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Measurement and characterization of particles by acoustic methods

Part 2: Guidelines for linear theory

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National foreword

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Measurement and characterization of particles by acoustic methods —

Part 2:
Guidelines for linear theory

Caractérisation des particules par des méthodes acoustiques —

Partie 2: Théorie linéaire

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Contents

Foreword

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The committee responsible for this document is ISO/TC 24, *Particle characterization including sieving,* Subcommittee SC 4*, Particle characterization.*

ISO 20998 consists of the following parts, under the general title *Measurement and characterization of particles by acoustic methods:*

- *Part 1: Concepts and procedures in ultrasonic attenuation spectroscopy*
- *Part 2: Guidelines for linear theory*

Introduction

It is well known that ultrasonic spectroscopy can be used to measure particle size distribution (PSD) in colloids, dispersions, and emulsions (References [1][2][3][4]). The basic concept is to measure the frequency-dependent attenuation or velocity of the ultrasound as it passes through the sample. The attenuation spectrum is affected by scattering or absorption of ultrasound by particles in the sample, and it is a function of the size distribution and concentration of particles (References [5][6][7]). Once this relationship is established by empirical observation or by theoretical calculations, one can estimate the PSD from the ultrasonic data. Ultrasonic techniques are useful for dynamic online measurements in concentrated slurries and emulsions.

Traditionally, such measurements have been made off-line in a quality control lab, and constraints imposed by the instrumentation have required the use of diluted samples. By making in-process ultrasonic measurements at full concentration, one does not risk altering the dispersion state of the sample. In addition, dynamic processes (such as flocculation, dispersion, and comminution) can be observed directly in real time (Reference [8]). These data can be used in process control schemes to improve both the manufacturing process and the product performance.

ISO 20998 consists of two parts:

- 20998-1 introduces the terminology, concepts, and procedures for measuring ultrasonic attenuation spectra;
- 20998-2 provides guidelines for determining particle size information from the measured spectra for cases where the spectrum is a linear function of the particle volume fraction.

A further part addressing the determination of particle size for cases where the spectrum is not a linear function of volume fraction is planned.

Measurement and characterization of particles by acoustic methods —

Part 2:
Guidelines for linear theory

1 Scope

This part of ISO 20998 describes ultrasonic attenuation spectroscopy methods for determining the size distributions of a particulate phase dispersed in a liquid at dilute concentrations, where the ultrasonic attenuation spectrum is a linear function of the particle volume fraction. In this regime, particle–particle interactions are negligible. Colloids, dilute dispersions, and emulsions are within the scope of this part of ISO 20998. The typical particle size for such analysis ranges from 10 nm to 3 mm, although particles outside this range have also been successfully measured. For solid particles in suspension, size measurements can be made at concentrations typically ranging from 0,1 % volume fraction up to 5 % volume fraction, depending on the density contrast between the solid and liquid phases, the particle size, and the frequency range.

NOTE See References [9][10].

For emulsions, measurements may be made at much higher concentrations. These ultrasonic methods can be used to monitor dynamic changes in the size distribution.

While it is possible to determine the particle size distribution from either the attenuation spectrum or the phase velocity spectrum, the use of attenuation data alone is recommended. The relative variation in phase velocity due to changing particle size is small compared to the mean velocity, so it is often difficult to determine the phase velocity with a high degree of accuracy, particularly at ambient temperature. Likewise, the combined use of attenuation and velocity spectra to determine the particle size is not recommended. The presence of measurement errors (i.e. “noise”) in the magnitude and phase spectra can increase the ill-posed nature of the problem and reduce the stability of the inversion.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 14488:2007, *Particulate materials — Sampling and sample splitting for the determination of particulate properties*

ISO 20998-1:2006, *Measurement and characterization of particles by acoustic methods — Part 1: Concepts and procedures in ultrasonic attenuation spectroscopy*

3 Terms and definitions

For the purposes of this document, the terms and definitions in ISO 20998-1 and the following apply.

3.1
coefficient of variation
ratio of the standard deviation to the mean value

3.2
dimensionless size parameter
representation of particle size as the product of wave number and particle radius

3.3
particle radius
one-half of the particle diameter

3.4
wave number
ratio of 2π to the wavelength

4 Symbols and abbreviated terms

$\mathbf{A}$	matrix representing the linear attenuation model
A_n	coefficients of series expansion in ECAH theory
a	particle radius
c	speed of sound in liquid
C_p	specific heat at constant pressure
C_PF	particle projection area divided by suspension volume
CV	coefficient of variability (ratio of the standard deviation to the mean value)
E	extinction at a given frequency
ECAH	Epstein-Carhart-Allegra-Hawley (theory)
f_i	frequency
$\mathbf{H}$	identity matrix
h_n	Hankel functions of the first kind
I	transmitted intensity of ultrasound
I_0	incident intensity of ultrasound
i	the imaginary number
inv()	matrix inverse operation
K	extinction efficiency (extinction cross section divided by particle projection area)
$\mathbf{K}$	matrix representation of the kernel function (the ultrasonic model)
$\mathbf{K}^\mathrm{T}$	transpose of matrix **K**
$k(f, x)$	kernel function
k_c, k_T, k_s	wave numbers of the compressional, thermal, and shear waves
ka	dimensionless size parameter
P_n	Legendre polynomials
PSD	particle size distribution

$\boldsymbol{q}$	solution vector (representation of the PSD)
$q_3(x)$	volume weighted density function of the PSD
$Q_3(x)$	volume weighted cumulative PSD
s	standard deviation
x	particle diameter
x_{10}	the 10th percentile of the cumulative PSD
x_{50}	median size (50th percentile)
x_{90}	the 90th percentile of the cumulative PSD
x_{min}	minimum particle size in a sample
x_{max}	maximum particle size in a sample
α	total ultrasonic attenuation coefficient
$\boldsymbol{\alpha}$	attenuation spectrum
$\tilde{\alpha}$	absolute attenuation coefficient divided by the frequency, $\tilde{\alpha} = (\alpha/f)$
α_{exc}	excess attenuation coefficient, $\alpha_{\mathrm{exc}} = \alpha - \alpha_{\mathrm{L}}$
$\alpha_{\mathrm{exc'}}$	alternate definition of excess attenuation coefficient where $\alpha_{\mathrm{exc}}' = \alpha - \alpha_{\mathrm{int}}$
$\boldsymbol{\alpha}_{\mathrm{exp}}$	measured attenuation spectrum
a_{int}	intrinsic absorption coefficient of the dispersion
α_{L}	attenuation coefficient of the continuous (liquid) phase
$\boldsymbol{\alpha}_{\mathrm{mod}}$	attenuation spectrum predicted by the model, given a trial PSD
α_{P}	attenuation coefficient of the discontinuous (particulate) phase
α_{sc}	elastic scattering component of the attenuation coefficient
α_{th}	thermal loss component of the attenuation coefficient
α_{vis}	viscoinertial loss component of the attenuation coefficient
β_{T}	volume thermal expansion coefficient
Δ	error in the fit, $\Delta = \left\lVert \alpha_{\mathrm{exp}} - \alpha_{\mathrm{mod}} \right\rVert$
$\mathit{\Delta}$	Tikhonov regularization factor
Δl	thickness of the suspension layer
ΔQ_2	fraction of the total projection area containing a certain particle size class
η	viscosity of the liquid
κ	thermal conductivity

λ	ultrasonic wavelength
μ	shear modulus
ρ, ρ'	density of the liquid and particle, respectively
ϕ	volume concentration of the dispersed phase
χ^2	chi-squared value
Ψ_c	compression wave
Ψ_s	shear wave
Ψ_T	thermal wave
ω	angular frequency (i.e. 2π times the frequency)

5 Mechanism of attenuation (dilute case)

5.1 Introduction

As ultrasound passes through a suspension, colloid, or emulsion, it is scattered and absorbed by the discrete phase with the result that the intensity of the transmitted sound is diminished. The attenuation coefficient is a function of ultrasonic frequency and depends on the composition and physical state of the particulate system. The measurement of the attenuation spectrum is described in ISO 20998-1.

5.2 Excess attenuation coefficient

The total ultrasonic attenuation coefficient, α, is due to viscoinertial loss, thermal loss, elastic scattering, and the intrinsic absorption coefficient, α_{int}, of the dispersion (References [1][10]):

$$\alpha = \alpha_{\text{vis}} + \alpha_{\text{th}} + \alpha_{\text{sc}} + \alpha_{\text{int}} \tag{1}$$

The intrinsic absorption is determined by the absorption of sound in each homogenous phase of the dispersion. For pure phases, the attenuation coefficients, denoted α_{L} for the continuous (liquid) phase and α_{P} for the discontinuous (particulate) phase, are physical constants of the materials. In a dispersed system, intrinsic absorption occurs inside the particles and in the continuous phase, therefore,

$$\alpha_{\text{int}} \approx (1-\phi)\cdot\alpha_{\text{L}} + \phi\cdot\alpha_{\text{P}} \tag{2}$$

The excess attenuation coefficient is usually defined to be the difference between the total attenuation and the intrinsic absorption in pure (particle-free) liquid phase (References [4][7]):

$$\alpha_{\text{exc}} = \alpha - \alpha_{\text{L}} \tag{3}$$

With this definition, the excess attenuation coefficient is shown to be the incremental attenuation caused by the presence of particles in the continuous phase. Combining Formulae (1), (2), and (3), it can be seen that

$$\alpha_{\text{exc}} = \alpha_{\text{vis}} + \alpha_{\text{th}} + \alpha_{\text{sc}} + \phi\cdot(\alpha_{\text{P}} - \alpha_{\text{L}}) \tag{4}$$

The viscoinertial, thermal, and elastic scattering terms depend on particle size, but α_L and α_P do not. Thus, the excess attenuation coefficient contains a term that does not depend on size. When working with aqueous dispersions and rigid particles, this term can often be neglected, so that

$$\alpha_{exc} \approx \alpha_{vis} + \alpha_{th} + \alpha_{sc} \tag{5}$$

However, in some emulsions, the ultrasonic absorption in the oily phase can be significant. In that case, the definition of the excess attenuation coefficient given in Formula (3) may be modified as

$$\alpha_{exc'} = \alpha - \alpha_{int} \tag{6}$$

In this situation, Formula (5) is still valid. It should be noted that some authors express attenuation coefficient as a reduced quantity $\tilde{\alpha} = (\alpha / f)$, dividing the absolute attenuation coefficient by the frequency.

