The assessment of different metrics of the concentration of nano (ultrafine) particles in existing and new industries

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D Wake
Health and Safety Laboratory
Exposure Control Section
Harpur Hill
Buxton
Derbyshire
SK17 9JN

This report describes work carried out in order to determine which metric for very small particles best relates the exposure measurement to the health risk posed by them.

An experimental rig was constructed in which it was possible to expose three instruments, simultaneously, to aerosols generated in a range of concentrations. These aerosols contained ultrafine particles of different chemical composition and particle shape. The relationships between the mass, number and active surface area of these particles, and how they are affected by characteristics such as chemical composition and morphology for these instruments were investigated.

Consistent relationships were found for mass and active surface area with increasing number concentrations for the particle sizes investigated, but they were not consistent with size. The influence of particle morphology on the relationship between mass, number and surface area, was not significant for polydisperse ultrafine aerosols and the degree of agglomeration was more likely to be responsible for the inconsistency of instrument response to size. No simple relationship was found for predicting active surface area and mass from the results of size and number measurements. The findings indicated it is unlikely that nanoparticles will be present in a working environment in an unattached state.

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EXECUTIVE SUMMARY

It is currently unclear as to which property or metric of ultrafine and nanoparticles best relates the exposure measurement to the health risk, through inhalation, to humans. Mass is the current way in which exposure to inhalable, thoracic and respirable aerosols is measured but from the epidemiological and toxicological evidence this may not be appropriate for aerosols containing very fine particles such as nanoparticles and ultrafines. Other medical evidence has indicated possible correlations between toxicity and the number or surface area concentrations of very small particles.

The purpose of the work detailed in this HSE Research Report, which has been carried out by the Health and Safety Laboratory, is to determine what relationships exist between the mass, number and active surface area for current instrumentation measuring in terms of these parameters, and to determine how these relationships are affected by particle characteristics such as composition and morphology.

To achieve this, a test rig was constructed in the laboratory to provide a means of comparing a Matter LQ1-DC active surface area monitor, a TSI Model 3934 Scanning Mobility Particles Sizer and an R& P Tapered Element Oscillating Microbalance. These instruments were simultaneously exposed in the rig to five different polydisperse test aerosols generated at a range of number concentrations. The aerosols contained ultrafine particles of different chemical composition and particle shape.

Given that the process of generating ultrafine aerosols with a narrow size distribution in the laboratory is extremely difficult it seems unlikely that nanoparticles will be present in a working environment in an unattached or primary state i.e. they will be most likely agglomerated or aggregated. Also the air in any working environment, including those entirely dedicated to nanotechnology, will almost certainly contain a cocktail of the particles produced by the process together with other particles from exhaust, combustion and other sources, similar in size.

For each of the five aerosol types investigated, consistent relationships were found for mass and active surface area with increasing particle number concentrations for all the particle sizes investigated. However, these relationships were not consistent with particle size.

No simple relationship was found for predicting active surface area and mass from the results of measurements made with the benchmark instrument the SMPS. This instrument, therefore, should not be used to calculate surface area and mass unless a detailed knowledge of the aerosol is known. In view of this, the use of all three instruments, measuring in parallel, should continue despite the difficulty in arranging this in the workplace. Moreover, it is unwise to make measurements in terms of just one parameter, be it mass, active surface area or number/size, when assessing the potential for
engineered nanoparticles to cause ill health when the causal factor has not yet been established.

The findings indicated that for the types of particles investigated the influence of particle morphology on the relationship between mass, number and surface area for the three instruments was not significant for polydisperse ultrafine aerosols and that the degree of agglomeration of the aerosols was more likely to be responsible for the inconsistency of instrument response to size.

The response of the instrument that measured active surface area, the Matter LQ 1-DC, showed reasonable agreement with the instrument measuring size and number for aerosols sized below 100 nm but not for larger sizes.

The device chosen for measuring aerosol mass, the R&P TEOM Series 1400a, showed that it tended to overestimate the mass of aerosols sized below 100 nm due to relatively small numbers of particles larger than this size. The suitability of this instrument for measuring ultrafines and nanoparticles in the workplace is therefore doubtful.

It was observed that under certain circumstances the SMPS might have the potential to alter the structure of the sampled aerosol due to the bi-polar charging process it employs in the size classification of the aerosol.

If the particles under investigation cannot be isolated from all other types of nanosized/ultrafine particles present in the workplace then it is unlikely, or at best very difficult, that an adverse health effect can be directly attributed to exposure to that specific type of engineered nanoparticle.

Since the start of this research project an instrument called the NanoMet, which can discriminate between ultrafine/nano particle species, has become generally available. The performance of this instrument and others like it should now be fully investigated because of the potentially useful measuring role they may play in the nano engineering workplace.
1 INTRODUCTION

1.1 BACKGROUND

Nano-scale science and engineering, which is now established as a mainstream activity in the UK and worldwide, makes it possible for us to manufacture and manipulate extremely small particles with relative ease. We have discovered that certain types of these particles have very different chemical and physical properties from larger particles composed of the same material and so have developed new applications that exploit these special and unique properties. This has resulted over the last few years in the so-called “Nanotechnology” industry growing exponentially on a worldwide scale. Nanotechnology has become influential on many aspects of life and the uses for nanoparticles include: the production of reactants for more efficient rechargeable batteries, cosmetics and constituents in sun creams and sun barriers. They are used in the production of novel pharmaceuticals and as catalysts and are used widely by the electronics industry where there is a burgeoning requirement for miniaturisation of electronic components.

With the development of any radically new technology or material, there usually follows a polarisation of opinion as to its worth and much debate and concern over the possible adverse effects on health. There is now a popular perception that exposure to nanoparticles is somehow much more injurious to health than exposure to larger particles. In the absence of a large body of conclusive medical evidence we must assume that they are.

Initially, the health concerns were for the workers exposed directly in those industries where engineered small particles are produced. Now these concerns extend to workers involved in other areas, such as the coatings and composite manufacturing industries, who also come in contact with the products of the nano-technology industry as end users. Medical research (Churg et al, 1998) has shown that 200 nm diameter is the size below which there is the greatest tendency for particle deposition in the deep pulmonary tissues. Other medical research in relation to ill health has implicated inhaled ultrafine aerosol mass as a causational factor (Donaldson et al, 1998), or the total inhaled ultrafine particle number (Oberdorster, 2000) and also the total active or “Fuchs” surface area (Brown et al, 2001).

1.2 EXISTING GUIDANCE FOR AEROSOL MEASUREMENT

The current European Standard for dust measurement in terms of health for workplace atmospheres is EN 481. This standard defines sampling conventions for the inhalable, thoracic and respirable aerosol mass fractions (see also MDHS 14/3). In other circumstances it is more appropriate to determine the potential health risk of aerosols in terms of the number of particles they contain. For instance, mesothelioma can be caused by just one of the asbestos fibres that have accumulated in the lung during a person’s
lifetime. So personal exposure to asbestos, because it is much more toxic than a dust like coal dust, is usually measured in terms of the number fibres contained in a known volume of air, (see MDHS 39/3). There is another European Standard, EN 13205:2002, which is for the performance assessment of instrumentation used to measure airborne particle concentrations in the workplace. There is no provision made specifically for ultrafine aerosols and engineered nanoparticles produced by the nanotechnology industry in this standard or in EN 481.

In the UK the British Standards Institute (BSI) has responsibility for standardisation in the field of nanotechnology. Dr Peter Hatto, Director of Research for Ionbond Ltd, chairs the BSI NTI/1 Committee for Emerging Nanotechnologies and Dr Trudy Phelps of the Association of British Healthcare Industries Ltd (ABHI) chairs the CEN/TC 352 - Nanotechnologies, initiated by BSI. BSI has also been instrumental in forming an international committee entitled ISO/TC229-Nanotechnologies. This also is chaired by Dr Hatto.

To date there is no International Standard for measuring and characterising ultrafines or nanoparticles but an ISO working document at final draft stage. The current version, ISO/TC 146/SC 2/WG1 N 320 is entitled “Characterizing and assessing occupational exposures to ultrafine nanometre-diameter and nanometre-structured aerosol particles. It must be stressed that this document will not be an International Standard, but will be a Technical Report for guidance only.

The progression of diseases such as pneumoconiosis or silicosis is directly related to the respirable mass of airborne coal dust or silica to which a worker has been exposed and to how much of this is accumulated in the lungs. The personal mass exposure rate can be conveniently and accurately measured, for particles larger than ultrafine, by using size selective respirable or inhalable personal samplers containing filters that are connected to small sampling pumps and worn on the body. The filters are weighed before and after exposure and the time weighted average dust concentration for worker exposure, is calculated from the quotient of the mass of dust collected and the total volume of air that has been sampled. Instantaneous or real time dust exposure levels in the workplace can be measured by devices such as optical particle counters (OPC’s) or particle mass monitors such as the Piezobalance and the Tapered Element Oscillating Microbalance (TEOM). The latter instrument however appears to be the only one that is sufficiently sensitive to detect nanoparticles.

1.3 MEASUREMENT RATIONALE

The methods and instrumentation for measuring ultrafines and nanoparticles are not as straightforward as those for aerosols containing coarser particles. The constituent particles in a nano aerosol are too small to be effectively detected with instruments such as optical particle counters (OPC’s) because the wavelength of light, approximately 500 nm, is the limit of resolution. Also, ultrafine and nanoparticles, unless they are abnormally high in density, have insufficient mass to be detected, easily weighed or collected effectively by filtration involving mechanical capture mechanisms.
An earlier study carried out by HSL (Wake, 2000) in industries based in the UK, found that industrial processes involving heat, such as welding, soldering and plasma spraying, produced high levels of aerosol in the ultrafine size region. The study also found that in the industries directly involved in the production and handling of ultrafine powders, or in processes that may produce ultrafine particles, control appeared to be very good. This was thought to be due to effective containment and production methods and through effective use of LEV. During the time of the study ultrafine aerosol concentrations in the environment, outside the industries visited, were found to be sometimes much higher than the levels of ultrafine aerosol occurring inside. The study recommended that the various industries concerned should to be monitored at greater length before significant conclusions could be drawn and that the contribution and significance of outside ultrafine aerosols should be investigated fully as a matter of some urgency.

In this present report, three instruments, which may have the appropriate level of sophistication and sensitivity to measure nano particles, in terms of one of the three parameters, are described and discussed. Their performance has been evaluated and compared, under laboratory conditions against various challenge ultrafine aerosols with different particle composition and morphology. The three instruments were tested simultaneously in the laboratory with each type of challenge aerosol. These were generated for a number of tests such that they consisted of particles with different size distributions and different number concentrations for each test. This was done in order to determine the relationships between the three measured parameters and the effect on those relationships due to particle composition and morphology.

The findings of this current study will form the basis of developing a measurement strategy to be employed in any new study, concerning exposure to ultrafine particles and nanoparticles, that should be carried out in order to fulfil the recommendations of the initial study.
2 ULTRAFINE AND NANOPARTICLES IN THE WORKPLACE

In this report the term nanoparticle is used to refer to particles that have been intentionally engineered and the term ultrafine particles to refer to naturally occurring particles and those produced during an industrial process. For these definitions and others please refer to the Appendix for the Nomenclature.

It is important to remember that very fine particles are not only produced in the nanotechnology industry but also in any type of industry where there is likely to be a nucleation process, either as combustion products, or from the saturated vapours arising from sources such as the melting or ionisation of metals. It should also be borne in mind that very fine particles are also naturally occurring in the general environment and that these will inevitably find a route into the working environment.

2.1 ENGINEERED NANOPARTICLES

The word “nanoparticle” was used originally by materials scientists to refer to the particles they had engineered specifically to exploit the unique physical and chemical properties of very small particles. These include particles formed from carbon blacks, fumed silica, titanium dioxide, metallic oxides, Fullerines, carbon nano-tubes and quantum dots etc. Thus the “Nanotechnology” industry was born. In a workplace associated with nanotechnology therefore, it is likely that nanoparticles and nanostructured particles will be present in the air if they are not contained during their manufacture.

2.2 NATURALLY OCCURRING ENVIRONMENTAL ULTRAFINE PARTICLES

Very small particles have always been present in the environment and are constantly being generated or removed by natural processes (see Appendix, Figure 49). These processes are also directly applicable to the way in which nanoparticles are engineered and ultrafine particles are produced by industry. The presence of naturally occurring ultrafine particles could complicate measurements carried out in the workplace so it is worthwhile to include a brief description of the generation and removal processes involved for these.

