

Miniature nanoparticle sensors for exposure measurement and TEM sampling

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Abstract. Nanoparticles in workplaces may pose a threat to the health of the workers involved. With the general boom in nanotechnology, an increasing number of workers is potentially exposed, and therefore a comprehensive risk management with respect to nanoparticles appears necessary. One (of many) components of such a risk management is the measurement of personal exposure. Traditional nanoparticle detectors are often cumbersome to use, large, heavy and expensive. We have developed small, reliable and easy to use devices that can be used for routine personal exposure measurement in workplaces.

1. Introduction

Exposure measurements should be a part of a general risk-management strategy for workplaces where nanoparticles are produced or processed. Since the prime exposure route is over inhalation, measuring airborne nanoparticles in such workplaces seems like a sensible idea, and it can be done in different ways: (I) measurements by an industrial hygienist (II) with stationary equipment that is always present at a sensible location (similar to a fire detector), or (III) as personal exposure measurement with small instruments carried by the workers, similar to dosimeters in the nuclear industry. Ideally, for personal monitoring, the instruments should be small, lightweight, affordable, simple to use and reliable, and provide an online measurement so that an alarm can be raised if a threshold value is exceeded. Unfortunately, most current particle detectors have severe drawbacks for this type of application: Optical detectors are generally simple to use, and low-maintenance, but are not sensitive to nanoparticles – sub-100nm particles cannot be detected. Condensation particle counters that first grow the particles to larger sizes before an optical detection are very precise devices, but need a working fluid that needs regular replenishment, and they need to be held level to prevent internal spilling of the working fluid. They are thus reasonable for occupational hygiene professionals, but cannot be used for measurements of types II and III. Filter samples can be taken, but are not real-time, and need a lot of effort after the sampling. Fortunately, there is one class of particle instruments that is nano-sensitive, reliable, and real-time – electrical particle detectors. This class of instrument has been known for a long time, and already exists in the market. Our new instruments are similar in performance to existing electrical particle detectors, but much smaller and easier to use.



2. Standard electrical detection by unipolar charging of aerosols

Unipolar charging of nanoparticles is at the basis of many current aerosol instruments (e.g. TSI FMPS, Cambustion DMS500, Dekati ELPI, Pegasor PPS etc). The simplest possible instrument that can be built based on unipolar charging is known as a diffusion charger (DC). A scheme of such an instrument is shown in figure 1.

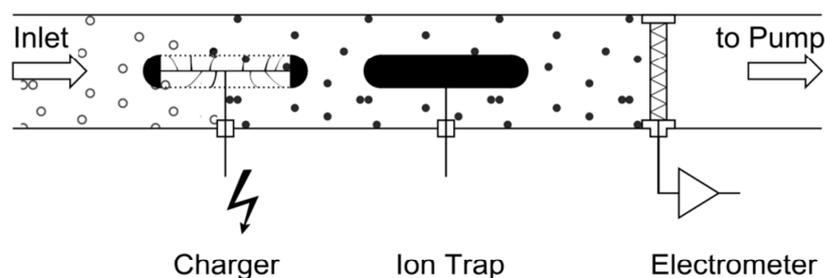


Figure 1: Scheme of a standard diffusion charger (DC)

The diffusion charger consists of 3 basic elements: the unipolar charger (usually a corona charger), where ions are generated and mixed with the particles to charge them, the ion trap, where excess ions are removed, and finally a filter, where all particles are captured and the current deposited by the particles onto the filter is detected with a sensitive electrometer, which must be able to measure currents in the order of fA. This type of instrument has been commercially available for some time (Matter LQ1-DC, Ecochem 2000-DC, TSI EAD, TSI NSAM, TSI Aerosotrak 9000). It measures the final charge state of the aerosol after the unipolar diffusion charger. The particles take up a charge that can well be described by a power law:

$$q(d) = c \cdot d^x$$

where x is usually in the range of 1.1 – 1.2. The signal of the DC is thus nearly proportional to an “aerosol length concentration” (with units e.g. mm/cm^3), and this is true over a very wide size range, from about 10 nm to 10 μm . Diffusion charging is unspecific, i.e. it hardly depends on the particle material, so all particles are detected with this instrument. An interesting interpretation of the DC signal was given by Wilson et al. [1]: for particles in a more limited size range (about 20nm – 350nm), the DC signal is approximately proportional to the lung-deposited surface area (LDSA) concentration of nanoparticles in the human lung, expressed in units of $\mu\text{m}^2/\text{cm}^3$, indicating how much particle surface area in μm^2 is deposited in the lung for every cm^3 of inhaled air. Since many toxicological studies have shown that particle surface area usually correlates better than particle mass or particle number with health effects, the LDSA concentration is a potentially highly interesting particle metric.

In summary, the DC is thus an interesting instrument, because it is simple (and thus robust and potentially low-cost), measures a probably relevant quantity, operates over a very large size range and needs no consumables.

