Aerosol Particle Size Analysis:
Good Calibration Practices

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Preface

Particle size analysis is extremely important in the characterisation of aerosol ensembles. The transport of such particles (and droplets) is determined by a combination of factors, of which a knowledge of the size distribution is particularly important. Hence, equipment used to measure particle (and droplet) diameters and size distributions need to be operated with competence and confidence. A Manual of Good Calibration Practices has therefore been prepared, with guidance from the National Calibration Forum for Aerosol Analysis (NCFAA) established through a Valid Analytical Measurement Programme (VAM14) of the National Measurement System Policy Unit (NMSPU), UK Department of Trade and Industry. The aim has been to prepare a starting document to aid non-specialists in their understanding, valid operation and calibration of aerosol particle-size analysers, so that the various types of equipment are used correctly and traceable quantitative data are obtained with confidence.

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CHAPTER 1

Introduction

Many of the necessary procedures for the calibration of aerosol instruments are ill-defined and lack proper instructions and documentation. Under normal circumstances, initial calibrations of new instruments are carried out by the instrument manufacturers or their agents, with further calibrations being provided when the instruments are returned to them for cleaning and service. In addition, a very small number of specialist laboratories provide calibration and characterisation services for various aerosol samplers and monitors. However, in a recent survey of user needs (Lewis *et al* (1993)), it was found that 58% of the aerosol instruments used at that time were either calibrated in-house, or not calibrated at all. Clearly this situation is unsatisfactory as the quality of calibration may vary from one laboratory to the next, and there is no co-ordination of these laboratories to establish the extent of the variability. This situation could lead to considerable differences in the measurement of aerosol concentrations and the characterisation of aerosol ensembles. Such inconsistencies are particularly important when sampling is carried out for legislative purposes to determine whether a workplace or an environmental emission complies to laid-down standards. It is also important in the quality control of some industrial processes.

In recognition of this situation, the National Measurement Infrastructure for Aerosols and Particulates in the Gas Phase was set up by the UK Department of Trade and Industry to coordinate and improve methods employed for the calibration of a range of aerosol instrumentation. This exercise constitutes part of the Valid Analytical Measurement (VAM) programme which has been charged with improving the quality and validity of all analytical measurements made in the UK.

The National Calibration Forum for Aerosol Analysis (NCFAA) forms the driving force for technical advice, supported by a number of technical projects designed to provide a range of certified test aerosol particles and recommended procedures that enable calibration processes to have some degree of traceability.

This manual is intended to provide guidance on the best methods for calibrating aerosol instruments, and represents a product of the NCFAA. Guidance is given in generic terms for eight types of aerosol instrument, with reference to specific dedicated texts for more detailed advice.

1.1 Importance of Calibration

All instruments require some form of calibration to ensure that the results they give relate to the parameter being measured and are of a consistently high quality. Ideally, all measurements should be traceable to a set of primary standards, possibly through the use of secondary standards.

1.2 Terminology

d_{ae}	Aerodynamic diameter
d_{cc}	Circumscribing circle equivalent diameter
d_{ve}	Volume equivalent diameter
d_F	Feret diameter (statistical diameter)
$\bar{d}_g$	Geometric mean diameter
d_M	Martin's diameter (statistical diameter)
d_P	Physical diameter (geometric diameter)
d_{PA}	Projected area diameter
d_{St}	Stokes diameter
d_{DC}	Equivalent diffusion coefficient diameter
d_{EM}	Electrical mobility equivalent diameter
d_{EZ}	Electrical sensing-zone equivalent diameter
d_{LS}	Equivalent light scattering diameter
ξ	Collection efficiency
μ	Gas viscosity
σ_g	Geometric standard deviation
χ	Dynamic shape factor
NCFAA	National Calibration Forum for Aerosol Analysis
NMSPU	National Measurement System Policy Unit
SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
VAM	Valid Analytical Measurement

Other terms and parameters occur only in association with specific equations, and are not included in the above list. Their definition can be more conveniently found in close proximity to the relevant equations in the main text.

