Methodology for generating stable concentrations of nano-objects

Beata Kaczorowska
Central Institute for Labour Protection – National Research Institute,
Czerniakowska 16, 00-701, Warsaw, Poland.
e-mail: bekac@ciop.pl

With an increasing number of companies using and producing nanomaterials, also the number of workers who are exposed to nano-objects is increasing. Nano-objects, because of their very small size, can very easily overcome the human systemic barrier and rapidly penetrate into the body, settling mainly in the lungs. It is important to establish standards for nanomaterials, because of the health and safety of workers who are exposed to nanomaterials in their workplace. During the exposure evaluation, it is important to determine the parameters of nano-objects in real-time and thus it is necessary to validate the measuring apparatus used during researches.
The purpose of the project is to provide the possibility of obtaining stable concentrations of the nano-objects to validate the measuring apparatus for real-time testing of parameters of the nano-objects.
The literature review [1-4] on methodology for generating nano-objects using techniques of nucleation and spark discharge was made. After analyzing different models, which were found in the literature [1-4], an experimental set-up was created. The experimental set-up is composed of: an aerosol generator, an aerosol neutralizer, a high-temperature furnace, a heat exchanger, a dilution system and a sampling chamber. Our set-up has many advantages:
– it can generate different types of nano-objects (carbon, cooper and silver nano-objects) with stable concentration;
– it can generate nano-objects with different concentration;
– it allows to take four samples at the same time and measure their parameters by using various measurement apparatus.
Thanks to the built set-up, it will be possible to validate measuring apparatus for testing parameters of nano-objects in real-time using an ELPI+ (Dekati) as a reference apparatus.
Keywords: nano-objects, aerosol generator, aerosol neutralizer, high-temperature furnace, validation, number concentration.

Introduction

Currently, there is no provision closely associated with nanomaterials in Polish law. However, the guidelines related to the protection and safety of human health against nano-objects are included in the major provisions of the European Union: Directive 89/391/EWG, 89/655EWG, 98/24/WE, 99/92/WE, 2004/37/WE, as well as legislation concerning REACH system.

Due to the fact that the number of companies using and producing nanomaterials is annually increasing, also the number of workers, who are exposed to nano-objects, is increasing. Therefore, it is important to establish standards relating to nanomaterials, in order to implement good practices in view of the health and safety of workers exposed to nanomaterials in their workplace.

Currently, in order to determine the exposure to dusts, the filtration-weight method is used, where the mass concentration of the inhalable fraction and the respirable fraction suspended in the air in the work environment is defined (gravimetric method). In the case of exposure to nano-objects, the gravimetric method does not fully reflect the size of exposure, because nano-objects are a very small fraction of a total mass of dust. So, there are used methods for determining the parameters of the particles in real time. However, in the case of significant concentrations of emitted particles, it is advisable to use also the filtration-weight method. In view of the fact that during the evaluation of the exposure, it is important to determine parameters of nano-objects in real time, there is a need of validating measuring instruments which are used in research. However, in the case of significant concentrations of emitted particles, it is advisable also to use the filtration-weight method. Therefore, during assessment of the exposure to nano-objects in real time, there is a necessity to validate measuring apparatus used in researches.

The purpose of the project is to provide the possibility of obtaining stable concentrations of the nano-objects to validate measuring instruments for real-time testing of number concentration of the nano-objects.

State of the art about generating stable concentrations of nano-objects

The literature review [1-21] on methods of generating nano-objects using techniques of nucleation and spark discharge was made. The production of airborne nano-objects by e.g. spark discharge or sintering has been studied by different researchers in several studies for different applications [1-17].

An experimental set-up [18] was based on the method of homogeneous nucleation, coagulation and sintering. It was consisted of two tube furnaces arranged in series, of which one was used to generate the nano-objects, and the second was used for the sintering. The generated objects were characterized by a stable concentration, but there was possibility to take only one sample during the test and the parameters of the nano-objects were measured just by two measuring apparartus.

The next set-up [19] was based on the phenomenon of spark discharge. It was built with an aerosol generator and two dilution chambers. In this case, the nano-objects also were obtained with stable concentrations. Additionally, by using various electrode materials in the generator, it was possible to generate different types of particles. In this case, there was also a possibility to take just one sample for testing.

