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Environmental Monitoring of Nanoparticles

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¹⁰

Abstract

The aim of this work was to review the existing instrumental methods to monitor airborne nanoparticle in different types of indoor and outdoor environments in order to detect their presence and to characterise their properties. Firstly the terminology and definitions used in this field are discussed, ¹⁵ which is followed by a review of the methods to measure particle physical characteristics including number concentration, size distribution and surface area. An extensive discussion is provided on the direct methods for particle elemental composition measurements, as well as on indirect methods providing information on particle volatility and solubility, and thus in turn on volatile and semivolatile compounds of which the particle is composed. A brief summary of broader considerations related to ²⁰ nanoparticle monitoring in different environments concludes the paper.

1. Introduction

1.1 Sources of Nanoparticles

The beginning of the twenty-first century has witnessed an explosion of interest in the science and ²⁵ technology of engineered nanoparticles - structures that range in size from a few, up to about 100 nm. These particles can escape into the environment, and along with an increasing demand for

nanomaterials in terms of both quantity and quality, there have also been growing concerns regarding their potential impacts on human health. However, nanomaterial engineering is not the only source of nanoparticles in ambient air. To the contrary, there are many natural and anthropogenic processes which can lead to the formation of large quantities of nanoparticles, and as a result, they are omnipresent in both indoor and outdoor air. The most significant sources of nanoparticles are combustion processes, both natural and anthropogenic (the later including vehicle and industrial emissions, biomass burning and tobacco smoking), but also natural processes, in particular those leading to secondary particle formation via nucleation. In the urban environment, motor vehicle combustion is the main source of secondary airborne nanoparticles, which are not emitted directly by the source but formed in the air from precursors originating from one or more sources. For example, considerable progress in engine combustion technologies has led to more complete combustion, whereby the size of primary black carbon soot particles in vehicle exhaust has decreased substantially from the micrometer into the nanometre size range. These smaller soot particles have a reduced surface area for the volatile organic compounds in vehicular exhaust to condense upon and as a result, instead of condensing onto soot particles, these semivolatile species homogeneously nucleate to form high concentrations of nanoparticles. Sometimes formation processes also involve photochemistry and in such cases, light is an essential factor for the process to proceed. Examples of these processes include the formation of secondary nanoparticles from biogenic emissions in forest or marine environments, as well as from sources found in the indoor environment, including modern office equipment (e.g. printer emissions) or consumer products (e.g. detergents or paints).

1.2 Impacts of Nanoparticles

The potential hazards from the inhalation of nanoparticles by humans are very different to those from the inhalation of larger particles because nanoparticles are not readily removed from the airstream of inhaled air in the upper parts of the respiratory tract and therefore, they are inhaled into much deeper

regions of the lung¹. When in the small containments of the alveoli region, diffusional deposition of the particles on the epithelium becomes an efficient physical mechanism, with an alveolar deposition of about 40% for 50 nm particles compared to about 10% for 700 nm particles². The nanoparticles deposited in this oxygen/blood exchange region can penetrate very quickly and efficiently into the blood stream. If these particles are charged, they pose an added risk to human health, since inhaled charged particles have a five to six-fold increased probability of depositing in the lung than uncharged particles of the same size³.

To date, the toxicity of these nanoparticles, their penetration across the blood-brain barrier and the pathways leading to nanoparticle-related cardiovascular diseases have been demonstrated. In addition to health effects, these man made nanoparticles have also been shown to have significant impacts on the environment, more specifically on atmospheric properties and climate modification, by providing seeds for atmospheric nucleation processes, as well as changing the optical properties of the atmosphere.

Considering these potential risks to human health and the environment, it is of critical importance to not only monitor the presence of nanoparticles in the air, but also to obtain a good quantitative understanding of their physical and chemical properties, as well as spatial and temporal trends in indoor and outdoor environments. The instrumental methods which are now available to monitor the presence of these particles in the air, as well as characterise their properties, are the main focus of this review.

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2. Definition of ‘Nanoparticles’

Many terms have been used in relation to particles in the nanosize range, which extends from about 1 to over 100 nm, with the most common terms being ultrafine particles and nanoparticles. Within the

field of aerosol science the term “ultrafine particle” has been used in relation to particles smaller than 100 nm⁴, while nanoparticles are generally referred to as those smaller than 50 nm⁴. Both these terms constitute a somewhat arbitrary classification of particles in terms of their size, indicating the significant role of this physical characteristic on particle fate in the air. Common to the various definitions of ultrafine particles was “at least one dimension less than 100 nm”^{5,6}. While there has not been universal agreement on these terms, they have been used to differentiate between particles formed through different mechanisms. In particular, in the field of vehicle emissions, primary particles, which are generated during a combustion processes, are generally referred to as ultrafine particles, while secondary particles (i.e. those that are not emitted from a source but formed in the air) and those originating from homogenous or heterogeneous nucleation are referred to as nanoparticles. In contrast to the fields of ambient aerosol or combustion emissions science, the term “engineered nanoparticle” is the preferred term when describing nanosize particles originating from various manufacturing or engineering processes.

A more rigorous definition of these terms has been introduced by the International Standards Organisation (ISO). In particular, ISO/TC 146/SC 2/WG1 N 320 defines a **nanoparticle** as “A *particle with a nominal diameter smaller than about 100 nm*”, a **nanoaerosol** as “An aerosol comprised of or consisting of nanoparticles and nanostructured particles” and a **nanostructured particle** as “A *particle with structural features smaller than 100 nm, which may influence its physical, chemical and/or biological properties*”. This means that a nanostructured particle may have a maximum dimension substantially larger than 100 nm, since a 500 nm diameter agglomerate of nanoparticles would be considered a nanostructured particle. The same document defines an **ultrafine particle** as “A particle sized about 100 nm in diameter or less” and thus, an **ultrafine aerosol** would contain a majority of particles of this diameter or less.

It should be mentioned here that the 100 nm cut-off for nanoparticles is not derived from particle behaviour in the respiratory tract following deposition, and therefore it is not a health based metric ⁷. A health based metric will need to consider the fact that as particles become smaller, surface curvature, the arrangement and percentage of atoms on the particle surface, and the size dependent quantum effects, such as quantum confinement, play an increasingly significant role in determining behaviour ⁷.

When referring to nanoparticle measurements, an unspoken assumption is made that the instrumental methods used provide information on particles in the specific size range, which is below 100 nm. This is possible if the instrumental method enables measurements of particle number size distribution, usually in a broader range, from which the sections of data encompassing nanoparticles are then extracted. If, rather than employing instrumentation for particle size distribution measurement, only a particle counter is used, the outcome of the measurement is the total particle number concentration in the detection size range of the instrument. This means that the outcomes of the measurements are not specifically nanoparticle concentrations, unless specific inlets are used which restrict the range of particles entering the instrument's sensing volume. While it is true that, in most typical environments, particle number concentration is dominated by nanoparticles, it is important to keep in mind that these are not the same and that there are environments where there are significant particle modes outside the nanosize range.

In the view of the fact that the instruments detecting nanoparticles do not strictly restrict particle size (as discussed above), when discussing the instrumental techniques for nanoparticle monitoring, it is generally not essential to use a rigorous definition of the particles, and therefore, in relation to the review, there is no need to accept a particular definition. For simplicity, through the paper only the term "nanoparticle" is used, unless refereeing to published data using other terms.

3. Particle Concentration and Size Distribution

3.1 Particle number concentration measurements

The particle detection and counting techniques used in environmental monitoring primarily employ optical detection methods and this is also true of nanoparticle sampling. However particles smaller than about 50 nm do not interact strongly with electromagnetic radiation of optical or near optical wavelength, and so are not detected efficiently by light blocking or scattering. To overcome this range limitation, environmental nanoparticle number concentration measurements must employ Condensation Particle Counters (CPC's) which effectively enlarge the particles to detectable sizes by condensing a low vapour pressure material onto the original particles from the gas phase. Condensation Particle Counters (CPCs) typically contain water or butanol as the condensable species used to grow the particles to a detectable size, although a small number, such as TSI's PTrak, use propenol. A list of water-based and butanol-based CPCs are provided in Table 1. The mass diffusivity of condensable species dictates the design of the instrument and therefore, instruments using species' with a lower diffusivity than air, such as the butanol based instruments, rely on the greater diffusivity of air to carry heat away from a warm vapour enriched aerosol stream as it passes through a cooler condensing tube, thereby increasing the vapour concentration to the super-saturation levels needed for particle growth. In contrast, instruments relying on highly diffusive species for particle growth, such as water vapour, may achieve super-saturation by passing a cooler aerosol stream through a warm tube coated with the condensable species, so that the more mobile condensable species carry heat to the cooler aerosol, thereby reaching super-saturation⁸. Alternatively, such instruments may rely on the rapid mixing of two flows, each saturated at different temperatures, to produce super-saturation^{9,10}.

