BSI PD 6699-2:2007 - Nanotechnologies – Part 2: Guide to safe handling and disposal of manufactured nanomaterials

Comments on suggested benchmark exposure levels

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Introduction

In December 2007, BSI published PD 6699-2 – Nanotechnologies – Part 2: Guide to safe handling and disposal of manufactured nanomaterials (referred to herein as **BSI PD** 6699-2:2007). As part of the suggestions and recommendations made to working as safely as possible with new and emerging nanomaterials, the guide introduced a series of suggested exposure levels for different classes of nanomaterial, referred to as "benchmark exposure levels" (section 8.3). Quoting from the guide:

"These are intended to provide reasonably cautious levels and are based in each case on the assumption that the hazard potential of the nanoparticle form is greater than the large particle form. This assumption will not be valid in all cases. Although these benchmark levels relate to current exposure limits, they have not been rigorously developed. Rather, they are intended as pragmatic guidance levels only and should not be assumed to be safe workplace exposure limits."

The levels are suggested for four categories of nanomaterial (section 7.1). These categories are considered within the guide as broadly covering the types of airborne nanomaterials of particular concern that might be encountered in workplaces. They are:

Fibrous nanomaterials, defined as high aspect ratio insoluble nanomaterials;

CMAR nanomaterials, defined as any nanomaterial which is already classified in its larger particle form as carcinogenic, mutagenic, asthmagenic or a reproductive toxin (hence "CMAR");

Insoluble nanomaterials, defined as insoluble or poorly soluble nanomaterials not in the previous two categories; and

Soluble nanomaterials, being soluble nanomaterials not in the fibrous or CMAR categories.

As I have noted previously,¹ these categories appear to be a useful simplification of nanomaterials of concern in the workplace, if the intent is to develop pragmatic and

¹ "Safe nanotechnology in the workplace: A practical guide" <u>http://community.safenano.org/blogs/andrew_maynard/archive/2008/01/18/safe-nanotechnology-in-the-workplace-a-practical-guide.aspx</u>. Accessed 27 March 2008.

simple guidelines to avoid harm.

In essence, the benchmark exposure levels were introduced as guidelines that might be used or be useful when working with the four categories of nanomaterials, *in the absence of any better information*.

Since publication of BSI PD 6699-2:2007, these benchmark exposure levels have come under some scrutiny. Here, I would like to discuss briefly my own perspective on the relevance and usefulness of the levels as a scientist and analyst closely involved in the development of safe nanotechnologies. In considering the levels, I address four questions:

- Is there an immediate need for nanomaterial-specific occupational exposure limits?
- Should governments be establishing legal exposure limits for nanomaterials?
- Are the Benchmark Exposure Levels presented in BSI PD 6699-2:2007 reasonable?
- Are the Benchmark Exposure Levels in BSI PD 6699-2:2007 measurable?

These comments are provided in the interest of aiding and informing a science-based discussion around the proposed benchmark exposure levels. They represent my personal and professional perspective, and do not necessarily reflect the views and opinions of the Project on Emerging Nanotechnologies.

1. Is there an immediate need for nanomaterial-specific occupational exposure limits?

Here I believe we have to consider three questions:

- Are people currently working with nanomaterials?
- Can we rely on existing exposure limits while working with these materials?
- Can businesses, occupational health professionals and others make effective decisions on workplace safety in the absence of nano-specific exposure limits?

To address the first question; engineered nanomaterials are already in commerce, and thus by implication in the workplace. The Project on Emerging Nanotechnologies maintains an inventory of manufacturer-identified nanotechnology enabled consumer products, which currently contains over six hundred entries.² The total number of nanotechnology-based products and materials on the market is likely to be substantially higher than this, as not all nano-manufacturers identify their products as nanotechnology-based. There are also commercial nanotechnology materials and products in commerce that are not considered consumer products, and are not listed in the inventory.

² An inventory of nanotechnology-based consumer products currently on the market. <u>http://www.nanotechproject.org/inventories/consumer/</u> Accessed 24 March 2008.

