Particle Size Measurements

Particle Size Measurements

Fundamentals, Practice, Quality

Henk G. Merkus

Springer

Drs. Henk G. Merkus
Former Ass. Professor
Delft University of Technology
Park Berkenoord 30
2641 CZ Pijnacker
The Netherlands

Printed on acid-free paper

9 8 7 6 5 4 3 2 1

springer.com

Preface

Following my graduation in physical organic chemistry at the University of Amsterdam, I started to work at the Royal Dutch Shell Laboratories in Amsterdam. My first assignment was research in the field of detergents and industrial chemicals. It was followed by development work on thermal wax cracking for production of $C_2 - C_{14}$ olefins and on acid-catalyzed synthesis of carboxylic acids from $C_3 - C_6$ olefins.

Then, I made a significant change to analytical chemistry, first at Shell's process development department and later in the chemical engineering department of Delft University of Technology. In both departments, there was a large variety of analytical techniques and development of new methods for automated analysis of small process streams. It was the time that gas chromatography conquered the world. In this field, a firm basis was given by Henk Boer, Arie Kwantes and Frits Zuiderweg at Shell Research Laboratories in Amsterdam, both for packed and for capillary columns. The potential of gas chromatography was huge and, therefore, also in Delft, its use increased enormously. Moreover, the growth of this technique was facilitated significantly by the rapidly developing electronics industry. It not only led to digital peak integrators and personal computers but also enabled complex measurement techniques. In addition, I became involved in surface area and porosity characterization of catalysts and adsorbents, on which topic the research had been initiated by Prof. J.H. de Boer.

Then, Prof. Brian Scarlett came to Delft to set up education and research in particle technology. He had a very broad vision for research topics in Delft. The responsibility for particle size analysis came to my laboratory, soon followed by a Malvern 2600 laser diffraction instrument and a Coulter counter. This was the time of modernization of particle size and shape analysis techniques and many conferences on this subject. We in Delft took our part in these developments and also acquired more commercial instruments. We were lucky to have outstanding PhD students to improve the techniques of laser diffraction, dynamic light scattering and image analysis as well as their application for in- and on-line measurement: Arthur Boxman, Sigrun Drescher, Michiel van Drunen, Erik Gommeren, Camiel Heffels, Zhenhua Ma, Evelien Nijman and Alexander Willemse. Moreover, Jan Marijnissen had joined the Delft Particle Technology Group and started research on analysis and synthesis of aerosols. Also several researchers from abroad contributed during a visiting year in Delft to my work: Dan Hirleman, Jusuke Hidaka, Houyuan Liu and

Tatsushi Matsuyama (laser diffraction), Yasushige Mori (sedimentation field flow fractionation), Margarida Figueiredo (electrical sensing zone), Hitoshi Ohya (gold particle preparation) and Lihui Peng (process tomography). Some of the work was directed to technique development, other work to application of the instruments in, for example crystallization, paint dispersion, milling and coarse dust emission (the latter in cooperation with Ernest Vrins). And, of course, we went to conferences where I met many experts from other universities, institutes and companies. It was a fascinating time.

Now, most measurement techniques have been developed as commercial instruments. Of course, some further improvement is still possible, but the really new developments seem to get scarce. There are Particle Characterization Groups in various countries, including one in the Netherlands and the UK, to improve understanding and practice. We participate in ISO to write International Standards for sampling, dispersion, measurement techniques and representation of results to improve standardization and practices. There are Proficiency Testing Schemes to improve the performance of analysts and laboratories. And there are Certified Reference Materials and attempts to certify new materials for calibration and qualification of instruments and for validation of operational procedures. And we were and still are involved in giving courses. Here, we not only teach but also learn from other lecturers and hear from participants about their experiences and problems in characterization of particulate products for industrial, environmental and scientific applications. Altogether, I have come to the conclusion that the first remaining challenge lies in the selection of appropriate characteristic PSD parameters for adequate representation of the behavior and performance of products. This, of course, requires good understanding of the quality aspects of particle sizing results coming from different techniques.

The existing textbooks reflect the development of the field. Most of them deal with the theoretical background of the techniques. Some give overviews of the many applications that presently exist. None of them, however, gives a clear view on the quality aspects of all techniques and deals with problems and solutions related to reach the best practice in the characterization of products through particle size analysis. Therefore, I decided to write such a book, for which I seem to have most of the background from the various tasks, in which I was involved, as well as have sufficient knowledgeable friends. Moreover, it gave me a new challenge after my retirement, which has given me a lot of fun. Of course, it is impossible to write a book completely on your own. I am indebted to many people for their stimulating advice and comments as well as for their good friendship. Most of all, my thanks go to Brian Scarlett (†), Henk Nugteren, Jan Marijnissen, Peter Verheijen, Bas van Laarhoven, Louk Peffer, Loes Schouten, Valérie Butselaar, Ed Jansma (†), Johan Groen, Reg Davies, Robert Finsy, Ralph Haswell, Kari Heiskanen, Kurt Leschonski (†), Maurice Wedd and all PhD and undergraduate students and foreign visitors who gave their contribution to my education. Furthermore, I am grateful to Oliver Bischof, who helped me with the text and figures of aerosol instruments in Chapter 6, to Virgil Marple, who did the same for impactors, to Frank Babick for help on electro-acoustics, to Ton van Duynhoven for assistance on nuclear magnetic reso-

nance and to Maarten Alderliesten, who helped me with the moments of a distribution. Moreover, John Dodds and Michael Stintz were very helpful in providing me with adequate French and German for the multilingual terminology in Chapter 19. Finally, I am indebted to all those companies, who gave permission to reproduce figures from their books, journals and brochures, and to the reviewers of the original manuscript, especially Alan Rawle, for their useful comments on both content and English.

And, last but not least, my wife Addy contributed in a significant way through letting me carry out this hobby.

I wish all readers as much pleasure in the field of particle size measurement as I had. I hope that my book will enable them to select the best particle size parameter(s) and analysis procedure for the given task and that it will contribute to optimum practice in all elements of particle size analysis.

June 2008
Henk G. Merkus

Particle Size Measurement

A large variety of particulate products exists, viz. abrasives, cement, sand, pharmaceutical powders and sprays, margarine, paint, toothpaste, sugar, pulverized coal, catalysts, etc., etc. Their behavior and performance is usually linked to characteristic parameters of the particle size distribution. Therefore, such parameters are often used in product specifications. This is the reason for frequent particle size determinations, for which a variety of techniques has been developed.

The contents of this book concentrate on the practical aspects of particle size measurement in its relationship with adequate characterization of product quality. This is a major difference with existing books, which have a more theoretical approach to particle sizing techniques. Of course, the emphasis in this text still lies with the measurement techniques. For optimum application, their theoretical background is accompanied by quantitative quality features, limitations and problem identification. In the first two chapters, the concepts of equivalent sphere diameters and of characteristic parameters for particle size distributions and particle shape are described. Also, a relation is made to product performance, both during processing as well as in final application. In following chapters, sampling and dispersion of powders is treated, since one or other of them is usually dominant in the overall analysis error. Furthermore, there are chapters on the general aspects of quality for particle size analysis, on quality management, on reference materials and written standards, on in- and on-line measurement, on definitions and multilingual terminology and on the statistics required for adequate interpretation of results. Finally, names and (web site) addresses of relevant institutes and companies in this field are given in an annex.

