



Ultrafine Particle Generation through Atomization Technique: The Influence of the Solution

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ABSTRACT

The present work is focused on the characterization of a sub-micrometer aerosol generation system (TSI 3940) in terms of particle number distributions and total concentrations as a function of the solution. Fourteen soluble salts were tested, and different solution molar concentrations were considered.

The experimental apparatus was composed of a Submicrometer Aerosol Generator TSI 3940, a Scanning Mobility Particle Sizer spectrometer (SMPS 3936, TSI), and a Condensation Particle Counter (CPC TSI 3775).

Particle number distributions and total concentrations were found to change as a function of the molar concentration of the solution. In addition, at a fixed molar concentration of the solution, different particle number distributions and total concentrations were measured as a function of the salt used in the solution preparation. The mode and standard deviation of the distribution also varied as the solution changed, and thus salts able to provide number concentrations higher than the NaCl ones at low diameter ranges were obtained. For example, ammonium chloride (NH₄Cl) provided particle number concentrations at 8 nm and 10 nm about 40-fold and twice the NaCl ones, respectively.

Keywords: Particle generation; Ultrafine particles; Atomization; CPC calibration; SMPS.

INTRODUCTION

In the last decades a growing interest in airborne particle measurements was detected since negative health effects due to exposure to particles were observed (Simkhovich *et al.*, 2008; Franck *et al.*, 2011; Schmid *et al.*, 2009). Even if the regulatory authority policies to reduce people exposure to particles are still mostly based on particle mass concentration standards, PM₁₀ or PM_{2.5} (U.S. Environmental Protection Agency, 1997; European Committee for Standardization, 2001; European Committee for Standardization, 2005; European Commission, 2008; European Parliament and Council, 2008; European Parliament and Council, 2010; Buonanno *et al.*, 2011a), during the last years the scientific community is focusing on new exposure metrics mainly related to sub-micrometric and ultrafine particles (UFPs) such as particle number (Franck *et al.*, 2011) and surface area concentrations (Giechaskiel *et al.*, 2009a; Cauda *et al.*, 2012).

The main goal of toxicological studies is to determine an exposure-dose-response correlation for each particle metrics (Sayes *et al.*, 2007). To this purpose, air quality experts should be able to characterize people exposure to particles

in different microenvironments (Buonanno *et al.*, 2011b; Stabile *et al.*, 2013) in order to provide accurate data to toxicological and epidemiological researchers. Therefore, an adequate evaluation of the exposure-dose-response correlation can only be pursued if particle concentration measurements performed are worthy from a metrological point of view. Thus, instrument calibration represents a key aspect in this research field.

The Need of Calibration

Particle number concentration measurements are mainly performed through particle counters based on both condensation (Condensation Particle Counters, CPCs; Kulkarni *et al.*, 2011) and electrical techniques (Marra *et al.*, 2010; Buonanno *et al.*, 2013). The CPCs are usually characterized by better metrological performances and, for this reason, they are also used in Mobility Particle Sizer spectrometer configurations to measure particle number distributions (Buonanno *et al.*, 2009; Kulkarni *et al.*, 2011). Moreover, on the basis of the findings of the Particle Measurement Programme (PMP) (Giechaskiel *et al.*, 2009b), CPC represents the only particle counter device provided by the regulatory authorities (Economic Commission for Europe of the United Nations, 2012) on particle number measurement recently introduced in Euro 5/6 light duty vehicle legislation (European Commission Regulation 692/2008). According PMP regulation, CPCs must guarantee

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metrological performances such as: linear response to particle concentrations over the full measurement range in single particle count; counting accuracy of $\pm 10\%$ across the range in single particle count mode; minimum counting efficiencies at particle electrical mobility diameters of 23 ± 1 nm ($50\% \pm 12\%$) and 41 ± 1 nm ($> 90\%$). To meet these metrological requirements, the CPCs should be calibrated at least annually (Giechaskiel *et al.*, 2009b; Commission for Europe of the United Nations, 2012).

Summarizing, both i) the CPC metrological requirements stated by the PMP in particle number emission measurements, and ii) the adequate particle number exposure-dose-response correlation evaluation are based on a rigorous CPC calibration procedure. The calibration (ISO/IEC Guide 99–12, 2007) is performed comparing the CPC under investigation with either a calibrated Aerosol Electrometer (primary method, Liu and Pui, 1974) or a reference CPC directly calibrated by the primary method (secondary method) when simultaneously sample the same aerosol. In particular, such calibrations are performed measuring particles properly produced in generators.

Particle Generation

In order to perform CPC calibration through primary method as well as to evaluate the response of the CPCs as a function of the particle size, monodisperse particles are usually needed in calibration processes. Monodisperse aerosols can be obtained in different ways: i) aerosolizing engineered particles (e.g., PSL particles), ii) directly generating monodisperse particles (e.g., through an Inkjet Aerosol Generator; Yli-Ojanperä *et al.*, 2012), and iii) classifying particles from polydisperse aerosol previously generated. The latter is actually the only useful technique to generate monodisperse particles in the size range lower than 50 nm. It requires a sub-micrometer aerosol generator able to produce polydisperse aerosols and an electrostatic classifier able to: a) electrically neutralize such particles, and b) classify monodisperse particles according to their electrical mobility diameter (Liu and Pui, 1974; Fletcher *et al.*, 2009). Thus, the number of particle flowed to the CPCs under calibration is function of the Boltzmann equilibrium charge distribution provided to the particles by the neutralizer (Wiedensohler *et al.*, 1986; Kulkarni *et al.*, 2011); as an example the fraction of particle smaller than 20 nm carrying one positive elementary charge is lower than 10%; therefore, in order to calibrate CPC at very small particle size, very high particle concentrations need to be generated.

