P_d$  and T are the vapor pressure and temperature on the surface of the growing particle; T the temperature of the surrounding vapor; S the saturation ratio of the vapor. The generator presented here uses the same evaporation condensation precept. The only (but significant) difference is the use of singly charged atmospheric ions as nuclei. This allows to simplify considerably the set up and give better results in the sense that there is no multi charged droplets or spheres in the final aerosol. The method no longer asks a neutralizer nor dryer in the case of atomization. The source of seed ions can be unipolar (corona) or any bipolar (radioactive or soft X ray source) based neutralizer. The method is not exactly evaporation condensation but ion induced nucleation through evaporation condensation. Ion induced nucleation has been widely studied theoretically and experimentally because of its importance in atmospheric science.

Previous designs have focused on the monodispersity generation (standard deviation between 1.2 and 1.4 in the case of the Liu and Lee (1975)) or quasi monodispersity (Sinclair–Lamer (1949), Ristovski et al. 1998)). The main goal of the present generator concept is to produce a broad continuum of polydisperse unipolar particles, as is the case of the atomizers. Nevertheless, there is a difference with the atomizers. The fundamental difference may be in the charge state of the generated droplets or spheres. Atomizers indeed produce bipolar multi charged particles.

The present generator is designed as singly charged polydisperse unipolar source to be used with a DMA. Geometric standard deviation of the final droplets diameters varies from 1.7 to 2.4, which is considered polydisperse (Chen, 1993).

Charles Thomson Rees Wilson (1896) have shown the ability of positive and negative atmospheric ions produced with Röntgen X ray source to form particle droplets in a clean and free atmosphere 124 years ago. He was the first to talk in terms of ion induced-nucleation.

During the last decades mixing and laminar condensation particle counters (CPCs) have shown their ability to activate and detect positive and negative atmospheric ions produced with a radioactive source neutralizer and or a corona source (Gamero (2000, 2002), Iida et al. 2011, Hering et al. 2016, Kangasluoma et al. 2016). Water, butanol, ethylene glycol, dibutyl phtalate and di ethylene glycol as working fluid in CPCs have been used to activate atmospheric ions (Maisser & Hogan 2017, Kangasluoma & Attoui 2019) with detection efficiencies between 30 and 70 % (Attoui (2018), Hering et al. (2016), Vanhanen et al. (2011)). The present generator uses these findings to produce singly charged particles in a laminar device given in the figure 1 or mixing device given in the figure S3.

As in the case of laminar or turbulent mixing CPCs singly charged atmospheric ions are activated and grown in a condenser (growth tube). The carrier gas (air in the present study) is saturated with vapor from heated high boiling point and viscous liquids or low melting point solids.

The probability to produce doubly charged atmospheric ions with unipolar (corona) or bipolar (soft X-ray or radioactive material) device is equal to zero. As the consequence of that the droplets or particles produced by the final coated ion keep the same electrical charge that the original residue ion. NO<sub>x</sub> and O<sub>3</sub> production presents the unique disadvantage when corona source is used to produce ions.

Tandem DMA experiments with a Kr85 neutralizer in the middle (Kim et al. 2005) to check if multi charged particles could appear by coagulation have been carried for glycerol and stearic acid as suggest by one of the reviewers. After 10 hours experiments for each compound no multi charged particles have been detected.

## 2\*/ Description of the generator.

Two generators based on two different designs have been built and characterized during this study: laminar based generator and turbulent mixing generator. The paper presents only the results of the laminar design.

The figure 1 gives the schematic of the laminar generator. Aluminum square pipe (25x25 mm) with 20 mm ID, 15 cm length forms the reservoir-saturator. The maximum temperature  $T_s$  of the saturator is limited to 150°C in this study. The length of 15 cm length of the saturator is needed to give time to the carrier gas to be saturated before the inlet of the condenser with flowrates up to 6 lpm (Reynolds number  $\sim 450$ ). Thirty watts heater is used to heat up the saturator to the desired temperature. The saturator and the heater are shrouded with 2 cm thickness glass wool to equalize the temperature of the saturator ( $T_s$ ) and the product inside. Two different inner diameters (ID) cooled tubes of the same length are used and tested as condensers: 10 and 20 mm. The temperature of the air at the condenser outlet is fixed to 20°C. The corresponding Reynolds numbers in the condensers are 743 and 448.

Digital thermometer controllers (Chauvin-Arnoux) with a thermocouple K-type are used to set the temperatures at  $T_s$  (saturator temperature) and  $T_c$  (condenser temperatures). Stainless steel tubes (6mm OD, 4 mm ID) at the inlet and at the outlet of the saturator are disposed over the pool. The outlet tube of the saturator is horizontal contrarily to the laminar CPCs. In laminar CPC design the condenser is on the top of the saturator which causes contamination of the working fluid by the condensed vapors on the wall of the condenser.