For an insoluble species, the predicted lower detection size limit is the Kelvin diameter corresponding to the super-saturation ratio achieved in the aerosol. However, a species which is soluble in the condensing species will have an associated equilibrium vapour pressure for the condensing species lower than that for an inert particle such that the particles may be detectable at smaller sizes.

Therefore, the solubility of the aerosol in the condensable species can affect the lower detection limit achieved by an instrument.

Several studies have been conducted to compare the performance of butanol and water based CPCs for different types of aerosol. These have examined the relative response of the instruments to aerosols for different particle sizes, compositions and concentrations. Biswas et al.¹¹ conducted a study comparing a butanol based CPC (BCPC) with a water based instrument (WCPC) for NH_4SO_4 , NH_4NO_3 , glutaric acid, and adipic acid aerosols generated in the laboratory. The concentration ratio (WCPC/BCPC) recorded by the two instruments ranged from 1.0-1.1 for particles sizes in the range 10-50 nm, while a slightly higher WCPC/BCPC ratio was obtained for particle sizes of less than 15 nm. In addition, Hering et al.⁸ compared an ultrafine water-based CPC TSI 3785 with a BCPC TSI 3025. Comparable results of WCPC and BCPC (within $\pm 3\%$ differences) were observed for 80 nm Oleic acid, and 50 nm NaCl particles. They also showed that the water based instrument responded with varying sensitivity near the lower size limit depending on the composition of the aerosol with detection efficiency for the smallest particles being greater when water soluble species were present in the particles.

Iida et al.¹² also compared the performance of the WCPC TSI 3786 and BCPC TSI 3025 under field conditions using different particle sizes. The tests were conducted in freeway tunnels and ambient environments. For ambient air, the WCPC and BCPC values were comparable for particles > 5 nm and at 3 nm, the BCPC showed higher detection efficiency than the WCPC. In contrast, the tunnel data showed that the WCPC/BCPC ratio was larger than 1.0 for the smaller particles. The authors suggested that the difference in performance between the WCPC and BCPC, in ambient and freeway tunnel environments, may be due to differences in the instrumentation or differences in particle composition. In addition, Biswas et al.¹¹ observed that the WCPC/BCPC ratio varied with particle concentration, with the WCPC/BCPC ratio being > 1.0 when the particle concentration was below $3 \times 10^4 \text{ cm}^{-3}$ but < 1.0 for higher concentrations ($3 \times 10^4 - 8 \times 10^4 \text{ cm}^{-3}$). Similarly, Mordas et al.¹³ used 15 and 30 nm

silver particles to compare the performance of a WCPC with respect to an electrometer. The results showed that WCPC/Electrometer ratio was > 1.0 for particle concentrations below $3 \times 10^3 \text{ cm}^{-3}$, close to 1 for particle concentrations in the range $3 \times 10^3 - 5 \times 10^4 \text{ cm}^{-3}$ and < 1 for larger concentrations.

The results of the above studies do not support any firm conclusions regarding the reasons behind the observed differences between the WCPC and BCPC. In Biswas et al.¹¹, the chemical composition of the aerosol did not affect the relative particle concentrations recorded by the water and butanol based instruments, however Iida et al.¹² suggested that the chemical properties of the aerosol play a role near the instruments lower size limit, showing a difference in performance for water and butanol based instruments with the same 3 nm nominal detection limit when measuring 3 nm ambient and freeway tunnel particles. Higher concentrations were recorded by the butanol based instrument for ambient air but lower concentrations were recorded for vehicle emissions. Consistent differences in response were observed for a WCPC and BCPC in both Biswas et al.¹¹ and Mordas et al.¹³, where the WCPC consistently counted more particles than the BCPC under lower concentrations, but counted fewer particles at higher concentrations. Further comparisons of WCPC and BCPC performance are needed to investigate the impact of differing aerosol types near the lower cut-off sizes of the instrument.

Table 1. Commercial CPCs and their specifications.

Water-Based CPCs									
Manufacturer	Model	Size range (nm)		¹ Conc. range (p/cm ³)		Response time to 95% conc. (sec)	² Flow rate (lpm)		Working fluid
		From	To	From	To		Aerosol flow	⁵ Inlet flow	
TSI	3781	6	> 3000	0	5 x 10 ⁵	< 2	0.12 ± 0.012	0.60 ± 0.12	water
TSI	³ 3782	10	> 3000	0	5 x 10 ⁴	< 3	0.60 ± 0.06		water
TSI	⁴ 3785	5	> 3000	0	1 x 10 ⁷		1.0 ± 0.1		water
TSI	3786	2.5	> 3000	0	1 x 10 ⁵	< 2	0.3	0.60 ± 0.03	water
Alcohol-Based CPCs									
TSI	³ 3010	10	> 3000	0.0001	1 x 10 ⁴		1.0 ± 0.1		N-butyl alcohol
TSI	^{2,3} 3022A	7		0	9.99 x 10 ⁶	< 13	0.3 ± 0.015	1.5 ± 0.15 (H) 0.3 ± 0.015 (L)	N-butyl alcohol
TSI	^{2,3} 3025A	3		0	9.99 x 10 ⁴	< 1 (H), < 5 (L)		1.5 ± 0.15 (H) 0.3 ± 0.03 (L)	N-butyl alcohol
TSI	^{1,3} 3760A	11	> 3000	0.0001	1 x 10 ⁴	< 3 (decreasing conc.) < 1.5 (increasing conc.)	1.5 ± 1.5		N-butyl alcohol
TSI	^{1,3} 3762	11	> 3000	0.0001	1 x 10 ⁴	< 1.5 (decreasing conc.) < 1 (increasing conc.)	3.0 ± 0.3		N-butyl alcohol
TSI	3771	10	> 3000	0	1 x 10 ⁴	3	1.0 ± 0.05		N-butyl alcohol
TSI	3772	10	> 3000	0	1 x 10 ⁴	3	1.0 ± 0.05		N-butyl alcohol
TSI	² 3775	4	> 3000	0	1 x 10 ⁷	4 (H), 5 (L)	0.3 ± 0.015	1.5 (H), 0.3 (L)	N-butyl alcohol
TSI	² 3776	2.5	> 3000	0	3 x 10 ⁵	< 0.8 (H), < 5.0 (L)	0.05 (with 0.25 lpm sheath flow)	1.5 (H), 0.3 (L)	N-butyl alcohol
TSI	3790	23	> 3000	0	1 x 10 ⁴	< 5	1.0		N-butyl alcohol
TSI	3007	10	>1000	0	1 x 10 ⁵	< 9	0.1	0.7	isopropyl alcohol
GRIMM	² 5.401	4.5	> 3000	0	1 x 10 ⁷	3.9 (at 90%)	0.3	1.5 (H), 0.3 (L)	N-butyl alcohol
GRIMM	² 5.403	4.5	> 3000	0	1 x 10 ⁷	3.9 (at 90%)	0.3 (with 3 lpm sheath flow)	1.5 (H), 0.3 (L)	N-butyl alcohol
GRIMM	5.412	23		0	1.2 x 10 ⁴	≤ 4	0.6		N-butyl alcohol
Kanomax	¹ 3885	10		0	~105		4.2 ± 0.4		Propylene Glycol

- Notes: ¹ External vacuum pump used in TSI 3010, 3760, 3762, 3771, 3772; Kanomax 3885.
² For some CPCs, high and low flow modes available which stated with H or L in the bracket.
³ Discontinuous models
⁴ TSI 3785 also marketed as Quant Technologies 400
⁵ Inlet flow equals aerosol flow plus transport flow.

3.2 Particle size distribution

3.2.1 Differential Mobility Particle Sizer /Scanning Mobility Particle Sizer

Particle size distribution in the submicrometer size range is generally measured with a differential mobility particle sizer (DMPS) or a scanning mobility particle sizer (SMPS). Component systems feature an electrostatic classifier with a differential mobility analyser (DMA) that selects the size bins and a condensation particle counter (CPC) that counts the number of particles in each bin. The sample first passes through a bipolar ion neutralizer which uses a radioactive source such as Kr-85 or Po-210 to ionize the particles into positive and negative ions and brings their charge level to a Fuch's equilibrium charge distribution. The charged and neutral aerosols next enter the DMA where they are deflected by an electric field. Only particles within a narrow range of electrical mobility and, therefore size, are allowed to pass through an open slit into the CPC. In the DMPS, the voltage giving the electric field is increased in discrete steps to cover the entire particle size distribution to be measured. In the SMPS, the voltage is continuously ramped over a user-selected period of time. Associated software controls instrument operation and calculates the number-size distributions, taking into account multiple charge effects and detection efficiency. The versatility afforded by the individual components enables the selection of a system that best fits the sizing requirements. For example, the TSI SMPS's are capable of measuring aerosols in a wide number concentration ranging from $1-10^8$ particles cm^{-3} in varying size windows between 3 nm and 1.0 μm . Data may be acquired in up to 167 size channels. The lower size limit cannot be smaller than the lower size detection level of the CPC which can range from 3 to 23 nm (Table 1) while the width of the size window is controlled by the ratio of the sheath to the sample flow rate which is usually kept around 10:1 L min^{-1} .

