Characterization of
particles · powders · pores

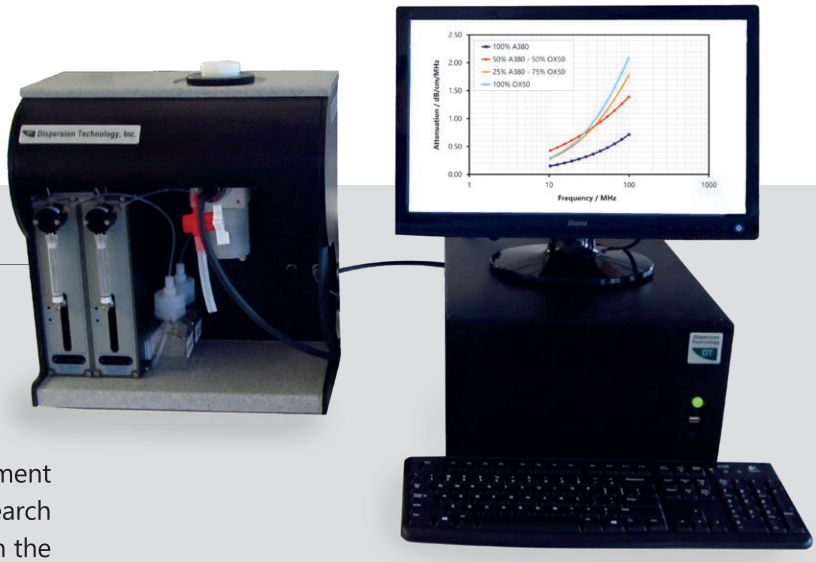
DT Series

- Particle size and zeta potential measurement in original concentrated dispersions
- Wide range of concentration: 0.1 – 60 Vol.-%
- Wide size range from 5 nm to > 100 µm
- Flexible sample amount (more than 3 ml)

Particle size and zeta potential

using acoustic and electro-acoustic Spectrometry

DT Series Overview / Contents



Acoustic spectrometry

Particle size measurement in concentrated dispersions

The particle size distribution of an emulsion or suspension is a key parameter to evaluate the quality of the dispersion. Thus, the choice of a suitable size measurement method is essential for an efficient quality control of research on these systems. Many instruments and methods are on the market, but most of them like light scattering systems require a special sample preparation/dilution due to their limited concentration range. Image analysis methods (REM, TEM, etc.) on the other hand can analyze only a limited sample amount – thus the results are not representative. Due to the fact that modification/dilution is always influencing the electrochemical properties and particle size distribution of concentrated dispersions, a suitable measurement method must be able to characterize the system in its original state without any modification.The acoustic spectrometry is a technique which exactly fulfils this task. Concentrated suspensions like ceramic slurries, cements or paints, even paste-like, can be characterized easily in order to analyze particle size distribution and the state of agglomeration. The size range extends from nano-sized to the upper micro-size range.

Electroacoustics

Zeta potential measurement in concentrated dispersions

The zeta potential is defined as the electrical potential difference at the shear plane of a moving particle in a liquid medium. Thus, it is a characteristic parameter for the electrochemical properties of an emulsion droplet or rigid particle in a liquid: it gives some indication of the dispersion stability and the particle mobility in external electric fields. The isoelectric point (IEP), the zero point of the zeta potential is an important value: the particles agglomerate and the dispersion tends to flocculate.

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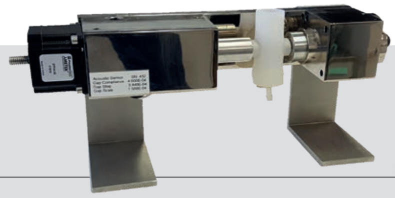

DT-100/110

- Particle size analyzer based on acoustic attenuation spectroscopy (ISO 20998-1)
- Characterization of suspensions and emulsions; aqueous, polar and non-polar solvents
- Extended measurement range: 5 nm – 1000 µm
- Measurement of the non-diluted original sample (0.1 – 60 Vol.-%)
- No calibration necessary
- Frequency range: 1 to 100 MHz
- Variable sender-detector-gap
- Can be equipped with additional probes for temperature, pH-, electric conductivity and titration
- **DT-100**: allows sample agitation with magnetic mixer or peristaltic pump, sample volume > 15 – 20 ml
- **DT-110**: stable samples, sample volume > 3 ml, sample cell disposable

DT-300/310/330

- Zeta potential analyzer based on electroacoustic method (ISO 13099)
- Characterization of suspensions and emulsions; aqueous, polar and non-polar solvents
- Measurement of the non-diluted original sample (0.1 – 60 Vol.-%)
- Minimal sample volume: 2 ml
- Determination of the dynamic mobility and double layer thickness (Debye length)
- Can be equipped with additional probes for temperature, pH-, electric conductivity and titration
- **DT-300:** zeta potential in concentrated dispersions and emulsions
- **DT-310:** analogue to DT-300, additionally equipped with an automated titrator (2 burettes)
- **DT-330:** analogue to DT-300, determination of zeta potential of:
  - Dispersions of solid particles, emulsions, dispersions of porous particles with sizes up to millimeters
  - Sediments of solid and porous particles
  - Monoliths, e.g. geological cores, ceramic tiles
  - Membranes

DT-1202/1210

- Acoustic spectrometer combination to measure particle size (ISO 20998-1) and zeta potential (ISO 13099)
- Can be equipped with additional probes for temperature, pH-, electric conductivity and titration
- **DT-1202**: combination of DT-100 and DT-300
- **DT-1210**: combination of DT-110 and DT-300

1 Particle size measurement with acoustic attenuation spectrometry

1.1 Principle of measurement and technical performance

The acoustic spectrometers DT-100/110/1202/1210 measure the attenuation of ultrasound for a set of frequencies, typically from 1 to 100 MHz. These ultrasound attenuation frequency spectra contain information on particle size distribution. The software performs a fitting search procedure for the particle size distribution that provides the best fit to the experimental data. A comprehensive overview about this system can be found in [6].

The principle of operation is shown in Fig. 1: A sound transducer transforms a high-frequency signal into an ultrasound wave. It is a short-wave package with a very constant amplitude and wavelength that will be launched into the dispersion to be characterized. Every “burst” is shorter than the time of transmission, so that there are no overlap-effects. This technique is called “tone-burst-method”.

During transmittance of the wave through the dispersion, it will be attenuated due to different mechanisms (see below). Thus, it is an acoustic wave transmission method. The attenuated signal is detected by the sound receiving transducer and forwarded to the computer for signal-conditioning and analysis. Apart from the specific effects in the dispersion (I_0 to I), the attenuation is dependent on the gap L between sender and detector as well as on the sound frequency f:

$$\text{attenuation}\left[\frac{\frac{\text{dB}}{\text{cm}}}{\text{MHz}}\right]=\frac{10}{f[\text{MHz}]L[\text{cm}]}\log\frac{I_{\text{in}}}{I_{\text{out}}}[\text{dB}] \qquad (1)$$

The dependency of the attenuation on sound frequency can be used to analyze the particle size distribution in the dispersion.

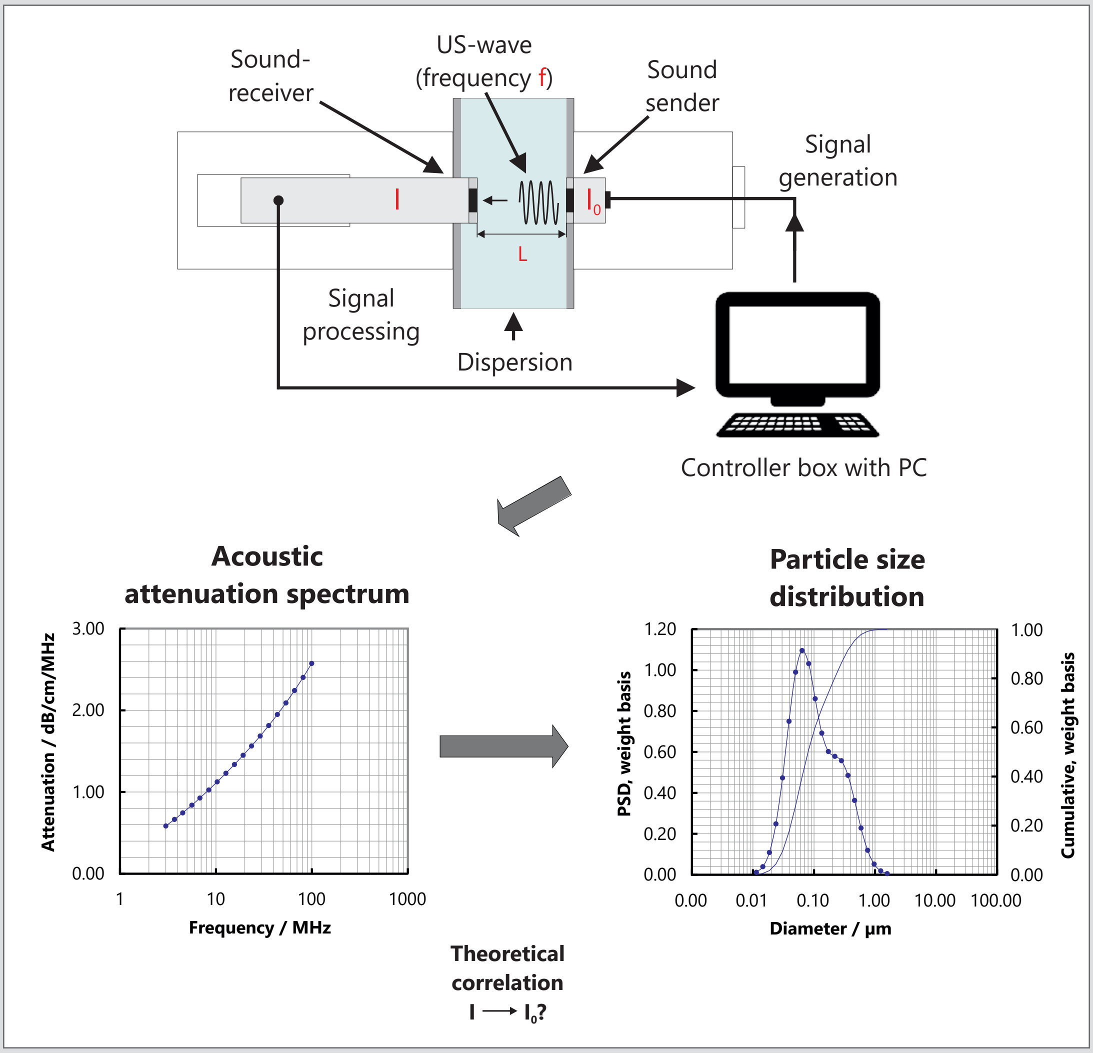

Figure 1 *Measurement principle of the acoustic spectrometers DT100/110/1202/1210*

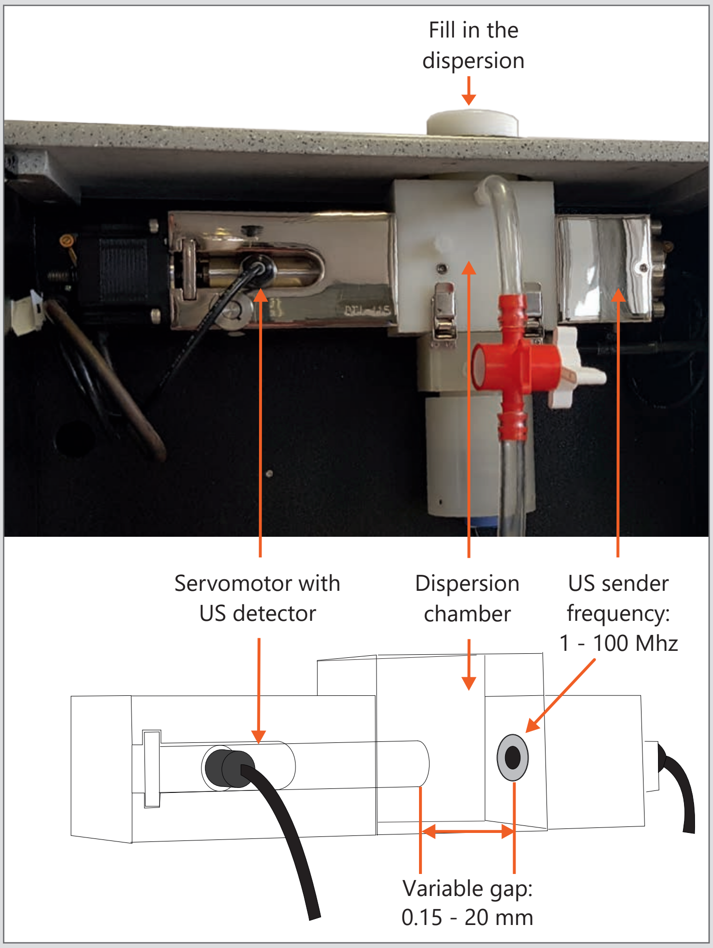

Figure 2 *Acoustic measurement cell for particle size analysis*

The technical implementation of the tone-burst-method into the DT-spectrometers is shown in Fig. 2.