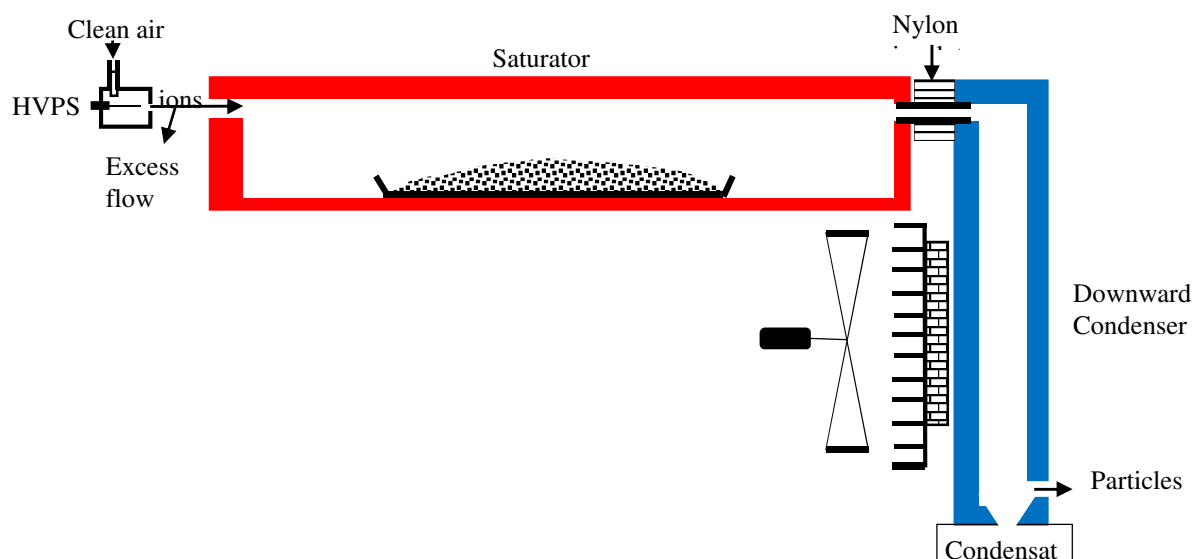


Figure 1  
Design of the laminar ion induced nucleation generator

The solution enacted here allows to the condensed vapors on the walls of the condenser (condensate) to trickle out of the pool in separate chamber. The condensate are drained and collected for recycling. The 6 mm OD stainless tube at the outlet of the saturator fits in a Swagelok nylon connector. The Swagelok connector serves to insulate the tube at high temperature from the condenser kept at room temperature. This nylon connector prevents the use of the device for temperature higher than  $T_s = 150^\circ\text{C}$ . The nylon can be changed to TEFLON or even PEEK (poly ether ether ketone) which can accept operating temperatures up to 250°C. The condenser is 250 mm length aluminum tube cooled with a thermo-electrical cooler Peltier (TEC).

## 3\*/ Experimental set up for the size distribution characterization of the generator.

The mobility measurements of the positive and negative ions from the corona source have been done with a high flow high resolution DMA Attoui-type (Heim et al 2009) in closed loop. Home-made Faraday cup coupled to a Keithly electrometer is used as detector of the high flow DMA.

The penetration of the ions in the saturator have been measured with the same Faraday cage-Keithley electrometer. The experimental set up used to characterize the generator for particles smaller than 1  $\mu\text{m}$  is given in the figure 2. It's the classical method using a DMA, a bipolar high voltage power supply and CPC. A computer program controls the voltage of the DMA with a ramp from a data acquisition card (DAC). The same DAC acquires and records the signal of the CPC for each voltage applied to the DMA. A long cylindrical TSI differential mobility analyzer (44.44 cm length; 1.905 & 0.937 cm radii coupled to a CPC (TSI 3025) are used to characterize the size distribution. The study is limited to diameters smaller than 950 nm at 2 lpm sheath and 0.3 lpm aerosol sample with  $\pm 10\text{kV}$  maximum voltage. Bipolar (Applied Kilovolt HPZ10ZIP025) power supply is used to study positive and negative populations of particles. A logarithmic bipolar ramp is used in scanning mode of the high voltage power supply applied to the inner electrode of the DMA.

The electrical mobility of the particles measured by the DMA is converted to the diameter through the equation (2) that relates the particle diameter to collector rod voltage, number of charges on the particle flow rate and geometry of the long DMA.

$$\frac{D_p}{C} = \frac{2neVL}{3\mu Q_{sh} \ln \frac{r_2}{r_1}} \quad (2)$$

Where  $Q_{sh}$  = sheath flow,  $r_2$  outer radius of annular space,  $r_1$  inner radius of annular space,  $L$  = length between exit slit and polydisperse aerosol inlet,  $V$  voltage on the inner collector rod,  $e = 1.610^{-19}\text{Cb}$ ,  $C$  the Cunningham correction factor.

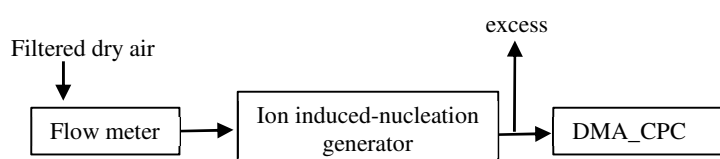


Figure 2

Experimental set up used for the size distribution measurement of the particles generated by the ion induced nucleation generator.

Compound	State	Formula	Vapor pressure	Melting point	Mw(g/mol)	Density
Glycerol	Liquid	$\text{C}_3\text{H}_8\text{O}_3$	0,0228Pa	18°C	92,09	1,26g/cc
Dibutyl phthalate (DBP)	Liquid	$\text{C}_{16}\text{H}_{22}\text{O}_4$	0,0027Pa	-35°C	278,34	1,045g/cc
Di octyl sebacate (DOS)	Liquid	$\text{C}_{26}\text{H}_{50}\text{O}_4$	0,000024Pa	-48°C	426,68	0,9g/cc
Ethylene glycol	Liquid	$\text{C}_2\text{H}_6\text{O}_2$	7Pa	-12,7°C	62	1,1g/cc
Di ethylene glycol	Liquid	$\text{C}_4\text{H}_{10}\text{O}_3$	2Pa	-7°C	106,12	1,12g/cc
PEG 300*	Liquid	$\text{C}_{2n}\text{H}_{4n+2}\text{O}_{n+1}$	0,088Pa	4-8°C	300	1-1,2g/cc
PEG 600*	Liquid	$\text{C}_{2n}\text{H}_{4n+2}\text{O}_{n+1}$	0,053Pa	20°C	600	1-1,2g/cc
PEG 1500*	Solid	$\text{C}_{2n}\text{H}_{4n+2}\text{O}_{n+1}$	0,019Pa	44-48°C	1500	1-1,2g/cc
PEG 8k*	Solid	$\text{C}_{2n}\text{H}_{4n+2}\text{O}_{n+1}$		50-60°C	8000	1-1,2g/cc
PEG 40k*	Solid	$\text{C}_{2n}\text{H}_{4n+2}\text{O}_{n+1}$		60-80°C	40000	1-1,2g/cc
PEG 50k*	Solid	$\text{C}_{2n}\text{H}_{4n+2}\text{O}_{n+1}$		75_95°C	50000	1-1,2g/cc
Potassium sodium tartrate	Solid	$\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$		75°C	282,1	1,79g/cc
ter butanol	Solid	$\text{C}_4\text{H}_{10}\text{O}$		25°C	74,12	0,78g/cc
Stearic Acid	Solid	$\text{C}_{18}\text{H}_{36}\text{O}_2$		69°C	284,47	0,94g/cc