5.3 Specific attenuation mechanisms

5.3.1 Scattering

Ultrasonic scattering is the redirection of acoustic energy away from the incident beam, so it is elastic (no energy is absorbed). The scattering is a function of frequency and particle size.

5.3.2 Thermal losses

Thermal losses are due to temperature gradients generated near the surface of the particle as it is compressed by the acoustic wave. The resulting thermal waves radiate a short distance into the liquid and into the particle. Dissipation of acoustic energy caused by thermal losses is the dominant attenuation effect for soft colloidal particles, including emulsion droplets and latex droplets.

5.3.3 Viscoinertial losses

Viscoinertial losses are due to relative motion between the particles and the surrounding fluid. The particles oscillate with the acoustic pressure wave, but their inertia retards the phase of this motion. This effect becomes more pronounced with increasing contrast in density between the particles and the medium. As the liquid flows around the particle, the hydrodynamic drag introduces a frictional loss. Viscoinertial losses dominate the total attenuation for small rigid particles, such as oxides, pigments, and ceramics. An explicit calculation of the attenuation due to viscoinertial loss is given in Annex A for the case of rigid particles that are much smaller than the wavelength of sound in the fluid.

5.4 Linear models

5.4.1 Review

The attenuation of ultrasound in a dispersed system is caused by a variety of mechanisms (see 5.3), the significance of which depends on material properties, particle size, and sound frequency. Moreover, for some material systems, a linear relationship between sound attenuation and particle concentration can be observed up to concentrations of 20 % volume fraction or more, while for others, such a relationship exists only at low concentrations. This situation has led to a variety of models; two principal approaches may be distinguished.

The first is the scattering theory, which aims at the scattered sound field around a single particle. Based on this, the propagation of sound through the dispersed system can be calculated. By assuming independent scattering events and neglecting multiple scattering, the attenuation turns out to be linearly dependent on the particle concentration.

The fundamentals of the scattering theory were already presented by Rayleigh, but his approach ignored the energy dissipation by shear waves and thermal waves (viscoinertial and thermal losses). A well-known scattering theory is the ECAH (Epstein-Carhart-Allegra-Hawley) theory, a short introduction to which is given in Annex B. The ECAH theory includes sound scattering as well as the viscoinertial and the thermal losses. It can be applied to homogenous, spherical particles with no limit regarding material properties, particle size, or sound frequency.

The second principal approach in modelling is to consider only the attenuation by viscoinertial and thermal losses, which is admissible in the long wavelength limit (where $x \lll \lambda$ or, equivalently, $ka \lll 1$) only. That restriction facilitates the inclusion of nonlinear concentration effects that are caused by the interaction of shear waves and/or thermal waves. Consequently, most of these theories are beyond the scope of this part of ISO 20998. However, linear solutions can be obtained in the limiting case of vanishing particle concentration ($\phi \rightarrow 0$). In general, these theories then agree with the ECAH theory (with regard to the modelled attenuation mechanism). Purely linear models are that of Reference [11] for the viscoinertial loss mechanism and that of Reference [12] for the thermal loss mechanism, both of which agree with ECAH results (Reference [7]).

The theoretical models may fail to accurately explain measured attenuation spectra since they hold true only for homogenous, spherical particles and require the knowledge of several physical parameters of the dispersed system. In such situations, semi-empirical approaches may be used that are based on the observation that for spheres we get

$$\tilde{\alpha}_{\text{vis}} = \mathrm{f}(x^2 f) \ ,$$

$$\tilde{\alpha}_{\text{th}} = \mathrm{f}(x^2 f) \ ,$$

and

$$\tilde{\alpha}_{\text{sc}} = \mathrm{f}(xf) \ .$$

The application and derivation of such a semi-empirical model is described in Annex C.

5.4.2 Physical parameters

A number of physical properties affect the propagation of ultrasound in suspensions and emulsions. These properties (listed in Table 1) are included in the ECAH model described in Annex B. In most practical applications, many of these parameters are not known, and it is therefore difficult to compare theory with experimental observation directly. Fortunately, approximate models can be employed for many situations (cf. 5.3.1), which reduces the number of influential parameters. Moreover, some of these parameters only weakly affect the attenuation and, therefore, do not need to be known with high accuracy. Typical material systems are listed in Table 2 together with the material properties that most significantly affect the attenuation.

Table 1 — The complete set of properties for both particle and medium that affect the ultrasound propagation through a colloidal suspension

Dispersion medium	Dispersed particle	Units
Density	Density	kg · m^{-3}
Shear viscosity (microscopic)		Pa · s
	Shear modulus	Pa
Sound speed	Sound speed	M · s^{-1}
Absorption	Absorption	Np · m^{-1}, dB · m^{-1}
Heat capacity at constant pressure	Heat capacity at constant pressure	J · kg^{-1} · K^{-1}

Table 1 *(continued)*

Dispersion medium	Dispersed particle	Units
Thermal conductivity	Thermal conductivity	$W \cdot m^{-1} \cdot K^{-1}$
Thermal expansion	Thermal expansion	K^{-1}

NOTE The decibel (dB) is commonly used as a unit of attenuation, so absorption is often expressed in units of $dB \cdot m^{-1}$ or $dB \cdot cm^{-1}$.

Table 2 — Material properties that have the most significant effect on ultrasonic attenuation

System	Properties of the particle	Properties of the liquid
Rigid submicron particles	Density	Density, sound speed, shear viscosity
Soft submicron particles	Thermal expansion	Thermal expansion
Large soft particles	Density, sound speed, elastic constants	Density, sound speed
Large rigid particles	Density, sound speed, shape	Density, sound speed

6 Determination of particle size

6.1 Introduction

This section describes procedures for estimating the particle size distribution from an ultrasonic attenuation spectrum.

In general, the observed ultrasonic attenuation spectrum, which forms the data function $\boldsymbol{\alpha}$, is dependent on the particle size distribution and on the particle concentration. In dilute suspensions and emulsions, the sound field interacts with each particle independently. That is, the attenuation of sound is formed by the superposition of individual, uncorrelated events, and the spectrum is a linear function of concentration. In this case, a linear theory such as the ECAH model described in Annex B can be applied to determine the particle size distribution.

Within the linear theory, the attenuation of sound is related to a PSD by the following formula:

$$\tilde{\alpha}_{\text{exc}}(f_{\text{i}})=\phi\cdot(\tilde{\alpha}_{\text{P}}(f_{\text{i}})-\tilde{\alpha}_{\text{L}}(f_{\text{i}}))+\phi\cdot\int k(f_{\text{i}},x)\cdot q_3(x)dx \tag{7}$$

where ϕ is the volume concentration of the dispersed phase and $q_3(x)$ is the volume weighted density function of the PSD. The function $k(f, x)$ is called the kernel function, and it models the physical interactions between the ultrasound and the particles.

The inversion problem, i.e. the determination of the continuous function $q_3(x)$ from a (discrete) attenuation spectrum, is an ill-posed problem. Any measured discrete attenuation spectrum cannot reveal all details of $q_3(x)$. Moreover, signal noise further reduces the amount of accessible information on $q_3(x)$. For that reason, the inversion problem has to be modified by restricting the space of possible solutions. Two principal approaches may be distinguished:

a) the approximation of $q_3(x)$ by a given PSD function, where the parameters of this function are determined by a nonlinear regression;

b) the discretization of the size axis x plus imposing additional constraints on the solution vector $\mathbf{q}$ (regularization.)

These two approaches are described in 6.2.

NOTE The choice of inversion approach does not depend on the choice of theory used to calculate the attenuation spectrum.

The performance of the algorithms depends on the material system, on the measurement instrument, as well as on the size distribution. It is further related to the information content of the measured attenuation spectrum, which is determined by the covered frequency range, by the signal noise, to a lower extent by the number of frequencies, and primarily by the structure of the kernel functions $k(f, x)$ (Reference [13]).