The other set-up to generate nano-objects [20] was built with a small ceramic heater with a local heating area. The numerous advantages of this concept in relation to the method using a tube furnace was noticed. Except that there were generated non-agglomerating nano-objects with stable concentrations, this method of generating was characterized by reduced time needed to reach thermal stability, lower energy use required to raise the temperature of a material or a smaller occupied surface of set-up. A drawback was the possibility to take only one sample, which was not possible to measure simultaneously several parameters of nano-objects.

The last experimental set-up [21] was composed of an aerosol generator, aerosol neutralizer and a high-temperature furnace. That set-up had many advantages, such as: the ability to produce different types of non-agglomerating nano-objects with stable concentrations or the ability to take simultaneously four samples and then measure them using various measuring apparatus.

Methodology for generating stable concentrations of nano-objects

This section describes methodology for generating nano-objects with stable and repeatable concentrations for the validation of measuring instruments for real-time testing of physical parameters of the nano-objects, such as a number concentration or size distribution of the particles.

The methodology includes issues important for providing the generation of stable concentrations of nano-objects, such as:

- control the volume flows of compressed air and argon,
- preparation of compressed air to generate nano-objects,
- control the flows of air and argon,
- generating nano-objects,
- neutralization of nano-objects,
- sintering nano-objects,
- cooling of an aerosol,
- dilution of an aerosol,
- taking samples,
- measuring apparatus for testing a number concentration and a size distribution of the particles in real time.

The scheme of an experimental set-up is shown in Figure 1.

Control the volume flows of compressed air and argon

During the tests, argon is taken from the cylinder, and air is taken from a compressed air installation. The air is first pre-filtered in an air preparation unit (TSI model 3074B), and then it is separated into several streams, depending on the system configuration (1 stream only at generating of an aerosol, 2 streams at generating and neutralizing of an aerosol or at generating and diluting an aerosol, 3 streams at generating, neutralizing and diluting of an aerosol). One of the streams of air and the stream of argon are directed to an aerosol generator Palas GFG-1000. Then, if it is necessary to neutralize, the prepared nanoaerosol moves to an aerosol neutralizer Topas EAN 581. The need of neutralizer's use is checked by observing the currents' changes on the graph in ELPI+ software (function 'charge meas'). If the ELPI+ charger is turned off, a reading of negative currents indicate that the particles have a negative charge state and the aerosol does not require neutralization. If the original charge of the particles is positive, in some cases there might be a need to neutralize the particles before they enter the ELPI+. The neutralizer is powered by the next of the air streams, so that it is possible an ions exchange. It causes change in the final charge on the particles when they exit from the apparatus. A high-temperature furnace can be used in order to test the impact of temperature on the number concentration of the particles. The aerosol coming out of the generator (or neutralizer) goes to the furnace VecStar Ltd. VTF7 and then the aerosol is directed to a heat exchanger. A dilution system can be used in order to obtain lower number concentrations, or to check the impact of dilution on the number concentration of the particles. In this case the aerosol passes through the dilution system Palas VKL-10 powered by another air stream and then it gets into the sampling chamber, where one of the outlet stub-tubes is connected to a HEPA PN 12144 filter (Pall Corporation) and it is an outlet of an excess aerosol. In the sampling stage, there is determined the number concentration and the size distribution of the particles in real time.

Preparation of compressed air to generate nano-objects

During the tests argon is taken from the cylinder and the air—from compressed air installation. The air, which is used to generate the nano-objects with stable concentrations, should be cleaned in order to remove particles which might affect the

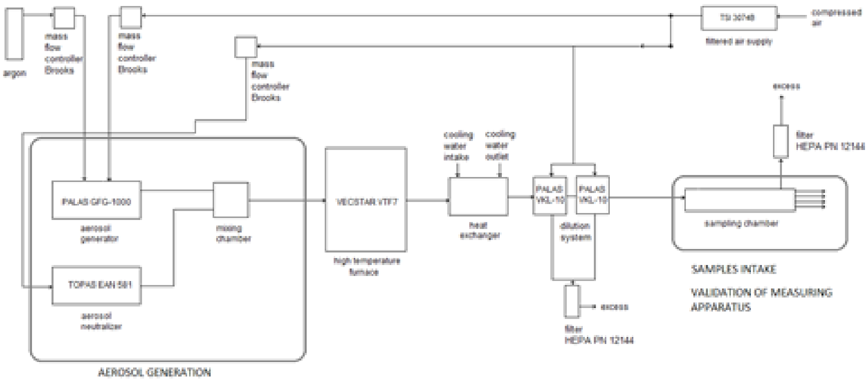

Figure 1. The experimental set-up used to generate nano-objects with stable concentrations

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process of generating nano-objects. The compressed air system is equipped with a pressure regulator with a pressure gauge and filter system connected in series. The filter system (see Figure 2) includes:

– pre-filter for particles with diameters of ≥1 µm with the possibility of draining the condensate water+oil,
– a fine filter for particles with diameters of ≥0.1 µm with the possibility of draining the condensate water+oil,
– a filter for particles with diameters of ≥0.01 µm.