Paraffin	Solid	$C_nH_{2n+2}$	50-57°C	~785	0,94g/cc
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Table I  
List of the compounds tested in this study.

The table 1 gives a list of liquid and solid compounds tested in this study with their properties that can be used to produce liquid (spherical) and solid particles. The most important parameters are their low vapor pressure at room temperature and their low boiling point.

The table ST2 (in the annex) gives other solid compounds as candidates for solid particles which can be used to produce vapor for the generation of liquid particles. The table ST3 shows a list of liquid compounds. The compounds given in ST2 and ST3 lists have not been tested.

#### 4\*/Results and discussion.

##### 4-1\*/ Characterization of the corona source.

The study uses a corona unipolar source for the ions generation. Radioactive or soft x ray source will give more or less the same results in terms of size distributions of the final particles or droplets. The concentrations could be different since the bipolar sources produce less ion concentrations because of the recombination neutralization. On the other hand a corona source solves the problem of the regulation in terms of radiation protection.

The figure 3 gives an example of the mobility diameter distribution of the positive and negative ions produced by the corona source at different flowrates of clean dry compressed lab air with +5 kV and -5 kV. The distributions show different classical peaks corresponding to a mixture of different atmospheric ions produced with corona, radioactive or soft X ray source (Liu et al 2020). One can see that there is a significant difference between positive and negative distributions. While the negative distribution shows two main well defined peaks the positive distribution shows a series of more complicated unresolved peaks. Indeed there are more abundant peaks poorly resolved forming a mixture of different species. On the other hand the mobility at low flowrate (2 lpm) shows a flat continuum signal trend without any peak below 1.15 nm. The other difference between positive and negative distributions is the signal strength. The concentration of the negative ions seems higher than the concentration of the positive ones because of the monodispersity in the case of the negative ions. But the total concentration (average concentration) measured with an electrometer of positive ions is much higher than the total concentration of the negative ones. At 6 lpm for example one can see more peaks (species) of high mobility than at low flow rate (2 lpm). This point will have a consequence on the size distribution of the final particles at the outlet of the condenser. Indeed at high flowrates there are more candidates to grow in the condenser including the smallest ones which are hard to activate.

The measured mobility diameter distributions of the figure 5 (A and B) are at the outlet of the DMA without taking into account the transmission of the DMA. Since the corona source is used without classification in the generator, at least the concentrations of the different peaks are much higher. On the other hand additional species peaks could be present because the transmission inside the DMA is size dependent. The highly mobile ions could have been lost inside the DMA. This point is illustrated in the figure 5A for 2 lpm. The mobility diameter distribution can change from one day to the other of course because of the chemical composition of the vapors present in the atmosphere.

The measured ion mobility ( $Z_p$ ) was converted to mobility equivalent diameter according to the Stokes-Cunningham formalism (Ude & Fernandez de la Mora, 2005):

$$Z_p = \frac{e}{3\pi\mu d_z} \left( 1 + K_n \left[ A + B e^{-C/K_n} \right] \right) \quad (3) \quad K_n = \frac{2\lambda_g}{d_z} \quad (4) \quad \lambda_g = \frac{\mu}{\rho_g} \sqrt{\frac{\pi M_g}{2RT}} \quad (5)$$

Where  $d_z$  is the mobility equivalent diameter,  $\mu$  is the dynamic viscosity,  $e$  is the elementary charge ( $1.610^{-19}C$ ),  $Kn$  is the Knudsen number,  $\lambda_g$  is the mean free path of the gas,  $\rho_g$  is the gas density, and  $T$  is the gas temperature.  $A = 1.257$ ,  $B = 0.4$ , and  $C = 1.1$  (Kim et al. 2005; Larriba et al., 2011).