The cell-chamber is made of Kynar, a very resistant polymer. The measured frequency range is 1 – 100 MHz. A specialty of the acoustic DT spectrometer is the variable gap between sound-sender and -detector: this allows a bigger range of dispersion-concentration. With the DT100 and 1202, the gap varies between 0.1 and 20 mm, with the DT110 und 1210 between 0.1 and 14 mm. At smaller gaps, the higher concentrated systems show a much better signal to noise ratio, while more diluted dispersions attenuate adequately only at bigger gaps and can be measured therefore only under these conditions. During the measurement process, at least 800 signals for each gap and frequency will be detected and averaged. Further, the sound speed at 10 MHz will be measured at every experiment.

The mixing of the dispersion can be carried out using the integrated magnetic stirrer (Fig. 2) or, in case of concentrated, higher viscous systems, by means of a peristaltic pump. Stable dispersions can be measured without mixing.

1.2 Ultrasound absorbing mechanisms and analysis of the attenuation spectrum

A suspension is a liquid dispersion with a solid dispersed phase. In case of an emulsion, the dispersed phase is also a liquid. Both dispersion types can be characterized regarding particle size using the acoustic attenuation spectrometers of the DT series, but the absorbing mechanisms are different. An ultrasound wave, which is transmitting through a liquid dispersion, will be attenuated with the increasing path length (gap between sender and detector). Basically, there are three effects responsible for this:

- Intrinsic absorption,
- dissipative absorption and
- sound scattering.

1.2.1 Intrinsic absorption

This is the attenuation of the sound wave in the continuous as well as in the dispersed phase of the dispersion. In solids, i. e. the rigid particles of a dispersion, the attenuation is relatively small and can be neglected for the acoustic attenuation. In pure liquids, the sound wave will be predominantly attenuated due to the formation of compacted and expanded areas, which results in temperature gradients and pressure relaxation processes. These effects are energy intensive (Fig. 3). In case of coarser molecules, relaxation effects like rearrangements of molecules can be responsible for an additional attenuation of the sound wave.

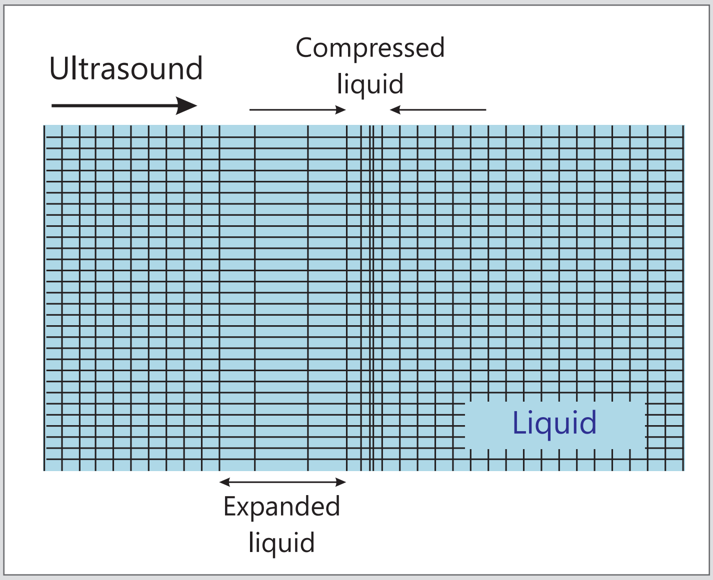

Figure 3 *Effect of the ultrasound wave in a pure liquid – formation of expanded and compacted areas [6]*

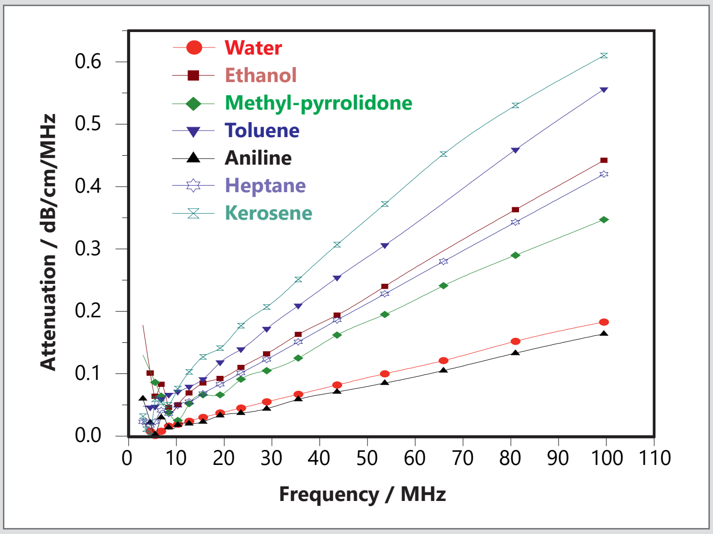

Figure 4 *Ultrasound attenuation spectra of pure liquids*

Examples for intrinsic attenuation spectra of pure liquids are shown in Fig. 4. Two different types of liquids can be distinguished: Newtonian and non-Newtonian liquids. In case of Newtonian liquids, the attenuation shows a linear dependency on the frequency. This is the case for water or cyclohexane respectively. On the other hand, Glycerine or propylene-glycol 400 are examples of non-Newtonian liquids.

1.2.2 Dissipative absorption

This is the ultrasound attenuation due to dissipative interactions between continuous and dispersed phase. Dissipative means, that a system is losing energy which will be transformed into thermal energy. Three different effects can be distinguished which are described below.

Viscous-inertial effect

This is a hydrodynamic mechanism that will increase with an increasing density contrast (difference in density) between the dispersed phase and the medium. During the transmission of the wave through the dispersion, the density contrast causes a relative movement of the particles to the continuous phase. This leads to a shearing of the liquid layers at the liquid-solid interphase: the wave will be attenuated due to shear friction (Fig. 5). This effect is predominant for suspensions with rigid, coarse particles < 4 µm (ceramics, pigments, ...).

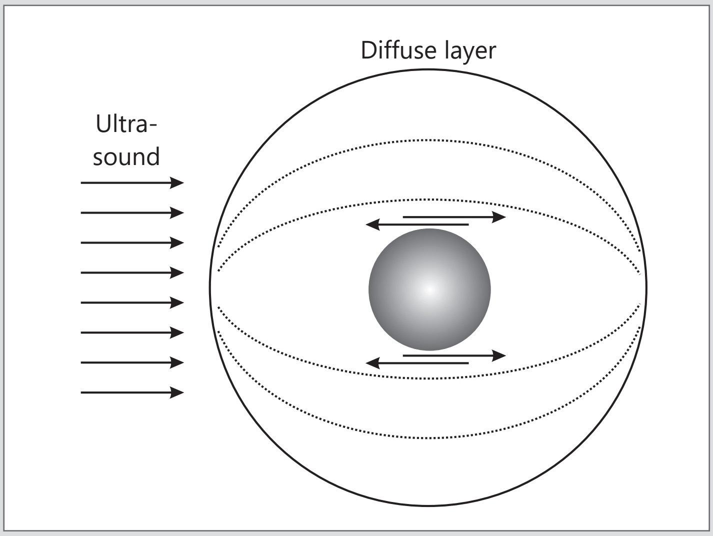

Figure 5 *Mechanism of the viscous-inertial effect*

Fig. 6 shows the complete attenuation spectrum of similar suspensions which differ only in the particle diameter of the dispersed phase (3.0 µm, 0.4 µm and 0.05 µm). In addition, it was assumed that a continuous spectrum from the KHz to the GHz range could be recorded.

All spectra show a maximum of the attenuation at a characteristic frequency f_{cr}, which shifts to higher frequencies with increasing particle size.

$$f_{cr} \sim \frac{\eta}{\rho d^2} \qquad (2)$$

The red rectangle in Fig. 6 shows the shape of the spectrum of the respective suspension as it would look after a measurement using a DT spectrometer (1 – 100 MHz).

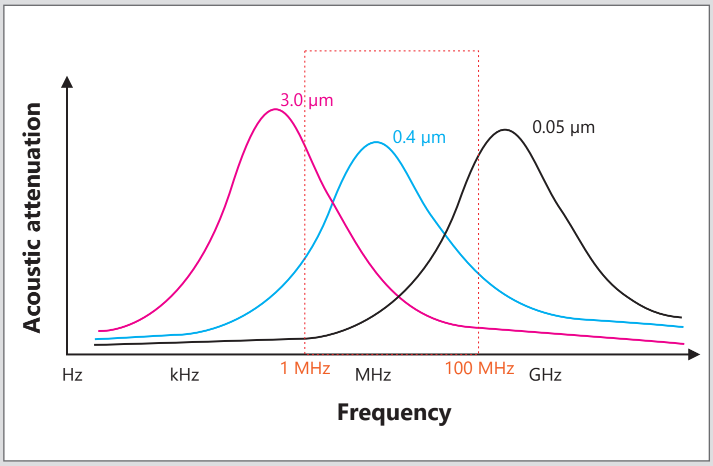

Figure 6 *Characteristic frequency of similar suspensions with a different particle size*

The experimental description of the viscous effects started already in the 1940s with the works of Urick [1] and Ament [2]. The model of Ament points out that the individual phases can appear with certain amounts and provides a possibility to take several different dispersed phases into account. The most common acoustic theory is surely the ECAH theory, which was developed by Epstein, Carhart, Allegra and Hawley [3-4]. It is applicable only for diluted systems and describes the viscous as well as the thermal attenuation mechanism. The theory to analyze the viscous-inertial effect integrated in the DT-100/110/1202/1210 spectrometers is the so-called advanced coupled phase model (PKM) developed by Dukhin and Goetz [5-6].

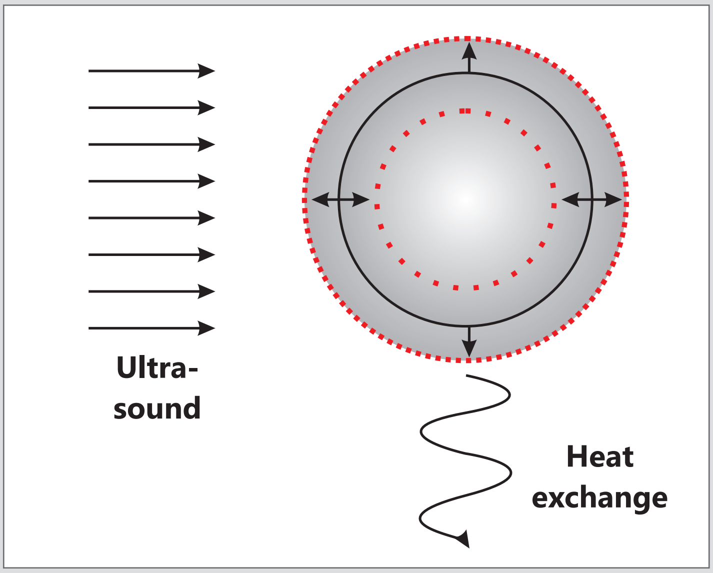

Figure 7 *Thermal effects*

Thermal effects

The nature of this mechanism is thermodynamic: The transmitting ultrasound wave leads to pressure- and density-fluctuations in the dispersed as well as in the continuous phase. The consequence is the appearance of different temperature fluctuations inside the phases due to the thermodynamically coupling of pressure and temperature. These fluctuations lead to the formation of temperature gradients at the phase boundary (Fig. 7). The temperature compensation results in an increase of the oscillation energy. This effect is dominant for emulsions and plays a role in e.g., latices. For aqueous suspensions, it is negligible.

The thermal effects in a latex suspension (mean particle size of 160 nm) can be seen in Fig. 8. The attenuation of the suspension is shown versus the latex weight fraction.