Clear figures on the quantity of nanomaterials in production and use are not readily available, although a number of indicators have been published. In 2004, the Royal Society and Royal Academy of Engineering predicted production rates for many simple nanomaterials as being in the hundreds to thousands of metric tons per year by 2005 - 2010.³ Taking one specific class of nanomaterials, the chemicals company Bayer have a stated vision for producing 3000 metric tons of carbon nanotubes per year by 2012. And this is just one company in a global market for carbon nanotubes that is forecast to exceed one billion dollars in 2014.⁴

These figures only hint at the quantities of nanomaterials that people are and will be handling, and will potentially be exposed to. But the bottom line is that simple nanomaterials—including metal and metal oxide nanoparticles and carbon nanotubes— are in production and use now, and occupational exposures will be occurring.

Where nanomaterials are being used, workers, occupational health professionals and business managers need to be able to make decisions on how to work with them as safely as possible. The health of employees and avoidance of potentially harmful environmental releases depends on following the best possible practices. But good workplace health and safety decision-making is also central to good stewardship, managing liability and maintaining customer, stakeholder and shareholder trust. In short, good occupational health practices make for good business.

Yet good occupational health practices cannot be made in the absence of benchmarks, against which actions can be evaluated. A decision to control exposures without guidance on how low is low enough makes little sense from a health perspective, and no sense from a business perspective. It is hard to justify actions—especially costly ones— if there is no way of evaluating whether they are useful or not. As a result, irrespective of whether exposure limits for engineered nanomaterials are developed from robust scientific data or rules of thumb, they are essential to effective occupational health strategies.

If no nanomaterial-specific limit exists for a given material, health and safety managers have three broad choices open to them:

- Assume existing limits for similar non-nanoscale materials apply;
- Adopt a zero exposure policy; or
- Make an informed estimate of an appropriate exposure limit, and modify it as new information becomes available.

³ RS/RAE (2004). Nanoscience and nanotechnologies: Opportunities and uncertainties, The Royal Society and The Royal Academy of Engineering, London, UK, 113 pp.

⁴ Carbon Nanotubes By The Metric Ton. Ann M. Thayer. Chemical & Engineering News, 85(46), November 12, 2007

The first option is clearly far from ideal, as data from fifteen years plus of research have shown that some nanoscale materials present a greater hazard than their larger scale counterparts.⁵ For example, the National Institute for Occupational Safety and Health (NIOSH) have assessed the comparative hazard of nanoscale and non-nanoscale TiO₂, and concluded that the exposure limit for nano-TiO₂ should be reduced by a factor of 0.066—based on evidence of scale-specific behaviour.⁶ And a number of studies have demonstrated unusual and potentially harmful biological behaviour associated with carbon nanotubes,⁷ that differs significantly from other allotropes of carbon.

The second option is also problematic, for two reasons. First, it makes no business sense to go to extraordinary costs to contain materials where total containment is not necessary, and indeed going to such lengths would be prohibitive to many nanomaterial industries. But perhaps more importantly, exposures can only be reduced to the limit of detection of the best available measurement techniques, and so true "zero exposure" is never achievable. If the exposure metric selected is particularly sensitive, even getting to exposure levels below the limit of detection may be impossible to achieve. For example, using particle number as a measure of exposure, "zero exposure" nanomaterial facilities would need to operate under conditions significantly more stringent than an ISO Class 1 cleanroom.⁸

This leaves option three. Using informed estimates as the basis for exposure limits is not ideal, as it relies on setting limits that are based on educated guesswork rather than strong scientific data. But it is the most pragmatic approach available, and provides industries with the benchmarks they need to develop effective health and safety strategies. And if it is accepted that these interim exposure limits are continually revised in the light of new understanding, adaptability is built into the process that will ensure worker health is protected to the best extent possible *in the absence of more formal exposure limits*.

⁵ For example, see Oberdörster, G., Stone, V. and Donaldson, K. (2007). Toxicology of nanoparticles: A historical perspective. *Nanotoxicology* 1:2 - 25.

⁶ NIOSH (2005). NIOSH CURRENT INTELLIGENCE BULLETIN: Evaluation of Health Hazard and Recommendations for Occupational Exposure to Titanium Dioxide. Draft, National Institute for Occupational Safety and Health, Washington DC.

