Characterization of Powders & Aerosols

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WILEY-VCH

Weinheim · New York · Chichester · Brisbane · Singapore · Toronto

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Library of Congress Card No. applied for

A catalogue record for this book is available from the British Library

Die Deutsche Bibliothek – Cataloguing-in-Publication Data
Kaye, Brian H.:
Characterization of powder and aerosols / Brian H. Kaye. – 1. Aufl. – Weinheim ; New York ; Chichester ; Brisbane ; Singapore ; Toronto : Wiley-VCH, 1999
ISBN 3-527-28853-8

Printed on acid-free and chlorine-free paper

Composition: Text- und Software-Service Manuela Treindl, D-93059 Regensburg
Printing: strauss offsetdruck, D-69509 Mörlenbach
Bookbinding: Wilhelm Osswald + Co., D-67433 Neustadt
Printed in the Federal Republic of Germany

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Preface

I first started working with powders in 1955. In the 43 years since that initial activity there has been a multitude of developments of instruments and sources of information on the performance of these instruments. Back in 1955 the Coulter Counter was becoming well known and the height of sophistication was the Photosedimendometer. I began my studies using an Andreason bottle and moved on to study the possibility of using divers and developed all the way to fractals. In the period covered by my activities in particle size analysis the type of book required for people active in the field has changed. When I began my work there was no journal devoted to the subject but as of now we have three journals, Aerosol Science, Particle and Particle Systems Characterization and Particle Technology. I was involved in setting up of both of these latter journals and they have both grown into many volumes. Also in the early days there was difficulty in finding information on the performance of instruments whereas today many manufactures provide comprehensive notes on operational variables with their machines. The availability of the journal information and literature from manufacturers means that the role of potential textbooks has changed. In this book we have tried to set out the basic methods for characterizing powders and aerosols and have tried to indicate the questions that the investigator should use when trying to choose a method for his particular needs. The inter-method comparison of data generated in particle size is still a complex problem and one of the useful features of this book is the provision of many graphs showing the relative performance of different machines in assessing powder properties.

The question of particle shape is a complex problem and we are still at the stage where we are developing methods to see if we can characterize adequately the range of shapes within a powder and their effect on the powder system and/or the aerosol system. It is becoming apparent that some complex problems will require more than one method of characterization thus if one was inhaling a complex soot particle the aerodynamic diameter which governs the penetration of the lung is one parameter whereas the fractal structure is another needed to assess the potential health hazard of the inhaled aerosol particle.

A problem facing the investigator in powder technology is that many of the earlier publications use methodologies to characterize the powders that are no longer avail-

able. To enable the analyst to assess the information presented in earlier publications we have reviewed the physical principles and have set out the problems associated with some of the classical instruments such as the micromerograph which for many years was a standard method in the powder metallurgy industry but is now only of historic interest. Sometimes the problems associated with methods are posed by the cessation of manufacturing of a given procedure. Thus the M.S.A. Centrifuge method was very widely used in occupational health and safety but the manufactures decided to discontinue the manufacturing of equipment so for continuity of interpretation the method has been outlined. Emphasis has been placed on references to enable the reader to recover detailed information for their own investigations. Unfortunately normal systems of training in industry such as pharmaceuticals, chemical engineering, and powder metallurgy do not present a great deal of information on characterization procedures and because methods have developed in different subjects different scientists tend to use different words for the same concept. Therefore we have attempted to clarify some of the vocabulary which has been used in different fields of endeavor which generate information of interest to a wider audience of scientists than those who have immediately carried out the work.

Any author has his own biases when writing a book and since we have been very active at Laurentian University in developing shape methodologies this aspect of powder technology has been fully covered in this text.

Hopefully the advanced reader will find references to work relevant to their own studies and student reader will find this book a useful introduction to methods for characterizing powders and aerosols.

Acknowledgments

Many students have contributed to the development of this book and the typing of the script. I thank then the following people who have been particularly active: Cherie Turbitt Daoust, Lorna Mac Lod, Heather Eberhardt and my two daughters Sharon Kaye and Alison Kaye have also contributed to the text preparation. Cherie undertook the difficult task of copyright clearance and the help of Garry Clark in preparing the diagrams and in general proof reading the scripts have been invaluable. I also wish to thank the manufactures of the various machines who have been most helpful in providing data and material describing their instruments. In particular Morris Wed of Malvern Instruments was most helpful in supplying of literature on diffractometers. I also wish to thank the personal at Wiley-VCH especially Barbara Böck, for encouraging me to finish this project.

