

The characterisation of nanoparticles

Nanoparticles are of current interest because of an emerging understanding of their possible effects on human health and environmental sustainability, and owing to the increasing output of man-made nanoparticles into the environment. Nanoparticles are used in many different applications and created by many different processes. Their measurement and characterisation pose interesting analytical challenges.

What is a nanoparticle, where do they come from, and why are they important?

Nanoparticles are entities some billionths of a metre in size. The formal definition of a nanoparticle is a “nano-object with all three external dimensions in the nanoscale”¹ (ISO/TS 27687:2008), although in practice the term is often used to refer to particles larger than 100 nm. The reason for this is that the behaviour of nanoparticles and the applicability of measurement techniques vary with size and environment, to the extent that 500 nm particles can either be considered very large or very small depending on the frame of reference!

Nanoparticles can be both natural and man-made entities, and are widely found in the environment as well as the laboratory. Their origins and properties are highly varied, making their study a rich branch of analytical science.

Box 1- Sources of Nanoparticles

Nanoparticles are produced by a wide range of natural (biogenic) and man-made (anthropogenic) processes. Although the deliberate manufacture of nanoparticles (referred to as ‘manufactured nanoparticles’) is a relatively new human activity, we have been generating them for many years (for example from internal combustion engines) and adding to the natural background. Some of the main biogenic sources of nanoparticles include mineral erosion, atmospheric chemistry processes and evaporation of sea spray. Anthropogenic sources include combustion, mining/quarrying and industrial processes including the deliberate manufacture of engineered nanoparticles.

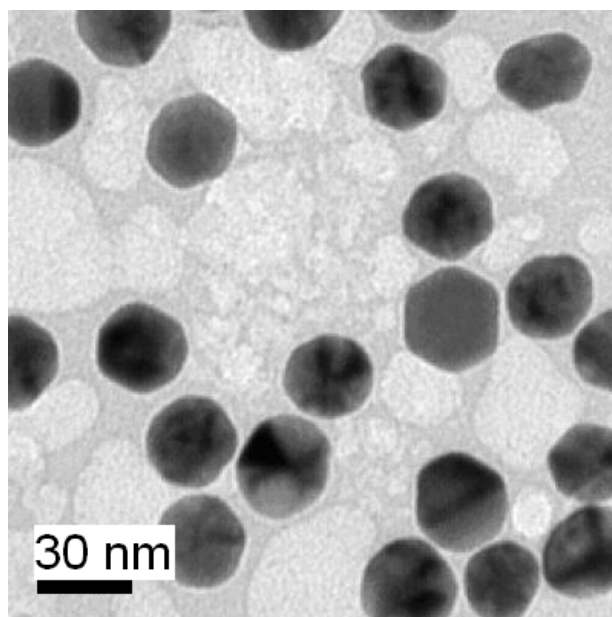


Figure 1. Transmission electron micrograph of a collection of gold nanoparticles.

The properties of nanoparticles often bridge the microscopic and macroscopic regimes, meaning that conventional theories do not necessarily allow us to predict their behaviour. It is this uncertainty that lies at the heart of concerns surrounding the health and environmental impact of nanoparticles, but also of the excitement around opportunities for their application in new areas of science and technology. Therefore, it is important to have robust analytical approaches for characterising nanoparticles, to maximise our benefit from them whilst mitigating their impact.

Material properties

Chemical properties of interest for those studying nanoparticles include total chemical composition, mixing state (internal/external), surface composition, electrochemistry and oxidation state. Physical properties of interest include number and mass concentration, size, surface area, total mass, morphology and optical properties. Because of their very high surface area to mass ratio (see Table 1), and high surface curvature, nanoparticles may be particularly chemically active.

¹ A nano-object is defined to be “material with one, two or three external dimensions in the nanoscale” and the nanoscale is defined as “size range from approximately 1 nm to 100 nm”.

Table 1. Comparison of the properties of nominally spherical nanoparticles and their likely penetration into the human respiratory system. Particle size has a dramatic effect on the physical properties of a collection of particles. Mass-based measurements are heavily weighted towards the largest particles, whereas smaller particles have a much larger surface area per unit mass.

Particle Diameter (nm)	Relative Mass per Particle	Relative Surface Area per Unit Mass	Respiratory Penetration
10 000	8 000 000	1	Nasal Passage
2 500	125 000	16	Trachea, Bronchi
1000	8 000	100	Alveoli
50	1	40 000	Bloodstream?

Nanoparticle characterisation methods are required to cover a range of requirements, from long term environmental monitoring campaigns over entire continents where only basic properties are measured, to one-off laboratory measurements on a specially prepared samples where a full chemical and physical analysis is performed.

Box 2- Uses of Nanoparticles

Nanoparticles have many uses beyond the laboratory, such as: fuel additives to moderate emissions, sunscreen and cosmetics to look after our skin, and antibacterial agents in clothing. However, man has unwittingly been using nanoparticles for centuries, for instance as pigments in stained glass and during the vulcanisation of rubber.

Characterisation techniques

Characterisation techniques can be subdivided by both general measurand and the phase in which the nanoparticles reside. Measurements of each type present their own difficulties and often have subtly different interpretations. Moreover, comparison of results between phases is very difficult, and matrix effects can be significant due to the high surface area to mass ratio of nanoparticles. The techniques presented below give a general overview of common measurements made on nanoparticles for a range of applications.

Solid Phase

Nanoparticles in the solid phase exist either as a powder or encapsulated in a solid medium. The former can take several forms including loose powders and wet or dry 'powder cakes' for convenience of handling. As such, any analysis must take into account how the particles will eventually be used because this will affect their final agglomeration state and other properties.

