Annex 2: Short Summary on the fibre measurement issues raised by BSI Published Document PD 6699-2:2007 Guide to safe handling and disposal of manufactured nanomaterials

Introduction

PD 6699-2:2007 suggested a use the asbestos-derived exposure limits as the basis for carbon nanotubes (CNTs) and choose a proposed benchmark exposure limit of 0.01 fibres/ml based on the lowest asbestos limit in use. This annex outlines the implications for monitoring airborne concentrations of nanotubes and nanofibres at the suggested benchmark exposure limit.

Physical size and shape of nanotubes and nanofibres

Nanotubes and nanofibres come in various diameters and lengths with single walled carbon nanotubes (SWCNT) being the thinnest and having the least mass, with diameter down to 1 nm. They may however be relatively long up to a few millimeters (mm). Multi-wall carbon nanotubes (MWCNTs) tend to be have larger diameters up to 100 nm. Nanowires have a range of diameters but have been produced down to ~30 nm diameter but may be manufactured to very long continuous lengths.

CNTs have a high tendency to agglomerate in tangles of fibres and are difficult to disperse into individual fibres unless the lengths are considerably shortened to a few micrometres. These large tangles and balls of fibres are typical of bulk materials and can form larger agglomerates of all sizes up to a few mms but not necessarily with aspect ratios which would make them identifiable as fibres.

Current UK asbestos limits

In the UK asbestos concentration should be kept below a 4- hour control limit of 0.1 f/ml and a peak level measured over 10 minutes of 0.6 f/ml (HSE L143, 2006). EU and US have 8-hour exposure limits of 0.1 f/ml. A clearance indicator of 0.01 f/ml in air is used in the UK for assessing whether it is safe to take down an enclosure after the asbestos removal has been completed and the area thoroughly cleaned. The above values are based on counts of >5 µm long fibres with aspect ratios of >3:1 visible under x500 magnification phase contrast microscopy (PCM). In practice, the refractive index difference between the filter mount and the asbestos fibre and phase contrast illumination, allows fibres down to ~200 nm (0.2 µm) in width to be seen and counted.

PCM counting

Individual nanotubes are at least one – two orders of magnitude thinner than PCM countable asbestos fibres but can group together to form larger agglomerates (as found with asbestos). However, the relationship with the current index of exposure for asbestos cannot be applied particularly as large tangles of fibres will not be recognisable as “fibre” bundles so much higher magnifications using electron microscopy need to be used capable of resolving individual fibres.

Electron microscopy

There are a number of EM methods that can be used: the two main types are scanning electron microscopy (SEM) and Transmission electron microscopy (TEM). SEM forms an electronic image from secondary electrons and/or backscattered electrons produced by the incident beam reacting with the surface of the object. The TEM uses the incident electron beam passing through the thin sample to form an image on a phosphor screen. There is a considerable range of performances in each type, depending mainly on the type and intensity of the electron sources and many other features but under best conditions SEMs can resolve particles in the 1-10 nm range and the TEM can resolve to an order of magnitude lower (1- 0.1 nm). However, best conditions are rarely present especially with carbon materials which have low atomic number and produce much fewer backscattered and secondary electrons for the SEM image and have limited scattering for the TEM image.

SEM capabilities

Given the cost and availability of the the SEMs available at present and the very poor signal to noise ratios that will form the electronic image, it is unlikely that they will detect individual SWCNTs, in a normal search mode used for asbestos fibres and will struggle with some thin MWCNT. Although by using integration of many images signal to noise ratios can be improved visibility and resolution of the fibres, this is more suited to taking pictures rather than searching for fibres.

TEM capabilities

The TEM screen image is not electronic and is formed instantly giving a much higher signal to noise ratio than the SEM so is much more suited to scanning an area to look for fine fibres. Using solid-state cameras to take pictures of the screen can also give high resolution images with comparative ease.

Achieving a 0.01 f/ml limit for nanoparticles

Other than being able to detect the fibre, the main challenge is the time and cost it takes to scan sufficient area of the filter to achieve the suggested exposure limit.

Currently, to achieve the PCM evaluation that the air concentration of fibres is below 0.01 f/ml a minimum volume of (480 L) of air is sampled through a filter and 1.5 mm^2 of filter area is scanned (based on a 25 mm diameter filter) at X500 magnification. The 1.5 mm^2 area is scanned by observing 200 circular fields of view of ~100 µm diameter.

Assuming a similar filter loading and the same area has to be scanned (1.5 mm^2) but at higher magnifications the numbers of FOvs will be increased. The calculated number of TEM fields of view that would need to be inspected is given in the table 1.

Clearly the higher the magnification that has to be used to reliably detect a SWCNT will greatly increase the time and cost of the analysis but if X 60,000 magnification is necessary and an average of 10 fovs are checked per minute, some 1146 hours of TEM time will be required to scan the required filter area. Although there are other factors are involved this is a reasonable first estimate of the amount of effort required by TEM to measure the same filter area as used at present, to monitor fibres by PCM down to 0.01 f/ml.

Table 1: Approximate number of fields of view to required to assess 1.5 mm^2 of filter area based on a 100mm diameter fov on the TEM screen v magnification.

TEM MAGNIFICATION	Effective screen diameter of the fov (µm)	Number of fields of view to scan 1.5 mm^2
1000	100.0	191
2000	50.0	764
5000	20.0	4775
10000	10.0	19101
20000	5.0	76404
30000	3.3	171909
40000	2.5	305616
50000	2.0	477525
60000	1.7	687635
70000	1.4	935948
80000	1.3	1222463
90000	1.1	1547179
100000	1.0	1910098

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