A size selective nanoparticle collection device based on diffusion and thermophoresis

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Abstract. There is a growing industry fabricating products that are based on nanoparticles (particle diameter \(d_p\leq100\) nm). The production of these particles requires detection, classification and characterisation of even smaller particles because of, e.g. preventing unwanted particle emissions from the processes and health issues. Monitoring of the processes is needed on one hand for product quality determinations, on the other hand to ensure safe and particle-free working conditions. Thus simple, fast and reliable measurement devices are needed for particle characterisation.

1. Introduction

The ideal "particle monitor" would be based on on-line detection, and would measure particle number (e.g. CPC) (and mass) size distribution (e.g. DMA connected to a CPC and controlled by SMPS software) and would also analyse the morphology and chemical composition (elemental, for a start) of the measured particles. This is important because it is known [1, 2] that there is no single particle property parameter that would describe, e.g. the health effects or particle exposure adequately. In addition, if the chemical composition of the particles could be determined at the same time as the physical particle parameters are measured this would indicate the source of the measured particles, e.g. do the particles originate from the process itself or is the source somewhere else. Another requirement for the "particle monitor" is that it should be small in size to make the transportation easy in industrial environments. However, research is still needed to achieve these features, although some promising techniques are already available, e.g. aerosol mass spectrometry (AMS) [3] and laser-induced breakdown spectroscopy (LIBS) [4]. The problem with these techniques is, however, that they are currently quite bulky and/or not so easy to operate.

In this study the target was to develop a particle sampler that would be simple to use, durable, preferably small in size, and should be suitable for use in industrial environments. Because there already are a number of particle measurement devices based on particle number and mass concentration and size distribution measurements, there is no need to develop a device based on similar techniques. Therefore, a different approach by sampling particles on a grid (\(d_p=3\) mm) used for electron microscopy (EM) samples was developed. The grid is placed on top of a tube-like resistor
heater. The collection of particles is based on diffusion of the nanoparticles and thermophoretic repulsion (antithermophoresis; temperature difference between the aerosol flow and the grid) of the large particles (\(d_p>200\) nm). Samplers based on particle collection on electron microscopy grids have been developed before but these samplers are based on different collection techniques, e.g. electrostatic precipitation with a point-to-plate ESP [5, 6], and do not classify particles in any way.

2. Experimental methods

2.1. The heated electron microscopy (EM) grid sampler

The collection of the particles by the heated EM grid sampler is based on diffusion of the nanoparticles and thermophoretic repulsion [7, 8]; temperature difference between the aerosol flow and the grid) of the large particles (\(d_p>200\) nm). The size of the heated EM grid sampler is a compact, pocket-size model approximately 80 mm by length and 20 mm by diameter with ½-inch Swagelok fittings. However, these dimensions do not include the resistor heater controller needed for accurate temperature control of the sampler. The temperature of the heated EM grid sampler is adjusted via a heating controller equipped with a CAL 3300 PID regulator. The heating of the EM grid is fast, typically on the order of minutes or less.

![Figure 1. Schematics of the compact heated EM grid sampler.](image)

The heating resistor element (\(P=100\) W, \(l_{\text{element}}=40\) mm, \(d_{\text{element}}=6.5\) mm) in the heated EM grid sampler is a commercial, cylindrical shaped HHP-type made by Hotset GmbH. The shell of the resistor element is made of stainless steel. The resistor element is inserted inside a brass tube, whose outside diameter is \(d_{\text{tube1, out}}=8\) mm and length \(l_{\text{tube1}}=40\) mm. This 8 mm tube is inserted inside another tube of length \(l_{\text{tube2}}=30\) mm and outside diameter of \(d_{\text{tube2, out}}=12.5\) mm. This tube section has a ½-inch Swagelok tube fitting. The temperature of the heating resistor is controlled by a K-type thermocouple inserted inside the heating element. The head of the heated EM grid sampler (\(l_{\text{head}}=10\) mm, \(d_{\text{head}}=3.3-7\) mm), where the grid is mounted, is screwed into the brass tube (\(d_{\text{tube1, out}}=8\) mm, \(l_{\text{tube1}}=40\) mm) surrounding the heating resistor element making the thermal contact between the resistor element and the head (Figure 1).
Mounting of the EM grid on top of the heated sampler may be done in two ways: either with the help of a brass hat (Figure 2a) or with carbon tape (Figure 2b). In the case of the carbon tape the EM grid is glued directly on top of the collecting head of the EM grid sampler with the tape (Figure 2b). By using carbon tape instead of the brass hat the passing flow may sweep directly the surface of the grid. Because the dimensions controlling the balance between diffusion and anti-thermophoresis may be small, this may have an effect on the collection efficiency. In the case of the brass hat the grid is located in a pit of approx. 1 mm deep (the thickness of the brass hat; Figure 2a).