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1 Basic Concepts in Characterization Studies, Representative Samples and Calibration Standards

1.1 Who Needs to Characterize Powders and Spray Systems?

The list of industries using powders, or processes in which there is a substance used as spray or a mist, is long and increasing. My first exposure to the problems of powder technology began in 1955 when I studied the characterization of powders used to fabricate parts of nuclear weapons. One study involved the metal beryllium which was used in powder form. The production of dense beryllium required powders having a specific size and shape distribution. Beryllium powder is however a respirable health hazard and to characterize the powder in a safe atmosphere required the development of new methods of characterizing powders.

After working with beryllium I moved on to study nuclear reactor fabrication. In this study I worked on determining the surface area, size and shape distributions of uranium dioxide and plutonium dioxide powders used to fabricate fuel rods. Looking back I see that my initiation into powder technology was a baptism of fire since all of these powders were extremely toxic and dangerous. The technology that I studied in those years is currently very applicable to the study of modern ceramic materials and powder metallurgical routes to finished products [1, 2].

After my studies of the technology for creating nuclear weapons I soon became involved in studying the fallout from nuclear weapons tests and similar problems of occupational diseases, such as pneumoconiosis and silicosis caused by the inhalation of fineparticles. The study of respirable hazards in industry and from nuclear fallout requires detailed knowledge of the shape and size of fineparticles [3, 4].

The same type of information required to predict the respirable hazard for grains of powder is also vital to the success of therapeutic aerosol technology in which drugs are delivered to the lungs in aerosol form [5]. The same technical information is used by military experts to design the delivery of biological warfare agents, such as clouds of toxic dust. The other side of the military problem is to design filters which will protect military personnel against these toxic clouds of fineparticles; a task requiring detailed size, shape and aerodynamic behaviour information for the aerosol fineparticles. Other industrial activities where detailed knowledge of the size and shape distributions of powder grains are important include industries involved in food processing, cosmet-

ics, paint, pesticide manufacture and delivery, pharmaceutical products, and the manufacture of explosives, abrasive powders, metal powders used in the creation of magnetic tape, and the dry inks used in xerographic copiers.

Size characterization studies have often evolved in parallel in many of these industries and sometimes there is vocabulary confusion because of the different perspectives of scientists from the various industries. We will attempt to develop and use a consistent terminology as we study the multitudes of powders used in various industries.

1.2 The Physical Significance of Size Measurements

If one is concerned with the characterization of dense smooth spheres, the concept of size is elementary and straight forward. If however one must deal with some of the powder grains found in industry, exactly what is meant by size has to be defined very carefully. Consider for example the carbonblack profile shown in Figure 1.1(a) [6].

One measure of the structure of the carbonblack profile is it's circle of equal area as shown in Figure 1.1(b). Another simple descriptor, which has been widely used to describe such objects is the Aspect Ratio. This is the length, defined as the longest dimension of the profile, divided by the width of the profile (right angles to the length measurement.) This is a dimensionless number which is defined as a geometric index of shape. Many different geometric shape factors have been described by different workers [7–11].

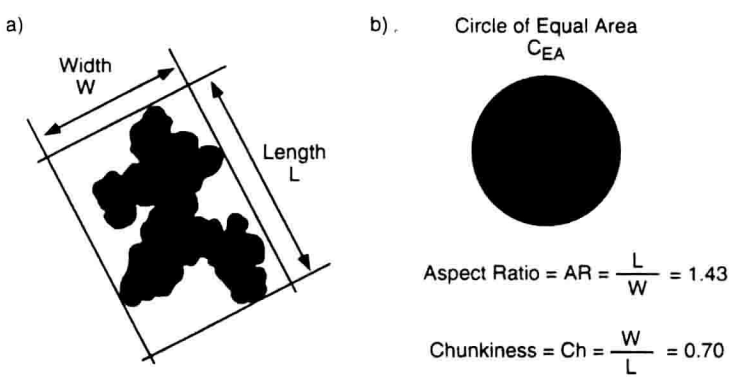

Figure 1.1. To specify the size and shape of a complex fineparticle, many equivalent and operational parameters may be required, as demonstrated by the parameters required to describe a carbonblack profile originally described by Medalia [6]. a) Simple, classical dimensions of a carbonblack profile. b) Typical size and shape descriptors of the profile of (a).