Several aerosol generation techniques were designed to produce either monodisperse and polydisperse aerosols carrying liquid and/or solid particles. Amongst these, one of the most reliable, repeatable, flexible, and cheap techniques is based on the atomization of a properly prepared solution and the consequent evaporation of the solvent from the solution droplets (Liu and Lee, 1975; Park *et al.*, 2012).

Aims of the Work

Although the sub-micrometer aerosol generator based on atomization technique can be used with different solutes, such technique was only characterized for few of them

(TSI Inc., 2005). In particular, most of the data in the scientific literature were obtained using sodium chloride (NaCl) as solute; only few studies reported experimental campaigns using other solutes (e.g., NaNO_3 , $(\text{NH}_4)_2\text{SO}_4$), and they were not designed to show the influence of the solute on particle generation process (Hogrefe *et al.*, 2004; Mikuška *et al.*, 2004; Liu *et al.*, 2007; Kulkarni *et al.*, 2009; Hu *et al.*, 2011).

The aim of this paper is to characterize the sub-micrometer aerosol generation system TSI 3940 in terms of particle number distributions and total concentrations as a function of solute type in order to evaluate the effect of the solution on the particle atomization/generation technique. To this purpose different soluble salts were tested (e.g., sulfates, nitrates, carbonates and halides) at the same molar concentration of the solution: molar concentrations ranging from 2×10^{-6} to 2×10^{-3} mol/L were considered.

EXPERIMENTAL ANALYSIS

Generation Equipment Description

The sub-micrometer aerosol generation system TSI 3940 is based on the atomization of the solution and evaporation of the solvent (Liu and Lee, 1975) in order to obtain dried salt particles (Fig. 1). In particular, the solution, obtained by dissolving the salt in deionized water, is constantly drawn from a plastic-coated glass bottle into the atomizing section through a vertical passage (Bernoulli effect) where is atomized by the high-velocity air jet produced by the compressed air expanding through an orifice. The atomization leads to the formation of droplets with a mode of 350 nm and a standard deviation less than 2 (TSI Inc., 2005). Anyway, the droplet size distribution and concentration can be partially regulated by changing the air pressure (1.5–2.5 bar; TSI Inc., 2005). Therefore, large droplets are removed by impaction on the wall opposite the jet, whereas small droplets leave the atomizer moving to the diffusion dryer to complete the water absorption as the wet aerosol passes through. Therefore, the generation process theoretically produces one dry salt particle for each solution droplet.

Experimental Apparatus

In order to perform number distribution and total concentration measurements of aerosol produced by atomization technique, the following apparatus were used:

- a Submicrometer Aerosol Generator TSI 3940 made up of a Constant Output Atomizer (TSI 3076; Shoreview MN, USA), a Filtered Air Supply (TSI 3074B; Shoreview MN, USA), and a silica gel Diffusion Dryer (TSI 3062; Shoreview MN, USA). It is able to generate particles in the size range 0.01–1.0 μm with a generation rate of 10⁶ part/s. Particle concentrations and flow rates at the exit of the generator are adjustable with the dilution bridge;
- a Scanning Mobility Particle Sizer spectrometer (SMPS 3936, TSI; Shoreview MN, USA) made up of an Electrostatic Classifier (TSI 3080) and a Condensation Particle Counter (CPC TSI 3775; Shoreview MN, USA) able to measure particle number distributions in sub-micrometric range;