6.2 Inversion approaches used to determine PSD

6.2.1 Optimization of a PSD function

In the case of colloidal dispersions, i.e. in the long wavelength regime, the spectra are very smooth so that very little information appears to be contained in the data. In order to extract the PSD from the attenuation data, a model function might be assumed, effectively reducing the number of free parameters to be fit to the data (Reference [9]). A typically used model function is the log normal distribution (cf. ISO 9276-2:—,[33] Annexes A and B):

$$q_3(x) = \frac{1}{sx\sqrt{2\pi}} \exp\left[-\frac{1}{2}\left(\frac{1}{s}\ln\frac{x}{x_{50}}\right)^2\right] \tag{8}$$

where x_{50} is the median size and s is the standard deviation of $\ln(x)$. The solution of the inversion problem is found by minimizing the residual Δ:

$$\Delta = \left\| \alpha_{\text{exp}} - \alpha_{\text{mod}} \right\| \tag{9}$$

where $\boldsymbol{\alpha}_{\text{exp}}$ is measured and $\boldsymbol{\alpha}_{\text{mod}}$ is calculated by Formula (7) using, for example, viscoinertial loss (see Annex A), ECAH (see Annex B), or some other suitable model. The model parameters of the best fitting function can be obtained from an optimization strategy. These are iterative algorithms, the general principal of which is described in Annex D. Care must be taken to ensure that the optimization strategy does not result in a local minimum of the residual Δ, which could cause a significant error in the estimated PSD.

6.2.2 Regularization

Model functions restrict the solution $q_3(x)$ with regard to the number of modes or the skewness, which may obscure relevant details in the distribution function. As shown in Annex C, it is possible to derive an inversion without model parameters for the estimated PSD (References [14][15][16]). If the information content of $\boldsymbol{\alpha}$ is sufficient, an alternative approach is to introduce size fractions and to re-write Formula (7) in its discrete form:

$$\alpha = \phi \cdot (\alpha_p - \alpha_L) + \phi \cdot \mathbf{K} \cdot \boldsymbol{q} \tag{10}$$

where the matrix **K** is the discrete representation of the ultrasonic model, giving the attenuation as a function of particle size. Solving this formula is an ill-conditioned problem, as the signal noise is extremely magnified. Formal solution may yield results that are physically unacceptable, for example, negative size fractions or a discontinuous PSD. To avoid such results, one can modify the problem by assuming certain properties of the shape of the distribution function (or the solution vector $\boldsymbol{q}$, respectively). The most popular regularization is based on the smoothness of the distribution function, which can be quantified via $\boldsymbol{q}^{\mathrm{T}} \cdot \mathbf{H} \cdot \boldsymbol{q}$ leading to the modified objective function:

$$\chi^2 = \left\| \alpha_{\mathrm{exp}} - \mathbf{K} \cdot \boldsymbol{q} \right\|^2 + \delta \cdot \boldsymbol{q}^{\mathrm{T}} \cdot \mathbf{H} \cdot \boldsymbol{q} \tag{11}$$

Here, **H** is the identity matrix, $\mathbf{K}^{\mathrm{T}}$ is the transpose of matrix **K**, and δ is a suitable Tikhonov regularization factor (Reference [14]). The solution is then obtained from:

$$\boldsymbol{q} = \mathbf{inv}(\mathbf{K}^{\mathrm{T}}\mathbf{K} + \delta^2 \cdot \mathbf{H})\mathbf{K}^{\mathrm{T}} \alpha_{\mathrm{exp}} \tag{12}$$

For small values of the regularization factor δ, the solution $\boldsymbol{q}$ is highly affected by the signal noise showing strong oscillations with large negative values. In contrast, very large regularization factors yield such smooth solutions that the characteristic features of the PSD are lost. In order to select an optimal regularization factor, different strategies can be applied (References [17][18][19][20]).

6.3 Limits of application

The typical particle size for ultrasonic analysis ranges from 10 nm to 3 mm, although particles outside this range have also been successfully measured. Measurements can be made with a linear model for concentrations of the dispersed phase ranging from 0,1 % volume fraction up to 5 % volume fraction or more, depending on the density contrast between the continuous and the dispersed phases. In the case of emulsions, measurements may be made at much higher concentrations (approaching 50 % volume fraction).

The application of linear theoretical models requires the knowledge of the relevant model parameters. Users should therefore be aware of possible changes in those parameters, e.g. variation of the particle concentration. In particular, processes including a change of the phase (e.g. dissolution) or a change in temperature may defy an analysis with theoretical models. In such a case, users are referred to the world of chemometrics, i.e. to methods for data treatment and statistical modelling (e.g. with neural networks, multiple regression, etc.).

7 Instrument qualification

7.1 Calibration

Ultrasonic spectroscopy systems are based on first principles. Thus, calibration in the strict sense is not required; however, it is still necessary and desirable to confirm the accurate operation of the instrument by a qualification procedure. See ISO 20998-1 for recommendations.

7.2 Precision

7.2.1 Reference samples

For testing precision, reference samples with an x_{90}/x_{10} ratio in the range of 1,5 to 10 should be used. It is desirable that reference samples used to determine precision are non-sedimenting and comprising spherical particles with diameters in the range of 0,1 µm to 1 µm. The concentration shall be in the range of 1 % to 5 % volume fraction.

7.2.2 Repeatability

The requirements given in ISO 20998-1 shall be followed. The instrument should be clean, and the liquid used for the background measurement should be virtually free of particles. Execute at least five consecutive measurements with the same dispersed sample aliquot or dispersed single shot samples. Calculate the mean and coefficient of variation (CV) for the x_{10}, x_{50}, and x_{90}. An instrument is considered to meet this part of ISO 20998 for repeatability if the CV for each of the x_{10}, x_{50}, and x_{90} is smaller than 10 %. If a larger CV value is obtained, then all potential error sources shall be checked.

7.2.3 Reproducibility

Reproducibility tests shall follow the same protocol as that for repeatability. At least three distinct samples of the same reference material shall be measured, and the mean and CV for the x_{10}, x_{50}, and x_{90} shall be calculated. A CV larger than that of repeatability may be expected due to differences in sampling or dispersion or between analysts or instruments. The certification for the reference material will contain information about the acceptable error for that material.

7.3 Accuracy

7.3.1 Qualification procedure

In the qualification step, the accuracy of the total measurement procedure is examined. It is essential that a written procedure is available that describes the sub-sampling, the sample dispersion, the ultrasonic measurement, and the calculation of the PSD in full detail. This procedure shall be followed in its entirety and the title and version number reported.

7.3.2 Reference samples

Certified reference materials (see ISO 35) are preferred in the measurement of accuracy. These materials have a known size distribution of spherical particles with an x_{90}/x_{10} ratio in the range of 1,5to 10. It is preferred that the median size of the certified reference material be chosen so that it lies within the size range contemplated for the end-use application. For single shot analysis, the full contents of the container shall be used. If sub-sampling is necessary, this shall be done with due care while using a method that has been proven to yield adequate results (see ISO 14488). If a protocol for sampling, dispersion, or measurement is not available, the procedure that is used shall be reported with the final results.

7.3.3 Instrument preparation

The advice given in ISO 20998-1 should be followed. The instrument should be clean, and the liquid used for the background measurement should be free of particles.

7.3.4 Accuracy test

The written test protocol defined in 7.3.1 shall be followed for the accuracy test, which measures the PSD of the selected reference material. Single shot analysis may be applied. Analysis of sub-samples is permitted if the procedure for sub-sampling is also written and is documented to provide good repeatability. Analysis shall be made on five consecutive sample aliquots, and the average value and CV of the median size shall be calculated.

7.3.5 Qualification acceptance criteria

The 95 % tolerance limits stated for each certified size value of the standard reference material specification form a set of maximum and minimum values that define the stated parameter. The qualification test shall be accepted as passing the requirement of this part of ISO 20998 if the resulting measured particles size distribution achieves both of the following criteria.

a) The reported average value of the median size measured in the qualification test is no smaller than 90 % of the minimum value and no larger than 110 % of the maximum value.

b) The reported CV of the median size does not exceed 10 %.

If a larger deviation is obtained, then all potential error sources should be checked. If it is not possible to meet the qualification criteria of this section, then this failure shall be noted on the final PSD report.

If a higher standard of accuracy is required for any reason, then a reference material should be chosen with a narrow confidence interval and a total protocol for sampling, dispersion, and measurement should be used that guarantees minimum deviation.

8 Reporting of results

The particle size distribution results shall be reported according to the guidelines in ISO 20998-1, Clause 5.

Annex A
(informative)

Viscoinertial loss model

Viscoinertial loss (see 5.3.3) may be calculated in the long wavelength limit from Formula (A.1). The form shown here is from Reference [5], but it is derived from the explicit analytical solutions of Reference [7] and is mathematically equivalent to results obtained by many authors (References [11][21][22]).

$$\alpha_{\text{vis}} = \left(\frac{\phi}{2}\right)\left(\frac{C_d^{\infty}}{c\rho}\right)\frac{\left(\rho' - \rho\right)^2}{\left[\left(\rho' + \rho C_i^{\infty}\right)^2 + \left(C_d^{\infty}\right)^2 \omega^{-2}\right]} \tag{A.1}$$

where the dissipative and inertial drag coefficients (Reference [5]) are given by

$$C_d^{\infty} = \frac{9\eta}{2a^2}(1+Y) \tag{A.2}$$

$$C_i^{\infty} = \frac{1}{2}\left(1 + \frac{9}{2}Y^{-1}\right) \tag{A.3}$$

with the dimensionless parameter Y defined by

$$Y = a\sqrt{\frac{\omega\rho}{2\eta}} \tag{A.4}$$

In the formulae above,

α_{vis}	is the viscous attenuation coefficient
a	is the particle radius
c	is the speed of sound in liquid
ω	is the angular frequency of ultrasound (i.e. 2π times the frequency)
ρ, p'	is the density of the liquid and particle, respectively
η	is the viscosity of the liquid
ϕ	is the volume concentration of the particle

Annex B
(informative)

ECAH theory and limitations

B.1 Introduction

The Epstein-Carhart-Allegra-Hawley (ECAH) theory is derived from Reference [6] on sound attenuation in liquid/liquid systems (emulsions). Reference [7] later generalized that theory to include elastic solid particles as well as fluid particles in a liquid suspending medium. This theory is one of many linear scattering theories, each of which has made assumptions about the particle system and how it reacts to sound waves (see Figure B.1).