The reciprocal of the Aspect Ratio has recently become quite widely used to describe the shape of fineparticles. The reciprocal quantity is called the Chunkiness of the fineparticle. (The physical significance of this measure will be discussed in Chapter 2.)

Relating the equivalent measure of a fineparticle to its physical properties is not always easy and for this reason what is known as an operational diameter of the fineparticle is sometimes used. Thus, the equivalent area of the carbonblack of Figure 1.1(a) is probably related to the opacity of the fineparticle when it is used as a pigment. However, if it is to be used to be part of a defensive smoke screen in a military operation the opacity of the profile, with respect to scattered light, has to be measured and in this situation some of the diffractometer measurements discussed in Chapter 6, may be a more direct measure of the operational behavior of the profile.

Soot fineparticles produced by a combustion processes are similar in structure to the carbonblack profile of Figure 1.1(a). When one is looking at the dispersal dynamics of a smoke and/or the health hazards of the smoke fineparticles, one must use an operational diameter known as the aerodynamic diameter. The aerodynamic diameter is the size of the smooth dense sphere of unit density which has the same dynamic behavior as the soot particle. Several procedures for measuring the aerodynamic diameter of airborne fineparticles will be discussed in various chapters of this book.

When looking at a complex profile such as that of Figure 1.1(a) one can sometimes clearly identify subunits in the structure of an agglomerate. In some instances workers report the size distribution of the subunits in the agglomerate as the operational size of the fineparticle system but this can be confusing and lead to difficulty interpreting the data. Thus in Figure 1.2(a) a set of fineparticles captured on a whisker filter and studied by Schafer and Pfeifer are shown [12]. The size distribution of the fineparticles on the filter whiskers were studied by two methods. The distributions reported by Schafer and Pfeifer are shown in Figure 1.2(b). It is quite surprising that the image analysis data shows much smaller fineparticles than those that are obviously visible under a microscope in the array of Figure 1.2(a). The reason for this is that Schafer and Pfeifer measured what they called "obvious units" contributing to clusters which they claimed were formed on the filters as capture trees [13]. Deciding whether a cluster of smaller fineparticles has grown on the filter fiber or existed in the aerosol being filtered is a value judgment for which different scientists would reach different conclusions. In the case of the study reported by Schafer and Pfeifer the decision as to the reality of the structure of the cluster is not critical since they were studying alumina fineparticles used to create visible trails in wind tunnel experiments. However, looking at a typical cluster such as that shown enlarged in Figure 1.2(c), if the study had been on the health hazard of the dust, the hazard would be very different if the cluster was a single entity of the size of 3 microns long or if it was in fact 20 or 30 small particles less than half a micron in size.