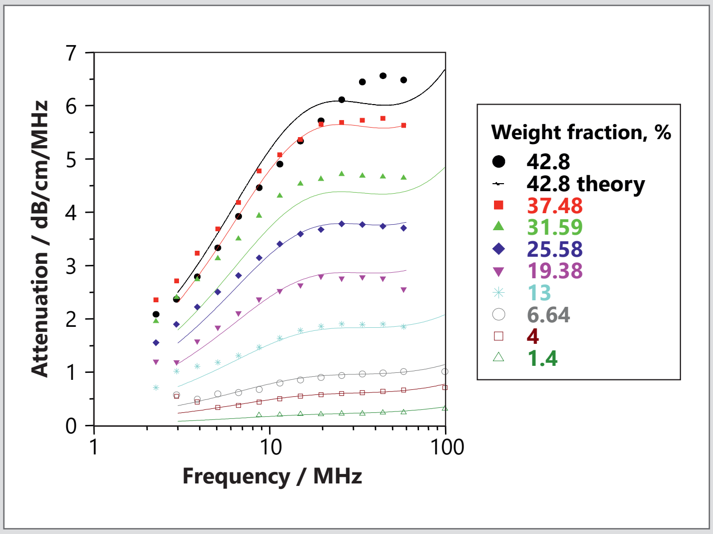

Figure 8 *Thermal effects in a latex suspension at different latex contents (d50 = 160 nm) [6]*

To focus on the history of the modelling of the thermal effects, it is necessary to reach once again for the ECAH theory. The theory for the description of this effect which is integrated in the DT-acoustic spectrometers is the model of the „particle-medium-coupling" (PMK) of Isakovich [7].

Structural effects

This attenuation mechanism appears in structured dispersion (highly concentrated dispersions or systems with binders). The individual mobility of a particle in the continuous phase is strongly influenced by the others. Such structured systems have dissipative as well as elastic properties. For this case, one can imagine the particles as interconnected by springs (Fig. 9, Rouse-Bueche-Zimm model, integrated in the DT-100 [8]). The springs are representing the elastic fraction. The viscous fraction of the particles moving through the liquid is represented by the attenuation module. It is inversely proportional to the Stokes resistance value. This additional energy loss can be determined by means of the Hooke's law (3):

$$F^{hook} = H_1 \, \Delta X + H_2 \frac{\delta X}{\delta t} \tag{3}$$

$H_1 \Delta X$...... elastic force (H_1...elastic coefficient;
ΔX...displacement of the particle)

$H_2 \frac{\delta X}{\delta t}$ .... dissipative force (H_2...dissipative coefficient;
$\frac{\delta X}{\delta t}$...particle speed)

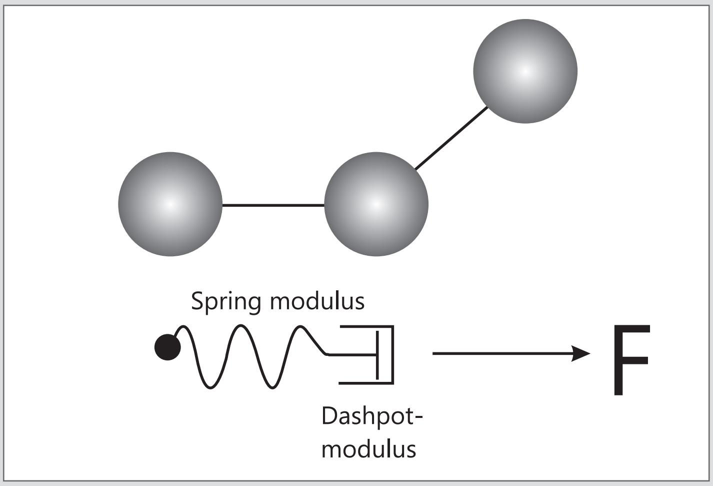

Figure 9 *Structural losses*

According to the theory it can be concluded that the relevant mechanism for sound attenuation is the dissipative fraction here. This can be seen clearly in Fig. 10: the left image shows the influence of the Hooke elasticity coefficient on the attenuation of a 40 Vol.-% alumina suspension (d50 = 1 µm).

Apparently, the curve shape remains unaffected by this parameter, only the attenuation maximum shifts to higher frequencies. The right graph shows the influence of the Hooke loss coefficient on the attenuation spectrum of this dispersion. In this case, the curve shape is changing significantly – the parameter is used as an additional fit parameter.

1.2.3 Sound scattering

Scattering of sound waves by particles in a dispersion works according to similar laws as for light scattering. This is not a dissipative effect but the sound wave will be partially deflected in other directions in space. The total energy will be conserved (Fig. 11). Effects that play a role in this process are reflection and refraction at the phase-boundaries as well as diffraction directly at the particle itself. The scattering effect is only important in the so-called long wave regime. This means that the wave length of the ultrasound wave is much bigger than the particle size diameter. For ultrasound spectrometry, this is the case for particles bigger than ca. 5 µm.

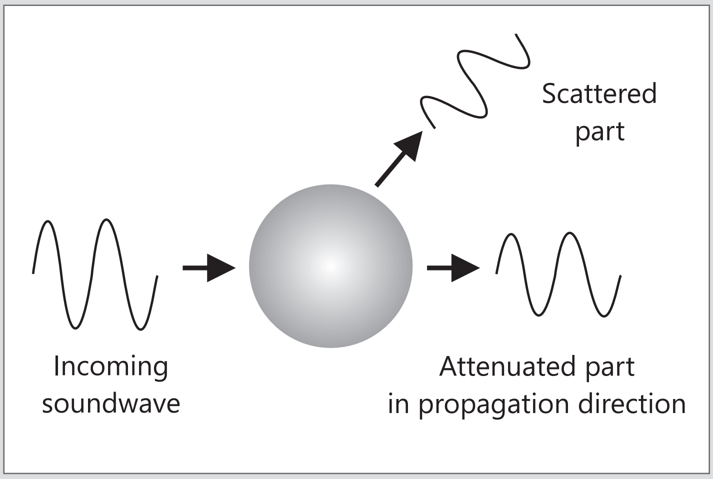

Figure 11 *Sound scattering*

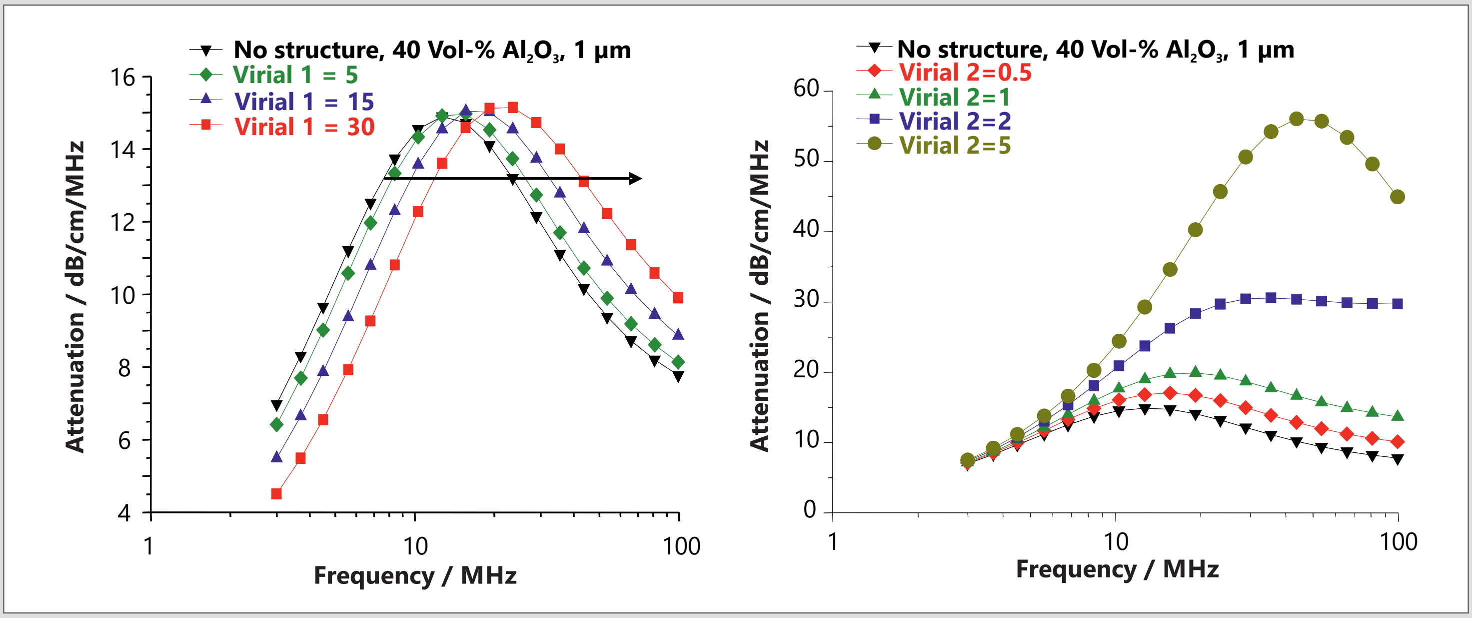

Figure 10 *Structural effects at a 40 Vol.-% Al_2O_3 suspension (d50 = 1 µm),*
left: the Hooke elasticity coefficient (virial 1); right: the Hooke loss coefficient (virial 2) [6]

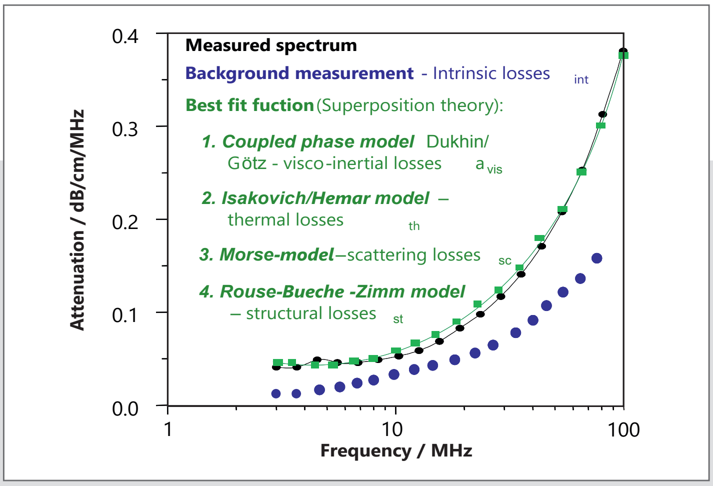

Figure 12 *Principle of superposition demonstrated in a diagram*

The first approaches to describe sound scattering at an individual particle can be found in a paper of Rayleigh in 1880. The ECAH-Theory on the other hand describes the scattering for diluted systems. The model for concentrated dispersions which is integrated in the DT100 is a modification of the Morse theory [9].

1.2.4 Analysis of the attenuation spectrum

The intrinsic and the dissipative effects as well as the sound scattering are independent from each other The acoustic approach of superposition [6] states that the total acoustic attenuation αT of an acoustic wave in a dispersion can be written as the sum of all individual attenuation mechanism:

$$\alpha_T = \alpha_{int} + \alpha_{vis} + \alpha_{th} + \alpha_{st} + \alpha_{sc} \tag{4}$$

Fig. 12 demonstrates the superposition approach in a diagram: the measured spectrum (black curve) is an overlay of all mechanisms 1 to 5. The intrinsic loss in the pure solvent is independent of the particle size and is subtracted from the total spectrum as a background. The remaining spectrum consists of the particle size depending mechanisms 1 to 4. On the basis of the specific theory for each mechanism integrated in the software, this remaining spectrum is fitted in and the particle size is calculated from this.

2 Electroacoustic measurement for zeta potential

2.1 Principle of measurement and technical performance

A comprehensive summary of the electroacoustic method is given in [6]. The principle of this zeta potential measurement is shown in Fig. 13: A high frequency signal (RF-pulse) is transferred into an ultrasound wave by means of a piezo transducer. This wave passes a quartz delay rod (internal calibration), then a buffer rod and launches into the dispersion as a narrow frequency, short pulse. The colloidal particles in the dispersion start a frequent motion relative to the surrounding liquid because of their mass inertia. Thus, the particles are shifted relative to their diffuse double layer: an oscillating electric field is generated which induces a measurable, alternating current – the colloidal vibration current (CVI). This is measured as a potential between two electrodes and can be used to determine the colloidal properties of the sample. The two important measurement parameters are the magnitude of the CVI signal which determines the absolute amount of the zeta potential and the phase shift θ between the ultrasound wave as well as the CVI signal which determines the sign.