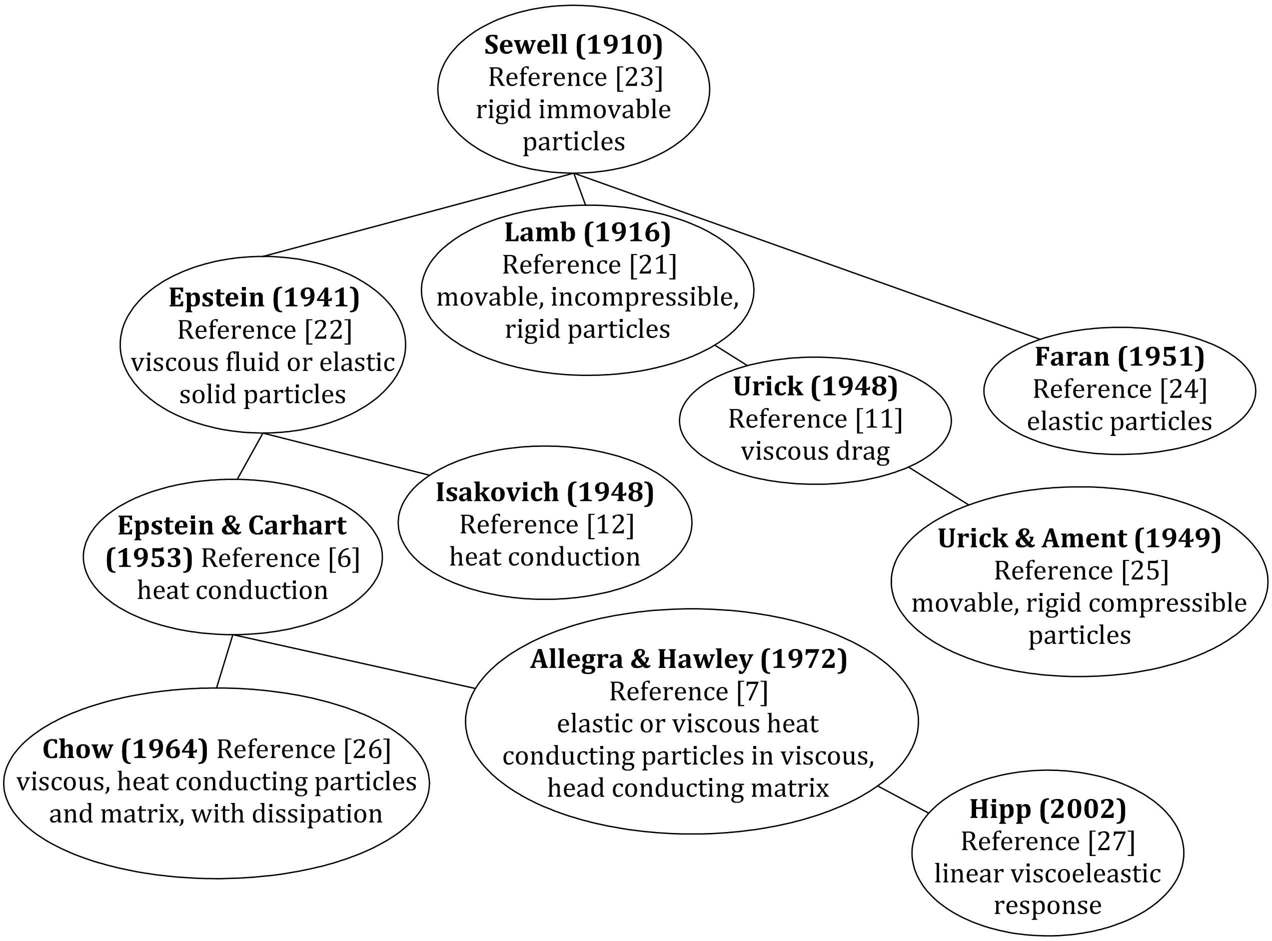


Figure B.1 — Linear models of ultrasonic scattering

B.2 Calculation of attenuation

ECAH theory considers the propagation of sound through a suspension or emulsion via three distinct types of wave: a compression wave, ψ_c, a thermal wave, ψ_T, and a shear wave, ψ_S. Since the incident sound beam is generally a compression wave, the other two types are generated at the boundary of the discontinuous phase. These waves are solutions of the wave formulae:

$$\left(\nabla^2+k_c^2\right)\psi_c=0 \tag{B.1}$$

$$\left(\nabla^2+k_T^2\right)\psi_T=0 \tag{B.2}$$

$$\left(\nabla^2+k_s^2\right)\psi_s=0 \tag{B.3}$$

Here, the wave numbers k_c, k_T, and k_s are defined by

$$k_c=\frac{\omega}{c}+i\alpha_0 \tag{B.4}$$

$$k_T=\left(1+i\right)\sqrt{\frac{\omega\rho C_p}{2\kappa}} \tag{B.5}$$

$$k_s=\sqrt{\frac{\omega^2\rho}{\mu}} \tag{B.6}$$

where ω is the angular frequency, c is the speed of sound, α_0 is the absorption, ρ is the density, C_p is the specific heat at constant pressure, κ is the thermal conductivity, μ is the shear modulus, and i is the imaginary number. These waves appear in the interior of the particle and in the continuous phase (the fluid). Within the fluid, the wave number corresponding to the shear wave [Formula (B.6)] is calculated by replacing the shear modulus μ with the factor $-i\omega\eta$, where η is the viscosity.

In the case of a spherical particle, the general solution of this system of formulae can be represented as an expansion of Legendre polynomials. The reflected compression wave, for example, is

$$\Psi_c^r=\sum_{n=0}^{\infty}i^n\left(2n+1\right)A_n h_n\left(k_c a\right)P_n\left(\cos\theta\right) \tag{B.7}$$

where h_n are Hankel functions of the first kind and P_n are Legendre polynomials. The coefficients A_n specify the reflected compression wave completely. In total, there are six sets of coefficients that describe the three waves in the medium and the three waves inside the particle. These coefficients are related through the boundary conditions, which require continuity of these physical parameters at the surface of the particle: radial velocity, tangential velocity, temperature, heat flux, radial stress, and tangential stress. Explicit formulae for the boundary conditions for emulsions, are given in Reference [2], pp. 114–115 and the boundary conditions for suspensions of solids are discussed in Reference [7].

The resulting system of formulae is solved to determine the coefficients A_n in Formula (B.7). The ultrasonic attenuation, α, is then given by Reference [6]:

$$\alpha_\mathrm{exc} = -\frac{3\phi}{2k_\mathrm{c}^2 a^3}\sum_{n=0}^{\infty}(2n+1)\,\mathrm{Re}\,A_\mathrm{n} \qquad \text{(B.8)}$$

where a is the radius of the particle. In the long wavelength limit, where $k_\mathrm{c}a < < 1$, coefficients of order $n > 1$ can be ignored. This limiting case applies to many suspensions of microscopic particles when the ultrasonic frequency is well below 100 MHz (Reference [10]). In this case,

$$\alpha_\mathrm{exc} = -\frac{3\phi}{2k_\mathrm{c}^2 a^3}\mathrm{Re}\left[A_0 + 3A_1\right] \qquad \text{(B.9)}$$

Formulae for determining A_n are given in Reference [28]. Explicit analytical solutions for A_0 (thermal loss) and A_1 (viscous loss) are given in Reference [7] for the long wavelength limit in the case of rigid, dense particles.

B.3 Limitations of ECAH theory

It should be noted that Formulae (B.8) and (B.9) are only valid for dilute suspensions, where particle-particle interactions can be neglected.

Annex C
(informative)

Example of a semi-empirical model

There are many semi-empirical models; this annex provides one example.

