

# PARTICLE WORLD

Technical Papers of QUANTACHROME

Edition 4 • March 2010

**New: Aquadyne DVS - the new dual balance arrangement DVS Water Sorption Analyser**

**Criteria for the selection of analysers for characterisation of surfaces and pores**

**International Particle Characterisation Seminars 2010**

**Comprehensive characterisation of concentrated dispersions**



Dear Reader,

with our PARTICLE WORLD 4 we want to inform about the latest developments in the field of Characterisation of Dispersions, Powders and Porous Solids. The 4<sup>th</sup> English issue of our PARTICLE WORLD starts with the **characterisation of nano- and other fine particles in original concentrations by use of the analyser DT-1200**. The DT-1200 is the unique instrument to determine parallel the particle size distribution, the zeta potential and its pH-dependency, sound speed, dynamic mobility and other parameters in original concentrations and therefore without the need of changing the system.



Additionally you can read about particle size and shape analysis by use of the new sophisticated **CILAS particle size analysers in combination with the EXPERT SHAPE** option. Only with CILAS plus EXPERT SHAPE it is possible to combine laser diffraction and particle shape analysis, i.e. to get results according ISO 13320 for particle sizing with additional particle shape parameters for a moderate price.

The most recent development in water vapour sorption by use of the Dynamic Vapour Sorption (DVS) method is the **Aquadyne DVS**, which offers the unique capability of two parallel sample analyses of water adsorption isotherms by DVS method. Pharmaceutical products and foods, building or ceramic materials are typical applications for the **Aquadyne DVS**.

As distributor for FORMULACTION we offer the following instruments as part of a comprehensive dispersion characterisation:

- The patented **TURBISCAN** (Lab, Online and automated AGS version) to characterise the stability of original dispersions by use of both transmitted and backscattered light.
- The **HORUS** for characterisation of drying behaviour of films.
- The recently developed **RHEOLASER Lab** for determination of  $\mu$ -rheological properties of soft materials as emulsions, suspensions, gels or polymers.

For Belgium, Netherlands and Luxembourg we start with this year to offer the analytical devices from FORMULACTION and all connected services (after-sales service, lab capabilities for test and contract analyses, instruments demonstrations and educational seminars) as we successfully do for a while in other European countries.

We invite you to our seminars 2010 in Antwerpen, Copenhagen, Delft, Leoben, Ljubljana, Pecs, Munich or Zurich. We look forward to welcome you to discuss the newest developments in the field of characterisation of dispersions, powders and porous solids. Please check [www.quantachrome.eu.com](http://www.quantachrome.eu.com) and don't hesitate to contact us for further information.

All the best for you,

Yours sincerely Dr. Dietmar Klank

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**Imprint**

**Editor:**  
 QUANTACHROME  
 Office of Benelux  
 Schanspoort 21  
 NL-4791 HA Klundert  
 Phone: +31 168 370 241  
 Fax: +31 168 405 113  
[ton.goverde@quantachrome.nl](mailto:ton.goverde@quantachrome.nl)  
[www.quantachrome.eu.com](http://www.quantachrome.eu.com)

**Editorial Staff:**  
 Dr. Dietmar Klank, Ton Goverde

**Illustrations:**  
 Quantachrome, Fotolia

## Comprehensive determination of particle size, zeta potential, stability and $\mu$ -rheological parameters in concentrated dispersions

The extensive characterisation of dispersions in original concentrations is one of the most important tasks and challenges in very different branches as for pharmaceutical products, beverages and foods, cosmetics, ceramics, metallic nanoparticles and oxides or concentrated cement slurries. It is important for fields like research and development as well as quality control. The particle size distribution and the zeta potential of slurries are of key importance in slurry characterisation and in optimizing performance. In ceramics e.g. the size of the particles is closely related to inhomogeneities, which in turn relate to fracture origins as well as shape distortion/cracking during drying, pyrolysis and sintering. Moreover, the zeta potential of the slurry particulates



can be used as a tool for optimizing chemical dosage to achieve the desired colloid stability and size distribution. For such complex application there is normally a necessity for more than one analytical method as demonstrated for different milling products in figure 1. The different analytical methods of Fig. 1 can characterise not only the particle size, zeta potential or particle shape of milling products, but additionally can give information about surface and pore characteristics as pore volume and pore size distributions, different densities (TAP, raw and true densities) and water vapour uptake behaviour, measured with the new AQUADYNE DVS from QUANTACHROME.



Figure 1 Characterisation of milling products by use of different analytical methods

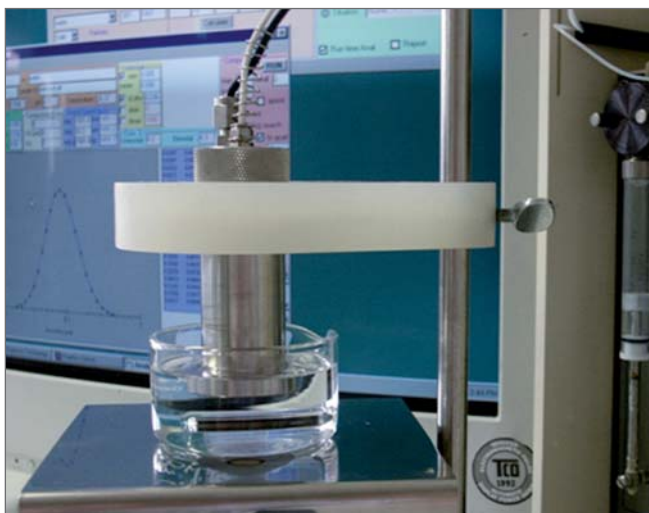


Figure 2A and 2B DT-1200 with acoustic (particle size) and electroacoustic (zeta potential) method: the zeta potential probe can be used for external experiments, like special titrations or online-monitoring (left); DT-1200 (right) with acoustic (upper block), electroacoustic (zeta probe in centre) and sensors for temperature, conductivity measurement and titration.

**Especially the combined acoustic and electroacoustic spectrometer DT-1200 ([www.dispersion.com](http://www.dispersion.com)) is a unique tool for complex characterisation of dispersions in original concentrations.** With the DT-1200 there is a combination of the acoustic spectrometer DT-100 and the electroacoustic spectrometer DT-300 available with sensors both for measuring acoustic and electroacoustic signals. The gap between the transmitting and receiving transducer of the DT-1200 is variable in steps from 0.15 mm up to 20 mm and computer controlled by means of a stepping motor. The signal level at the output transducer is measured for a set of discrete frequencies and gaps. The resulting attenuation spectra are used by the DT-software to calculate the particle size distribution over a range from 0.005 to 1000 micrometers. The acoustic sensor also measures the sound speed at one chosen frequency. A complete DT-1200 can determine the following parameters and properties:

- Particle size from 5 nm up to 1000  $\mu\text{m}$ ,
- zeta potential in aqueous and non-aqueous dispersions,
- temperature and pH-dependency of parameters as the zeta potential,
- conductivity of aqueous and non-aqueous dispersions,
- electrical permittivity of the dispersion,
- sound speed of the dispersion,
- longitudinal viscosity and bulk viscosity for Newtonian systems,
- liquid compressibility, Newtonian test, rheological properties.

The following examples represent the capability of the DT-1200 system for characterisation of original dispersions. As only one example out of the wide range of applications ceramics shows that the acoustic and electroacoustic spectrometry can be employed for research as well as for the whole manufacturing process. Typical applications are in this field

- quality control of raw materials,
- control and manipulation of grinding processes,

- optimizing stability and performance of ceramic slurries at minimum chemical cost,
- operating the process under the best conditions,
- characterising of non aqueous slurries e.g. for electrophoretic deposition processes,
- finding the optimum of flocculant dosage in ceramic waste water treatment.

Please register also the examples for nanoparticles in general, micro-emulsions, stability characterisation of dispersions and the characterisation of

- food samples (mayonnaises) by use of the new **RHEOLASER** for  $\mu$ -rheological characterisation,
- drying behaviour characterisation by use of the **HORUS**,
- stability of dispersion under original conditions by use of the unique **TURBISCAN** principle with determination and interpretation both of transmitted and backscattered light.