The generation processes are termed Primary Production, to refer to aerosol produced by direct ejection into the atmosphere and Secondary Production to refer to the aerosols produced by physical and chemical processes within the atmosphere. Examples of the latter include the aerosols formed during the evaporation of liquid droplets, those by gas to particle reactions or those through homogenous nucleation. It is these aerosols found in the general environment that are likely to contain extremely small particles that will carry over into the work environment in significant numbers. Other aerosols, such as wind blown dusts, emissions, sea sprays, dust from volcanoes and plant particulates such as
spores and seeds will also be present. These however are significantly larger than the ultrafine/nano size region and will only be present in low concentrations, as most of them will have been excluded through sedimentation, their primary route of removal from the atmosphere.

Aerosols containing very small particles in the 1nm to 100 nm size range produced by heat in an industrial process are likely to be examples of particles formed through transient nucleation via the hot vapour, condensation, primary particle formation, coagulation and aggregation route. Unless these are removed during an industrial process they can carry over into the ambient atmosphere where rainout or washout is their primary route of removal from this. Rainout or washout is also the primary route of removal of particles in the accumulation mode, which ranges from about 50 nm through the nucleation range up to roughly 1000 nm. The accumulation range for environmental aerosols also includes coalesced or coagulated particles formed through the chemical conversion of gases to low volatility vapours, from low volatility vapours to homogenous nucleation to condensation route. Environmental aerosols tend to be transient phenomena but the process of their creation and removal from the atmosphere is continual so particle numbers may fluctuate but they will never completely disappear.

2.3 PREVIOUS MEASUREMENTS OF ULTRAFINE AND NANOPARTICLES IN THE WORKPLACE

From between about 1 to 50 nm is the primary particle diameter size range of combustion aerosols generated by heat through nucleation, condensation processes and vapour reactions. These are the processes through which carbon black is formed for example, which was an industrial process examined in a previous measurement study (Wake 2000). The number of primary particles contained in the newly formed carbon black aerosol at these sizes will influence their rate of coagulation and hence for how long they remain at their primary size. That study showed only a single momentary instance of when the carbon black aerosol, in a factory producing it, was close to the primary size, when measurements were made over the bagging area. For combustion aerosols in general, which initially contain great numbers of primary sized particles, the rate of coagulation will be very rapid, so as the foregoing observation suggests, they are more likely to be encountered in the workplace as agglomerated aerosols.

In industry in general ultrafine aerosols are produced in abundance as unwanted byproducts in any processes involving heat such as welding, metal founding, soldering and metal surface coating or treating operations. The working environment may therefore contain a complex mixture of ultrafine particles produced by the indigenous processes and also any others carried over from the surrounding environment. Industry tends to be focussed in urban regions near to major transport routes, so cross contamination from one industry to another and the presence of ultrafine particulate, from vehicle exhaust emissions is also a distinct possibility. The author has observed that the nanotechnology industry existing in the UK during the year 2000 was sparsely distributed in rural areas and that the containment that was witnessed in those industries was extremely good. If this is still the case then the possibility of cross contamination from engineered nanoparticles might not be an issue. The ingress of nearby vehicle exhaust emissions and
ultrafines from the general environment, however, will still present problems for any measurements that are carried out there.

The measurements made in the HSL (Wake, 2000) study, were carried out in a small number of nanotechnology industries and in several other industries not specifically nanotechnology based. In these other industries, however, it was suspected that very small (ultrafine) particles occurred because of the types of processes involved. The results of those measurements, in addition to those made in the nanotechnology industries, also indicated that newly formed ultrafine particles did not remain in the unattached state for long but quickly grew or in some way combined as there was no incidence when a particle size approaching the suspected primary size was observed. This was also true when the industrial process was solely concerned with the handling of engineered nano powders, not their production. Overall however, during that study, the observed aerosols generally remained in the ultrafine/nano size region.

On another occasion the author was involved in the investigation of polymer fume fever (Keen, 2003) from the welding of plastics, particularly PTFE. By using several P-Trak particle detectors in the welding room and with no operational containment, it was possible to indicate that in the region close to the welder, the time scale for agglomeration or growth out of the ultrafine size region, for the aerosol being produced, was of the order of seconds during the operation. It is worth noting that this investigation also indicated that the containment, when it was in operation (LEV), was extremely effective, for the welder, in reducing exposure to the fume produced. Also, on occasions, there were more ultrafine particles due to vehicle exhaust fume in the welding room than those particles actually produced by the welding operation.
3 FACTORS AFFECTING THE MEASUREMENT OF ULTRAFINE AND NANOPARTICLES

For the instrumentation chosen for this study for the purpose of measuring ultrafine and engineered nano aerosols in terms of their mass, their number or their surface area, the following factors will influence the accuracy of the results. These factors may have a greater significance for one particular type of instrument compared to another employing a different method of detection.

3.1 PARTICLE MORPHOLOGY AND COMPOSITION

An ultrafine or nanoparticle of known geometry and density can be directly characterised in terms of its shape and mass through simple calculation. Thus for single unattached ultrafine or nanoparticles, with a common dimension of 100 nm and assuming unit density, we obtain the following data shown in Table 1.

Table 1 Comparative surface areas and volumes for a spherical, cubic, pyramidal and cylindrical shaped particle with a common dimension of 100 nanometres

<table>
<thead>
<tr>
<th>Morphology And Size (nm)</th>
<th>Surface Area (nm²) ( (x \ 10^3) )</th>
<th>Volume (nm³) ( (x \ 10^4) ) (or mass for unit density)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CUBE (each edge =100)</td>
<td>60</td>
<td>100</td>
</tr>
<tr>
<td>SPHERE (diameter = 100)</td>
<td>31</td>
<td>52</td>
</tr>
<tr>
<td>PYRAMID (height and base = 100)</td>
<td>32</td>
<td>33</td>
</tr>
<tr>
<td>CYLINDER (height and diameter = 100)</td>
<td>47</td>
<td>79</td>
</tr>
</tbody>
</table>

Although their physical scale is similar, if they were particles made from the same material, a cubic shaped particle of that scale would have almost twice the surface area and volume (and hence mass), compared to a similar scaled spherical particle. Clearly the mass of similar scaled but polymorphic ultrafine or nanoparticles of homogenous composition will be substantially different depending on their individual shape. Their effective diameter, however, is very small so they will behave very similarly aerodynamically (Brown, 1993; Davies, 1973). If they were inhaled as individual particles they would all be capable of reaching the pulmonary alveoli in the respiratory system. The health risk they pose will be a function of their relative toxicity. The extent
of their individual surface area could possibly contribute more to this function than their difference in mass because it is the surface of the particle that is available to interact with the blood supply and gas exchange regions in the pulmonary alveoli. This surface would also facilitate a site of attachment for other materials at a molecular level that also could be capable of interacting with the blood supply and gas exchange regions possibly in a more harmful way as toxicity could be enhanced.

3.2 AGGLOMERATION, AGGREGATION AND COAGULATION

Exposure to ultrafine and engineered nanoparticles is obviously not experienced on a single particle basis but to many numbers of them. The constituent particles in the ultrafine/nano aerosol, in all probability from the evidence so far, will not be unattached as in the analogy above and so will be inhaled in the workplace as agglomerates, as aggregates or as particles that have coagulated. Any measurement technique applied to ultrafine/nano aerosols in a workplace context therefore, to be accurate and appropriate to the way they effect health, must not have the potential to break up or increase the formation of these agglomerates, aggregates and coagulates, prior to detection.

The degree of aggregation/agglomeration/ coagulation has more significance for instruments that measure aerosols in terms of their number and active surface area than for instruments that measure aerosols in terms of their mass.

3.3 PARTICLES LARGER THAN ULTRAFINE AND NANOPARTICLES

Problems will also arise when measuring ultrafine and engineered nanoparticles in the workplace air due to the presence of particles that are greater in size than those under investigation. These must be separated from the ultrafines and nanoparticles and removed from the sampled air by a process of elutriation. If elutriation of the larger fraction is by a process likely also to disrupt the ultrafine/nano fraction of the aerosol sampled then that process should be avoided. This is important for methods that measure the ultrafine or nano aerosol in terms of number and size and active surface area. It is less of a problem for methods that measure in terms of mass. In this latter case for mass, however, if the elutriation process is not entirely effective then gross overestimates of the aerosol mass supposedly associated with just the ultrafines or nanoparticles, could result. Conversely, the presence of a few large particles in a number or surface area analysis would not be too detrimental.
4 INSTRUMENTATION

4.1 INSTRUMENTATION FOR MEASURING PARTICLE NUMBER AND SIZE
(TSI Model 8525 P-Trak, TSI Model 3370 CNC and the TSI Model 3934 Scanning Mobility Particle Sizer (SMPS))

Figure 1 The TSI Model 3370 Condensation Nucleus Counter (CNC)

4.1.1 Number Concentration

A Condensation Nucleus Counter (CNC) can count ultrafine and nano aerosols by a process that involves the condensation of a vapour (usually 1-butanol, 1-propanol or water) onto the surface of the constituent particles to make them large enough to be detected by optical light scattering. This is achieved after the sampled aerosol enters a chamber saturated by the vapour where, due to adiabatic expansion, the vapour condenses onto the particles so that they grow to about 10 µm in diameter. On example of such a counter is the Model 8525 P-track manufactured by TSI Inc of Minneapolis, USA. This instrument is portable and hand-held and it can detect particles in the 20 nm to 1 µm diameter size region. The P-Trak can be used as an investigative field instrument to detect localised or fugitive sources of ultrafine particles. A more sensitive but otherwise identical version of this instrument, with a size range down to 10 nm, is the TSI Model 3370 CNC (see Figure 1). The maximum measurable number concentration for these two
instruments is \(5 \times 10^5\) particles cm\(^{-3}\) in the case of the former and \(1 \times 10^5\) particles cm\(^{-3}\) for the latter. This means that they are only really suitable for use in situations where it is unlikely that these levels will be continually exceeded. In places like clean rooms, which are well isolated from exhaust emissions, for instance. Examples of both of these instruments were used to measure background levels in the laboratory for the purpose of this study.

### 4.1.2 Number Concentration and Size

The size of particles in the ultrafine/nano size region is measured using a differential mobility analyser (DMA) in the Scanning Mobility Particle Sizer (SMPS). Several versions of this instrument are currently available from different manufacturers. All versions of these, however, essentially follow the same principle of operation. The most sophisticated version is capable of counting particles between 1 nm to 1000 nm in diameter. The SMPS system used in this study is shown below in Figure 2.

![Figure 2 The TSI Model 3934 Scanning Mobility Particle Sizer (SMPS)](image)

The Model 3934 SMPS is capable of measuring the size and number distributions of aerosols in the size range from 5 nm to 1000 nm. Particles are size classified with a Model 3071A Electrostatic Classifier (EC) one of two major components of the system, prior to the concentration of each size fraction being measured with a Model 3022A Condensation Nucleus Counter (CNC) being the other major component. The aerosol is initially charged to a Boltzmann Equilibrium level through contact with the bi-polar ions produced by radioactive source located in the EC. The particles are then classified according to their electrical mobility. The electrical mobility of the particles will govern their ability to traverse the electrical field produced in the EC during the analysis. The electric field is continually increased under computer control to produce the required size spectrum. The particles that have traversed the applied electric field pass out of the EC as
a monodisperse aerosol stream into the CNC. Each particle is then individually counted by the CNC providing that a threshold of $10^3$ particles cm$^{-3}$ is not exceeded. In the instances when this threshold is exceeded, the CNC will then operate in the photometric mode. In this mode the CNC measures the total light scattered by all particles in the sensing volume and the concentration it indicates for these is based on calibration data held in internal memory look-up tables. The entire SMPS system is automated. The data reduction and analysis is carried out on an attached PC running proprietary software. The software can be adapted to produce output data in the form of graphs, tables or statistics that provide the number, surface area or volume (and hence mass if the density of the individual particles in the measured aerosol is accurately known) concentrations versus the particle electrical mobility diameter.

Using Figure 3 as a reference, the theory behind the operation of the EC is as follows:

![Diagram of Electrostatic Classifier](image)

**Figure 3** The Electrostatic Classifier

The mobility $\mu$ of particles larger than the mean free path of gas molecules ($\sim 66$nm) follows from the Stokes equation for viscous drag $F$ of a particle of diameter $D_p$ travelling at velocity $V$ in an air medium of dynamic viscosity $\eta$ ($1.81 \times 10^{-5}$ N.s.m$^{-2}$)

$$F = \frac{3\pi \eta D_p V}{C_n}$$

\[ (1) \]
Where \( C_n \) is the Cunningham slip correction factor.