In view of its structure, this book is well suited to stimulate good practice in particle size measurement for product characterization as well as to support courses on particle size measurement.

<div align="right">Henk G. Merkus</div>

Contents

Chapter 1
Introduction

Contents

1.1   Objectives of This Book

The main objective of this book is to give guidance to good practice in particle size analysis. Good practice starts with adequate understanding of the relationship between the performance of a particulate product and its particle size distribution. Furthermore, it requires good knowledge of the concepts of particle size and its measurement as well as of the background and error sources of sampling, dispersion and measurement techniques. Note that either sampling or dispersion is more often the major error source rather than the size measurement itself.

In the next paragraph of this introductory chapter, the relevance of particle size is illustrated. Also a standardized nomenclature for fineness of powders and their size distribution width is proposed. A later paragraph describes the contents of the book.

Good practice requires:

- quantitative description of product quality requirements
- knowledge of methods for particle characterization
- a plan for sampling/dispersion/characterization.

1.2   Relevance of Particle Size

When we look around us, we observe many particles or particulate materials. In fact, more than 75% of all materials processed in industry are in particulate form. The "particles" may be solid, liquid or gaseous, occurring in any of these three phases. Some are natural, others are industrially processed from natural products, again others are completely synthetic (Table 1.1).

Table 1.1   Examples of particulate materials

• **Dry powders**	sugar, flour, starch, sand, cement, coal, pigments, polymer beads, peas, diamond, toner powder, etc.
• **Liquid mixtures**	emulsions (L/L) + suspensions (S/L)
	milk, butter, margarine, creams, bacteria, blood, paint, etc.
• **Solid mixtures (S/S)**	rocks, sediments, pharmaceuticals, etc.
• **Aerosols (L/G +S/G)**	fog, mist, sprays, etc., which may consist of dust, salt, sand, coal, ore, inhalers, etc.
• **Gas bubbles in medium**	whipped cream (G/L), insulating foam (G/S), etc.

Fig. 1.1 Illustrates that the particle size of natural and industrial particulate materials ranges from nanometers to millimeters. Some products have a (very) narrow size distribution; others show a wide range of sizes.

An example of a cumulative undersize particle size distribution is presented in Fig. 1.2. In this example, some volume-based characteristic features are: mean diameter D_{mean} = 3.29 μm, median diameter D_{50} = 3.00 μm, D_{10} = 1.73 μm, D_{90} = 5.21 μm, and D_{90}/D_{10} = 3.02. Various ways of representation and characteristic features are discussed in Chap. 2.

Fineness of particles and width of particle size distributions are defined differently in different fields of application. In my opinion, it seems best to standardize to:

Fineness (D_{90}):

- Nanoparticles   < 0.1 μm
- Ultrafine   0.1–1 μm
- Fine   1–10 μm
- Medium   10–1,000 μm
- Coarse   1–10 mm
- Very coarse   > 10 mm

PSD width (D_{90}/D_{10} ratio)[1]:

- Monosized   < 1.02 (ideally = 1.00)
- Ultra narrow   1.02–1.05
- Narrow   1.05–1.5
- Medium   1.5–4
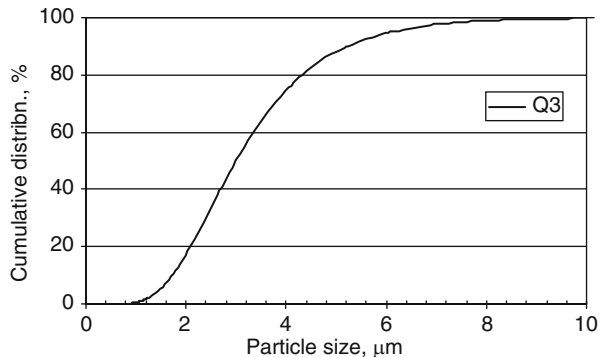- Broad   4–10
- Very broad   > 10

Fig. 1.2   Example of a volumetric size distribution

---

[1] Note that NIST uses the word "monodisperse system" for a collection of particles for which at least 90% lies within a range of 5% of the median size, and "polydisperse system" for a particle collection, where more than 10% differs at least 5% from the median size [8].
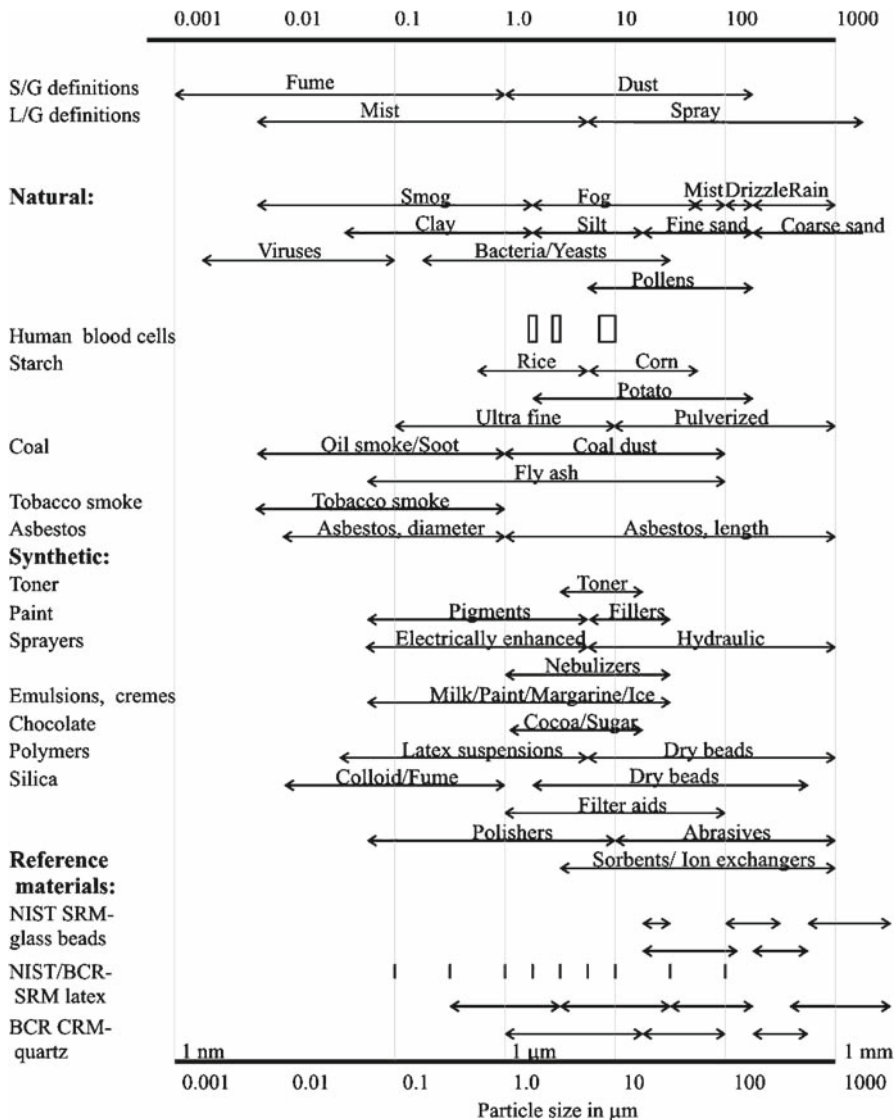
Fig. 1.1 Particle size range of some particulate materials

Note that the D_{90} and the D_{10} in a normal Gaussian distribution are separated by about 2.6 times the standard deviation of that distribution.