1.3 Scope

Up-to-date guidance is given in the following sections on the calibration of a range of aerosol instrumentation techniques. This advice is restricted to the calibration of instruments to measure and/or select the particle size distribution of aerosol ensembles. Although aerosol concentration (number of particles m^{-3} and kg m^{-3}) represents another important ensemble characteristic that needs to be determined with confidence, calibration procedures for this parameter are not included in this document. Such valid measurements could constitute a worthwhile topic in a future manual. Furthermore, no consideration is given to the sampling and transmission efficiences of the instruments (guidance is given in an equivalent document produced during the VAM programme that covers a series of sampling guidelines).

CHAPTER 2

Measurement Techniques

2.1 Particle Size Parameters

Particle size is the most important parameter used to assist in defining the physical characteristics and behaviour of airborne particles. The size distribution of an aerosol ensemble is generally polydisperse, with sometimes up to a one hundred-fold range between the smallest and largest particles (Hinds (1982)). An appreciation of how aerosol properties can vary with particle size is fundamental to the understanding of their behaviour. It is necessary to make use of a 'particulate approach' to characterise aerosol properties in terms of the size of the individual particles which constitute the ensemble.

Aerosol particles are normally sized in terms of a characteristic dimension, or more often a diameter of a 'selectively equivalent' spherical particle. These dimensions are expressed in the units of micrometre and/or nanometre. Some authors size particles in terms of their radius rather than the more usual diameter, although the latter is to be preferred. Aerosols are often described as being in the micrometre ($\sim 1\ \mu$m) and sub-micron size range ($< 1\ \mu$m), and can vary in diameter from 0.001 μm to greater than 100 μm. Dust particles, fungal spores and pollen are generally larger than 1 μm, and fumes and smokes are smaller.

Airborne liquid droplets are spherical (unless under hydrodynamic stress), but solid particles usually have complex geometries which makes the process of describing their behaviour more difficult. Most authors have considered only simple spherical geometries to facilitate the development of mathematical theories in describing aerosol behaviour and related phenomena. It has been necessary to make use of various 'correction factors', usually expressed in terms of a spherical 'equivalent diameter', to characterise mathematically the behaviour of non-spherical particles. In general terms, equivalent diameter is defined as the diameter of the spherical particle that has exactly the same behavioural characteristic as that of the non-spherical particle under consideration. Very often this physical property refers to a parameter which describes the aerodynamic behaviour of the particle.

2.1.1 Geometric Diameters

Microscopic examination of aerosol particles permits *direct* measurement of particle size. This procedure contrasts with *indirect* methods such as sedimentation, impaction, mobility analysis and light scattering, where the particle size is estimated from the measurement of another property which is related to size. Microscopy can be used to obtain 2-D information relating to the shape of the particle, in addition to allowing an assessment of size. The linear measurements that can be made by microscopy can be traced back to accurate optical calibrations using certified calibration graticules or grids. Microscope measurements therefore provide a fundamental basis upon which other aerosol particle measurements can be related. It is necessary to employ these alternative, indirect methods in practice, because microscopy can be rather tedious and expensive.

It is generally found necessary to assign to each particle a size based upon a 2-D projected image or silhouette. For spherical particles this is the diameter of the circular silhouette, but for geometrically complex particles it is necessary to make use of a series of 'equivalent diameters' based on the geometry of the 2-D silhouette. These 2-D based equivalent diameters are geometry dependent, and differ from the more generally applicable property-based 3-D equivalent diameters.

The smallest dimension in a 2-D image is called Martin's diameter (d_M). This parameter is the length of the line parallel to a given reference line that divides the projected area of the silhouette of the particle into two equal parts. This diameter is often referred to as a 'statistical diameter', because the value depends on the orientation of the particle, and only the mean value for all particle orientations is unique for a given particle. In practice, this orientation average is rarely estimated, and it is more common when sizing particles to measure a single d_M for each of the many particles oriented randomly with respect to the reference line.

Another statistical diameter is the Feret diameter (d_F), which is the length of the projection of the image of the particle along a given reference line, or the distance between left and right tangents that are perpendicular to this reference line.