### 1. Nanoparticle size distributions

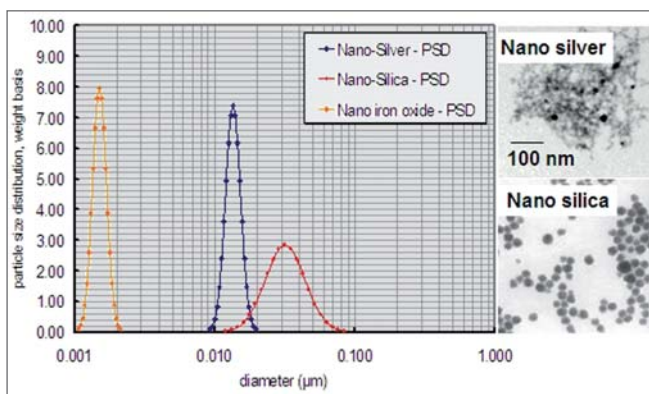


Figure 3 Aqueous iron oxide (5 wt-%) and silver suspension and aqueous silica suspension (10 wt-%), particle size measurements by use of DT-1200

## 2. Particle size of micro-emulsion

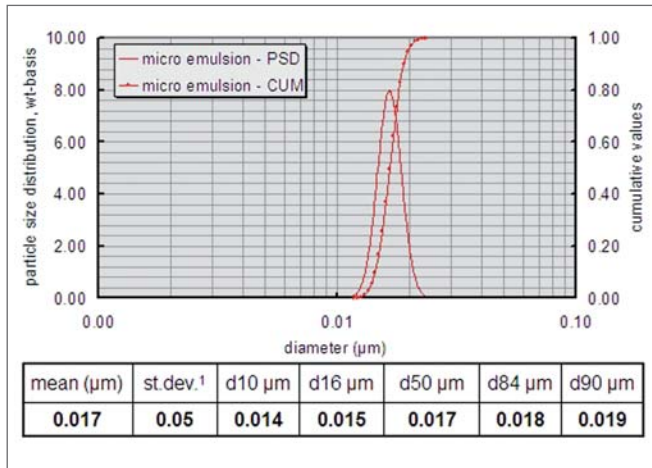


Figure 4 Complex oil phase in water (3 wt-%) with cumulative and differential oil drop size distribution (mean diameter 17 nm), measured with DT-1200

## 3. Influence of the milling time on the particle size distribution

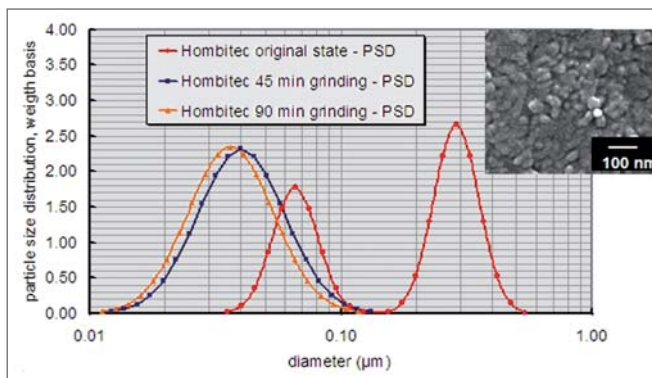


Figure 5 Aqueous  $TiO_2$  (Hombitec) suspension, 35 wt-%, online-measurements with DT-1200 show significant shift of the particle size to smaller particles and change from bimodal to monomodal distribution with additional small influence of milling time between 45 and 90 minutes.

## 4. Titration experiment, zeta potential in dependence of the pH

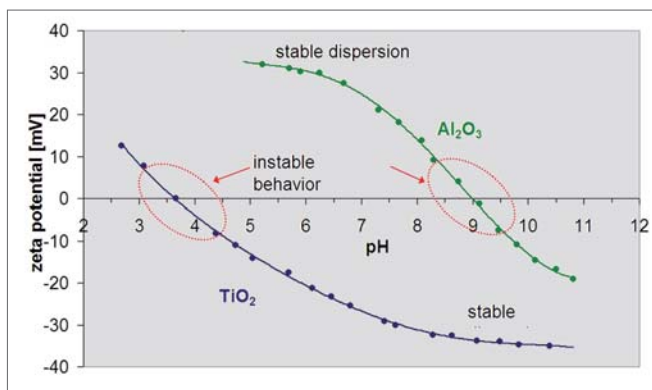


Figure 6 Aqueous  $Al_2O_3$ - und  $TiO_2$ -suspensions (submicron powders), determination of the isoelectric point (IEP) for setting of the optimal pH concerning stability or viscosity, measured with DT-1200 by use of automated titration option.

## 5. Zeta potential measurement to find optimum dosage of flocculants

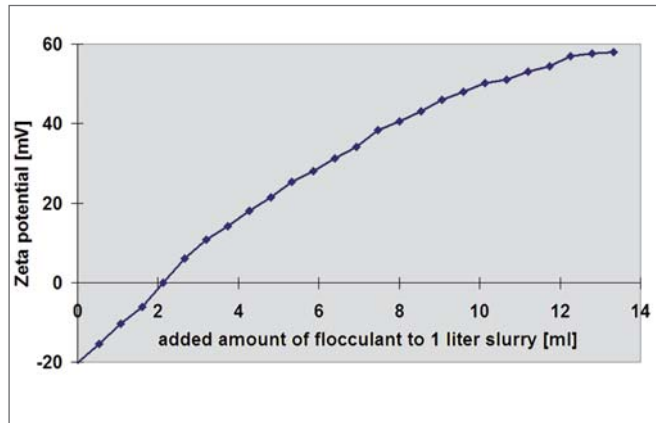


Figure 7 It can be appreciated to work with unstable slurries near the isoelectric point as it is in the case of filtration or flocculation. In many plants it becomes more and more important to recycle the process water. Waste water treatment is usually performed by flocculation. If recycling the process water the optimum dosage of flocculants is crucial. If the amount of flocculant is too low particles will remain in the water. On the other hand leads overdosing to remaining flocculant in the process water which has a devastating effect during the production process. Optimum dosage of flocculant is given by the isoelectric point and can therefore be measured by zeta potential; measured with DT-300 zeta potential probe.

## 6. Complex zeta potential titration to study sample history

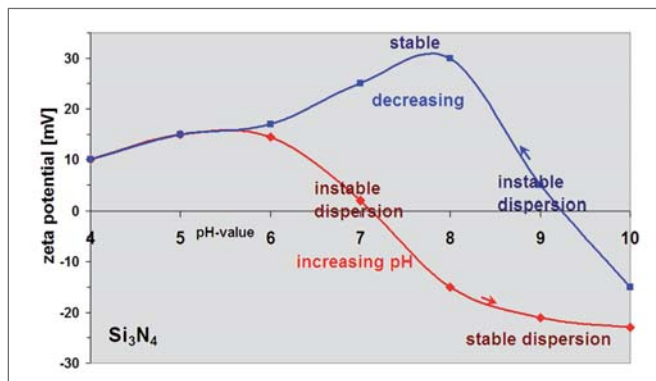


Figure 8 Slurry stability depends not only on chemical state but how one reaches this state. Laboratory titration of production silicon nitride slurry to low pH indicates high zeta potential and good stability at  $pH=7-8$ . However, process engineers found that this pH did not provide good operating performance. Actual process included an acid wash of slurry. Subsequent back-titration to alkaline conditions shows dramatic shift in isoelectric point that required shift in plant operating conditions. The explanation for this shift in isoelectric point is that the initial slurry had a very small level of contamination, which was insignificant in terms of the overall zeta potential and stability of the system. However, under acid conditions this minor component dissolved. Upon subsequent change to more alkaline conditions, this dissolved material then re-precipitated on the surface of the bulk of the silicon nitride surface. This minor component, although present in seemingly insignificant quantity, nevertheless finally dominated the surface chemistry of the silicon nitride material. By realizing that the final state is dependent on the history of the sample the process could be modified to accommodate this change; measured with DT-1200.

## 7. Characterisation of high concentrated cement dispersions

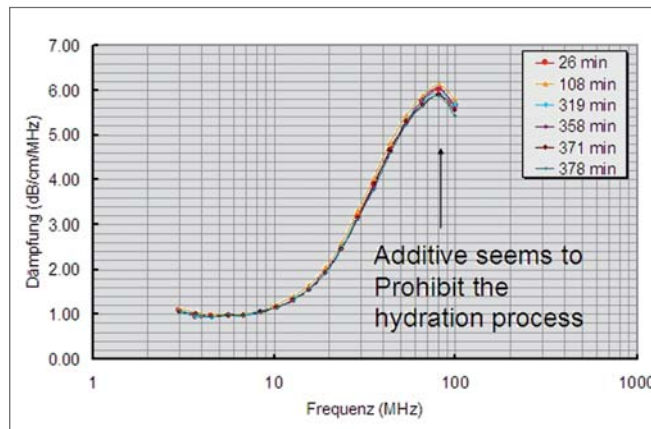
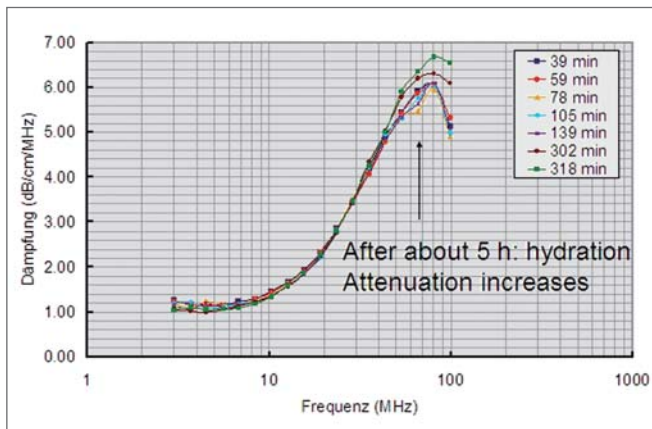


Figure 9a and 9b Measurement of the acoustic attenuation spectra of cements vs. time by use of DT-1200, Fig. 9a shows the time-dependent spectra of 20 wt-% cement dispersion (CEM I 42.5 R). It is clearly to see that after about 5 hours there starts a hydration process and causes step by step higher attenuation at high frequencies (Note: such experiment shows the importance to use a DT-1200, which offers a frequency range up to 100 MHz and flexible distance between transducer and receiver!). Fig. 9b shows the time-dependent spectra of 20 wt-% cement dispersion (CEM I 42.5 R) + 1 wt-% FM 2453, that means with additional additive. The additive prohibits the hydration process significantly.