The particle size and size distribution (PSD) of particulate products determines—together with particle shape—many properties of these products. The relationships can be grouped in three directions:

- To *quality of processes*, in which particles are produced. Here, size and PSD are coupled to the variables of design and operating conditions of processes, often on the basis of a theoretical or empirical model of the process mechanism (proc-

ess property function). Often, the mean, the median or some "maximum" size is used to express the progress of the process (in terms of "conversion" to a desired product), whereas PSD width and number of modes can be applied to express its quality. The availability of in- and on-line measurement instruments and powerful computers has largely stimulated research in this area (See also Chap. 14).

- To *product properties*, related to further *processing*. Typically, these properties relate to particle size in a so-called "product property function" through laws of physics, in which mass, mass transfer and surface area are involved. A weighted mean particle size can often be applied in such property functions. In cases, where the amount of material in a given size class limits product functionality, this amount or, if possible, the corresponding characteristic size parameter can be used.
- To *product properties*, in a given *application* of the product. Here too, product property functions may be used, although they may be quite complex and empirical due to the complex nature of the relationship. A weighted mean size, the PSD width as well as the amount of material in some defined "critical" size class or, if possible, a corresponding characteristic size parameter may be used in the property function.

Table 1.2 gives some examples of processes and properties involved.

Sometimes, one encounters an example of the influence of particle size on product properties in one's everyday life:

- Compare the poor flowability of powdered sugar with the easy flow of crystal sugar.
- Taste the difference of coffee extracted from different milling grades.
- Notice that sometimes sand dust from a desert travels over thousands of kilometers, for example from the Sahara desert to the Netherlands or even to the USA.
- See the difference between clear pilsner beers and turbid white beers or milk.

Some examples of relationships with industrial relevance are shown in Figs. 1.3–1.8.

The Geldart diagram clearly shows that type C powders with particle diameters below some 20–50 μm are cohesive due to relatively strong attractive forces between particles, meaning that these powders are sticky and show poor flow and fluidi-

Table 1.2 Examples of particulate processes and product properties

Process quality	Product properties	Application
Classification	Dissolution rate, reactivity	Abrasive/polishing properties
Comminution	Drying rate/efficiency	Cement/ceramic strength
Crystallization	Dusting behavior	Dosability fertilizer/pharmaceutical
Dispersion/milling	Explosion sensitivity/severity	Gloss/light fastness paints
Emulsification	Flowability	Suspension viscosity
Filtration	Fluidization possibilities	Taste chocolate/chewing gum
Polymerization	Inhalation/penetration in lungs	Toner quality
Spraying	Segregation	Transparency/hiding power
	Suspension/emulsion stability	

Fig. 1.3 Geldart fluidization diagram [6] (reproduced with permission; copyright John Wiley & Sons Ltd.)
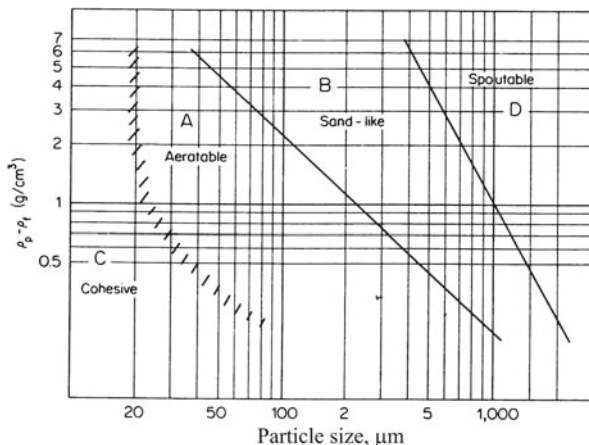

zation behavior. At larger particle size, flow becomes easier, since inertial forces become larger than inter-particle forces. For type A powders, aeration and fluidization become easy: when a stream of air passes through a bed of particles above some minimum flow rate, particles and air mix nicely to a semi-homogeneous mixture, which behaves as a liquid. At again larger particle size (type B and D powders), fluidization becomes more difficult again due to the increased particle mass. This results in so-called spouting beds above about 1 mm particle size, where the air is transported through only one or a few channels in the particulate bed and only the particles at the top of these channels are lifted by the air (are spouting) [5, 6].

At the end of a production process, particulate material often has to be separated from a gas or air stream. Sometimes, the objective is collection of the powder product having a given size range; sometimes, it is (also) particulate reduction in stack gases. Fig. 1.4 shows some typical grade efficiency curves for gas-particle separators [12]. First of all, it is clear that the curves show a fairly slow, gradual increase in efficiency with particle size. Also, it can be concluded that it is advantageous to apply a combination of separator systems working at different conditions or based on different principles, each with its own optimum working range, for collection or reduction of emission of particles having a very broad size range.

Fast dissolution of particles in a liquid is desired in many situations, both in household applications such as sugar in tea or coffee and for pharmaceutical products in the human gastric juices. Fig. 1.5 clearly shows the increase of dissolution rate of phenacetin particles with decreasing particle size (here, after adequate wetting by the presence of a surfactant) [4]. Therefore, particle size is often reduced to increase dissolution rate. This inverse relationship between dissolution rate and particle size is to be expected in view of the increasing specific surface area at decreasing particle size (related to D^2/D^3 or $1/D$).

Often, problems related to surface wetting greatly influence this relationship. The same authors found, for example, that a mass of larger particles of phenacetin dissolved faster in water than the same mass of smaller particles, if no surfactant was added [4].

Fig. 1.4 Typical grade efficiency curves for gas-particle separators [12] (reproduced with permission; copyright John Wiley & Sons Ltd.)
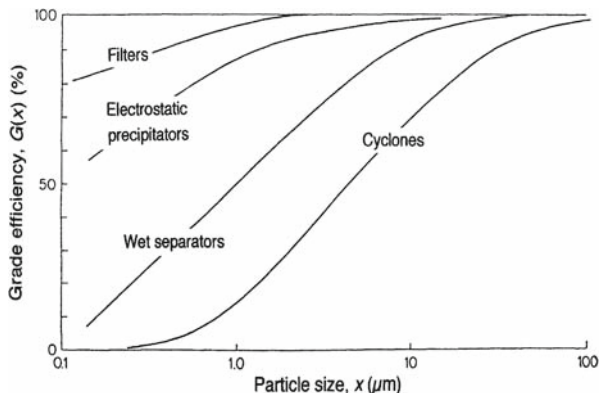

Diffusion in a stagnant layer around the particle has been found to limit evaporation of particles (droplets) in still air [9, 10]. This results in an evaporation rate per unit mass that is proportional to $1/D^2$.

Explosion of dust can lead to great damage. Often, it occurs quite unexpectedly, as the material seems to be quite harmless such as flour, milk powder, wood dust, or metal powder. Fig. 1.6 shows an increase of explosion sensitivity with decreasing particle size through both minimum ignition energy (MIE) and—though to a lesser extent—lower explosion limit (LEL). Also, the severity of the explosion increases, as shown by both the maximum rate of pressure rise and the maximum pressure obtained. Here too, the surface area per volume of particles is the determining property.