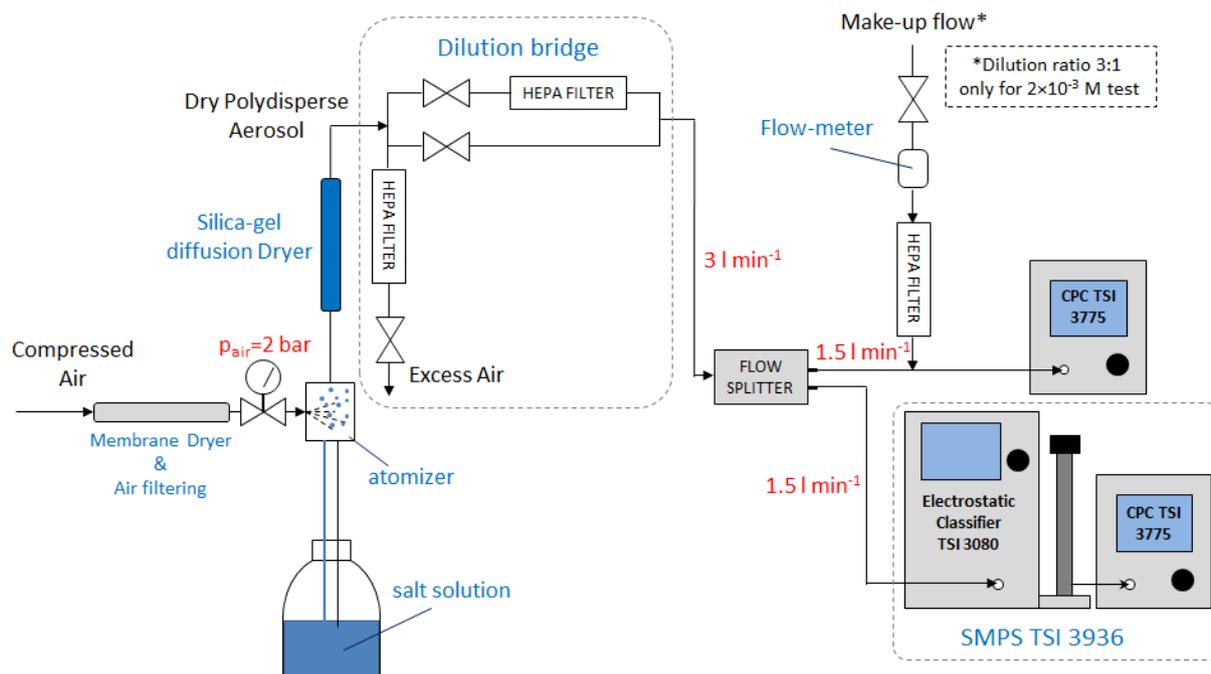


Fig. 1. Detailed scheme of aerosol generator and measurement systems used in the experimental campaign.

- a further Condensation Particle Counter (CPC TSI 3775; Shoreview MN, USA) to measure number concentrations up to 1×10^7 part/cm³ of particles down to 4 nm;
- a Flow meter TSI 4410 (Shoreview MN, USA) to check flow rates in the tubing connecting the generation system to the measuring devices.
- a balance with a capacity of 1200 g and resolution of ± 0.001 g to weigh the salt amount during the preparation of the solutions;
- a deionized water generation system based on reverse osmosis technique (Human Power I Plus, Human Corporation, Korea) which produced deionized water with an electrical conductivity equal to 1×10^{-6} S/cm.

Methodology

Preparation of the Solutions

To evaluate the influence of the solution on particle generation through atomization, 14 different soluble salts were tested (Table 1); moreover, deionized water was also tested in order to take into account for possible impurities in the solvent. Salts were selected according to the following criteria: very common (i.e., belonging to common families of soluble salts), cheap and relatively not-hazardous salts. In Table 1 the salts considered in our experimental campaign are summarized. Main chemical properties of the solutions considered are also reported.

The comparison of particle number distributions and concentrations obtained through the different salts was performed using equal molar concentration of the solution; in particular, four different molar concentrations were considered for each solution: 2×10^{-3} M, 2×10^{-4} M, 2×10^{-5} M, and 2×10^{-6} M. 2×10^{-3} M solutions were prepared by weighing the corresponding salt mass (molar mass and density data are reported in Table 1) and, then, dissolving

it in deionized water, produced through the Human Power I Plus, up to final solution volume equal to 1 L. Deionized water was produced through a reverse osmosis technique in order to guarantee lower residual particle number than commercially available one (Park *et al.*, 2012). In order to avoid errors in salts weighing, the hydrated forms were used for hygroscopic salts operation weighing. Anyway, the salts mass reported in Table 1 refers to the anhydrous forms. The more dilute solutions were obtained diluting the 2×10^{-3} M solution in deionized water with a dilution factor of 1:10, 1:100, and 1:1000 to obtain 2×10^{-4} M, 2×10^{-5} M, 2×10^{-6} M solutions, respectively. The same molar concentration for the different salts was chosen in order to dissolve the same number of unit formula in the different solutions considered. In Table 1 solution mass concentration data corresponding to the molar mass concentrations tested are reported: these data confirm that all the salts can be considered soluble at the solution concentration tested. Three different solutions were prepared for each salt and molar concentration tested. Since the presence of residual particles can be affected by water impurity amount, water pH, material of the storage container, and storage time, the same procedure in the preparation of all the solutions was applied: in particular, freshly generated deionized water was used to prepare the solutions, moreover short sampling (about 30 min, major details are provided in the next sections) were performed in order to reduce the effect of possible leaching from the bottle walls which lead to an increase of residual particle number concentration during storage time (LaFranchi *et al.*, 2002; Knight and Petrucci, 2003).

Aerosol Measurements

Measurements of particle number distributions and total concentrations were performed through the following

Table 1. Summary of the chemical properties of the 14 tested salts and corresponding solutions. Solution mass concentrations corresponding to the considered molar concentrations are also reported.

Salt	family	Molar mass (g/mol)	Density (g/cm ³)	Solubility in water @20°C (g/L)	Solution mass concentration (g _{salt} /L)			
					Test 2 × 10 ⁻³ M	Test 2 × 10 ⁻⁴ M	Test 2 × 10 ⁻⁵ M	Test 2 × 10 ⁻⁶ M
Sodium chloride	Chlorides	58	2.2	359	0.116	0.0116	0.00116	0.000116
Potassium chloride	Chlorides	75	2.0	344	0.148	0.0148	0.00148	0.000148
Caesium chloride	Chlorides	168	4.0	1865	0.336	0.0336	0.00336	0.000336
Magnesium chloride	Chlorides	95	2.3	543	0.190	0.0190	0.00190	0.000190
Calcium chloride	Chlorides	111	2.2	745	0.222	0.0222	0.00222	0.000222
Barium chloride	Chlorides	208	3.9	358	0.416	0.0416	0.00416	0.000416
Ammonium chloride	Chlorides	53	1.5	372	0.107			
Potassium iodide	Iodides	166	3.1	140	0.332	0.0332	0.00332	0.000332
Sodium nitrite	Nitrites	69	2.2	848	0.138	0.0138	0.00138	0.000138
Lithium nitrate	Nitrates	69	2.4	900	0.138	0.0138	0.00138	0.000138
Potassium carbonate	Carbonates	138	2.3	1120	0.276	0.0276	0.00276	0.000276
Sodium sulfate	Sulfates	142	2.7	48	0.284	0.0284	0.00284	0.000284
Potassium sulfate	Sulfates	177	2.7	120	0.354	0.0354	0.00354	0.000354
Disodium hydrogen phosphite	Phosphites	126	2.4	n.a.	0.252			

