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Measurement and characterisation of airborne nanoparticles

Summary

As far as concerns the risks of nanotechnology, the focus of attention is on nanomaterials and in particular on free nanoparticles. Alongside the investigation of their possible toxicity, the question of the exposure of humans and the environment is an essential element of their risk assessment. Nanoparticles suspended (distributed and embedded) freely in the air are of particular relevance, since they can easily penetrate the human body via the lungs. In addition, it is extremely difficult to monitor the spread of nanoparticles in the air.

Commercially available particle counters can be used to determine the concentration of particles and droplets in the air down to a size of a few nanometres. In the light of the high background concentration of natural nanoparticles and those generated by human activity, the first priority is to distinguish between natural and synthetic nanoparticles. While an on-site concentration measurement can be carried out in a few minutes, the analysis of the nanoparticles contained in the air, that is the determination of their form and composition is only possible using complex electron microscopy procedures in the laboratory. This situation currently constitutes the main problem for determining the concentration of synthetic nanoparticles and will do so for the near future.

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Introduction

There is broad agreement that direct risk to health and the environment in the field of nanotechnology can above all result from nanoparticles and their aggregates and agglomerations. Two aspects are to the fore in the associated assessment of the risk: the exposition, i.e. the release of nanoparticles in the environment and the resulting possible absorption by humans, and the effects that they might have in the human body or in nature. The latter depend strongly on the properties of the particles themselves. In addition to their size and shape, their structure, chemical composition and, very decisively, the surface properties play a role. Exposure is an important factor in particular for ensuring safety at the place of work. In order to be able to determine exposure and particle properties, it is necessary to be able to detect, i.e. measure and characterise the particles. The present dossier presents a number of the most important currently available measurement methods for detecting and characterising nanoparticles in the air. The focus here is less on a precise description of the technical methods and more on their capacities and limits.

General preliminary comments

Ordinary outside or room air consists of a mixture of gases (individual molecules or atoms), but also contains aerosols. Aerosol is the generic name for all solids (particles) or liquids (droplets) present in the air. The aerosols in the air may be of natural origin, for instance caused by forest fires or volcanic eruptions, condensed salt particles from the sea or disturbed soil or plant components. However, particularly in urban centres, they are mostly due to human activities (anthropogenic). Here, aerosols that originate from combustion processes (traffic, industry, household) or through friction on road surfaces, brakes and tyres or are generated by machines with movable parts predominate. Moreover, machines emit extremely fine oil droplets. The concentration and size distribution of these particles depends very strongly on local conditions (see Table 1) and there are roughly between 10,000 and 40,000 particles per cm³. Conventional dust measurement distinguishes between fine and ultrafine particles. Fine dust consists of particles (particulate matter, PM) with a diameter of around 10 µm (PM10). Very fine dust refers to dust with particles of a diameter of between 0.5 µm and 2.5 µm (PM2.5), while ultrafine dust (UFP) consists of particles with a diameter of below 0.1 µm, i.e. below 100 nm.

Table 1: Typical concentrations of man-made nanoparticles, according to Berges.¹

Process/place	Number of aerosols with a diameter of 14–673 nm [particles/cm ³]	Particle diameter at maximum concentration [nm]
Outdoor air/office	ca. 10.000	
Metal grinding	up to 130.000	20–170
Soldering	up to 400.000	35–65
Bakery	50.000–640.000	30–110
Airport	up to 1.570.000	< 10
Welding	100.000–40.000.000	40–600

Synthetic nanoparticles differ from natural anthropogenic nanoparticles by the fact that they are manufactured intentionally with defined properties and mostly with a narrow size distribution. The main challenge for the measurement of synthetic nanoparticles consists in distinguishing them from natural particles or those produced accidentally. In particular if the synthetic particles were to have a high toxicity, they would have to be detectable in low concentrations in order to exclude risks for man and the environment.