For the relationship between scattered light intensity by a single particle and its particle size there are three different regions, as shown in Fig. 1.7. Below a particle size of about 0.1 μm, we find the Rayleigh region where the intensity is related to the 6th power of particle size (volume squared). In the middle part, the intensity gradually increases with size, but with strong fluctuations—this is generally called the Mie region. The width of this region and both amplitude and frequency of the fluctuations are strongly dependent on refractive index of particles and medium and on scattering angle. Above about 30 μm, diffraction is the dominating scattering

Fig. 1.5 Relation between dissolution rate and particle size of phenacetin [4] (in presence of surfactant; size fractions from upper to lower curve: 0.11–0.15; 0.15–0.21; 0.21–0.3; 0.3–0.5, and 0.5–0.71 mm) (reproduced with permission; copyright American Pharmacists Association)
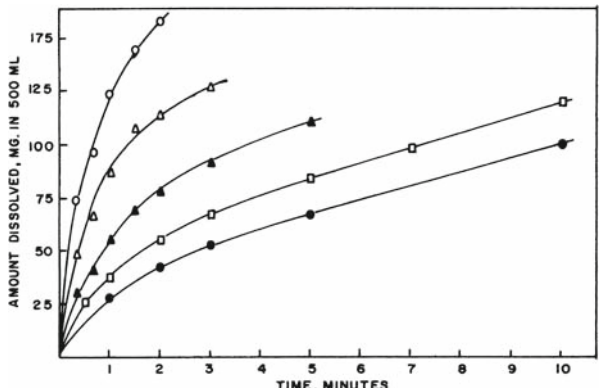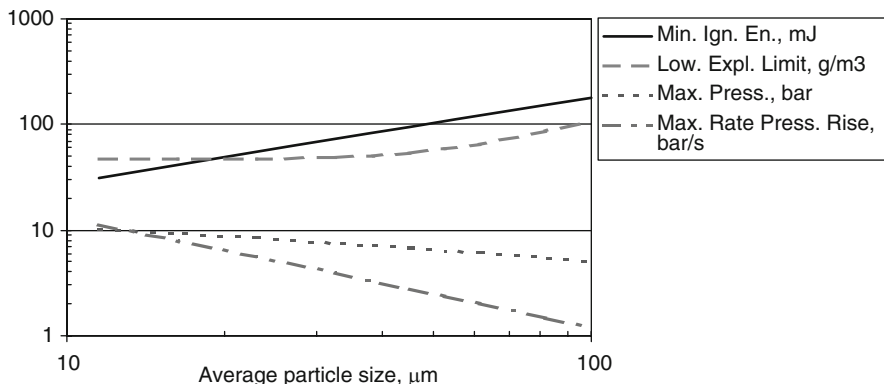
Fig. 1.6 Explosion sensitivity and severity of aluminum powder; after [11]

mechanism, which gives a relationship with the particle diameter squared (cross sectional area). This relationship is not only important for particle size measurement (See Chaps. 6, 10 and 12) but also for product properties such as color and hiding power [7]. Note the differences in color during size reduction of colored pigment particles in a mortar.

Particulate emissions by industrial activities may cause health hazards as well as nuisance to the local neighborhood. Therefore, measurement campaigns are held to quantify these emissions and to minimize them. Fig. 1.8 presents some results of monitoring the concentration of particles having a size range of about 15–100 μm in the vicinity of some coal and ore transshipment companies at the Rotterdam Harbor area (Maasvlakte) in the Netherlands [14]. The results (1-hour averages) clearly show the decrease of the concentration during nights and weekends and, thus, the relationship with loading, unloading and transport activities. In this study relationships between emission and both meteorological and working conditions were quantified. Studies such as these allow effective measures for emission reduction to be formulated.

The above examples show that there is a clear relationship between properties of particulate materials and their particle size distribution, which may be complex.
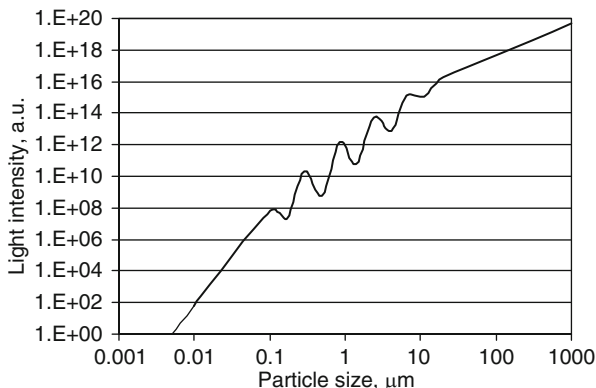

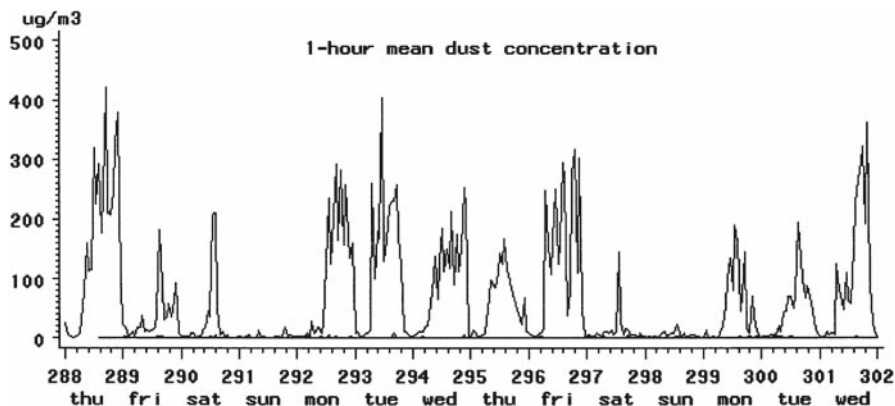**Fig. 1.7** Scattered light intensity versus particle size

Fig. 1.8   Coal and ore coarse dust concentration in the Rotterdam Harbor area [14]

Usually, the product property functions are simplified by using only a single size value of the PSD. Often, the median size or an arbitrary mean size is chosen for this purpose, since these can be determined with good accuracy. This, however, excludes or reduces the influence of the width of the distribution, which exists as well. In my opinion, a weighted mean size (moment) offers the best general solution for this purpose, if particles of all sizes contribute in a significant way to the product properties (See also Chap. 2). Here, the type of both weighting and equivalent diameter should be chosen on the basis of the proven or expected relationship between particle size and product performance, or in other words on the product property function. In this way, the weighting includes the effect of the width of the size distribution. An old example is the application of the area-weighted Sauter mean diameter, for example in equations for atomizing efficiency of sprayers and rate of mass transfer for scrubbers. Some new examples are presented in [1–3, 13]. In cases where the quantity of particles in a specific size class (or larger or smaller than a stated size) determines product quality, this quantity should be measured and applied in relation to quality (after a proper weighting by number, area, etc.). Examples are the number of coarse particles in paint (deteriorating gloss), the amount of near-mesh particles during sieving (that may reduce the sieving rate) and the percentage of small particles during filtration (that may hamper its rate). At the extremes of a PSD, such values can sometimes be converted to a corresponding characteristic size parameter (e.g., D_{90} or D_{10}) for specification purposes. Adequate reasoning on this choice in the property function and/or robust regression analysis is required.

It must be realized, however, that particle shape or particle–particle interactions may play a significant or even dominant role in product performance. Moreover, the influence of particle shape in most particle-sizing techniques limits the possibilities for adequate calculation of a weighted mean size. Finally, different aspects of product performance are often to be satisfied, which may ask for compromises in product composition. This emphasizes that due care is to be given to the selection of measurement technique in relation to relevant size and shape characteristics.