methodology: once the properly prepared solution was placed in the bottle, the compressed air (p = 2 bar) was turned on and the solution was flown to the atomizer. The aerosol produced was sent to a flow splitter since particle number concentration and distribution measurements were performed simultaneously through the CPC 3775 and the SMPS 3936, respectively. Both the CPC and the SMPS operated at 1.5 L/min, therefore, the total flow rate at the flow splitter was 3.0 L/min: possible excess flow rate was automatically flown through the excess air flow at the dilution bridge. In order to correctly measure particle number concentrations with the CPC 3775, a dilution ratio of 3:1 was considered during 2 × 10⁻³ M solution testing by using a filtered make-up flow; in fact, concentrations higher than 1 × 10⁷ part./cm³ (CPC maximum concentration) are expected for most concentrated solutions. Flow rates were monitored with the Flow meter TSI 4410.

Measurements performed during the first 10 minutes were not considered in order to avoid measurement uncertainties due to possible unsteady conditions during the start-up of the generation device. Moreover, after each test, cleaned air was flown in the experimental apparatus for 10 minutes in order to remove salt particles previously generated and likely deposited in the tubing. The bottle was also cleaned after each test by means of deionized water. The diffusion dryer was kept in active condition during all the experimental campaigns: the regeneration of the silica gel was performed by placing it into a baking furnace at a temperature of 105°C for 4–6 hours.

Ten 180-s samples (plus a retrace of 15 s) were continuously measured through the SMPS for each test. The SMPS operated with an aerosol flow and sheath flow equal to 1.5 L/min and 15.0 L/min, respectively, and the corresponding measurement range was 6–225 nm. CPC measurements were performed simultaneously for a total sampling length of 32.5 min. Results reported in the following section represent the average of the three tests for each salt and solution concentration.

RESULTS

In Table 2 particle number concentrations measured through the CPC 3775 are reported as a function of the salt and the molar concentration of the solution. These data represent the average of three sets of measurements on the basis of the procedure described in the section 2.3.2. All the solutions show a decrease in particle number concentration moving toward more diluted solutions. This behavior, at the moment only recognized for NaCl and NaNO₃ (Mikuška, 2004; TSI Inc., 2005; Chen and Chein, 2006), can be partly explained observing that in more concentrated solutions a larger volume of salt precipitated after the evaporation of the water. A more detailed and comprehensive explanation is proposed in the Discussion section. Average particle number concentrations, when all the solutions were considered, were measured equal to 1.67 × 10⁷, 3.06 × 10⁶, 9.37 × 10⁵, and 5.40 × 10⁵ part./cm³ for 2 × 10⁻³ M, 2 × 10⁻⁴ M, 2 × 10⁻⁵ M, and 2 × 10⁻⁶ M solution tests, respectively. The corresponding standard

Table 2. Total particle number concentrations and particle number distribution modes measured through the CPC 3775 and SMPS 3936, respectively, for different solutions and molar concentrations. Each data represent average (and standard deviation) of three tests.