In the light of the extremely highly developed chemical detection methods, it might appear strange that detecting nanoparticles, which are several times bigger than molecules, should be a problem. The reason is that potential toxicity could be primarily due not to the chemical elements but rather to factors associated with size and shape. Asbestos is an example of a substance that causes lung cancer not as a result of its chemical ingredients but rather because of its physical properties (bio-persistence, shape, size and rigidity). Since the toxicity of particles is influenced both by chemical composition, shape, size, surface properties and by optical properties (photocatalysis), these properties must be included in the survey when counting the particles contained in the air. A purely chemical analysis of the composition of the air, on the other hand, would only result in a large number of different elements, without indicating whether they were contained in gaseous form, in the form of droplets or as particles in the air. This does not permit any conclusions about the shape, size, composition and concentration of the individual aerosols.

One of the commonest ways of determining the dust load is to pass a defined quantity of air through a filter and measure the mass of the particles collected on this filter. However, since only a few large particles are equivalent to the mass of thousands of small particles (see Table 2), this provides practically no information about concentrations of nanoparticles, in other words although the number of nanoparticles in the air can be much larger than the number of large particles (see Fig. 1), their share in the mass of aerosols found in the air is as a rule too small for the use of mass-sensitive measurement methods.

Table 2:
Calculated particle concentrations for 0.1 mg/m³ according to Berges (see footnote 1).

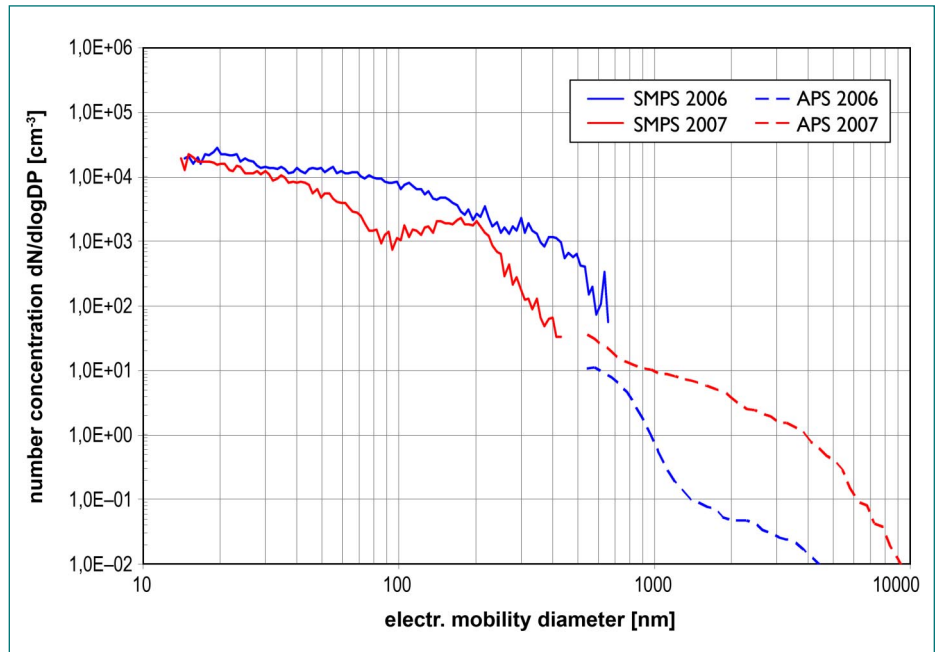


Figure 1: This figure shows a comparison between two measurements (2006, 2007) of the particle concentration in outdoor air. The dotted lines represent measurements with an APS (aerodynamic particles sizer) which is suitable for particles of between 500 and 20,000 nm, and is likewise based on the DMA principal (see text). The representation is in double logarithmic form: this means that both the x-axis and the y-axis are scaled in powers of 10. The illustration clearly shows that the number of nanoparticles also clearly outweighs the total number of particles in the outside air. While for instance only 1 to 10 particles per cm³ were measured with a diameter of 1000 nm, concentrations of 10,000 particles per cm³ were detected for particles with a diameter of around 20 nm. With particle size 100 nm, a clear difference of a factor of 10 can be identified between the 2006 measurement (the top line) and the 2007 measurement. This difference shows how particle concentrations depend on local and temporal conditions. (Source: Berges¹)