Sample collection with the heated EM grid sampler is simple. The grid is mounted on the EM grid sampler, and the sampler is mounted on the collection location, in this case a 1/2-inch T-fitting on the sampling tubing. Parallel or perpendicular mounting of the EM grid sampler in relation to the aerosol flow may be used. The heater controller is set to the desired temperature to achieve temperature difference between the heated EM grid sampler and the passing flow. After reaching the preset temperature the EM grid sampler is ready for sampling. The warm-up usually takes on the order of minutes. The sampling is initiated by opening the on-off valve upstream the sampler and switching on the pump.

2.2. Aspiration sampler for comparison measurements
To compare the performance of the heated EM grid sampler to another individual particle sampler an aspiration EM grid sampler was built and designed. The sampler consists of a commercial preimpactor (orifice diameter 0.0457 mm) normally inserted in front of a TSI electrostatic classifier model 3080, an EM grid mounting head soldered with silver into 6 mm tubing and Swagelok fittings (Figure 3). By regulating the flow through the aspiration sampler to approximately 0.3 Nlpm with a critical orifice (CO) the aerodynamic cut size of the preimpactor is approximately at $d_{50,ae}=600$ nm.

In the aspiration sampler the sample flow enters the preimpactor, where the particles whose aerodynamic size is approximately $d_{p,ae}>600$ nm are deposited on the impactor collection plate because of their inertia. The smaller particles are able follow the flow and are collected on the EM grid after the preimpactor. The grid is installed on the mounting head with the help of a hollow screw, and a copper seal is mounted between the screw and the EM grid.
2.3. Measurement set-up

The experimental measurements were carried out using TiO$_2$ particles produced by thermal decomposition of TTIP (titanium tetraisopropoxide). The nanoparticle generator used in the experiments is described in detail elsewhere [9, 10].

The test matrix to study the performance of the revised heated EM grid sampler consisted of two different mounting set-ups of the EM grid sampler in relation to the passing flow (perpendicular and parallel), two types of grid mounting (carbon tape and brass hat), different collection times (from 1 min to 6 min) and temperature differences (dT=0, 10, 30, 70°C) between the EM grid sampler and the aerosol flow. In addition, the performance of the heated EM grid sampler was compared to an aspiration sampler (Figure 3) equipped with a preimpactor. The comparison measurements were done by measuring simultaneously with both samplers after the two-stage dilution of the measurement set-up (Figure 4). The temperature difference between the EM grid sampler and the aerosol flow was set to dT=10°C that ensured sound collection efficiency. During all the measurements the total particle number concentration was measured with a TSI CPC model 3022. Typical collection times with the aspiration sampler with the preimpactor were 5 and 10 s, and for the heated EM grid sampler 30 and 45 min at the total particle number concentration of $N_{tot}=6.0\times10^9$ #/cm$^3$ with dilution correction (DR=1001) and $N_{tot}=6.0\times10^6$ #/cm$^3$ after two-stage dilution, i.e. at the measurement location.

Figure 3. The aspiration sampler equipped with a preimpactor normally inserted in front of a TSI electrostatic classifier model 3080. a) The sampler with fittings. b) The sampler installed inside a ½-inch Swagelok 90 degree elbow, and the head of the aspiration sampler, where the grid is mounted (under the hollow screw).