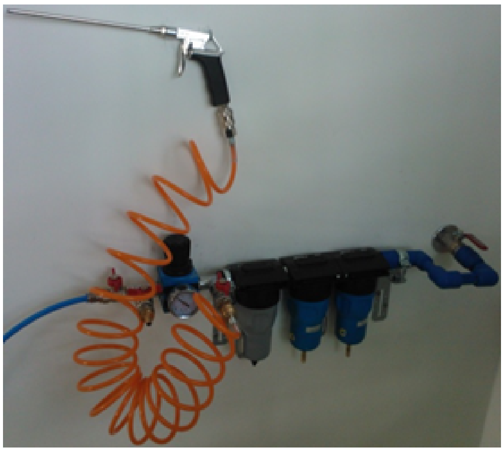

Figure 2. The filter system

The air from compressed air installation is directed to the filtered air supply TSI 3074B (see Figure 3), where it is split into several streams, depending on the system configuration (1 stream only at generating of an aerosol, 2 streams at generating and neutralizing of an aerosol or at generating and diluting an aerosol, 3 streams at generating, neutralizing and diluting of an aerosol).

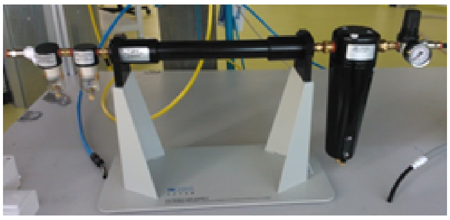

Figure 3. The filtered air supply TSI 3074B

The filtered air supply is designed to filter, dry and regulate the air pressure in a compressed air line. During operation, two coalescing filters (DX and BX grade) remove water/oil droplets and particles from incoming air supply. A membrane dryer removes moisture from the air stream and a final carbon-vapor filter absorbs any remaining oil vapors and provides a last stage of filtration. A gas regulator provides pressure adjustment.

During tests air is supplied into different parts of the set-up:

– to the aerosol generator,
– to the aerosol neutralizer,
– to the dilution system.

Control the flows of air and argon

Measurement and regulation of the argon and air flow in the set-up are carried out by mass flow controllers Brooks. Range of used controllers:

– to 50 dm^3/min (Brooks GF40),
– to 100 dm^3/min (Brooks SLA5851S—see Figure 4),
– to 40 dm^3/min (Brooks 4850).

Figure 4. The mass flow controller Brooks SLA5851S

Regulators are controlled by using a software Medson FC. That application allows to set the flow or to see the current volumetric flow.

Generating nano-objects

The aerosol is generated by the generator Palas GFG-1000 (see Figure 5), which is equipped with three different pairs of electrodes (graphite, cooper and silver). The generator is powered by a stream of argon or streams of argon and air.

Figure 5. The aerosol generator Palas GFG-1000

The GFG 1000 generates very fine carbon (cooper or silver) particles by spark discharge between two graphite (cooper or silver) electrodes. In order to avoid an oxidation of the carbon (cooper or silver), an argon stream is focused through a narrow slit into the space between the electrodes. The carbon (cooper or silver), evaporated in the spark, is transported by the argon flow through the space between the electrodes and condenses to very fine primary particles. These particles coagulate to more or less big agglomerates, depending on their concentration. The particle mass flow rate is adjustable over a wide range by means of the spark frequency. The electrode consumption is compensated by an automatic adjustment of the electrodes. This adjustment grants a very constant operation of the generator. Agglomerates are reduced by means of an exact dilution of the aerosol with clean pressurized air.

Neutralization of nano-objects

If the generated aerosol needs to be neutralized, it goes to the aerosol neutralizer Topas EAN 581 (see Figure 6), which is also supplied by the air stream, so that it is possible to exchange ions.

Figure 6. The aerosol neutralizer Topas EAN 581

Due to the charge exchange onto particle surfaces the particles become (dis)charged. The EAN 581 is based on the corona discharging principle and consists of a mixing chamber with two separate ionization heads and a control unit. The ion blowers generate positive and negative ions. They are then combined with the aerosol in the mixing chamber one after the other. Compressed particle free air is connected to both of the ionization heads.

