

# Particle size analysis — Small angle X-ray scattering method

ICS 19.120

## National foreword

This Draft for Development reproduces verbatim ISO/TS 13762:2001

### This publication is not to be regarded as a British Standard.

It is being issued in the Draft for Development series of publications and is of a provisional nature because it deals with emerging technology, in which insufficient experience has been gained for a full ISO standard to be appropriate. It should be applied on this provisional basis, so that information and experience of its practical application may be obtained.

Comments arising from the use of this Draft for Development are requested so that UK experience can be reported to the international organization responsible for the Technical Specification. A review of this publication will be initiated not later than 3 years after its publication by the international organization so that a decision can be taken on its status at the end of its 3-year life. Notification of the start of the review period will be made in an announcement in the appropriate issue of *Update Standards*.

According to the replies received by the end of the review period, the responsible BSI Committee will decide whether to support the conversion into an international standard, to extend the life of the Technical Specification for another 3 years or to withdraw it. Comments should be sent in writing to the Secretary of BSI Subcommittee LBI/37/4, Sizing by methods other than sieving, at British Standards House, 389 Chiswick High Road, London W4 4AL, giving the document reference and clause number and proposing, where possible, an appropriate revision of the text.

A list of organizations represented on this committee can be obtained on request to its secretary.

### Cross-references

The British Standards which implement international publications referred to in this document may be found in the *BSI Catalogue* under the section entitled "International Standards Correspondence Index", or by using the "Search" facility of the *BSI Electronic Catalogue* or of British Standards Online.

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*Analyse granulométrique — Méthode de dispersion par rayons X sous  
angle faible*



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## Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 3.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

In other circumstances, particularly when there is an urgent market requirement for such documents, a technical committee may decide to publish other types of normative document:

- an ISO Publicly Available Specification (ISO/PAS) represents an agreement between technical experts in an ISO working group and is accepted for publication if it is approved by more than 50 % of the members of the parent committee casting a vote;
- an ISO Technical Specification (ISO/TS) represents an agreement between the members of a technical committee and is accepted for publication if it is approved by 2/3 of the members of the committee casting a vote.

An ISO/PAS or ISO/TS is reviewed every three years with a view to deciding whether it can be transformed into an International Standard.

Attention is drawn to the possibility that some of the elements of this Technical Specification ISO/TS 13762 may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO/TS 13762 was prepared by Technical Committee ISO/TC 24, *Sieves, sieving and other sizing methods*, Subcommittee SC 4, *Sizing by methods other than sieving*.

Annexes A and B form a normative part of this Technical Specification. Annexes C to E are for information only.

## Introduction

The size range for which the small angle X-ray scattering (SAXS) method is applicable is approximately in the range of 1 nm to 300 nm. The success of the technique is mainly based on the fact that SAXS effect results from the difference of electron density between particles and their surroundings so that size  $X_{\text{SAXS}}$  always indicates the size of a primary particle rather than the internal crystallite or external agglomerate size; in other words, the requirement of particle dispersion of a sample for SAXS analysis is not as strict as that for other methods.

However, the SAXS method has its limitations: firstly, it cannot distinguish pores from particles; secondly, the interference effect between particles will arise as the sample is available only in concentrated form.

SAXS measurements and the interpretation of the data are currently not uniform. The purpose of this Technical Specification is to facilitate comparisons of size analysis made in different laboratories.

It is well known that X-rays can kill human tissue. However, this Technical Specification does not purport to address all the safety problems associated with the use of the SAXS method; it is the responsibility of the user to establish appropriate safety and health practices prior to its use.





# Particle size analysis — Small angle X-ray scattering method

## 1 Scope

This Technical Specification specifies the method for determining particle size distribution of ultra-fine powders by the small angle X-ray scattering technique. It is applicable to particle sizes ranging from 1 nm to 300 nm. In the data analysis, it is assumed that particles are isotropic and spherically shaped.

The method described in this Technical Specification is also applicable to particle suspensions.

This Technical Specification does not apply to:

- a) powders containing particles whose morphology is far from spherical, except by special agreement;
- b) powders consisting of porous particles;
- c) mixtures of powders.

## 2 Normative references

The following normative documents contain provisions which, through reference in this text, constitute provisions of this Technical Specification. For dated references, subsequent amendments to, or revisions of, any of these publications do not apply. However, parties to agreements based on this Technical Specification are encouraged to investigate the possibility of applying the most recent editions of the normative documents indicated below. For undated references, the latest edition of the normative document referred to applies. Members of ISO and IEC maintain registers of currently valid International Standards.

ISO 9276-1, *Representation of results of particle size analysis — Part 1: Graphical representation.*

ISO 9276-2:—<sup>1)</sup>, *Representation of results of particle size analysis — Part 2: Calculation of average particle sizes/diameters and moments from particle size distributions.*

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1) To be published.

### 3 Symbols and abbreviations

SAXS	small angle X-ray scattering
$x$	particle size, diameter of a sphere
$\Delta x_i$	length of particle size interval, $\Delta x_i = x_i - x_{i-1}$
$n$	total number of size classes
$\bar{q}_{3,i}$	average density distribution of the class $\Delta x_i$ by volume or mass
$\bar{q}_{3,i'}$	average density distribution in a representation with logarithmic abscissa
$Q_{3,i}$	cumulative volume fraction of particle sizes $x \leq x_i$
$\varepsilon$	scattering angle
$\Delta Q_{3,i}$	volume fraction within the class $\Delta x_i$ , $\Delta Q_{3,i} = \bar{q}_{3,i} \cdot \Delta x_i$
$\Phi(\zeta)$	scattering function of a spherical particle: $\Phi(\zeta) = 3(\sin \zeta - \zeta \cos \zeta) / \zeta^3, \quad \zeta = \frac{\pi x}{\lambda} (\varepsilon^2 + t^2)^{1/2}$
$\lambda$	wavelength of incident X-ray beam
$t$	angle variable along the slit-height direction
$F(t)$	slit-weighting function along the slit-height direction

### 4 Principle

As a narrow beam of X-ray passes through a powder layer containing ultra-fine particles, it will be dispersed around the incident beam at a small angle range resulting from the electron scattering in the particles. The distribution of scattered intensity is closely related to the particle size distribution.

The scattered intensity  $I(\varepsilon)$  from a dilute spherical particle system can be expressed by the integral equation:

$$I(\varepsilon) = c \int_{-\infty}^{+\infty} F(t) dt \int_{x_0}^{x_n} \omega(x) x^3 \Phi^2(\zeta) dx \quad (1)$$

where

$x_0$  is the size below which there are no particles;

$x_n$  is the size above which there are no particles;

$\omega(x)$  is the size distribution function by volume (without normalization);

$c$  is a synthetic constant.