It follows from the conditions described above that the determination of the concentration of specific nanoparticles in the air can only consist of a combination of a size-dependent determination of concentration followed by an analysis of shape or chemical composition of the particles counted. Whilst the size-related determination of the concentration is currently possible “online” (on-site), the analysis of the particle shape and composition can in the current state of the art only be carried out “offline”. Offline, in contrast to online, means that the particles must be collected on a sample holder and then analysed in the laboratory. The following explains the principle of the particle counters currently being used.²

Particle counter (Scanning mobility particle sizer, SMPS)

The commonest particle counters at present are based on the principle of differential mobility analysis (DMA) implemented as a scanning mobility particles sizer (SMPS) combined with an optical counter. This measurement method consists essentially of two stages. In the first, the collected particles are distinguished according to size while a second stage determines the number of particles of a specific size. The following describes the principle for the determination of size in more detail, since this also reveals some of the limits of the measurement method.

Material	Quantity for 0.1 mg/m ³ at 20 nm [particles/cm ³]	Quantity for 0.1 mg/m ³ at 2 μm [particles/cm ³]	Density [kg/m ³]
Buckyballs (C60)	14.500.000	14	1.650
TiO ₂	5.600.000	6	4.240
Silver	2.300.000	2	10.490

At the input of the measuring device, large particles (> 1000 nm) outside the measurement range of interest are first of all eliminated by means of what is known as a pre-impactor. The remaining particles and droplets are first electrically neutralised and given a defined negative charge according to their size. The charged particles are then passed in turbulence free flow through a tube. In the middle of this tube there is a second tube with a smaller diameter. An electric voltage is applied between the two tubes (up to 10,000 V) with the result that the charged particles are driven towards the central electrode by means of electrical attraction. This acceleration is limited by collisions with the gas molecules of the carrier gas (particle-free air), with the result that the effective drift speed that develops is related to the size of the particles. At the end of the inner cylinder there is a small outlet opening on the cylinder wall. Depending on the electrical voltage applied, only aerosols of a specific size can pass through this opening. The size of the aerosols can be determined by varying the voltage between the cylinders.

In a second stage, the number of these size-selected aerosols is determined optically in the detector. For this purpose, the air is saturated with H₂O (water) or butanol vapour, the particles and droplets acting as condensation nuclei. In this way, a larger drop forms around the aerosol and can then be counted optically. This principle is called the condensation particle counter (CPC).

This method can be used for aerosols with a diameter of between 2.5 and 1000 nm.³ The upper limit, however, means that large (< 1 μm) agglomerates of nanoparticles cannot be measured using this device.⁴ Measurement accuracy is around 5 % for the particle size and around 10 % for the determination of the concentration. Concentrations of between 1 and 10⁸ P/cm³ can be detected. The measurement devices are transportable and are therefore useful for determining the aerosol concentrations near production facilities and at the place of work. The disadvantage is that the measurements take a relatively long time (depending on accuracy between 20 and 300 seconds). This is then a problem if specific processes of a production process with brief peak values are to be examined (replacement of a container in a bottling plant).⁴

However, the method also involves a number of restrictions. It cannot distinguish between droplets and particles, nor can it determine the chemical composition, shape or surface properties of an aerosol of a specific size.

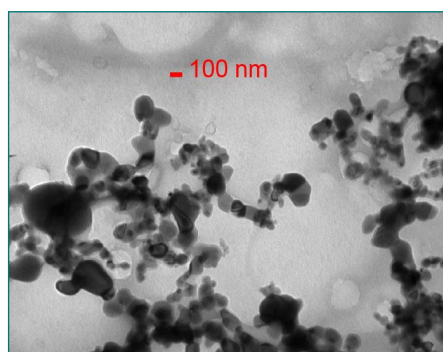
The size of the aerosol is only measured indirectly, namely on the basis of drift behaviour in the carrier gas. This, however, depends strongly on the shape of the particles. Fibre-shaped particles, entangled nanotubes, large-scale agglomerates, droplets and compact particles have different drift behaviours. This means that the mean diameter attributed to them (aerodynamics or mobility equivalent diameter) need not necessarily correspond with the actual diameter.

Electron microscopy

Since the aerosol counters cannot be used to determine what aerosols have been counted, in many cases an electron microscope analysis is carried out in addition. For this purpose, aerosols are deposited on special sample carriers at the place of the concentration measurement and investigated in the laboratory with an electron microscope.