In the intermediate regime where particle diameter is comparable to the mean free path of gas molecules

\[
\mu = \frac{V}{F} = \frac{C_n}{3\pi \eta D_p} \tag{2}
\]

The mobility or motion of particles can be quantified by a coefficient of diffusion. From equation (2) it can be seen that the mobility of the particle varies inversely with diameter. This manifests itself for nanoparticles and ultrafines as a very high coefficient of diffusion (see Table 2 below).

**Table 2** Coefficient of Diffusion of Aerosols at 20°C (Davies, 1973)

<table>
<thead>
<tr>
<th>Particle Diameter (micrometer)</th>
<th>Coefficient of Diffusion in air (m²s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00038</td>
<td>(~7 \times 10^{-5})</td>
</tr>
<tr>
<td>0.002</td>
<td>(1.3 \times 10^{-6})</td>
</tr>
<tr>
<td>0.01</td>
<td>(5.3 \times 10^{-8})</td>
</tr>
<tr>
<td>0.02</td>
<td>(1.4 \times 10^{-8})</td>
</tr>
<tr>
<td>0.05</td>
<td>(2.4 \times 10^{-9})</td>
</tr>
<tr>
<td>0.1</td>
<td>(6.8 \times 10^{-10})</td>
</tr>
<tr>
<td>0.2</td>
<td>(2.2 \times 10^{-10})</td>
</tr>
<tr>
<td>0.5</td>
<td>(6.3 \times 10^{-11})</td>
</tr>
<tr>
<td>1</td>
<td>(2.8 \times 10^{-11})</td>
</tr>
<tr>
<td>2</td>
<td>(1.3 \times 10^{-11})</td>
</tr>
<tr>
<td>4</td>
<td>(6.2 \times 10^{-12})</td>
</tr>
<tr>
<td>10</td>
<td>(2.4 \times 10^{-12})</td>
</tr>
</tbody>
</table>

Comparing, for instance, the value for the 10 µm particle with that of the 50 nm particle, the latter is three orders of magnitude or 1000 times more mobile.

The high mechanical mobility of particles also implies a high electrical mobility. Therefore the response to any applied electric field for particle, carrying as little as a single fundamental charge will be considerable.

The range of particle diameters that can be classified by the EC depends on the electrical mobility of the particles and also the internal geometry of the classifier and the airflow rate through it. The design of the instrument has followed on from work carried out by Knutson and Whitby (1975) who identified the optimum values for these parameters. Thus \( Z_p \) the electrical mobility of a particle of diameter \( D_p \) can be simply defined by the following equation: where \( n \) = the number of elementary charges, \( e \) = the elementary charge = \(1.6 \times 10^{-19}\) Coulomb, \( C_n \) = Cunningham slip correction, \( \eta \) = viscosity of air.
\[ Z_p = \frac{neC_a}{3\pi\eta D_p} \] .........................................................(3)

The relationship between particle electrical mobility and optimum EC parameters according to Knutson et al, 1975 is given by the following equation:

\[ Z_p = \frac{Q_{sh}}{2\pi VL} \ln \left( \frac{r_2}{r_1} \right) \] .........................................................(4)

And the bandwidth of the electrical mobility spectrum \( \delta Z_p \) by the following equation

\[ \delta Z_p = \frac{Q_a}{\pi VL} \ln \left( \frac{r_2}{r_1} \right) \] .........................................................(5)

Where \( Q_a \) = aerosol flow rate through the EC, \( Q_{sh} \) = sheath air-flow rate around collecting rod, \( V = \) average voltage on inner collecting rod, \( L = \) distance between monodisperse aerosol exit and polydisperse aerosol inlet, \( r_1 \) and \( r_2 \) are the radii of the inner and outer annular space around the collecting rod.

Therefore by combining equations (3) and (4) gives an equation that relates particle diameter to collector rod voltage, number of elementary charges on the particle and the EC flow rates and internal geometry

\[ \frac{D_p}{C_n} = \frac{2neVL}{3\eta Q_{sh} \ln \left( \frac{r_2}{r_1} \right)} \] .........................................................(6)

Thus : if the number of elementary charges on the aerosol is known the particle diameters passing through the Classifier monodisperse aerosol exit slit can be calculated from equation (6).

4.2 INSTRUMENTATION FOR MEASURING SURFACE AREA BY DIFFUSION CHARGING (DC) (The Matter Engineering diffusion charging particle sensor type LQ 1-DC active surface area monitor)

Electrical charge measurement can be used to measure the surface area of a particle directly and the diffusion charging type of instrument (DC) can be used to measure the active or Fuchs surface area. Fuchs, (1963, 1964) defines active surface area as the surface of a particle that is directly available or accessible to be involved in chemical and physical interactions with the surrounding gas. Thus it can simply be described as the fraction of the geometric surface of a particle that is directly accessible from outside. The active surface area of a particle has a direct relevance to adsorption kinetics and is a major influence on chemical reactions between the particle, if it acts as a catalyst, and the
surrounding gas phase or gas phase reactions. Active surface area also determines the growth of the particle by providing a surface for the attachment of material from the gas phase.

For small particles in the molecular regime where their diameter is smaller than the mean free path of gas molecules the mobility $\mu$ of the particle is inversely proportional to the particle diameter $D_p$ and if the particle is a sphere, its surface area $S = \pi D_p^2$

$$\mu = \frac{\phi \lambda}{1.5 \pi \eta D_p^2} \quad \text{..................................................(7)}$$

where $\phi$ is a scattering parameter (=1.695), $\lambda$ = the man free path of gas molecules (~66 nm)

Combining equation (7) with the surface area $S$ of a spherical particle with diameter $D_p$

$$S = \pi D_p^2 \quad \text{..................................................(8)}$$

We obtain a function that establishes the relationship between mobility and surface area

$$S = \frac{\phi \lambda}{1.5 \eta} \left( \frac{1}{\mu} \right) \quad \text{..................................................(9)}$$

Therefore for small particles the surface area is inversely proportional to the mobility of the particle.

Extending this relationship to particles of all sizes the active surface area $S_a$ is defined.

$$S_a = \frac{\phi \lambda}{1.5 \eta} \left( \frac{3 \pi \eta D_p}{C_n D_p} \right) = 2 \pi \phi \lambda \left( \frac{D_p}{C_n D_p} \right) \quad \text{..................................................(10)}$$

The response of the DC can therefore be calibrated against a monodisperse aerosol in conjunction with a DMA, to measure the electrical mobility of the particles and a CNC to measure their number. The ionic current produced by the captured monodisperse aerosol in the DC is a function of size, according to electrical mobility, and to the concentration and hence, to the total active surface area of the sampled particles.
The basic operating principle of the LQ 1-DC instrument chosen for this study seen below in Figure 5, and referring to Figure 4 is as follows: The sampled aerosol passes initially through a weak plasma created by corona discharge device located in the sampling inlet. In this device the corona is generated from a 50µm diameter platinum wire electrode connected to a positive high voltage of between 3.5 to 4.5kV potential. The aerosol is allowed to mix with the uni-polar air ions produced by the corona in a short plenum chamber situated immediately after the sampling inlet. The air ions diffuse and attach to the exposed surfaces of the particles. The excess unattached air ions are removed by a collecting electrode held at an electrical potential of -15V, after a suitable residence time in the cylinder to ensure that the charge is completely taken up by the particles. This potential is chosen, together with an airflow rate of 1.5 l min$^{-1}$ to ensure that only the particles that are as electrically mobile as the air ions are removed from the flow. The aerosol, comprising the particles with the attached charge, ultimately passes into a Faraday cup electrometer, which contains a fibrous media onto which the charged particles attach. The Faraday cup is completely electrically insulated from the rest of the system. The current produced by the charged particles in the Faraday cup is measured using a sensitive electrometer with a resolution of 1 f A (1 femto amp = A$^{-12}$). As described above, the current measured is a function of the concentration and size distribution of the sampled particles.
With calibration, using a DMA or SMPS, the current can be used to give a measure of the equivalent active surface area of the aerosol. This device is suitable for dynamic measurement because it has a short response time of around a few seconds. The measuring range is between 0 and 2000 $\mu m^2$ $cm^{-3}$ active surface area, with a quoted accuracy of +/- 2 $\mu m^2$ $cm^{-3}$. The aerosol charging mechanism (and hence response) is claimed by the manufacturer to be mainly independent of the chemical composition of the particles. It must be borne in mind however that it is factory calibrated against sodium chloride particles and that detection efficiency falls to below 80% for particles larger than about 100 nm and continues to fall with increasing particle size.

This instrument can be used simultaneously in conjunction with the Matter Engineering photoelectric aerosol sensor (PAS) a type of photo-ionisation detector (PID) to provide a measurement method that differentiates between particle types such as carbon based aerosols from exhaust and engineered nanoparticles. The manufacturers also claim that it is very good for measuring combustion aerosols because the dynamic processes involved during the generation can be observed by virtue of the instruments short response time (Matter et al, 1999). The L Q 1-DC does not have the ability to store any data gathered. So for the purpose of the test detailed here, it was interfaced with a PC via a peripheral interface-adapter (PIA) with an inbuilt A/D converted and opto-isolated relays to control the functions of the DC. The data was processed using a purpose written in house programme and stored on the PC as a sequence of time referenced readings.

An impactor designed to produce a 1$\mu m$ cut-off at an air flow-rate of 1.5 l min$^{-1}$ was added to the sample entry of the Matter LQ1-DC Active Surface Area Monitor to prevent the entry of particles larger than that size. This can be seen at the top of the picture in Figure 6.

Figure 5 Type LQ 1-DC active surface area monitor
4.3 AN INSTRUMENT FOR MEASURING AEROSOL MASS (the Rupprecht and Pastashnick TEOM Series 1400a Ambient Particulate (PM-10) Monitor)

In contrast to instruments that measure ultrafine particle concentration or number, there are not many instruments available that can be considered to be suitable to measure ultrafine aerosols mass. Of those that are available there is only one instrument potentially sensitive enough and that can be realistically and conveniently used to measure the real time mass of ultrafine aerosols in the workplace and this is the Tapered Element Oscillating Microbalance (TEOM). As the name suggests this instrument is based around the principle of a tapered element oscillating microbalance that has been patented by Rupprecht and Pastashnick (see Figure 6).

![Figure 6 The R & P Series 1400a Tapered Element Oscillating Microbalance (TEOM)](image)

The TEOM is in effect an instantaneous and continually monitoring mass balance transducer. The mass transducer comprises a tapered element, essentially a hollow cantilever, which incorporates a filter on to which sampled aerosol is deposited after passing through a sampling inlet. (The sampling inlet normally connects to a PM-10 device). The tapered element is fixed at one end and free to oscillate, at its natural frequency, at the other. The filter is coupled to the tip of the free end of the element. Sampled aerosol, at a constant airflow rate, passes through to the filter where it is collected. The air then passes down the tapered element. The frequency of oscillation of
the tapered element is monitored electronically in a positive feed back configuration. This configuration feeds back just the right amount of energy back to the system to restore the natural frequency of the element. The frequency tends to be reduced as the mass of dust is added to the filter. The tapered element and filter housing are held at a constant temperature of 50 °C in order to drive off any captured volatile material.

Because the tapered element is essentially an oscillating cantilever (see Figure 7) it will have a spring rate and mass. So as for any spring/mass system if the mass is increased the frequency of oscillation decreases. Thus following from simple mechanics. Where \( f \) = frequency in radians s\(^{-1}\), \( K \) = spring rate, \( M \) = mass

\[
f = \sqrt{\frac{K}{M}} \quad \text{..........................}(11)
\]

Thus, assuming \( K \) and \( M \) are in consistent units, the relationship between change in mass \( d_m \) and change in frequency, with \( f_0 \) as initial (Hz) and \( f_1 \) as final (Hz) and \( K_0 \) is the spring constant

\[
d_m = K_0 \left( \frac{1}{f_1^2} - \frac{1}{f_0^2} \right) \quad \text{..........................}(12)
\]

thus solving for the spring constant \( K_0 \)

\[
K_0 = \frac{d_m}{\left( \frac{1}{f_1^2} - \frac{1}{f_0^2} \right)} \quad \text{..........................}(13)
\]

Therefore the calibration constant for the instrument can be determined by measuring the oscillation frequency before and after a known mass is added to the tapered element.
The TEOM operates at an overall airflow rate of 16.7 l min\(^{-1}\), with 3 l min\(^{-1}\) passing through the filter. Airflow of 16.7 l min\(^{-1}\) is also the required rate for the particular combination of PM-1 sharp-cut cyclone and diffusion screens seen in Figure 6. This was added to the sample entry of the TEOM for the purpose of these tests, to prevent the entry of particles greater than roughly 1 µm in diameter. The mass detection limit of the instrument is 0.01 µg and the measurement precision +/- 5.0 µg m\(^{-3}\) averaged over a 10 minute sampling period or +/- 1.5 µg m\(^{-3}\) averaged over a 1 hour sampling period. The peripheral functions of the instrument, such as maintaining a constant airflow and the heating provided for the tapered element, are all controlled by a separate electronic unit in which all averaged mass data is also stored. The data can be accessed directly from a screen on the front panel using a membrane keyboard. Alternatively, the unit can be connected to a PC to download all the data. The PC can also act as the host, via a proprietary programme, to control the functions of the instrument and to display the averaged and real-time data.