### Comprehensive characterisation of dispersions

- HORUS:** Drying behaviour of dispersions
- CILAS:** Particle size and particle shape analysis
- DT-1200:** Particle size >5 nm, zeta potential, rheological and other parameters in original concentration
- RHEOLASER:** Micro-rheological parameters of dispersions
- TURBISCAN:** Stability of dispersions under original conditions

Figure 10 Comprehensive characterisations of dispersions by use of complementary analytical methods

The comprehensive characterisation is possible by use of different complementary analysis methods as is shown in Figure 10. The LabSPA (Laboratory for Scientific Particle Analysis) has these analytical methods available for testing your application in various fields of materials: Foods, pharmaceuticals and cosmetics, pigments and colours, ceramics and cement, synthesized nanoparticles and other materials. The analytical methods of the next application examples are developed by FORMULACTION:

- The **patented TURBISCAN-principle** to study the stability or instable processes in original dispersions under original storage conditions. Only the TURBISCAN measures both the transmitted and the backscattered laser light of a dispersion dependent on the height of the sample cell - and without any additional force which can change the complex structure of your emulsion or suspension, so that the TURBISCAN prevents the risk that the measurement will not characterise the nature of your original sample. With the TURBISCAN-principle there is a way to characterise opaque samples by interpretation of backscattered light intensities to not only detect sedimentation or creaming effects, but also coalescence of particles and droplets as a function of time.
- The **HORUS** instrument is a film formation analyser using an optical technology based on Diffusing-Wave Spectroscopy (DWS) to study the drying behaviour of thin films. When a laser illuminates a sample, the light diffuses into the sample, and encounters objects (particles...etc) that backscatter light as interfering waves. By using a video-camera as a detector, an interference image called 'Speckle' is displayed. If the sample is fluid and if scatterers in the sample are moving particles (ex: Brownian), the motion induces light intensity fluctuations of the speckle spots, and an overall deformation of the speckle pattern. In the case of a film forming sample, as the film progressively forms, the motion of the scatterers slows down, due to an increase in the film viscosity. As a consequence, the deformation speed of the speckle pattern decreases as the sample dries. Objective drying times as well as information on film formation mechanism can be extracted from the kinetics displayed in real time by specific software.



- The **RHEOLASER Lab** is a new analyser for  $\mu$ -rheological characterisation of soft materials, like emulsions, gels and polymers. DWS (Dynamic Light Scattering) is the basis of the RHEOLASER and is extended to opaque and concentrated media for determination of  $\mu$ -rheological parameters. MS-DWS consists in sending a coherent laser light beam into a sample. The light is multi-scattered by the particles, which leads to interfering backscattered waves. An interference image called "Speckle image" is detected by a multi-pixel detector.

In a soft material, the thermal energy leads to the motion of micron sized particles. This Brownian motion induces a deformation of the speckle image. The multi-pixel detector measures the speckle pattern deformation to quantify. No macroscopic deformation is applied to the sample. Instead, state-of-the-art optical techniques are used to measure the nanometer-scale motion of the sample constituents due to thermal energy. Rheological properties are deduced from this motion using a well-established formalism. Advantages of MS-DWS based  $\mu$ -Rheology include:

- measurements in the linear regime,
- no wall slip issues,
- samples contained in standard vials,
- no need to transfer the sample or to clean the rheometer tools,
- fast measurements that allow the sample evolution to be monitored.

### 8. Characterisation of stability of shaving foam

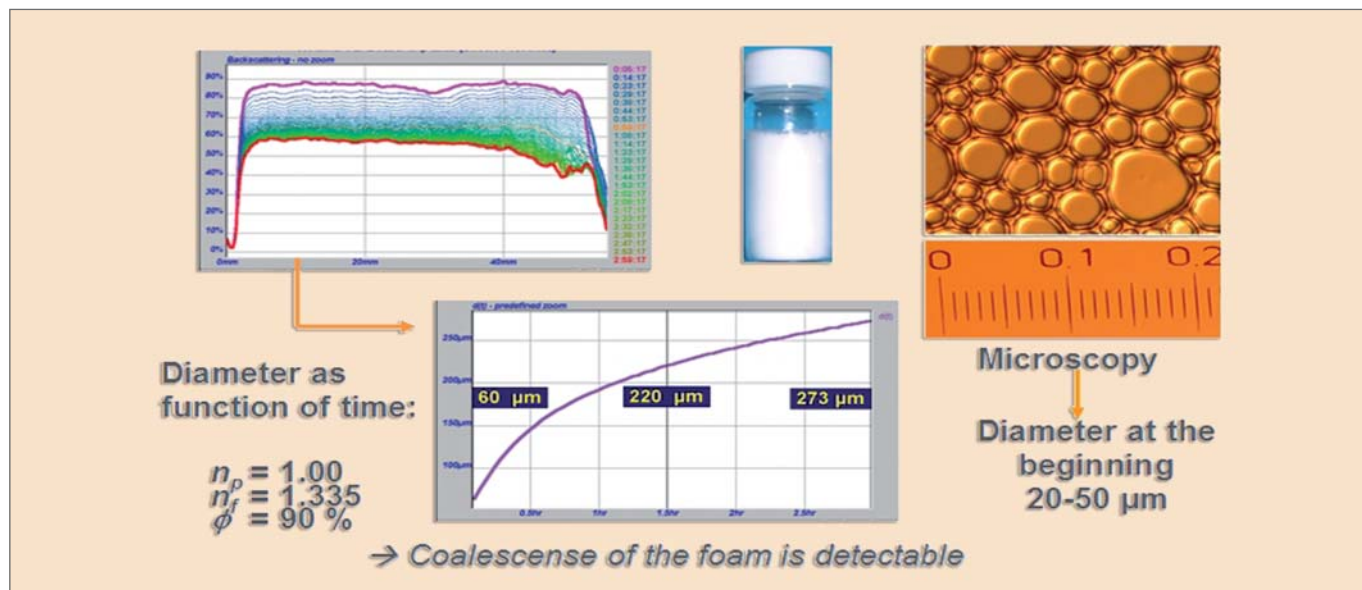


Figure 11 Characterisation of stability of shaving foam: The time-dependent measurements of the backscattered light signals show changes of the intensity over the full length of the measuring cell, this is caused by coalescence of the foam bubbles. The coalescence kinetics can be calculated and agrees very well with results from optical microscopy.

The TURBISCAN-principle is standard for many industries to characterise the stability or the instability behaviour of liquid dispersions. Liquid dispersions can be liquid/liquid (Emulsion), liquid/solid (Suspension) or liquid/gas (Foam) systems. Application notes about stability measurements of various liquid dispersions are available, e.g. do not hesitate to use [www.formulaction.com](http://www.formulaction.com) to get publications direct from the developer and producer of the TURBISCAN. Figure 11 shows the characterisation of foam by use of backscattered light signals to characterise not only the instability of the foam but additionally of the kinetics of this instability.

### 9. Characterisation of drying behaviour of thin films

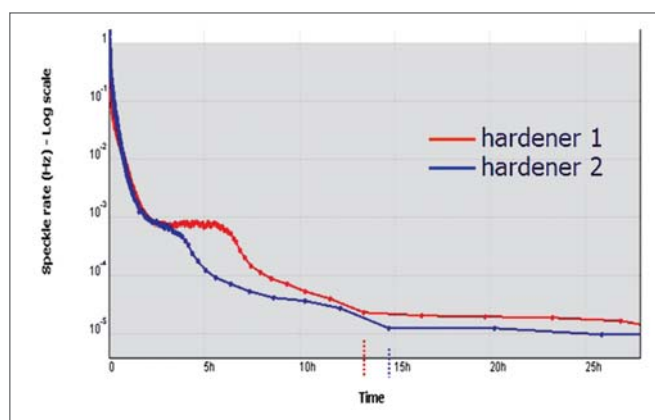


Figure 12 Characterisation of drying behaviour of paints by the HORUS: Parallel detection of the time-dependencies of the drying process of two paint samples over one day. It is clearly to see that hardener 2 reduces the drying time significantly in comparison to hardener 1.

### 10. Determination of μ-rheological parameters

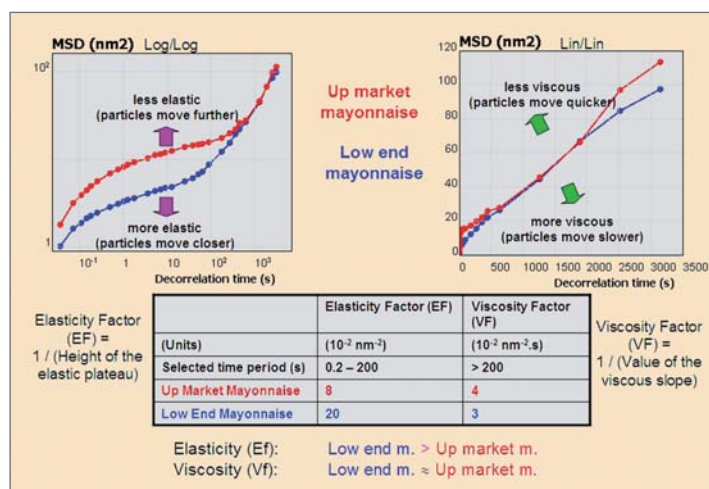


Figure 13 Characterisation of two mayonnaises by use of RHEOLASER Lab, the results show differences in rheological properties: whereas the viscosity factor is similar for both samples, the elasticity factor is significantly different.