The size range of  $x_0$  to  $x_n$  can be divided into  $n$  intervals and the lengths of the intervals,  $\Delta x$ , increase with  $x$  increasing. Let  $\omega_j$  represent the average distribution function of the class  $\Delta x_j$ , and then measure scattering intensities at a series of chosen angles to obtain  $n$  values of  $I(\varepsilon)$ . The angles are specified by the equation:

$$\varepsilon_i = 2\sqrt{5} \lambda / \pi(x_{i-1} + x_i) \quad (i = 1, 2, 3, \dots, n) \quad (2)$$

Approximately, the integral equation (1) is transformed into a set of a linear equations:

$$I(\varepsilon_i) = \sum_{j=1}^n a_{ij} \omega_j \quad (i = 1, 2, 3, \dots, n) \quad (3)$$

where

$$a_{ij} = \int_{-\infty}^{+\infty} F(t) dt \int_{x_{j-1}}^{x_j} x^3 \phi^2(\zeta) dx \quad (4)$$

All the coefficients,  $a_{ij}$ , in the set of linear equations are a group of constants for given  $\lambda$ , collimation geometry, classes and specific angles. We may calculate them one by one by using a numerical integration method as long as the slit-height weighting function,  $F(t)$ , has been measured (annex B). Thus, the values of distribution function corresponding to each class can be obtained from solving equation (3). Based on the solutions, the average density distribution, volume fractions, cumulative volume fractions and the mean size  $\bar{x}$  of the particles can be calculated as follows:

$$\bar{q}_{3,j} = \omega_j / \sum_{k=1}^n \omega_k \Delta x_k \quad (j = 1, 2, \dots, n) \quad (5)$$

$$\Delta Q_{3,j} = \bar{q}_{3,j} \Delta x_j \times 100\% \quad (j = 1, 2, \dots, n) \quad (6)$$

$$Q_{3,j} = \sum_{k=0}^j \Delta Q_{3,k} \quad (j = 1, 2, \dots, n) \quad (7)$$

$$\bar{x} = \sum_{j=1}^n \Delta Q_{3,j} (x_{j-1} + x_j) / 2 \quad (j = 1, 2, \dots, n) \quad (8)$$

The solution of equation (3) involves the inversions of an ill-conditioned problem but it can be improved through optimizing the coefficient matrix and introducing a diagonal matrix  $B$  and a stabilizer  $\eta$ . In matrix form, equation (3) can be modified as:

$$[A + \eta B] \omega = I \quad (9)$$

where

$$A = (a_{ij})_{n \times n};$$

$$B = \text{diag}(a_{11}, a_{22}, \dots, a_{nn});$$

$$0 < \eta < 0,3$$

$$\omega = (\omega_1, \omega_2, \dots, \omega_n)$$

$$I = (I_1, I_2, \dots, I_n)$$

## 5 Sample preparation and requirement

### 5.1 Preparation of collodion solution

The analytically pure acetone and collodion without small-angle scattering should be used to prepare the solution. In general, the concentration of the solution may be approximately 5 % to 10 %.

### 5.2 Requirements and preparation of the sample plate

#### 5.2.1 Requirements of the sample plate

The sample plate used for scattering measurement should meet the following requirements:

- a) the volume concentration of the test powder in the plate should be less than 1 %;
- b) to achieve maximum scattering intensity, the thickness of the sample plate shall be chosen to an optimum value where the monochromatic X-ray beam will be attenuated to 37 %;
- c) the sample plate should be uniform, flat, crack free and should ensure that the powder particles are separated as well as possible;
- d) the sample plate should have suitable dimensions, for example a length of 20 mm and a width of 10 mm.

#### 5.2.2 Preparation of the sample plate

Weigh out a given mass of test powder and pour onto it an appropriate volume of collodion solution. The quantities requested for the powder and solution may be estimated from the density of each and from their X-ray absorption coefficient, in order to meet the requirements in 5.2.1.

Stir the suspension in a small cup. A drop of wetting agent shall be added to the suspension if the solution does not readily wet the powder.

The dispersion of the powder in the suspension shall be made by the addition of dispersing agent and/or an ultrasonic treatment.

Place the cup containing the suspension into an oven at the temperature of 20 °C to 50 °C and with a relative humidity of below 50 %, until a dry sample plate has formed.

### 5.3 Preparation of dry powder sample

Place the dry powder in a special sample holder with a slot. If the requirements in 5.2.1 are met in this way, it shall be directly used for SAXS measurement.

### 5.4 Preparation of colloidal solution

The concentration of the colloidal solution should be less than 1 %. An appropriate surfactant may be added to prevent the colloids from agglomerating.

When preparing the sample for measurement, the method chosen should not affect the particle morphology.

## 6 Apparatus

The apparatus consists of:

- an X-ray generator combined with electronic circuit panel, detector and recording;
- a system, with synthetic stability superior to 1 %;

- a small angle scattering goniometer;
- a computation unit;
- an ordinary laboratory apparatus, such as an analytical balance, ultrasonicator and oven.

See also annex C.

## 7 Procedure

**7.1** Switch the X-ray diffractometer on and allow it to warm up.

**7.2** Adjust or check the small angle scattering goniometer according to the manual.

**7.3** Once the conditions of the instrument are stable, adjust the goniometer according to the instruction manual. Insert an appropriate number of absorber plates in front of the detector then set the goniometer at 0 scale of the angle. Register the intensity of the primary X-ray beam as an intensity of the goniometer's 0 degree.

**7.4** Fix the sample plate onto the sample holder, or inject the colloidal suspension sample into a special cell and then insert the holder with the sample into the shaft hole of the goniometer. Pull out the absorber plates.

**7.5** Measure the scattering intensities,  $I_a(\varepsilon_i)$ , at the angles specified by equation (2). The total pulse counts measured should reach at least 5 000 at each angle. The measured intensity,  $I_a(\varepsilon_i)$ , is composed of the small-angle scattering from the sample as well as the scattering background.

**7.6** Take out the sample. Reinsert the absorber plates, reset the goniometer to 0° and then measure the intensity of the primary beam. The relative deviation between this value and the intensity registered in 7.3 shall be less than 15 %; if this is not the case, repeat the procedures starting from 7.2.

**7.7** Place the sample between the X-ray window and the first slits of the goniometer. Measure the scattering background,  $I_b(\varepsilon_i)$ , under the same instrumental conditions and at the same angles as in 7.5. However, the pulse counts for  $I_b(\varepsilon_i)$  need not be specified.

**7.8** Subtract the intensity measured in 7.7 from that measured in 7.5, i.e. the small-angle scattering intensity,  $I(\varepsilon_i) = I_a(\varepsilon_i) - I_b(\varepsilon_i)$ .