1.3 Set up of the Book

The ultimate goal of a particle size analysis is almost always a measurement of product performance. There are many candidates for relevant parameters related to particle size, shape and porosity. Chap. 2 gives an overview of the possibilities. The various quality aspects of particulate analysis are treated in Chap. 3, together with advice on the design of the total procedure for characterization of a new product for some given application. In the size measurement of many powders, either collection of a sample from a product lot or dispersion of a dry sample in air or in a liquid is the dominant error source. Background and procedures are described in Chaps. 4 and 5, respectively. It is obvious that the procedure and technique used for PSD determination should be sensitive to the changes of the PSD that are relevant for product performance. Chap. 6 gives an overview of the size measurement techniques and their quality aspects, whereas Chaps. 7–13 give more details on techniques that are frequently used or show good potential. In- and on-line measurement for process monitoring and control is of increasing importance for manufacturing processes. Some background is presented in Chap. 14. There exist at present already a large number of national as well as international written standards for particle size analysis. Chap. 15 gives some basic information on these standards. For adequate calibration and qualification of instruments and for validation of measurement procedures, (standard) reference materials are required. They are treated in Chap. 16. In the modern world, good quality management accompanied by maximum self-criticism is a must. The background to this is given in Chap. 17. Although definitions and symbols are given in the relevant chapters, Chap. 18 is added, in which the main definitions, abbreviations and symbols, used in the field of particle technology, are summarized. Moreover, a terminology translation from English into French, German, Spanish and Dutch and vice versa is given in Chap. 19, to facilitate reading of this book by non-native English readers. The final Chap. 20 gives basic statistical concepts, relevant to size measurement and to hypothesis testing and, thus, for testing whether a given product has the required quality at a given significance level.

For more information, references to other books and articles are included in the various chapters. In some chapters, some exercises are given to improve understanding. In Annex I, names and addresses of the most important institutes and companies related to particle size measurement are given.

1.4 Definitions, Abbreviations and Symbols

Aerosol	dispersion of liquid or solid particles in a gas (usually air), which is usually stable over long periods of time
Dispersion	(preparation of) mixture of primary, non-clustered particles in another phase
Emulsion	(stable) dispersion of small liquid droplets in another, immiscible liquid

Foam	dispersion of gas (air) bubbles in a liquid or solid
Mean size	arithmetic mean particle size for a given population of particles, weighted according to number, volume, etc. (synonym to average size)
Measurement method	short description of the essential points of a measurement procedure
Measurement technique	(description of) principle and specific configuration of a measurement instrument
Median size	particle size at the point in the cumulative size distribution, where 50 % of the particles is smaller and 50 % larger
Particle	discrete piece of material
Particulate material	material consisting of particles
Powder	mixture of dry, solid particles
Procedure	written document describing all details of one or more operational steps (primary sampling, sample splitting, dispersion, instrument calibration and/or qualification, measurement, method validation and/or reporting) in the characterization of a particulate product property, leading to one or more specified parameter(s) with specified quality, either or not standardized
Protocol	written document describing the goals of analysis/testing, the required quality, the total procedure and the way of reporting for adequate characterization of a defined product property
Suspension	dispersion of solid particles in a liquid, in which they are not soluble
D	particle size (equivalent diameter)
D_{10}	particle size at the 10 % point of the cumulative, undersize PSD (other subscripts represent other percentile values, e.g., the 90 % point)
D_{50}	median particle size
G	gas
L	liquid
PSD	particle size distribution
S	solid
SOP	standard operating procedure
s	estimated standard deviation from a series of measurement results (absolute value for precision)
v	coefficient of variation (relative value for precision, standard deviation divided by related mean value, expressed as fraction or percentage)
ρ	density
ρ_{p}	effective particle density
ρ_{f}	fluid density
σ	true standard deviation

Bibliography

1. M. Alderliesten, Part. Part. Syst. Charact. *19* (2002) 373–386.
2. M. Alderliesten, Part. Part. Syst. Charact. *21* (2004) 179–196.
3. M. Alderliesten, Part. Part. Syst. Charact. *22* (2005) 233–245.
4. P. Finholt in L.J. Leeson and J.T. Carstensen, Dissolution Technology,1974 Publ. Dev. Corp. Whitlock Press Inc., USA, p. 108.
5. D. Geldart, Powd. Technol. *7* (1973) 285.
6. D. Geldart (ed), Gas Fluidization and Technology, 1986 Wiley & Sons.
7. F. Hund, Chem. Ing. Techn. *38* (1966) 423–428.
8. A. Jillavenkatesa, S.J. Dapkunas, L.-S.H. Lum, Particle Size Characterization; NIST Special Publication 960–961, 2001 NIST.
9. I. Langmuir, Phys. Rev. *12* (1918) 368–370.
10. H.W. Morse, Proc. Am. Acad. Sci. *45* (1910) 363–367.
11. J. Nagy, H.C. Versakis, Development and Control of Dust Explosions,1983 Dekker.
12. M.J. Rhodes, Introduction to Particle Technology,1998 Wiley & Sons, p. 176.
13. A.P. Tinke, K. Vanhoutte, R. De Maesschalck, S. Verheyen, H. De Winter, J. Pharm. Biomed. Anal. *39* (2005) 900–907.
14. E. Vrins, H.G. Merkus, B. Scarlett; Determination of Relationship between Dust Emission and Dust Plumes (in Dutch), 1998 ICES/VRMO/TUDelft report.

Chapter 2
Particle Size, Size Distributions and Shape

Contents

Abstract: Only for spheres, the size of a particle can be represented by a single parameter, being e.g., its diameter. For the description of a particle of any other shape more parameters are required. Many different descriptors exist. They can be directly related to visual or microscopic measurement, such as length or breadth, or they are based on the concept of equivalent sphere, yielding the diameter of a sphere that shows the same behavior as the particle or group of particles under consideration. Measurement of particle size by different principles may lead to different results for the same group of non-spherical particles. Examples of equivalent sphere diameters are equivalent sieve (or near-mesh) diameter, Stokes' diameter and volume diameter. Usually, the particles in a particulate product do not have the same size but a distribution of sizes. Here too, there are different possibilities for quantitative description. One example is a size distribution, based on number, volume or mass of the particles. Other possibilities are a mean size, a single or a small number of descriptors in the middle or at either side of the distribution, or parameters of a model-distribution. The choice of descriptors for particle size and size distribution should be made such that they give the best discrimination for the quality of the particulate product with respect to given properties or for characterization of a production process. If these properties also depend on particle shape, shape and shape distribution should be characterized in addition to size. This can be done in qualitative terms, such as fibers or flakes, or in quantitative terms, such as elongation, roundness, angularity, surface rugosity, percentages of given model shapes, or fractal dimension. Finally, the porosity of particles may play a role in their behavior. This chapter describes some of the many possibilities that exist.

> **Good practice requires:**
>
> - good data on PSD, shape, surface and porosity of product
> - known relationship between performance and PSD
> - adequate choice of PSD parameter(s)
> - the reasoning for this choice.