### Summary

In summary, acoustic and electroacoustic spectroscopy with the DT-1200 analyser offer a unique tool to characterise concentrated dispersions, e.g. concentrated slurries and emulsions. In combination with additional techniques like the new RHEOLASER, the HORUS and the TURBISCAN from FORMULACTION these methods provide not only a means for characterising the final aggregative state of different sample types, but more significantly gives us tools to understand, optimize, and control this state. These techniques will clearly become more and more important as users understand the benefits of supplementing data on diluted samples with measurements of the final concentrated product.



# Particle Size and Shape Analysis for Drilling in Petroleum Industry

N. Marchet, CILAS, nicolas.marchet@cilas.com



## Introduction

In order to drill a successful oil well, most drilling operators will use a good drilling fluid or mud. Mud cools and lubricates the drilling tool, helps to attack the rock by injection under pressure, and cleans out the hole, carrying away the pieces of crushed rock [1]. These mud systems are usually WBM (Water-Based Mud), OBM (Oil-Based Mud) or SOBMs (Synthetic Oil-Based Mud). One of the major problems with these systems, particularly when reused on different wells, is the build-up of very fine micron solids (less than 5 microns) known as Low Gravity Solids (LGS). The generation of LGS in the mud creates, slower penetration rates, high pump pressures and increased solids surface area or plastic viscosity. The main risk is the mud becomes stuck and to lose the hole drilled. Particle shape determination permits also to quantify the shape anisotropy of particles or to provide information relating to surface area regularity. In this article we show the importance of morphological analysis and show the benefits of combining laser diffraction size measurements with simultaneous shape analysis using the same sample.

## The use of Particle Size Analysis (PSA) for drilling in the petroleum industry

Particle Size Analysis (PSA) based on laser diffraction is an easy-to-use technique to measure liquids and dry products. All mud systems with their different carry liquids can be

tested, from WBM and OBM to SOBMs. In the figure 1, we can observe that the particle size distribution decreases during drilling process from 35  $\mu\text{m}$  to 2.6  $\mu\text{m}$ . This analysis makes it possible to detect the presence of 5- $\mu\text{m}$  particles in drilling fluids in order to avoid the cementing process in the well.

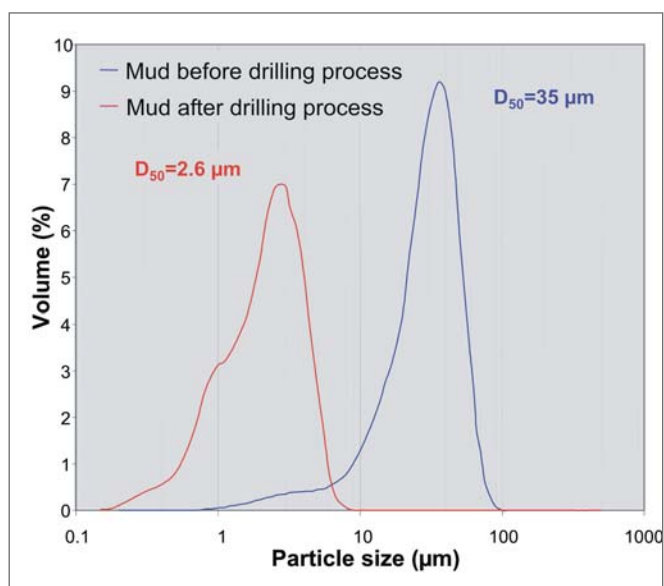


Figure 1 Particle size distributions of drilling fluids

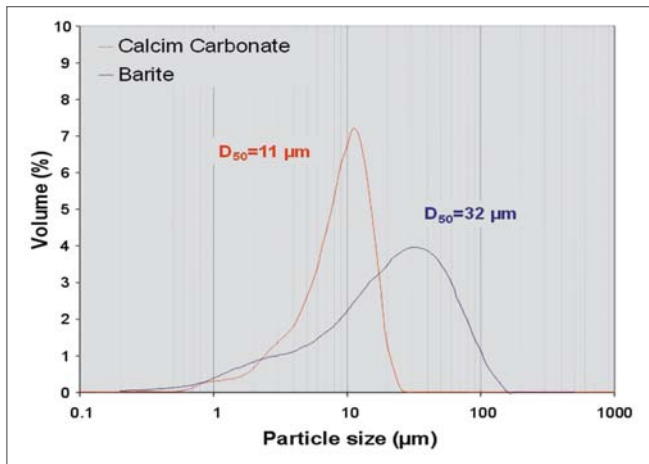


Figure 2 Size distributions of materials used in drilling fluids

Along with drilling mud, the particle size measurement of LCM (Lost Circulation Material), such as calcium carbonate ( $\text{CaCO}_3$ ) and barite ( $\text{BaSO}_4$ ) (figure 2), is significant. The latter are used as a weighting material to increase the apparent density of the mud and can be measured with adapted dispersion protocols.

By adjusting the viscosity of the carrying liquid, the stabilisation of weighting materials makes it possible to take the particle size measurement without sedimentation. Dispersing agents are usually added to provide steric stabilization. This mechanism is usually based on adsorption of polymers onto particle surfaces to reduce the van-der-Waals attractive forces. It is also possible to measure the particle size distribution in dry mode by selecting the air pressure to disperse agglomerates. The deagglomeration is obtained by airflow turbulence combined with particle-particle and particle-wall collisions. The resulting two phases flow is then directed to the laser path through a succession of venturi sections and a special nozzle.

### The influence of shape factor in drilling efficiency

In addition to particle size distribution, shape parameters provide much information on the drilling fluid's properties. In the figure 3 a), we have reported the influence of particle's morphology on the two main shape parameters. The aspect ratio defined as the ratio of Feret diameters corresponding to the length represented in figure 3 b) and the circularity ratio, proportional to the ratio of the area of the particle to its perimeter squared.

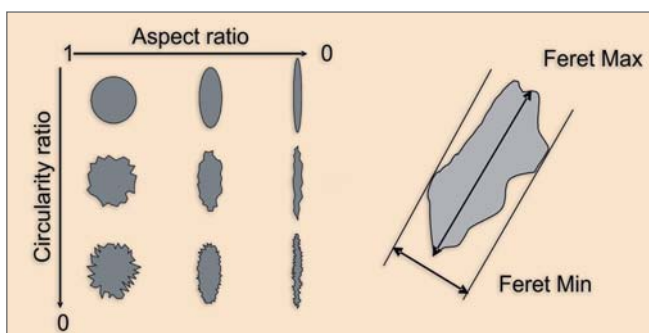


Figure 3 a) some shape parameters and b) the definition of Feret diameters

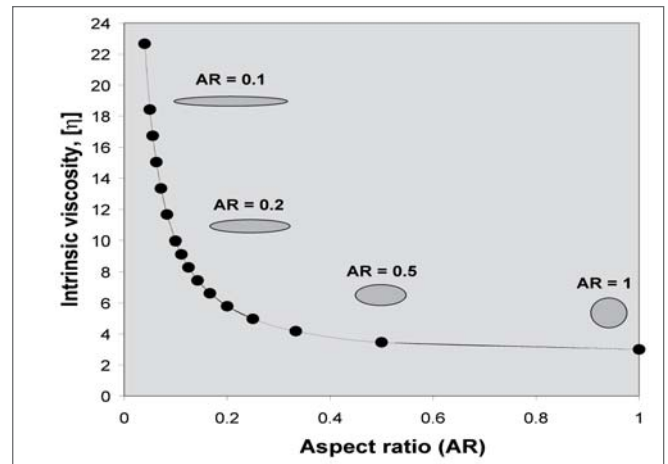


Figure 4 Variation of intrinsic viscosity as a function of the aspect ratio

The morphology of particles plays a role in the thixotropic behaviour of drilling fluids. Thixotropy is the property of some fluids to show a time-dependent change in viscosity. For example, the intrinsic viscosity  $[\eta]$  of particles with the same volume is directly related to their aspect ratio (figure 4) [1–2]. Furthermore, the rheological properties of some materials used in petroleum industry are of great importance in structural and geotechnical engineering.

The flow rate of particle suspensions may be of importance in transfer steps. The importance of particle morphology may be demonstrated, for example, by the intrinsic viscosity value for the solution, since this has an effect on the thixotropic behaviour of viscous solutions. Figure 4 shows the change in this variable as a function of the aspect ratio for particles at constant volume and concentration. This graph therefore shows a rapid increase in intrinsic viscosity when particles exhibit a high degree of shape anisotropy. This property may have important consequences when transferring solutions [2–4] or during the use of drilling mud in the oil industry.

### Technical benefits of combined particle size and shape analysis

Shape analysis coupled with laser diffraction provides quantitative information not only gives a more precise characterisation of the sample dispersion but also provides information on the presence of impurities or of synthesis by-products or to identify the differences in morphology as a function of their size.

The state of dispersion of particles is a step which has a direct effect on laser diffraction size measurements. The use of an appropriate dispersion protocol may involve optimising the conditions, the power and duration of ultrasound or the addition of chemical dispersants.

Figure 5 shows an improvement in the state of dispersion due to optimisation of the period of ultrasound treatment. The modification of the state of dispersion can also be seen through the change in the particle size distribution.