The ultrasonic extinction, E, of a suspension or emulsion of mono-disperse particles with the diameter x can be described by the Lambert-Beer's law according to Reference [4].

$$E = -\ln\left(\frac{I}{I_0}\right)_{f_\mathrm{i}} = \Delta l \cdot C_\mathrm{PF} \cdot K\left(f_\mathrm{i}, x\right) = \alpha \cdot \Delta l \tag{C.1}$$

The extinction, E, at a given frequency, f_i, is linearly dependent on the thickness of the suspension layer, Δl, the projection area-concentration, C_PF, and the extinction efficiency (normalized extinction cross section), K, where

$$C_\mathrm{PF} = \frac{\text{particle projection area}}{\text{suspension volume}} \tag{C.2}$$

$$K = \frac{\text{extinction cross section}}{\text{particle projection area}} \tag{C.3}$$

The extinction efficiency, K, is a function of frequency and particle size. In a polydisperse system, K is integrated over all particle size fractions from x_min to x_max:

$$E\left(f_\mathrm{i}\right) = \Delta l \cdot C_\mathrm{PF} \cdot \int\limits_{x_\mathrm{min}}^{x_\mathrm{max}} K\left(f_\mathrm{i}, x\right) \cdot q_2\left(x\right) dx \tag{C.4}$$

The integral in Formula (C.4) can be approximated as sum:

$$E\left(f_\mathrm{i}\right) \cong \Delta l \cdot C_\mathrm{PF} \cdot \sum_j K\left(f_\mathrm{i}, x_\mathrm{j}\right) \cdot q_2\left(x_\mathrm{j}\right) \cdot \Delta x_\mathrm{j} \tag{C.5}$$

If now extinction measurements are performed at various frequencies, this results in a linear system of formulae:

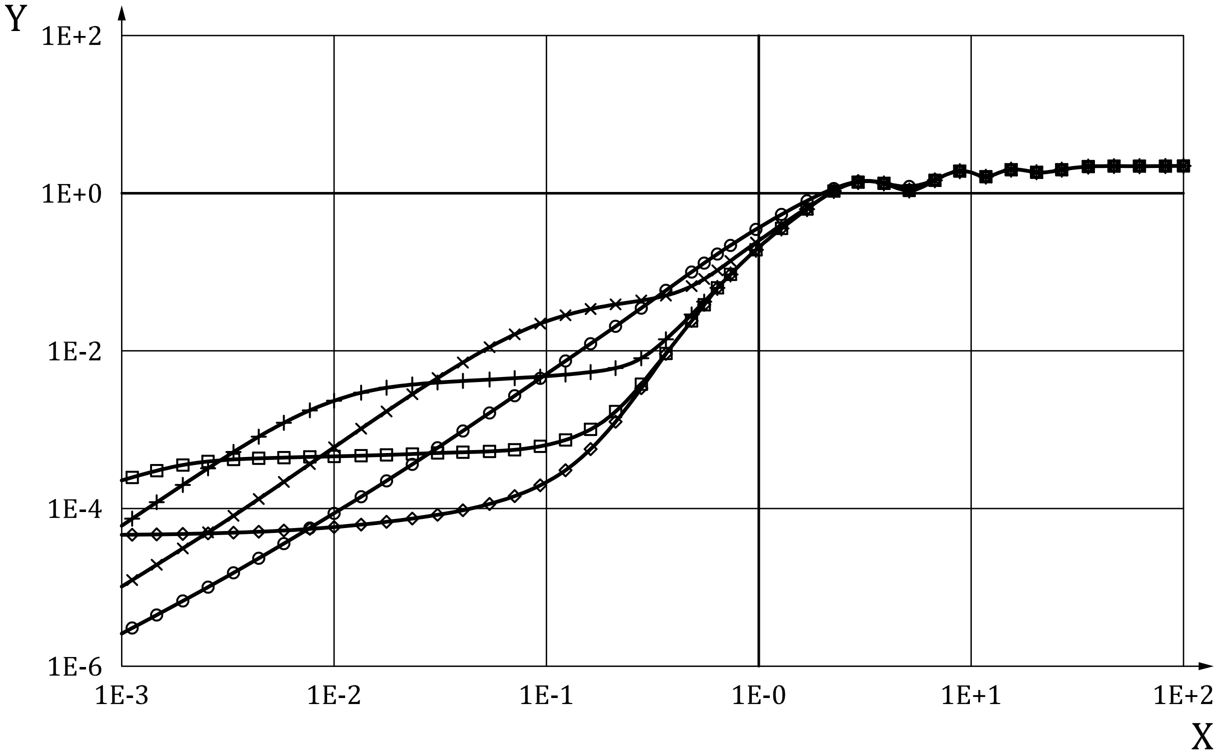
$$\begin{pmatrix} E(f_1) \\ \vdots \\ E(f_\mathrm{j}) \end{pmatrix} = \Delta l \cdot C_\mathrm{PF} \cdot \begin{pmatrix} K_{1,1} & \cdots & K_{1,\mathrm{j}} \\ \vdots & \ddots & \vdots \\ K_{\mathrm{i},1} & \cdots & K_{\mathrm{i,j}} \end{pmatrix} \cdot \begin{pmatrix} q_{21} \cdot \Delta x_1 \\ \vdots \\ q_{2\mathrm{i}} \cdot x_\mathrm{i} \end{pmatrix} \tag{C.6}$$

The system of formulae (C.6) is numerically unstable and must be solved by suitable algorithms.

To calculate the particle size distribution, one must know the extinction cross section K as a function of the dimensionless size parameter ka defined in Formula (C.7):

$$ka = \left(\frac{2\pi}{\lambda}\right)\left(\frac{x}{2}\right) \tag{C.7}$$

The dimensionless size parameter is defined as the product of wave number and particle radius, and it equals π times the ratio of particle diameter, x, to ultrasonic wavelength, λ, within the liquid. The wavelength is equal to the ratio of the frequency, f, and the speed of sound, c, of the liquid. Figure C.1 shows a typical extinction function for spherical particles.



Key

—○— *x* = 0,1 µm
—+— *x* = 10 µm
—◇— *x* = 1000 µm
—×— *x* = 1 µm
—□— *x* = 100 µm
X dimensionless size parameter *ka*
Y extinction efficiency *K*

Figure C.1 — Typical extinction function for spherical glass particles in water Reference [29]

For small dimensionless size parameters (long wavelength regime), the extinction cross section can be calculated with the ECAH theory. For larger dimensionless size parameters (short wavelength regime), scattering becomes more and more relevant. Particle shape gains a strong influence on the extinction behaviour of the particles. For systems with low density contrast between the continuous and the discontinuous phases, sound absorption within the particle becomes relevant. For many particle systems, the theoretical predictions for the extinction efficiency are not sufficient for the calculation of a particle size distribution.

This situation can be overcome by a semi-empirical approach, which takes advantage of the functional relationship

$$K\left(f,x\right)=\mathrm{f}(ka) \tag{C.8}$$

Firstly, the particle size distribution is measured with a suitable particle sizing method (e.g. laser diffraction), and the frequency dependent ultrasonic extinction is also measured. Secondly, the extinction portion caused by viscous and thermal losses is calculated by a suitable model. The remaining scattering portion of the measured extinction is the starting point for an algorithm which calculates the scattering extinction function with help of the measured particle size distribution. For this, Formula (C.5) is rewritten:

$$E(f_\mathrm{i})\cong\Delta l\cdot C_\mathrm{PF}\cdot\sum_j K\left(f_\mathrm{i},x_\mathrm{j}\right)\cdot\Delta Q_2\left(x_\mathrm{j}\right) \tag{C.9}$$

where ΔQ_2 is the fraction of a certain particle size class of the total projection area. Formula (C.9) is an ill-posed linear system of formulae, which can be solved according to the methods described in Clause 6. The resulting vector **K** gives the extinction efficiency as a function of the dimensionless size parameter.

The quality of the calculated extinction function depends on the accuracy of the measured particle size distribution. Therefore, the calculation should be carried out with measurements of at least five different samples with different particle size distributions as measured on a well-qualified instrument.

Annex D
(informative)

Iterative fitting

Due to the ill-posed nature of the inversion problem, the attenuation spectrum often cannot be inverted directly as in Formula (12) with adequate reliability. Instead, many workers have resorted to an iterative fitting scheme similar to that depicted in Figure D.1. Typically, the spectra are very smooth so that very little information appears to be contained in the data. In order to extract the PSD from the attenuation data, a model function (such as a log-normal or bi-log-normal distribution) is assumed, effectively reducing the number of free parameters to be fit to the data (Reference [9]).

1) Measure the attenuation spectrum $\boldsymbol{\alpha}_{\text{exp}}$.

2) Make an initial guess of the PSD, $\boldsymbol{q}$. If a particular shape is assumed for the PSD, this step is equivalent to making an initial guess for the PSD parameters and calculating the PSD. In the case of a log-normal distribution, the parameters are the median size and the geometric standard deviation, and Formula (8) is used to calculate $\boldsymbol{q}$.

3) Assuming that ϕ is the particle volume concentration (either known or estimated), the expected attenuation spectrum $\boldsymbol{\alpha}_{\text{mod}}$ is predicted by

$$\alpha_{\text{mod}} = \phi \cdot (\alpha_P - \alpha_L) + \phi \cdot \mathbf{K} \cdot \boldsymbol{q} \tag{D.1}$$

where **K** is a matrix representing the linear model that estimates attenuation as a function of particle size. In cases where the intrinsic attenuation is small, the first term of Formula (D.1) can be omitted.

4) Calculate the error Δ.

$$\Delta = \left\| \alpha_{\text{exp}} - \alpha_{\text{mod}} \right\| \tag{D.2}$$

5) Use an optimization strategy to update the estimate of $\boldsymbol{q}$ (or the parameters used to calculate it and iterate from step 3) until Δ becomes sufficiently small. If the concentration ϕ is unknown, it may also be varied to decrease the value of Δ. The best results are obtained when the value of ϕ is known.

6) The final $\boldsymbol{q}$ is the estimated PSD.

It is understood that simple iterative fitting schemes are prone to find local minima of Δ, so care must be taken to explore an adequately large region of the parameter space. Fitting algorithms are discussed in [17],[18], and [19].