Figure 4. Schematics of the measurement set-up. The empty rectangle drawn with a broken line indicates the location of the heated EM grid sampler during the comparison measurements with the aspiration sampler.
3. Results

3.1. Modelling
Deposition velocities as a function of particle size were calculated for the heated EM grid sampler placed perpendicular to the passing aerosol flow. The model calculations were based on a previous study [11]. The results of the calculations for passing flow velocities of 1 (Figure 5a) and 10 m/s (Figure 5b) indicated that the larger the temperature difference between the collecting grid and the passing flow, the stronger is the dependence of the collection efficiency on the particle size. However, reasonable nanoparticle collection efficiency and size classification (up to approximately 100 nm) is achieved already at temperature differences of \( dT=10^\circ \text{C} \).

![Figure 5](image_url)

**Figure 5.** Estimates of the deposition velocities as a function of particle size at various temperature differences (\( dT \)) for the perpendicular flow towards the heated EM grid sampler. a) flow velocity 1 m/s b) flow velocity 10 m/s.

3.2. Experimental

3.2.1. Heated EM grid sampler
The modelling calculations indicated that as low temperature difference as \( dT=10^\circ \text{C} \) between the passing flow and the heated electron microscopy (EM) grid sampler causes a significant, more than three orders of magnitude, difference in the deposition velocity compared to the unheated grid case, \( dT=0^\circ \text{C} \). However, the modelling results apply for the case where the flow was perpendicular to the heated EM grid sampler. In the following experimental measurements the heated EM grid sampler was also placed parallel to the passing flow to find out if there are any differences in collection efficiency and collected particles. Currently the flow velocity past (or towards in case of a perpendicular flow) the heated EM grid sampler is \( v=8.0 \text{ m/s} \).

The first experiments were carried out at temperature differences of \( dT=0, 10, 30, 70^\circ \text{C} \) for perpendicular flow towards the heated EM grid sampler with a brass hat and a carbon tape mounting using collection times of 1 and 3 min. Based on the experimental and previous modelling results, the temperature differences in the following experiments were set to \( dT=0, 10, 30^\circ \text{C} \). The position of the heated EM grid sampler in relation to the aerosol flow was also changed from perpendicular to parallel based on the experiments with hat and tape at \( dT=10, 30^\circ \text{C} \). At these temperature differences with perpendicular flow with hat mounting mainly large, almost spherical particles of \( d_p=300-700 \text{ nm} \) in diameter are observed. In the case of carbon tape mounting similar spherical particles are also seen together with chain-like aggregates. It seems that especially in the case of the hat mounting the collection of the particles is dominated by large particle impaction, and the temperature difference hinders the collection of the smaller particles \( (d_p<200 \text{ nm}) \). The structure of these spherical particles \( (d_p=300-700 \text{ nm}) \) is presented in Figure 6 for the case of perpendicular aerosol flow towards the collecting EM grid. Particle image velocimetry (PIV) was also carried out to found out the flow field around the heated EM grid sampler in the case of the perpendicular flow (Figure 7). Twisting of the
flow vectors/flow field is observed at the edges of the sampler thus indicating possible particle impaction points.

Figure 6. SEM image of TiO2 particles collected with the heated EM grid sampler, optimal collection time. Grid mounted on the heated resistor with a brass hat, aerosol flow perpendicular to the surface of the grid, sampling time 3 min, temperature difference $dT=30^\circ$C.

Figure 7. Particle image velocimetry (PIV) graph presenting the flow field (average velocity vectors) around the EM grid sampler mounted perpendicular to the flow.

For the carbon tape mounting this is not so evident, because the mounting of the carbon tape was not successful (one spot mount) thus making the thermal conduction from the heater resistor to the grid worse than in the case of the hat. This was fixed later on by applying two spot, opposite to each other carbon tape mounting (Figure 2). No significant difference in the size of the particles was found between $dT=10^\circ$C and $dT=30^\circ$C cases. Therefore, the further experiments with the heated EM grid sampler either with brass hat or carbon tape mounting were carried out at the temperature difference of $dT=0$ (reference), $10^\circ$C with parallel aerosol flow sweeping the surface of the grid.