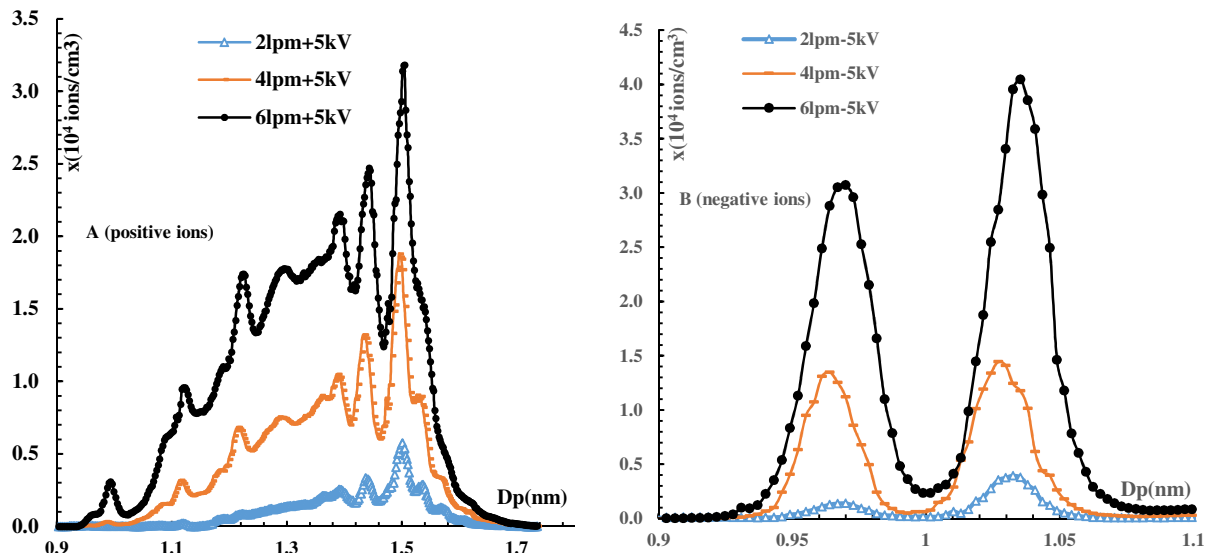


Figure 3  
Mobility diameter of the positive (A) and negative (B) ions for different flowrates at 5 kV.

The corona source outlet is connected directly to the Faraday cup of the aerosol electrometer. One can see that the corona source produces more or less two times positive ions than negative ions. The figure 4 gives an example of the total concentration of positive and negative ions at the outlet of the saturator (or the inlet of the condenser) for different flowrates at room temperature and at 100°C. The corona source is directly connected to the inlet of the saturator of the generator. The whole stuff produced by the corona source is introduced inside the saturator without crucible. The flowrate is measured at the inlet of the saturator at room temperature with a TSI mass flowmeter. The temperature of the saturator in the shown data is 100°C. The voltage of the corona needle is +/- 5kV. Because of the high temperatures in the saturator (up to 150°C) the flowrate will expand according to the ideal gas law by a factor of 1,44 at 150°C for example. This affects the residence time of the ions and the saturation ratio of the carrier gas.

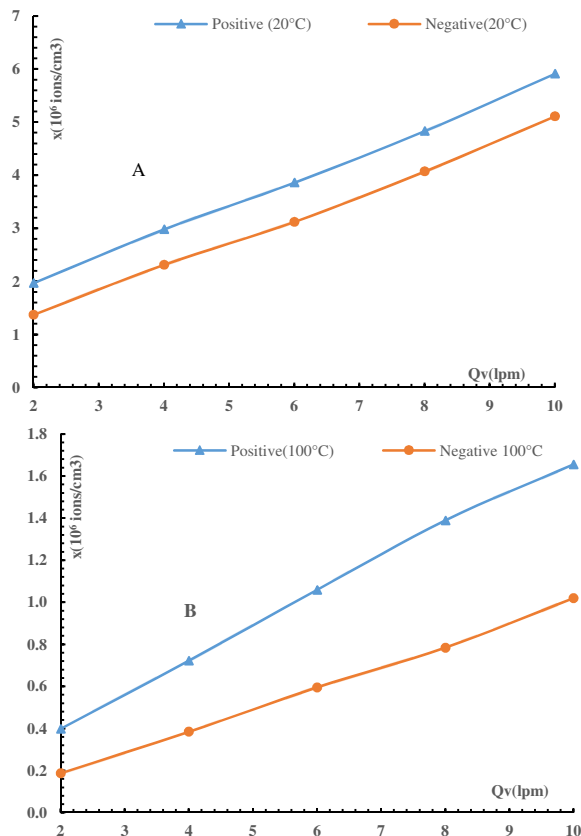




Figure 4  
Positive and negative ion concentrations at room temperature (A) and at 100°C (B) versus flowrate.

The populations of ions (positive or negative) are mixed (laminar mixing) alternatively with the vapors produced when a compound is present in the saturator. The total flowrate in the corona source in this study enters the saturator-condenser. A bypass (shown in the figure1) can be used at the outlet of the corona source to reduce the flowrate in the saturator condenser. That will affect the transmission of the ions in the saturator-condenser but will (at the same time) reduce the dilution rate of the vapor concentration. High flowrates in the generator have an effect on the concentration of ions produced in the corona source, their transmission up to the condenser and on the vapor concentration (by dilution) in the saturator. High flowrates decrease also the residence time in the saturator and in the condenser. Taken together, these factors reduce the quantity of vapors available at the outlet of the saturator and increase the concentration of ions candidates to grow. The flowrate affects the processes that take place in the saturator and in the condenser. High flow in the saturator minimizes the losses (increases the transmission) of the high mobility ions. At the same time it decreases the residence time and consequently decrease the saturation of the carrier gas. These antagonistic effects can be used by the user to get the size and the concentration of particles he needs. High flowrate in the condenser have a consequence on the residence time (of the vapors and ions) and growth of the particles. Short residence time decreases the saturation ratio which is the key for nucleation or condensation process. Beside the two effects cited one has to keep in mind that high flow has at least one positive effect. Indeed it suppresses the homogeneous nucleation which produces non charged droplets and consume vapor. The mean consequence of the high flow linked is the shift of the distribution to smaller diameters. This is because the concentration of ions to grow is higher. In the second hand the quantity of vapors is lower by dilution.