The most commonly used equivalent diameter is the projected area diameter (d_{PA}), which is the diameter of the circle that has the same area as the projected image of the particle. This is a useful measurement because, in the 2-D sense, it is independent of the orientation of the particle. Many investigators find that the circumscribing circle equivalent diameter (d_{CC}) is also useful, representing the diameter of the circle which has a perimeter just containing the outline of the irregular particle. Once again this diameter is independent of particle orientation in a 2-D sense.

The size measurements of irregular, non-spherical particles by microscopy are frequently dependent on the ability to convert the measured 2-D geometric diameters to other equivalent diameters which better describe the behaviour of the airborne particle. Shape factors, for example, can be assigned to many geometries, and these can be used to convert geometry-based diameters into more useful sizes such as the volume equivalent diameter (d_{ve}), which is the diameter of sphere which has the same volume as the non-spherical particle; this parameter can also be associated with the diameter measured by electrical sensing-zone techniques (ranging from 0.5 to 500 μm).

Optical microscopy can be used to carry out geometric measurements in the size range from approximately 0.5 to 50 μm. Smaller sizes require the use of electron microscopy: scanning electron microscopy (SEM) for the range 0.01 to 20 μm diameter, and transmission electron microscopy (TEM) in the range 0.01 to 10 μm diameter.

2.1.2 Equivalent Diameters Based on Behavioural Properties

As opposed to the 2-D dependent geometric equivalent dimensions discussed above, the following equivalent diameters are 3-D dependent, and are related to an equivalence of a selected physical property of the non-spherical particle. The Stokes diameter (d_{St}) is one of the most important examples of the 3-D, property-based equivalent diameters, representing the diameter of a sphere that has the same density and settling velocity under gravity as the particle.

The aerodynamic diameter (d_{ae}) is of somewhat more fundamental importance in obtaining an understanding of the behaviour of airborne particles, and is defined as the diameter of the sphere of unit density which has the same settling velocity under gravitational forces as the particle.

The volume equivalent diameter (d_{ve}), the Stokes diameter (d_{St}), and the aerodynamic diameter (d_{ae}) of an aerosol particle are related in terms of particle density and shape. Under Stokesian conditions, these relationships can be expressed in terms of simple equations. All three diameters can be defined in terms of particle aerodynamic diameter, rather than particle geometry. Aerodynamic diameter is the key particle dimension for describing airborne behaviour such as dispersion, filtration, respiratory deposition, and the performance of many types of air cleaner. Instruments such as the elutriator, impinger, cyclone, centrifuge, cascade impactor and particle relaxation devices use aerodynamic separation or characterisation to measure the aerodynamic or Stokes diameter.

Electrical sensing-zone equivalent diameter (d_{EZ}) has been equated with the volume equivalent diameter (d_{ve}), although d_{EZ} is obtained by measuring the disturbance the particle makes to an electrical field developed in an electrolyte. This disturbance is dependent upon the volume of the particle, but also depends upon the electrical conductivity of the particle and the electrolyte. The method is commonly used to size powders greater than a micron in diameter.

A number of other equivalent diameters are frequently adopted to describe the size distribution of aerosols. Often the utilisation of specific techniques for carrying out measurements is ultimately dependent upon the size range of the aerosol particles under investigation. Over the 0.003 to 1 μm range, for example, the electrical mobility method is used, and the size of the particle is expressed in terms of electrical mobility equivalent diameter (d_{EM}). Particles that have been electrically charged by diffusion under well-defined conditions acquire a known charge, and a unique electrical mobility is associated with every particle size. The distribution of particle size can therefore be determined by measuring the distribution of electrical mobility.

The diffusion of an aerosol ensemble is the net transport of these particles from a region of higher concentration to a region of lower concentration. This process is controlled by the diffusion characteristics of the particle, and for particles in the size range 0.001 to 2 μm, the diffusion process can be used in laminar flow to achieve separation. The equivalent diffusion coefficient diameter (d_{DC}) can therefore be used to describe the size of small aerosol particles.

Very small particles will increase in size when placed in a supersaturated environment to become micron-sized droplets that can be used to enumerate the original nuclei. Aerosol particles in the range 0.002 to 0.2 μm diameter may be saturated and cooled by adiabatic expansion to create the conditions of supersaturation for subsequent growth. Nuclei will grow to $\sim 10\,\mu$m, regardless of their original size, and the number of droplets and hence nuclei can be determined using condensation particle counters.