**Figure 7** The tapered element oscillating microbalance principle
5 LABORATORY MEASUREMENTS OF MASS, SURFACE AREA AND NUMBER

Using the three instruments described above, experiments were carried out in the laboratory with polydisperse aerosols, containing ultrafine particles, to establish what relationships exist between the three measurement parameters mass, surface area and number as determined by each instrument and how these relationships may be influenced by particle composition and morphology.

5.1 TEST RIG

The laboratory work was carried out in the aerosol test facility shown in Figures 8 and 9. The main components of the facility comprised two interconnected chambers, each with a volume of 1 m³. One of the chambers served as mixing chamber in which, various aerosols produced from different materials, were generated. Methods of generation for the soluble aerosol materials were by atomisation (see Figure 10) using either a Collison type atomiser for the low to intermediate particle number concentration range or a TSI Model 9306 Six Jet Atomiser for high particle number concentrations. A Grimm Model 78225 Aerosol Generator was used to atomise the latex particles that were supplied as aqueous suspensions with nominal particle sizes ranging from 90 nm to 750 nm in diameter. A TSI Model 3433 Small Scale Powder Disperser (SSPD) (see Figure 11) was used to disperse and aerosolise two nano-size fractions of zinc oxide powder. Whichever method of generation was employed, the aerosol was always conditioned before passing into the mixing chamber. Conditioning for those produced by atomisation involved passing the aerosol immediately through a heater and diffusion drier (see Figure 12), and through a small cylinder containing a 370 MBq Krypton¹³⁵ radioactive source to reduce any residual electric charge. Conditioning for the aerosols produced from powder by the SSPD involved only the radioactive source as the powders were dried before dispersal. Conditioning was carried out in order to “age” the aerosol to a similar state it would be in if it were encountered in a typical workplace. A typical aged ultrafine workplace aerosol, given a suitable length of time to establish itself, will tend not to settle out under gravity or be affected by nearby electrically charged surfaces.
The “aged” aerosol was drawn from the mixing chamber to the sampling chamber through a 5 cm diameter duct. The air velocity in the duct was maintained at 0.2 m.s⁻¹.
This was achieved by an electronic control loop circuit which utilised the voltage signal from a pressure sensor, connected across an orifice plate in the duct, to supply an appropriate signal to an electrically powered variable flow restrictor located between the sampling chamber and the laboratory extraction system. The laboratory extraction system provided the main airflow through the two chambers. The three instruments under comparison were arranged in the sampling chamber so that their sampling inlets were approximately equidistant from the point where the aerosol entered the chamber. This was a precautionary measure to ensure that each instrument would experience the aerosol at a similar concentration. Number concentration measurements, however, were made throughout the volume of the sampling chamber using a TSI Model 3003 Condensation Nucleus Counter P-Trak which confirmed that the aerosol concentration profile was very uniform throughout the sampling chamber, with all readings being within +/- 2% of each other, provided that the aerosol was left to establish over a suitable length of time.

All sources of air entering the test Aerosol Mixing chamber from the laboratory environment were filtered by electrical means to remove the coarse particles and as many of the ultrafines particles as possible present in the immediate environment. This also included any that might enter from outside. The electrical filtration process involved initially passing the main air supply through a filter constructed from electrostatic material and then through a electrostatic parallel plate elutriator held at an appropriate electrical potential with a high voltage power supply, to precipitate out any particles not removed by the electrostatic filter. To aid the electrical precipitation process, charge was applied to any particles that were electrically neutral. This was achieved using a corona wire, located in the elutriator inlet, which was connected to a separate power supply. The air inlets to the pumps used to supply the aerosol generators were situated downstream of the electrostatic filter and precipitator so that they were also drawing in the cleaned air. Absolute filters were used to filter the air leaving the pumps because they were the vane type and therefore likely to produce particles of carbon. These steps were taken not only to ensure that the test aerosols comprised mainly of particles of a known composition and morphology but also to reduce the presence of transient exhaust emissions and the possibility of them swamping the test aerosol. Background counts using a TSI Model 3003 CNC, were made in the Aerosol Sampling chamber, before generation of the test aerosol, but with all air sources used in the generation process flowing into the chamber. When there was no traffic or evidence of smoke from fires in the vicinity, the particle counts indicated were typically around 15 particles cm\(^{-3}\) or less. Particle counts in the ambient air made with the same instrument were around 3000 to 4000 particles cm\(^{-3}\) and up to ten times this when vehicle activity or smoke was evident.
Figure 10 Apparatus for producing ultrafine aerosols by nebulisation

Figure 11 Apparatus for producing aerosols by re suspension
**Figure 12** Apparatus for conditioning the test aerosols

### 5.2 TEST AEROSOLS

Details of the challenge aerosols are shown below in Table 3.

**Table 3** Details of the challenge aerosols

<table>
<thead>
<tr>
<th>Material</th>
<th>Density Of bulk material g/cm³</th>
<th>Median Mobility diameters (nm)</th>
<th>Geometric standard deviation σg</th>
<th>Particle shape</th>
<th>Method of generation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium fluorescein</td>
<td>1.9</td>
<td>120 - 257</td>
<td>2.3 – 2.4</td>
<td>Amorphous with inclusions</td>
<td>Atomisation</td>
</tr>
<tr>
<td>Sodium chloride</td>
<td>2.6</td>
<td>35 - 175</td>
<td>2.1 – 2.7</td>
<td>Cubic</td>
<td>Atomisation</td>
</tr>
<tr>
<td>Latex</td>
<td>1.0</td>
<td>88 - 773</td>
<td>1.6 – 2.3</td>
<td>Spherical</td>
<td>Atomisation</td>
</tr>
<tr>
<td>Caffeine</td>
<td>1.2</td>
<td>34 - 247</td>
<td>1.8 – 2.1</td>
<td>Rods with 6:1 aspect ratio</td>
<td>Atomisation</td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>4.8</td>
<td>91 - 167</td>
<td>2.4 - 2.7</td>
<td>Highly agglomerated Rods (aspect ratio ~ 3:1)</td>
<td>Re-suspension</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[See Figure 13][13]</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[See Figure 14][14]</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[See Figure 15][15]</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[See Figure 16][16]</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[See Figure 17][17]</td>
<td></td>
</tr>
</tbody>
</table>
**Figure 13** SEM image of 250 nm sodium fluorescein particles

**Figure 14** SEM image of 500 nm sodium chloride particles
Figure 15 SEM image of 750 nm diameter latex particle

Figure 16 SEM image of caffeine particles (size unknown) courtesy N Vaughan of HSL
5.3 TEST PROCEDURE

The procedure followed for each size and concentration of test aerosol for each material was to generate the aerosol for a sufficient period to enable the number of particles in the air throughout the volume of the sampling chamber to stabilise. This was determined by monitoring the concentration in the sampling chamber with a P-Trak attached to a robotic arm. Particle numbers generally increased over an initial period lasting around 30 minutes and then remained stable for about an hour providing the aerosol generation process was maintained. When it was evident that particle numbers had stabilised, the TOEM, SMPS and DC simultaneously sampled the aerosol for a period lasting approximately 30 minutes. The data gathered during this period was stored and processed later to determine the average reading returned by each instrument over the period of stability. For the aerosols produced by nebulisation, the aerosol generators were operated at various pressures to obtain a range of particle sizes and at different solution strengths and varying quantities of dilution air to obtain a range of particle concentrations for each material. The concentration of the aerosols generated from the zinc oxide powders by the SSPD were varied by varying the quantity of the dilution air required by the device during its operation. The zinc oxide powder was supplied in two grades each with a particular primary particle size. The concentration range for the latex particles for each of the sizes supplied was obtained by varying the concentration of particles added to the carrier fluid used in the nebulisation process and also the quantity of dilution air flowing through the aerosol generator.
During all tests the sample inlets of the Matter LQ1- DC and the TEOM were each fitted with an impaction device to prevent the entry of particles larger than about 1.0 µm in diameter. This was to prevent the entry of particles liberated from the walls of the Sampling Chamber through mechanical stress or vibration. The SMPS is equipped with an impaction device designed to cut off around 1 µm as a standard feature.

More comparative tests were carried out with the sodium chloride aerosols. Sodium chloride proved to be easier to generate in stable concentrations by nebulisation compared to the other materials. The reason for this is not known.
6 RESULTS OF LABORATORY COMPARISONS

6.1 AEROSOL SIZE DISTRIBUTION AND MEASURED VALUES OF SURFACE AREA AND MASS

For each of the five aerosol types a typical particle size distribution, at one of the sizes and concentrations investigated, is shown below. The numerical values, averaged over a 30 minute sampling period, returned by each instrument simultaneously sampling one of the five types of test aerosols at a particular size and concentration of aerosol for all the sizes and concentrations investigated are tabulated below. The results for each aerosol type are grouped together according to size and are ordered in terms of increasing concentration within each size group. Plots of measured values of mass against active surface area, active surface area against particle number and mass against particle number are shown for each aerosol type. The lines shown on all the following graphs, linking the points, are those showing the best fit produced by Microsoft Excel regression analysis.

From the particle number and size data measured during each test by the SMPS it was possible to calculate the equivalent geometric surface area and mass after the density of the particular material was factored into the calculation. These values are included in the tables in the two rightmost columns of the data for each material and are subsequently discussed in Section 6.2

6.1.1 Sodium Fluorescein

For this aerosol, two main size groups were generated from two different concentrations of sodium fluorescein in aqueous solution.

Figure 18 SMPS size distribution of sodium fluorescein aerosol of 138 nm median mobility diameter
The distribution of sizes seen in Figure 18, together with the geometric standard deviation values shown in Table 4, indicate that the sodium fluorescein test aerosols were very polydisperse. The geometric standard deviation values are very consistent. The average sizes of the two groups of aerosols are 133 nm for the smaller and 243 nm for the larger.

**Table 4** Readings returned by the three instruments simultaneously sampling sodium fluorescein aerosols comprised of particles of varying size and number concentration

<table>
<thead>
<tr>
<th>Average SMPS mobility diameter (nm)</th>
<th>Average SMPS Geometric standard deviation (μg m⁻³)</th>
<th>Average TEOM reading (μm² cm⁻³)</th>
<th>Average DC reading (μm² cm⁻³)</th>
<th>Average SMPS count (Particles/cm³)</th>
<th>Surface area calculated from SMPS data (μm² cm⁻³)</th>
<th>Mass calculated from SMPS data (μg m⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>129</td>
<td>2.3</td>
<td>18.6</td>
<td>286</td>
<td>7081</td>
<td>370.2</td>
<td>14.8</td>
</tr>
<tr>
<td>140</td>
<td>2.4</td>
<td>31.6</td>
<td>489</td>
<td>13107</td>
<td>807.1</td>
<td>35.0</td>
</tr>
<tr>
<td>138</td>
<td>2.4</td>
<td>55.4</td>
<td>869</td>
<td>21644</td>
<td>1294.9</td>
<td>55.4</td>
</tr>
<tr>
<td>122</td>
<td>2.3</td>
<td>72.2</td>
<td>1132</td>
<td>25785</td>
<td>1205.7</td>
<td>45.6</td>
</tr>
<tr>
<td>145</td>
<td>2.4</td>
<td>90.2</td>
<td>1461</td>
<td>33822</td>
<td>2234.0</td>
<td>100.4</td>
</tr>
<tr>
<td>120</td>
<td>2.4</td>
<td>120.3</td>
<td>1852</td>
<td>51171</td>
<td>2314.9</td>
<td>86.1</td>
</tr>
<tr>
<td>243</td>
<td>2.4</td>
<td>21.7</td>
<td>623</td>
<td>2300</td>
<td>426.7</td>
<td>32.1</td>
</tr>
<tr>
<td>257</td>
<td>2.4</td>
<td>27.8</td>
<td>842</td>
<td>3595</td>
<td>745.9</td>
<td>59.4</td>
</tr>
<tr>
<td>233</td>
<td>2.4</td>
<td>41.6</td>
<td>1233</td>
<td>4796</td>
<td>817.9</td>
<td>59.1</td>
</tr>
<tr>
<td>254</td>
<td>2.4</td>
<td>47.6</td>
<td>1558</td>
<td>7322</td>
<td>1484.0</td>
<td>116.9</td>
</tr>
<tr>
<td>236</td>
<td>2.4</td>
<td>63.7</td>
<td>1879</td>
<td>8703</td>
<td>1522.8</td>
<td>111.4</td>
</tr>
<tr>
<td>238</td>
<td>2.4</td>
<td>73.7</td>
<td>Over range</td>
<td>10028</td>
<td>1784.5</td>
<td>131.7</td>
</tr>
</tbody>
</table>

With sodium fluorescein it was not possible to generate stable aerosols smaller than the one sized at 129 nm median mobility diameter. The reason for this is not known.