3. Electrical detection by induced currents

We have developed a novel technique to measure LDSA by induced currents, rather than particle-deposited currents on a filter, and implemented it in an instrument called the partector. It works as follows:

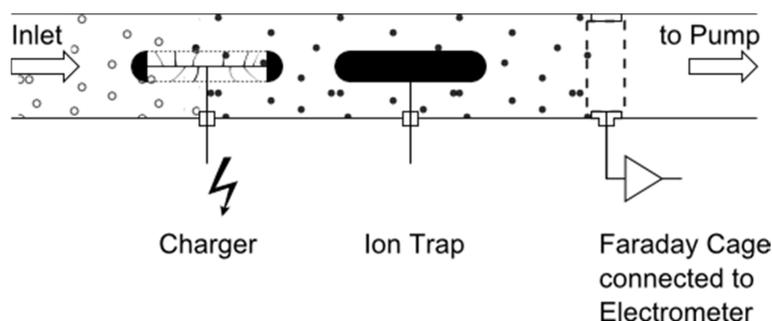


Figure 2: Scheme of an induced current detector

The only visible difference to the DC is the lack of the particle filter. It is replaced by an empty Faraday cage, which is connected to an electrometer, and thus virtually grounded. Since a grounded Faraday cage will not allow any electric field lines to escape, the total charge inside the cage and on the cage must be zero by the law of Gauss. Therefore, by measuring the charge on the cage, an indirect measurement of the charge in the cage is made. However, in our setup we are only measuring the current flowing to/from the cage, i.e. the time derivative of the charge, dQ/dt . Thus, a constant charge in the cage is not detectable. In order to always have a measureable signal, a temporal variation of the charge must be introduced. We do this by pulsing the unipolar charger, which turns on and off at a rate of 0.5 Hz. In this manner, we can detect an oscillating signal at the electrometer, whose amplitude is proportional to the charge transfer to the aerosol (see Fig. 3).

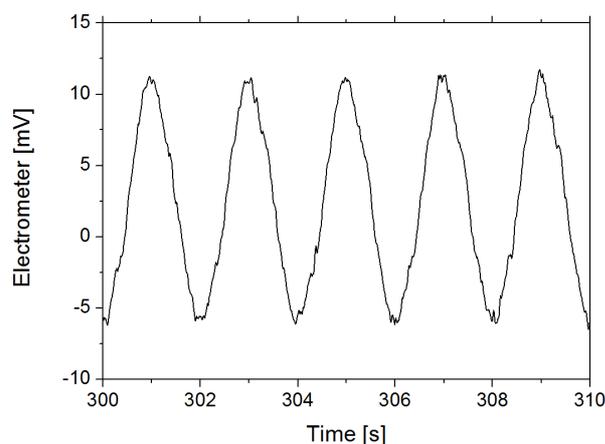


Figure 3: example electrometer signal from the Faraday cage

This approach has some important differences to the standard DC approach:

- It measures the charge transferred to the aerosol in the unipolar charger, and not the final charge state. In practice, this is mostly identical, since aerosols are usually neutral. However, if a highly charged aerosol is measured, this difference will be clearly visible. In particular, negatively pre-charged aerosols will give a larger signal than neutral aerosols, while positively pre-charged aerosols will give a smaller signal (since the unipolar charger uses positive charging).
- An amplitude of an AC signal is measured rather than a DC signal. This is much more robust, since all electrometers exhibit some zero offset that may drift with time and/or ambient conditions (such as temperature and humidity). In traditional electrometer-based aerosol instruments, warmup periods and regular zero checks are necessary, which are not needed here.
- A better monitoring of the instrument health status is possible in this version: (1) the electrometer zero offset is constantly monitored, because it is just the period-average of the

electrometer signal. Although a drift or high offset in itself does not influence the measurement, it is an indicator that something bad is happening to the instrument. The firmware can thus display a service warning while the instrument is still operational. (2) In the unipolar charger, the charging current reaching the ion trap is measured, and the high voltage is regulated for constant current. It is possible that a leak current flows to this counterelectrode via insulator due to water condensation or, over long times, contamination with particles. In traditional instruments, such leak currents are indistinguishable from real currents, whereas here, the charger is in an off-state half of the time, where we can monitor if the charging current is really 0 as it should be.

- Service intervals are longer. Since no particles are collected nominally, there is no need for cleaning or filter exchanges. Of course, particles are always deposited by diffusion and impaction in any instrument, so some service is required at some point. Nevertheless, service intervals are much longer than in previous instruments we have built.
- Finally, because this is a non-contact method of aerosol detection, the particles are still available after the measurement in a charged state, and can be further manipulated. We have built a version of the instrument where the particles can be deposited on a TEM grid for further analysis. This is described in section 4.

Overall, the Faraday cage variant of a DC seems to have more advantages to us than drawbacks. We used this principle to build an instrument designed for occupational hygiene / workplace safety, i.e. our goal was to build a small instrument that would be simple to use. The partector, has the following specifications:

- Small (13.4 x 7.8 x 2.9 cm)
- Light-weight (400 g)
- No consumables, such as working fluids in handheld CPCs
- Battery life of 14 hours
- Alarm capability when a threshold concentration is exceeded
- Only 16 s warmup time, and a time resolution of 1 s
- Concentration range: 1 – 20'000 $\mu\text{m}^2/\text{cm}^3$ (This corresponds to about 500 – 10⁷ particles/cm³)
- Size range: 10nm – 10 μm ; however, the interpretation as LDSA is only valid in a more limited size range of about 20-350nm. Nevertheless the instrument can be used to measure larger particles.