## 8 Calculation and expression of results

### 8.1 Calculation

#### 8.1.1 Evaluation of equation (3)

Substitute the values obtained in 7.8 and 7.9 in equation (3); each  $\omega_i$  can be calculated by means of a microprocessor. If the solution is not stable or reasonable enough, the equation (9) shall be used.

#### 8.1.2 Calculation of average density distribution and volume fraction

The average densities distribution,  $q_{3j}$ , and the volume fractions,  $\Delta Q_{3,j}$ , for each class shall be calculated from the values of  $\omega$  according to equation (5) and equation (6) respectively.

#### 8.1.3 Calculation of mean particle size

The mean particle size shall be calculated from the volume fractions according to equation (8).

## 8.2 Expression of results

The data may be presented in tabular and/or graphical form, see ISO 9276-1.

### 8.2.1 Tabular form

The report shall be made in accordance with Table 1.

Table 1

Class (nm)	$x_0 \sim x_1$	$x_1 \sim x_2$	.....	$x_{j-1} \sim x_j$	.....	$x_{n-1} \sim x_n$
Density distribution $\bar{q}_3$ ( $\text{nm}^{-1}$ )	$\bar{q}_{3,1}$	$\bar{q}_{3,2}$	.....	$\bar{q}_{3,j}$	.....	$\bar{q}_{3,n}$
Volume fraction $\Delta Q_3$ (%)	$\Delta Q_{3,1}$	$\Delta Q_{3,2}$	.....	$\Delta Q_{3,j}$	.....	$\Delta Q_{3,n}$
Cumulative percentage (%)	$\Delta Q_{3,1}$	$\Delta Q_{3,1} + \Delta Q_{3,2}$	.....	$\sum_{k=1}^j \Delta Q_{3,k}$	.....	100

The mean particle size,  $\bar{x}$ , is expressed in nanometres.

### 8.2.2 Graphical representation

#### 8.2.2.1 Histogram, $\bar{q}_3(x)$

In some cases, the results are presented as a histogram by using the data in the first and second rows of Table 1 in 8.2.1. A schematic normalized histogram is shown in Figure 1.

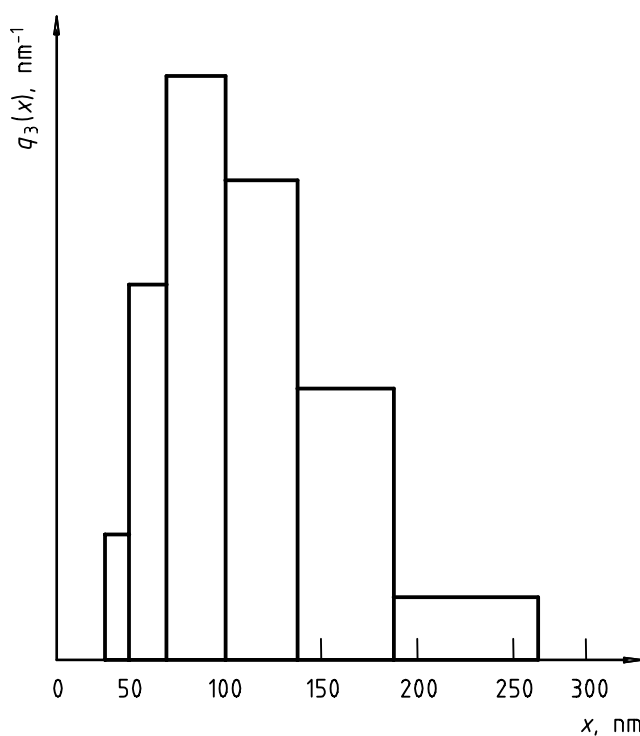


Figure 1 — Histogram of a density distribution function  $\bar{q}_3(x)$

In Figure 1, the area of each rectangular column represents the corresponding fraction  $\Delta Q$ , and the whole area beneath the histogram is normalized to 100 %.

### 8.2.2.2 Cumulative distribution graph, $Q_3(x)$

It is convenient to present the results as a cumulative curve by using the data in the first and fourth row of Table 1 in 8.2.1. A schematic cumulative graph is shown in Figure 2. The continuous curve is calculated by suitable interpolation algorithms. Each point on the curve defines a relative amount of particles smaller than a given size  $x$ , the median diameter,  $x_{50}$ , can be easily determined from the graph where the cumulative percentage reaches 50 %.

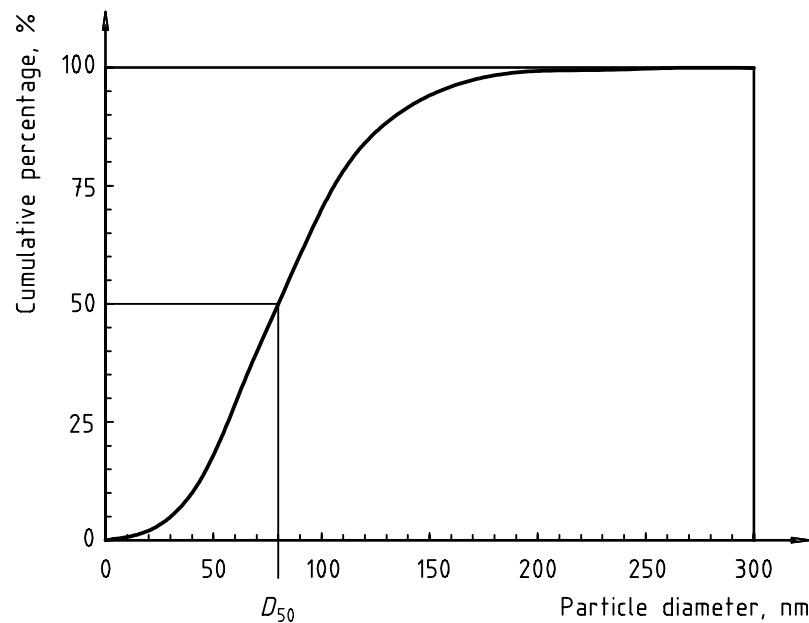


Figure 2 — Cumulative distribution,  $Q_3(x)$

## 9 Verification

Checking both the operational procedure and instrumental performance at regular intervals is essential to verify the test results. It is recommended that verification be made by the use of certified reference materials or a known “general sample” size distribution.

## 10 Reporting of results

The test report shall include the following information:

- a) reference to this Technical Specification;
- b) remarks about the sample;
- c) the test conditions and the type of instrument used;
- d) the result obtained;
- e) all operations not specified in this Technical Specification;
- f) details of any occurrence which may have affected the test result;
- g) date and operator.