3.2.2 Fast Mobility Particle Sizer

The Model 3091 Fast Mobility Particle SizerTM Spectrometer or FMPS marketed by TSI Inc, uses similar technology to the SMPS, namely electrostatic classification within a laminar flow and dynamic scanning, but rather than using a single CPC to detect particles as they exit from a fixed location at the base of the inner electrode, and scanning the mobility diameter across the entire range as occurs in the SMPS, the FMPS detects particles in situ as they reach the outer electrode and does so simultaneously at 22 different locations, greatly reducing the time required to examine the entire mobility range¹⁴. The FMPS achieves this by locating particle counting electrometers at multiple locations along the column. In this way the instrument is able to acquire a full size distribution in as little as 1 second. The instrument also differs from the SMPS/DMPS in that it uses an electrical unipolar ion generator to produce a predictable positive charge distribution on the aerosol instead of the predictable bipolar charge distribution applied in the SMPS/DMPS, which use radioactive source based neutralizers.

The FMPS sensitivity is generally poorer than that of the SMPS and DMPS systems because electrometer signal noise results in a minimum reading equivalent to an apparent particle number concentration of 100 cm^{-3} at the smallest detectable particle sizes, when a 1 second averaging time is used, however this improves to around 50 cm^{-3} for a ten second average. This is the worst case scenario and the sensitivity is better for larger particle sizes. The maximum concentration measurable also depends on diameter but can be as high as 10^7 cm^{-3} at the smallest sizes. The FMPS classifies particles into a total of 32 channels at a size resolution of 16 channels per decade. A total of 20 channels lie in the nanoparticle size range. The sensitivity of the instrument is poorest at the 6nm lower size limit, being 100 cm^{-3} when a 1 s averaging time is used and 50 cm^{-3} when a 10 s interval is used, however this improves to 0.9 cm^{-3} and 0.2 cm^{-3} at 500 nm when a 1 s and 10 s intervals are used, respectively.

3.2.3 Electrical Low Pressure Impactor (ELPI)

The Electrical Low Pressure Impactor (ELPI, Dekati Ltd., Tampere, Finland) ¹⁵ performs both real time size distribution measurement and the simultaneous collection of the size classified material for chemical analysis. Like the FMPS, the ELPI uses a unipolar corona charger to achieve a known aerosol charge distribution and detects particle concentration by using multiple sensitive electrometers, but uses inertial classification rather than electrical mobility to assess particle size. After being charged, the aerosol particles are classified according to their aerodynamic diameter onto a series of impactation stages and a final filter, while electrometers measure the rate at which the particles deliver charge to each stage. The ELPI classifies particles into a total of 12 channels at a size resolution of 4.3 channels per decade. A total of 3 channels lie in the nanoparticle size range. Although it is unable to measure particles in the coarse size range accurately, due to a low total charge carried by these particles, the ELPI can measure the number, mass concentration and size distribution of nanoparticles down to 30 nm, with a good time resolution (of a few seconds) very effectively ¹⁶. The sensitivity is again limited at the lower size limit by lower charge carried by smaller particles being 83 cm⁻³ for the 15 14 nm size classification for the 30 Lpm flowrate of the outdoor ELPI.

3.3 Particle surface area, surface topography and morphology

Total particle surface area is a parameter of interest from a health effects point of view since a good correlation has been found between particle surface area and certain health effects^{17, 18}. However, to date, there is no well established technique to measure it. In this section we review the existing techniques and discuss the different definitions of surface area that each technique measures.

In many cases, airborne particles are not smooth spheres and more commonly they are agglomerates, as is the case for diesel soot particles, and therefore, it is not clear what actually presents the particle

surface. The definition of particle surface that is measured also depends on the measurement method used. In principle, all instruments are based on the attachment of molecules or atoms to the surface of aerosol particles. Some of the definitions coming from different measurement methods are: the BET surface, the active surface and the equivalent surface.

5 The BET method, named after Brunauer, Emmett and Teller, measures the number of adsorption sites available on a particle. This is done by measuring the amount of a gas (most commonly N_2) that can be absorbed on the particle surface and in turn using this value as a measure of surface area¹⁹. Although this method has shown to correlate well with pulmonary inflammatory responses¹⁷, unfortunately it is very time consuming and often difficult to apply.

10 The active surface area is based on the integral collision cross section of the particles. The active surface of a single particle is approximately proportional to the inverse of the particle mobility. The total active surface can be calculated by integrating the measured mobility distribution or it can be measured directly via the adsorption of labelled species onto the particles²⁰. If the labelled species are radioactive atoms, then the method is called the '*epiphaniometer*', and if they are ions, then the method
15 is called '*diffusion charger*'.

The epiphaniometer was developed at the Paul Scherrer Institute²¹. The EPI is based on the attachment of lead atoms (^{211}Pb), produced by the radioactive decay of a long-lived ^{227}Ac source. The number of attached ^{211}Pb lead atoms is then determined by counting the α -decay events of its progeny, ^{211}Bi . It is a very sensitive, but slow instrument, with an integration time of 30 min and a detection limit of 0.003
20 $\mu m^2 cm^{-3}$. Therefore, it cannot be used to measure transient emissions such as those from motor vehicles.

In the diffusion charging sensor (referred to as DC), positive ions from a corona discharge diffuse onto the particles. After passing through the charging section of the instrument, the aerosol passes by an ion

trap electrode, to which a low voltage is applied, and this removes the remaining ions. The charged particles are then precipitated onto an electrically insulated filter. The filter current yields the ion attachment rate (number of ions attached in unit time), which is proportional to the active surface of the particle ensemble as shown by Konstandopoulos et al.²². The DC yields the same information as the epiphaniometer, but it is much faster and simpler to use, such that the response time is short enough to allow transient measurements. On the other hand, the DC is also significantly less sensitive, with a lower detection limit. This is because potential high particle charges have to be avoided, in order to avoid artifacts which may result from the repelling Coulomb force. The detection limit of around $1 \mu\text{m}^2/\text{cm}^3$ is sufficient for direct measurement of emissions from sources, such as vehicles and ambient air measurement in urban areas.

As the most common method of characterizing particle size is the measurement of number size distribution by mobility analysis, the surface area can be calculated from the measured number size distributions. In this case, the calculated surface area yields a mobility equivalent surface (i.e. the surface of spherical particles having the same size distribution as the measured ones). This surface area is easy to determine but in many cases has no physical meaning.

Particle morphology and surface topography can be examined directly using Scanning Electron Microscopy (SEM). SEM uses a high energy electron beam to scan the surface of a sample resulting in the production of secondary electrons as well as characteristic X-Rays, as atoms in the sample surface are ionised. Back scattered beam electrons can also be detected. Each of these signals can be independently examined. When secondary electron imaging is used the surface of particle and provides depth of field as well as resolution down to a few nanometres. Hence SEM is very useful for examining the surface structure of nanoparticles and the nanostructure of larger particles. Alternatively the back scattered electron signal can be used to produce an image in which intensity is proportional to the atomic numbers of element within the particle surface. Characteristic X-Rays representing specific

elements, are also produced when the electron beam removes inner shell electrons from the atoms in the particle surface and these can be used to probe the elemental composition within regions on the particle surface.

TEM can be used to image particles with much greater resolution than SEM, achieving lateral resolutions of fractions of a nanometre, however the technique is used for examining particle structure rather than surface topography. The sample is illuminated with a beam of high energy electrons and an image formed on film from the transmitted electrons. As with SEM characteristic X-Rays can be used to examine elemental composition.

3.4 Particle Light Scattering and Absorption

Nanoparticles play an important role in the Earth's radiation balance, directly through their ability to absorb and scatter light, and indirectly when they act as cloud condensation nuclei (CCN) and thereby alter cloud albedo and lifetime. Measurement of the potential for particles of various sizes to act as CCN is usually achieved through the use of CCN counters. These instruments determine the CCN content of bulk aerosol without discrimination in terms of the initial particle size and hence are not nanoparticle monitoring instruments as such.