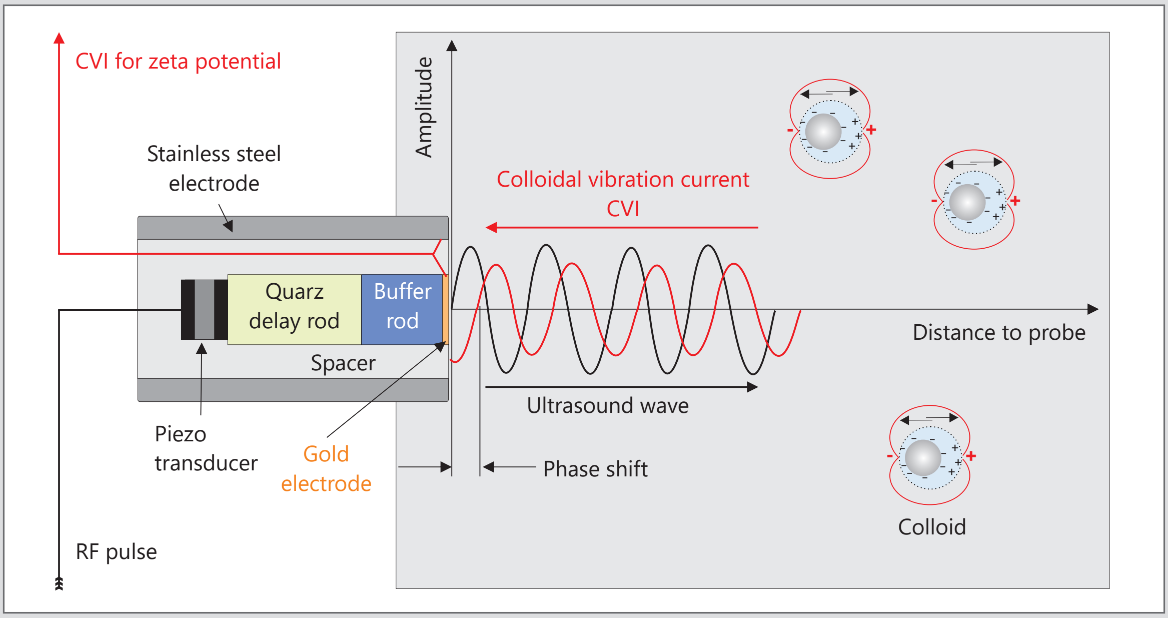

Figure 13 *Electroacoustic measurement principle*

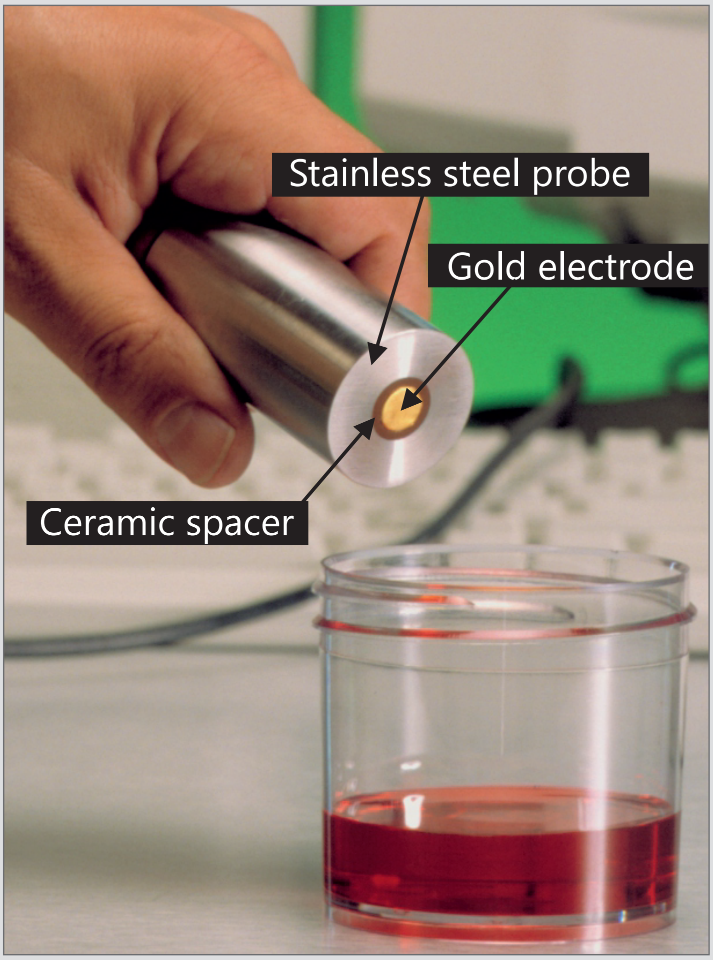

Figure 14 *Zeta potential probe*

The technical implementation of the electroacoustic method – the DT zeta potential probe implemented in the electroacoustic systems DT-300 / 310 / 330 / 1202 / 1210 – is shown in Fig. 14: This pulse-echo method enables a practical hand electrode design with a smooth, easy-to-clean surface. The isolation of the gold- and stainless-steel electrode is realized by a ceramic spacer.

The transmitted ultrasound wave has a wave length of 3 MHz by default, because it is commonly used in most applications. But it is also possible to vary the frequency. At least 800 sound pulses are sent into the sample. This number can be increased up to 1.6 million pulses in case of a very low signal or if the dispersion is not stable. In analogy to the particle size measurement via ultrasound attenuation, the zeta potential can be measured in flowing or a stationary dispersion.

2.2 Electroacoustic theories – determination of colloidal properties from the colloidal vibration current

2.2.1 Electric double Layer (EDL) at steady state (no external fields)

The double layer (EDL) structure can be described using the model of Gouy-Chapman-Stern [6]: Colloidal particles with a surface charge and a surface potential Ψ_S creates an electrostatic field, in combination with the thermal motion of the ions, creates a counter-charge, and thus screens the electric surface charge. The net electric charge in this screening diffuse layer is equal in magnitude to the net surface charge but has the opposite polarity. As a result, the complete structure is electrically neutral. The distribution of the electric potential in the EDL is shown in Fig. 15.

Basically, two colloidal parameters as shown in Fig. 15 are important for the characterization of the electric colloidal properties: the Stern potential Ψ_D effective at the Stern plane and the Debye length κ^{-1}, which is the thickness of the diffuse layer.

Taking into account the Boltzmann statistic and the Poisson equation, it follows for the ionic distribution κ^{-2} for a flat surface [10]:

$$\kappa^2 = F^2 \sum_i \frac{c_i z_i}{\varepsilon_0 \varepsilon_m RT} \qquad (5)$$

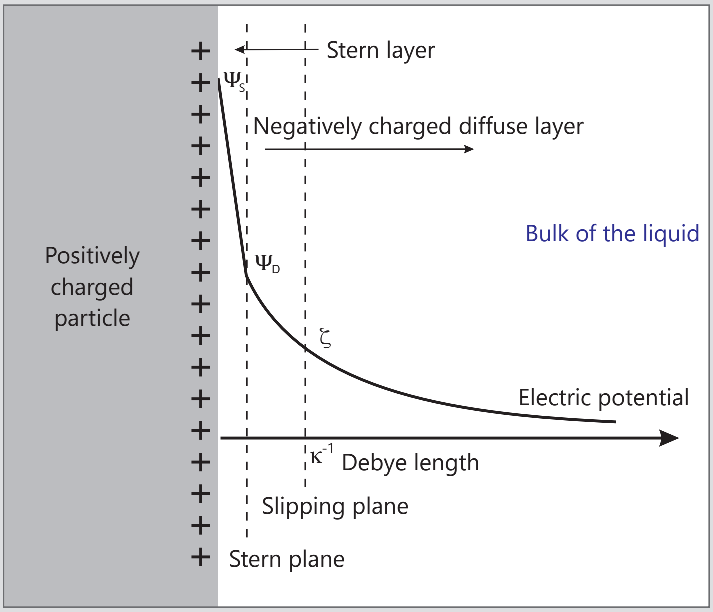

Figure 15 *Stern double layer model*

The Debye length is calculated from the reciprocal square root of this ionic distribution and correlates with the thickness of the diffuse double layer. In equation (1), c_i indicates the electrolyte concentration, z_i the ionic valence, ε_0 and ε_m the dielectric constant and permittivity, F the Faraday constant, R the gas constant and T the absolute temperature. Thus, the Debye length depends strongly on the "ionic strength" of the liquid. For an ionic strength of 0.1 M, it is approximately 1 nm and increases to about 10 nm if the ionic strength drops down to 0.001 M.

For a spherical electric double layer, the radius of the particle "a" is an additional geometrical parameter. The ratio of both, the "κa-value" is an important, dimensionless common parameter: It represents the relation between double layer size and particle radius. Three cases must be distinguished in order to describe the electric charge conditions surrounding the particle (Fig. 16):

Thin EDL

This model corresponds to colloids in which the DL is much thinner than the particle radius ($\kappa a >> 1$). This is the case for most aqueous dispersion (except very small particles). Progress of the electric potential and diffuse charge density can be calculated using the Debye-Hückel approximation if the Stern Potential Ψ_D is known [6, 23].

Thick EDL

corresponds to systems where the DL is much larger than the particle radius ($\kappa a << 1$). This is the case for many nanodispersions at low ionic strength and hydrocarbon media with very low ionic strength. Progress of the electric potential and charge density can also be calculated using the Debye-Hückel approximation [6, 23].

Overlapping double layers

The overlapping of the double layers in a dispersion depends strongly on the κa value (must be very small) and the volume fraction of the particles φ. The critical volume in a dispersion where the double layers overlap can be calculated with Eq. 6. The Debye-Hückel approximation is not valid here, the charge density can be calculated by a model of Shilov and Dukhin [6].

$$\varphi_{over} \approx \frac{0.52}{\left(1+\frac{1}{\kappa a}\right)} \tag{6}$$

The Debye length can be calculated by means of measuring the electric conductivity [6]. The Stern potential Ψ_D is a theoretical construct and cannot be measured directly. It is approximately in accordance with the zeta potential (see next column).

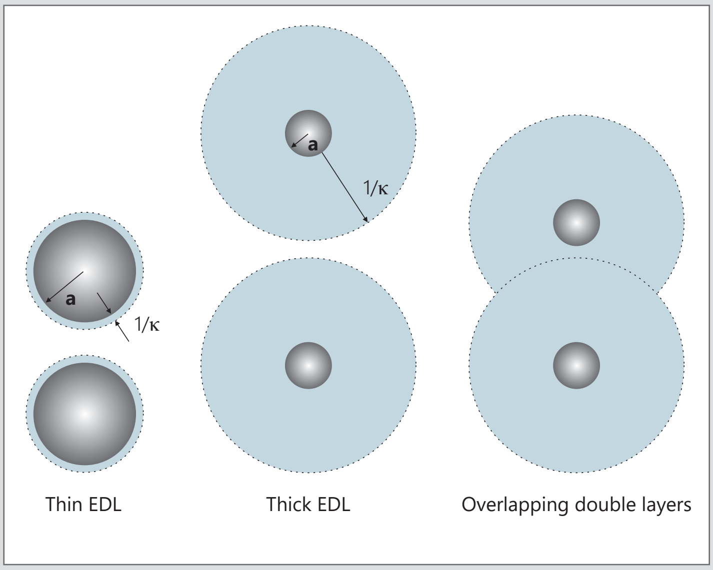

Figure 16 *Three possible cases for the electric charge conditions surrounding a colloid particle*

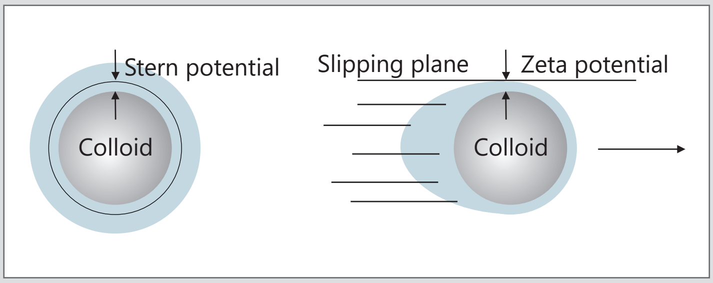

Figure 17 *Colloidal particle in steady state and in motion*

2.2.2 Electric double Layer (DL) at polarized state (applied acoustic field)

Applying a tangential stress in form of an acoustic field makes a colloid particle move and introduces a slipping plane in its diffuse layer that separates mobile fluid from fluid that remains attached to the surface (Fig. 17).

The electric potential at this plane is called the zeta potential, which can be measured directly in contrast to the Stern Potential. This slipping plane is located very close to the outer Helmholtz or Stern plane and thus equal or a little lower in magnitude than the Stern potential (Fig. 15).