The results of the collected particles for the heated EM grid sampler with carbon tape mounting and parallel flow over the grid for $dT=0$, $10^\circ$C (Figures 8 and 9; sampler placed before two-stage dilution, see Figure 4) indicate the effect of the temperature difference between the grid and the aerosol flow. For the $dT=0^\circ$C case, collection time 3 min (Figure 8a; no thermophoretic repulsion), the total particle number concentration during measurement after two-stage dilution is $6.0 \times 10^6$ #/cm$^3$ ($6.0 \times 10^6$ #/cm$^3$ at the measurement location; Figure 11a), and the chain-like aggregates are larger than in the case of $dT=10^\circ$C, total particle number concentration $6.3 \times 10^5$ #/cm$^3$ ($6.3 \times 10^5$ #/cm$^3$ at the measurement location), collection time 2 min (Figure 8b). In addition, in $dT=0^\circ$C case there are large, spherical particles of 300-700 nm in diameter that are absent in the $dT=10^\circ$C case. Longer collection times (Figure 9), in this case 6 min for $dT=0$, $10^\circ$C, lead to particle overlapping on the grid (on-top deposition).
Figure 8. SEM images of TiO$_2$ particles collected with the heated EM grid sampler, optimal collection time. Grid mounted on the heated resistor with carbon tape, aerosol flow sweeping parallel to the surface of the grid. a) Sampling time 3 min, temperature difference $dT=0^\circ C$, i.e. no thermophoretic repulsion, b) Sampling time 2 min, temperature difference $dT=10^\circ C$.

Figure 9. SEM images of TiO$_2$ particles collected with the heated EM grid sampler, too long collection time. Grid mounted on the heated resistor with carbon tape, aerosol flow sweeping parallel to the surface of the grid. a) Sampling time 6 min, temperature difference $dT=0^\circ C$, i.e. no thermophoretic repulsion, b) Sampling time 6 min, temperature difference $dT=10^\circ C$.

At identical experimental conditions as above but using the brass hat for mounting the grid almost similar effects on the collected particles are observed. For the $dT=0^\circ C$ case, collection time 2 min (Figure 10a), the total particle number concentration is $5.4 \times 10^9$ #/cm$^3$ ($5.4 \times 10^6$ #/cm$^3$ at the measurement location; Figure 11b), and similar chain-like aggregates as in the case of the carbon tape above are seen. However, the large, spherical particles of 300-700 nm in diameter are absent in the brass hat case. For $dT=10^\circ C$ case for brass hat mounting (Figure 10b), collection time also 2 min and total particle number concentration $5.5 \times 10^9$ #/cm$^3$ ($5.5 \times 10^6$ #/cm$^3$ at the measurement location; Figure 11b), the collected particles are almost identical in size compared to the carbon tape mounting case (Figure 8b), smaller than 200 nm (experimentally determined from the SEM micrographs) in diameter. Also the collected number of the particles seemed to be almost the same for the carbon and brass hat mounting. Thus it seems that under these collection conditions ($dT=10^\circ C$, $N_{tot}=5.5 \times 10^6$ #/cm$^3$ after two-stage dilution) the two different grid mounting types do not cause any significant difference on the collected particles.
3.2.2. Comparison between heated EM grid and aspiration sampler

To compare the performance of the heated EM grid sampler to other individual particle samplers an aspiration sampler (Figure 3) equipped with a preimpactor (orifice diameter 0.0457 mm) normally inserted in front of a TSI electrostatic classifier model 3080 was applied. Both samplers were operated simultaneously at identical locations of the sampling system (Figure 4). Because of the very different collection principles of these samplers, the collection times are very unequal. For the heated EM grid sampler at $dT=10^\circ\text{C}$ and collection time of 45 min after two-stage dilution (Figure 12) the collected particles are almost identical to the $dT=10^\circ\text{C}$ case with carbon tape mount before the two-stage dilution (Figure 8b). However, overlapping of the particles (longer chain-like aggregates than they actually are) in the case of the 45 min collection has occurred. Thus a shorter collection time should have been applied. The total particle number concentration during the measurement is approximately $6.9\cdot10^9$ #/cm$^3$ ($6.9\cdot10^8$ #/cm$^3$ at the measurement location; Figure 14).
Figure 12. SEM images of TiO$_2$ particles collected with the heated EM grid sampler, too long collection time causing partial particle overlapping. Grid mounted on the heated resistor with carbon tape, aerosol flow sweeping parallel to the surface of the grid, sampling time 45 min after two-stage dilution (Figure 4), temperature difference $dT=10^\circ$C. a) Overall view of the particles where overlapping is observed b) Detailed image of the individual particles, whose sizes are typically under $d_p=200$ nm when no mutual overlapping is present.