⁷ For example, see: Lam, C. W., James, J. T., McCluskey, R., Arepalli, S. and Hunter, R. L. (2006). A review of carbon nanotube toxicity and assessment of potential occupational and environmental health risk. *Critical Reviews in Toxicology* 36:189-217, Warheit, D. B., Laurence, B. R., Reed, K. L., Roach, D. H., Reynolds, G. A. M. and Webb, T. R. (2004). Comparative Pulmonary Toxicity Assessment of Single-wall Carbon Nanotubes in Rats. *Toxicol. Sci.* 77:117-125, Shvedova, A. A., Kisin, E. R., Mercer, R., Murray, A. R., Johnson, V. J., Potapovich, A. I., Tyurina, Y. Y., Gorelik, O., Arepalli, S., Schwegler-Berry, D., Hubbs, A. F., Antonini, J., Evans, D. E., Ku, B. K., Ramsey, D., Maynard, A., Kagan, V. E., Castranova, V. and Baron, P. (2005). Unusual inflammatory and fibrogenic pulmonary responses to single-walled carbon nanotubes in mice. *Am. J. Physiol.-Lung Cell. Mol. Physiol.* 289:698-708.

⁸ Perhaps the hardest task in achieving "zero exposure" is maintaining background levels of particles to below those associated with process-related releases. Failure to do this would prevent possibly harmful nanomaterials from a specific process or material being distinguished from presumably less-harmful ambient airborne particles.

2. Should governments be establishing legal exposure limits for nanomaterials?

While I make the argument that industry needs some form of nanomaterial exposure limits, even if they are based on informed estimates, exposure limits set by governments (and other authoritative bodies) are typically based on robust dose-response data. As these data do not currently exist for many nanomaterials, governments are not in general in a position to develop exposure limits for nanomaterials under the established systems for setting such limits. This in itself points to an urgent need for research to inform limit-setting. And indeed, given the warning signs of nearly 20 years' research, it is surprising that more action has not been taken to date.⁹

Unless government agencies are prepared to issue guidance exposure limits for nanoscale materials, the onus for developing interim exposure limits—what BSI PD 6699-2:2007 refers to as benchmark exposure levels—must lie with industry and non-government organizations. In this case, industry will need the best possible guidance to inform the development and use of such benchmark levels. This is a role that BSI and other organizations are attempting to fill.

3. Are the Benchmark Exposure Levels in PD 6699-2:2007 reasonable?

Fibrous nanomaterials.

BSI PD 6699-2:2007 states that:

"The most rigorous limit currently in place for fibres in air is 0.01 fibres/ml, used in the UK as the clearance limit in asbestos removal activities. A fibre is defined as a particle with aspect ratio greater than 3:1 and length greater than 5 000 nm. The counting method used is phase contrast optical microscopy. The proposed benchmark for fibrous nanomaterials is 0.01 fibres/ml, as assessed by scanning or transmission electron microscopy."

In the absence of any other information, it seems reasonable to assume that insoluble

⁹ For instance, research published in 1990 demonstrated the increased pulmonary toxicity of nanometerscale particles (Ferin, J., Oberdörster, G., Penney, D. P., Soderholm, S. C., Gelein, R. and Piper, H. C. (1990). Increased Pulmonary Toxicity of Ultrafine Particles .1. Particle Clearance, Translocation, Morphology. J. Aerosol. Sci. 21:381-384.). Epidemiology on ambient aerosol exposure in the 1990's suggested smaller particles are more potent than larger ones (Dockery, D. W., Pope, C. A., Xu, X., Spengler, J. D., Ware, J. H., Fay, M. E., Ferris, B. G. and Speizer, F. E. (1993). An association between air pollution and mortality in six U.S. cities. N. Engl. J. Med 329:1753-1759.) The discovery of carbon nanotubes prompted cautions on their asbestos-like behavior (Coles, G. V. (1992). Occupational risks. Nature 359:99.) In the context of recommendations for action in the UK, a report prepared for the Health and Safety Executive in 1999 raised concerns over the health impacts of nanomaterials (Kenny, L. C., Maynard, A. D., Brown, R. C., Crook, B., Curran, A. and swan, D. J. (1999). A scoping study into ultrafine aerosol research and HSL's ability to respond to current and future reasearch needs, health and Safety Laboratory, UK.)

fibrous nanomaterials will have the potential to exhibit asbestos-like behaviour, and should therefore be controlled to similar levels.¹⁰ Asbestos fibres are almost universally recognized as causing harm due to their ability to penetrate to the deep lung, their persistence and their length. There are other factors involved—the presence of metals in the fibres, and their ability to migrate to the mesothelium—but with no additional information, thin insoluble nanofibres that are longer than around 5 micrometers should probably be treated in a similar way to asbestos. And this leads to a working exposure limit of 0.01 fibres/ml in the UK.