## Annex A (normative)

### Determination of slit-height weighting function $F(t)$

Experimentally,  $F(t)$  is equal to the rocking curve taken in the slit-height plane. It is defined by the collimation geometry, intensity distribution in the primary beam and detector sensitivity. It can be determined as follows:

- set the goniometer at 0 scale;
- insert an appropriate number of absorber plates then put the X-ray generator to work;
- moving the detector with the receiving slit in the perpendicular direction, measure the intensity distribution in the absence of a sample by step-scanning.



## Annex B (normative)

### Calculation of coefficient, $a_{ij}$

It is recommended that the size range of 1 nm to 300 nm be divided in this way, i.e. 1 to 5, 5 to 10, 10 to 20, 20 to 35, 35 to 55, 55 to 80, 80 to 110, 110 to 150, 150 to 200, 200 to 300.

In order to optimize the diagonal element,  $a_{ij}$ , in the coefficient matrix, the scattering angle shall be selected according to equation (2).

Each  $a_{ij}$  can be calculated after introducing  $F(t)$  by a method of numerical integration according to equation (4).

The optimizing degree of the coefficient matrix,  $\bar{Q}$ , may be evaluated by the following equation:

$$\bar{Q} = \frac{\sum_{i=1}^n a_{ii} / (a_{ij})_{\max, j \neq i}}{n}$$

In general,  $\bar{Q}$  should be greater than 1,5.

**NOTE** In view of the fact that the stability of the solution of a set of linear equations becomes poor as the number of equations increases, the selection of classes should take the size range of the sample to be tested into account. It is recommended that only a few classes be chosen if the size range of the sample can be estimated in advance.

## Annex C (informative)

### Equipment for SAXS measurement

#### C.1 General

The following items concerning SAXS instrument should be further described.

#### C.2 X-ray sources

SAXS measurements can be performed by using sealed tubes or rotating anodes as sources of X-rays. Recently, the availability of synchrotron-radiation sources with intense, brilliant beams of variable wavelength has opened up new opportunities.

#### C.3 Small angle scattering goniometer

The small angle scattering goniometer is designed for the studies of SAXS by either the automatic recording method or the photographic method. However, the photographic method is currently seldom used for particle size analysis. The use of an SAS goniometer equipped with the Kratky collimation system is recommended when the measurable angle could reach  $1'$  and when higher intensity distribution might be acquired. It is particularly necessary to use such an apparatus for samples containing bigger particles having a size  $> 150$  nm.

In general, the angular range and accuracy can be specified as  $0'$  to  $2^\circ$  and  $0,1'$ , respectively. On the other hand, the minimum measuring angle depends on both what size range is to be determined and what kind of radiation is being used. Besides the size range, angular resolution also relates to how many classes are to be requested. As Co  $K_\alpha$  radiation was used, and  $n = 10$ , the Table C.1 could be a reference.

**Table C.1 — Classes**

Size range (nm)	1 to 300	1 to 200	1 to 150	1 to 100	1 to 50	1 to 20
Min. measuring angle (')	1,7	2,3	3,2	4,5	8,8	29
Angular range (')	1,7 to 90	2,3 to 90	3,2 to 90	4,5 to 90	8,8 to 90	29 to 90
Angular resolution (')	0,6	0,9	1,3	1,5	2	5

#### C.4 Detector

The scintillation counter is recommended as its rising time ( $0,2 \mu\text{s}$ ) to maintain a linear response over a broad range of intensities is very short, and its quantum counting efficiency is much higher for  $0,1$  nm to  $0,2$  nm radiation.

The position sensitive detector (PSD) allows simultaneous recording of the scattering intensities. It results in a reduction of the measuring time by a factor of 100 to 1 000 but it is not very suitable for determining the particle size of metallic or ceramic powders because of its longer dead time ( $12,5 \mu\text{s}$ ) and poor spatial resolution ( $100 \mu\text{m}$ ). It might be applicable to the study of biological samples.

A new type X-ray detector, “Image Plate”, has been developed recently. It can record the scattering intensity distribution simultaneously, has better resolution and allows a much higher counting rate.

**WARNING — Since the SAS apparatus is combined with an X-ray generator, the unit should be equipped with a proper radiation shield. The user also needs to take precautions to avoid X-ray hazards. No one should be permitted to use the equipment before having received proper instruction in safe practices.**

## Annex D (informative)

### Reproducibility and accuracy

A definite quantity of carbonyl nickel powder was drawn from the same batch (No. 90-3-5) of product then split into three portions. Determinations of particle size distribution of the powder were respectively carried out at laboratories A, B and C, according to GB/T13221-91. Five determinations on the test sample were made at each laboratory. The results are summarized in Tables D.1 to D.4.

**Table D.1**

$x_{i-1} \sim x_i$ (nm)	10 ~ 18	18 ~ 36	36 ~ 60	60 ~ 90	96 ~ 140	140 ~ 200	$\bar{X}$ (nm)
A1	20,2	47,2	20,0	10,2	1,0	1,3	36,5
A2	20,9	46,9	19,2	10,9	0,9	1,2	36,4
$\Delta Q_{3,i}$ (%) A3	20,8	46,8	19,1	11,0	0,7	1,5	36,7
A4	21,6	45,5	21,4	8,4	1,9	1,1	36,3
A5	21,5	45,4	2,3	8,6	1,6	1,6	36,7
$< \Delta Q_i >_A$ (%)	21,00	46,36	20,20	9,82	1,22	1,34	
$S_{\Delta Q_i,A}$ (%)	0,57	0,84	1,11	1,25	0,51	0,21	
$S_{\Delta Q,A} = 0,75 \%$ , $< \bar{X} >_A = 36,52$ nm, $S_{\bar{X}, A} = 0,18$ nm							

**Table D.2**

B1	21,7	47,3	23,6	4,4	1,7	1,3	34,7
B2	22,2	48,4	22,5	3,8	1,8	1,3	34,2
$\Delta Q_{3,i}$ (%) B3	21,1	46,3	24,7	5,1	1,6	1,2	35,2
B4	21,5	47,1	23,9	4,6	1,6	1,3	34,8
B5	21,2	46,6	24,4	4,9	1,6	1,3	35,1
$< \Delta Q_i >_B$ (%)	21,54	47,14	23,82	4,56	1,66	1,28	
$S_{\Delta Q_i,B}$ (%)	0,44	0,81	0,85	0,50	0,09	0,04	
$S_{\Delta Q,B} = 0,46 \%$ , $< \bar{X} >_B = 34,80$ nm, $S_{\bar{X}, B} = 0,39$ nm							