Figure 19 shows the results of plotting TEOM and DC values against each other for increasing concentration at these average sizes.
Figure 19 Surface area measured by DC plotted against measured TEOM mass concentration for sodium fluorescein aerosols

Figure 19 shows that a linear relationship exists between TEOM and DC measured values for each aerosol size group. The divergence of the two sets of points, however, indicates a size dependency on that relationship.

Figure 20 Surface area measured by DC plotted against SMPS number concentration for sodium fluorescein aerosols

DC measured surface area is plotted against SMPS measured number concentration for each average size group in Figure 20. A size dependant linear relationship between values for DC and SMPS is indicated.
**Figure 21** Mass measured by TEOM plotted against SMPS number concentration for sodium fluorescein aerosols

With the TEOM measured mass values we also see, in Figure 21, a size dependent linear relationship between TEOM and SMPS values. This naturally follows when the relationships shown in Figures 19 and 20 are linear.

### 6.1.2 Sodium Chloride

Seven size groups of sodium chloride aerosol were generated from seven different concentrations of aqueous sodium chloride solution.

**Figure 22** SMPS size distribution of sodium chloride aerosol of a 92 nm median mobility diameter
The range of sizes seen in Figure 22 indicates that the sodium chloride test aerosols were polydisperse but not to the same degree as the sodium fluorescein aerosols. The high values of geometric standard deviation in Table 5, however, indicate that the largest aerosols (89 to 170 nm) were very polydisperse.

Table 5 Readings returned by the three instruments simultaneously sampling sodium chloride aerosols comprised of particles of varying size and number concentration

<table>
<thead>
<tr>
<th>Average SMPS mobility diameter (nm)</th>
<th>Average SMPS Geometric standard deviation (Sg)</th>
<th>Average SMPS count (Particles/cm3)</th>
<th>Average DC reading (µm2 cm-3)</th>
<th>Average TEOM reading (µg m-3)</th>
<th>Surface area calculated from SMPS data (µm2 cm-3)</th>
<th>Mass calculated from SMPS data (µg m-3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>37</td>
<td>2.1</td>
<td>28970</td>
<td>198</td>
<td>19.7</td>
<td>124.6</td>
<td>2.0</td>
</tr>
<tr>
<td>35</td>
<td>2.1</td>
<td>91200</td>
<td>600</td>
<td>54.2</td>
<td>351.0</td>
<td>5.2</td>
</tr>
<tr>
<td>55</td>
<td>2.3</td>
<td>25190</td>
<td>144</td>
<td>16.3</td>
<td>239.4</td>
<td>5.6</td>
</tr>
<tr>
<td>56</td>
<td>2.3</td>
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<td>562</td>
<td>72</td>
<td>1046.3</td>
<td>25.0</td>
</tr>
<tr>
<td>55</td>
<td>2.4</td>
<td>147008</td>
<td>840</td>
<td>80.6</td>
<td>1397.1</td>
<td>32.8</td>
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<td>55</td>
<td>2.3</td>
<td>219608</td>
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<td>113.7</td>
<td>2087.0</td>
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</tr>
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<td>60</td>
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<td>268</td>
<td>110</td>
<td>598.1</td>
<td>18.6</td>
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<tr>
<td>77</td>
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<td>65</td>
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</tr>
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<td>1232</td>
<td>325</td>
<td>5296.4</td>
<td>384.2</td>
</tr>
</tbody>
</table>

The DC and TEOM results for each of the size groups are plotted against each other, below, in Figure 23.
The plots for each of the seven sizes of aerosols seen in Figure 23 show linear relationships between the DC and TEOM. Similarity in the slope of the lines indicates a grouping of the smaller sizes (35 and 55nm) and the larger sizes (75,92,124 and 170 nm) The 63 nm aerosol does not appear to fit in to either group. It is worth noting that the order of the slopes with size is the reverse of that for sodium fluorescein.

Figure 24 Surface area measured by DC plotted against SMPS number concentration, for sodium chloride aerosols

The plot of points for each size group in Figure 24 all indicate linear relationships between equivalent DC and SMPS readings and that the gradients increase with size.
The relationships between the TEOM and the SMPS readings, seen in Figure 25, are also linear and the order of the slopes with size is the same as that seen in Figure 24 for the DC.

6.1.3 Latex

Four size groups of aerosol were generated from stock suspensions of four nominal sizes of latex particles.

Figure 25 Mass measured by TEOM plotted against SMPS number concentration, for sodium chloride aerosols

Figure 26 SMPS size distribution of 306 nm median mobility diameter latex aerosol
Although the geometric standard deviations of the latex aerosols were low (see below in Table 6) the spread of sizes seen in Figure 26 indicates that the latex aerosols were very polydisperse. This is curious because these aerosols were generated from suspensions of monodisperse latex particles. The anomaly could be due to agglomeration and may be further evidence of ultafine and nanoparticles not remaining for long at their primary size.

Table 6 Readings returned by the three instruments simultaneously sampling latex aerosols comprised of particles of varying size and number concentration

<table>
<thead>
<tr>
<th>Average SMPS mobility diameter (nm)</th>
<th>Average Geometric standard deviation (Sg)</th>
<th>Average TEOM reading (µg m⁻³)</th>
<th>Average DC reading (µm² cm⁻³)</th>
<th>Average SMPS count (Particles/cm³)</th>
<th>Surface area calculated from SMPS data (µm² cm⁻³)</th>
<th>Mass calculated from SMPS data (µg m⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>90</td>
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<td>6.9</td>
<td>55</td>
<td>1429</td>
<td>36.4</td>
<td>0.6</td>
</tr>
<tr>
<td>94</td>
<td>1.7</td>
<td>18.2</td>
<td>144</td>
<td>3297</td>
<td>91.5</td>
<td>1.5</td>
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<td>26.9</td>
<td>181</td>
<td>4387</td>
<td>106.7</td>
<td>1.6</td>
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<tr>
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<td>2.6</td>
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<tr>
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<td>1203</td>
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<td>201.2</td>
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<td>10135</td>
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<tr>
<td>760</td>
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<td>1954.3</td>
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<td>680</td>
<td>4841</td>
<td>8970.3</td>
<td>1205.6</td>
</tr>
</tbody>
</table>

Figure 27 shows the results of plotting TEOM and DC values against each other for increasing concentration at these four average sizes.
Figure 27 Surface area measured by DC plotted against measured TEOM mass concentration for latex aerosols

For the four size groups linear relationships are indicated in Figure 27 between equivalent DC and TEOM readings. The gradients of the plots increase with size.

Figure 28 Surface area measured by DC plotted against SMPS number concentration for latex aerosols

For the data shown in Figure 28, for the 92 nm and 306 nm aerosols, the best fit from regression analysis indicates a power relationship. For the two larger aerosols the best fit is linear. None the less the aerosols are ranked more or less consistently in ascending order with size.
Figure 29 Mass measured by TEOM plotted against SMPS number concentration for latex aerosols

For the data shown in Figure 29 when TEOM values are plotted against those from the SMPS. The best fit from regression analysis is for a power relationship for the two smaller aerosols and linear for the two larger aerosols. There is no consistent order of the gradients with size.

6.1.4 Caffeine

Three size groups of caffeine aerosol were generated from three concentrations of aqueous caffeine solution.

Figure 30 SMPS size distribution of caffeine aerosol with 34 nm median mobility diameter
Figure 30 indicates that the 34 nm caffeine aerosol was bi-modally distributed. The first mode possibly indicates the primary size of the caffeine rods and the second mode the size of the agglomerates of these. Overall, the distribution of sizes in the 34 nm diameter aerosol is very polydisperse, however, the geometric standard deviations for the 44, 39,152 and 174 nm diameter aerosols, indicate less spread in the distribution of sizes. (See below).

**Table 7** Readings returned by the three instruments simultaneously sampling caffeine aerosols comprised of particles of varying size and number concentration

<table>
<thead>
<tr>
<th>Average SMPS mobility diameter (nm)</th>
<th>Average SMPS Geometric standard deviation (Sg)</th>
<th>Average SMPS count (Particles/cm³)</th>
<th>Average DC reading (μm² cm⁻³)</th>
<th>Average TEOM reading (µg m⁻³)</th>
<th>Surface area calculated from SMPS data (µm² cm⁻³)</th>
<th>Mass calculated from SMPS data (µg m⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>44</td>
<td>1.9</td>
<td>10293</td>
<td>37</td>
<td>59.4</td>
<td>62.6</td>
<td>0.6</td>
</tr>
<tr>
<td>34</td>
<td>2.1</td>
<td>15687</td>
<td>49</td>
<td>65.3</td>
<td>57.0</td>
<td>0.4</td>
</tr>
<tr>
<td>39</td>
<td>1.8</td>
<td>20597</td>
<td>66</td>
<td>72.2</td>
<td>98.4</td>
<td>0.8</td>
</tr>
<tr>
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<td>2</td>
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<td>66</td>
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<td>10085.4</td>
<td>351.0</td>
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<td>227882</td>
<td>458</td>
<td>431.9</td>
<td>31571.7</td>
<td>1326.0</td>
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</table>

Figure 31 shows the results of plotting TEOM and DC values against each other for increasing concentration at these three average sizes.
The points in Figure 31 show linear relationships between the TEOM and DC readings with little or no dependence on size for the larger two of the three aerosols because the gradients are similar. However, for the smallest 39 nm sized group, the steeper gradient indicates a lower sensitivity of the TEOM to particles of that size.

For the three size groups of caffeine aerosols, linear relationships are indicated in Figure 32 for DC readings plotted against equivalent SMPS readings. However, the gradients of the points are very similar, so there appears to be little dependence on size.
**Figure 33** Mass measured by TEOM plotted against SMPS number concentration for caffeine aerosols

For the two larger size groups of the caffeine aerosol seen in Figure 33 the best fit to the data for these from regression analysis is indicated by a power relationship. For the smallest aerosol, regression analysis indicated a linear relationship but curiously this did not intercept the y-axis at zero. Moreover, the slope of the gradients should increase with size but this is not the case.

### 6.1.5 Zinc Oxide

Two mean size groups of aerosol were generated from two nominally different sized zinc oxide powders. The sizes measured in this exercise were broadly similar to the mean sizes for the two zinc oxide powders quoted by the manufacturer. It is believed that the manufacturer used TEM analysis to obtain the average size of each powder.
**Figure 34** SMPS size distribution of zinc oxide aerosol with 158 nm median mobility diameter

The spread in the distribution of sizes, seen Figure 34, for the 158 nm aerosol and the high values of geometric standard deviation for the other zinc oxide aerosols, seen below in Table 8, indicates that the zinc oxide aerosols were very polydisperse.

**Table 8** Readings returned by the three instruments simultaneously sampling zinc oxide aerosols comprised of particles of varying size and number concentration

<table>
<thead>
<tr>
<th>Average SMPS mobility diameter (nm)</th>
<th>Average Geometric standard deviation (Sg)</th>
<th>Average TEOM reading (µg m⁻³)</th>
<th>Average DC reading (µm² cm⁻³)</th>
<th>Average SMPS count (Particles/cm³)</th>
<th>Surface area calculated from SMPS data (µm² cm⁻³)</th>
<th>Mass calculated from SMPS data (µg m⁻³)</th>
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</table>

Figure 35 shows the results of plotting TEOM and DC values against each other for increasing concentration for each of the two zinc oxide aerosol size groups.
**Figure 35** Surface area measured by DC plotted against measured TEOM mass concentration for zinc oxide aerosols

For the data shown in Figure 35 the best fit from regression analysis is for a power relationship for the 156 nm aerosol and a linear relationship for the 92 nm aerosol. The highly contrasting gradients indicate that there is a strong dependence on size. Also, the very steep gradient seen for the 92 nm aerosol indicates a comparatively lower response of the TEOM for the smallest sizes of aerosol.