Salt	Test 2 × 10 ⁻³ M		Test 2 × 10 ⁻⁴ M		Test 2 × 10 ⁻⁵ M		Test 2 × 10 ⁻⁶ M	
	Total concentration (part./cm ³)	Mode (nm)	Total concentration (part./cm ³)	Mode (nm)	Total concentration (part./cm ³)	Mode (nm)	Total concentration (part./cm ³)	Mode (nm)
NaCl	1.78 × 10 ⁷ ± 1.61 × 10 ⁵	42.4 ± 1.1	2.93 × 10 ⁶ ± 3.62 × 10 ⁴	41.4 ± 1.4	1.23 × 10 ⁶ ± 2.61 × 10 ⁴	37.9 ± 1.0	6.34 × 10 ⁵ ± 1.99 × 10 ⁴	31.1 ± 1.2
KCl	1.87 × 10 ⁷ ± 3.01 × 10 ⁵	42.6 ± 1.0	3.15 × 10 ⁶ ± 4.41 × 10 ⁴	41.6 ± 1.5	8.14 × 10 ⁵ ± 1.69 × 10 ⁴	35.6 ± 1.5	5.37 × 10 ⁵ ± 1.44 × 10 ⁴	27.7 ± 1.2
CsCl	1.71 × 10 ⁷ ± 1.30 × 10 ⁵	39.4 ± 1.1	1.94 × 10 ⁶ ± 1.71 × 10 ⁴	39.5 ± 1.9	6.93 × 10 ⁵ ± 2.28 × 10 ⁴	31.0 ± 1.4	4.45 × 10 ⁵ ± 1.41 × 10 ⁴	24.3 ± 1.0
MgCl ₂	2.85 × 10 ⁷ ± 1.90 × 10 ⁵	54.2 ± 2.5	3.84 × 10 ⁶ ± 5.39 × 10 ⁴	46.4 ± 0.6	1.14 × 10 ⁶ ± 2.42 × 10 ⁴	35.7 ± 1.7	5.98 × 10 ⁵ ± 1.59 × 10 ⁴	24.2 ± 1.0
CaCl ₂	2.39 × 10 ⁷ ± 2.02 × 10 ⁵	53.8 ± 0.9	3.01 × 10 ⁶ ± 2.76 × 10 ⁴	48.4 ± 3.4	9.54 × 10 ⁵ ± 2.77 × 10 ⁴	35.6 ± 1.5	4.18 × 10 ⁵ ± 1.74 × 10 ⁴	32.6 ± 0.6
BaCl ₂	1.68 × 10 ⁷ ± 2.01 × 10 ⁵	39.8 ± 1.1	3.48 × 10 ⁶ ± 2.80 × 10 ⁴	37.4 ± 0.5	9.98 × 10 ⁵ ± 2.20 × 10 ⁴	32.9 ± 0.9	5.71 × 10 ⁵ ± 1.70 × 10 ⁴	26.5 ± 0.5
NH ₄ Cl	4.66 × 10 ⁶ ± 3.56 × 10 ⁴	52.1 ± 1.0						
KI	2.21 × 10 ⁷ ± 5.57 × 10 ⁴	41.9 ± 2.3	3.52 × 10 ⁶ ± 2.85 × 10 ⁴	40.3 ± 1.0	1.07 × 10 ⁵ ± 5.20 × 10 ⁴	32.2 ± 1.1	5.36 × 10 ⁵ ± 1.42 × 10 ⁴	22.8 ± 1.1
NaNO ₂	2.11 × 10 ⁷ ± 7.21 × 10 ⁴	40.0 ± 0.4	2.83 × 10 ⁶ ± 3.21 × 10 ⁴	40.5 ± 2.0	7.59 × 10 ⁵ ± 1.77 × 10 ⁴	32.8 ± 1.1	5.18 × 10 ⁵ ± 1.71 × 10 ⁴	24.9 ± 1.2
LiNO ₃	7.24 × 10 ⁶ ± 6.11 × 10 ⁴	41.6 ± 2.2	1.46 × 10 ⁶ ± 2.94 × 10 ⁴	40.4 ± 0.9	5.86 × 10 ⁵ ± 1.53 × 10 ⁴	31.8 ± 0.6	5.06 × 10 ⁵ ± 5.89 × 10 ³	24.0 ± 1.0
K ₂ CO ₃	1.46 × 10 ⁷ ± 1.62 × 10 ⁵	42.9 ± 0.1	2.79 × 10 ⁶ ± 3.17 × 10 ⁴	40.0 ± 0.2	8.43 × 10 ⁵ ± 1.79 × 10 ⁴	34.8 ± 1.2	4.54 × 10 ⁵ ± 1.28 × 10 ⁴	26.1 ± 1.2
Na ₂ SO ₄	1.76 × 10 ⁷ ± 2.25 × 10 ⁵	33.1 ± 1.2	3.46 × 10 ⁶ ± 3.49 × 10 ⁴	31.5 ± 1.3	9.82 × 10 ⁵ ± 2.81 × 10 ⁴	26.9 ± 0.5	6.51 × 10 ⁵ ± 2.01 × 10 ⁴	28.1 ± 0.7
K ₂ SO ₄	1.77 × 10 ⁷ ± 5.88 × 10 ⁴	33.3 ± 1.2	3.16 × 10 ⁶ ± 4.49 × 10 ⁴	32.2 ± 0.2	9.46 × 10 ⁵ ± 2.36 × 10 ⁴	27.0 ± 0.4	5.51 × 10 ⁵ ± 1.45 × 10 ⁴	25.3 ± 0.9
Na ₂ HPO ₃	5.88 × 10 ⁶ ± 4.93 × 10 ⁴	56.5 ± 1.1						
Deionized water	Total concentration (part./cm ³)							
	3.74 × 10 ⁵ ± 4.62 × 10 ³						21.5 ± 1.4	

deviations were 41%, 19%, 18%, and 13%, respectively, demonstrating that the more diluted the solution, the less influencing is the salt used; in fact, moving towards the lowest molar concentration, the differences amongst the various solutions are nearly negligible. Moreover, the more diluted the solution, the more influencing are the water impurities. Particle number concentration due to the water impurities was measured equal to 3.74×10^5 part./cm³: therefore, such impurities are not negligible when 2×10^{-5} M and 2×10^{-6} M solutions are tested since they represent, on average, 41% and 70% of the total particle number concentration measured, respectively. On the contrary, the water impurities are negligible when 2×10^{-3} M and 2×10^{-4} M data are considered: in particular, when 2×10^{-3} M solutions are analyzed, the average impurity percentage in terms of total count is 3%. The presence of the impurities clearly explain that more diluted solutions have an amount of salt comparable to the impurities. Therefore, the possible effect of the solution is only detectable in more concentrated solution (2×10^{-3} M). The maximum particle number concentration for the 2×10^{-3} M solution was measured for MgCl₂ (2.85×10^7 part./cm³), whereas the minimum was measured for NH₄Cl (4.66×10^6 part./cm³): such difference of one order of magnitude demonstrates the strong influence of the solution. The concentration standard deviations measured for each salt and solution concentrations were in the range 0.25–4.87% confirming that measurements were performed in steady state conditions. In Table 3 the modes of the number distributions measured through the SMPS 3936 as function of the salt and solution molar concentration are also reported. The mode of the particle number distribution tends to decrease moving toward more diluted solution. In fact, average modes, when all the solution were considered, were measured equal to 43.9, 39.3, 32.8, and 26.2 nm for 2×10^{-3} M, 2×10^{-4} M, 2×10^{-5} M, and 2×10^{-6} M concentrations, respectively. The maximum mode was measured for Na₂HPO₃ 2×10^{-3} M (56.5 nm), whereas the minimum mode was measured for KI 2×10^{-6} M (22.8 nm) which is obviously very close to the water impurity mode (21.5 nm). More generally, 2×10^{-6} M solutions presents modes approaching the water impurity one. The standard deviations of the modes were in the range 0.1–3.4 nm confirming again the steady state conditions during the experimental analysis.