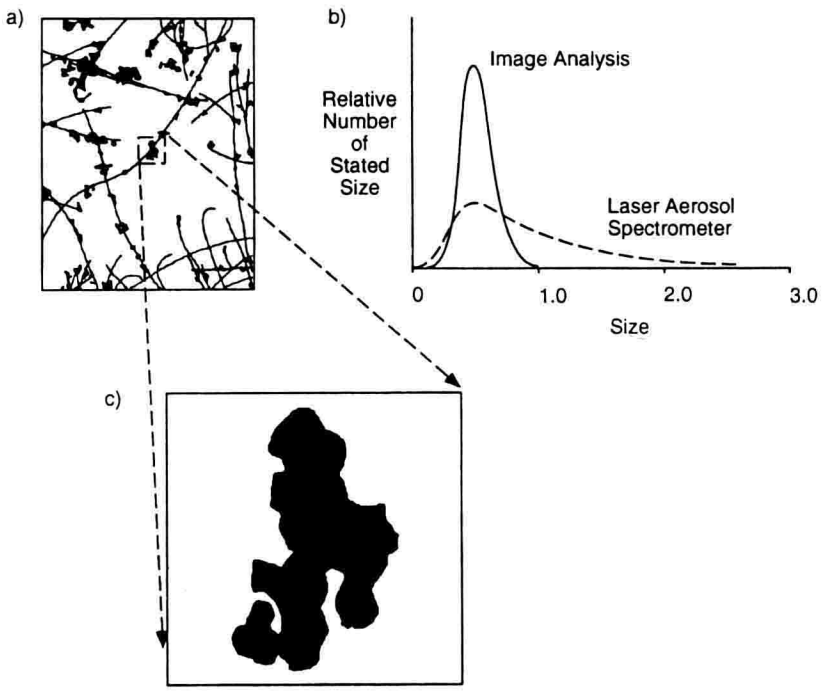

Figure 1.2. The decision as to what constitutes a separate fineparticle can lead to very different descriptions of a fineparticle population, as demonstrated by the data reported by Schafer and Pfeifer [12]. a) Low magnification field of view of fineparticles captured in the fibres of a filter. b) Size distributions by two different methods of the fineparticles of (a). c) A typical agglomerate which Schafer and Pfeifer describe as constituted from "obvious" subunits which they report as the effective unit in their image analysis size distribution.

The difficulties of using image analysis in health hazard studies is demonstrated by the profile of Figure 1.2(c). Predicting the aerodynamic diameter from the perceived physical structure of the profile is very difficult. (See discussion of the aerodynamic profiles of complex fineparticles in Chapter 6.) In the discussion so far of the profiles of the Figures 1.1 and 1.2, the term agglomerate has been used without definition. Unfortunately in powder technology literature the terms agglomerate and aggregate are used somewhat indiscriminately. One author's agglomerate may be another author's aggregate. In this book the term agglomerate is used to describe a structure which is strong enough to persist throughout the handling of the fineparticle in the process of interest. The term aggregate on the other hand is used to describe a temporary cluster which breaks down during the processing of the material. This is a logical use of the two terms since agglomerate means "made into a ball" whereas aggregate means be-

having like a flock of sheep. Anyone who has watched the behavior of a flock of sheep knows that the flock assembly disintegrates as soon as the dog and the shepherd walk away. Thus when looking at titanium dioxide powder taken out of a bag, the powder is often clustered into aggregates as large as 20 microns in diameter but when dispersed by high shear forces into a paint these agglomerates will breakdown into individual fineparticles of one micron or less.

When selecting a method of size characterization to study a powder, one should try to use an analytical procedure to disperse the powder resulting in fineparticles that will be the same operative size as those in the process under study. Thus, if we were to have a cluster of fineparticles which persisted throughout a pharmaceutical processing operation, it would be inappropriate to use a sizing procedure which used dispersing forces strong enough to rip the cluster apart. This aspect of size characterization will be discussed throughout the text when discussing the various characterization procedures.

Again, when choosing a method of size characterization, one should always choose a method close to the operational context for which the information is required. Thus if one wants to study the dust movement into and out of the lung one should use a method that actually measures the aerodynamic size of the fineparticle.

Sometimes it is necessary to measure several size description parameters for a more complete description of a fineparticle in the operational context. For example, if one is studying a soot fineparticle having a structure similar to that of the profile of Figure 1.1(a), one needs to know the aerodynamic diameter to predict the movement in the atmosphere and/or into or out of the lung; however to look at the health hazard of the fineparticle one needs to measure the structure and the surface of the fineparticle. Thus, an open textured, fluffy soot fineparticle would have a small aerodynamic diameter the magnitude of which would give very little indication of the probability of lodging on the surface of the lung or to the possibility of capturing the soot fineparticle in a respirator or filter. For such purposes, one would have to measure the physical dimensions of the profile such as the length and chunkiness.

Two other parameters which would be useful when evaluating potential health hazards of fineparticles, such as the soot profile of Figure 1.1(a), are the fractal dimensions of the structure and the texture of the profile. The fractal dimension of a boundary is a concept from the subject of applied fractal geometry [14, 15]. Fractal geometry, invented by Mandelbrot [16], describes the ruggedness of objects in various dimensions of space. (As will be pointed out in the various discussions in the use of the term fractal in powder science, the word fractal dimension can mean different things, in this case the word fractal dimension describes the rugged structure of the boundary of a profile.) To describe the ruggedness of lines in two dimensional space, the fractal dimension is a fractional addendum to the topological dimension of a line, which is 1, as illustrated for the various lines of Figure 1.3. It can be seen that this fractal addendum increases as the ruggedness, i. e. the ability of the line to fill space, increases.