**Figure 36** Surface area measured by DC plotted against SMPS number concentration for zinc oxide aerosols
For the data shown in Figure 36 the best fit from regression analysis is for a linear relationship and the similar gradients indicate little dependence on size.

![Graph showing TEOM Mass concentration (ug/m³) plotted against SMPS Number concentration (particles/cm³). The graph includes data points for 92 nm and 158 nm aerosols.]

**Figure 37** Mass measured by TEOM plotted against SMPS number concentration for zinc oxide aerosols

The regression analysis of the data shown in Figure 37, for the TEOM as it did for the DC, gives the best fit for a power relationship. Unlike the results for the DC, however, the contrasting gradients indicate a strong dependence on size. The points for the 92 nm aerosol are all close to the x-axis indicating a very low response of the TEOM to aerosols of this size.

### 6.2 MEASURED MASS AND SURFACE AREA CONCENTRATION FOR TEOM AND DC VERSUS CALCULATED FROM SMPS NUMBER SIZE DISTRIBUTION

In order to examine the feasibility of accurately predicting aerosol mass and surface area from SMPS data alone, this section includes a comparison of measured and calculated data. Graphs of the active surface area measured by DC and the mass measured by the TEOM are plotted against the corresponding surface area and mass values calculated from the SMPS data. This is carried out for each aerosol type using the actual DC and TEOM readings and the calculated numerical values shown in the two rightmost columns in the previous tables.

#### 6.2.1 Sodium Fluorescein Aerosols: Measured versus calculated SMPS data

Plotting the calculated values against those measured with the DC and TEOM for the two average size groups gives the relationships shown in Figure 38 for the DC and in Figure 39 for the TEOM.
**Figure 38** Surface area measured by DC plotted against SMPS calculated surface area for sodium fluorescein aerosols

The similar gradients for the two aerosol groups indicate a low dependence on size for the indicated linear relationships. However, assuming that the SMPS calculation was reasonably accurate, then a much steeper gradient for the larger aerosol would be expected.

**Figure 39** Mass measured by TEOM plotted against SMPS calculated mass for sodium fluorescein aerosols

The points for the smallest aerosol are very scattered and regression analysis gives the best fit for a linear relationship. For the larger of the two aerosol groups the best fit is for
a power relationship. However, for the 133 nm group the slope of the line is close to 45\degree indicating a better agreement of the TEOM and SMPS for particles of this size.

6.2.2 Sodium Chloride Aerosols: Measured versus calculated SMPS data

Plotting the calculated values against those measured with the DC and TEOM for each of the seven size groups gives the relationships shown below in Figure 40 for the DC and in Figure 41 for the TEOM.

**Figure 40** Surface area measured by DC plotted against SMPS calculated surface area for sodium chloride aerosols

**Figure 41** Mass measured by TEOM plotted against SMPS calculated mass for sodium chloride aerosols
In Figures 40 and 41, regression analysis gave the best fit for linear relationships for each of the seven size groups, which were roughly ordered with size with the steepest gradient being for the smallest aerosol. For the largest aerosol (170 nm) the SMPS prediction of mass is similar to that actually measured by the TEOM. Therefore, assuming the TEOM response is correct, the SMPS calculation underestimates the mass of the aerosols smaller than this and this effect becomes worse with decreasing size. For the DC the SMPS calculation of surface area is more accurate at predicting the surface area of the smallest sized aerosol and overestimates the surface area of the aerosols larger than this, assuming the response of the DC is correct.

6.2.3 Latex Aerosols: Measured versus calculated SMPS data

Plotting the calculated values against those measured with the DC and TEOM for the four average size groups gives the relationships shown in Figure 42 and Figure 43.

![Figure 42](image-url)

**Figure 42** Surface area measured by DC plotted against SMPS calculated surface area for latex aerosols
For the results shown in Figures 42 and 43, regression analysis gave the best fit for a linear relationship between results for each of the four sizes for both the DC and TEOM readings against the SMPS calculated values. Both are ordered with size with the steepest gradient being for the smallest aerosol. For the 306 nm aerosol the SMPS prediction of mass is the closest to that actually measured by the TEOM, assuming that the TEOM is reading correctly. The SMPS calculation overestimates the mass of the aerosols smaller than this and this effect becomes worse with increasing size. For the DC the SMPS calculation of surface area, as it was for the sodium chloride aerosol, is more accurate at predicting the surface area of the smallest sized aerosol, assuming that the response of the DC is correct.

6.2.4 Caffeine Aerosols: Measured versus calculated SMPS data

Plotting the calculated values against those measured with the DC and TEOM at the average sizes gives the relationships shown in Figure 44 and Figure 45.
Figure 44 Surface area measured by DC plotted against SMPS calculated surface area for caffeine aerosols

Figure 45 Mass measured by TEOM plotted against SMPS calculated mass for caffeine aerosols

For the results shown in Figures 44 and 45 regression analysis gave the best fit for a power relationship for the largest 228 nm sized aerosol and linear for the 163 nm aerosol. The SMPS calculation does not appear to predict the response of the TEOM to the 39 nm aerosol but is closer in predicting the response of the DC to this size of aerosol, compared to the two larger sizes. For the TEOM the SMPS calculation is most accurate in predicting the mass of the 163 nm aerosol assuming that the TEOM readings are correct.
6.2.5 Zinc Oxide Aerosols: Measured versus calculated SMPS data

Plotting the calculated values against those measured with the DC and TEOM at the average sizes gives the relationships shown in Figure 46 and Figure 47.

Figure 46 Surface area measured by DC plotted against SMPS calculated surface area for zinc oxide aerosols

For the data shown in Figure 46 the best fit from regression analysis is for a power relationship for the larger of the two aerosols and linear for the smaller. It is worth noting for this type of aerosol (which was composed of highly agglomerated rods) that the values calculated from the SMPS data are many times greater than those actually measured by the DC.

Figure 47 Mass measured by TEOM plotted against SMPS calculated mass for zinc oxide aerosols
As in the previous Figure, for the DC results, the data shown in Figure 47 for the TEOM results, the best fit from regression analysis is for a power relationship for the 158 nm aerosol and linear for the 92 nm aerosol. Unlike the DC response to the 158 nm aerosol however, which gets worse at higher concentrations assuming that the SMPS prediction is correct. The response of the TEOM improves at higher concentrations of this size of aerosol. Which possibly indicates that the effects of agglomeration are more significant for the DC.

6.3 EFFECT OF PARTICLE CHARACTERISTICS ON CALCULATIONS OF SURFACE AREA AND MASS

In all instances for the five different aerosol types, there is a good correlation between data for the DC and TEOM when the values returned by each instrument for a particular size of aerosol are plotted against concentration. This is illustrated below in Tables 14 for the measured and calculated surface area data and in Table 15 for the measured and calculated mass data, assuming power relationships to aid comparison. From the equation given by the regression analysis

\[ y = \text{Constant} \times x^{\text{power}} \]

\( y \) equals either the DC or the TEOM measured value and \( x \) equals the SMPS calculated values of surface area or mass.
Table 14 Data regression analysis of measured surface area versus surface area calculated from SMPS data

<table>
<thead>
<tr>
<th>Aerosol</th>
<th>Size class (Mobility Diameter nm)</th>
<th>Constant</th>
<th>Power</th>
<th>Goodness of Fit Parameter</th>
<th>R^2</th>
</tr>
</thead>
<tbody>
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<td></td>
</tr>
<tr>
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<td>1.0</td>
<td>0.9</td>
<td></td>
</tr>
<tr>
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<td>1.0</td>
<td></td>
</tr>
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<td></td>
</tr>
<tr>
<td>Latex spheres</td>
<td>92</td>
<td>0.4</td>
<td>1.4</td>
<td>0.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>306</td>
<td>0.01</td>
<td>1.6</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>470</td>
<td>0.13</td>
<td>1.0</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>767</td>
<td>0.2</td>
<td>0.5</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>Caffeine</td>
<td>40</td>
<td>1.8</td>
<td>0.8</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>163</td>
<td>0.03</td>
<td>1.0</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>229</td>
<td>0.0001</td>
<td>1.5</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>Zinc Oxide</td>
<td>92</td>
<td>0.01</td>
<td>1.2</td>
<td>0.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>158</td>
<td>1.2</td>
<td>0.5</td>
<td>0.8</td>
<td></td>
</tr>
</tbody>
</table>
### Table 15 Data regression analysis of measured mass concentrations versus mass concentrations calculated from SMPS data

<table>
<thead>
<tr>
<th>Aerosol</th>
<th>Mobility Diameter (nm)</th>
<th>Constant</th>
<th>Power</th>
<th>Goodness of Fit Parameter R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium Fluorescein</td>
<td>133</td>
<td>1.4</td>
<td>0.9</td>
<td>0.9</td>
</tr>
<tr>
<td></td>
<td>243</td>
<td>1.8</td>
<td>0.7</td>
<td>0.8</td>
</tr>
<tr>
<td>Sodium Chloride</td>
<td>36</td>
<td>2.6</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>55</td>
<td>0.3</td>
<td>1.1</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>63</td>
<td>0.1</td>
<td>1.2</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>75</td>
<td>0.1</td>
<td>1.2</td>
<td>0.9</td>
</tr>
<tr>
<td></td>
<td>92</td>
<td>0.2</td>
<td>1.1</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>124</td>
<td>1.4</td>
<td>0.9</td>
<td>0.9</td>
</tr>
<tr>
<td></td>
<td>173</td>
<td>108.5</td>
<td>0.3</td>
<td>1.0</td>
</tr>
<tr>
<td>Latex</td>
<td>92</td>
<td>13.3</td>
<td>1.3</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>306</td>
<td>0.1</td>
<td>1.5</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>470</td>
<td>0.1</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>767</td>
<td>0.1</td>
<td>0.9</td>
<td>1.0</td>
</tr>
<tr>
<td>Caffeine</td>
<td>40</td>
<td>71.3</td>
<td>0.1</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>163</td>
<td>1.2</td>
<td>0.9</td>
<td>0.9</td>
</tr>
<tr>
<td></td>
<td>229</td>
<td>0.0001</td>
<td>2.1</td>
<td>1.0</td>
</tr>
<tr>
<td>Zinc Oxide</td>
<td>92</td>
<td>0.1</td>
<td>1.2</td>
<td>0.9</td>
</tr>
<tr>
<td></td>
<td>158</td>
<td>0.00004</td>
<td>2.5</td>
<td>0.9</td>
</tr>
</tbody>
</table>

From equation $y = \text{Constant} \times x^{\text{Power}}$

What is striking, from the values given in Table 14 and Table 15 is there is no consistent order of response of the DC or the TEOM to size between the five aerosol types.

For the sodium fluorescein aerosols, which contain particles approximating in shape to spheres, the DC measured active surface area compares reasonably well with the equivalent surface area calculated from the SMPS data, for both size groups investigated (133 nm and 243 nm). However, returning to the values shown in Table 4, and assuming the SMPS predictions are correct, the DC measurement underestimates the surface area of the smallest sized aerosol and overestimates the surface area of the largest sized aerosol. Interestingly the DC measurement for the 133 nm sodium fluorescein aerosol compared to measurements for the other substances of a similar size and number concentration, shown below for this and other sizes below in Table 16, is much higher and closer to the value predicted from the SMPS results.
Table 16 Comparison of DC active surface area and TEOM mass results for aerosols of similar size and concentration according to SMPS

<table>
<thead>
<tr>
<th>Aerosol</th>
<th>Mobility Diameter (nm)</th>
<th>Number (SMPS) (Particles/cm³)</th>
<th>Geometric standard deviation (Sg)</th>
<th>DC reading (µm² cm⁻³)</th>
<th>Surface area from SMPS data (µm² cm⁻³)</th>
<th>TEOM reading (µg m⁻³)</th>
<th>Mass calculated from SMPS data (µg m⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Caffeine</td>
<td>163 39</td>
<td>32074 20597</td>
<td>2.0 1.8</td>
<td>66 66</td>
<td>2677 98</td>
<td>60 72</td>
<td>87 1</td>
</tr>
<tr>
<td>Sodium Chloride</td>
<td>175 89 37</td>
<td>17099 33168 28970</td>
<td>2.9 2.5 2.1</td>
<td>336 300 198</td>
<td>1645 704 124</td>
<td>65 114 19</td>
<td>128 31 2</td>
</tr>
<tr>
<td>Zinc Oxide</td>
<td>159 88</td>
<td>23414 28947</td>
<td>2.7 2.7</td>
<td>48 35</td>
<td>1859 704</td>
<td>20 6 20</td>
<td>236 49 2</td>
</tr>
<tr>
<td>Sodium Fluorescein</td>
<td>133</td>
<td>21644</td>
<td>2.4</td>
<td>869 1294</td>
<td>1294 55</td>
<td>55 55</td>
<td>55 55</td>
</tr>
</tbody>
</table>

This is consistent with a large surface area and is what might be expected from a very convoluted surface like that of the sodium fluorescein particle.