#### 4-2\*/ Characterization of the homogeneous nucleation in the generator.

The homogeneous nucleation produces large concentrations (up to  $10^5 \text{ p/cm}^3$ ) of particles in the absence of seed ions with  $T_s=150$  and  $T_c=20^\circ\text{C}$ . The positive point for this study is that they are not charged electrically. They will not be seen by the classifier used at the outlet of the generator. The homogeneous nucleation rate and size distributions are measured without corona source. The total concentration is measured with a CPC and the size distributions are determined with a TSI SMPS (long cylindrical DMA 3025 CPC and a 3088 soft X ray source) and *TSI AIM soft*. The threshold depends on the compound in the saturator, the temperature difference (DT or  $\Delta T$ ) and the flowrate. The  $\Delta T$  is more or less the same for all the tested compounds.  $T_c$  is fixed to  $20^\circ\text{C}$  to be close to the temperature at which the droplets or particles will be used (room temperature).  $T_s$  varies from 100 to  $150^\circ\text{C}$  maximum for safety material reasons. The flowrates varies from 2 to 6 lpm maximum to keep the flow laminar in the saturator and in the condenser. The homogeneous nucleation rate of glycerol is given in the figure 5 A as an example. The figure 5 B gives the size distribution of the homogeneous nucleation droplets (uncharged empty droplets).

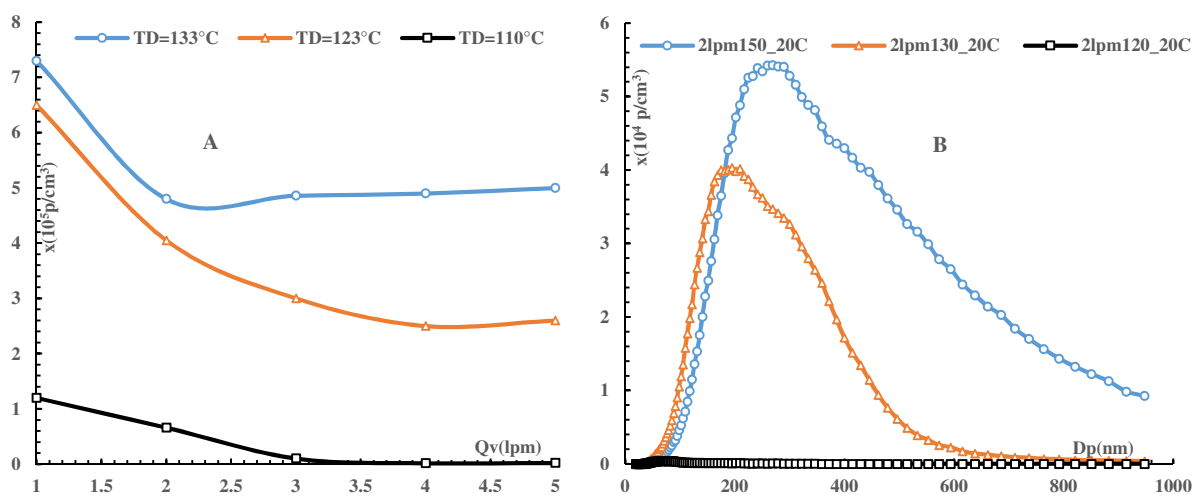


Figure 5  
Characterization of the homogeneous glycerol droplets in terms of concentration vs flowrate (A) and of size distribution (B) for 2lpm and different temperature differences (B).

### 4-3\*/ Characterization of the generator in terms of size distributions:

To keep the saturator clean and prevent contamination and or mixing of different used compounds, alumina crucibles are used. However this is not enough to have a clean saturator after use for another product to test or use. Indeed the vapors produced at high temperatures in the crucible diffuse to the walls of the saturator. More than five hours are needed to clean the walls of the saturator at high temperature (150°C) and high flowrate of clean air (up to 10 lpm) from the previous compounds. Of course the saturator can be disassembled and cleaned with a brush and a solvent to reduce the cleaning time. The cleaning of the generator is needed only when the user needs to change the working fluid. The condenser is kept at room temperature (20°C) during this cleaning time and the corona source at 5 kV positive or negative. A CPC (TSI 3025) is used to monitor the outlet of the generator during the cleaning time.

The generator is characterized with liquid and solid compounds. The table I gives the list of the compounds used during this study. The applied voltage to the needle within the corona chamber is intentionally limited to 5 kV in positive and negative mode for safety reasons. As seen in the figure 5 the ion concentrations produced at 5 kV is around  $10^6$  ions per  $\text{cm}^3$  of air. The concentration of particles per  $\text{cm}^3$  at the outlet of the condenser will be around  $10^4$  p/cc with an activation and growth efficiency supposed around 1%. In case higher concentrations are needed a multi needle saturator can be designed as shown in the appendix (figureS1).

The temperature in the saturator is limited to 150°C because of the use of nylon as insulator around the tube between the saturator and the condenser. A prototype using PEEK (polyetheretherketone) as insulator is build but not tested. PEEK can be used up to 250°C. On the other hand the results with a maximum of 150°C are good enough for particles smaller than 1  $\mu\text{m}$ .

Air flowrate, polarity of the ions (positive/negative) and  $T_s$  are the three parameters used to tune the size distributions of the generated particles of the different compounds. Two different inner diameter condensers (10; 20 mm) are also tested to study the effect of the residence time, axial and radial diffusion of vapors molecules on the size distributions. The three condensers are 250 mm length. Only few results are given in this paper.

#### 4-3-1\*/ Effect of the saturator temperature.

The key factor for the condensation of the vapors produced in the saturator on the seed ions is the saturation ratio in the condenser. The temperature  $T_c$  inside the condenser is kept constant and close to the room temperature (20°C). The temperature sensor (thermocouple K) is installed inside the flowrate at the outlet of the condenser. To prevent contamination and vapor deposition on the thermocouple of the saturator the temperature  $T_s$  is measured on the outer wall of the saturator. The saturation ratio which is a function of temperature difference  $\Delta T = T_s - T_c$  (or  $T_D$  for temperature difference) is then controlled by the changes of  $T_s$  since  $T_c$  is always constant.  $T_s$  in the case of the present prototype ING (ions induce nucleation generator) varies from 120 to 150°C maximum for long terms measurements safety reasons.