Besides external forces, surface conductivity effects can influence the measurement of the zeta potential. Surface conductivity is an additional electric conductivity of the electrolyte in the vicinity of the charged interface: The diffuse layer consists of counter ions of the opposite polarity to the surface charge (in the example in Fig. 18, the diffuse layer is negatively charged).

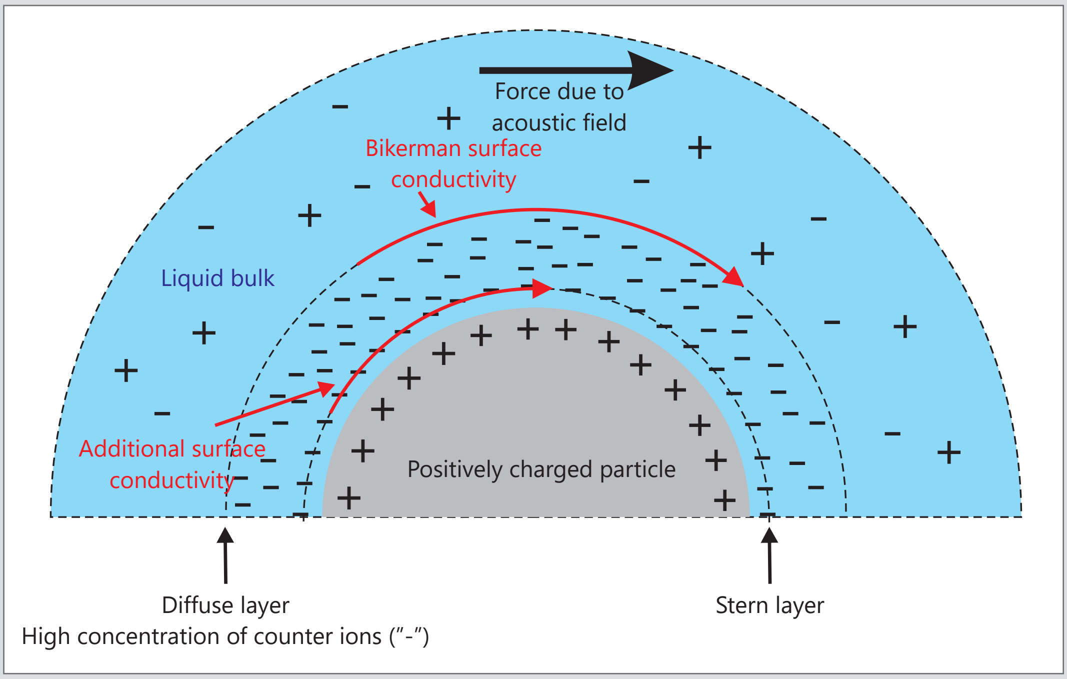

Figure 18 *Electric double layer at polarized state*

The charge concentration is much higher as compared in the liquid bulk. This leads to a higher electric conductivity of this layer. This so called "surface conductivity K^σ" has two parts: the one between the bulk liquid and the diffuse layer (Bikerman surface conductivity) and another between the diffuse and Stern layer (additional surface conductivity). Both effects can influence the measurement of the zeta potential depending on the colloid system. This surface current increases the total current and is proportional to the surface area of the particle a^2.

Besides this effect, the particle itself is non-conducting. This non-conductivity of the particle reduces the total current because the current cannot pass to this nonconductive volume. This current depends on the electric conductivity of the liquid K_m and is proportional to the particle volume a^3. Both additional effects are opposite and the balance of them depends on the dimensionless Dukhin number Du:

$$\mathrm{Du} = \frac{a^2 K^\sigma}{a^3 K_m} = \frac{K^\sigma}{a K_m} \qquad (7)$$

Thus, Du is a measure of the relative importance of the surface conductivity for a colloid dispersion. The parameter can be measured using the electric conductivity of the medium and the solids content of the dispersion.

2.2.3 Analysis of the zeta potential using electroacoustic technique and CVI-signal

An important value for electrophoresis is the so-called electrophoretic mobility μ: it is the particle speed v normalized by the applied electric field E (μ=v/E, [6]).

The key parameter for the determination of the zeta potential out of the CVI measurement is the dynamic mobility μ_D. It is the equivalent value of μ for high frequent oscillating particle motion as it is the case in acoustic fields. The dynamic mobility for the electroacoustic experiment is defined as:

$$\mu_D = CVI\left[\frac{\rho_m}{\varphi\left(\rho_P - \rho_m\right)}\right]\left[\frac{1}{A(\omega)F(Z)}\right] \qquad (8)$$

CVI........magnitude of the CVI electroacoustic signal
$A(\omega)$ ......instrument constant found by calibration
$F(Z)$ ....function of the acoustic impedances of the transducer and the dispersion under investigation describing reflection of ultrasound on the surface of the electroacoustic probe
ρ_P; ρ_m... Density of particle and medium
φ... ....volume fraction

The zeta potential ζ is then calculated from the dynamic mobility using a theory that correctly describes the present colloidal conditions. The three different situations are shown in Fig. 16.

Smoluchowski limit theory for electroacoustic (SDEL)

The SDEL-theory is the electroacoustic equivalent for the most widely used electrophoretic theory of Smoluchowski [6, 23]. It is very simple and applicable for particles of any size, any shape and almost any concentration in aqueous systems. The relation between μ_d and ζ for this theory is given by:

$$\mu_d = \frac{\varepsilon_m \varepsilon_0 K_S}{\eta K_m} \frac{\left(\rho_p - \rho_s\right)\rho_m}{\left(\rho_p - \rho_m\right)\rho_s} \qquad (9)$$

The SDEL-theory can be used to calculate the zeta potential out of μ_D under the following conditions:

1. Thin double layer ($\kappa a >> 1$, benchmark is $\kappa a > 10$, Fig. 16): a limit are very small nanoparticles and very low conductive systems; a very good overview is given in Fig. 17
2. Negligible surface conductivity effects ($Du << 1$)
3. Isolated double layers: the solids content is limited at a certain conductivity and particle size.

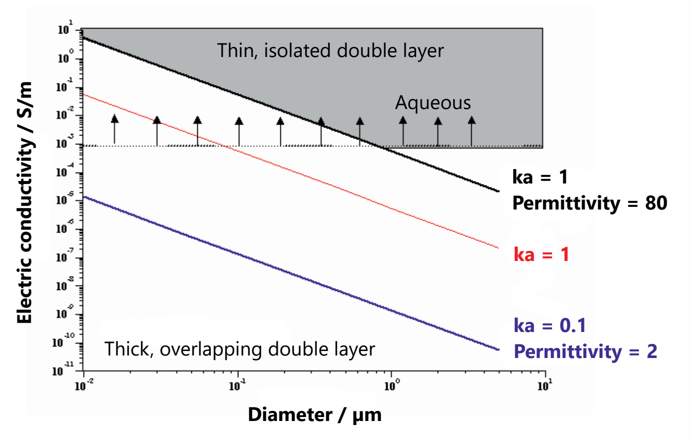

Figure 19 *Scope of application of the SDEL-theory*

Further, the applied frequency ω of the acoustic field is restricted: it must be smaller than the so-called critical frequency of hydrodynamic relaxation (ω_{hd}) which is related to the particle inertia. In addition, it must be much smaller than the Maxwell Wagner frequency (ω_{MW}). Above that, the diffusion time of the ions through the double layer is high in comparison to the fluctuation of the double layer and surface charge effects plays a role. Details to this can be found in [6, 23, 24]. The calculation of the zeta potential regarding the SDEL theory requires:

1. CVI signal
2. Solids content

Advanced theory for polar systems

Advanced theories for the determination of the zeta potential out of the dynamic mobility are rather complex. Such a theory for polar systems which takes into account particle interactions and eliminates restrictions on the surface conductivity effects (restriction 1 and 2, see SDEL-theory C.1) has been developed by Dukhin, Shilov, Ohshima and Goetz [19]. Thus, the remaining limitation of this model are isolated, non-overlapping double layers.

The approach for this theory is that a poly-disperse colloidal system is assumed and the relationship between CVI and zeta is determined for each fraction on the basis of a „cell model". In addition, the model is extended to systems with surface conductivity via the Dukhin number. Then the relationship between μ_D and ζ results from superposition of all fractions [6] to:

$$\mu_D = \frac{2\epsilon_m \epsilon_0 (\rho_s - \rho_m)\rho_s}{3\eta(\rho_s - \rho_m)\rho_s} \frac{\sum_{i=1}^{N} \frac{9\rho_s \varphi_i h(s_i)}{4j\varphi(1-\varphi)s_i I(s_i)\left(\rho_p - \rho_m\left(\frac{3H_i}{2I(s_i)} + 1\right)\right)} \frac{3}{2 + \varphi + 2Du_i(1-\varphi)}}{1 - \frac{\rho_p}{1-\varphi} \sum_{i=1}^{N} \frac{\left(\frac{3H_i}{2I(s_i)} + 1\right)\varphi_i}{\rho_p - \rho_m\left(\frac{3H_i}{2I(s_i)} + 1\right)}} \qquad (10)$$

As shown in Fig. 19 the theory covers the complete aqueous range ($K_{Dispersion} > 10^{-3}$ S/m). The calculation of the zeta potential regarding this "advanced CVI-theory" requires the information as follow:

1. CVI signal
2. Electric conductivity of the dispersion
3. Electric conductivity of the dispersion medium K_m (Dukhin number)
4. Solids content

Advanced theory for non-polar systems

A specific theory for non-polar, non-aqueous systems with thick, overlapping DLs has been developed by Shilov, Dukhin and Borkovskaja [22]: In case of non-polar systems, the diffuse layer is expanding extremely although the permittivity is small. The reason for this is that the number of charge carriers in the dispersion is low. The values of κa are getting very small – depending on the solids content, an overlapping of the double layers is most likely. In strong non-polar systems, the double layers overlap already at a concentration of 0.04 %. The SDEL- as well as the advanced-theory for polar systems described in C1) and C2) is not valid for this special case. The dynamic electrophoretic mobility can be calculated using:

$$\mu_D = \frac{2\sigma a}{3\eta\Omega} \frac{\rho_m}{\rho_s + i\omega(1-\varphi)\frac{2a^2}{9\eta\Omega}\rho_p \rho_m}. \qquad (11)$$

Ω is a drag coefficient well known from the Stokes law (F = 6πηaΩv, hydrodynamic interaction) and *σ* is the surface charge. In case of ion adsorption in systems with thick DL, *σ* is a suitable parameter to characterize the amount of this adsorption. In addition, the electric conductivity which is not always easy to get, must not be measured for its calculation. The relation between the zeta potential and the surface charge is given by:

$$\sigma = \frac{1}{3}\frac{RT}{F}\frac{1-\varphi}{\varphi}\varepsilon_m a\kappa^2 sinh\tilde{\zeta} \tag{12}$$

Thus, the electric conductivity must be known to determine the zeta potential.

Literature

[1] Urick, R.J., „The absorption of sound in Suspensions of irregular Particles“, J. Acoust. Soc. Am. 20, 3, 283-289 (1948).

[2] Ament, W.S., „Sound propagation in Gross mixtures“, J. Acoust. Soc. Am. 25, 641-683 (1953).

[3] Allegra, J.R., Hawley, S.A., „Attenuation of Sound in Suspensions and Emulsion: Theory and Experiments“, J. Acoust. Soc. Am. 51, 1545-64 (1972).

[4] Epstein, P.S, „On the Absorption of sound by suspension and emulsions“, in Applied Mechanics (Th. Von Karman Anniversary Volume), 162-188 (1941).

[5] Dukhin, A. S.; Goetz, P. J., Langmuir (1996), 12, 4336-4344.

[6] Dukhin, A. S.; Goetz, P. J., Characterization of Liquids, Dispersions, Emulsions, and Porous Materials Using Ultrasound, third edition, Elsevier, 3. Edition (8.8.2017); ASIN: B074PN87R5

[7] Isakovich, M.A., Zh. Experim. I Teor. Fiz. 18, 907, (1948).

[8] Mason, W.P., „Dispersion and Absorption of sound in high polymers“, in Handbuch der Physik, vol.2, Acoustica, part 1 (1968).

[9] Morse, P.M., Uno Ingard, K., „Theoretical Acoustics“, 1968 McGraw-Hill, NY Princeton University Press, NJ, 925 p (1986).

[10] Lagaly, G.; Schulz, O.; Zimehl, R., „Dispersionen und Emulsionen“, Steinkopf, Darmstadt, ISBN 3-7985-1087-3 (1997).

[11] Debye, P., „A method for the determination of the mass of electrolyte ions“, J. Chem. Phys., (1933), 13-16.