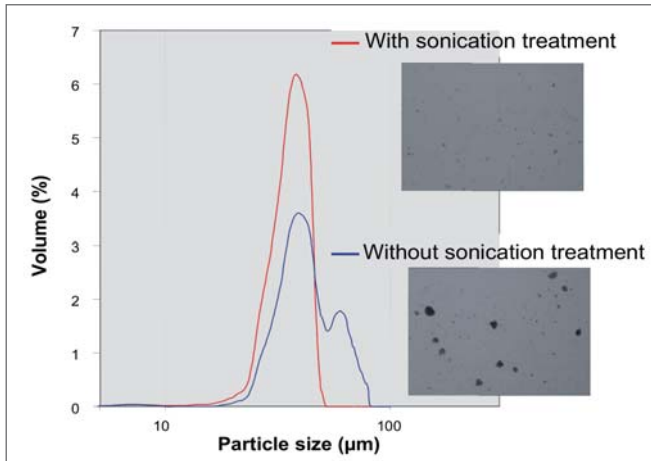


Figure 5 Effect of ultrasound treatment on the dispersion of oxide particles, particle size distribution and observations using optical microscopy

A second benefit lies in the quantification of the state of agglomeration, for example through the circularity or degree of sphericity of particles or of agglomerates of particles. The photographs in figure 6 show that the production sequence for the glass beads has either produced particles with a high degree of shape anisotropy (a), adhering particles of very variable sizes (b), or that contaminants have been introduced into the production batch (c). In this last case, the difference in morphology and the transparency of the material provide information about its chemistry.

This specific design makes it possible to perform a shape analysis with the same sample analysed by laser diffraction and to compare these two techniques. Laser diffraction measurement of particle sizes can be carried out both via a dry process and via a wet process. After optimisation of the sample dispersion conditions, the results obtained can be correlated with those obtained by optical microscopy (figure 7). For the three modes of measurement, the particle size distributions are similar and median diameters of 50 µm are obtained.

## Conclusions

The measurement of particle size is a key point for drilling fluid formulation, which itself plays an important role in the efficiency of drilling wells. CILAS Particle Size Analysers are

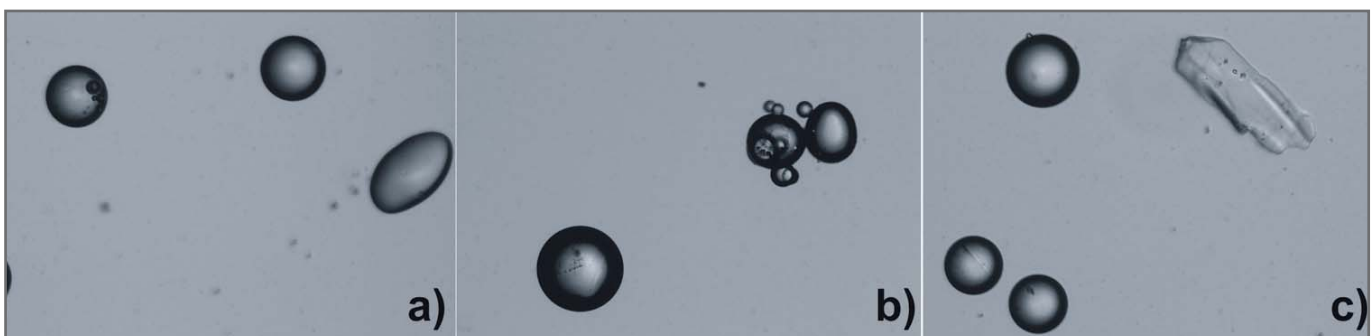


Figure 6 Examples of pictures indicating, a) shape anisotropy, b) agglomerated by-product and c) presence of impurities (Magnification x10)

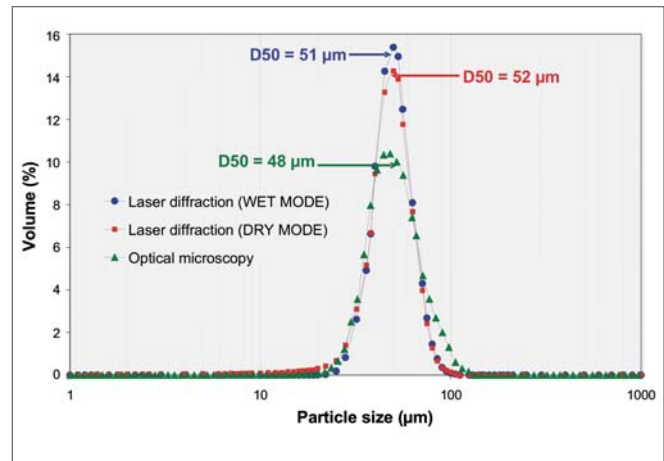


Figure 7 Correlation between particle size distributions obtained by laser diffraction using a dry process, using a wet (liquid) process, and by optical microscopy

easy to use, fast, accurate and very reliable with liquid and dry formulations. With their robust design, they enable testing and analysis to be performed in the field without being affected by dust or vibration, and provide reliable analysis even under adverse industrial conditions for routine analysis. From this information, the condition of the drilling fluid can be quickly and accurately assessed. Shape analysis makes it possible to control the particle morphology to complete knowledge of the material's properties. Decisions can be made based on this accurate data to correct the problem in the most efficient way before a serious incident occurs. By employing robust analytical methodologies, formulators can use this tool to generate reproducible particle size data rapidly, which in turn facilitates the development of formulations suitable for drilling in diverse geologies.

## References

- [1] Alteration of permeability by drilling fluid invasion and flow reversal *Journal of Petroleum Science and Engineering*, Volume 58, Number 1–2, p. 227–244, (2007)
- [2] Rheology modification in mixed shape colloidal dispersions. Part I: Pure components, *Soft Matter*, Volume 3, p. 1145–1162, (2007)
- [3] Rheology modification in mixed shape colloidal dispersions. Part II: Mixtures, *Soft Matter*, Volume 4, p. 337–348, (2008)
- [4] Intrinsic viscosity and the polarizability of particles having a wide range of shapes *Advances in Chemical Physics*, Volume XCI, (1995)

## **Aquadyne DVS - the new dual balance arrangement DVS Water Sorption Analyser**

**W**ater sorption behaviour plays an important role in the development and use of many common and advanced materials. Some examples include:

- stability of pharmaceutical excipients and drug actives,
- drying and storage of grains,
- texture and shelf life of food products,
- PEM fuel cell components,
- mortar, grout and other cementitious materials,
- paper and coatings,
- hydrophobic surface treatments,
- microporous and nanostructured carbons.

The Aquadyne DVS is a fully automated, gravimetric, dual sample water vapour sorption analyser. It measures adsorption and desorption isotherms of water vapour both accurately and sensitively, including sorption kinetics, with minimal operator involvement. The weight(s) of one or two sample(s) is/ are constantly monitored and recorded as the relative humidity is automatically varied by the blending of dry carrier gas with a saturated gas stream. The Aquadyne DVS unit has two micro-balances. The heads are housed in a chamber whose temperature is controlled separately from that of the weighing chamber. Dry gas can be flowed into the balance chamber to prevent moist air from the weighing chamber entering the balance head. The dual balance design allows increased analysis throughput, side-by-side comparison with known or reference materials, or an extended mass range for a single sample. The independently temperature-controlled balance head environment ensures long term stability. The small sample chamber ensures rapid changes in sample atmosphere conditions when the relative humidity is altered during an analysis. Samples can be pre-dried in situ at up to 80°C in a flow of dry gas.



Figure 2 Aquadyne DVS from QUANTACHROME

### **Application areas and types of studies**

The Aquadyne DVS may be used in research and development, manufacture, quality control, storage and packaging of products, the study of natural and manmade materials. The information gained about samples include

- polarity of surfaces,
- surface area accessible to water molecules,
- surface porosity,
- crystallinity,
- solubility,
- reactivity with water.



Figure 1 Applications for use of the new dual sample water vapour sorption analyser Aquadyne DVS

Isotherms monitor the equilibrium water uptake and release of samples at different relative humidities. Kinetic studies record mass changes of the samples with time, in response to step changes in the relative humidity and/or temperature. Temperature experiments study moisture uptake or release by samples in response to changes in the temperature with or without simultaneous changes in the RH. There are different types of studies possible with the Aquadyne DVS:

- water sorption isotherms of samples,
- kinetics of water uptake and release,
- hydration of materials,
- temperature-dependence of water sorption,
- irreversible changes mediated by adsorbed water,
- porosity of sample surfaces,
- effect of mixing compounds,
- effect of compacting powders,
- quality assurance testing for material conformity.

### Summary

The unique dual balance system of the Aquadyne DVS is the right choice to increase the sample throughput for accurate water vapour adsorption and desorption isotherms. The Aquadyne DVS is a new developed water vapour sorption analyser for a broad range of applications, e.g.

- Deliquescence: certain salts exhibit the property of dissolving in self-adsorbed water.
- Equilibrium moisture content: quantitatively the amount of water associated (adsorbed/absorbed) with the material under given atmospheric conditions of temperature and relative humidity. (Organic materials may be subject to moulding according to atmospheric humidity, for example).
- Hysteresis working range: adsorption and desorption usually differ by hysteresis - this gives a range of stability in which subsequent sorption cycles produce no change in equilibrium moisture content.
- Hydrophobicity/Hydrophilicity: the shape of the isotherm reveals relative strength of affinity between water and the surface, due to polar or other chemical interactions.
- Micropore investigations: even hydrophobic materials can take up moisture if their pores are small enough.
- Crystallization phenomena: certain amorphous materials will undergo crystallization as a function of water sorption due to, for example, shifts in glass transition points.
- Sample form: sorption kinetics can be altered by the physical form of a material - powder, granule, pellet, tablet, monolith etc.