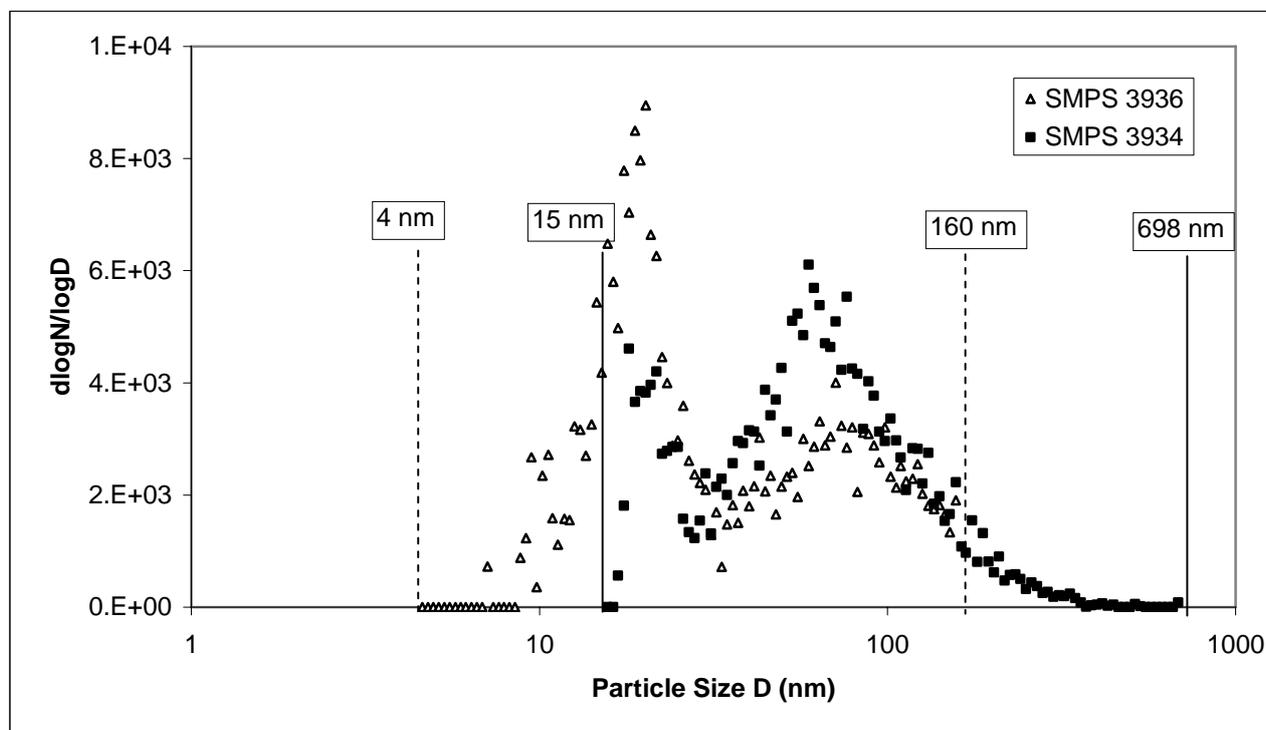
Light scattering relevant to the direct effect is commonly measured non-size-selectively using the integrating light scattering nephelometer. This is also a bulk method which does not distinguish between scattering by nanoparticles and by larger particles or by gases. Light scattering and absorption by bulk aerosol is typically dominated by those particles larger than the wavelength of the light so that nanoparticles typically make only a minor contribution to the overall signal. Hence measurement of the direct effect for nanoparticles is not usually sought.

Light absorption can be measured by collecting nanoparticles on a filter as is the case in black carbon measurements, and a number of instrument exist for this purpose, however light scattering and absorption by nanoparticles accumulated on a filter may not be representative of their behaviour when suspended in air²³. Instruments which assess optical properties for suspended particles typically become insensitive when particles are smaller than the wavelength of the radiation in question, making them ineffective at diameters of less than a few hundred nanometres.

3.4 Comparison between CPC and SMPS number concentration monitoring in the environment

Over the last twenty years, the CPC and SMPS have emerged as the most popular instruments for monitoring particle number concentration in the environment. While the CPC is used to measure total particle number concentration, the SMPS provides number-size distributions within given size ranges. Most of the published reports on environmental particle number and number-size distribution have used instruments manufactured by TSI Incorporated. In interpreting the results from these instruments, a parameter that is of crucial importance is the lower end of the measurement size range. This lower size limit is determined both by instrumental factors and operator decisions. For example, the lower size limit of the CPC is determined by the capability of the instrument and ranges from 3-23 nm (Table 1). However, the lower end of the detection window of the SMPS is set to a value above this, in the range from 10 – 30 nm, which is up to 10 nm higher than the achievable lower limit. This is done to achieve a compromise as to the overall size of the window. The loss of a few nanometres at the lower end enables a significant extension of the window at the upper end. This is generally a desirable option when monitoring submicrometer particles in the environment. However, when a study specifically focuses on nanoparticles and formation of secondary particles through nucleation, it is preferable to use a narrower window with a lower size cut-off. The TSI Model 3936 SMPS, for example, can be used with a 3085 nano differential mobility analyser (DMA) and a Model 3025 CPC to monitor

particles in the size range 3-150 nm. Where a number concentration within a specific size range is required (for example below 100 nm), it is sometimes possible to extract this information from a measurement of particle number size distribution in a broader size range.



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Figure 1. Particle number-size scans obtained by the authors with two different SMPS's in a rural outdoor environment. While the SMPS 3936 is able to detect the full nucleation mode centred at 18 nm, the SMPS 3934 is not able to do this due to the higher lower size cut-off. The lower and upper size cut-offs of the two instruments are shown as pairs of broken lines (3936) and solid lines (3934).

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Figure 1 shows the particle number size distributions obtained simultaneously by the authors in a rural outdoor environment using two different SMPS systems. The 3934 operated on a size window of 15-698 nm while the 3936, using a nano DMA, was set at 3-160 nm. Note that, while it counts particles up to a much larger size, the 3934 loses its detection efficiency at the lower end of the window and is

unable to see the complete nucleation mode centred at about 18 nm, which is clearly detected by the SMPS 3936 with the nano DMA. We believe that this nucleation mode occurred due to the photo-oxidation of biogenic precursors as it lasted only for a few hours close to mid-day and was shown to consist of volatile substance that evaporated completely when passed through a thermodenuder heated to 200°C. The total ambient particle number concentration was about 3800 cm⁻³. The count median diameters reported were 59.5 nm and 24.9 nm, for the SMPS 3934 and 3936, respectively. This large difference is a direct result of the different size detecting ranges employed and illustrates the importance of caution when comparing results from various instruments.

Where only a CPC is used, the outcome of the measurement is the total particle number concentration in the detection size range of the instrument. In interpreting this result, there are two important aspects to be considered. Firstly, the result does not reflect the nanoparticle concentrations, unless specific inlets are employed to restrict the range of particles entering the sensing volume of the instrument. Secondly, as stated earlier, the detection range of the CPC often extends to lower sizes than the window set by the SMPS. Therefore, CPC's are able to detect particles in the earlier stages of nucleation, and the presence of the nucleation mode which is below the size detection limit set by the SMPS. As a result, CPC's would detect more particles than the SMPS, the difference being significant in environments where a nucleation mode is frequently present.

This fact is often overlooked when comparing particle number concentrations, specifically nanoparticles, reported in different studies using instruments with different size range windows. In order to assess the impact which these differences have on the reported particle number concentrations, data from 60 studies reporting total particle number concentrations in a wide range of environments was compiled and the results grouped according to the instrumentation used, that is CPC or SMPS. The CPC and SMPS results were extracted from the following papers: Aalto et al.²⁴, Harrison et al.²⁵, Kittelson et al.²⁶ and Shi et al.²⁷ who used both the CPC and SMPS; Vakeva et al.²⁸, Zhu et al.²⁹,

Imhof et al. ³⁰, Paatero et al. ³¹ and Westerdahl et al. ³², Schnieder et al. ³³, Lechowicz et al. ³⁴, Asmi et al. ³⁵, Bergmann et al. ³⁶ and Weimer et al. ³⁷ who used only the CPC and McMurry and Woo ³⁸, Tuch et al. ³⁹, Morawska et al. ⁴⁰, Hitchins et al. ⁴¹, Junker et al. ⁴², Jamriska and Morawska ⁴³, Pitz et al. ⁴⁴, Ruuskanen et al. ⁴⁵, Cheng and Tanner ⁴⁶, Molnar et al. ⁴⁷, Morawska et al. ⁴⁸, Thomas and Morawska ⁴⁹, Wehner et al. ⁵⁰, Zhu et al. ⁵¹, Zhu and Hinds ⁵², Ketznel et al. ⁵³, Longley et al. ⁵⁴, Tunved et al. ⁵⁵, Wehner and Wiedensohler ⁵⁶, Gidhagen et al. ⁵⁷, Gramotnev and Ristovski ⁵⁸, Gramotnev et al. ⁵⁹, Hussein et al. ⁶⁰, Jamriska et al. ⁶¹, Janhall et al. ⁶², Jeong et al. ⁶³, Ketznel et al. ⁶⁴, Morawska et al. ⁶⁵, Stanier et al. ⁶⁶, Gidhagen et al. ⁶⁷, Holmes et al. ⁶⁸, Imhof et al. ⁶⁹, Rodriguez et al. ⁷⁰, Janhall et al. ⁷¹, Virtanen et al. ⁷², Wahlin et al. ⁷³, Woo et al. ⁷⁴, Abu-Allaban et al. ⁷⁵, Laakso et al. ⁷⁶, Hussein et al. ⁷⁷, Mejjia et al. ⁷⁸, Pey et al. ⁷⁹, Barone and Zhu ⁸⁰, Yue et al. ⁸¹, Wu et al. ⁸², Westerdhal et al. ⁸³, Buonanno et al. ⁸⁴ and Minoura et al. ⁸⁵ who used only the SMPS. Other studies, such as Hameri et al. ⁸⁶ and Kaur et al. ⁸⁷, which measured particle concentration without using a CPC or SMPS (e.g. P-trak etc.) were not included in the analysis, nor were the four tunnel studies, Abu-Allaban et al. ⁷⁵, Gpuriou et al. ⁸⁸, Jamriska et al. ⁶¹ and Imhof et al. ⁶⁹.