[12] Hermans, J., Philos. Mag., 25, 426 (1938).

[13] Rutgers, A. J.; Rigole W., „Ultrasound vibration potentials in colloid solutions, in solutions of electrolytes and pure liquids“, Trans. Faraday. Soc., 54, 139-143 (1958).

[14] Booth, F. and Enderby, J. “On Electrical Effects due to Sound Waves in Colloidal Suspensions”, Proc. of Amer. Phys. Soc., 208A, 32 (1952).

[15] Marlow,B.J., Fairhurst, D. and Pendse, H.P., “Colloid Vibration Potential and the Electrokinetic Characterization of Concentrated Colloids”, Langmuir, 4,3, 611-626 (1983).

[16] Levine, S.; Neale, G.H., „The Prediction of Electrokinetic Phenomena within Multiparticle Systems. 1. Electrophoresis and Electroosmosis“, J. Coll. Interface Sci., 47, 520-532 (1974).

[17] O’Brien, R.W. “Electro-acoustic Effects in a dilute Suspension of Spherical Particles”, J. Fluid Mech., 190, 71-86 (1988).

[18] M. v. Smoluchowski, Elektrische Endosmose und Strömungsströme, in: Handbuch der Elektrizität und des Magnetismus, L. Graetz, Editor. (1921), Leipzig, S. 366-387.

[19] Dukhin, A.S., Shilov, V.N., Ohshima, H., Goetz, P.J. “Electroacoustics Phenomena in Concentrated Dispersions. New Theory and CVI Experiment”, Langmuir, 15, 20, 6692-6706, (1999).

[20] Dukhin, A.S., Shilov, V.N., Ohshima, H., Goetz, P.J. “Electroacoustics Phenomena in Concentrated Dispersions. Effect of the Surface Conductivity”, Langmuir, 16, 2615-2620 (2000).

[21] Lyklema, J., „Fundamentals of Interface and Colloid Science“, vol. 1-3, Academic Press, London-NY, 1995-2000.

[22] Shilov, V.N., Borkovskaja, Yu.B., and Dukhin A.S. “Electroacoustic theory for concentrated colloids with overlapped DLs at Arbitrary ka. Application to Nanocolloids and Nonaqueous Colloids. J. Colloid Interface Sci. 2004, 277 pp. 347-358

[23] ISO/FDIS 13099-1, Colloidal systems – Methods for Zeta Potential Determination – Part 1: Electroacoustic and electrokinetic phenomena. 2009

[24] ISO/FDIS 13099-3, Colloidal systems – Methods for Zeta Potential Determination – Part 3: Acoustic methods, 2014

3 Applications

3.1 Acoustic measurements on nano- and submicron rigid materials

A key application for acoustic spectrometers of the DT series is the characterization of rigid nano- and submicron particles. For the determination of the particle size, the main absorbing mechanism is the visco-inertial effect (see below).

In the first example, acoustic attenuation measurements were carried out on aqueous dispersions of two nano scaled silica powders (Aerosile OX 50® and A 380®) and their mixtures using the DT-100. The primary particle size of OX 50 is about 50 nm and of A 380 about 10 nm. Fig. 20 shows exemplarily the attenuation spectra of aqueous dispersions with 20 wt.-% solids content with OX 50, A 380 and mixtures with 25 and 50 wt.-% A 380 fraction, respectively. The four attenuation spectra differ clearly in their run. The attenuation at higher frequencies (> 30 MHz) decrease with an increasing fine powder content and flatten. The curves have no maximum in the frequency spectrum 1 to 100 MHz.

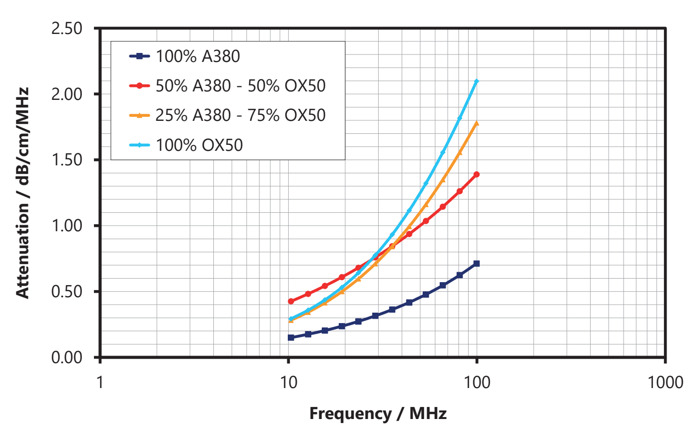

Figure 20 *Acoustic attenuation spectra of 20 wt.-% aqueous dispersions containing different mixtures of OX 50 and A 380*

Fig. 21 demonstrates the analyzed particles size distributions of the four dispersions: The mean particle sizes are shifted to smaller values with an increasing fine powder content. At the same time, the standard deviation is increasing.

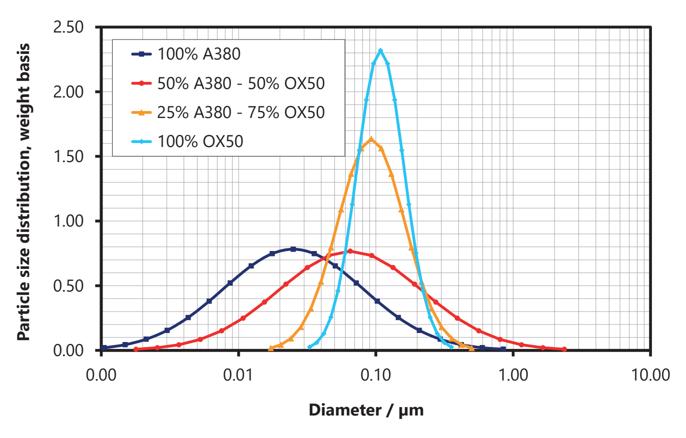

Figure 21 *Particle size distribution of 20 wt.-% aqueous dispersions containing different mixtures of OX 50 and A 380*

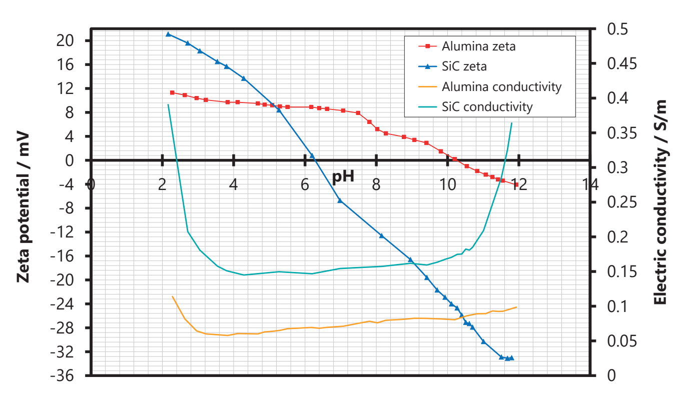

Figure 22 *Zeta potential and electric conductivity of the aqueous SiC- and alumina-slurries in dependence of the pH*

In the second example, electroacoustic and acoustic measurements were were carried out on aqueous SiC- and alumina-slurries using the DT-1202. The SiC suspension had a solids content of 35 wt.-%, the alumina slurry of 20 wt.-%. Both systems were titrated regarding pH using a 1 mol HCl and KOH. Fig. 22 shows the zeta potential and electric conductivity of both suspensions in dependence of pH. The SDEL theory was applied for the analysis.

The alumina shows an isoelectric point (IEP) at about pH = 10.3, the IEP of SiC is around 6.4. Assuming a low electrical conductivity and a large zeta potential in terms of magnitude for good stability of the particles in dispersion, a pH of around 4 for alumina and a pH of around 11 for SiC seems to be suitable.

Fig. 23 presents the attenuation spectra of both suspensions at these suitable pH values, Fig 24 the associated particle size distributions.

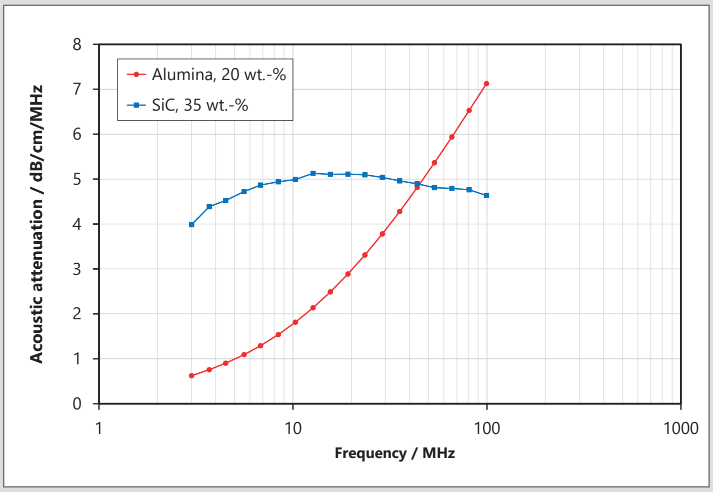

Figure 23 *Attenuation spectra of different aqueous ceramic slurries*

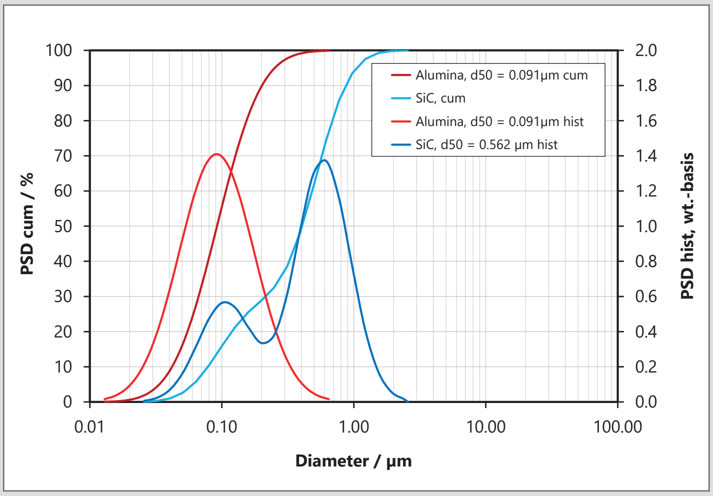

Figure 24 *Particle size distribution of different aqueous ceramic slurries*

Conclusion

Original concentrated nano- and submicron suspensions can be fully characterized regarding size and colloidal properties using electroacoustic and acoustic spectrometer DT-1202.

3.2 Zeta potential on high conductive systems

The measured electroacoustic signal as described above contains – in addition to the CVI of the colloidal particles – also a component that is caused by ions: the ion vibration current (IVI). In most of the cases, this part is negligible compared to CVI. However, in case of a high ion concentration, e. g., for cements or electrolyte baths, the IVI must be taken into account. The CVI is the difference between the measured value (total ion vibration current, TVI) and the IVI:

$$\text{CVI} = \text{TVI} - \text{IVI} \qquad (13)$$

The subtraction is vectorial in nature and not scalar, a comprehensive description can be found in [6]. The technique is called “method of the electroacoustic background”.

From a colloidal perspective, when a dispersion has an extremely high concentration of ions (such as cement), the diffuse layer will be thinned out and will sometimes collapse normally. Such a collapse does not happen in the case of hydrophilic surfaces like cements, because the formation of a hydrate-layer displaces the ions in outwards direction and the collapse will be inhibited (Fig. 25). That is the reason why zeta potential can be measured even for such systems.