Of course, with more information, this limit can be adjusted, and possibly relaxed. The degree of adjustment will depend on the type and nature of the fibrous nanomaterial—whether it is comprised of are single walled or multi-walled carbon nanotubes for instance; whether the nanotubes are straight and stiff, or tangled and flexible; whether they are heavily aggregated, or discrete fibres; whether they contain significant quantities of metals like iron; and so on. Data exist on some of these variations that would enable different "benchmark" exposure levels to be set. But the seriousness of asbestos-related diseases would suggest that, in the absence of such data, the most stringent exposure limits are applied to this class of material.

CMAR Nanomaterials.

BSI PD 6699-2:2007 states that:

"The potentially increased solubility of CMAR materials in nanoparticle form could lead to increased bioavailability. To provide a margin of safety, a benchmark level of $0.1 \times$ material WEL is suggested. Typically, this would be expressed as a mass concentration."

First, it should be acknowledged that legal exposure limits for CMAR materials provide an upper ceiling, and exposures to such agents in the workplace should be kept as low as is reasonably practicable *below this ceiling*. That said it is likely, based on current data, that some nanoscale forms of such materials will require a lower ceiling, as they may be more capable of entering the body, penetrating to organs, and releasing material in a bioavailable form, than their non-nanoscale counterparts. Thus in the absence of any additional information, it would seem prudent to set benchmark exposure levels for nanoscale CMAR materials at some factor below those for equivalent non-nano materials.

Choice of a suitable factor is somewhat subjective without relevant experimental or

¹⁰ Since this document was originally written, the potential for *some* forms of carbon nanotubes to show asbestos-like behavior has been demonstrated by Poland et al. (Carbon nanotubes introduced into the abdominal cavity of mice show asbestos-like pathogenicity in a pilot study. Nature Nanotechnology 3:423-428. 2008). See also <u>http://2020science.org/2008/05/21/8521-carbon-nanotubes-the-new-asbestos-not-if-we-act-fast/</u>, accessed 11/28/08.

comparative data. Pragmatically though, a factor as low as 2 is likely to be insufficiently stringent in some cases, while reducing ceiling limits by something like a factor of 200 would be too stringent in others. While the factor of 10 used in BSI PD 6699-2:2007 might seem rather arbitrary, it actually represents a good compromise between being over-cautious, and not cautious enough.

Once again though, this rule of thumb evaluation should be just a starting point, and benchmark exposure levels should draw on other relevant information where available.

Insoluble Nanomaterials.

BSI PD 6699-2:2007 states that:

"For insoluble nanoparticles, work recently published by NIOSH [13] recommends exposure limits of 1.5 mg/m^3 for fine TiO₂ (particles greater than 0.1 µm in diameter) and 0.1 mg/m³ for ultrafine particles as time-weighted averages. In the absence of other published approaches, this seems to be a reasonable basis to judge other nanomaterials. On this basis, a benchmark level of $0.066 \times \text{WEL}$ is suggested. Typically, this would be expressed as a mass concentration. An alternative would be to develop a benchmark based on particle number concentration. In the UK, current urban pollution is in the range 20 000 to 50 000 particles/ml. It is suggested that the lower end of this range 20 000 particles/ml discriminated from the ambient environmental particle concentration is an appropriate benchmark."

When developing benchmark exposure levels for such insoluble nanomaterials, two factors need to be addressed: which metric should exposures be evaluated against, and how should exposure levels for non-nanoscale materials be scaled to nanoscale counterparts?