Sintering nano-objects

A high-temperature furnace VecStar Ltd. VTF7 (see Figure 7) is used to determine the effect of temperature on the number concentration of the particles.

The furnace is heated by silicon carbide elements. The temperature is controlled by a PID controller using a type R thermocouple to control the temperature. The green light on mains will illuminate when power is applied to the furnace. Instruments on/off switch and the controller will illuminate when turned to the on position. The amber light will illuminate whenever the elements are drawing power. The red light will illuminate if the furnace goes over a set temperature. This is controlled by either a thermal fuse located in the chamber or a resetable electronic controller.

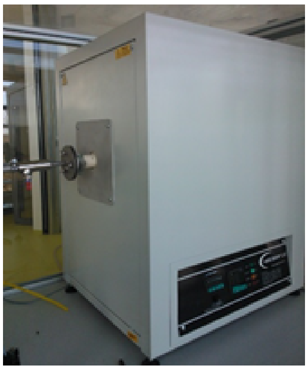

Figure 7. The high-temperature furnace VecStar Ltd. VTF7

Cooling of an aerosol

A shell and tube heat exchanger (see Figure 8) is used to reduce the temperature of the aerosol leaving the furnace. The heat exchanger is supplied of cooling water from the water installation. It is important because of the maximum allowable temperature of the sample (60°C) collected by a measurement apparatus (ELPI+).

Figure 8. The heat exchanger

Dilution of an aerosol

A dilution system is used to obtain lower number concentration of the particles or to check the effects of dilution on the number concentration of the particles. Depending on needs, the aerosol is diluted with one or two serially connected dilution chambers Palas VKL-10.

The system for the representative dilution of aerosols by a factor of 10. The particle size range is between 0.01 and 20 μm. The dilution factor VF is calculated according to the following formula:

$$V_F = \frac{(V_R + V_{An})}{V_{An}} \quad (1)$$

where:

- V_R – clean air flow rate [dm³/min],
- V_{An} – aerosol flow rate at the inlet to the dilution chamber [dm³/min].

In order to change the flow rate of clean air at the inlet, adjust pressure, through a pressure reducer located in the upper part of the panel. Aerosol flow rate during the tests does not change.

Taking samples

If dilution is not needed, the aerosol can go directly to the sampling chamber (see Figure 9).

Figure 9. The sampling chamber

The chamber is equipped with a thermometer to monitor the temperature of the aerosol. At the outlet of the chamber there is a splitter, which allows to take four samples at the same time and measure them at four different measuring apparatus. The chamber is also equipped with an outlet stub-tube connected to the HEPA filter (PN 12144 Pall Corporation), which is a place, where the excess aerosol is leaving the set-up. In the sampling stage, there is determined the number concentration and the size distribution of the particles in real time.

Measuring apparatus for testing a number concentration and a size distribution of the particles in real time

System ELPI+ Dekati (see Figure 10) is used as a reference apparatus for the measurements of the number concentration and the size distribution of the particles in real time. It is used because of its wide particle size range (6 nm to 10 μm).

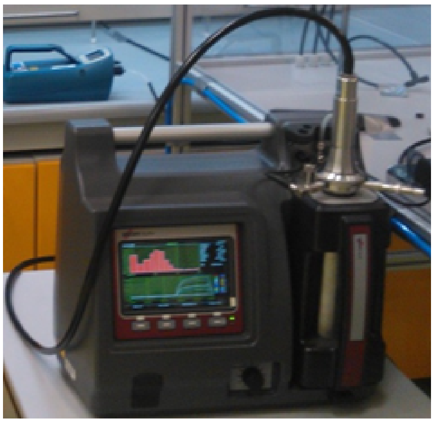

Figure 10. The reference apparatus Dekati ELPI+

The particles are first charged into a corona charger. After charging, the particles are size classified in a low-pressure cascade impactor according to their aerodynamic size. The impactor stages are electrically insulated and sensitive electrometers are connected to each impactor stage. The charged particles collected in a specific impactor stage produce an electrical current, which is recorded by the respective electrometer channel. This current is directly proportional to the number concentration of particles on that stage.