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The mean concentrations measured by the CPC's and SMPS's were $58.7 \times 10^3/\text{cm}^3$ and $50 \times 10^3/\text{cm}^3$, respectively, and the median concentrations were $28.3 \times 10^3/\text{cm}^3$ and $21.4 \times 10^3/\text{cm}^3$, respectively. In other words, the mean and the median CPC measurements were 17% and 32% higher than the SMPS measurements, respectively. The difference in median concentrations was analysed using a Students t-
20 test and found to be statistically significant at a confidence level of over 99%. These differences are expected to be larger for environments where a nucleation mode is present and smaller where aged aerosol dominates. It is, therefore, important to take these differences into consideration when attempting to establish quantitative understanding of variation in particle concentrations between different environments, which is of significance for human exposure and epidemiological studies.

Both CPC and SMPS have been also employed in engineered airborne particle characterisation. There have been a handful of studies conducted in the work environment of several nanotechnology facilities where engineered nanoparticles are formed, which included measurements of size distribution, concentration, mass, and physico-chemical characterisation of the particles ⁸⁹⁻⁹³. Most of these studies, which were conducted in the ambient air of the facility (not just inside the particle reactor), showed an increase in particle concentration, which was usually higher closer to the production site. This elevation in concentration - even if it is not large - is of significant concern, due to unknown health effects of these particles. However, as concluded by the Royal Academy of Engineering ⁹⁴, experience with occupational monitoring during nanoparticle production is still in its infancy, with many uncertainties regarding an appropriate metric and empirical method.

4. Measurements of Nanoparticle Elemental Composition

Chemical characterization of airborne nanoparticles is important, since, in addition to size particle chemical properties further influence the impacts of the particles on human health and global climate ⁹⁵⁻⁹⁷. Several recent reviews have discussed the methods used for chemical characterization and their application to atmospheric chemistry ⁹⁸⁻¹⁰⁴, however these methods often are difficult to implement in the nanometre size range due to the small mass of the particles involved. The purpose of this section is not to describe in detail the operation principles of the different available techniques capable of measuring nanoparticle composition, but to compare and discuss their strengths and limitations.

4.1 Offline Measurements

The most direct method for the chemical analysis of aerosols is to pass a sample flow through a filter and analyse the collected material in the laboratory using well-established analytical procedures. A common method of analysing the sample collected on the filter is to dissolve the material in water or

another solvent, and analyse the solution using regular analytical methods, including gas chromatography–mass spectrometry (GC-MS), ion chromatography (IC) and/or proton nuclear magnetic resonance (HNMR). The sample can also be analysed in situ, without transferring it to water or other solvents, by using X-ray fluorescence, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and/or secondary-ion mass spectrometry (SIMS). Chow ¹⁰⁵ discussed suitable filter materials for various analytical methods, species sampling artefacts and analytical techniques that can be used for various species.

Although filters are inexpensive and easy to use, and they have been widely used in traditional atmospheric chemistry in the past, unfortunately, the very small mass of nanoparticles has posed a new challenge when using this sampling technology to determine their size-dependent chemical composition. As a result, when collecting size-classified nanoparticles for chemical analysis, impactors are the most frequently used devices ¹⁰⁶⁻¹⁰⁹. For example, the NanoMOUDI (Nano-micro-orifice Uniform Deposit Impactor, MSP Corp, Shoreview, MN, USA) can collect particles classified by aerodynamic diameter down to 10 nm ¹¹⁰. The second generation of MOUDI includes 10-13 stages covering the size range 0.01 – 18 µm and up to 6000 micro-orifice nozzles as small as 50 µm diameter are used in the 30 L/min Model 122 to reduce pressure drop, jet velocity, particle bounce and re-entrainment ¹¹¹. To achieve enough mass for laboratory analysis, the NanoMOUDI ambient sampling process generally need to continue for days. In order to shorten this sampling time, Geller et al. ¹¹² utilized a USC Ultrafine Concentrator to concentrate nanoparticles by a factor of 20-22 before the NanoMOUDI sampling. This system was employed to collect enough nanoparticles in 3 consecutive 3 h time intervals (i.e. morning, midday, and afternoon) for examining diurnal variations of size-fractionated ultrafine particle chemistry in the Los Angeles Basin.

Advantages of impactors include their relatively high sampling rate, simplicity of operation and compatibility of sampling substrates with commonly used analytical methods. Bounce is a major

disadvantage of using impactors to collect nanoparticles, as they rely on the particles sticking to the substrates when they impact, and after impaction, the dislodged particles become re-entrained in the air flow, such that they are then able to deposit on subsequent stages.

In addition to impaction, electrostatic precipitation is another effective sampling method for collecting nanoparticles. For example, the Nanometer Aerosol Sampler, consisting of a grounded cylindrical sampling chamber with an electrode at the bottom of the chamber, can be used to sample aerosols that have been conditioned and positively charged, like those from the output of a DMA, onto sample substrates for further analysis, such as SEM/TEM and GC-MS¹¹³⁻¹¹⁵. The instrument is designed to collect 2-100 nm particles and the size of the captured particles can be controlled using two electrode sizes, in order to get a uniform deposition size that is optimal for the particular analysis system. The electrostatic precipitation technique can also be used as a sampler in some online analysis instruments (discussed below). One limitation of these off-line methods is the poor time resolution associated with collecting a large enough sample for bulk analysis. Gas-phase partitioning after collection and contamination during handling are other issues that also need to be considered.

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4.2 Online measurements

The on-line measurement of particles avoids potentially significant sampling artefacts caused by the evaporation, adsorption and chemical reaction of particulate species which can result when aerosols remain on substrates for long periods of time¹⁰⁰, and also from gas-particle partitioning after collection

20 ¹¹⁶.

4.2.1 On-line bulk sampling and analysis methods

A more general approach has also been used for the automated and in-situ sampling of aerosols by absorption into water, using the Particle Into Liquid Sampler (PILS)¹¹⁷, the Steam Jet Aerosol

Collector (SJAC) ¹¹⁸ or the Semi-Continuous Measurement System for Ionic Species (SCMSIS) ¹¹⁹. Particles grown by supersaturated water are impacted on a surface, over which water continuously flows and an ion chromatographer (IC), with a suitable detector, is employed to periodically analyse the collected water sample to give the quantitative soluble ion composition of the aerosol with a high time resolution (minutes). NH_4^+ , K^+ , Na^+ , Mg^{2+} , Cl^- , NO_3^- , SO_4^{2-} , as well as some short-chain organic acids, can be measured in this way and the collection efficiency for particle diameters between 0.03 - 10 μm is greater than 97% ¹¹⁷. Recent improvements in the design have enabled measurements down to 10 nm diameter ¹²⁰.

Thermal desorption aerosol GC-MS/FID (TGA) is another novel continuous measurement method ¹²¹⁻
¹⁰ ¹²³. Nanoparticles are collected in bulk, by impaction onto a cooled surface, which is then isolated after collection and heated, vaporizing the components either for total mass concentration by GC-FID (flame ionization detector) or for compound identification by GC-MS. This method can be used to measure the organic fraction of aerosols with a one hour time resolution. Overall, these automated instruments are less labour-intensive and more suitable for continuous monitoring. The inherent
¹⁵ limitation of the online bulk sampling instruments, however, is that they cannot provide any information regarding size-dependent distribution of chemical compounds because size-resolved data are not available ¹¹⁶.