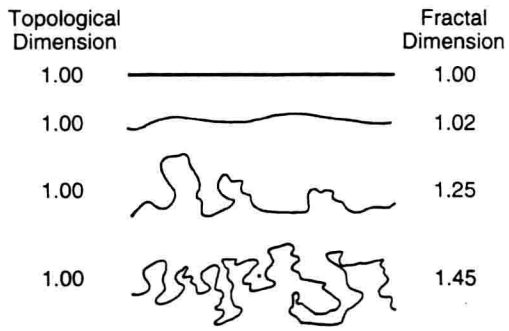

Figure 1.3. The fractal dimension of a profile can be used to describe the ruggedness of a fineparticle profile. The fractal dimension consists of a fractional number, which is related to the ruggedness or space filling ability of a profile, added to the topological dimension of a line or other structure [13].

We will show in Chapter 2 that the carbonblack profile of Figure 1.1(a) has two fractal dimensions, one describing the gross structure of the agglomerate and the other the texture. The magnitude of the structural fractal dimension is about 1.32. The structural fractal dimension of the agglomerate is useful information concerning the way in which the agglomerate formed in the smoke in which it was created. The other fractal dimension used to describe the carbon black agglomerates, called the textural fractal dimension, describes the texture of the agglomerate. This parameter has information on the way in which the subunits are packed together to form the agglomerate [17]. The techniques for measuring the fractal dimensions of profiles such as that of Figure 1.1(a) will be described in detail in Chapter 2.

Because the various methods for characterizing aspects of a complex structure explore different aspects of that structure, the data generated from a given study of the system may not correlate directly with data generated by another technique. From time to time in the body of the text the differences in the data generated by different studies of the same type of population by various methods will be discussed. In the final chapter we will collect together various comparative studies illustrative of the usefulness of the information generated by different size characterization techniques. Predicting the physical properties of a powder system from the size distribution study is not usually a direct procedure. For this reason in Chapter 9 we will look at assessing by direct study, physical properties of powder systems such as the flow of a powder system, the packing of a powder assembly, and permeability/porosity of compressed powder systems.

1.3 Standard Powders for Calibrating Powder Measurement Techniques

Sometimes the interpretation of data generated in a method for studying the size of a fineparticle can be carried out using physical relationships. Thus when studying the sedimentation of a fineparticle in a viscous fluid, the Stokes diameter of the fineparticle can be established using known values of viscosities and densities along with measured falling speeds and a well known formula developed by Stokes (see Chapter 4). However, in other techniques, the physical significance of data generated by a method is interpreted by carrying out calibrations using standard fineparticles. For example, when looking at the size of fineparticles using a stream counter, such as the HIAC system described in Chapter 6, the instrument is calibrated using standard latex spheres. The data generated for a particular powder is then reported in terms of the size of the equivalent spheres which would represent the fineparticles.

Standard latexes, and other reference materials, are available from various organizations [18–24]. One of the calibrations standards available to fineparticle scientists are latex spheres which were made on board the space shuttle in 1985. Because these spheres were formed in the absence of gravity they are perfectly spherical. The National Bureau of Standard makes available standard reference material in the form of ten micron microspheres mounted on glass slides. In the first type of slide a few thousand microspheres are deposited as a regular array on a glass microscope slide. In the other type, the fineparticles are randomly distributed [18]. A series of standard non-spherical fineparticles have been prepared by the Community Bureau of Reference Commission of the European Community for use in comparing the performance of size methods. These reference powders are known as BCR standards and several publications are available describing the use of such reference materials [19].

1.4 Representative Samples

Often in the laboratory one is given a sample of a few grams taken from a large supply of powder. It should be self obvious that if this sample is not representative of the original bulk supply of powder then one is wasting time characterizing the sample in the laboratory. Unfortunately this fundamental step in powder technology is often overlooked sometimes simply because the laboratory is separated in time and space from the original bulk supply of powder. Several times in my career I have been in charge of laboratories providing size analysis data to other groups. When