The ELPI+ measures particles in 14 size fractions in the range from 6 nm to 10 μm. The 13 impactor stages operating in the range of 16 nm to 10 μm collect the sample on a foil/filter that can be analyzed after the real-time measurement to get chemical composition of particles in each particle size class. The final stage measuring real-time particle concentration in the range of 6 nm to 16 nm is a back-up filter stage.

Conclusion

Created set-up and methodology will enable measurements of physical parameters of generated nano-objects in stable conditions. Knowledge of how to generate such particles may be used in predicting the exposure to nano-objects in the workplace. It may also be used in designing of technological processes in such a way to reduce the risks associated with the release of nano-objects.

Elaborated method enabled the validation (in a size range 20-100 nm) of measuring apparatus of such parameters as:

– number concentration,
– size distribution of the particles.

References

[1] A. Schmidt-Ott, New approaches to in situ characterization of ultrafine agglomerates" in Journal of Aerosol Science, 1988, 19, 553–563

[2] M. Shimada, et al. „Size change of very fine silver agglomerates by sintering in a heated flow" in Journal of Chemical Engineering of Japan, 1994, 27, 795–802

[3] T. Seto, et al. "Sintering of polydisperse nanometer-sized agglomerates" in Aerosol Science and Technology, 1997, 27, 422–438

[4] A. P. Weber and S. K. Friedlander "In situ determination of the activation energy for restructuring of nanometer aerosol agglomerates" in Journal of Aerosol Science, 1997, 28, 179–192

[5] S. Schwyn, et al. "Aerosol generation by spark discharge" in Journal of Aerosol Science, 1988, 19(5), 639-642

[6] C. Helsper, et al. "Investigations of a new aerosol generator for the production of carbon aggregate particles" in Atmospheric Environment, 1993, 27(8), 1271-1275

[7] C. Roth, et al. "Do inhaled ultrafine particles cause acute health effects in rats? I: Particle production." in Journal of Aerosol Science, 1998, 29, S679-S680

[8] J. S. Brown, et al. "Generation of Radiolabeled "Soot-Like" Ultrafine Aerosols Suitable for Use in Human Inhalation Studies" in Aerosol Science & Technology, 2000, 32(4), 325-337

[9] D. E. Evans, et al. "The generation and characterization of metallic and mixed element aerosols for human challenge studies" in Aerosol Science & Technology, 2003, 37(12), 975-987

[10] H. Horvath and M. Gangl "A low-voltage spark generator for production of carbon particles" in Journal of Aerosol Science, 2003, 34(11), 1581-1588

[11] C. Roth, et al. "Generation of ultrafine particles by spark discharging" in Aerosol Science and Technology, 2004, 38(3), 228-235

[12] J. P. Borra "Nucleation and aerosol processing in atmospheric pressure electrical discharges: powders production, coatings and filtration" in Journal of Physics D, 2006, 39(2), R19-R54

[13] J. H. Byeon, et al. "Spark generation of monometallic and bimetallic aerosol nanoparticles" in Journal of Aerosol Science, 2008, 39(10), 888-896

[14] N. S. Tabrizi, et al. "Generation of nanoparticles by spark discharge" in Journal of Nanoparticle Research, 2009, 11(2), 315-332

[15] N. S. Tabrizi, et al. "Synthesis of mixed metallic nanoparticles by spark discharge" in Journal of Nanoparticle Research, 2009, 11(5), 1209-1218

[16] N. S. Tabrizi, et al. "Generation of mixed metallic nanoparticles from immiscible metals by spark discharge" in Journal of Nanoparticle Research, 2010, 12(1), 247-259.

[17] S. Bau, et al. "Experimental study of the response functions of direct-reading instruments measuring surface-area concentration of airborne nanostructured particles" in Journal of Physics: Conference Series. IOP Publishing, 2009, p. 012006

[18] B. K. Ku and A. D. Maynard "Generation and investigation of airborne silver nanoparticles with specific size and morphology by homogeneous nucleation, coagulation and sintering" in Journal of Aerosol Science, 2006, 37.4: 452-470

[19] S. Bau, et al. "Electrical properties of airborne nanoparticles produced by a commercial spark-discharge generator" in Journal of Nanoparticle Research, 2010, 12.6: 1989-1995

[20] J. H. Jung, et al. "Metal nanoparticle generation using a small ceramic heater with a local heating area" in Journal of aerosol science, 2006, 37.12: 1662-1670

[21] J. Jacoby, et al. "Caiman: a versatile facility to produce aerosols of nanoparticles" in Journal of Physics: Conference Series. IOP Publishing, 2011, p. 012014

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