2.1 Particle Size

In the ideal world of particle characterization, all particles would be homogeneous spheres. Moreover, they would have uniform properties such as density, chemical composition, color, and opacity. Then, all size measurement methods would yield the same size for a particle, being its diameter, and the same particle size distribution (PSD) for a collection of particles, regardless of the principle applied in the technique. It will be clear that such particles would constitute the ideal standard reference material for particle size measurement methods. It will also be clear that this world would be rather dull.

In the real world, most particles are not spherical, but have different shapes and often rough surfaces. Materials of different chemical composition have different properties (e.g., density, conductivity, refractive index) and, even when the bulk
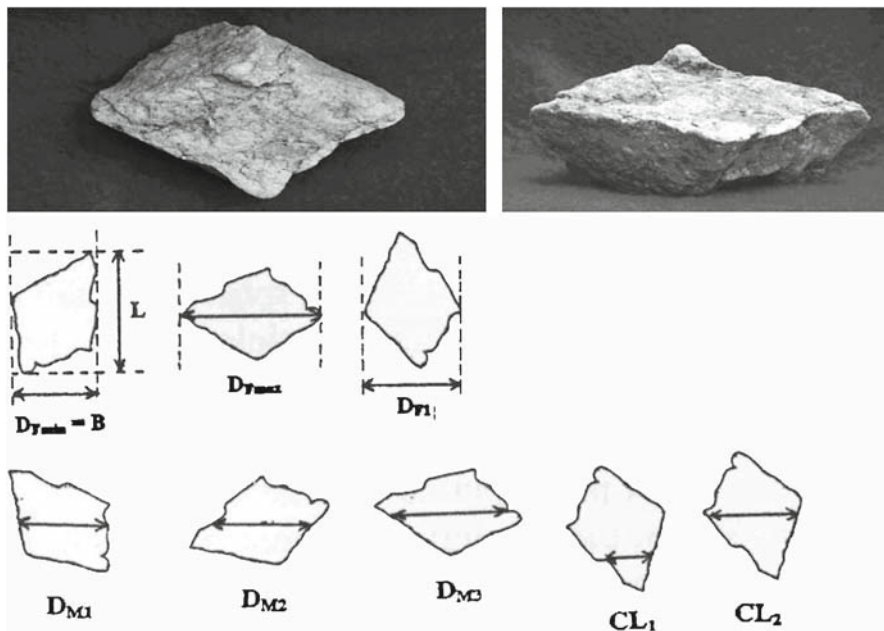

Fig. 2.1 Vertical (l) and horizontal (r) projection of a particle in most stable resting position, together with some Feret and Martin diameters and chord lengths

composition is the same, different crystal structures or impurities may lead to different properties. These differences have a different influence in the principles that are responsible for appearance and behavior of particles, for example color and flow properties, but also behavior during sieving, sedimentation or light scattering. Consequently, different PSDs will often result from different techniques. This is what makes the real world colorful, exciting and challenging, not only for people in general but also for those dealing with particle characterization [22, 25, 40, 55, 56].

In the early days of particle characterization, when light microscopy was often used, some characteristic size of a particle was determined. Some of these characteristic sizes are illustrated in Fig. 2.1.

Feret diameter, D_F	distance between two parallel tangents on opposite sides of the image of a randomly oriented particle (sometimes, the average value over many orientations is used)
Martin diameter, D_M	diameter of the particle at the point that divides a randomly oriented particle into two equal projected areas (sometimes the average value over many orientations is used)
Breadth, B	minimum Feret diameter of the projection of a particle, when it is resting in its position of maximum stability
Length, L	Feret diameter perpendicular to the breadth (in some literature, the maximum Feret diameter is meant)
Chord length, CL	distance of intersection of a particle, starting at a randomly chosen point at the perimeter in a random direction
Thickness, T	height of a particle when it is resting in its position of maximum stability

Of course, both Feret and Martin diameter are dependent on the orientation of the particle with respect to tangents or bisection. Thus, a single measurement has little significance. However, when all possible orientations of the particle projection are taken into account, there is, for convex particles, a relationship between the mean Feret diameter $<D_F>$ and the particle perimeter P according to the second Cauchy theorem [31]:

$$< D_F >= P / \pi$$

If the particle is not convex, there is no such relationship between the mean Feret diameter and the perimeter.

A similar relationship is given by the first Cauchy theorem between the mean projected area in different particle orientations <A> and the particle surface area S [27]:

$$< A >= S / 4$$

The minimum Feret diameter is best used to describe the breadth of a particle's projection, when resting in its most stable position [37, 41]. The length of the particle can be defined in that projection as the distance between the two tangents perpendicular to those of breadth. Sometimes, however, the maximum Feret diameter is taken as

length. The thickness is the height in the most stable position. Breadth and thickness then define the minimum aperture size of a sieve through which the particle can pass—that is if the particle is capable of taking an optimum position for passage.

The chord length is a special case, since even a sphere can be represented by a set of different chord lengths. In general, chord lengths of a particle can range from zero to its maximum Feret diameter. The curvature of particles, however, often leads to a smaller range of chord lengths, e.g., because only part of the reflected beams may be caught by the detector. Still, if the response of an instrument to the curvature of particles is known, many particles are being measured in a random way and statistic requirements are fulfilled, then a series of chord lengths can be related to particle size and, thus, used for characterization (given particle shape). A drawback of all these characteristic lengths, however, is that they give only a single dimension per particle, where the other dimensions may be important as well for its behavior. Moreover, these characteristic lengths are usually not well suited to describe PSDs. On the other hand, distributions of these characteristic lengths can sometimes be used to monitor or control a particulate process.

The equivalent sphere concept has been introduced in the field of particle technology to enable PSD measurements for collections of particles in a less ambiguous way. Here, an arbitrary particle and its equivalent sphere have identical properties in relation to a given principle. The diameter of the equivalent sphere characterizes the size of that particle. The nice consequence of this concept is that an arbitrary particle can still be characterized by a single size parameter, the equivalent sphere diameter[1]. When the linear dimensions of the arbitrary particle all change by a constant factor—and, thus, the particle shape remains unchanged—then the diameter of the equivalent sphere changes by the same factor. For example, when all linear dimensions of a particle double, then the equivalent surface diameter and the equivalent volume diameter also double, although the surface increases fourfold and the volume eightfold. When another principle is involved in the measurement of the same arbitrary particle, then the diameter of the sphere with equivalent behavior often is different. Sometimes, the behavior of a non-spherical particle in a measurement technique corresponds to a single equivalent sphere. This is the case for the volume-equivalent sphere or when the particle has a specific orientation during analysis. Examples are microscopy, sieving and sedimentation. But, for example, in laser diffraction, different orientations of a non-spherical particle may occur, giving different scattering patterns, which are averaged during analysis. Thus, non-spherical particles of a single size may yield here a size distribution, where the smaller size corresponds to that of the smaller cross section and the larger size to that of the larger cross section. Some examples of equivalent diameters are given below and in Fig. 2.2. A consequence of the above is that the same collection of particles may and often will yield different PSD's coming from different measurement techniques.

---

[1] ISO 9276-1 [1] recommends the use of symbol x or D for this diameter. In this book, the symbol D will be used.