Essentially, two methods can be distinguished: transmission electron microscopic (TEM) and scanning electron microscopy (SEM). The two devices are relatively expensive, a TEM being considerably more expensive than an SEM. However, with a TEM, it is usually possible to carry out both methods in one device, the preparation of samples is very different. What both methods have in common is that they must be carried out in a high vacuum (> 10⁻⁷ atm), which makes the investigation of a large number of different samples a time-consuming enterprise. The droplets contained in the aerosol cannot be investigated using both methods, since they evaporate immediately in the vacuum.

Figure 2:
TEM image of diesel soot. Although the particles have a diameter of 100 – 210 nm, they agglomerate to create the structures of several μm shown in the figure.
(Source: Berges¹)



With TEM, the focused electron beam transmits the sample. Accordingly, the sample must be prepared in such a way that particles are not superimposed on each other, and the matrix in which the particles are held must be in strong contrast to the material of the particles (see Fig. 2).

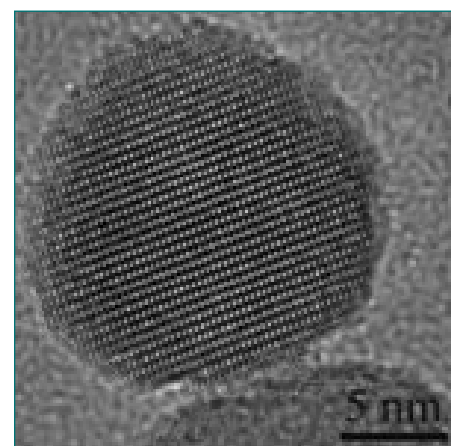
If the crystalline structure of the particle is also to be determined, the point in the sample where the particle is located must be thinned to a few layers of atoms. This is necessary, since otherwise a number of crystal levels would be superimposed and the crystalline structure could not be identified (cf. Fig 3). Because of this complex preparation of the sample, this method is primarily used for research purposes or for the analysis of layer systems such as those used in the semiconductor industry.

In SEM, the sample is scanned by moving a focused electron beam in lines across it. The current of the secondary electrons emitted by the sample is measured according to the position of the electron beam.⁷ This results in topographic image of the sample. Hence SEM can be used to determine the shape of the particles (cf Figs. 4, 5).

The devices usual today can resolve particles down to the size of a few nm. With special devices, a resolution of down to 1 nm can be achieved with samples with a high electrical conductivity.

With larger particles, the electron beam can be used to eject electrons out of the atoms and measure their energy distribution. This is known as the Auger electron measurement, and can determine the elements that

Figure 3:
TEM image of an approximately 15 nm Fe₃O₄ particle, prepared in such a way that the individual atom layers are visible.
(Source: Pinna⁶)



comprise the particle. A very similar way of determining composition is energy dispersed x-ray (EDX) measurement. Here, instead of measuring the ejected electrons, the emitted x-rays are measured. Since the electron beam excites not only the surface of the sample but also penetrates into the material below its surface, the detection of particles less than 3000 nm in size involves considerable uncertainty.

Particles that, while having different crystal structures, are comprised of the same elements can however not be distinguished with this method. This restriction is particularly relevant in the case of carbon-based nanoparticles such as all types of fullerenes, for example buckyballs. They cannot be distinguished chemically from the ubiquitous soot particles.

However, a further restriction is that an analysis of the composition of the particles is only possible on a random sample basis and in addition, with small particles, involves a high degree of uncertainty.

In principle, both methods, SEM and TEM, can be used to determine particle concentration in addition to structure. To this purpose, a defined quantity of the air to be measured is pumped through a special filter. The filter is then inserted into an electron microscope in the laboratory and analysed. In order to determine the concentration, sections of a defined size are selected at random and the particles in this section are counted manually. In order to minimise systematic and statistical errors, a sufficient number of different sections of the sample must be counted. The advantage of this method is that it can be used not only to determine the concentration but also to

obtain information about particle size and structure. There is currently no alternative, in particular for the determination of concentrations of fibrous particles ("high aspect ratio nano-objects", HARN). On the other hand, it is extremely time and labour intensive.⁵ The particles must be counted according to size and structure. This method involves considerable uncertainty and only provides limited information, particularly in the case of samples where a large number of different particles of different sizes, shapes and compositions have been deposited on the sample carrier.⁶ Moreover, electron microscopes are relatively expensive devices and can only be operated by well trained and experienced personnel