The figure 6 (A and B) gives the results for stearic acid positive and negative particles at 2 lpm air for different  $T_s$ . The figure 7 (A and B) gives the results for paraffin (solid particles). The concentrations of small particles (below 200 nm) are not changed by the changes in temperatures. It seems that the increase of the vapor concentrations in the saturator does not affect the growth of the ions activated at low temperatures for both polarities even if the chemistry compositions of the ions are very different. The effect of  $T_s$  (molecule concentration of working fluid) is not identical in terms of size distribution for all the compounds. Glycerol for example in the figure 8 (A and B) gives larger diameter droplets in positive and in negative mode for the same ID condenser. This is due to the volatility of the liquids versus the solids. The solid compounds to melt use a part of the thermal energy given in the saturator. It is not the case for the liquids. This phenomenon appears also in the activation of sub 2 nm particles in the CPCs. Indeed the activation and the detection efficiency is strongly linked to the working fluid and to the chemistry of the particles. Di ethylene glycol for example have a low activation efficiency for organic ions (Kangasluoma and Attoui 2019) and high detection efficiency for non-organic (metal oxides for example) of the same mobility diameters.

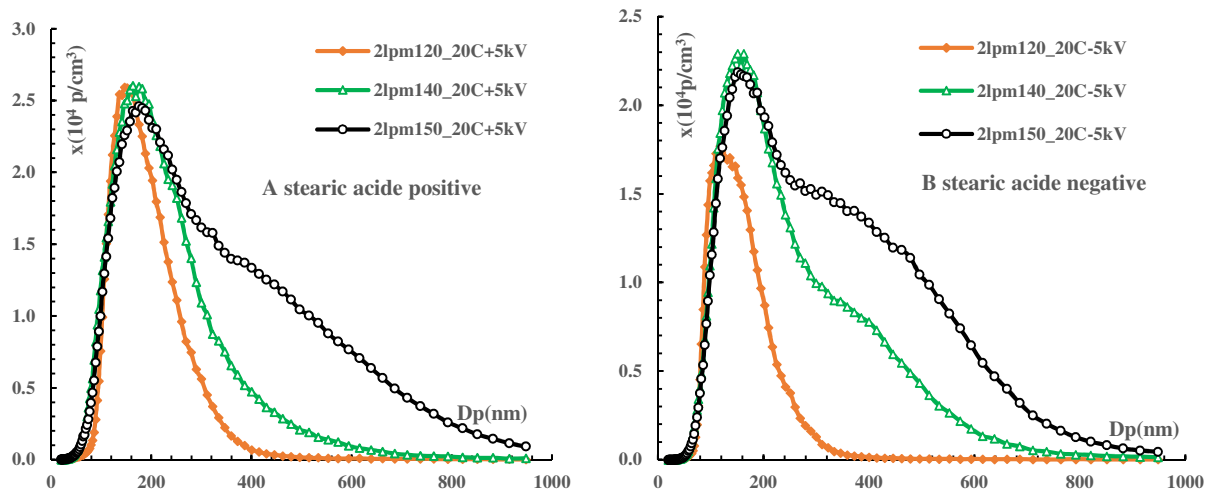


Figure 6

Size distributions of stearic acid solid particles at 2 lpm for different saturator temperatures A positive particles; B negative particles. The inner diameter of the condenser is 20 mm.

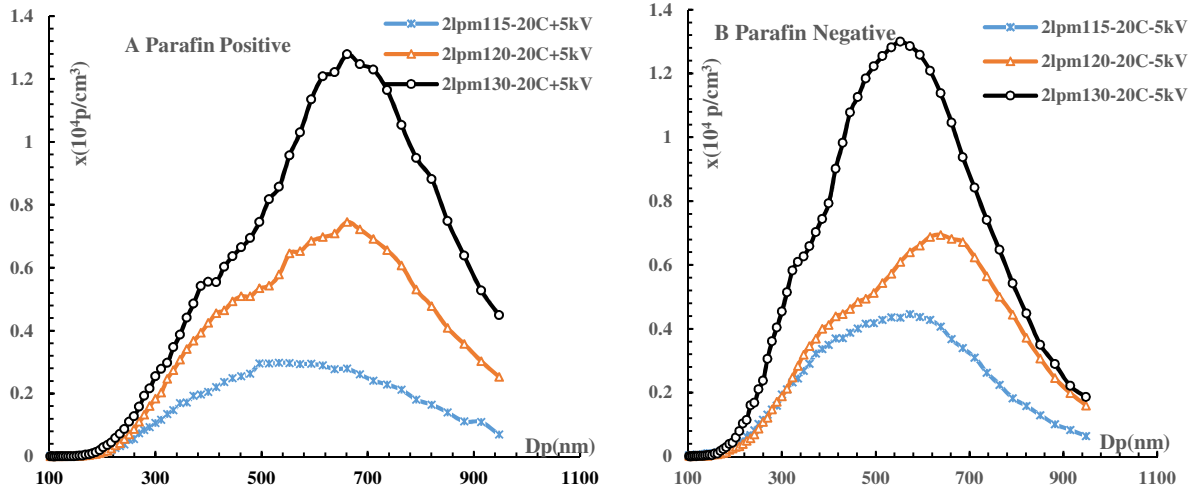


Figure 7

Size distributions of solid paraffin (A positive and B negative) particles for different saturator temperatures for 2 lpm flowrate in a 20 mm ID condenser.