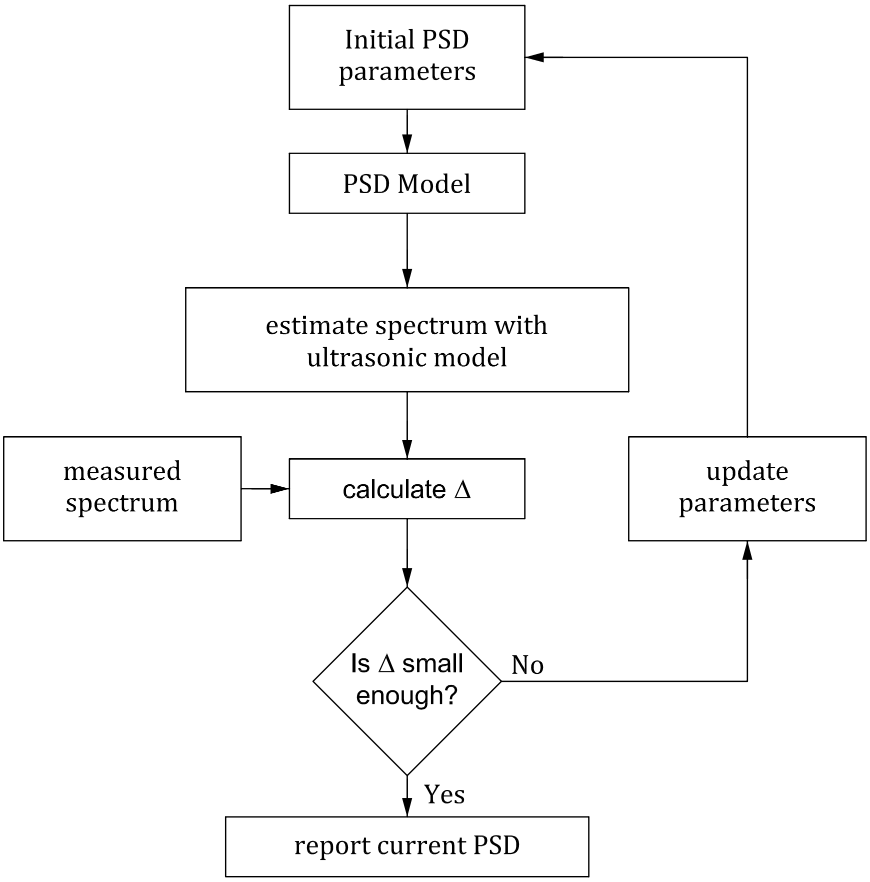


Figure D.1 — Iterative method of determining the PSD from the measured ultrasonic attenuation spectrum

Annex E
(informative)

Physical parameter values for selected materials

Tables E.1 and E.2 show physical parameter values for a few selected materials; other materials are listed in References [10][30]. Table E.3 lists examples of standard methods used to measure these parameters.

Table E.1 — Physical constants for selected solids, as compiled in Reference [10]

Parameter	Polystyrene	Silica	TiO_2	Iron
c (m·s^{-1})	$2{,}330 \times 10^3$	$5{,}968 \times 10^3$	$7{,}900 \times 10^3$	$5{,}900 \times 10^3$
ρ' (kg·m^{-3})	$1{,}053 \times 10^3$	$2{,}185 \times 10^3$	$4{,}250 \times 10^3$	$7{,}900 \times 10^3$
μ (N·m^{-2})	$1{,}27 \times 10^9$	$3{,}09 \times 10^{10}$	$3{,}54 \times 10^{10}$	$6{,}56 \times 10^{10}$
κ (W·m^{-1}K^{-1})	0,140	1,6	4,98	$8{,}04 \times 10^1$
C_p (J·kg^{-1}K^{-1})	$1{,}193 \times 10^3$	$7{,}29 \times 10^2$	$9{,}30 \times 10^2$	$4{,}44 \times 10^2$
α/f^2 (Np·s^{2}m^{-1})	$1{,}0 \times 10^{-13}$	$2{,}6 \times 10^{-22}$	$1{,}2 \times 10^{-16}$	$5{,}7 \times 10^{-14}$
β_T (K^{-1})	$2{,}1 \times 10^{-4}$	$1{,}35 \times 10^{-6}$	$8{,}61 \times 10^{-6}$	$3{,}3 \times 10^{-5}$

Table E.2 — Physical constants for selected liquids at 20 °C, as compiled in Reference [30]

Parameter	Water (25 °C)	Water (20 °C)	Hexadecane	Isopropanol	Olive oil
c (m·s^{-1})	$1{,}487 \times 10^3$	$1{,}483 \times 10^3$	$1{,}358 \times 10^3$	$1{,}181 \times 10^3$	$1{,}440 \times 10^3$
ρ (kg·m^{-3})	$9{,}97 \times 10^2$	$1{,}0 \times 10^3$	$7{,}7 \times 10^2$	$7{,}9 \times 10^2$	$9{,}00 \times 10^2$
η (Pa·s)	$8{,}91 \times 10^{-4}$	$1{,}00 \times 10^{-3}$	$3{,}10 \times 10^{-3}$	$2{,}35 \times 10^{-3}$	$8{,}40 \times 10^{-2}$
κ (W·m^{-1}K^{-1})	0,59	0,59	0,14	0,13	0,19
C_p (J·kg^{-1}K^{-1})	$4{,}182 \times 10^3$	$4{,}182 \times 10^3$	$2{,}090 \times 10^3$	$2{,}494 \times 10^3$	$2{,}00 \times 10^3$
α/f^2 (Np·s^{2}m^{-1})	$2{,}5 \times 10^{-14}$	$2{,}5 \times 10^{-14}$	$1{,}0 \times 10^{-13}$	$2{,}7 \times 10^{-13}$	$1{,}35 \times 10^{-12}$
β_T (K^{-1})	$2{,}1 \times 10^{-4}$	$2{,}1 \times 10^{-4}$	$7{,}0 \times 10^{-4}$	$1{,}04 \times 10^{-3}$	$7{,}2 \times 10^{-4}$

NOTE Constants for water at 25 °C from Reference [10] are included for comparison in Table E.2.

Table E.3 — Example standards used to measure parameters listed in Tables E.1 and E.2

Parameter	Symbol	Standards
Sound speed	c	ISO 15086-2:2000
Density	ρ	ISO 1183-1:2012, ASTM C128-07a
Shear modulus	μ	ASTM E1875-08
Viscosity	η	ISO 3104:1994, ASTM D445
Thermal conductivity	κ	ASTM E1952
Specific heat	C_p	ISO 11357-4:2005, ASTM E1269-11
Thermal expansion	β_T	ISO 1768:1975

NOTE Standards listed in Table E.3 are for information only and may not be applicable to all materials.

Annex F
(informative)

Practical example of PSD measurement

F.1 Purpose

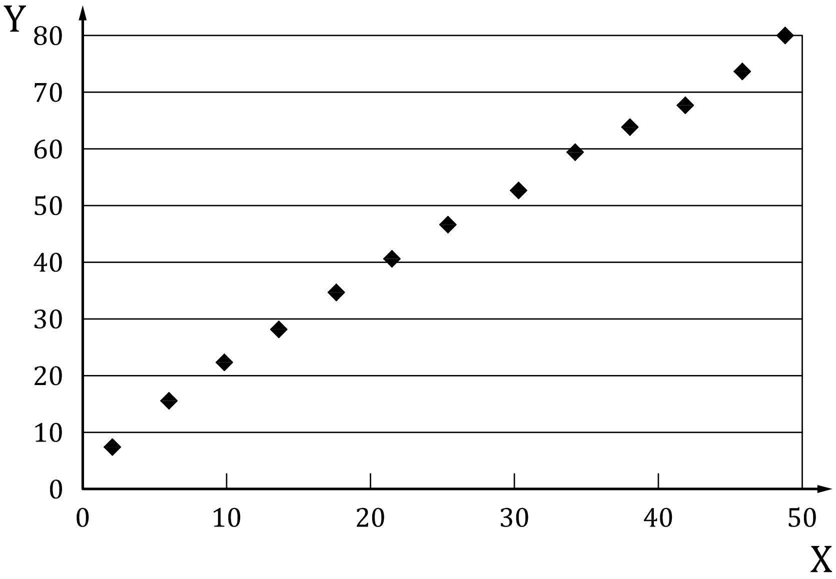
The purpose of this annex is to provide one example of how to estimate PSD from an attenuation spectrum using the methods described in this International Standard. This example uses the “Solver” tool in Excel[1] to perform the inversion.

NOTE The example given here is for the purpose of demonstration only. Other specimens within the scope of this part of ISO 20998 can be measured, provided a suitable attenuation model is used in the inversion of the observed attenuation spectra, and other inversion techniques could be used.

F.2 Attenuation spectrum

The measured attenuation spectrum shown in Figure F.1 is reproduced from an ultrasonic study of various grades of titanium dioxide (TiO_2) (Reference [9]). The concentration of the TiO_2 sample is 1,9 % volume fraction. Discrete values taken from this curve are shown in Table F.1 for convenience in subsequent calculations.

NOTE Data shown in Figure F.1 and Table F.1 have been extracted from Reference [9], Figure 4. The original attenuation data were given in units of nepers per centimetre; here, they are converted into decibels per centimetre.



Key

X frequency (MHz)

Y attenuation (dB/cm)

Figure F.1 — Attenuation spectrum of one TiO_2 grade, measured at a concentration of 1,9 % volume fraction (Reference [9])

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[1] Excel is the trade name of a product supplied by Microsoft. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of the product named. Equivalent products may be used if they can be shown to lead to the same results.