In Fig. 2 the average particle size distributions measured through the SMPS 3936 for all the solutions tested at the more concentrated (2×10^{-3} M) and the more diluted (2×10^{-6} M) solutions are reported. The figure clearly shows the overall shift of the distributions toward smaller diameters, and, in particular, toward pure water impurity distribution (Fig. 2(b); 2×10^{-6} M) as also shown in terms of total number concentration. The Fig. 2(b) highlights that NaCl, which is the salt typically used in generation through atomization technique, only presents the highest number concentration for 2×10^{-6} M solution in the diameter range larger than 30 nm: thus, other salts should be looked at in particle generation though atomization technique if CPC calibration at smaller diameters are needed. This is confirmed by the Fig. 2(c) where the same particle number distributions

Table 3. Percentage of water impurities in particle number concentration measured for different solutions and molar concentrations.

Molar concentration	NaCl	KCl	Na ₂ SO ₄	MgCl ₂	KI	K ₂ CO ₃	LiNO ₃	CaCl ₂	NaNO ₂	CsCl	BaCl ₂	K ₂ SO ₄	NH ₄ Cl	Na ₂ HPO ₃
2×10^{-3} M	2.1%	2.0%	2.1%	1.3%	1.7%	2.6%	5.2%	1.6%	1.8%	2.2%	2.2%	2.1%	8.0%	6.4%
2×10^{-4} M	12.8%	11.9%	10.8%	9.8%	10.6%	13.4%	25.7%	12.4%	13.2%	11.9%	10.7%	11.9%	11.9%	
2×10^{-5} M	30.4%	46.0%	38.1%	32.8%	35.1%	44.4%	63.8%	39.2%	49.3%	40.4%	37.5%	39.6%	39.6%	
2×10^{-6} M	59.0%	69.6%	57.5%	62.6%	69.8%	82.4%	73.9%	89.5%	72.2%	73.2%	65.5%	68.0%	68.0%	

are zoomed in the range lower than 50 nm: the figure shows that, in this particle range, ammonium chloride (NH_4Cl) presents larger particle number concentrations, in fact, at 8 nm and 10 nm it provides concentrations about 40-fold and twice the NaCl ones. In the range 11–25 nm the salt showing the highest concentrations is the Na_2SO_4 (about twice the NaCl ones), whereas for particles larger than 30

nm (up to more than 200 nm) the salt with the best performances is the MgCl_2 (concentrations from 2 to 4 times the NaCl ones). The authors point out that the present results were obtained through a CPC 3775 using n-butyl alcohol (butanol) as a working fluid. Anyway, the type of vapor condensed on liquid droplet is important as the sizes of sampled particles decrease. In particular, the minimum