Do not hesitate to contact us for further information, for test measurements and also for paid analyses in our LabSPA (Laboratory for Scientific Particle Analysis) in case you have only very limited number of samples to test.

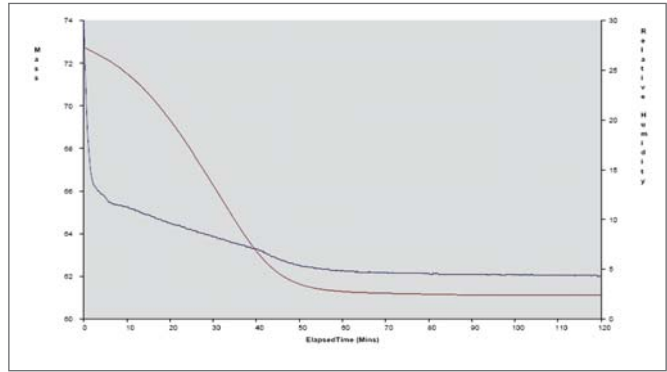


Figure 3 Drying behaviour of an active carbon, the upper curve left shows the mass lost of the sample [mg] especially during first 50 minutes; the lower curve shows the humidity [%] in the sample chamber during the drying process.

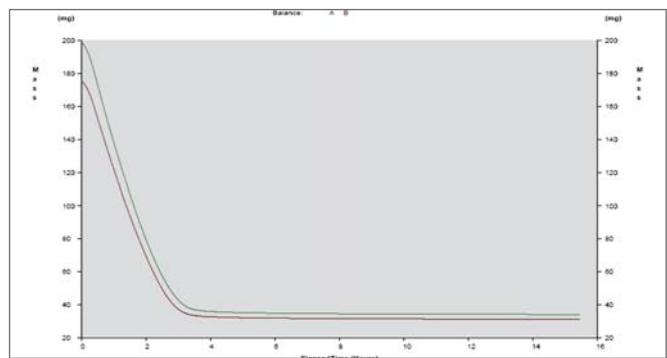


Figure 4 Drying behaviour of two pieces of apple at 50°C, both curves show a similar drying process and about 80 weight-% losses after 4 hours.

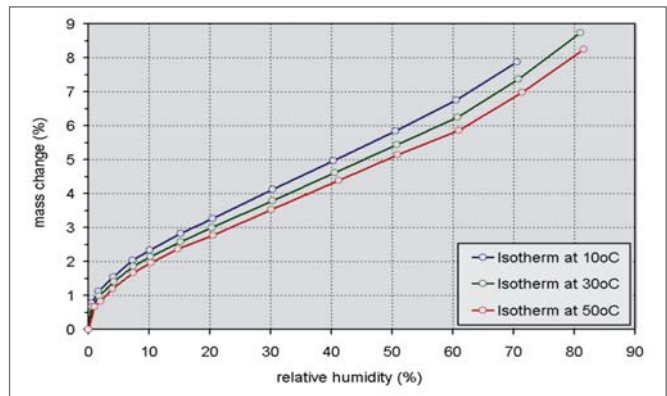


Figure 5 Water sorption isotherms of a powder at three different temperatures: Such analyses at different temperatures can be defined as one experiment, so that it is started one time only to get all three isotherms

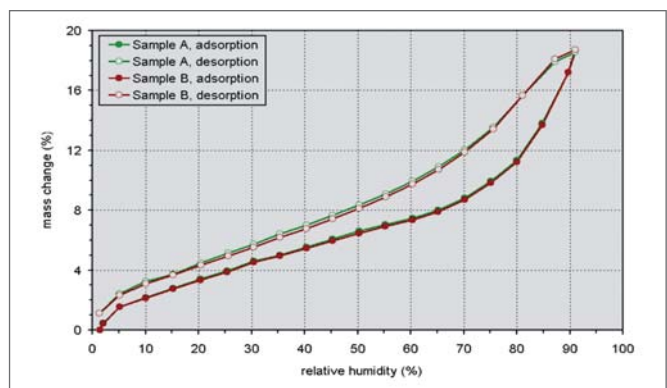


Figure 6 Reproducibility tests of two powdered samples of one batch, the dual balance configuration of the Aquadyne DVS increase the sample throughput and allows the comparison of two samples with one experiment only.

## Criteria for the selection of analysers for characterisation of surfaces and pores

Since the development of different categories of analysers for the same analysis method interested parties are confronted with the need to decide which system to be the most suitable regarding tasks and budget. To give you assistance in making the decision please find in the following an overview of features of the equipment for surface and pore analysis, of physisorption and chemisorption testing as well as for variable sample capacities within the scope of gas and vapour sorption. Chemisorption, vapour sorption and mercury porosimetry will be treated at the end of this survey; within the first paragraphs criteria for surface (BET-surface area) and pore analysis by gas adsorption are outlined.

The pore size range of the gas adsorption method reaches from 0.35 – 400 nm. Larger pores can be analysed by mercury porosimetry. QUANTACHROME offers with the POREMASTER also in this field state-of-the-art equipment, so that one can characterise pores from 0.35 nm up to 950 µm by use of gas adsorption and mercury porosimetry in combination. With the POREMASTER it is also possible to determine the skeletal as well as the bulk density.

Which equipment category makes sense for which conditions, in which aspects are the differences to find for the AUTOSORB, the QUADRASORB SI, the NOVAe-series and the MONOSORB? In the following we will try to give an answer without claiming to clear with it all kinds of possible questions. We are ready for discussions and to provide you with further information any time but perhaps this summary points out for you the essential differences in features.

The following order of analysers equates to an increasing grade of components, additional possibilities and reaches therefore from the lower to the higher price range. Most analysers of a higher price category offer all analysis possibilities of those with a lower price; an exception hereof can be the number of sample stations.

### MONOSORB

The decision for or against the **MONOSORB** is an easy one: Do you exclusively want to determine the BET surface area according to the single point BET-method? Will you stay with this method also in future and don't you plan, e.g. for budget reasons or the high speed of the one point method, to acquire equipment with further possibilities? In this case the MONOSORB is the adequate analyser: **precise BET-surfaces according to the single point-BET-method**, most efficient and timesaving measurement, especially for production controls, as well as simple handling of this approved technique are convincing reasons to decide for the MONOSORB.

All other gas adsorption analyser categories (AUTOSORB, QUADRASORB SI and NOVA) allow the simple practice of the multipoint method for the determination of the BET surface area as well as of the pore volume and pore size distribution from adsorption and desorption measurements. Which are the most significant distinctions between them?



### NOVAe-series

For BET-measurements and for pore analysis the NOVA is available as 1-, 2-, 3- and 4- sample stations equipment and is used in research and development as well as in quality control. It is characterised by a very good price-performance-ratio and guarantees with the multipoint configuration a sufficient quantity of measurements for many applications.

There are naturally certain limitations of the NOVA compared with the more expensive QUADRASORB SI and AUTOSORB. During the measurement all samples are in one dewar for the adjustment of temperature. Therefore the sample stations can't be refilled and a new measurement can't be started, before the analyses at all sample stations are finished. Parallel measurements with the QUADRASORB SI and the AUTOSORB-6B are



faster also because of their pressure sensor configuration. For these reasons it can be advantageous for an extensive quality control with a high quantity of measurements to decide for the QUADRASORB SI or the AUTOSORB-6B.

A further criterion against the NOVA can be the necessity of a turbo molecular pump and additional pressure transducers. These configurations are needed for high-resolution micropore measurements of different solids and for the determination of very small BET surfaces by means of krypton adsorption at 77 K. In these cases the QUADRASORB SI-MP or the AUTOSORB-1-MP are first choice.

QUANTACHROME offers also for the NOVAe-series solutions for many tasks. Therefore the hardware disadvantage, which is connected with a price advantage, of the NOVA compared with the AUTOSORB-1-MP is no problem, if

- you don't need high-resolution micropore distributions,
- your sample throughput is so large that there remains no time for long micropore analysis and you need timesaving alternatives,
- the determination of the micropore volume (instead of the micropore distribution) is sufficient,
- your needs are satisfied with the NOVA potential to determine average micropore diameters or its alternatives, e.g. CO<sub>2</sub> adsorption at 273 K with state-of-the-art evaluation of micropore-distributions.

### QUADRASORB SI-series

This analyser series consists of the **QUADRASORB SI** and the **QUADRASORB SI-MP**. Both analysers have 4 sample stations with a pressure sensor for each of them, 4 separate stations for continuous determination of the saturation vapour pressure  $P_0$  as well as 4 dewars to enable individual measurements and independent re-start of each sample station. With these options the QUADRASORB SI realizes a significant higher throughput of samples than the NOVA.

The **QUADRASORB SI-MP** is fitted with a turbo molecular pump and an additional 10 Torr pressure transducer. With this configuration the determination of smaller BET surfaces by krypton adsorption is possible. Furthermore can the measurement range for certain micropore examinations be extended to low pressure range although – to remark it already here – the low pressure option of the QUADRASORB SI can't be completely compared with this of the AUTOSORB-1-MP as the latter one is equipped with a 1 Torr pressure transducer for high resolution low pressure measurements.