Fig. 2.2 Equivalent sphere concept for arbitrary particles
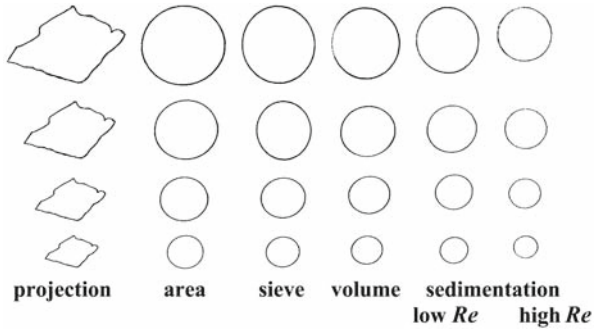
Equivalent projected area diameter, D_A — diameter of a circle having the same area as the particle's projection

Equivalent surface area diameter, D_S — diameter of a sphere having the same surface area as the particle

Equivalent volume diameter, D_V — diameter of a sphere having the same volume as the particle

Equivalent sieve (near-mesh) diameter, D_{Si} — diameter of particles that just pass through the apertures of a sieving medium (near-mesh diameter; sometimes, calibrated or nominal aperture size of sieve)

Stokes' diameter, D_{St} — diameter of a sphere having the same settling rate as the particle under conditions of Stokes' law

Often, the area equivalent diameter is larger than the other equivalent diameters. The sieve diameter is usually smaller, since a particle can pass the sieve apertures in an orientation, represented by its smallest cross section. Generally, the Stokes' diameter is again smaller, since the larger surface area of the particles causes an increased drag (resistance) during settling. Moreover, some particles take a preferred orientation of maximum cross section perpendicular to the direction of flow, resulting in maximum drag. Note that the increased drag force at high Reynolds number (Re) causes the sedimentation diameter at high Re to be smaller than the Stokes' diameter (low Re).

The volume equivalent diameter has the advantage that it relates to the volume or the mass of the particulate material. Therefore, equal volumes of various particles were taken as the basis in Table 2.1 for calculation of some of the size parameters discussed above.

The data clearly show the similarities and differences in the various equivalent sphere diameters. For compact particles having an aspect ratio close to 1, such as cubes and granules, the equivalent diameters are similar. Since spheres have the lowest surface area per unit volume, compact particles have a D_S close to, but slightly larger than D_V. D_A may both be smaller and larger than D_V, depending on the particle's projection. Elongated particles show significantly larger values for

Table 2.1 Equivalent sphere diameters for various particles having the same volume ($D_{V,rel}$[a] = 1; volume = 10^{-6} cm^3 = 10^{+6} μm^3)

Shape	Dimensions, l×b×h or l;diam, μm	D_A rel.[a]	D_S rel.[a]	D_{Si} rel.[a]	L, μm	B, μm	T, μm	D_{Fmax}, μm
Cube	100×100×100	0.91	1.11	0.81	100	100	100	141
Sphere	124	1	1	1	124	124	124	124
Granule	172;86	1.11	1.10	0.69	172	86	86	192
Granule	108;108	0.99	1.07	0.87	108	108	108	153
Granule	Flat projection	0.87	1.07	0.87	108	108	108	108
Disk	68;137	1.10	1.10	1.10	137	137	68	137
Thin disk	23;234	1.88	1.46	1.5–1.9	234	234	23	234
Flake	215×215×21.5	1.96	1.52	1.4–1.7	215	215	21.5	304
Column	232×93×46	1.33	1.23	≥0.8[b]	232	93	46	250
Needle	585×58×29	1.68	1.46	≥0.5[b]	585	58	29	588
Fiber	6,828;13.7	2.78	2.46	—	6,828	13.7	13.7	6,828

[a] Relative to sphere
[b] Depends on sieving conditions

both D_A and D_S than for D_V. Sieve diameters depend on the size of the smallest cross section if optimum particle position during sieving can be realized. Thus, their ratio to D_V is smaller than 1 if the cross section of the particle is smaller than that of the equivalent volume sphere. Large differences between the various diameters exist for very elongated or flaky particles (large aspect ratios).

As discussed above, different particle sizes and size distributions may result from the different techniques available, for non-spherical particle ensembles having an aspect ratio much larger than 1. Moreover, different types of size may be relevant in different aspects of application. Therefore, an important product or process requires adequate attention for the choice of an appropriate particle size (linear dimension or some equivalent diameter) that can be measured with adequate quality (See Chap. 3) for characterization of that product or process or for application in its property functions. Note that often measurement quality dominates in this choice.

Usually, an identical density for the particle and its equivalent sphere is assumed. There are two exceptions, however. The first one is in the *aerodynamic diameter* of aerosol particles. Here, the density of the equivalent sphere is assumed to be 1,000 kg/m^3. The second exception is in the *hydraulic diameter* of sediments. Here, the density of quartz (2,650 kg/m^3) is assumed. These assumptions are often necessary since the densities of different particles in aerosols and sediments may be different and/or unknown.

In the world of geologists, the Phi-notation (Φ) for particle size is often used [22, 55]:

$$\Phi = -log_2 D(mm)$$

where D(mm) is the particle size in mm.

Table 2.2 Correlation between Φ and D

Φ	D, μm	Φ	D, μm
0	1,000	4	**63**
1	500	5	**31**
2	250	6	**16**
3	125	7	**8**

Table 2.3 Correlation between D_{Si} and mesh number

Aperture size, $D_{Si}\,\mu$m	Mesh number ASTM E11	Mesh number Tyler series	Mesh number BS 410:1962
38	400	400	—
45	325	325	350
63	230	250	240
125	120	115	120
250	60	60	60
500	35	32	30
1,000	18	16	16

Table 2.2 clearly shows the inverse relationship between Φ and D for some values of Φ.

In some countries, e.g., USA, it is still common to use the mesh number to indicate the size of woven-wire sieve apertures as well as of the size fractions obtained by sieve analysis [11]. The number of apertures (or wires) per linear inch defines this mesh number. It will be clear from this definition that the relationship between aperture size and mesh number is an inverse one. A severe drawback of the mesh number as size indicator is that the corresponding size is dependent on the wire diameter, which has changed in the past and varies in different countries. Correspondingly, several sieve series exist. Some examples are given in Table 2.3.

The characteristic size for a specific application is to be chosen such that it is easily analyzed with adequate quality and best relates to the property of interest of the particulate product or process. Often, this relation is not straightforward. Then, the choice should be based on thorough investigation.

2.2 Particle Size Distributions

A collection of particles always shows a PSD, since there are always some deviations during their generation or production. Sometimes, these deviations are small and all particles have nearly the same size: the PSD is narrow. According to NIST, the particles are called monodisperse if at least 90% lies within 5% of the median size (See Chap. 1 for classification of PSD widths). Often, however, PSD's are broad

and the larger and smaller particles vary in size largely. Now, the size distribution of the particles is called polydisperse. Sometimes, the sizes differ by a factor of 10 or more. It will be clear that the surface of these particles then has a difference of more than a factor of 100 and the volume and mass more than a factor of 1,000. In measurement, the occurrence of particles of certain sizes is usually expressed as the amount present in defined size classes. The width of these size classes depends on the intrinsic resolution of the measurement technique, the measurement range and the width of the PSD. Narrow size classes, of course, have better possibilities to show tiny differences in particle size than wide classes.

The results of a PSD measurement are expressed in tables and/or in graphs. The data can be expressed in a differential way or in a cumulative way. Generally, the data are normalized so that the sum of all fractions equals 1 or 100% (through division of the amounts per class by the total amount of sample). In differential size distributions, either the fractional frequency of material in each of the size classes or the fractional density is given, either as a histogram or as a smoothed curve. Cumulative size distributions present the fraction smaller (undersize) or larger (oversize) than stated sizes. Table 2.4 and Figs. 2.3–2.5 give an example of representations. Note that, in this example, size classes of equal width are used.