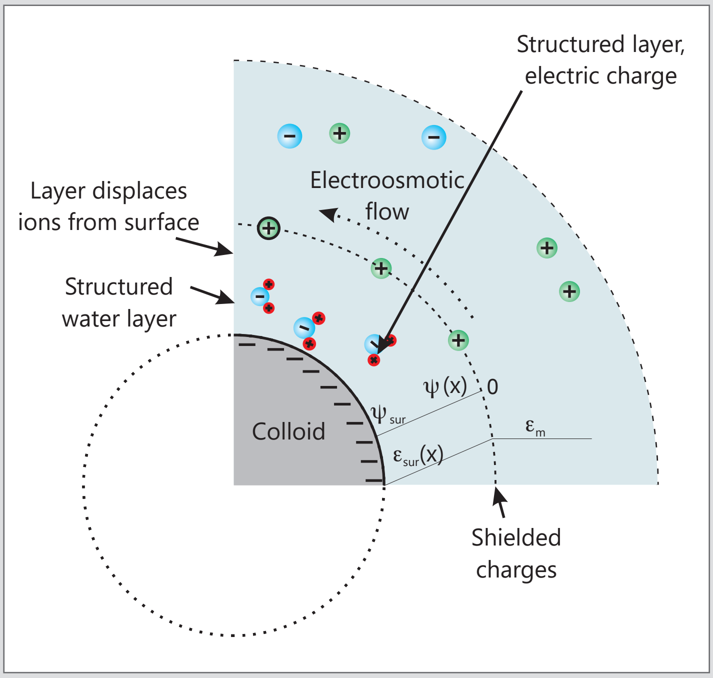

Figure 25 *Electric double layer for hydrophilic particles in dispersions at a high ionic strength*

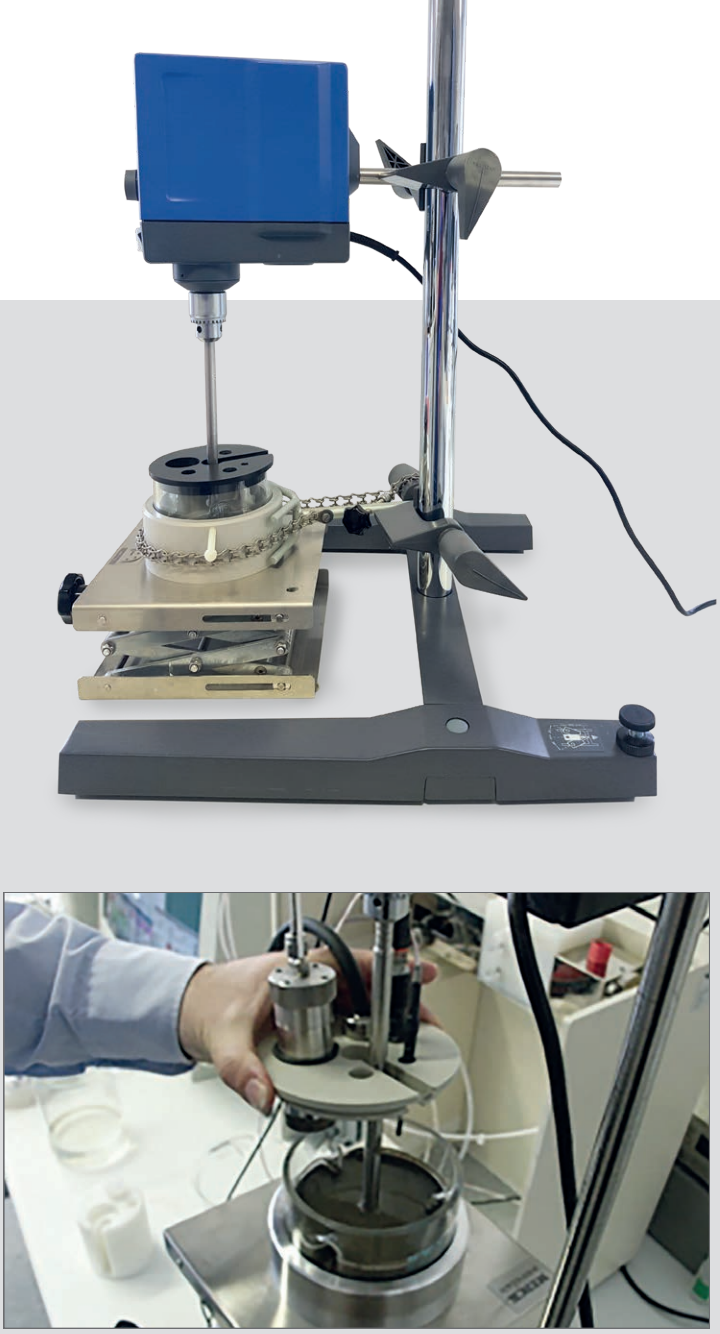

Figure 26 *Measuring stand for high viscous dispersions (top) and application for a 66.7 wt.-% cement in water paste (bottom)*

Measurements of the zeta potential on typical cement slurries (CEM 2925, 66.7 wt.-% in water) by means of the DT-310 with different amounts of various additives were carried out using the “method of the electroacoustic background” described above. In order to do this, the background liquid of the identical cement measurement was first separated off with the aid of a suction filter and the IVI was measured before each measurement. This value was taken into account in the subsequent measurement as IVI background. For the zeta potential measurement, a special stand was used (Fig. 26).

Fig. 27 represents exemplarily the zeta potential of the CEM 2925 suspension in dependence on the added amount of naphthalene sulfonate (ml), measured with the DT-310.

It can be observed that the higher the zeta potential, the more additive is added. A saturation is reached at about 2 ml additive. Obviously, naphthalene sulfonate acts as an electrostatic flux material. In contrast to this, the zeta potential of the same cement is decreasing by increasing the amount of polycarboxylate (Fig. 28). Nevertheless, this additive decreases the viscosity, it works as a steric additive. The reason for the decrease of the zeta potential is a shift of the hydrostatic shear layer in case of the adsorption of polymers with longer side chains. If this layer moves outwards, lower zeta potentials will be measured than without adding these adsorbed polymers.

Conclusion

The method of the electroacoustic background using the DT-310 can be applied to characterize dispersions even with a high electric conductivity regarding their zeta potential. Due to the beneficial geometry of the zeta probe (flat, robust surface), this is even possible in a concentrated slurry using the special designed zeta stand (Fig. 26).

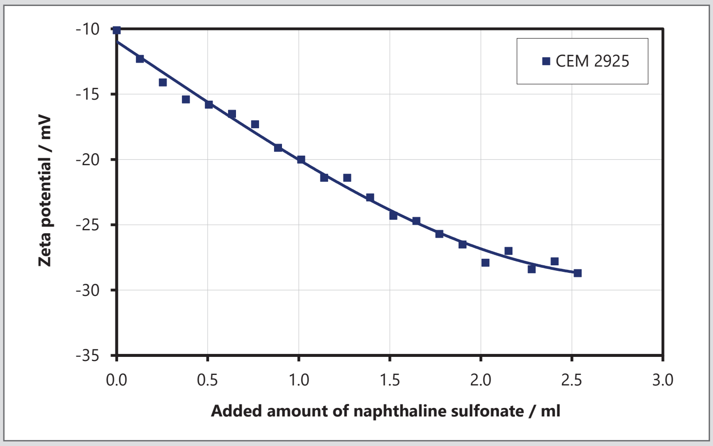

Figure 27 *Zeta potential of an aqueous cement slurry (66.7 wt.-% CEM 2925) in dependence of the added amount of naphthalene sulfonate*

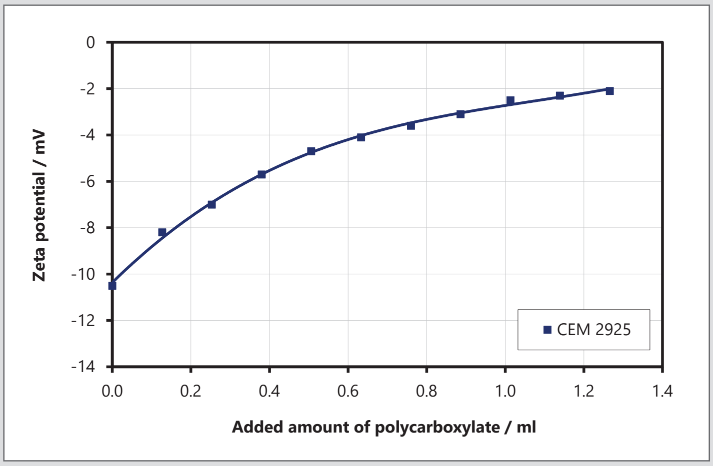

Figure 28 *Zeta potential of an aqueous cement suspension (66.7 wt.-% CEM 2925) in dependence of the amount of polycarboxylate*

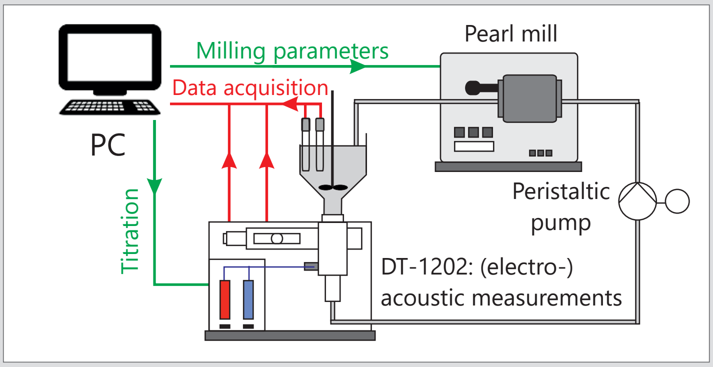

Figure 29 *Scheme of the bypass experiment of a milling process using a DT-1202*

3.3 Bypass or online experiments

Due to the fact that acoustic attenuation and electroacoustics can be applied for original concentrated systems, near-process-bypass or -online experiments can be realized. This is no challenge for zeta potential due to the easy design of the DT zeta probe (pulse-echo method, flat surface, see above).

A bypass-experiment for particle size distribution analysis using the DT-1202 is shown in Fig. 29: The purpose here is to control the milling process of a concentrated suspension. After the data acquisition and -analysis, the milling process parameters can be adjusted.

In this example, a milling process of a $CaCO_3$ dispersion will be discussed exemplarily. For this purpose, a high concentrated non-milled $CaCO_3$ powder was milled using a commercial pearl mill. The particle size distribution was measured every 10 minutes by means of the DT-1202. Fig. 30 shows the measurement data (acoustic attenuation) of the particle size measurement in dependence of the grinding time.

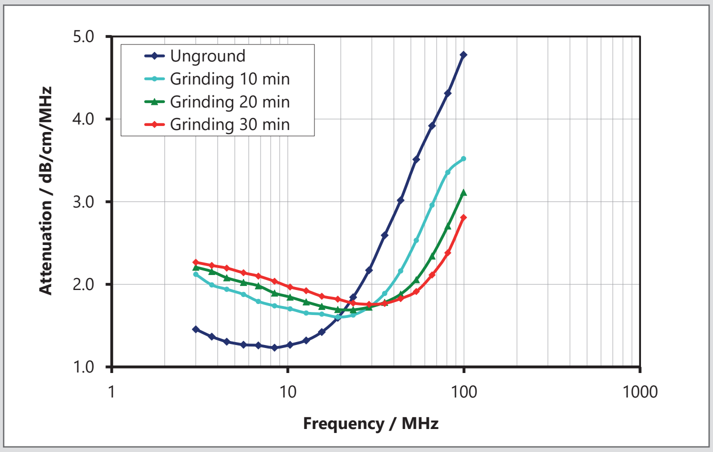

Figure 30 *Influence of the grinding time on the acoustic attenuation spectra of the chalk sample*

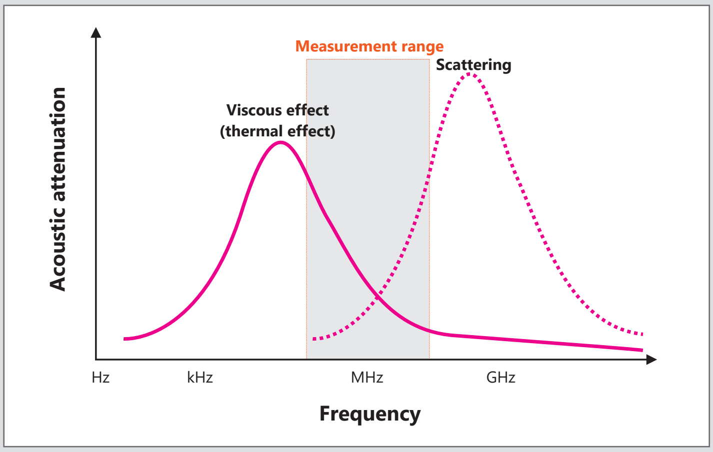

Figure 31 *Interference of the attenuation mechanism viscous effect and scattering*

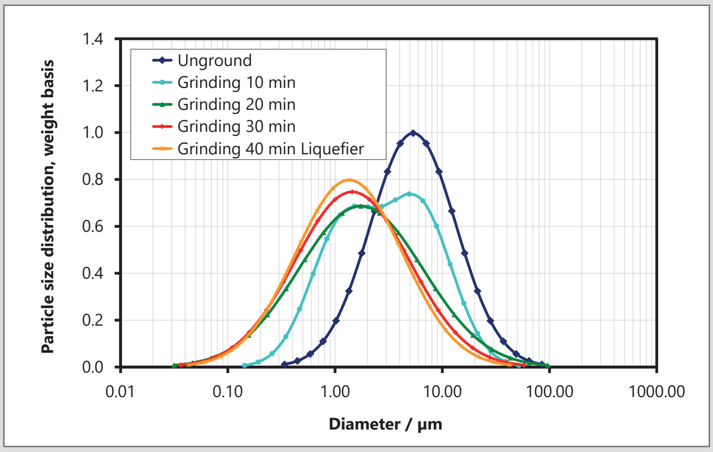

Figure 32 *Particle size distribution of the $CaCO_3$ particles in dependence of the grinding period*

Obviously, the ungrounded educts show a huge attenuation in the frequency range > 20 MHz, which decrease significantly with an increasing grinding time. In the lower frequency range (< 20 MHz), the effect is inverse, the spectrum increases with an increasing grinding time. The explanation is given in Fig. 31. Two effects are responsible for the attenuation of the ultrasound: scattering at the $CaCO_3$ particles and viscous friction at the particle-water boundary – both processes interfere with each other. The scattering is predominant for bigger particles (> 5 µm), while the viscous loss is the important effect for smaller particles. In the current example, the scattering forms the higher frequency range and the viscous loss the lower frequency part of the spectrum. Thus, the attenuation spectrum decreases in the higher frequency range with an increasing grinding time, because the scattering effect of the particles decreases – for the viscous loss, the situation is conversely.