### AUTOSORB-series

The AUTOSORB is available as 1-station and 6-stations analyser (**AUTOSORB-1 und -6B**) as well as basic- and micropore instrument with turbo molecular pump and additional pressure transducers (**AUTOSORB-1-MP, -6B-MP**). The **AUTOSORB-1-C** is an AUTOSORB-1-MP with supplementary chemisorption option to characterise active surfaces of catalysts.

There are at least 4 settings of tasks that make the decision for an analyser out of the AUTOSORB series recommendable:



### Highest sample throughput of AUTOSORB-6B:

With the AUTOSORB-6B the maximum throughput of samples is possible. Six independent sample stations guarantee continuous re-start at free sample stations. So very often this measurement system is used when an extensive amount of samples has to be processed. But just as well the AUTOSORB is employed for special applications, e.g. the measurement of large sample specimen.

### High-resolution micropore characterisation with the AUTOSORB-1-MP:

The characterisation of micropores (pore diameter < 2 nanometres) often needs a long-term stable method of measurement with turbo molecular pump vacuum and adequate configuration at the pressure transducers. The AUTOSORB-1-MP meets these requirements, e.g. by enabling long-term measurements



because of special dewars, by creating an oil-free vacuum and as a 1 Torr pressure transducer measures the adsorption equilibrium directly at the sample cell in the low pressure range. By separation of the other dosing system (manifold) from the sample cell during the adsorption equilibrium the leakage rate of the system is minimized as well is the sensitivity of the measurement maximized because of the reduced free space volume (dead volume). Basic decisions for or against the AUTOSORB MP can result from the following questions:

- Do your samples not have micropores or are you not interested in long-term measurements (20 – 60 hours) for the determination of micropore size distribution then you will tend in your decision towards the NOVA or the QUADRASORB SI.
- You will be interested in the AUTOSORB-1-MP if you want to determine the micropore size distribution or to make other high-resolution measurements.
- If you (also) have samples with very small BET-surfaces for which nitrogen cannot be used you can analyse them by krypton adsorption with the AUTOSORB MP or the QUADRASORB SI-MP.
- A decision for the AUTOSORB-1 (basic version) without krypton-, micropore- or chemisorption versions is in general only made, if for budget reasons the mentioned options are planned to be upgraded at a later date.

### *Chemisorption and temperature programmed reactions as TPD, TPR or TPO:*

For such applications, mostly for catalyst characterisation, the AUTOSORB-1-C and the CHEMBET analysers are suitable analysers. If a combination of physisorption (BET and pore analysis) and chemisorption is required in one instrument, please ask for further information regarding the AUTOSORB-1-C with according options as **TCD for temperature programmed reactions** or an **additional port for the connection with a mass spectrometer**. If your sample throughput is limited because of high-resolution micropore-measurements we recommend as separate analyser for such task our CHEMBET-series: the CHEMBET Pulsar TPR/TPD and the CHEMBET TPR/TPD: The CHEMBET Pulsar TPR/TPD runs the pulse titration for the determination of active surfaces, the change between the necessary gases for the sample preparation and the measurement fully automatic. The illustration shows a CHEMBET Pulsar TPR/TPD connected to a mass spectrometer for the analysis of the temperature programmed reactions and their reaction products.



### *Vapour adsorption:*

For vapour sorption measurements it is possible to fit the **AUTOSORB-1-MP with a vapour option**, so that the adsorption of volatile liquid vapours can be determined. The distinguishing feature of the vapour option compared with usual analysers is that the whole manifold is heated to 50°C to prevent condensation. If a combination of gas sorption (BET and pore analysis) and vapour sorption is required in one equipment please ask for further information on the AUTOSORB-1-MP with vapour option.

### *Dynamic Vapour Sorption by use of gravimetric method:*

#### **AQUADYNE DVS: the new dual balance arrangement DVS Water Sorption Analyser**

If you are interested in a separate analyser to determine the water adsorption and desorption by gravimetric Dynamic Vapour Sorption (DVS) you should request more information to the **AQUADYNE DVS**.



### **POREMASTER-series**

In contrast to the above mentioned analysers the **POREMASTER** is a **high pressure mercury porosimeter**. The **POREMASTER-series** complete the coverage of the range of measurement in allowing the determination of large pores until almost 1 mm.

If measurement tasks are completely solvable by gas adsorption this method is sufficient as a rule. If the pore analysis in the micrometer range is important for the characterisation of porous samples, e.g. of building materials, compact ceramics or pharmaceutical tablets, so is the mercury porosimetry or are both methods (mercury porosimetry and gas adsorption) in combination to apply.

The four POREMASTER-models differ from each other in the pore size range (3 nm – 950 µm respectively 6 nm – 950 µm pore diameter) and in the sample throughput, as in the GT-models two samples can be measured parallel in the high pressure station.

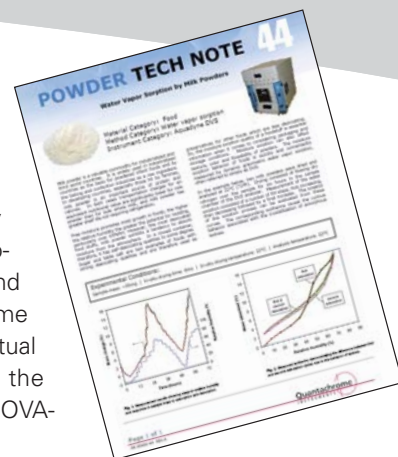




## POWDER TECH NOTES from QUANTACHROME

You can order the following Powder Tech Notes from QUANTACHROME in sending an email to [ton.goverde@quantachrome.nl](mailto:ton.goverde@quantachrome.nl) or [info@quantachrome.de](mailto:info@quantachrome.de) and we will provide it free of charge. Please be informed especially about the latest innovations as the **Dynamic Vapour Sorption (DVS) analyser Aquadyne DVS** (Note 44 and 45), the new way for gas adsorption measurements in temperature range from 77 - 120 K (Note 43, **Customized Optistat<sup>®</sup> DN Cryostat for Advanced**

**Adsorption and Structural Characterisation Studies**) and the kernel library for calculation of pore size distribution according Density Functional Theory and Monte-Carlo-Simulation (e.g. Note 27, 31, 36 and 40) - only available from Quantachrome with all software versions of the actual gas adsorption instruments of the AUTOSORB-, QUADRASORB and NOVA-series.



TN#	TITLE
45	Kinetics of Water Vapor Sorption by Fruit (Aquadyne DVS) <b>New</b>
44	Water Vapor Sorption by Milk Powders (Aquadyne DVS) <b>New</b>
43	Application of Customized Optistat <sup>®</sup> DN Cryostat for Advanced Adsorption and Structural Characterisation Studies <b>New</b>
42	Mercury Porosimetry for the Characterisation of Specialty Papers
41	Thermal conductivity detectors (TCD's) for flow-based measurements
40	Application of QSDFT (quenched solid density functional theory) - a novel density functional theory for an accurate pore size analysis of disordered porous carbons
39	Characterising thin-film low-k dielectrics using krypton adsorption
38	Pycnometers Aid Osteoporosis Research
37	Hydrogen Adsorption: Experiment and Application
36	Comments on the Proper Selection of Adsorption or Desorption Branches for Mesopore Size Analysis
35	Micropore Size Analysis of Porous Carbons Using CO <sub>2</sub> Adsorption at 273 K (0°C)
34	Some Aspects of Quantachrome's NOVA (NO Void Analysis) Technology
33	Pore Network Modelling from Mercury Intrusion/Extrusion Porosimetry
32	Practical Methods to Prevent Sample Elutriation in Vacuum Volumetric Gas Sorption Analysers
31	Pore Size Analysis by Gas Adsorption, Part I: Aspects of the Application of Density Functional Theory
30	Tapped Density in the Pharmaceutical Industry
29	Elevated Saturation Vapor Pressure of Liquid Nitrogen
28	Attaching a Mass Spectrometer to the ChemBET
27	A New Method for Zeolite Characterisation
26	Percentage of Solids in a Slurry
25	Catalyst Evaluation by Temperature Programmed Reaction (TPR)
24	Geometric (Envelope) Density without Mercury (Tap Density)
23	Advantages of Using Thermistor and Motorized Dewar for LN <sub>2</sub> Coolant Control
22	Alternate Method to Determine Density of Cement
21	Achieving High Accuracy and Precision in Helium Pycnometry
20	Submicropore Analysis
19	A Method for the Determination of Ambient Temperature Adsorption of Gases on Porous Materials
18	Determination of Micropore Surface Area by Nitrogen Adsorption
17	Method for Estimation of Micropore Volume and Micropore Surface Area
16	Effect of Coating of Catalyst Supports in Mercury Porosimetry
15	Contact Angle Measurement for Mercury Porosimetry
14	Sample Conditioning
13	Hysteresis, Entrapment and Wetting Angle in Mercury Porosimetry
12	Contact Angle in Mercury Porosimetry
11	Isotherms from Mercury Porosimetry
10	Pore Spectra from Mercury Porosimetry
9	Hysteresis in Mercury Porosimetry
8	Desorption Isotherms by Continuous Flow
7	B.E.T. Constant and Site Occupancy
6	Chemisorption Surface Titration
5	Representative Sampling for Surface Area Measurements
4	Particle Structure
3	Low Surface Area Using Krypton
1/2	Small Volume Calibration for BET and Low Surface Area Measurements



## LabSPA (Laboratory for Scientific Particle Analysis) Rent the Lab!



**R**ent the Lab is an initiative of the LabSPA - Laboratory for Scientific Particle Analysis - in providing you for a day of your visit with the wide range of its analysers for the very effective characterisation of dispersions, powders and porous solids as well as to develop the most suitable analysis method for your application in general as for your special requests, plans or ideas. Rent the Lab means that our experienced laboratory staff will demonstrate the handling, discuss your application and interpret results together with you. Rent the Lab can also include longer measurements only to be started during the day of your visit but take a longer time to finish, e.g. for stability of dispersions with the TURBISCAN, for determination of water adsorption isotherms by use of the new AQUADYNE DVS or for low pressure adsorption isotherms to characterise microporous adsorbents. By arrangement samples can be sent in advance to be prepared, e.g. degassing them at a special temperature, so that the time for Rent the Lab can be used in the most effective way for you to get results, interpretation of data and experience with the analytical methods.