From Table 14 it can be seen that the DC has the most consistent response with size to the sodium chloride aerosols. However, the DC measurement is almost invariably less than the surface area calculated from the SMPS data. The TEOM measured mass of sodium chloride aerosols is almost always greater than the mass calculated from the SMPS data. Significantly, the only exceptions to these observations occur at the largest particle sizes investigated, (173 nm) for the mass comparison and at the smallest sizes investigated (36 nm), for the surface area comparison. The order of the slopes of the points of TEOM measured mass plotted against DC measured active surface area shown in Figure 23 are not consistent with size, but this is not the case when each of these parameters are plotted against particle number as in Figures 24 and 25. This indicates that the degree of agglomeration or aggregation of the sodium chloride aerosol, rather than the actual shape of the particles contained in the aerosol, could have a greater bearing on the results. This is also borne out by the values of geometric standard deviations from the measured SMPS data for each aerosol group. The geometric standard deviation is an indicator of the spread of particle sizes within the aerosol and the observed geometric standard deviations for the sodium chloride aerosols show a significant variation but not a consistent order with size.

The results for the latex aerosols, which contain particles with a true spherical geometry, show a similar behaviour to those for the sodium fluorescein aerosols, but in a reverse sense. The DC measured values are invariably less than the values of surface area calculated from the SMPS data for the largest sizes and invariably greater for the smallest sizes. But unlike the sodium fluorescein aerosols, the disparity appears to increase with particle size. The mass returned by the TEOM for latex aerosols greater in size than the
92 nm group is lower by a factor of 3 for the 306 nm aerosol group, rising to a factor 40 for the 470 and 767 nm groups. The TEOM, assuming that the SMPS calculations are correct, grossly overestimates the mass of the aerosols sized below 100 nm (i.e. the 92 nm group) as it has for all the other aerosols except zinc oxide.

For caffeine aerosols the data for the aerosol mass measured by TEOM against those calculated from SMPS data compares reasonably well for aerosols around the 150 nm mobility diameter sizes and is lower by roughly a factor of four for the aerosols greater in size than 200 nm. At sizes below 150 nm, however, the TEOM appears to overestimate by approximately a factor of 100. This is probably due to the TEOM detecting the mass of the fraction of particles larger than the median size of the aerosol. The aerosols are polydisperse so particles larger in size than the median diameter will be present in the distribution but in lower numbers. In terms of their mass, however, they will dominate the distribution. A good indication of this can be seen in the size distribution of the 34 nm mobility diameter aerosol (Figure 30), this shows the presence of a significant number of particles, probably agglomerates, in the 100 nm to 400 nm mobility diameter region. The DC measured active surface area values, on the other hand, agree reasonably well for sizes of 34, 39 and 44 nm median diameter with the SMPS calculated surface areas. The lower DC values returned for larger sizes, however, indicates either the DC response is flattening off or that the influence of surface area, due to the aerosols becoming more agglomerated, becomes less important with increasing size.

For zinc oxide aerosols the TEOM measured mass in all instances is less than the mass calculated from the SMPS data. This is apparent for sizes below 100nm by roughly a factor of two and for the sizes above by roughly a factor of five. The DC active surface area measurements are invariably less than the values calculated from the SMPS data by roughly a factor of twenty.

The results of DC and SMPS measurements for the smallest particles investigated in this study are broadly in line with some of the findings of a similar study carried out with monodisperse aerosols (Ku and Maynard, 2005) which showed that for monodisperse particles, DC and SMPS measurements of surface area agree for particles below 100 nm in diameter. That study also found that for monodisperse aerosols below 100 nm with spherical and fractal-like geometries the response of the DC instrument, which was identical to the one used in this study, is proportional to the mobility diameter squared and for larger particles up to 200nm in diameter the response changes from this to the theoretically expected value of mobility diameter raised to the power of 1.5.
7 DISCUSSION

It is relatively easy to draw ultrafine or nano particles into a sampling device with a pump since their aerodynamic diameter is extremely small they can be considered to effectively follow the motion of the air transporting them into the sampling device. As an aside this means also that it is likely that most forms of local exhaust ventilation (LEV) including low volume high velocity (LVHV) which is inefficient against large particles, may be very effective at capturing ultrafine particles. However unlike respirable, thoracic or inhalable particles, which can be effectively captured on a filter, it is difficult to filter ultrafine particles because their geometric size rules out particle capture by interception. Moreover, their small aerodynamic diameter, unless they are abnormally dense, precludes capture involving aerodynamic forces or gravitational settling. They cannot be effectively captured by mechanical filtration involving interception or inertial impaction (other than low pressure impactors such as the MOUDI or ELPI) or by cyclones, settling chambers and parallel plate elutriators. However, inertial impactors could be used to remove the larger fraction of aerosol from the sample as they have been for this exercise.

For devices that measure mass, the presence of a relatively low number of extraneous large particles would result in a serious overestimation of the actual mass under investigation, which appears to be the case for the TEOM. It was found during the latter part of this investigation that the TEOM uses a mechanical filter to collect the particles, so it is likely that the TEOM will also underestimate the mass of ultrafine aerosols with a very small mobility median diameter. In the workplace newly formed ultrafines and nanoparticles are highly mobile and very large numbers of particles could be present in a relatively small mass of aerosol. Although PM-10, PM-2.5 is supposed to include all particles less than the cut-point, the TEOM is specifically designed to sample the mass of aerosols equivalent to and greater in size than the PM-1 fraction, and the makers make no claims about the instruments suitability to sample ultrafine aerosols. The inability of the TEOM filter to efficiently capture ultrafines was demonstrated by configuring a CNC with a lower size limit of detection of 10 nm in the exhaust air-flow line between the filter and the pump. The count did not fall to zero as it should with perfect filtration but reduced to a significant fraction of the count observed when the CNC was sampling freely in the ambient air. Under normal conditions the significant fraction was roughly 10% but this increased to between 20% and 30% when vehicle exhaust emissions were evident in the ambient air. There is a further disadvantage associated with the TEOM when sampling ultrafines and nanoparticles. This is due to what happens when volatile material is captured on the filter. The filter and tapered element are held at a temperature of 50°C in order to help drive off the volatiles. However when this occurs the balance tries to momentarily compensate for the loss of mass and negative readings are returned. If this occurs over a significant fraction the sample interval then it has the effect of reducing the short-term average. If instantaneous sampled masses are already very low, as usually is the case with ultrafine and nanoparticles, this leads to a significant reduction in the short-term averaged value and if it occurs frequently then the long-term average suffers also.
The SMPS is an ideal tool for measuring the size of monodisperse ultrafine and nanoparticles but are we correct to assume that the SMPS should be employed as the “bench mark” instrument for measuring the size distribution of polydisperse ultrafine and nano aerosols in the workplace? Instruments such as the differential mobility analyser (DMA), which forms a vital part of the SMPS, may not be entirely reliable for accurately analysing polydisperse aerosols containing agglomerates because the aerosol is pre-charged before classification and the charging process is bi-polar. The presence of bi-polar charged ions in the sampled aerosol may have the potential to further agglomerate the aerosol. This could in some way explain why the results of these laboratory comparisons are not very consistent. In the workplace the settling velocity of chains of particles is not very different from that of individual particles and thus the mobility of the particles will decrease more or less linearly with the number of components in the agglomerate (Brown, 1993). The result of this would be a reduction in the diffusional depositional efficiency of attached particles and an increase in their interception efficiency. These factors obviously have implications for the way in which ultrafine and nano aerosols are inhaled and what happens in the lung. Moreover, if it could be determined whether inhaled agglomerations of ultrafine particles remain in the same agglomerated state after they have settled in the tissues of the body, then it would be easier to predict their toxicity. The ability of the charging process in the DMA to alter the size distribution (and probably the degree of agglomeration of the sampled aerosol) can be demonstrated by carrying out an SMPS analysis of ambient aerosol when it was known to be stable in concentration, with and without the charger present in the DMA. Stable ambient aerosol usually carries a level of electric charge which is similar to a Boltzmann equilibrium level (Wake et al, 1991) The author carried out such a measurement in the HSL laboratory where conditions are usually very stable. The comparison was made by repeating the measurement with and without the Krypton85 radioactive source (the bi-polar charger) installed in the DMA. The two size distributions were different as shown in Figure 48.

![Figure 48 SMPS size distributions of nominally identical concentrations of ambient HSL laboratory air](image-url)
As can be seen the size has changed and the overall count reduced, for nominally the same aerosol, after it was passed through the radioactive charger. Also, the distribution has broadened, evidenced by an increase in the geometric standard deviation from a value of 1.9 to 2.1. In terms of the observed size shift of the aerosol it could be argued that these results are as expected because the correct operation of the mobility analyser requires the level of charge to be known and prescribed, (i.e. Boltzmann equilibrium). But this does not explain why the count reduced by approximately 20% when the charger was used and why the distribution broadened after the aerosol had passed through the radioactive charger. A second SMPS (Grimm) sampling at the same time confirmed that the concentration and size of the aerosol in the laboratory did not change. The most likely explanation is that the degree of agglomeration of the sampled aerosol, post and prior to passing through the radioactive charger, was different.

Other workers in the field (Bon Ki Ku and Maynard, 2004. Charron and Harrison, 2005) have suggested an approach of using the SMPS information relating to aerosol mass and surface area from a measurement made with the instrument to reasonably accurately predict these parameters without the need to actually measure them directly. This may be true for monodisperse aerosols of known composition but the author has serious reservations about this being applied to a workplace scenario where aerosols may be in different states of agglomeration.

The DC type of instrument appears to give good surface area results, in comparison with the SMPS data, when the median size of the aerosols investigated here is smaller than about 200 nm. But it should be borne in mind, however that the response of the DC is initially calibrated using an SMPS and monodisperse sodium chloride aerosols around and below this median size. Curiously the only significant instances when the DC does not agree well with the SMPS data are when the DC is used to measure sodium chloride aerosols. The charging process in the DC is however unipolar so it is less likely to alter the degree of aggregation of the sampled aerosol and this could account for why the results for sodium chloride vary so markedly.

From the evidence so far it is doubtful whether the measurement in terms of any single property of nanosized or ultrafine particles will be sufficient to identify their potential for causing ill health. Moreover, exposure to the engineered nanoparticles created specifically in the nanotechnology industry is in conjunction with all the other types of very small airborne particles that have been described in this report, which may be present in a workplace environment. This is also true for any other type of working environment in which very small particles are created. The problem of isolation of one from the other is no easy task but it would appear to be crucial to the way we now approach the problem of how to measure them in the most appropriate way. The author knows of only one measuring technique, photo-ionisation detection (PID) which, when used in conjunction with a device like the DC, is capable of discriminating between ultrafine particle species. During the time of writing this report an instrument called the “NanoMet”, which embodies the principles of DC and PID in its operation has become
available on the market. It would be very prudent to include this instrument in any future investigation. This instrument is briefly described in the Appendix.

We should look at the combined effects of exposure to all ultrafine particles both naturally occurring and man made, rather than approach the problem of consequence of exposure to ultrafines by simply focussing on the specific threat from engineered nanoparticles. We must do this if we are to fully understand how they will impact on the health of everyone not just the workers engaged in the industries that produce them
8 CONCLUSIONS

Stable polydisperse aerosols composed of nanoparticles of five different substances have been successfully generated in the laboratory in a range of sizes and number concentrations. This has enabled simultaneous comparisons of the performance of an SMPS, which measures an aerosol in terms of particle size and number, a Diffusion Charging device which measures an aerosol in terms of the particle active surface or Fuchs surface area and a Tapered Element Oscillating Microbalance, which measures and aerosol in terms of its mass. The aerosol types were chosen to produce particles, which individually are of a specific shape. This was to enable the influence of the particle morphology to be investigated. From the findings of these tests the following conclusions can be made.