4.2.2 Real-time mass spectrometry of aerosols

²⁰ In order to improve the source apportionment of atmospheric particles and determine causality between potential toxic particles and increased human morbidity, a comprehensive approach that simultaneously characterizes single particles for aerodynamic diameter and chemical composition is needed in place of bulk chemical analysis ¹²⁴. Due to its high sensitivity, mass spectrometers are often used when studying single particles in the atmosphere ¹²⁵. Although it has been recently demonstrated

that laser induced breakdown spectroscopy, coupled with an aerodynamic lens, is able to determine the elemental composition of metal nanoparticles ¹²⁶, real-time aerosol mass spectrometry (RTAMS) is the most widely used technique capable of simultaneously sizing and speciating single aerosol particles in situ. Since Davis ¹²⁷ began the online chemical analysis of single particles using a Surface/Thermal Ionization Mass Spectrometry over 35 years ago, scores of RTAMS with different approaches have been developed and applied to various laboratory and field measurements. Two reviews provided a chronological survey of the RTAMSs and discussed their design principles and operation ^{128, 129}. However, two main challenges emerge when these methods are extended to nanoparticles. One is how to achieve efficient sampling of particles from air under ambient atmospheric pressure into the high-
10 vacuum environment of a mass spectrometer source, the other is the small particle mass ¹³⁰. Due to these limitations some existing RTAMS cannot be used for nanoparticle measurement. For example, the Aerosol Composition Mass Spectrometer (ACMS), developed by Schreiner, can only detect particles with a diameter greater than 300 nm ¹³¹. Table 2 lists the name, measurement technology, detection limit and selected publications relating to those RTAMS with the capacity to measure
15 nanoparticles. This list is not exhaustive, but represents a wide spectrum of the novel techniques used in the nanoparticles field. All of the abbreviations for the instruments and methods mentioned in this paper (including those listed in Table 2) can be found in Table 3.

Table 2. Instruments capable of measuring nanoparticles composition using mass spectrometry

Instrument	Vaporization & Ionisation ^a	Mass spectrometer	Sizing ^b	Optimum size range	Species	Detection limit	Selected literature
AMS	Thermal-EI	Quadruple	PA	40-1000nm	SO ₄ , NH ₄ , NO ₃ & Organics (nonrefractory)	~ 2 µg/m ³	132, 133
A-TOFMS	Single laser	Bipolar RETOF	POA	30-3000 nm	SO ₄ , NH ₄ , NO ₃ & Organics	< 1 µg/m ³	134, 135
IT-AMS	Thermal-EI	3D Quadruple Ion Trap	PA	60 – 600 nm	Nitrate, sulphate	0.16 µg/m ³ for nitrate 0.65 µg/m ³ for sulphate	136
NAMS	Single laser	RETOF	NA	7-25 nm	Atomic composition	10 ⁵ particles/cm ³	130, 137, 138
Particle Blaster	Single laser	RETOF	NA	17 – 900 nm	Atomic composition	NA	139
PIAMS	Single laser	RETOF	POA	< 300 nm	Organic	50-500ng/m ³	140
RSMS III	Single laser	Bipolar Linear TOF	MA	50 – 750 nm	Nitrate, sulphate, carbon, metal	NA	141-143
SPLAT I/II	Dual laser	RETOF	POA	50-3500/125-600 nm	Atomic composition	NA	144, 145
SI-PBMS	Thermal-SI	Quadruple	NA	14 - 1000 nm	Alkali metal	10 ³ atoms	146
TD-CIMS	Thermal-CI	Triple quadruple	NA	6 - 20 nm	Molecular composition	50 pg/m ³	147-151
TDPBMS	Programmable thermal-EI	Quadruple	NA	20-500 nm	Molecular composition	~ 0.1 µg/m ³	152, 153

^a SI, surface ionization; EI, electron impact ionization; CI, chemical ionization;

^b NA, not available; PA, Polydisperse aerodynamic; POA, Polydisperse opto-aerodynamic;

Table 3. List of Instrumental and Method Abbreviations

ACMS	Aerosol composition mass spectrometer
ADL	Aerodynamic lens
AMS	Aerosol mass spectrometry
ATOFMS	Aerosol time-of-flight mass spectrometry
B/WCPC	Butanol / water based condensation particle counter
CPC	Condensation particle counter
DMA	Differential mobility analyser
DMPS	Differential mobility particle sizer
ELPI	Electrical low pressure impactor
FMPS	Fast mobility particle sizer
GC-FID	Gas chromatography-flame ionization detector
GC-MS	Gas chromatography–mass spectrometry
HNMR	Proton nuclear magnetic resonance
HR-TOF	High resolution TOF mass spectrometer
IC	Ion chromatography
ICP-MS	Inductively coupled plasma mass spectrometer
INAA	Instrumental neutron activation analysis
LDI	Laser desorption/ionization
LIF	Laser-induced fluorescence
MALDI	Matrix-assisted laser desorption ionization
NAMS	Nanoaerosol mass spectrometer
NanoMOUDI	Nano-micro-orifice uniform deposit impactor
PERCI	Photoelectron resonance capture ionization
PIAMS	Photoionisation aerosol mass spectrometry
REMPI	Resonance enhanced multiphoton ionization
RETOF	Reflecting time of flight
RSMS	Rapid single-particle mass spectrometer
RTAMS	Real-time aerosol mass spectrometry
SEM	Scanning electron microscopy
SIMS	Secondary-ion mass spectrometry
SI-PBMS	Surface ionization particle beam mass spectrometer
SMPS	Scanning mobility particle sizer
SPLAT-MS	Single particle laser ablation time-of-flight MS
TDCIMS	Thermal desorption chemical ionization MS
TDLIBS	Laser-induced breakdown spectroscopy
TDPBMS	Thermal desorption particle beam MS
TEM	Transmission electron microscopy
TGA	Thermal desorption aerosol GC-MS/FID
TD-GC×GC- TOF/MS	Thermal desorption coupled to comprehensive gas chromatography-time of flight mass spectrometry
VUV	Vacuum ultraviolet

There are currently two transportable aerosol mass spectrometers that are commercially available and able to be used for field measurements: the TSI model 3800 Aerosol Time of Flight Mass Spectrometer (ATOFMS) ¹³⁵, which is based on the desorption/ionization of single particles by the 260

nm light from NdYAG laser, and the Aerodyne Research Inc. Aerosol Mass Spectrometry (AMS)¹³²,¹³³, which focuses on a broader range of particle sizes using the continuous electron impact (EI) ionization method. ATOFMS uses a reflecting time of flight (RETOF) spectrometer for collecting both positive and negative ions, and delivers quantitative size and largely qualitative composition information on individual particles. AMS can give quantitative data on both the size and composition of the entire aerosol ensemble, but gives only limited data on specific particles and cannot measure refractory components¹¹⁶. The three versions of the AMS (Q-AMS, TOF-AMS and HR-TOF-AMS) currently in use vary in the type of mass spectrometric detector used, being either a quadrupole mass spectrometer (Q), a TOF mass spectrometer or a high resolution TOF mass spectrometer (HR-TOF).

A typical RTAMS configuration includes three component blocks: (1) sample introduction system; (2) vaporization/ionization source region; and (3) mass analyser. The sample introduction system is one of the most important factors determining whether a RTAMS can be used to measure nanoparticles because if insufficient nanoparticles enter the instrument, no measurements can be conducted in this size range. Vaporization and ionization methods influence not only its capacity to analyse nanoparticles but also the resulting data formats (atomic or molecular mass spectra). This is a very important factor to consider when analysing the composition of organic compounds and/or other refractory matters (salts and metals), or if the number concentration of particles is quite low. All of the three major mass analysers in aerosol mass spectrometers (TOF, quadrupole mass filter and the quadrupole ion trap) can be employed for nanoparticles analysis. However, only the TOF and the ion trap instruments can be used as a true single particle mass spectrometer⁹⁹.

Two methods have been employed to introduce particles into aerosol mass spectrometry. Electrostatic¹⁵⁴ and electrodynamic¹³⁰ fields can be used to transmit and select particles at the lower end of the nanometer size range, less than 50 nm and 10 nm, respectively, which are designated a charge prior to entering the inlet. This method becomes less effective as the particle size increases because the particle

kinetic energy grows too large to handle with electrostatics or electrodynamic alone ¹⁰³. Instead, a so-called aerodynamic lens (ADL) developed by McMurry et al ¹⁵⁵, tends to be more effective for particles at the higher end of the nanometer size range. Generally, ADL consists of a 100 μm flow limiting orifice attached to a 1 cm inner diameter, 30 cm long tube. The particles are gently forced to the centre of the tube while passing through a series of carefully designed and machined apertures before they reach the end of the lens where a 2 mm nozzle accelerates the particles into the next vacuum chamber for measurements ^{156, 157}. It is advertised that TSI 3800-030 ATOFMS, with an ADL, has a transmission of the inlet system from 30-300 nm. The major difficulties in relation to focusing nanoparticles arise from their low inertia and high diffusivity. McMurry et al ¹⁵⁵ also developed a tool to design and evaluate ADL systems. After optimizing certain parameters, the ADL system transfers particles 3–30 nm in diameter with 50-80% efficiency, respectively ^{158, 159}. This technique bridges the gap between particles less than 3 nm in diameter, which can only be focused by an electrodynamic lens, and larger particles which are not easy to focus using electrodynamics ⁹⁹.

There are many more choices than the particle inlet technique when using vaporization and ionization methods in RTAMS. The most popular method is laser desorption/ionization (LDI), which has been employed by ATOFMS. LDI is a single laser technique and has been found to be highly sensitive. It is ideal for measuring salt and metal containing particles, which are very hard to be ionized by other ways. Strong ion signals can be achieved from most types of materials (refractory and semivolatile, organic and inorganic etc), however considerable fragments induced by LDI, can make it difficult to identify the organic compounds in the particles. Some techniques, such as lower pulse energy laser beam and matrix-assisted laser desorption ionization (MALDI), have been used to reduce the fragmentation.