Table F.1 — Table of attenuation values depicted in Figure F.1

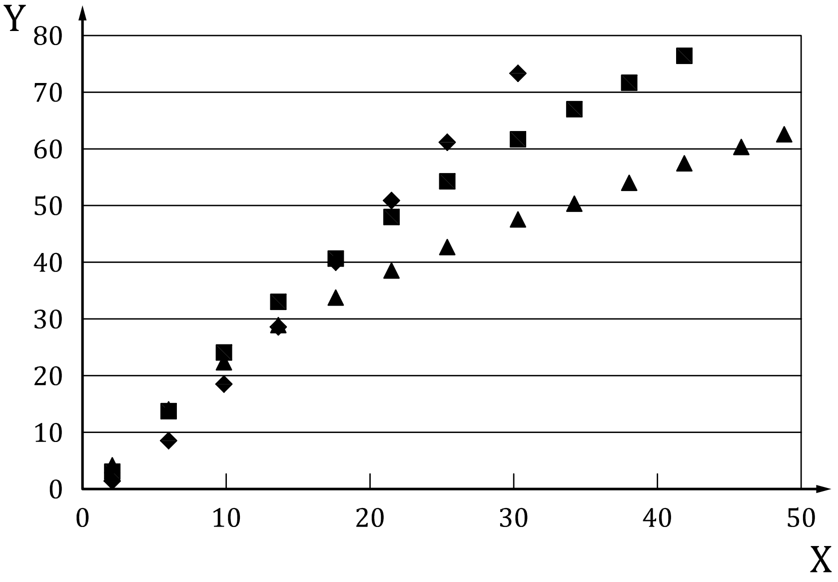
Frequency (MHz)	Attenuation (dB/cm)
1,95	7,60
5,85	15,74
9,76	22,25
13,67	28,22
17,57	34,74
21,48	40,71
25,39	46,50
30,27	52,47
34,17	59,35
38,08	63,69
41,99	67,31
45,89	73,28
48,82	79,44

F.3 Choice of model

Titanium dioxide particles are dense (4 250 kg·m^{-3}) and fine (< 10^{-6} m), so viscous loss is expected to be the dominant attenuation mechanism. The attenuation coefficient is calculated from the viscous loss model shown in Formula (A.1), using the physical parameter values for TiO_2 and water (at 25 °C) from Reference [10] as shown in Appendix E. The calculation may be implanted as a user-defined function to simplify the spreadsheet. Attenuation is a function of both particle size and frequency; Figure F.2 and Table F.2 show example results of this calculation at three selected values of particle radius.

NOTE 1 The model uses particle radius, but PSD results are generally expressed as particle diameter. This detail must not be overlooked when inverting the attenuation spectrum.

NOTE 2 The calculation shown here is the attenuation per unit volume concentration. This result must be multiplied by the volume fraction ϕ (where $0 < \phi < 1$) to obtain the expected attenuation.



Key

X frequency (MHz)

Y attenuation (dB/cm)

Figure F.2 — Viscous-loss model [Formula (A.1)**] for unit concentration TiO_2 at three values of particle radius: 8,439 × 10^{-8} m (diamonds), 1,458 × 10^{-7} m (squares), and 2,100 × 10^{-7} m (triangles)**

Table F.2 — Attenuation coefficient values depicted in Figure F.2

Frequency (MHz)	a= 8,439 × 10^{-8} (m)	a= 1,458 × 10^{-7} (m)	a= 2,100 × 10^{-7} (m)
1,95	1,19	2,70	3,92
5,85	8,12	13,19	14,07
9,76	17,93	23,54	21,92
13,67	28,75	32,61	28,21
17,57	39,68	40,53	33,51
21,48	50,42	47,61	38,18
25,39	60,77	54,01	42,38
30,27	73,07	61,26	47,12
34,17	82,40	66,57	50,60
38,08	91,34	71,55	53,87
41,99	99,88	76,25	56,96
45,89	108,03	80,68	59,88
48,82	113,94	83,87	61,98

F.4 PSD model

Assuming that the volume-weighted PSD can be described as a log-normal distribution (Reference [9]), then Formula (8) gives the probability that a fraction of the particles' volume lies in the interval *dx* between x_0 and x_0 + dx (Reference [31]). The cumulative PSD, i.e. the volume fraction of particles with diameters between 0 and x, is obtained by integrating Formula (8):

$$Q_3(x)=\int_0^x q_3(x)dx=\left(\frac{1}{s\sqrt{2\pi}}\right)\int_0^x \exp\left[-\frac{1}{2}\left(\frac{1}{s}\ln\frac{x}{x_{50}}\right)^2\right]\frac{dx}{x}=\frac{1}{\sqrt{\pi}}\int_{-\infty}^{z}\exp\left(-z^2\right)dz \tag{F.1}$$

where the substitution variable z is defined by

$$z=\frac{1}{s\sqrt{2}}\ln\left(\frac{x}{x_{50}}\right) \tag{F.2}$$

Since the “error function” is defined by the second integral in Formula (F.1), the cumulative PSD is evaluated as

$$Q_3(x)=\frac{1}{2}+\frac{1}{2}\mathrm{erf}\left[\frac{1}{s\sqrt{2}}\ln\left(\frac{x}{x_{50}}\right)\right] \tag{F.3}$$

Excel1) has a built-in function, *lognormdist*, that calculates the cumulative log-normal distribution $Q_3(x)$, so it is simple to determine the volume fraction ϕ_n in a size class bounded between sizes $x_\mathrm{n-1}$ and x_n:

$$\phi_\mathrm{n}=Q_3\left(x_\mathrm{n}\right)-Q_3\left(x_\mathrm{n-1}\right) \tag{F.4}$$

NOTE 1 In order to conform to the definitions used here, the correct function call is LOGNORMDIST(x,LN(x_{50}),s).

NOTE 2 The geometric standard deviation (GSD) of the PSD is equal to exp(s).

In the example shown in Table F.3, a set of 41 logarithmically spaced particle diameters is defined in Column A: { x_1 = 1,00 × 10^{-8} m; x_2 = 1,20 × 10^{-8} m; x_3 = 1,44 × 10^{-8} m, ..., x_{41} = 1,47 × 10^{-5} m}. These diameters define a set of 40 size intervals (i.e. size classes) where the average particle size X_n of the nth class is the geometric mean:

$$X_\mathrm{n}=\sqrt{x_\mathrm{n-1}x_\mathrm{n}} \tag{F.5}$$

Using an arbitrary initial guess of x_{50} = 1 x 10^{-7} m and s = 0,40, the trial cumulative PSD is calculated in Column B using the *lognormdist* function to evaluate $Q_3(x_\mathrm{n})$ at each particle size. The set of {ϕ_n} is determined from Formula (F.4) in Column C, and the geometric mean diameter of each size class in Column D is calculated from Formula (F.5).

Table F.3 — Partial listing of initial entries in Excel1) spreadsheet

	A	B	C	D
1	x	P(x)	vol fraction	GM diameter
2	1,00E-08	0,0000		
3	1,20E-08	0,0000	5,34E-08	1,095E-08
4	1,44E-08	0,0000	5,76E-07	1,315E-08
5	1,73E-08	0,0000	5,06E-06	1,577E-08
6	2,07E-08	0,0000	3,62E-05	1,893E-08
7	2,49E-08	0,0003	2,11E-04	2,272E-08
8	2,99E-08	0,0013	1,00E-03	2,726E-08
9	3,58E-08	0,0051	3,89E-03	3,271E-08
10	4,30E-08	0,0174	1,23E-02	3,925E-08
11	5,16E-08	0,0490	3,16E-02	4,710E-08

Table F.3 *(continued)*

	A	B	C	D
12	6,19E-08	0,1154	6,63E-02	5,652E-08
13	7,43E-08	0,2289	1,13E-01	6,783E-08
14	8,92E-08	0,3871	1,58E-01	8,139E-08
15	1,07E-07	0,5671	1,80E-01	9,767E-08

NOTE The sum of Column C over all 40 values must equal 1.

F.5 Inversion

Following the scheme outlined in Annex D, the next step is to estimate the attenuation spectrum expected from the trial PSD. Table F.4 shows a portion of the spreadsheet used for this calculation. The mean radius in Row 7 is one-half of the diameters transposed from Column D in Table F.3, and Row 8 is the transpose of Column C in Table F.3. Columns F and G contain the measured attenuation spectrum from Table F.1.