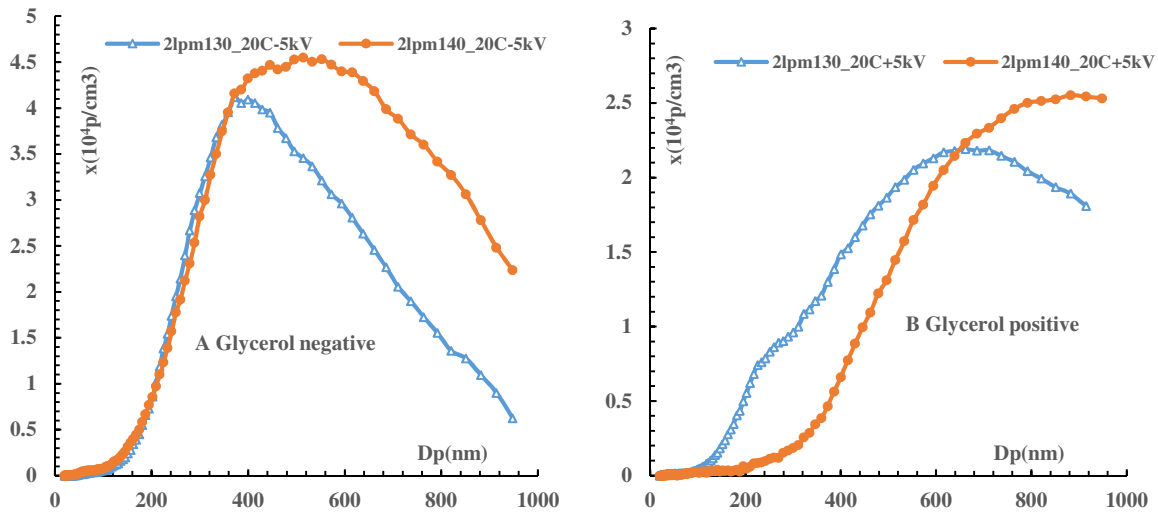


Figure 8

Size distribution of liquid particles of glycerol for  $T_s = 130$  and  $140^\circ\text{C}$  at 2 lpm in a 20 mm ID condenser.

#### 4-3-2\*/ Effect of the ion concentrations.

The concentration of ions to activate and grow in the concentration play an important role. Indeed for the same concentration of molecule vapors the final droplet diameters will be the same for low or high concentration of candidates. In simple words the ions have to share the same quantity of vapor produced in the saturator however they are numerous or not. This will affect the final size of the droplets or spheres they will form at the outlet of the condenser.

To study the effect of the ion concentrations on the size distribution of the droplets one can use the flowrate of the carrier gas or the voltage applied to the needle of the corona source. As seen in the figure 5 the concentration of ions is proportional to the flowrate in the corona source. At the same time the concentration of the vapor molecules in the saturator is inversely proportional to the flowrate. The main benefit of the high flowrate resides in the axial transmission of the ions and the vapor molecules in the saturator. Then to keep the concentrations of vapor molecules constant one can use only the voltage of the corona source. The figure 9A (di octyl sebacate) and 9B (paraffin) give a clear message on the effect of the losses inside the saturator for three different voltages of the corona source (-3; -6; -8 kV and -3;-5;-7 kV). Indeed for the same flowrate in the corona source (and in the saturator-condenser), the same  $\Delta T$  ( $\Delta T$ ), the same vapor molecules concentration and of course the same compound one can see that the shape of the size distributions are more or less the same. The DOS droplet concentrations for example at -8 kV are tiny higher because the ion concentrations produced at -8 kV are higher than at -6 and -3 kV. At 2 lpm all the ions have time to be activated and grow which gives the same shape of the distribution. The maximum of the distribution shifts to the small sizes (from 150 to 80 nm) and the ion concentrations increase significantly. The particle diameters are smaller because there are more ions candidates to grow for the same quantity of vapors.

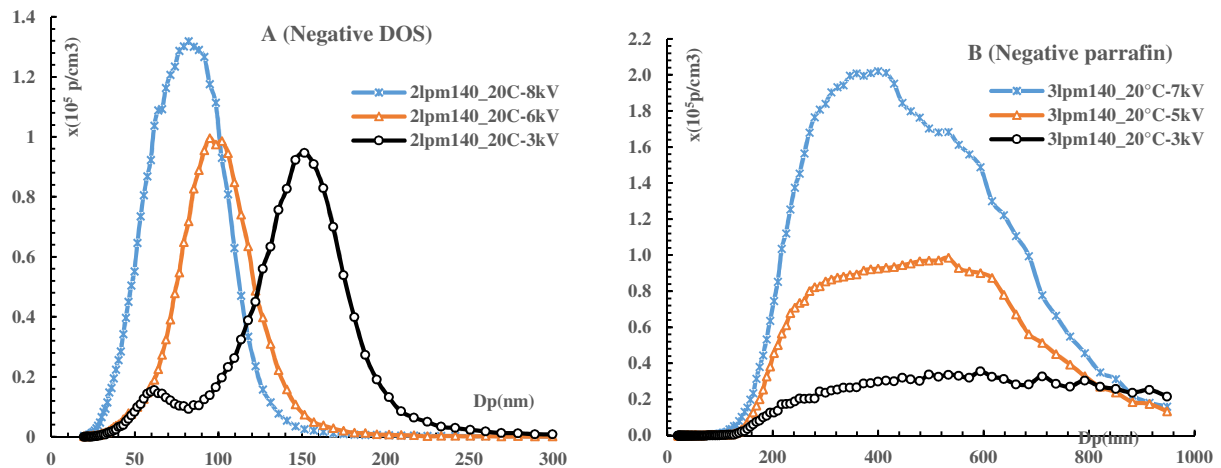


Figure 9  
Size distributions of DOS (A) and Paraffin (B) negative particles with different high voltage values in the corona source.