On the issue of exposure metric, it is likely that different nanomaterials will require different metrics, if potential health impacts are to be predicted and avoided as effectively as possible. In some cases, this will mean that aerosol surface area is the most relevant metric, while in others particle number concentration might give a better indication of risk. And in some cases, aerosol mass concentration will be sufficient. For this reason, my co-authors and I recommended the development of exposure monitors that measure aerosol mass, surface area and number concentration simultaneously, in the 2006 Nature commentary "Safe Handling of Nanotechnology".¹¹ Yet in the absence of such a device, simple and relevant guidelines are needed on what to measure.

Particle number concentration measurements are very sensitive to airborne nanoscale

¹¹ Maynard, A. D., Aitken, R. J., Butz, T., Colvin, V., Donaldson, K., Oberdörster, G., Philbert, M. A., Ryan, J., Seaton, A., Stone, V., Tinkle, S. S., Tran, L., Walker, N. J. and Warheit, D. B. (2006). Safe handling of nanotechnology. *Nature* 444:267-269.

particles, and could be effective in controlling against excessive exposure. Yet I would hesitate to establish benchmark exposure levels based on particle number. Number concentration measurements contain no information on particle size, shape, mass and surface area. But studies to date suggest that these may all be important parameters in determining material toxicity, suggesting that number concentration measurements alone would be extremely limited in their usefulness. Number concentration measurements are also biased towards extremely small particles, which may or may not be relevant to the potential health impact of an aerosol. For instance, when sampling a broad distribution aerosol with a mass median diameter of 10 nm, if two particle counters are used—one capable of counting particles down to 10 nm in diameter, the other extending down to 3 nm diameter particles—measured concentrations from the two instruments could vary by over a factor of 30. And as if this wasn't sufficient, in all but the cleanest workplaces, number concentration measurements tend to be swamped by background aerosols. For these reasons, I would recommend nanoparticle number concentration measurements for identifying sources of exposure, but not as a general tool for evaluating exposures.

If a single exposure metric is needed, aerosol surface area is attractive—it is sensitive to smaller particles, and contains information that would appear to correlate with biologically relevant parameters of some nanomaterials. Yet despite the emergence of new monitors in recent years, the means to routinely measure exposure against surface area are not yet widely available.

As a fallback, mass exposure measurements offer a reasonable compromise in many cases. For an aerosol that is consistent from day to day, it should be possible to derive mass-based benchmark exposure levels that underpin effective health and safety strategies, as long as an appropriate scaling factor can be derived between nanoscale and non-nanoscale counterparts of the material. And the means to measure aerosol mass concentration are readily available.

As an example, the NIOSH draft exposure limit for nanoscale TiO_2 cited in BSI PD 6699-2:2007 follows an extensive analysis of available data, and represents a well-reasoned and scientifically sound decision. It demonstrates how a mass-based limit can be derived for a nanomaterial, even though other exposure parameters are probably more closely associated with biological impacts. Yet sound as this assessment is, it is hard to justify extending it to other nanomaterials without careful consideration.

As a very crude rule of thumb, and in the absence of any additional information, a reasonable starting point for setting mass-based nanomaterial benchmark exposure levels is to assume that pulmonary toxicity of an insoluble material scales with specific surface area—the greater the surface area for a given mass of material, the greater the potential to cause harm. Specific surface area varies as the inverse of particle diameter, and so a reduction in diameter by a factor of ten leads to an increase in surface area for a given mass of material by a factor of ten.

With this in mind, if the particle size of a conventional form of a material is known, and the particle size of a new nanoscale form of the material is also known, a reasonable first

stab at a benchmark exposure level would be the ratio of the small to large particle diameter. For instance, if the established exposure limit for zinc oxide (for sake of argument) is based on particles approximately 1 μ m in diameter, and a new nanoscale form of the material is developed where the particles are 100 nm in diameter, the benchmark exposure level for nanoscale ZnO (in the absence of other information) would be 0.5 mg/m³—based on the NIOSH REL for ZnO

This rule of thumb would seem more reasonable than the factor of 0.066 suggested in BSI PD 6699-2:2007. However, it does rely on knowledge of two particle sizes. In the absence of such knowledge, a factor of 0.1 would seem neater than 0.066, but not necessarily more legitimate.