Table F.4 — Listing of entries in Excel[1] spreadsheet

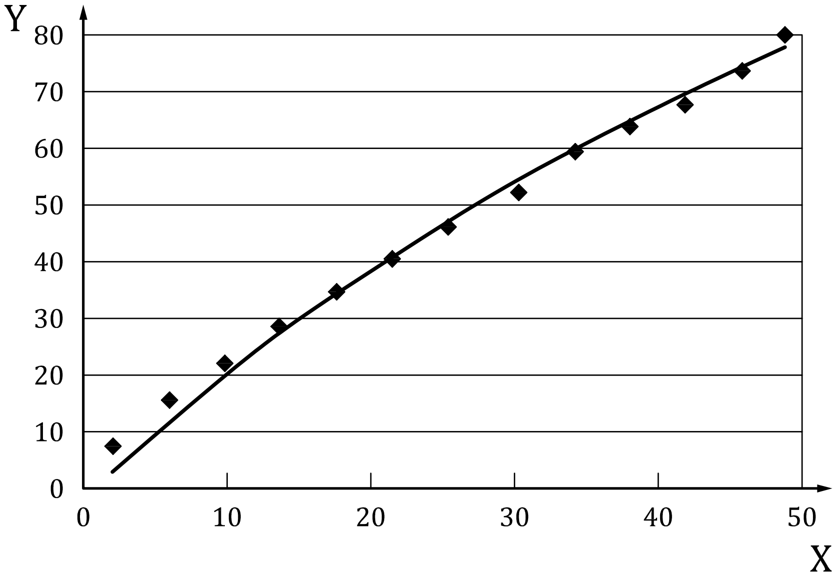
	F	G	H	I	J	K
7			mean radius:	5,477E-09	6,573E-09	7,887E-09
8			vol fraction:	5,340E-08	5,758E-07	5,059E-06
9						
10	freq (MHz)	α expt (dB/cm)	α model (dB/cm)	**Weighted attenuation**		
11	1,95	7,60	0,60	3,46E-10	5,36E-09	6,75E-08
12	5,85	15,74	4,32	3,08E-09	4,76E-08	5,98E-07
13	9,76	22,25	10,17	8,51E-09	1,31E-07	1,65E-06
14	13,67	28,22	17,33	1,66E-08	2,56E-07	3,20E-06
15	17,57	34,74	25,33	2,73E-08	4,19E-07	5,25E-06
16	21,48	40,71	33,92	4,05E-08	6,23E-07	7,79E-06
17	25,39	46,50	42,90	5,64E-08	8,66E-07	1,08E-05
18	30,27	52,47	54,45	7,97E-08	1,22E-06	1,52E-05
19	34,17	59,35	63,86	1,01E-07	1,55E-06	1,93E-05
20	38,08	63,69	73,37	1,25E-07	1,92E-06	2,39E-05
21	41,99	67,31	82,92	1,52E-07	2,32E-06	2,88E-05
22	45,89	73,28	92,45	1,81E-07	2,76E-06	3,43E-05
23	48,82	79,44	99,60	2,04E-07	3,12E-06	3,87E-05

The attenuation coefficient at a given frequency is the sum of contributions from each size class, weighted by the corresponding volume fraction. For example, cell J11 in Table F.4 is calculated by multiplying the volume fraction in J8 by the attenuation predicted by the model shown in F.2 for the particle radius shown in cell J7 at the frequency shown in cell F11, and at the stated volume concentration of 1,9 %. If the concentration is unknown, it may be used as a free parameter in the fitting procedure. The expected attenuation at 1,95 MHz, shown in cell H11, is the sum of the cells in the range I11:AV11. This value may be compared with the measured attenuation shown in G11, and the error may be calculated from Formula (D.2).

Using the "Solver" tool in Excel,[1] the error signal is minimized by adjusting the values of x_{50} and s (and also ϕ in cases where the concentration is unknown), subject to the constraint that they remain positive. An effective scheme is to adjust x_{50} (holding s constant) first, then to adjust s (holding x_{50} constant), then to adjust both values simultaneously. After Solver converges on a solution, the PSD can be read from Columns A and B (cumulative distribution) or Columns A and C (differential distribution). Alternatively, the PSD can be calculated from Formula (8), Formula (F.3), or *lognormdist* using the final values of x_{50} and s.

F.6 Results

In this example, Solver converged on $x_{50} = 3{,}180 \times 10^{-7}$ m and $s = 0{,}5647$. The fitted attenuation model and the measured attenuation spectrum are compared in Figure F.3 and Table F.5. This fit appears to be the same as that obtained in the original study.



Key

X frequency (MHz)

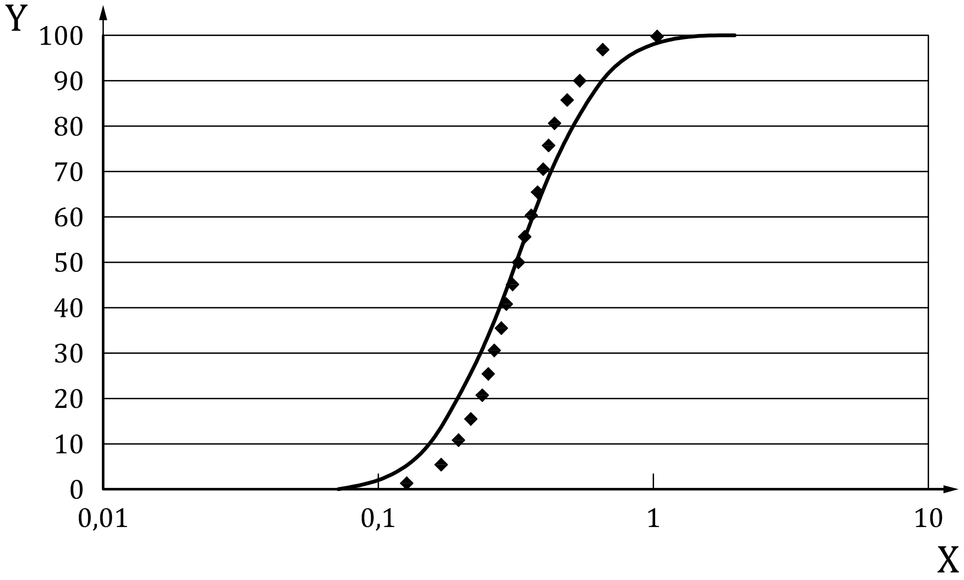
Y attenuation (dB/cm)

Figure F.3 — Comparison of measured attenuation spectrum (diamonds) and fitted model (line)

Table F.5 — Comparison of measured and fitted attenuation spectra depicted in Figure F.3

Frequency (MHz)	α experiment (dB/cm)	α model (dB/cm)	Error (%)
1,95	7,60	2,90	−61,9
5,85	15,74	11,43	−27,4
9,76	22,25	19,71	−11,4
13,67	28,22	27,36	−3,0
17,57	34,74	34,40	−1,0
21,48	40,71	40,95	0,6
25,39	46,50	47,07	1,2
30,27	52,47	54,21	3,3
34,17	59,35	59,57	0,4
38,08	63,69	64,68	1,6
41,99	67,31	69,55	3,3
45,89	73,28	74,21	1,3
48,82	79,44	77,59	−2,3

Finally, the Solver's optimum values for x_{50} and s are used as inputs to *lognormdist* in order to generate the cumulative PSD that is consistent with the attenuation spectrum shown in Table F.1. This result is shown in Figure F.4 and Table F.6, where it is compared with an X-ray disc centrifuge (XDC) measurement of this TiO_2 sample's PSD included in Reference [9]. The result obtained here is identical to the original estimate, which the authors based on ECAH calculations rather than the simpler viscous-loss model. They note that their result gives a reasonable estimate of the median size but over-estimates the width of the distribution in this case, as seen in Figure F.4. The corresponding differential PSD curves are shown in Figure F.5.



Key

X particle diameter (micrometres)

Y cumulative volume fraction (%)

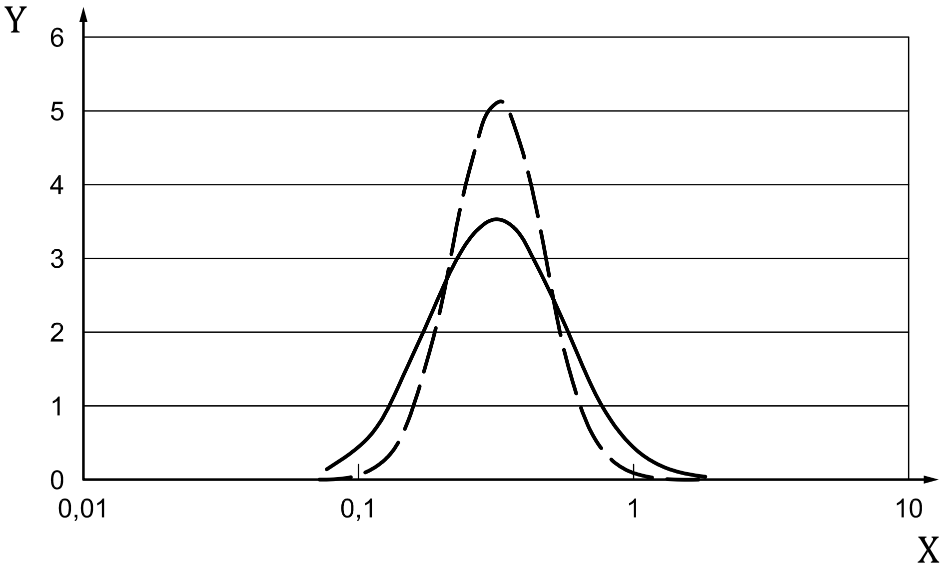
Figure F.4 — Comparison of PSD from this estimate (line) and X-ray disc centrifuge data presented in Reference [9]

Table F.6 — PSD values shown in Figure F.4

Size (µm)	XDC data (Reference [9]) % volume fraction undersize	Present estimate % volume fraction undersize
0,13	1,25	5,09
0,17	5,21	13,38
0,20	10,42	19,91
0,22	15,21	25,17
0,24	20,42	31,10
0,25	25,21	34,27
0,27	30,42	37,55
0,28	35,21	40,93
0,29	40,42	44,38
0,31	45,00	47,87
0,32	50,00	51,38
0,34	55,42	54,88
0,36	60,21	58,34

Table F.6 *(continued)*

Size (µm)	XDC data (Reference [9]) % volume fraction undersize	Present estimate % volume fraction undersize
0,38	65,42	61,73
0,40	70,21	65,04
0,42	75,42	68,24
0,44	80,42	71,31
0,48	85,42	76,98
0,53	90,21	81,97
0,65	96,62	89,72
1,02	99,38	98,02



Key

X particle diameter (micrometres)

Y differential volume fraction (%)

Figure F.5 — Differential form of the cumulative PSDs shown in Figure F.4; the dashed line is the XDC result, and the solid line is the ultrasonic result

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