As already mentioned above, it would also be conceivable to investigate particles deposited on a filter using known and highly sensitive chemical analysis methods. However, it is only in the rarest cases that it can be assumed that the particles deposited on the filter are of only one specific composition. Instead, it must be assumed that the particles on the filter are of very varying chemical composition. A list of the elements contained in the material investigated only allows conclusions about the composition of the particles in very special circumstances (e.g. where the elements are rare and chemically inert such as gold). In addition, a few large particles can dominate the analytical investigation of the sample as a whole.

Glossar

Aerosol Aerosol is a generic term for all solids (particles) or liquids (droplets) present in the air.

Butanol (C₄H₁₀O) Butanol is an alcohol with four carbon atoms.

Saturated A saturated gas (or solution) is a gas (or liquid) in which the maximum quantity of a particular substance has been dissolved. If parameters such as pressure or temperature are reduced, droplets form on what are known as condensation nuclei in the gas (or solids on crystallisation nuclei in the liquid (crystallite)).

nm Nanometre = 10⁻⁹ metre

µm Micrometre = 10⁻⁶ metre

Suspension A mixture of solid elements in a liquid or a gas.

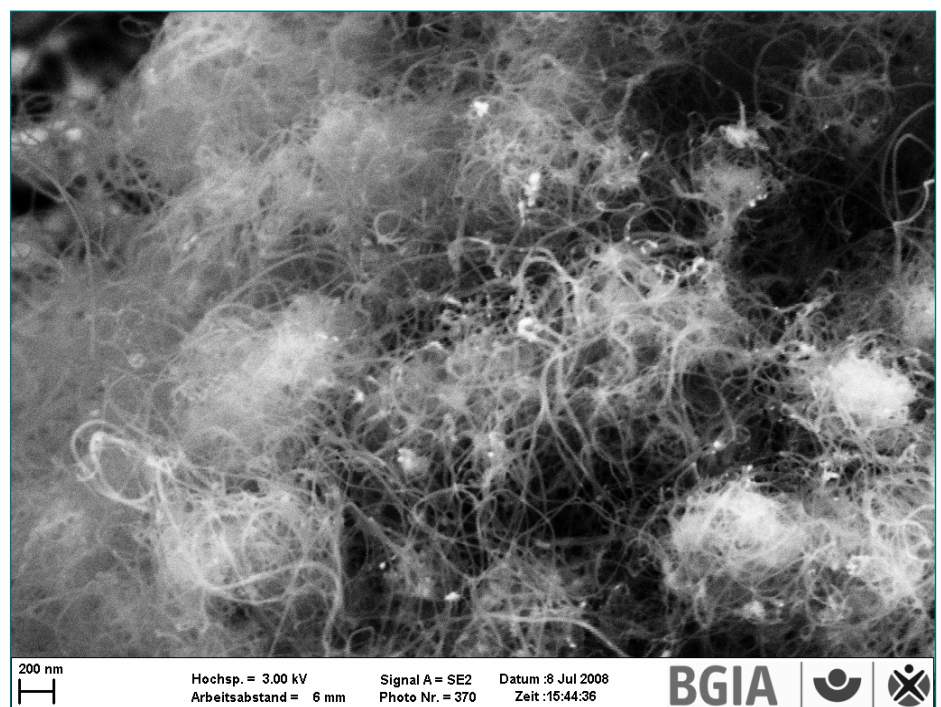
A chemical analysis may make sense if thanks to the background conditions (e.g. direct proximity to a specific production facility) the specific nanoparticles that might be involved are already suspected. However, it can be used more to exclude the possibility of the particles originating from the facility if for instance the sample shows no Ti although the facility is one that produces TiO₂ nanoparticles.