Fig. 32 shows the particle size distributions calculated from the spectra of Fig. 30. Starting with a size of about 6 µm and a lognormal distribution, a fine fraction is appearing after a grinding time of about 10 minutes with a maximum at 1,5 µm. After 20 minutes grinding, the coarser fraction has disappeared. A further milling of about 10 minutes does not lead to a further significant improvement.

Conclusion

By means of the ultrasound spectrometer DT-1202, an online/bypass characterization of particle size and zeta potential of a milling processes is possible. These processes can be controlled in high concentrations as well as in the range of nano scaled particles.

3.4 Characterization of mixtures of emulsions and rigid particles

Mixtures of emulsions and rigid materials are important for, e. g., sun creams. These normally contain titanium oxide dispersed in an O/W-(Oil-in-water)-emulsion. The emulsion guarantees the spreading of the titanium oxide on the skin, while the ceramic powder works as an UV-adsorbing material. Another application are special lubricants. In the following example, a manganese oxide-in-emulsion suspension was examined regarding particle size distribution using the DT-100. This type of materials is important for lubrication of bore holes. The pure emulsion is an O/W-basis system, stabilized with emulsifiers and other additives. Its attenuation spectrum is given in Fig. 33. The particle size distribution, analyzed on the basis of the thermal effect (see above), is presented in Fig. 34.

In the emulsion, manganese oxide was dispersed with a concentration of 80 wt.-%. The acoustic attenuation spectrum of this complex mixture is also given in Fig. 33. It should be noted that the y-axis is represented logarithmically: The amounts of the attenuation values of the base emulsion and the manganese dispersion differ significantly.

The particle size was calculated using the attenuation spectrum of the basis-emulsion as background (intrinsic loss) and is shown in Fig. 34. Finally, the size data are summarized in Tab. 1.

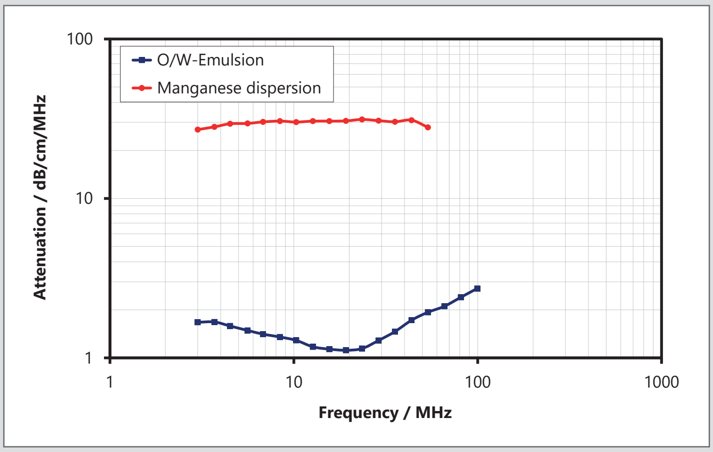

Figure 33 *Acoustic attenuation spectrum of the O/W-Emulsion and the complex manganese oxide dispersion*

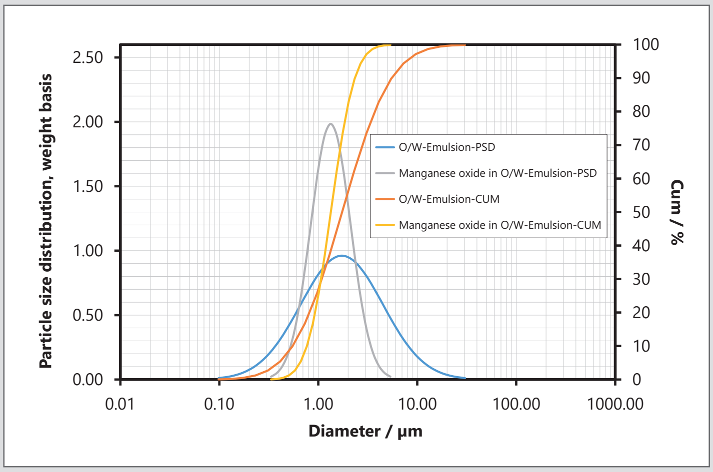

Figure 34 *Particle size distribution of the basis-emulsion and manganese oxide dispersion*

Conclusion

Emulsions and complex emulsion-rigid particle mixtures can be characterized by means of acoustic attenuation spectrometry.

Table 1 *Summary of the particle size distributions*

Sample	St. dev.	d10 / µm	d16 / µm	d50 / µm	d84 / µm	d90 / µm
O/W-emulsion	0.40	0.55	0.77	1.73	4.30	5.44
Manganese oxide-dispersion	0.20	0.77	0.87	1.33	2.07	2.33

DT Series Specifications

Specifications	**DT-100/110** **Particle size**	**DT-300/310/330** **Zeta potential**	**DT-1202/1210** **Particle size and Zeta potential**
Calculated parameter			
Particle size / µm	0.001 – 1,000	–	0.001 – 1,000
Lognormal parameter	Yes	–	Yes
Bimodal parameter	Yes	–	Yes
Zeta potential / mV	–	-200 – 200 (± 0.1)	-200 – 200 (± 0.1)
Porosity / %	–	1-99 (DT-330)	–
Measured parameters			
Temperature / °C	0 – 100 ± 0.1	0 – 100 ± 0.1	0 – 100 ± 0.1
pH	0.5 – 13.5 ± 0.1	0.5 – 13.5 ± 0.1	0.5 – 13.5 ± 0.1
Frequency range / MHz	1 – 100	1 – 100	1 – 100
Acoustic attenuation / $\mathrm{dB\cdot cm^{1}\cdot MHz^{1}}$	0 – 20, ± 0.01	–	0 – 20, ± 0.01
Sound speed / $\mathrm{m\cdot s^{1}}$	500 – 3,000 ± 0.1	–	500 – 3,000 ± 0.1
Electroacoustic signal	–	± 1 %	± 1 %
Electric conductivity / $\mathrm{S\cdot m^{1}}$	10^{-4} – 10^{1} ± 1 % opt.	10^{-4} – 10^{1} ± 1 % opt.	10^{-4} – 10^{1} ± 1 % opt.
Measurement time (in min)			
Particle size	1 – 10	–	1 – 10
Zeta potential – aqueous systems	–	0.5	0.5
Zeta potential – non-aqueous systems	–	0.5 – 5	0.5 – 5

DT Series Specifications

Specifications	**DT-100/110** **Particle size**	**DT-300/310/330** **Zeta potential**	**DT-1202/1210** **Particle size and Zeta potential**
Sample requirements			
Sample volume range / ml	20 – 70 (> 3 DT-110)	0.1 – 100	20 – 150 (>3 DT-1210)
Volume fraction % <?>	0.1 – 60	0.1 – 60	0.1 – 60
Electric conductivity	No restrictions	No restrictions	No restrictions
pH	0.5 – 13.5	0.5 – 13.5	0.5 – 13.5
Temperature / °C	< 50	< 50	< 50
Viscosity medium / cP	Up to 20,000	Up to 20,000	Up to 20,000
Micro-viscosity medium / cP [1]	Up to 100	Up to 100	Up to 100
Viscosity colloid / cP	Up to 20,000	Up to 20,000	Up to 20,000
Particle size / µm	0.001 – 1,000	< 100, porous monoliths	0.001 – 1,000
Zeta potential / mV)	No restrictions	No restrictions	No restrictions
Physical specification			
Output (power)	100 – 250 V AC, 50 – 60 Hz, < 300 W	100 – 250 V AC, 50 – 60 Hz, < 300 W	100 – 250 V AC, 50 – 60 Hz, < 300 W
Weight	50 kg (30 kg DT-110)	27 kg	50 kg (30 kg DT-1210)
Available options			
Electric conductivity probe	Yes	Yes	Yes
Permittivity measurement system	Yes	Yes	Yes
Peristaltic pump	Yes	Yes	Yes
Automatic titration	Yes	Yes	Yes
Non-aqueous application	Yes	Yes	Yes
Upgradeable to DT-1202/1210	Yes	No	–

[1] The decisive viscosity for particle size- and zeta potential-measurements is the one, at which the particle expires, when it moves into the acoustic field. This „micro-viscosity" can be – for gelatinous or structured systems e. g. – much smaller than the value measured by means of a conventional rheometer. In this case, the sphere of influence exceeds clearly the dimension of the particle.

DT Series Application fields

Ceramics

The properties of ceramic components depend on the quality of the starting powders. In addition, the type and execution of the shaping process is decisive: e.g. in wet processes (suspension route), the slip properties influence the properties of the green body in addition to the process parameters. A central quality characteristic is the stability of the suspension against sedimentation and agglomeration, with the zeta potential playing an important role in electrostatically or -sterically stabilized systems.

Anorganic Pigments & Inks

Inks are suspensions of pigments as a disperse phase and a liquid as a continuous phase. The challenge is to stabilize the suspension and control certain properties in the printed image. A decisive parameter for the stability of an ink is, for example, the particle size of the pigments. In addition, the suspensions are stabilized via additives that influence the surface charge (zeta potential). The zeta potential of these suspensions can be determined using acoustic spectrometry.

Building Materials

In the field of building materials, various mineral starting, intermediate and end products are produced. Cement slurries are often used as intermediate products. Their particle size and zeta potential can be characterized in undiluted state, e.g. by the DT-1202 acoustic spectrometer.

Battery Research

The development of new materials for hydrogen storage and lithium-ion batteries should lead to high energy and power densities, which should, for example, be quickly retrievable in vehicles when needed. Especially in the development of electrodes for fuel cells and supercapacitors, acoustic spectrometry can provide important parameters for assessing the materials.

LabSPA

Laboratory for Scientific Particle Analysis

The LabSPA (Laboratory for Scientific Particle Analysis) offers a wide range of contract analyses for the characterization of dispersions, powders and porous materials.

Contract analysis can be performed as individual analyses, call-off orders for a large number of samples in a defined period of time or as a comprehensive laboratory project. Individual sample preparation and/or measurement routines can be coordinated with our excellently trained laboratory staff. We are looking forward to your inquiry and we will gladly submit you an offer. An overview of our services and further information can be found at:

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R&D department working at scientific projects and solutions

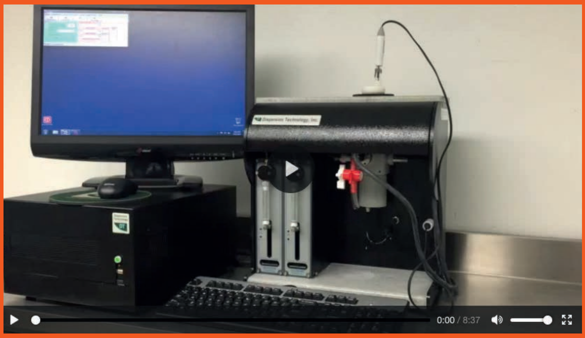
Experienced service team with direct access to test instruments

Customer service and instruction briefing by highly qualified expert team

Instrument rental and leasing is possible

Friendly administration, optimized business processes, very short response times

Watch the video of the DT-1202 in action:



3P Instruments GmbH & Co. KG
Rudolf-Diesel-Str. 12
85235 Odelzhausen | Germany

Tel. +49 8134 9324 0
info@3P-instruments.com
www.3P-instruments.com

RIFERIMENTO PER L'ITALIA

Qi technologies

Qi srl
t +39 06 9105461
www.qitech.it | sales@qitech.it

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