Interestingly, pursuing the example of ZnO, NIOSH also has a REL for ZnO fume, which is most likely a nanoscale material. This would seem a reasonable benchmark exposure level for the nanoscale version of zinc oxide, rather than scaling between nano and non-nano particle sizes, unless there is a good reason why the fume REL does not apply to nano ZnO. In this case, the fume REL is the same as for conventional ZnO particles—5 mg/m³.

Soluble nanomaterials.

BSI PD 6699-2:2007 states that:

"For materials which are highly soluble in any case, nanoparticle forms are unlikely to lead to greater bioavailability. Nor are the types of effects associated with insoluble particles likely to occur. Therefore, for these materials, a benchmark of $0.5 \times WEL$ is suggested."

The toxicity of soluble nanomaterials is unlikely to be associated with their size or structure, unless the timescale over which they act is significantly less than their rate of dissolution. And so existing exposure limits for such materials would seem a reasonable starting point for benchmark exposure levels. However, it is possible that the size, and possibly shape and surface chemistry, of soluble nanoparticles will lead to increased dose rates, or material doses to parts of the body not usually exposed to such materials. And so there is some justification to taking a cautious approach to working with soluble nanoscale materials.

Where there is a possibility of new translocation routes and significantly enhanced dose rates, a reduction in current exposure limits would seem prudent. In the absence of any additional information, the factor of 0.5 suggested in BSI PD 6699-2:2007 seems reasonable—any smaller would be over-cautious, and any larger, and the factor would seem irrelevant.

4. Are the Benchmark Exposure Levels in PD 6699-2:2007 measurable?

Fibrous nanomaterials.

Except for fibrous nanomaterials close to 100 nm in diameter, phase contrast optical microscopy techniques routinely used for assessing fibrous aerosol exposure will not be applicable to determining exposure to such materials. Instead, electron microscopy techniques will be required—both Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) have the necessary resolution to identify and count nanoscale fibres.

Methods exist to use SEM and TEM for assessing airborne fibre levels—including asbestos fibres. For instance, NIOSH Manual of Analytical Methods Method #7402 describes the assessment of asbestos using TEM,¹² and asbestos exposure assessment methods used routinely in France depend on electron microscopy. An extensive literature on the use of electron microscopy and asbestos exposure assessment exists, suggesting a significant level of knowledge and experience exists in this area.¹³

However, asbestos fibre counting has never been a precise science, and many fibrous nanomaterials will be even less straight forward to evaluate than asbestos fibres. Taking carbon nanotubes as an example, while these may be as thin as a nanometre and as long as tens to hundreds of micrometers in some configurations, they frequently form into complex aggregates. Where the nanotubes are not straight, these aggregates may vary from very open to very compact forms that resemble tangles of wool when observed in the electron microscope.¹⁴ Assessing such aggregates as fibres will be complex—and probably impossible in some cases. Yet where well-separated and long fibres are released from a nanomaterial, TEM and SEM-based techniques should be adequate to estimate exposure against the suggested benchmark exposure level. And it could be argued that complex aggregates may be better evaluated against an alternative benchmark—either counting the number of aggregates, or using a mass-based level.

Sampling fibrous nanomaterials for electron microscopy analysis will present some different challenges from sampling asbestos fibres, but variations of current techniques should be able to be used. For SEM analysis, direct collection to track-etched polycarbonate filters should suffice, and indeed I have successfully used this method in the past to examine carbon nanotube aerosols. For TEM analysis, I have used collection directly onto carbon film support grids to qualitatively examine carbon nanotube

¹² NIOSH (1994). Method 7402: Asbestos by TEM, in *NIOSH Manual of Analytical Methods*, P. E. Eller, ed., NIOSH, Cincinnati.

¹³ 229 papers are returned on a Web of Knowledge search on "asbestos" + "exposure" + "electron microscopy". Search date: 27 March 2008. [Added 11/28/08: Also see Baron, P. A. (2001). Measurement of airborne fibers: A review. Ind. Health 39.]

¹⁴ Maynard, A. D., Ku, B. K., Emery, M., Stolzenburg, M. and McMurry, P. H. (2007). Measuring particle size-dependent physicochemical structure in airborne single walled carbon nanotube agglomerates. *J. Nanopart. Res.* 9:85-92.

aggregates. Despite fears that such grids may contain carbon nanotubes that will interfere with quantitative exposure assessment, I have never observed this to be a significant problem. In each case, the ability exists to collect fibrous nanomaterials for analysis using electron microscopy—all that is lacking is the knowledge of how to use these techniques analytically.