In the light of the high background level of natural and anthropogenic nanoparticles,

Figure 4: SEM image of three crystallites roughly 1000 to 3000 nm long. The characteristic shadowing of SEM images is clearly visible, creating the impression that the objects viewed have been lit from the side. The small particles and the stripes are 70 to 150 nm in size. (Source: Fiedeler⁸)



Figure 5: SEM image of carbon nanotubes (CNT). (Source: Berges¹)



there is currently essentially only one possibility of directly measuring the synthetic nanoparticles carried in the air. To this purpose, the concentration of particles is continuously measured at the place of work and compared with the activities carried out. The opening of a production facility for nanoparticles or the bottling of nano-materials can then under certain circumstances lead to an increase in particle concentration. However, one cannot be certain whether the increase is actually the cause of the activity recorded. Accordingly, there must be certainty that no other activities took place at the same time (the opening of a window or a door, a diesel vehicle passing by or another production process). Fig. 6 shows a comparison of two measurements carried out before and after the bottling of nano-materials. A leak in the bottling plant identified in this way led to a difference in concentration by a factor of 4 to 5 with 20 nm particle size.

Notes and References

- ¹ Berges, Markus (2010), Lecture at the NanoTrust Autumn Workshop on 23.9. 2010 in Vienna.
- ² For a more in-depth discussion, see Pelzer et al. in Endnote 5 and BSI, 2010, Nanotechnologies – Part 3: Guide to assessing airborne exposure in occupational settings relevant to nanomaterials, PD 6699-3:2010.
- ³ Pelzer, J et al., 2010, Geräte zur Messung der Anzahlkonzentration von Nanopartikeln – Aktueller Überblick über die Messtechnik, Gefahrstoffe – Reinhaltung der Luft, 70 (11/12), pp. 469-477, p. 471.
- ⁴ Thus it may be useful to determine the particle concentration using a purely optical particle counter (OPC) (Endnote 4, BSI, p. 13).
- ⁵ Using a fast mobility particle sizer (FMPS), the measurement of the concentration according to size can be done within a second. The particles are likewise selected by size according to the DMA principle, but because of the different structure of the detection device the particle fractions can be measured at the same time. However, these devices are large and expensive and less sensitive with respect to small nanoparticles than the SMPS described above (cf. Endnote 5, p. 472 (Pelzer) and Endnote 4, BSI, p.16).

Figure 6:
Comparison of two measurements before and after bottling nano-materials in a production facility with a leak in the bottling system. (Source: Berges¹)