Table D.3

C1	13,3	55,1	22,5	6,1	2,1	0,9	36,3
C2	13,4	55,0	23,0	5,5	2,1	0,9	36,2
$\Delta Q_{3,i}$ (%) C3	14,4	53,1	23,1	5,8	2,6	1,0	36,6
C4	17,2	49,2	24,3	6,5	1,7	1,2	36,5
C5	19,9	46,1	25,2	5,7	2,0	1,1	36,1
$\langle \Delta Q_i \rangle_C$ (%)	15,64	51,70	23,60	5,92	2,10	1,02	
$S_{\Delta Q_i, C}$ (%)	2,86	3,94	1,09	0,39	0,32	0,13	
$S_{\Delta Q, C} = 1,46 \%$ , $\langle \bar{X} \rangle_c = 36,34 \text{ nm}$ , $S_{\bar{x}, C} = 0,21 \text{ nm}$							

Table D.4

$\langle \Delta Q_i \rangle_{A,B,C}$ (%)	19,38	48,40	22,55	6,77	1,66	1,21
$S_{\Delta Q_i, A,B,C}$ (%)	3,17	3,28	1,97	2,43	0,49	0,20
$S_{\Delta Q, A,B,C} = 1,93 \%$ , $\langle \bar{X} \rangle_{A,B,C} = 35,89 \text{ nm}$ , $S_{\bar{x}, A,B,C} = 0,84 \text{ nm}$						

Laboratory A — Central Iron & Steel Research Institute:

- Rigaku 3014 X-ray diffractometer;
- modified Rigaku 2202E1 small angle scattering goniometer equipped with Kratky U slit;
- Co  $K_\alpha$  radiation.

Laboratory B — Wuhan University of Technology:

- Rigaku D/Max-3A X-ray diffractometer;
- Rigaku D/Max-rB X-ray diffractometer;
- Rigaku 2203E7 small angle scattering goniometer equipped with Kratky U slit;
- Co  $K_\alpha$  radiation.

Laboratory C — State-operated Factory No. 857:

- Rigaku D/Max-rB X-ray diffractometer;
- Rigaku 2203E7 small angle scattering goniometer equipped with Kratky U slit;
- Co  $K_\alpha$  radiation.

$$\langle \bar{x} \rangle = \frac{1}{n} \sum_{j=1}^n x_j \quad S_{\bar{x}} = \frac{1}{n-1} \sqrt{\sum_{j=1}^n \{ \langle \bar{x} \rangle - \bar{x}_j \}^2}$$

$$\langle \Delta Q_i \rangle = \frac{1}{n} \sum_{j=1}^n \Delta Q_{ij}$$

$$S_{\Delta Q_j} = \frac{1}{n-1} \sqrt{\sum_{j=1}^n \{ \langle \Delta Q_i \rangle - \Delta Q_{ij} \}^2}$$

$$\langle \bar{S}_{\Delta Q} \rangle = \frac{1}{m} \sum_{i=1}^m S_{\Delta Q_i}$$

## Annex E (informative)

### Verification and examples for determination of particle size distribution of ultra-fine powders by SAXS method

#### E.1 Introduction

The small angle X-ray scattering (SAXS) technique is an effective method by which a particle size distribution of an ultra-fine powder sample can be determined when the particle size ranges from 1 nm to 300 nm. The SAXS signal is easily distinguished when the particles have a certain electron density contrast with the medium in which they are dispersed (see reference [1] in the bibliography). The intensity profile from a SAXS scan is closely related to the particle size distribution of the sample. SAXS always provides the primary particle size rather than the internal crystallite or external agglomerate size. It is relatively easy to prepare samples in an as-received state, and the result reflects the behaviour of a larger number of particles (in the order of  $10^{10}$  to  $10^{13}$ ) having participated in the scattering.

Compared with other methods which extract the particle size distribution from SAXS data, such as the Guinier tangent method and the successive logarithmic graphical (SLG) procedure, the dividing distribution function (DDF) method needs fewer measuring data. In addition, the coefficient matrix is determined solely by the measuring device and prerequisites. It is ready to compute without an assumed distribution function and the solution is relatively stable with optimized coefficient matrix (see references [2] and [3] in the bibliography). A wide variety of samples, such as metallic and ceramic powders, colloidal suspensions and precipitates in matrices have been tested. The results for some typical samples are shown in Table E.1.

In order to examine the reliability of the DDF method, the results of SAXS were compared with the images obtained with an EM-400 model transmission electron microscope (TEM). The validity of calculating specific surface was also checked by the BET absorption method.

#### E.2 Experimental examination by electron microscopy

The TEM method is often used in direct observation of particle sizes in a range of 1 nm to 1 000 nm. After a powder suspension sample has been dispersed, the particles are deposited on a thin membrane of approximately 10 nm to 20 nm, laid on a grid. In order to obtain reliable results from the measurement, a large number of particles must be examined.

The detailed procedure of DDF can be found elsewhere (see reference [4] in the bibliography).

Figures E.1 to E.4 show the relative frequency, cumulative distribution and the mean particle size ( $D_m$ ) of four different samples. All of them were obtained from SAXS measurement. The correspondent TEM micrographs are given in the Figures E.5 to E.8.

It can be seen that the results of SAXS and the TEM micrograph are consistent with each other.

Table E.1 — Particle size distribution of different samples by SAXS method

No.	Sample	Size range (nm)	2-10	10-20	20-30	30-40	40-60	60-80	80-120	120-160	160-220	220-280	Mean size $\bar{x}$ (nm)
1	Carboxyl	%	5,6	24,4	21,1	16,6	12,5	8,3	6	0,8	3,5	1,2	43,9
	Nickel	$\omega$	56,5	240,9	208,6	163,7	61,6	41,2	14,8	1,9	5,8	2,9	
2	Carboxyl	%	7	23,7	24,7	17,4	12	8	4,7	2,7			36,2
	Iron	$\omega$	61,3	204,3	213,9	150,0	51,6	34,3	10,1	5,8			
3	Fe <sub>3</sub> O <sub>4</sub>	%	19,9	33,9	21,9	12,7	5,9	2,5	1,0	0,5	0,5	1,2	26,5
	Powder	$\omega$	178	298	192	111,7	26,1	10,9	2,2	1,1	0,8	1,7	
4	Si <sub>3</sub> N <sub>4</sub>	%	9,5	13,7	19,3	17,0	14,5	10,1	5,5	4,3	3,0	3,2	52,8
	Powder	$\omega$	189	265	374	329	141,3	97,5	26,5	20,7	9,6	10,3	
5	CaCO <sub>3</sub>	%	7,6	9,2	17,1	20,4	15,8	10,1	3,8	3,9	3,8	8,3	65,4
	Powder	$\omega$	62,4	74,1	138	165,4	63,5	40,7	7,6	7,9	5,1	11,2	
6	Tungsten	%	0,3	0,5	2,3	8,2	18,1	18,7	17,8	14,4	10,6	9,0	106,4
	Powder	$\omega$	23,7	47,2	20,6	73,7	81,1	84,7	40,0	32,4	15,9	13,5	
7	Tin	%	0,6	4,6	11,0	14,3	17,2	16,7	14,1	10,3	6,0	5,2	81,7
	Powder	$\omega$	5,2	38,2	90,2	117,5	70,6	68,7	29,1	21,1	8,2	7,2	
8	Ni <sub>3</sub> Al	%	2,5	6,4	13,4	19,5	37,2	16,0	3,7	0,2	0,1	0,9	47,5
	Powder	$\omega$	13,3	33,1	69,2	100,4	95,8	41,3	4,8	0,2	0,1	0,8	
9	Al	%	0	21,8	43,4	18,3	12,3	3,3	0,8	0,1			29,9
	Powder	$\omega$	0	131	262	110	37,0	10,0	1,2	0,2			
No.	Sample	Size range (nm)	2-4	4-6	6-10	10-16	16-24	24-36	36-52				Mean size $\bar{x}$ (nm)
10	Nickel	%	22,5	27,5	33,6	13,4	2,0	0,3	0,7				7,2
	Catalyst	$\omega$	409	500	305	8,9	0,9	0,9	1,7				
11	SiO <sub>2</sub>	%	1,7	2,6	10,7	16,0	37,7	29,9	1,4				20,2
	Suspension	$\omega$	39,5	59,4	129	122	215	113	4,0				