- *Size*: there are many methods of measuring particle size (or, more correctly, size distribution) but electron

microscopy is widely used, in conjunction with other measurements. Laser diffraction is a common technique for measuring bulk samples under ambient conditions and powder X-ray diffraction may also be used by examining peak broadening.

- *Surface Area*: the most common technique is the nitrogen adsorption technique based on the BET isotherm, and is routinely carried out in many laboratories.
- *Pour Density*: this requires the weighing of a known volume of freshly poured powder.
- *Composition*: suitable surface techniques include X-ray photoelectron spectroscopy (and other X-ray spectroscopy methods) and secondary ion mass spectrometry. Bulk techniques generally use digestion followed by conventional wet chemical analyses such as mass spectrometry, atomic emission spectroscopy and ion chromatography.
- *Crystallography*: powder X-ray or neutron diffraction may be readily used to determine the crystal structure of simple lattice structures. It can also be applied to crystalline organic solids, but the data analysis is much more challenging.
- *'Dustiness'*: this is the propensity of a powder to become aerosolised by mechanical agitation. The dustiness of a particular sample is very dependent on its moisture content and static electrical properties.
- *Morphology*: particle shape and aspect ratio are most readily determined by image analysis of electron micrographs.

Liquid Phase

Nanoparticles suspended in the liquid phase are often mixed with surfactants to moderate their agglomeration state. Furthermore, a range of chemical or even biological species may be present and affect the results obtained, especially in samples taken from the environment. Therefore, care must be taken to prepare the sample to prevent unwanted matrix effects or changes to the sample.

- *Size*: dynamic light scattering (photon correlation spectroscopy) and centrifugation are commonly used techniques. Other methods include image-tracking instruments.
- *Surface area*: simple titrations may be used to estimate surface area but are very labour intensive. NMR experiments may also be used and dedicated instrumentation has recently been developed.
- *Zeta potential*: this gives information relating to the stability of dispersions. It cannot be measured directly but is often measured indirectly using an electrophoretic method.
- *Composition*: chemical digestion of the particles allows a range of mass spectroscopy and chromatography methods to be used. Interference from the matrix needs to be carefully managed.
- *Morphology*: it is difficult to measure morphology of particles moving freely in a fluid. Deposition onto a surface for electron microscopy is most commonly used (see Figure 1).

Gas Phase (Aerosols)

Nanoparticles in the gas phase may be monitored using a range of commercially available and relatively low cost equipment. Generally, these instruments are quite robust and can be used for prolonged periods with little attention. They are also generally resistant to matrix effects. However, relative humidity and volatile organic species can sometimes affect measurements. Unlike the condensed phases, aerosols cannot be stored for later analysis and so reproducible sampling is very important. A range of inlets has been designed for different applications to reduce inconsistencies in this respect.

- ‘*Concentration*’: usually expressed as a number concentration or mass concentration. The latter will strongly weight the distribution curve in favour of larger particles - a single 10 µm diameter particle weighs the same as 1 million 100 nm particles!
- *Size*: there are many methods for measuring particle size but comparability between them is a problem. They include optical and aerodynamic methods, but these give no information about variations in morphology.
- *Surface area*: There are few routine surface area techniques available. The most common involves charging the aerosol using a corona discharge and measuring the charge concentration. Such methods are usually calibrated against size distribution measurements.
- *Charge*: collisions of air ions with particles result in a steady state charge distribution. This distribution is Boltzmann-like, with small particles being much less likely to carry any charge than larger particles. This distribution is usually measured in the laboratory and subsequently utilised by other measurement techniques.
- *Morphology*: there are few instruments available for measuring morphology. The most common technique is to capture particles either electrostatically or by filtration for subsequent imaging using electron microscopy.
- *Composition*: measuring aerosol composition is very challenging owing to the small amounts of matter present. Most speciation methods require the particles to be collected and then subjected to spectrometric or wet chemical techniques.

Assessing Toxicology

Assessing the toxicology of a particular sample is challenging. Not only do the nanoparticles need to be suitably characterised using the techniques above, but their biological effect must be evaluated. To do this, all the relevant routes of exposure need to be explored and assessed. These are inhalation, ingestion and dermal exposure, and it cannot be assumed that two different types of particle behave identically. For example, airborne microparticles, which are still too small to see with the naked eye, behave very differently to nanoparticles. The larger particles do not penetrate as far into the lungs as the smaller ones (see Table 1), meaning that their biological effects are likely to be different.

Current research and standardisation activities

Research into and involving nanoparticles is vast and expanding rapidly. A simple literature search for ‘nanoparticle’ shows that the number of papers published in this area has increased from just a few per year in the late 1980s to many thousands in 2009. With such a breadth of research and wealth of measurement techniques, standardisation is becoming an important aspect of research in this area. International standardisation working groups ISO TC229 and CEN TC352 are currently busy delivering much of this activity internationally, and several documents relating to definitions, nomenclature and standard methods have already been produced. This work is shadowed in the UK by BSI committee NTI/1□

Further Reading

- W C Hinds. *Aerosol Technology: Properties, Behaviour & Measurements*. 2nd Edition, Wiley-Blackwell, 1999.
- R Hester and R M Harrison. *Nanotechnology: Consequences for Human Health and the Environment*. RSC Publishing, 2007.
- H-G Rubahn. *Basics of Nanotechnology*. 3rd Edition, Wiley VCH, 2008.

This Technical Brief was prepared for the Analytical Methods Committee by Richard J J Gilham and Richard J C Brown of the National Physical Laboratory.

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