- For each of the five aerosol types investigated the response of the TEOM and the DC at a particular size is consistent with increasing particle number concentration measured by SMPS but overall the response of the TEOM and the DC shows no consistent ranking with size.

- The difficulty in generating nano aerosols in the laboratory with a narrow size distribution, even when the test primary particles are close to being monodisperse, (like the gold aerosols generated in a tube furnace by Ku and Maynard, 2004) reinforces the view that nano aerosols in the workplace will be highly agglomerated and will contain few particles exhibiting the primary size.

- No simple relationship was found for predicting the active surface area, as measured by DC, from SMPS measurements. But for aerosols smaller than 100 nm the DC results for most of the materials investigated were broadly similar to those calculated from the SMPS data.

- Care should be exercised if using the SMPS to measure the polydisperse and probably highly agglomerated ultrafine aerosols found in some workplaces. This is because the charging process in the SMPS technique is bi-polar and could potentially alter the degree of agglomeration of the sampled aerosol.

- Because of the lack of consistent relationships found in this study between measurements of mass, number and surface area, we should continue to measure all three parameters despite the difficulty in arranging this in the workplace.

- It will be impossible to directly attribute a health response of exposure to a specific type of engineered nanoparticle if these cannot be isolated from all the other types of ultrafine particles, such as those produced from combustion processes etc, that will be also present with them.

- The TEOM, despite the use of an inlet size selector with a cut-point at 1 µm to match that of the SMPS and DC, is not suitable in the present form for measuring
ultrafine and nano aerosols because the presence of a relatively small number of particles larger than ultrafine and nano will lead to overestimation of the associated mass. Although the TEOM probably measures the mass of particles greater than 1 µm very efficiently, it is likely that the inclusion of a more suitable size selector with a lower cut size could improve the performance of this instrument for nano and ultrafine particles.

- The filter in the TEOM is mechanical in action and so is not totally efficient in capturing ultrafine or nanoparticles. This should be changed for a more efficient filter.

- The morphology of the nanoparticles investigated in this exercise, which did not include carbon nano tubes but did include spheres, rods and cubes etc, is probably not as significant a factor in the response of the three instruments investigated compared to the state of agglomeration of the measured aerosol.
9 RECOMMENDATIONS

- Measurements in terms of just one parameter, be it mass, active surface area or number/size, should not be made, when assessing the potential for ultrafines or nanoparticles in the workplace to cause ill health. None of these parameters taken in isolation can give sufficient information to predict toxicity.

- The performance of any device, currently available, that can discriminate between ultrafine/nano particle species should be investigated. These devices are few in number so the development of more of these should also be encouraged.

- For reasonable accuracy the SMPS must not be used to calculate surface area and mass without prior knowledge of aerosol composition and state of agglomeration.

- Improve the efficiency of the TEOM filter.
10 REFERENCES


Charron, A., Harrison, R.M., (2005). “Comparison between SMPS, Nano-SMPS and Epiphaniometer data at an urban background site (Bloomsbury) and a roadside site (Marylebone Road)” Report to DEFRA by University of Birmingham and Cassella Stanger under contract EPG 1/3/184


EN 481, Workplace atmospheres – Size fraction definitions for measurement of airborne particles.

EN 13205:2002, Workplace atmospheres – Assessment of performance of instruments for measurement of airborne particle concentrations


Wake, D., (2001), “Ultrafine Aerosols in the Workplace”. Health and Safety Laboratory Report number IR/ECO/00/18


11 APPENDIX

11.1 NOMENCLATURE

Rainout is the process by which the particles in an aerosol act as the nuclei for the condensation of cloud droplets, which in rain clouds, produce sufficiently large drops that then fall under gravity and settle to the earth's surface as rain.

Washout is the removal of the aerosol that becomes incorporated into an already existing cloud droplet that then becomes large enough to fall as rain.

ISO/TC 146/SC 2/WG1 N 320 defines a nanoparticle as “A particle with a nominal diameter smaller than about 100 nm” and a nanoaerosol as “An aerosol comprised of or consisting of nanoparticles and nanostructured particles. The same document defines a nanostructured particle as “A particle with structural features smaller than 100 nm, which may influence its physical, chemical and/or biological properties. A nanostructured particle may have a maximum dimension substantially larger than 100 nm. For example, a 500 nm diameter agglomerate of nanoparticles would be considered a nanostructured particle. “

ISO/TC 146/SC 2/WG1 N 320 defines the accumulation aerosol as “An aerosol associated with coalescence or coagulation of particles within the nucleation range into larger particles. Distribution modes typically extend from 50 nm to 1 mm, but are not confined to these limits”.

An ultrafine particle is defined, in ISO/TC 146/SC 2/WG1 N 320 as “A particle sized about 100 nm in diameter or less”. Thus an ultrafine aerosol will be dominant in particles of this diameter or less.

ISO/TC 146/SC 2/WG1 N 320 defines agglomerate as “A group of particle held together by relatively weak forces, including van der Waals forces, electrostatic forces and surface tension”. An aggregate is defined in this document as “A heterogeneous particle in which the various components are not easily broken apart”, and coagulation is defined as “The formation of larger particles through the collision and subsequent adhesion of smaller particles”

11.2 OTHER MEASURING DEVICES CONSIDERED

Several other types of aerosol measuring or collection devices were considered for use in this project but for the reasons discussed below they were not used.
11.2.1 The TSI Model 3320 Aerodynamic Particle Sizer (APS)

The TSI Model 3320 Aerodynamic Particle Sizer (APS) which uses the principle of time of flight to count and size particles according to their aerodynamic size which is a function of how long the particle lags behind the air, moving in the sensing zone, due to it’s inertia. This instrument is sometimes used in conjunction with an SMPS to obtain information over a wide size distribution encompassing the ultrafine size region, the Fine Particle region and the near Coarse Particle region. It is worth discussing this instrument as it suffers from a problem that could give rise to misleading results.

The manufactures claim that this instrument has a lower size limit of approximately 0.2 µm but under normal use this is not realistic as most industrial ultrafine aerosols would have very low inertia and so particles with diameters below about 0.5 µm would essentially be moving at the same speed as the air and could not therefore be resolved. The instrument tends to place all counts between these sizes in the initial channel of data leading to a distorted size distribution of the counts in this region. Moreover, a more subtle effect of this miss-sizing is that some of these small particles can be misinterpreted as larger phantom particles (Wake, 1989) due to the different scattering properties produced by slight changes in orientation, and hence incomplete detection, as they pass between the two laser beams. This can produce a false or distorted distribution and could be extremely misleading if particle mass is inferred. The work that the author carried out was based on the original version of the APS The APS 3300. The problem does not seem to have been successfully resolved, however, in the latest Model 3320 version. Thus the APS 3320 cannot be considered to be a good device for sizing and counting ultrafine particles.

11.2.2 Filtration involving electrostatic capture mechanisms.

It could be argued that the ultrafine aerosol could be simply captured on to a filter providing it is not mechanical in its action, as is the case for larger aerosols. Mechanical filters are ineffective against ultrafine aerosols because of their low inertia but with electrostatic filtration the capture of charged particles takes place by Coulombic attraction if the filter fibres are themselves charged and by electrical image forces if they are not.

For the workplace, the concept of collecting ultrafine particles by electrical means on to a filter using a simple sampling device like a personal pump for subsequent mass, number and surface area assessment is very appealing. The airflow resistance of electrostatic filters is usually very low so sampling pumps could operate for long periods using the batteries currently available. But realistically this is not practical because the mass of those captured would be extremely low and therefore sampling periods would need to be very protracted. Moreover, not all ultrafine particles are electrically charged and a significant number will be neutral. It would be extremely difficult to measure the mass increase on a filter with laboratory balances of less than at least six figure precision. For numerical analysis involving TEM for instance, the captured particles would be extremely difficult to recover from the fibers of the filter because they adhere through
strong electrostatic forces rather than weak Van der Waals forces. For surface area analysis using a technique such as BET (Brunauer et al, 1938, Reed, 1988) the collection filters would need to be those compatible with that analysis technique which means that they must be mechanical (membrane) filters of a specific type and porosity (and very likely high air flow resistance). The approach of re-dispersing the collected dust from the electrostatic filter on to these membrane filters makes the accuracy of the method then questionable due to the break up of any sampled aggregates or agglomerates. Also, BET is not a measure of the external surface area but rather the total surface area of the particle including pores and occlusions. It also requires a relatively large deposit of the dust on the analysis filter to be accurate.

11.2.3 The Micro-Orifice Uniform Deposit Impactor (MOUDI)

The micro-orifice uniform deposit impactor (MOUDI), is a sampling device that has the ability to capture ultrafine and nanoparticles by impaction despite their low inertia. The device impacts particles on to a system of 12 weighable plates according to their size. The MOUDI however cannot be considered to be a convenient way to measure ultrafines and nanoparticles in the workplace because it does not provide instantaneous results. More seriously, in order to give the particles a Stokes number sufficiently high enough for impaction to be effective, the device takes the sampled particles from atmospheric pressure to near vacuum conditions via a system of highly engineered channels so the break up of any agglomerates or aggregates is more than likely. Also, there is a problem associated with water condensing on the particles due to the low operating pressures. Moreover, in addition to the results not being available in real time, they have to be subsequently interpreted in the laboratory by very accurately by weighing the series of impaction plates.

11.2.4 The Epiphaniometer

A device called the Epiphaniometer (Pandis et al, Gaggeler et al 1989) is also available as an alternative to the DC method for measuring surface area. This cannot be considered as suitable for workplace measurements, however, because the availability of this instrument is very limited. Also, it is very unwieldy and employs a radioactive source of significant activity.

11.3 DETAILS OF THE NanoMet INSTRUMENT

(taken from manufacturers literature)

“The NanoMet is a recently introduced instrument which produces relatively fast response information on particle surface properties. NanoMet consists of two separate but nearly identical measurement channels which operate simultaneously. In both channels, the incoming aerosol flow is charged; the two channels differ in the way that the aerosol is charged. In the case of the first channel, a corona discharge is used to provide diffusion charging to the aerosol, while in the second channel, an excimer lamp (a monochromatic
UV source) is used to charge the aerosol photoelectrically. Once the two aerosol flows have been charged, they are collected on filters. The total electrical current produced by the charged aerosol being collected on the filters is then measured.

While the aerosol charge distribution resulting from diffusion charging is proportional only to the total “active surface area” of the aerosol, the charge distribution resulting from photoelectric charging is also dependent on a material coefficient. Consequently, the resultant charge distribution on each of the two aerosol flows (and thus the total current measured) will differ by a factor which is equal to the material coefficient. This material coefficient depends on the composition of the surface material of the aerosol and has been repeatably characterized for aerosols from a wide variety of different sources (e.g. diesel engine exhaust aerosol, spark ignition engine exhaust aerosol, cigarette aerosol, iron oxide, etc.). Thus, NanoMet can distinguish both the general surface properties of an unknown aerosol, as well as smaller variations within the surface properties of a known type of aerosol. NanoMet can also provide an absolute measure of the total active surface area of an aerosol.

The NanoMet system is currently capable of measuring particles in the size range from approximately 10 nm – 1000nm (without the ability to differentiate between different sizes) with a time “resolution” of approximately 1 second (the actual time constant of the instrument is likely to be closer to 5 seconds). NanoMet (with included dilution system) currently sells for approximately £50,000 in the United Kingdom’
11.4 Principal modes, size ranges, sources, particle formation and removal mechanisms for naturally occurring atmospheric aerosols (after Whitby and Cantrell, 1976 and Sienfeld and Pandis, 1998)
The assessment of different metrics of the concentration of nano (ultrafine) particles in existing and new industries

This report describes work carried out in order to determine which metric for very small particles best relates the exposure measurement to the health risk posed by them.

An experimental rig was constructed in which it was possible to expose three instruments, simultaneously, to aerosols generated in a range of concentrations. These aerosols contained ultrafine particles of different chemical composition and particle shape. The relationships between the mass, number and active surface area of these particles, and how they are affected by characteristics such as chemical composition and morphology for these instruments were investigated.

Consistent relationships were found for mass and active surface area with increasing number concentrations for the particle sizes investigated, but they were not consistent with size. The influence of particle morphology on the relationship between mass, number and surface area, was not significant for polydisperse ultrafine aerosols and the degree of agglomeration was more likely to be responsible for the inconsistency of instrument response to size. No simple relationship was found for predicting active surface area and mass from the results of size and number measurements. The findings indicated it is unlikely that nanoparticles will be present in a working environment in an unattached state.

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