$\omega$  the distribution frequency.



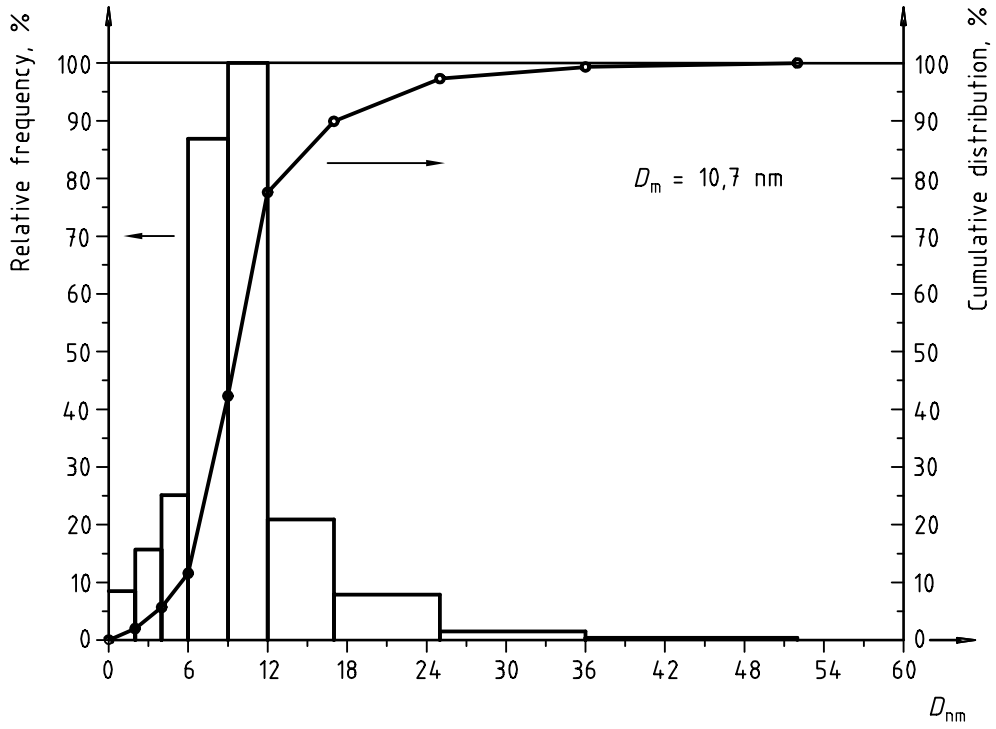


Figure E.1 — Size histogram of JAP-100 nickel

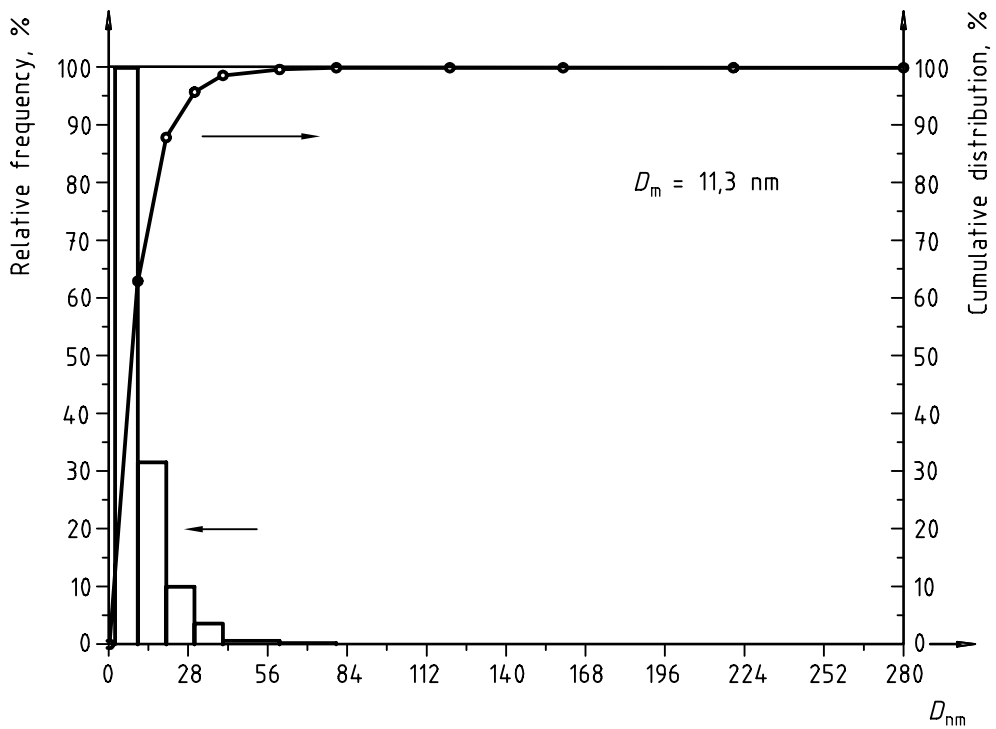


Figure E.2 — Size histogram of  $ZrO_2$  powder

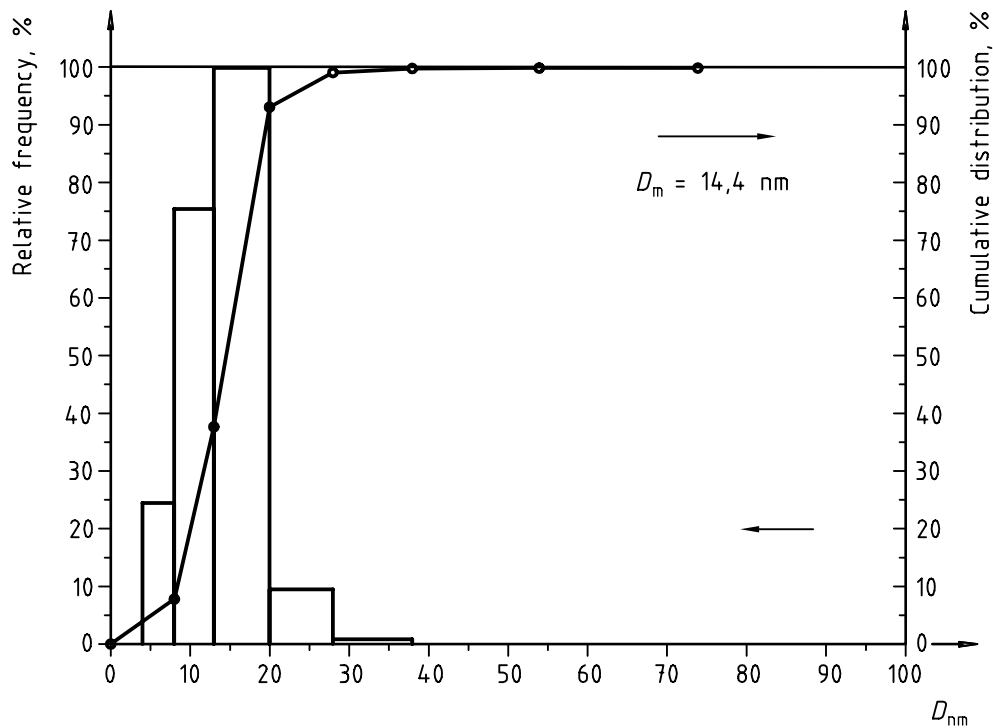


Figure E.3 — Size histogram of SiO<sub>2</sub> colloidal solution

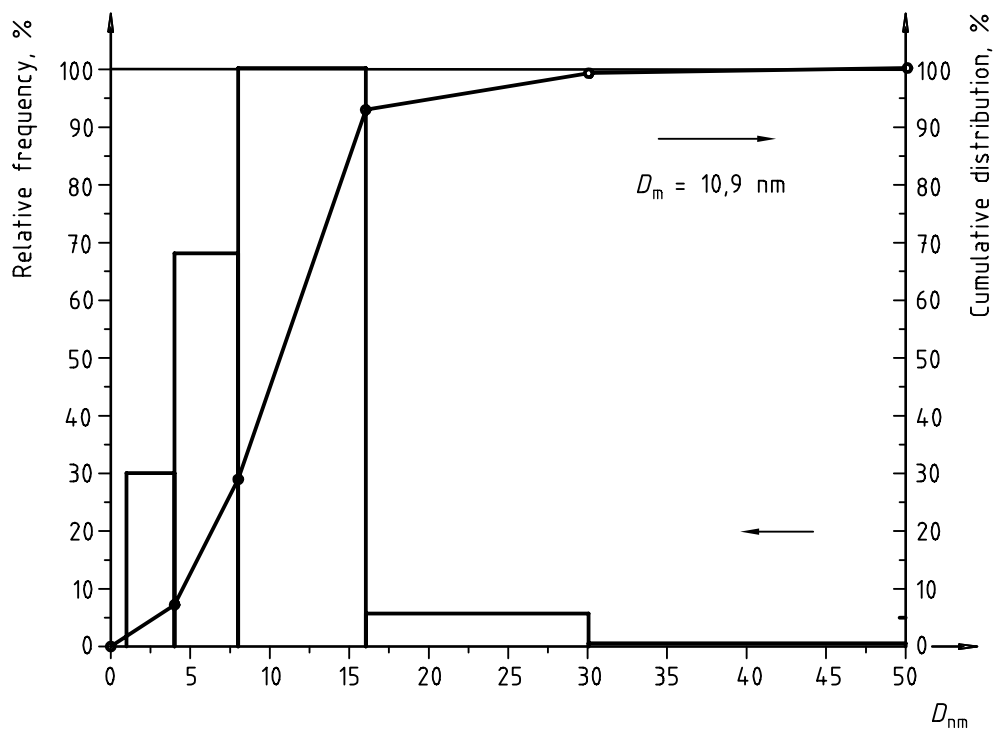


Figure E.4 — Size histogram of Fe<sub>3</sub>N magnetic fluid

### E.3 Experimental examination by specific surface measurement

The specific surface of a powder sample is defined as the total surface area of the particles per unit mass of the powder and it is usually expressed in units of  $\text{m}^2/\text{g}$ . The magnitude of specific surface of a powder sample depends on its particle size distribution and the morphology of the particles. It can be approximately calculated based on the shape and size distribution of the particles. For spherical particles, we have:

$$S_x = \frac{6}{\rho} \sum_{i=1}^n \frac{\Delta Q_{3,i}}{R_{i-1} + R_i} \times 10^3$$

where

$\rho$  is the density of the particle ( $\text{g}/\text{cm}^3$ );

$R$  is the radius of the particle;

$\Delta Q_{3,i}$  is the mass fraction in the size range of  $R_{j-1}$  to  $R_j$  (%);