Laser induced plasma is a similar ionization source to LDI except that a much higher laser irradiance is used. It can be used to quantitatively convert particles to atomic cations. Reents et al. ^{139, 160} developed

an aerosol mass spectrometer, the Particle Blaster, using this ionization technique to measure both the complete elemental composition and particle size of individual particles. The instrument can measure particles in the size range of 17 - 900 nm diameter. Zachariah et al ^{161, 162} extended this work and discussed quantitative measurements using the laser induced plasma method.

5 EI as a universal ionization method has also been used in RTAMS. There are three obvious advantages associated with EI ionization: universal detection of all vaporized molecules with similar sensitivity; easy identification of the compounds based on the well-established standard spectra database; and quantification of a molecules concentration relying on the proportionality between the total ion intensity and the total number of electrons in the molecule. However, EI ionization still leads to
10 extensive fragmentation and complex mass spectra and several groups have coupled aerosol mass spectrometers with soft ionization sources to develop methods that reduce this fragmentation, including resonance enhanced multiphoton ionization (REMPI) ¹⁶³, photoelectron resonance capture ionization (PERCI) ¹⁶⁴, Li⁺ ion attachment ¹³², chemical ionization (CI) ^{165, 166} and vacuum ultraviolet (VUV) single photo-ionization ¹⁶⁷. Although these softer ionization techniques have been shown to
15 simplify the complexity of organic mass spectra in both gas-phase and aerosol phase mixtures, the detection limits of most instruments using these methods are not sufficiently low enough to measure single nanoparticles in the ambient environment.

Another method for the real-time chemical analysis of individual aerosol particles is to combine a surface ionization with mass spectrometry (e.g. SI-PBMS) ^{127, 146}. Elements with sufficiently low
20 ionization potentials are ionized in contact with a hot metal surface, and the emitted positive ions are analysed by mass spectrometry. This technique may provide high sensitivity for certain elements in individual aerosol particles and has the potential to quantitatively analyse single nanoparticles down to the size of individual molecules¹⁴⁶. This instrument is very robust and suitable for field measurement applications.

Recently a nanoaerosol mass spectrometer (NAMS) has been designed especially for the real-time characterization of individual airborne sub-10-nm nanoparticles^{130, 137, 138}. The NAMS consists of an aerodynamic inlet, a quadruple ion guide, a quadruple ion trap and a time-of-flight mass analyser. Charged particles in the aerosol are drawn through the aerodynamic inlet, focused through the ion guide and captured in the ion trap. A high-energy laser pulse is employed to completely disintegrate the trapped particles into atomic ions, so that the atomic composition of the particle is attained from the relative signal intensities of the atomic ions.

4.3 Tandem measurements

As summarized by Park et al.¹⁶⁸, more complete information on particle transport and physicochemical properties can be obtained when using multiple instruments in tandem. For example, Cai et al.¹⁶⁹ used a technique that combined MALDI, laser-induced fluorescence (LIF) and a dual quadruple ion trap mass spectrometer. It was demonstrated that the mass spectra of fluorescently labelled nanoparticles with a size of 27 nm in diameter can be acquired by utilizing the unique tandem trap arrangement along with a frequency scan scheme.

In the field of chemical composition of nanoparticles, several instruments have been developed and applied in laboratory and field studies. For example, Neville et al.¹⁷⁰ analysed the combustion-generated particles (down to 10 nm) selected with Differential Mobility Analyser (DMA), using an Instrumental Neutron Activation Analysis (INAA), to determine the size dependence of elemental concentration (e.g. Mg, Ca, Fe, Al et al.). Smith et al.¹⁴⁸⁻¹⁵⁰ also successfully measured the chemical composition of atmospheric aerosols in the 6-33 nm diameter range using a nano-DMA with a 20-min-resolution, in tandem with TDCIMS. Average ion molar ratios for nitrate, organics and sulphur species

were measured, including nitrogen-containing organic compounds, organic acids and hydroxyl organic acids.

DMA can also be used with aerosol mass spectrometry to investigate the composition-dependent mixing characteristics. Park et al.¹⁶⁸ used ATOFMS to sample mobility-classified particles and observed that the particles with same mobility diameter were clearly separated into two groups with different vacuum aerodynamic diameter and with different chemical composition. Okada et al.¹⁷¹ also designed a spectrometer, which consisted of a DMA and inductively coupled plasma mass spectrometer (ICP-MS), to simultaneously measure the size-dependent concentration and chemical composition of nanometer-sized metal particles. For a particle size of 30 nm, the lower detection limit of the spectrometer for particle concentration was about 1×10^5 particles/cm³.

Recently, a novel nanoparticle sampler, which includes up to three UPC-Nano DMA systems in tandem with one electrostatic precipitator, was developed by McMurry et al.¹⁰⁸ to provide sufficient nanoparticle mass for chemical analysis over sampling periods of about 10 min. It was demonstrated that this sampler can collect 150pg of particles with the diameter of about 8 nm per hour, which is comparable to the amount collected by impactors and 100-300 times higher than mass spectrometers that collect particles at low pressure.

Several other instruments can also be used in tandem to measure particle transport and physicochemical properties, without using a DMA. For example, Hamilton et al. used online thermal desorption coupled with comprehensive gas chromatography-time of flight mass spectrometry (TD-GC×GC-TOF/MS) to analyse ambient and laboratory aerosols. Over 10, 000 individual organic components were isolated from around 10mg of aerosol material in a single procedure^{172, 173}.

In many circumstances, the tandem measurement methods are powerful and quite effective. For example, integrating DMA and different RTAMS has the potential to be quite useful when monitoring nanoparticles. At present, the biggest challenge for nanoparticle elemental composition measurement is the specification of individual organic compounds on single particles. The further development of softer ionization techniques, as well as tandem mass spectrometry (MS X MS), will almost certainly provide a better solution to this issue.

4.4 Indirect methods

Accurate time and size resolved data on the chemical composition of ambient submicrometer aerosols using standard methods of chemical analysis has limitations due to the difficulty of collecting sufficient material for analysis, as discussed above. Alternative physicochemical methods have therefore been developed that infer the composition and structure of the particles through indirect measurements. A typical example of such an indirect measurement method is based on the Tandem Differential Mobility Analyser technique (TDMA). The method was first introduced by Liu et al.¹⁷⁴ with the aim of studying the change in particle electrical mobility (diameter) due to a specific aerosol process with which the particles were conditioned. The authors named the system an aerosol mobility chromatograph. The term that is used today to refer to this measurement technique (TDMA) was introduced years later by Rader and McMurry¹⁷⁵.

The basic design of any TDMA consists of 2 DMA's, a conditioning device and one or two CPC's. The first differential mobility analyser (DMA) selects a narrow size distribution of particles centred on a set electrical mobility. This quasi-monodisperse particle size distribution is then "processed" within a conditioner and the change of the particle diameter and/or size distribution due to the conditioning is measured by a second DMA in conjunction with a CPC. The second DMA with the CPC can operate either as a Scanning or Differential Mobility Particle Sizer S(D)MPS. The term TDMA comes from

the fact that there are two DMA's used in tandem. In general the second DMA, as well as the conditioning process, can be replaced by another device that measures a different particle property such as mass, morphology, composition, aerodynamic size, etc. A detailed review of these tandem techniques has been recently published ¹⁷⁶.

5 There are a number of different ways the particles can be conditioned/processed in between the first size classification and the second size measurement. By far the most common way is to expose the dry selected particles to a well-defined relative humidity (RH) and to measure the water uptake of the particles, a set-up which is known as hygroscopicity TDMA or H-TDMA. The water uptake is measured through the distribution of growth factors (*Gf*) or sometimes called the growth factor
10 probability density function (*Gf*-PDF). The hygroscopic growth factor, *Gf*, is the ratio of humidified (d_w) to dry particle diameter (d_d) at a well-defined relative humidity RH. The H-TDMA's have been extensively used in various environments. A detailed review of the H-TDMA techniques and their applications in various environments has been recently published by Swietlicki et al. ¹⁷⁷. Duplissy et al. ¹⁷⁸ give a more technical overview with an intercomparison of several H-TDMA models. The authors
15 also propose a more standardised application of the H-TDMA techniques aiming at high data quality and data comparability. The importance of the inversion procedure to obtain the full information from the *Gf*-PDF has been recently shown by Gysel et al. ¹⁷⁹. They also propose a standardization of the H-TDMA inversion scheme and provide an excellent discussion of the measurement errors in TDMA systems. Although there algorithm has been developed for H-TDMA systems it can be used in other
20 TDMA arrangements.