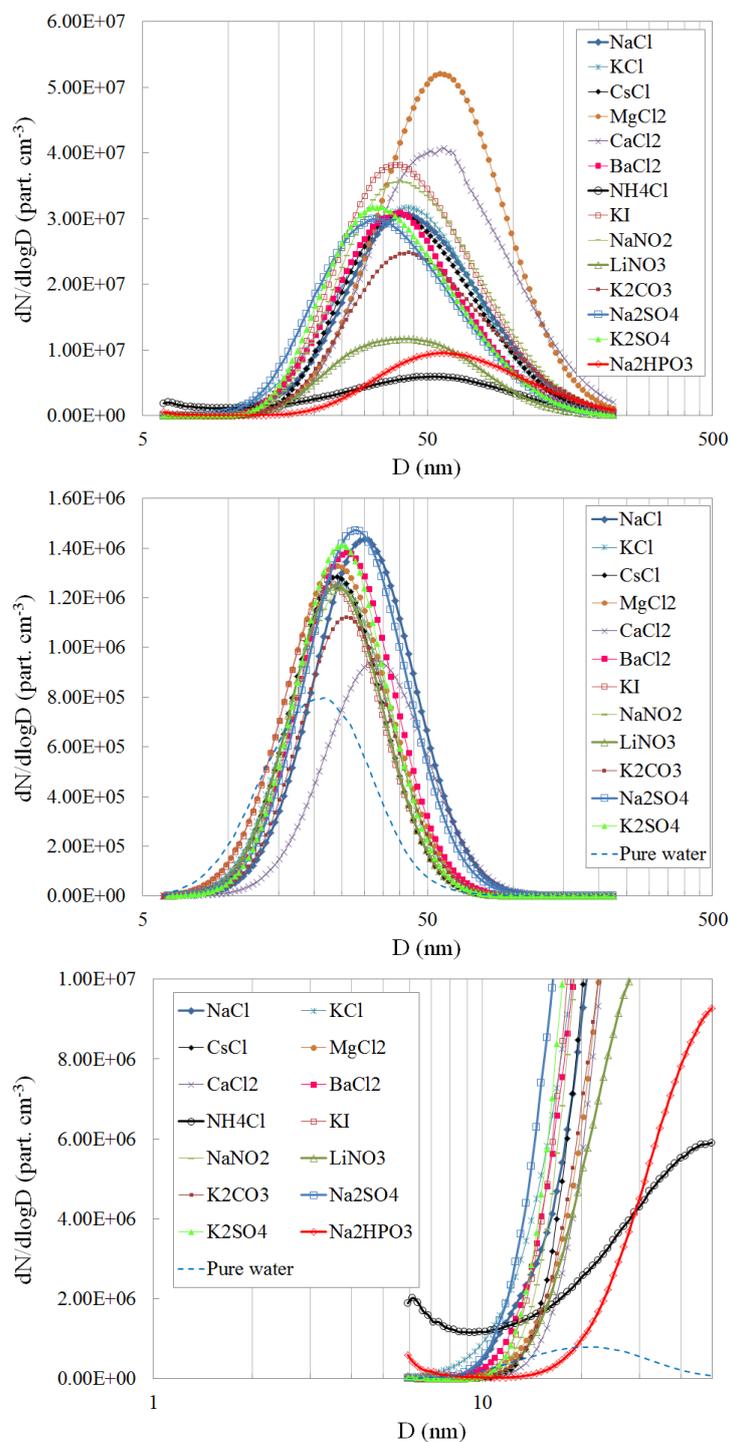


Fig. 2. Particle number distributions (N) measured through the SMPS 3936 for all the salt considered at a) 2×10^{-3} M, and b) 2×10^{-6} M. Details of the particle number distributions in the mobility diameter (D) range < 50 nm measured for 2×10^{-3} M solutions are also reported (c).

detectable size is influenced by the particle solubility in condensing vapor, therefore, the present results could be not correct for a water-based CPC as its detection limit may be different because of the different particles' hygroscopicity (Hu *et al.*, 2010, 2011). Future investigations will be performed to provide inter-comparison of 14 salt solutions involving CPCs using different working fluids, in particular, comparison will be focused in the smallest diameter range where the influence of the fluid can be significant.

DISCUSSION

The abovementioned results clearly demonstrate the effect of the solution on aerosol generation through atomization technique. An effect of the solution could be addressed to the subsequent water evaporation and salt precipitation. To evaluate these possible phenomena the expected mode of the salt particles precipitated has been evaluated through the Eq. (1) (Hinds, 1999; Chen and Chein; 2006) and considering i) all the droplets having the same diameter (D_d , mode of the droplets equal to 350 nm), ii) from each droplet only one spherical dry salt particle is generated (in the following the particle generated from a single droplet will be referred as "primary particle"):

$$D_{pp} = D_d \times (V)^{1/3} \quad (1)$$

where D_{pp} is the primary particle mode, and V is the volume fraction of the precipitated salt with respect the droplet; V can be easily obtained since droplet volume and molar concentration of the solution are known. As an example, the 2×10^{-3} M solutions of NaCl and KCl should generate primary particles with mode equal to 13.2 and 14.7 nm, respectively. Similarly, the 14 solutions analyzed at 2×10^{-6} M should generate spherical particles with modes ranging from 1.3 to 1.7 nm. Actually, data reported in the Results highlighted that modes larger than the expected ones are obtained: average modes of the 14 salts were found equal to 43.9, 39.3, 32.8, and 26.2 nm for 2×10^{-3} M, 2×10^{-4} M, 2×10^{-5} M, and 2×10^{-6} M solutions, respectively, whereas the corresponding average primary particle expected modes were evaluated equal to 15.6, 7.3, 3.4, and 1.6 nm. Anyway, such differences amongst measured and expected modes cannot be addressed to the simplified evaluation of the expected modes. Chen and Chein (2006) hypothesized that the differences amongst expected and measured modes was due to the presence of water impurities sticking on salt primary particle and leading to larger particles. Even if they maybe used less pure water (they measured water impurities mode larger than one, about 26 nm), in our opinion the presence of the water cannot explain the huge difference between theory and experiments results: in fact, when 2×10^{-3} M tests were performed the amount of the impurities is negligible and cannot drive so intense coagulation phenomena. The authors suggest that the reason of this difference can be related to the rapid coagulation phenomena involving the small dry salt primary particles which, after precipitation, lead to the formation of larger (measured) particles, independently from the presence of