For the aspiration EM grid sampler the collection times are usually very short. No overlapping of the collected particles (particles collected on top of each other) is observed (Figure 13a), and individual particle structure is still visible (Figure 13b). The particles are generally smaller than 200 nm in diameter. At the total particle number concentration of approximately $6.6\cdot10^8$ #/cm$^3$ ($6.6\cdot10^6$ #/cm$^3$ at the measurement location; Figure 14) after two-stage dilution the optimal collection time is on the order of 5 s.

Figure 13. SEM images of TiO$_2$ particles collected with the aspiration EM grid sampler equipped with a pre-impactor (aerodynamic cut size $d_{ae,cut}=600$ nm), sampling time 5 s.

a) Overall view of the particles. b) Detailed image of the individual particles, sizes typically under $d_p=200$ nm.
Figure 14. Total particle number concentration measured after the dilution, dilution ratio DR=1001 (Figure 4). The particle samples are collected simultaneously with the heated EM grid and aspiration sampler, grid mounted with carbon tape, aerosol flow sweeping parallel to surface of the grid. The images of the collected particles are shown in Figures 12 and 13.

4. Conclusions

An electron microscopy grid sampler based on nanoparticle diffusion and large particle thermophoretic repulsion (anti-thermophoresis) was designed. The dimensions of the current version are 79x22 mm at the largest. In addition, the performance of the heated EM grid sampler was compared to an aspiration EM grid sampler built and designed at VTT equipped with a commercial preimpactor (aerodynamic cut size approximately d_{50,ae}=600 nm).

Based on the experimental results a temperature difference of dT=10°C between the heated EM grid sampler and the passing parallel aerosol flow is high enough to hinder large particle (d_{p}>200 nm) collection on the EM grid. Mounting the grid on the sampler either with carbon tape or with a brass hat does not seem to cause any significant difference on the collected particles (d_{p}<200 nm; experimentally determined from the SEM micrographs) at these conditions (dT=10°C and N_{tot}≈5.3-5.5⋅10^6 #/cm^3 after two-stage dilution, DR=1001). Because the brass hat is currently much easier to mount it is preferred over the carbon tape mounting. However, dimensions in nanoparticle diffusion are very small and this may cause some error for sampling, as the passing aerosol flow cannot sweep the surface of the grid (actually first sweeps the surface of the hat) when reaching the grid sampler, and the grid cannot be mounted exactly on top of the grid sampler, it is approx. 1-2 mm below the surface of the hat. This cannot be totally avoided with hat-type mounting of the grid.

In addition, when using carbon tape for mounting the EM grid, it is important to ensure that the grid has been mounted properly. If the contact between the grid and the head of the heating resistor is poor thermophoretic repulsion is very weak or even non-existent. However, there are possibilities to make the carbon tape mounting easier and better to ensure good contact between the head of the resistor and the grid. Partial solution to this problem would be to increase slightly (approximately dT=20-30°C instead of dT=10°C) the temperature difference between the passing flow and the grid.

The performance of the heated EM grid sampler was also compared to another individual particle sampler called an aspiration sampler equipped with a commercial preimpactor (orifice diameter 0.0457 mm) normally inserted in front of a TSI electrostatic classifier model 3080. The sampling times for the aspiration sampler are usually very short, usually two orders of magnitude shorter than with heated EM grid sampler. Therefore, at low concentrations when sampling times should be kept short, the aspiration sampler is a good choice. However, overloading of the sampling grid is a potential problem because of the very short collection times. For optimal operation of the aspiration sampler a more suitable preimpactor than the commercial one applied in this study could be designed.
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