The Organic TDMA (O-TDMA) has a similar setup to the H-TDMA but instead of water vapour the particles are exposed to an organic vapour, such as ethanol ¹⁸⁰. The uptake of ethanol is proportional to the organic content enabling estimates of the organic fraction in even the ultrafine newly formed particles^{181, 182}. The Volatility TDMA, on the other hand, exposes the size selected particles to a

controlled elevated temperature. The volatilisation (reduction in the size of the particle after heating) of particles is measured as a function of temperature. The technique provides a suitable tool to measure online physico-chemical properties of aerosol particles with a high size resolution by heating the aerosol (typically up to 300°C). Where the aerosol particles are composed of a mixture of several chemical species with differing volatilisation or decomposition temperatures, the volatilisation curve shows distinct features associated with the removal of various components and the volume fraction of these components can be calculated. Comparing with laboratory measurements of “pure” species the chemical composition of the aerosols can be inferred. The technique has been extensively used for atmospheric measurements from characterising the presence of sulphuric acid in marine aerosols¹⁸³, nucleation events in the urban¹⁸⁴ and marine¹⁸⁵ environments as well as diesel exhaust¹⁸⁶.

The hygroscopic and volatile measurements have been recently combined into one instrument the volatile and hygroscopic TDMA (VH-TDMA)¹⁸⁷. Although several versions of the technique have been developed^{188, 189} the main goal is to measure the change of the hygroscopic properties as the more volatile components are evaporated from the particles. In this case more information on the composition of the particles can be inferred. The technique has been successfully applied in various environments such as marine environments^{188, 190, 191}, free troposphere¹⁹², smog chamber measurements¹⁹³ as well as diesel exhaust¹⁹⁴.

It is important to point out that TDMA measurements can only infer the chemical composition of the aerosols and should be used in conjunction with other online techniques for aerosol composition measurements such as the Aerodyne Aerosol Mass Spectrometer (AMS).

5. Monitoring design considerations

There are many different settings, as well as types of environments, where airborne nanoparticles are present and monitored. The settings include nanoparticle source emission characterisation, examples of which are vehicle emission testing or monitoring processes in a reactor where particles are engineered.

5 The environments include the outdoors, ranging from clean background to very polluted air as well as indoor environments, including residential buildings, non-industrial workplaces and occupational workplaces where the engineering of nanoparticles takes place. When developing an experimental design for nanoparticle monitoring under these different conditions, several factors need to be taken into consideration, including the fact that:

- 10 1. Particle concentrations could be very high, exceeding the range of the instruments used and thus, requiring the application of a dilution system ¹⁹⁵;
2. Variation in some operation parameters may lead to very rapid variations in source emissions ^{196, 197};
3. Spatial variation of particle concentration could be very high, under certain circumstances
15 exceeding an order of magnitude within a few meters of distance ^{25, 27, 51, 198};
4. Temporal variation in particle concentration may reach several orders of magnitude in seconds ^{74, 197};
5. Rapid formation of secondary nanoparticles may occur and the sampling process itself may actually affect this process ^{199, 200};
- 20 6. Initial size of the newly formed nanoparticles could be below the size detection limit of the instrument used and therefore, they may pass undetected or they may be detected only if they grow to sufficiently large sizes; and
7. Losses of particles could occur within the sampling system and sampling lines ^{201, 202}.

While an in depth discussion of the above aspects of nanoparticle monitoring is outside the scope of this review, several comments are made below in relation to the impact of monitoring design on nanoparticle formation, as well as on the monitoring requirements stemming from spatial and temporal variation in particle concentration. For further information, the reader is also referred to Baron & Willeke²⁰¹.

5.1 Impact of monitoring design on particle formation and losses

An example of a monitoring process where design may have a significant impact on particle formation is motor vehicle exhaust sampling. The exhaust plume, composed of thousands of particle, gaseous and vapour pollutants, often exits the exhaust pipe at the temperature of up to several hundred degrees Celsius. As it cools down and it is diluted by the ambient air and/or the clean, filtered air of a dilution system, rapid particle nucleation and/or condensation of vapours on the surface of existing particles (condensation seeds) may occur. Therefore, large discrepancies have been observed when comparing the results of particle number concentrations measured directly from vehicle exhaust. While particle volume/mass showed reasonable reproducibility between different studies, results of particle number measurements (with the vast majority of them being nanoparticles) were difficult to reproduce, even in the same study. Some artefacts and poor reproducibility in vehicle emission measurements were due not only to the different instruments used but also to the fact that the majority of particles (in terms of number) belonged to the nucleation mode and were formed in the process of dilution. The number of particles formed in the nucleation mode is very sensitive to the dilution conditions and small changes (of the dilution temperature, for example) can result in a significant change in particle number concentration. A detailed discussion on the effects of dilution conditions on sampling and measurements of particle numbers in vehicle emissions can be found in Kasper et al²⁰³. In order to develop a reproducible and comparable method that could be used in laboratories around the world, the

UNECE-GRPE Particulate Measurement Program (PMP) was formed, with a focus on the future regulation of nanoparticle emissions from light duty vehicles and heavy duty engines, with the goal of amending existing approval legislation to stipulate an extensive reduction of particle emissions from mobile sources²⁰⁴. Based upon the recommendation of the PMP, the European Commission has added a particle number limit to its Euro 5/6 proposed emission standards for light-duty vehicles. Only solid particles are counted, as volatile material is removed from the sample, according to the PMP procedure.

The monitoring design can also affect the measured concentration and size distribution by contributing to particle losses. Impaction losses, and gravitational settling which are important considerations in handling larger particles are less important for nanoparticles, however as particle size decreases, diffusion becomes more important, increasing the rate of particle deposition on the walls of the sample inlet tubing. Hence the sample inlet must be designed to minimise the sample residence time. Hence the tubing used to carry the sample to the instrument must be kept as short as possible. The flow rate may also have to be increased through the use of an auxiliary flow pump at the instrument end to augment the flow generated by the instrument.

5.2 Spatial and temporal variation in particle characteristics

A recent review⁴ showed that the average levels of particle number concentration in clean outdoor environments (not affected by anthropogenic activities) are of the order of $2.67 \pm 1.79 \times 10^3 \text{ cm}^{-3}$, while levels at urban sites are 4 times higher and levels at street canyons, roadside, road and tunnel sites are 27, 18, 16 and 64 times higher, respectively. Thus the range of concentrations between clean and vehicle effected environments spans over two orders of magnitude. Of importance in relation to particle monitoring is that it is often only a very small shift in time or space between these very different environments. For example, Kaur et al.⁸⁷ showed that there is a considerable variability in

UF particle exposure, of up to an order of magnitude above background, within a few seconds and over a few metres as people move through the polluted microenvironments. The study investigated exposures of volunteers walking or travelling by bus, car or taxi, along two busy roads and carrying P-Trak Ultrafine Particle Counters (TSI Model 8525). Similar conclusions were derived by Gouriou et al.⁸⁸ who showed that particle concentration encountered by car passengers may present high peaks, up to 10^6 particles cm^{-3} . An example of spatial variation in particle concentration in indoor environments is given by Ning et al.²⁰⁵, who showed that significant spatial variation in indoor particle number concentration was present even before the air was well mixed.

To account for temporal variation, monitoring should be conducted for a sufficiently long period of time to include changes in source operation (indoor or outdoor), meteorological parameters variation (outdoor), and operation of ventilation system (indoor). To account for spatial variation in particle concentration, two design options are available: either employing several sets of instruments, which could be prohibitive due to the costs, or the designation of a reference site, which would enable measurements with only one or two sets of instruments. In the later case, particle concentration is measured at the reference site either during the whole monitoring campaign, or the monitoring alternates between the reference site and the other sites. In the former case, two sets of instruments are required²⁰⁶, and in the latter case, it is done with only one set of instruments²⁰⁷.

20 **6. Summary**

The demand for quantitative methods to characterise airborne nanoparticles has led to significant progress in the design and manufacture of the fast response instruments required for detecting individual nanoparticles and their characteristics. This review showed that these instruments are now

capable of counting and size classifying the particles in real time, and also of providing insight into particle structure and chemical composition. The new generation of condensation particle counters, time-of-flight mass spectrometers or systems such as Volatilization/Humidification Tandem Differential Mobility Analysers, enable sufficient insight into the physicochemical nature of nanoparticles, so that the science of nanoparticle formation, as well as their post-formation dynamics can be revealed.

Data from the 60 studies reporting total particle number concentrations in a wide range of environments found a statistically significant difference between the median concentrations measured by the CPC's and SMPS's. These differences are expected to be larger for environments where a nucleation mode is present and smaller where aged aerosols dominate. It is, therefore, important to take these differences into consideration when attempting to establish quantitative understanding of variation in particle concentrations between different environments, which is of significance for human exposure and epidemiological studies.

Application of many of these techniques is still in the research domain rather than in everyday use, and requires knowledge and experience to provide meaningful data. It is expected that the coming years will bring further development of the techniques to make them cheaper, more robust and applicable to the diversity of the environments when nanoparticle monitoring is required.

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