Ultimately, the ability to measure exposure to fibrous nanomaterials against the suggested benchmark exposure limit will need to be evaluated on a case-by-case basis. But technology and expertise exists to devise methods to measure such exposures effectively in the cases where harm due to particle aspect ratio is most likely.

CMAR Nanomaterials.

Filter-based aerosol collection techniques used for larger scale particles should be useable for nanoscale particles, as filter collection efficiency typically increases below approximately 300 nm. Respirable and inhalable samplers will most likely provide an acceptable approach to sampling such materials, unless there is a specific rationale for separating sub-100 nanometre airborne particles from super-100 nanometre particles. In these cases, samplers do not yet exist, but the technology is there to develop them. However, in many cases, exposure will be a mix of individual nanoparticles and aggregates that are larger than 100 nm, and in this situation, respirable sampling will be essential to capture all particles of interest.

An ability to measure airborne concentrations of a CMAR nanomaterial at a benchmark exposure level that is 10% of established limits will depend entirely on the material, and on the accepted analytical techniques applied to its detection and analysis. Chemical speciation-based techniques like Inductively-Coupled Plasma Atomic Adsorption Spectroscopy and Inductively-Coupled Plasma Mass Spectrometry typically have extremely low detection limits, and in many cases are likely to provide the analytical capabilities to measure exposures to very low levels.

Insoluble Nanomaterials.

As with CMAR nanomaterials, applicable technologies exist to sample insoluble nanomaterials onto filters for subsequent analysis. Where personal aerosol samplers are used, gravimetric analysis will be pushed to its limits in many cases with the benchmark exposure levels recommended in BSI PD 6699-2:2007. In contrast, high volume area samplers should provide sufficiently large samples for weighing the material collected, and calculating mass concentration.

Where benchmark exposure levels are below the detection limit of gravimetric analysis techniques, chemical speciation should allow exposures to be quantified in most cases for this class of materials.

A number of instruments are available that enable the mass concentration of nanoscale aerosols to be measured or estimated in near real-time; many of these are described in the International Standards Organization Technical Report ISO/TR 27628.¹⁵ These are often expensive and complex to use, but they do provide a means for measuring concentrations against reduced mass-based exposure levels, and often provide insight into alternative exposure metrics, including number and surface area. Real-time aerosol monitors routinely used in the workplace for non-nanoscale particles typically rely on light scattering, and are insensitive to particles smaller than 100 - 500 nm in diameter. However, where exposure to nanoparticle agglomerates predominantly occurs, such instruments may be useful in measuring exposure against benchmark exposure levels.

Soluble nanomaterials.

Most of the approaches for measuring exposure to insoluble nanomaterials discussed above will also be applicable to soluble nanomaterials. If semi-volatile materials are being sampled, a combination of particulate and vapour samplers may be needed. But the sampling requirements here will not differ substantially for those employed to measure exposure to non-nanoscale soluble materials.

Closing thoughts

If effective health and safety plans are to be implemented in research laboratories and workplaces generating and using nanomaterials, guideline exposure limits are essential. In the absence of further information, the benchmark exposure levels presented in BSI PD 6699-2:2007 appear reasonable. Furthermore, the context surrounding the levels— which is clearly stated in the document—allows people following the recommendations to adapt the levels to their specific circumstances, depending on the best available information. In other words, they are not binding, but rather present a clear starting point for an informed process of setting relevant exposure levels. And thus, where evidence exists to suggest that the benchmark exposure levels are overly stringent or not measurable for a given material, it is left to the discretion of the person setting the levels to adjust the accordingly.

These suggested levels are not a substitute for workplace exposure limits, and do not remove the need for targeted research leading to the development of evidence-based limits. But until such levels are developed, they fulfil a role that is essential to underpinning the development of safe and successful nanotechnologies. As such, BSI should be applauded for publishing them.

¹⁵ ISO (2006). Workplace atmospheres - Ultrafine, nanoparticle and nano-structured aerosols - Inhalation exposure characterization and assessment, International Standards Organization, Geneva.