Optical measurements of aerosols are extremely sensitive and nearly instantaneous, resulting in no physical contact with the particles. Light scattering by aerosol particles of $\sim 0.05\,\mu$m diameter is described by Rayleigh's theory of molecular scatter. With larger diameter particles, the light scattering process is more complex and may be described in terms of the Mie theory, in which the particle size and the wavelength of light are of the same order of magnitude.

Aerosol particles are illuminated by a beam of light which they scatter and absorb to diminish the intensity. This extinction process involves only the attenuation of the light along the projecting axis, but has been successfully adopted to define the visibility of an aerosol-containing atmosphere. Since it is impractical to analyse the refracted and reflected light scattered from particles smaller than 50 μm, the interaction of light and aerosol particles is described in terms of the angular distribution of the scattered light which is dependent on the refractive index and the size of the particle. The refractive index parameter is dependent on the wavelength of the light, and therefore this parameter should be noted when equivalent diameters are quoted using light scattering techniques.

Standard conventions have been adopted to describe the angular distribution of light scattered by an aerosol particle. Light which deviates only slightly from the incident direction has a small scattering angle and is said to be 'forward-scattering light'; light reflected or scattered back towards the source is called 'back-scattered light'; light can also be scattered anywhere between the two extremes (such as 90° to the incident light). Either type of scattering can be used, under appropriate conditions, to size single aerosol particles in terms of an equivalent light scattering diameter (d_{LS}). Optical counters are particularly effective in measuring aerosol particles in the size range 0.1 to 50 μm.

Table 2.1 *Aerosol analysers—Measurement techniques*

Particle size parameter	*Measurement technique*	*Types of instrument*	*Comments*	*Generic references*	*Example of application*
Geometric diameter	Microscopy	Optical, SEM and TEM	Choice of method dependent on size range to be measured	Bradbury (1991)	Direct measurement of 2-D geometric diameters Application of image analysis for speed
Aerodynamic diameter	Particle relaxation	APS, API, ESPART *etc.*	Dependent on particle density and shape	Wilson and Liu (1980), Marshall *et al* (1991)	Real-time particle size distributions, quality control of powders, sampler tests, monodispersity of test aerosols
Aerodynamic diameter	Inertial separation	Cascade impactors, impingers, inertial impactors, cyclone samplers, centrifuges and inertial spectrometers	Wide range of measurement by appropriate selection of instrument	Hinds (1982)	Size distribution measurements of aerosol drug delivery systems
Stokes diameter	Gravitational sedimentation	Timbrell spectrometer and elutriators/ sedimentometers	Measurements made only under viscous conditions	Timbrell (1972)	Classification of aerosols, and measurement of true d_{ae} through d_{St} and density

(continued)

Table 2.1 *Continued*

Particle size parameter	*Measurement technique*	*Types of instrument*	*Comments*	*Generic references*	*Example of application*
Electric sensing-zone diameter	Electrical sensing, distortion effects of particle volume on electric field	Coulter counter and ELZONE	Closely related to volume equivalent diameter but also dependent on particle conductivity	Coulter sales literature	Measure size distribution of dusts, cells, test materials
Electrical mobility diameter	Particle electrical mobility dependent on surface area	Electrical mobility analysers and differential mobility analysers	Diffusion charging required to establish relationship between particle mobility and size	Liu and Pui (1975), Knutson and Whitby (1975)	Measuring size distribution of particles $< 1 \mu m$ diameter
Diffusion coefficient diameter	Measurement determined by diffusion coefficient of particle	Diffusion batteries and denuders	Used to separate and collect gases or vapours from airborne particulate	Knutson and Sinclair (1979), Hinds (1982)	Sub-micron particles; diffusion denuding to separate and collect gases or vapours from airborne particulate
Light scattering diameter	Single particle light scatter	Optical and laser size analysers such as the Royco and Polytec Many others	ϕ_{LS} dependent on shape and, depending on particle size, on the refractive index of the particle	Pinnick and Auvermann (1979)	Remote sensing of aerosols; fast-acting alarm systems in industrial applications

(continued)