Apart from other flexible ways to organize such a use of our LabSPA capabilities, we would like to let you have the following two practical examples:

**1. Rent the Lab** can include for comprehensive **Characterisation of dispersions** the following analysis methods, e.g. for characterisation of complex emulsions regarding stability or determination of rheological parameters or suspensions including characterisation both the powders and the suspension:

- particle size in diluted or concentrated dispersions,
- zeta potential,
- stability of dispersions,
- determination of  $\mu$ -rheological parameters,
- particle shape analysis and other methods.

In this way you can use the instruments in combination with our manpower and experience for analysis of your samples and parallel for discussion of the analysis methods, pro and contra to use a special method and for detailed interpretation of results. During the measurements we can discuss the detailed analyses plan for further measurements, deadlines and criteria to continue an analyses program.

**2. Rent the lab** can include for comprehensive **Characterisation of powders and porous solids** the following analysis methods:

- surface and pore characterisation by use of gas adsorption and mercury porosimetry,
- particle size,
- zeta potential,
- water vapour adsorption,
- density (true, raw, tap and bulk density),
- particle shape analysis,
- chemisorption studies and other methods.

In a similar way as for the characterisation of dispersions you can use the instruments together with our manpower. Parallel to the practical accomplishment of the measurements, there is time for discussion of the analysis methods, potential problems regarding the sample types and for detailed interpretation of results. An analyses plan for further measurements, deadlines and criteria to continue an analyses program can be discussed and decided.

Do not hesitate to contact us with your special application and ideas for the **Rent a Lab** action of the LabSPA - Laboratory for Scientific Particle Analysis.



## International Particle Characterisation Seminars 2010

With our new seminar plan we get started into 2010. Our seminars are intended to provide a platform to discuss recent developments and state-of-the-art interpretation of data as well as to demonstrate new methods and experiences - we look forward to meeting you.

### Characterisation of Dispersions, Powders and Porous Solids

Antwerpen/Belgium,	23 <sup>rd</sup> March, 2010
Delft/Netherlands,	24 <sup>th</sup> March, 2010
Zurich/Switzerland,	8 <sup>th</sup> June, 2010
Leoben/Austria,	14 <sup>th</sup> September, 2010
Pecs/Hungary,	15 <sup>th</sup> September, 2010
Ljubljana/Slovenia,	16 <sup>th</sup> September, 2010
Copenhagen/Denmark,	21 <sup>st</sup> September, 2010

### Characterisation of Porous Solids and Powders

Jülich/Germany	25 <sup>th</sup> March, 2010,
Leipzig/Germany	13 <sup>th</sup> April, 2010,
Karlsruhe/Germany	10 <sup>th</sup> June, 2010,
Hamburg/Germany	23 <sup>rd</sup> September, 2010
München/Germany	28 <sup>th</sup> September, 2010

### Characterisation of Dispersions and Powders

Potsdam/Germany	14 <sup>th</sup> April, 2010,
Darmstadt/Germany	15 <sup>th</sup> April, 2010,
Saarbrücken/Germany	9 <sup>th</sup> June, 2010,
Hamburg/Germany	22 <sup>nd</sup> September, 2010



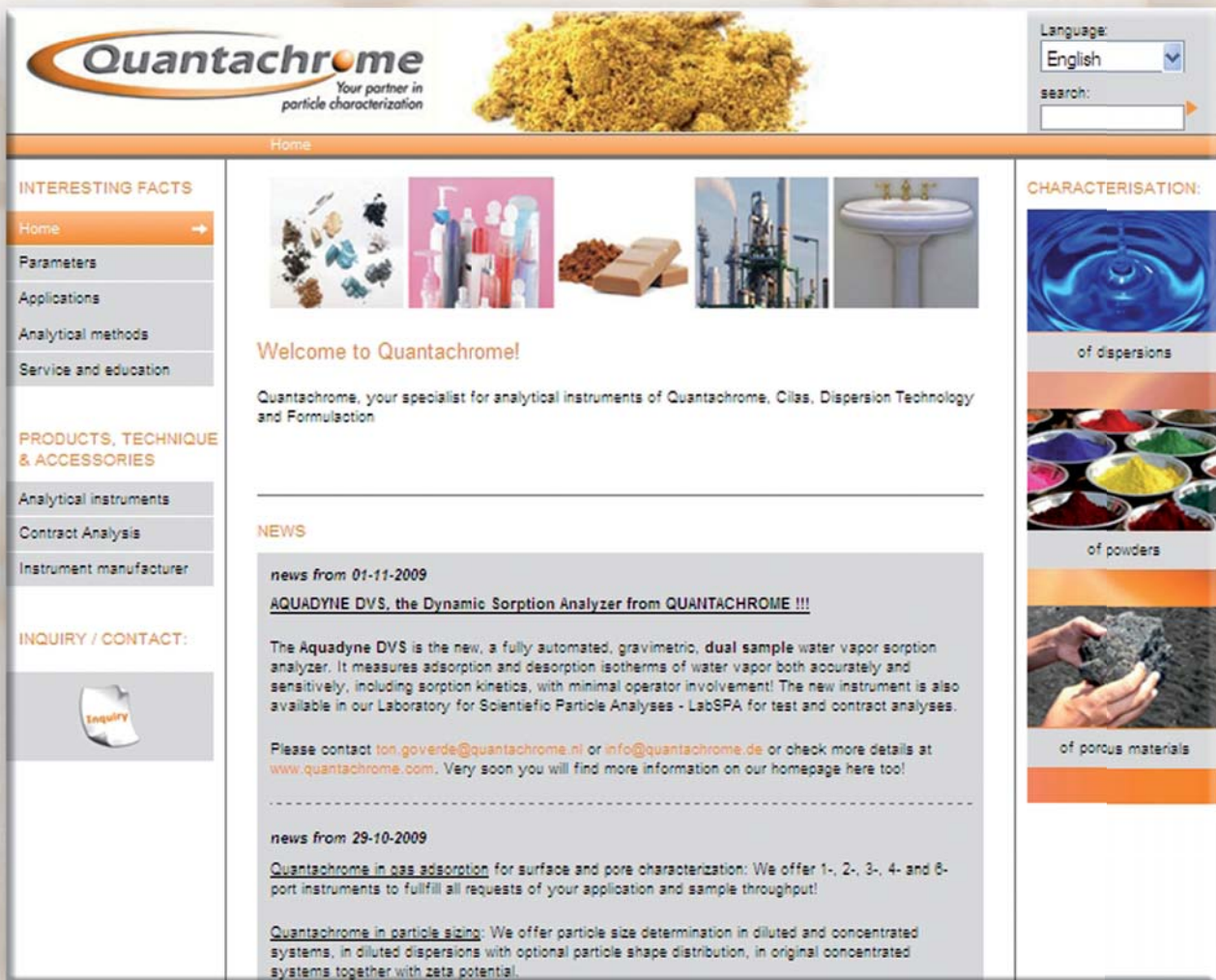
## Exhibitions

Please find us soon at the important analytical and powder exhibitions:

<b>ANALYTICA 2010</b>	23.-26. March 2010 in Munich/D Hall A2, Booth 522
<b>POWTECH 2010</b>	27.-29. April 2010 in Nuremberg/D Hall 9, Booth 9-502

# QUANTACHROME

Your partner in particle characterisation



The screenshot shows the Quantachrome website homepage. At the top left is the Quantachrome logo with the tagline "Your partner in particle characterization". To the right is a large image of a yellow powder. In the top right corner, there is a language selection dropdown menu set to "English" and a search bar. Below the header is a navigation bar with "Home" selected. The main content area is divided into three columns. The left column contains a sidebar with "INTERESTING FACTS" (Home, Parameters, Applications, Analytical methods, Service and education), "PRODUCTS, TECHNIQUE & ACCESSORIES" (Analytical instruments, Contract Analysis, Instrument manufacturer), and "INQUIRY / CONTACT:" with an "INQUIRY" button. The middle column features a "Welcome to Quantachrome!" message, a "NEWS" section with two news items from 2009, and a "CHARACTERISATION:" section with three sub-sections: "of dispersions" (with a blue liquid image), "of powders" (with a multi-colored powder image), and "of porous materials" (with a porous material image).

to find at

[www.quantachrome.eu.com](http://www.quantachrome.eu.com)

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Your partner in  
particle characterization