#### 5\*/ Generation of ultrafine particles

From the previous results it came out that ultrafine droplets or spheres can be produced by the generator if

- the concentration of ions as candidate to grow is high enough ( $> 10^6$  ions/cm<sup>3</sup>) in the condenser.
- the concentration of vapor is low (low  $T_s$ )
- the residence time in the condenser is short.

To increase the concentration of ions (as candidates to grow) in the condenser the solution is to install the corona source between the saturator and the condenser. This decreases the losses of the candidate to growth in the saturator. To lower the concentration of condensable vapors,  $T_s$  needs to be low or the flowrate needs to be increased. Indeed high flowrate dilute the vapor concentration. To shorten the residence time in the condenser the inner diameter must be small and the flowrate high.

The figure 10 (A and B) gives glycerol results at  $T_s = 120^\circ\text{C}$  for 4 and 6 lpm with a 10 mm condenser and  $\pm 5\text{kV}$ . The corona source is between the saturator and the condenser in this experiment.  $120^\circ\text{C}$  is the minimum temperature to produce enough glycerol vapors. The corona needle supplied with + and - 5kV produces high ion concentrations. Flowrates 4 and 6 lpm induce short residence and growth times in the 10 cm condenser. These

conditions are suitable for the generation of small droplets as seen in the figure 10 (A and B). The size of the peak of positive particles shifts from 57 to 41 nm when the flow rate increases from 4 to 6 lpm. For the negative particles the shift is more pronounced: 98 to 46 nm.

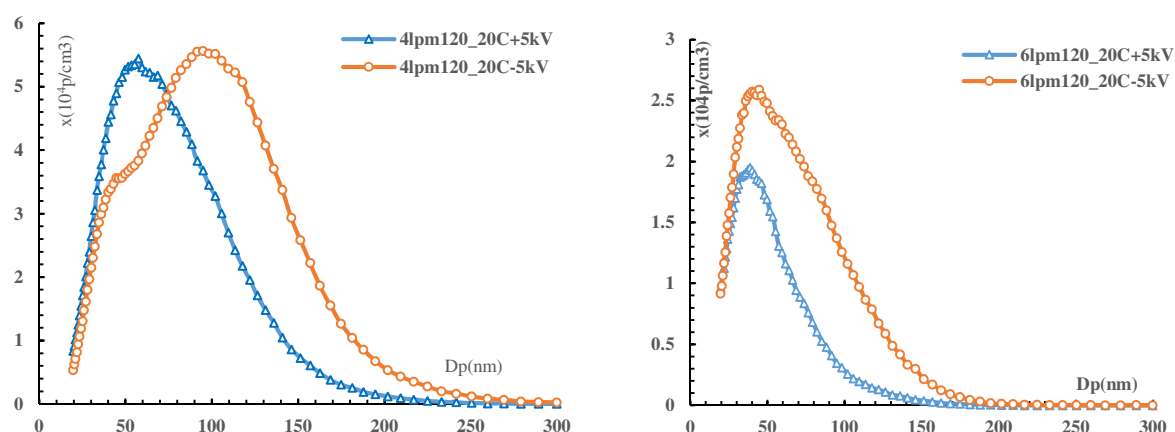


Figure 10  
Effects large flow rates in the generator on the size distributions of positive and negative particles of glycerol.

## 6\*/ Parameters governing the particles size distributions:

The ING (ion induced nucleation generator) is based on the concept of activation and growth of atmospheric ions in an evaporation-condensation device. The device is similar to the continuous CPC. The particles (solid or liquid) produced by the generator are not monodisperse. The objective of the instrument is to produce singly charged particles as polydisperse as possible. The device is supposed to be used in serial with a differential mobility analyzer to select monodisperse particles from the continuum of polydisperse particles. The width of the polydisperse distributions are as large as possible to cover the whole range of a DMA for each compound (liquid or solid). The temperature difference  $\Delta T = T_D = (T_s - T_c)$ , the air flowrate  $Q_v$  and the concentration of the seed ions are the parameters which determine the size distributions of the final droplets or solid particles.

Large  $\Delta T$ s and low flowrate give large particles. Small  $\Delta T$  combined with large flow rate give small particles.  $T_s$  is limited to 150°C in this study and  $Q_v$  the air flowrate to 6 lpm.  $T_s$  between 120 and 150°C and flowrate between 2 and 6 lpm had performed satisfactorily in the range of DMA for positive and negative, liquid and solid particles. High flowrates increase the concentration of the ions and their transmission in the saturator down to the condenser inlet. At the same time high flowrates decrease the concentration of vapors produced in the saturator by dilution.

## 7\*/ Conclusion

Ion induced nucleation based generator of singly charged particles is designed and tested in this study. The goal of the study is to design singly charged polydisperse particles generator to use with a classifier. The generator produce a continuum distribution singly charged up to 1  $\mu\text{m}$  with concentrations between  $10^3$  and  $10^5$  p/cm<sup>3</sup>. The generator has the same design than the continuous flow condensation particle counter.

The generator produces singly charged spherical particles (liquid and solid) with different chemical composition and density without neutralization device. The seed ions are produced by a unipolar corona source supplied with filtered atmospheric dry air. Low vapor pressure liquids or low melting point solids are used to produce vapors in the saturator which condense in the condenser on the ions to form droplets or spheres. The final droplets or spheres carry the charge of the seed ions. All the droplets and spheres are singly positively or negatively charged. The generator produces a large amount of zero charged particles by homogeneous nucleation because the temperature difference  $\Delta T$  between the saturator and the condenser is set at high values to activate the atmospheric ions. The homogeneous particles are zero charged. They are not de facto interesting since the generator is designed to be used as a polydisperse source of electrically charged particles for a DMA.

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