Often, differential data are reported in the form of histograms of frequency against particle size. Here, the height of the histogram bar represents the amount (e.g., number or volume) of material in a size class. This allows only good comparison with other data if the same size classes are used. Direct comparison is impossible, however, if the data have different size classes. This can be seen by comparing the top and bottom part of Fig. 2.3, where in the latter the same amount of material in the size range 340–400 μm was divided over two classes instead of one. This same drawback also makes data comparison difficult, if not impossible, if the data come from two instruments or techniques with different size classes, which is usually the case.

Table 2.4   Particle size distribution of an arbitrary product

1 Class number	2 Diameter D_v μm	3 Frequency dQ_3 g/100 g	4 Density q_3 fraction/μm	5 Cumulative Q_3 g/100 g
	100			0
1	160	0	0.000	0
2	220	4.2	0.042	4.2
3	280	14.2	0.142	18.4
4	340	26.0	0.260	44.4
5	400	23.8	0.238	68.2
6	460	16.5	0.154	84.7
7	520	9.6	0.096	94.3
8	580	4.7	0.047	99.0
9	640	1.0	0.010	100.0
10	700	0	0.000	100.0
Sum		100	1.000	

Fig. 2.3 Frequency representation of differential particle size distribution. Top: original; bottom: size class 340–400 μm split in two equal halves
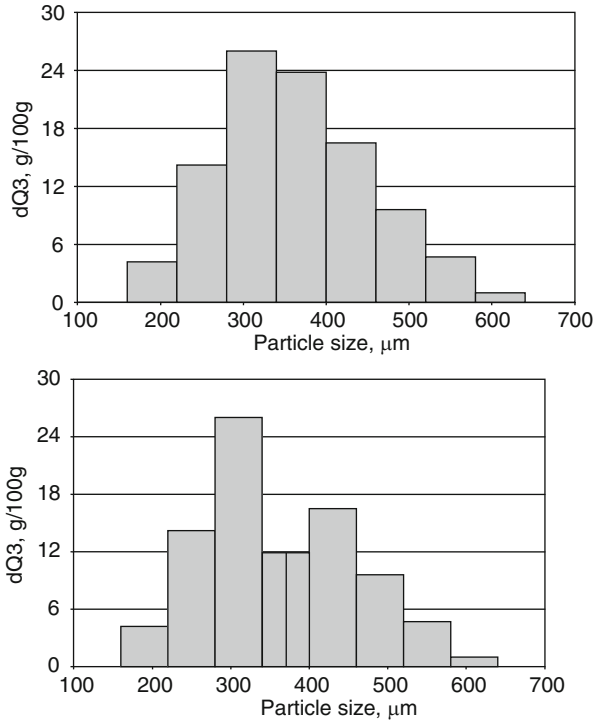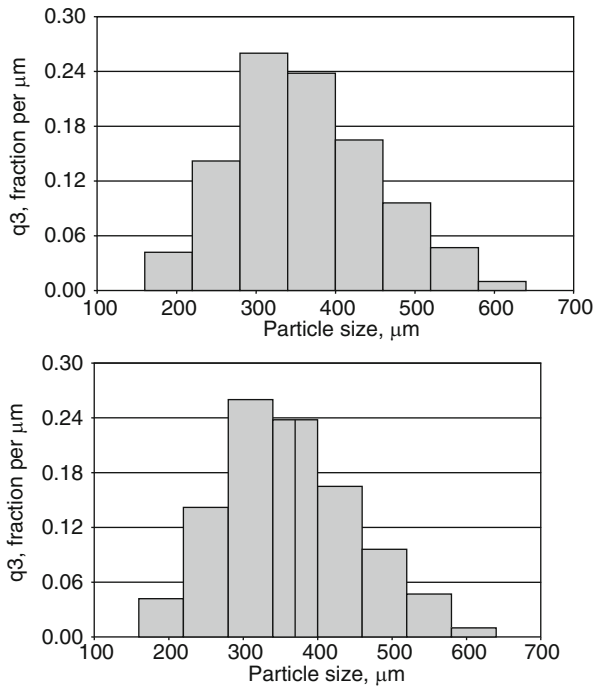
Fig. 2.4 Density representation of differential particle size distribution Top: original; Bottom: size class 340–400 μm split in two equal halves

Therefore, ISO 9276-1 [1] recommends the use of fractional density, which does not have this drawback. It is obtained from the frequencies by dividing them by the width of their respective classes and subsequent normalization. Now, the area of the histogram bar (height multiplied by width) represents the amount of material in the size class. Figure 2.4 gives the example for the same two cases as used in Fig. 2.3. The top parts of both figures look the same, because of the equal size class width. Note the differences in the Y-axis due to the different normalization (100 and 1, respectively). In Fig. 2.4, the top and bottom parts are equal.

Sometimes, these density curves are smoothed. Then, they are mostly obtained by differentiating the smoothed cumulative curve. Figure 2.5 gives an example of the smoothed density and cumulative (undersize) PSD representation. Note that the amount of material in each size class should remain the same in the smoothed density curve as in the histogram. Thus, the areas above and below the top of each histogram bar should be equal, which is illustrated for size class 6 (400–460 µm). The cumulative undersize amounts Q_3 are obtained by addition of the respective differential data at the corresponding particle sizes (columns 5 and 2 in Table 2.4; See also the points in the cumulative curve of Fig. 2.5 (bottom), through which a smoothed line is drawn).

The smoothed differential graphical representation usually shows better resolution of the PSD curve than the cumulative one, in case of shoulders or bimodal distributions. The density representation has the advantage of directly showing the modal (most frequently occurring) particle size. The cumulative curve gives easy access to percentile PSD parameters such as the median (D_{50}) or the D_{10} and the
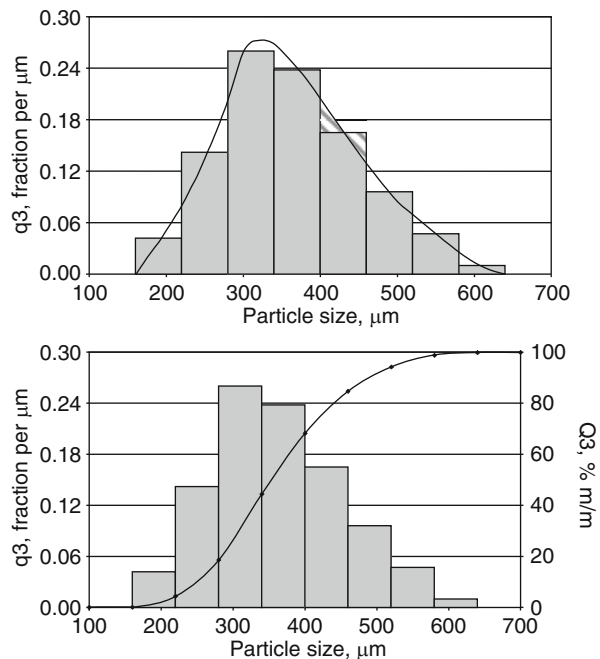

Fig. 2.5 Density and cumulative undersize PSD representation (smoothed)