Summing up, the partector has a very wide detection range both in terms of particle concentration and particle diameter, making it suitable even for workplaces with very high concentrations of nanoparticles (e.g. welding). The electrical charging principle is very sensitive even to nanoparticles, which cannot be detected with optical means.

4. TEM sampling

The partector can serve as a simple instrument in occupational hygiene to easily make a quick survey of nanoparticle concentrations. However, like all instruments measuring physical parameters (mass, number, size distribution etc), it cannot distinguish between different types of particles – whether they are harmless (e.g. salt particles) or potentially dangerous (e.g. metal particles, fibers), they are all seen by the instrument. Furthermore, as always in occupational hygiene, there is the general difficulty of distinguishing between the always present background aerosol and nanoparticles released by a process in the workplace. In such cases, a deeper analysis of the particles is necessary. The transmission electron microscope (TEM) is the most powerful analytical technique for analysing nanoparticles; in particular for morphology and single-particle chemical analysis. We thus designed a second instrument (partector TEM) which adds a sampling stage for TEM probes. Since the particles passing through the partector are already charged, it is natural to use electrostatic deposition to collect the

particles on the TEM grid. The partector TEM contains a small insert that holds the TEM grid, and a strong electric field can be applied to deposit the particles on the grid. Since TEM grids are notoriously difficult to handle due to their small size, the entire insert is exchanged at once when a new sample needs to be taken – the instrument comes with 6 inserts which can be prepared with TEM grids before the actual sampling.

One of the biggest challenges in TEM sampling is to produce samples with optimal coverage. If too many particles are sampled, they will form agglomerates on the grid, and it remains unclear whether they were agglomerated in the gas phase. If only very few particles are sampled, then the sample is not very representative. For traditional methods to collect TEM samples (on holey grids by flow-through filtering, by thermophoretic or electrostatic deposition), it is therefore necessary to either take multiple samples with different sampling time, or to estimate the necessary sampling time from a concentration measurement made with a second instrument. The partector TEM is unique, because it can directly estimate the area of the grid covered by nanoparticles by integrating the electrometer signal. This works because the time-integrated signal is approximately proportional to the area coverage of the grid: for the area A covered with N nanoparticles of diameter d we can write:

$$A = N \cdot d^2 = \eta \cdot nt \cdot d^2 = d^{-1} \cdot nt \cdot d^2 = nd \cdot t$$

Where n is the nanoparticle concentration in the air, η is the deposition efficiency, and t is the sampling time. Because smaller particles have a higher electric mobility after diffusion charging than larger particles, the deposition efficiency is approximately proportional to d^{-1} , and thus the area covered is proportional to the instrument signal integrated over time. This calculation once again breaks down for large particles ($d \gg 300\text{nm}$) where the mobility becomes more or less constant, so large particles will lead to a higher coverage of the grid. Nevertheless, especially for particles in the nano size range, integrating the LDSA signal over time gives an excellent estimate for when to stop sampling.

The partector TEM is thus a very interesting instrument, as it allows an occupational hygienist to first make a quick survey of nanoparticle concentrations in a workplace, and then, if there is some concern about the levels or the types of particle that might be produced, to take a sample with a single push of a button. TEM analysis is expensive due to the high cost of the instrument and the skilled operator involved, so, although the partector TEM is much more expensive than simple filter samplers, it can easily pay off through decreased operating costs in the TEM analysis.

5. Applications and Conclusions

We have developed a new method of aerosol detection, by induced currents. This method is sensitive to nanoparticles, and non-collecting, thus leading to long service intervals. As demonstrated, it can be used to create miniature nanoparticle detectors that are very easy to use. These instruments can for example be used for personal exposure monitoring in the workplace, but also, due to the long service intervals, for ambient monitoring where it seems that 1 year 24/7 operation is possible. Another application is to combine it with a CPC measurement; the ratio of the two instrument signals is then proportional to the average particle diameter over a very wide size range, allowing (crude) particle sizing in real time (1s) from 10nm to 10 μm [2].

References

- [1] Wilson W.E., Stanek J., Han H.-S., Johnson T., Pui D.Y.H., Turner J., Chen D.-R. and Duthie, S. (2007). Use of the Electrical Aerosol Detector as an Indicator of the Surface Area of Fine Particles Deposited in the Lung. *J. Air Waste Manage. Assoc.*, 57:211-220.
- [2] Bukowiecki N., Kittelson, D.B., Watts, W.F., Burtscher, H., Weingartner, E. and Baltensperger U. (2002). Real-time Characterization of Ultrafine and Accumulation Mode Particles in Ambient Combustion Aerosols, *J. Aerosol Sci.* 33: 1139-1154