impurities. Primary particle coagulation tendency is expected to influence the measured mode since the particles tend to reduce their Gibbs free energy through the surface area reduction of coagulating particles (Friedlander, 2000). To this purpose, for each solution we evaluated the ratio between the volume of the particles (calculated by considering all the particles as large as the particle mode) over the volume of the primary particle generated from 350 nm droplet, in the following this ratio will be referred as "coagulation ratio": namely the coagulation ratio represents the number of primary particles contained into the mode particles. As example, for 2×10^{-3} M NaCl were considered 1.78×10^7 part./cm³ of 42.4 nm measured particles, and 4.19×10^8 part./cm³ of 13.2 nm primary particles leading to a ratio of 33. Similarly, for 2×10^{-3} M Na₂SO₄ and K₂SO₄ were measured lower ratios (8 and 6, respectively), it is interesting to notice that these two salts are the ones showing the lowest modes amongst the 14 salt solutions. In Fig. 3 coagulation ratio data are compared to the modes measured through the SMPS 3936 for all the 2×10^{-3} M and 2×10^{-4} M solutions tested. The figure shows a good linear correlation amongst the two parameters confirming that the coagulation ratio is a valuable metrics of the physical phenomena involving water evaporation, salt precipitation and particle generation processes. As regards the differences between the different salts, it is not easy to evaluate the governing parameters of this rapid coagulation. Particle coagulation phenomena have been thoroughly modeled by Smoluchowski (1917). In particular, collision frequency functions involving coalescing spherical particles were evaluated when different flow conditions and external forces are applied (Friedlander, 2000; Lehtinen, 1997). Anyway, none of these coagulation theories (both for free-molecule and transition regimes) is able to explain the significant increase in diameter measured during our experiments as well as the differences in coagulation of the different tested salts. In fact, the expected size of dry salt particles is quite similar for all the considered salts (standard deviations of the modes for 2×10^{-3} M and 2×10^{-6} M solutions are evaluated as 1.3 nm and 0.1 nm, respectively) leading to similar collision frequencies (Brownian coagulation). More generally, coagulation models are not able to take into account for the material of the particles: the reduction in Gibbs free energy is only associated to the surface area reduction of the coagulated particles (Friedlander, 2000). Therefore, the different salt material (e.g., surface energy, unit formula) could somehow represents a governing parameter of such rapid coagulation phenomena also able to explain the different behavior of the different salts.

A further parameter maybe influencing the distributions and concentrations measured at the end of the generator is the solution conductivity: in fact, solution conductivity is influenced by solution molar concentration (it decreases with lower salt fraction in the solution, Ijsebaert *et al.*, 2001). Generally, the higher the solution conductivity the higher the charge levels of residual solid particles after drying, then leading to possible more significant particle losses in the different parts and tubing of the generator. The authors point out that further *ad-hoc* experimental

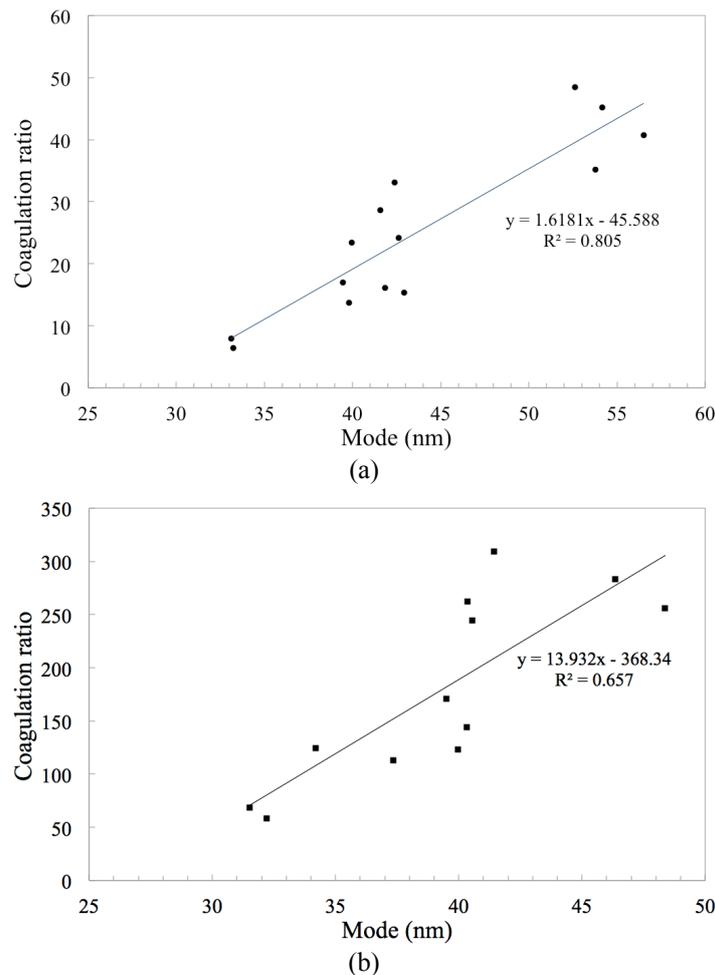


Fig. 3. Dry salt particle coagulation ratio as function of particle measured mode: for 2×10^{-3} M (a) and 2×10^{-4} M (b) solutions.

campaigns should be designed to deepen the knowledge in finding key parameters and phenomena affecting the particle generation through atomization.

CONCLUSIONS

The paper deals with the generation of sub-micrometric particles through atomization salt solutions. In particular, 14 different solutions made up of common soluble salts were considered and tested through a commercial sub-micrometric aerosol generator. Different molar concentrations were also considered.

The main finding of the experimental campaign was the effect of the solution on particle generation process. In fact, different particle number distributions and total concentrations were measured when different solutions were considered.

Higher particle number concentrations and distribution modes were measured for more concentrated solutions, in particular, the highest concentration was obtained for MgCl_2 2×10^{-3} M solution showing the total particle number concentration almost twice than the one obtained through NaCl. Besides number concentration data, the effect of the

solution is very interesting in terms of particle number distribution, in fact, the number concentration at very small diameter was found to be strongly dependent on the solution type. As example, the ammonium chloride (NH_4Cl) presents particle number concentrations at 8 nm and 10 nm about 40-fold and twice the NaCl ones. More generally, the NaCl, which is the salt typically used in ultrafine particle generation, was recognized as one of the worst salt in terms of generation performance. This is a really interesting result in terms of CPC calibration, in fact, at very small particle sizes is usually hard to generate particle concentrations adequate to perform calibration metrologically accurate.

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Received for review, March 19, 2013

Accepted, May 16, 2013