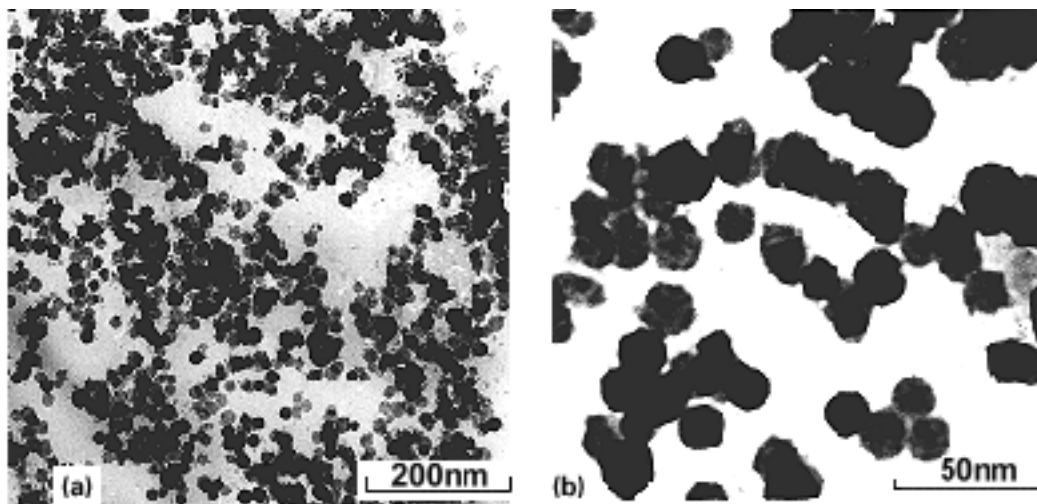


Figure E.5 — TEM micrograph of JAP 100 nickel powder

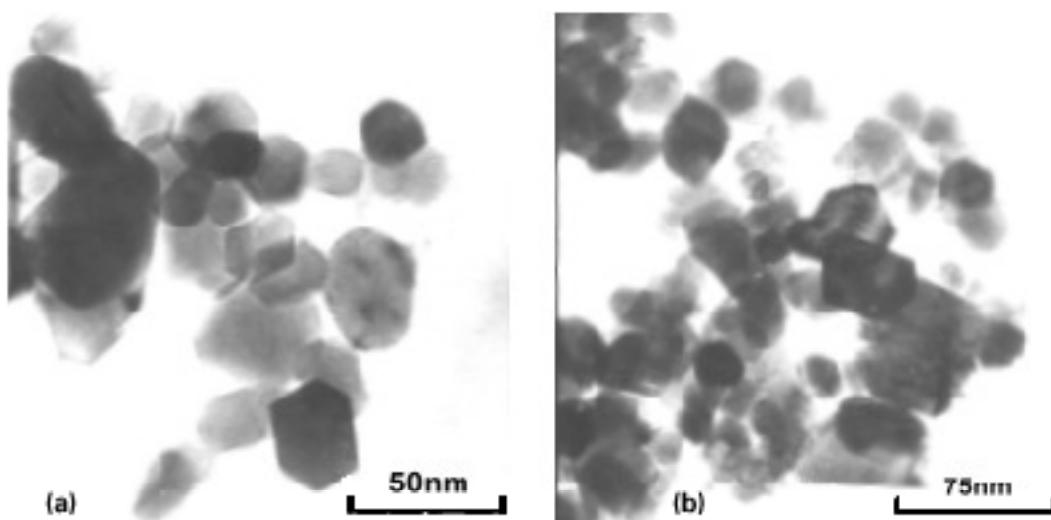
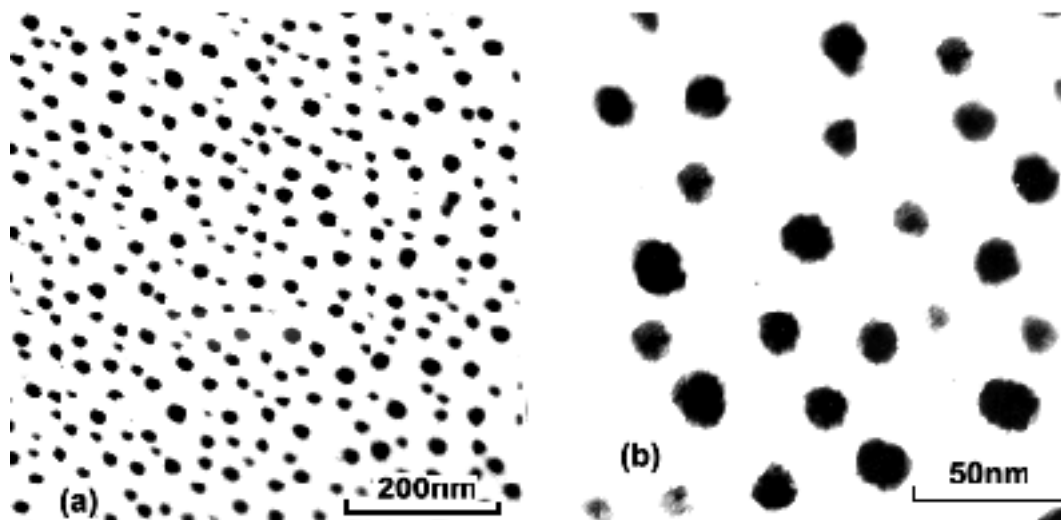
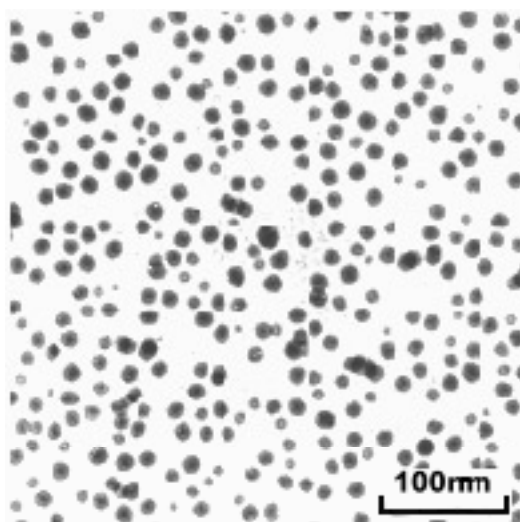


Figure E.6 — TEM micrograph of ZrO, ultrafine powder

Figure E.7 — TEM micrograph of  $\text{SiO}_2$ , colloid solFigure E.8 — TEM micrograph of  $\text{Fe}_3\text{N}$ , magnetic fluid

The BET method is commonly used in measuring the specific surface of a powder sample based on the gas-absorption technique. The SAXS method, on the other hand, can also derive the specific surface information from the measured particle size distribution and the mass density of the powder particle. For the comparison, a set of carbonyl nickel powder samples, with an observed near-spherical shape, were tested by both SAXS and BET methods. The results are listed in Table E.2.

Table E.2 — SAXS and BET results on carbonyl nickel powder samples

Sample	1-15	B-14	4-3	4-4	4-15	4-8	4-11	1-5	4-13	1-8
Sx ( $\text{m}^2/\text{g}$ )	16,0	19,1	19,9	21,3	24,9	24,9	24,5	30,7	26,5	24,8
SB ( $\text{m}^2/\text{g}$ )	16,3	19,6	22,7	26,0	29,3	31,0	32,4	34,5	34,4	36,4

It can be seen from Table E.2 that the values of SB obtained from BET are slightly greater than Sx from SAXS. This may indicate the irregularity of the real surfaces of powder particles. Clearly, the two sets of results are systematically comparable.

## E.4 Conclusion

Through comparison of SAXS results with TEM and BET absorption results, the DDF method is proved to be a reliable and effective method to extract the particle size distribution from the SAXS data of powders.

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