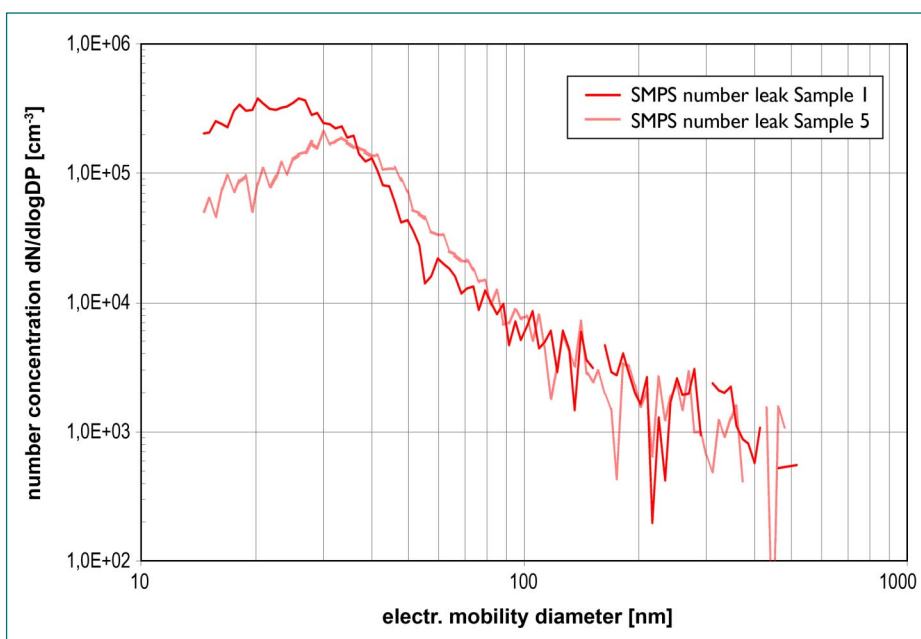
Fine dust and synthetic nanoparticles

At the latest since the Industrial Revolution, the contamination of air with combustion residues has become a serious problem. The replacement of coal stoves by oil or gas fired central heating and the development and use of filter systems have made a major contribution to a significant improvement in the air quality, particularly in towns. On the other hand, technical developments both in the field of combustion engines and in the field of measurement technology have meant that ultrafine dust concentrations have increased or become measurable. Ultrafine dust refers to dust consisting of particles with a diameter below 100 nm. In towns, the concentration of these particles is around 10,000 per cm³ (see Table 1). In contrast to these particles created in part naturally (forest fires, friction etc) and in part by human activity (man-made particles or incidental particles), synthetic nanoparticles are made systematically and have a defined composition, shape and, as a rule, a very narrow size distribution. Mostly, the concentration of these synthetic nanoparticles is far lower than the background concentration of natural and man-made nanoparticles. This fact is currently the largest problem in the determination of the concentration of synthetic nanoparticles in the ambient air.

Conclusions

At first sight, it might be assumed that determining the exposure of synthetic nanoparticles in outside air is so difficult because there are no measurement devices that can detect particles down to the nanometre size range. However, this is not the case. There are a number of particle counters that can detect nanoparticles with sufficient accuracy. The problem of determining the concentration of synthetic nanoparticles is that these devices cannot distinguish between natural and synthetic nanoparticles. This is all the more serious because the background load of natural nanoparticles and those accidentally generated by human activity (e.g. through combustion processes) is very high. Against a high background concentration, a small increase in concentration of synthetic nanoparticles is therefore hardly detectable.

Admittedly, electron microscopy also provides instruments for the detailed analysis of nanoparticles, but their time and labour-intensive operation means that these are only of limited suitability for practical application for the comprehensive monitoring of production facilities. Even if technically appropriate methods could be developed, the systematic monitoring of the concentration of synthetic nanoparticles in the air would also require a significant increase in personnel effort.



- ⁶ Pinna, N. et al., 2005, Magnetite Nanocrystals: Nonaqueous Synthesis, Characterization, and Solubility, *Chem. Mater.* 17, p. 3044.
- ⁷ The injected electrons eject electrons from the sample (secondary electrons). These are used to generate the image.
- ⁸ Fiedeler, U. 2002, Rekombination und Diffusion in CuGaSe₂ – Solarzellen, Freie Universität Berlin, Dissertation.
- ⁹ In order to show the expense, we refer to the limit value of less than 0.01 fibres/cm³ for carbon nanotubes (CNTs) proposed by the British Health and Safety Executive in 2008 (cf. UK Health and Safety Executive HSE: 'Summary on the issues raised by BSI Doc. PD 6699-2:2007 Short Summary on fibre measurement issues' (2008), www.hse.gov.uk/aboutus/meetings/iacs/acts/watch-2008-10-annex2.pdf).
- In order to monitor this requirement, a large volume of air would have to be sucked through a filter and checked with a TEM (on an area of 1.5 mm² in order to be able to identify the small CMT fibres. The enlargement required (60,000 times or more) means that this, together with the small optical field of vision for each observation, means that an exorbitant number of individual observations is needed.
- ¹⁰ Tiede, K., et al., 2008, Detection and characterization of engineered nanoparticles in food and environment, in: *Food Additives & Contaminants, Part A*, 25, (7), p. 795-821.

MASTHEAD:

Owner: Austrian Academy of Sciences; legal person under public law (BGBl 569/1921; BGBl I 130/2003); Dr. Ignaz Seipel-Platz 2, A-1010 Vienna

Editor: Institute of Technology Assessment (ITA); Strohgasse 45/5, A-1030 Vienna; www.oew.ac.at/ita

Mode of publication: The NanoTrust Dossiers are published irregularly and contain the research results of the Institute of Technology Assessment in the framework of its research project NanoTrust. The Dossiers are made available to the public exclusively via the Internet portal "epub.oew" : epub.oew.ac.at/ita/nanotrust-dossiers

NanoTrust-Dossier No. 025en, March 2012: epub.oew.ac.at/ita/nanotrust-dossiers/dossier025en.pdf

ISSN: 1998-7293



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