

# PARTICLE WORLD

Technical Papers  
of 3P Instruments  
EDITION 24  
SEPTEMBER 2023

New small volume **dispersion units**  
for special particle size measurements

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How **isothermal** is a sorption isotherm?

The new **BeNano** series for particle size analysis,  
zeta potential measurement and with microrheology option



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Dear Readers,

this 24<sup>th</sup> edition of the Particle World is dedicated to the creator of the Particle World, CEO Dr. Dietmar Klank. The occasion is a special one: **he celebrates his 25<sup>th</sup> company anniversary!** In 2002, after working four years in the company as account manager, he became head of marketing and released the very first issue of the **"Partikelwelt"** (in German language). In these days, the application magazine was sent as hard copy to the customers and generated great feedback. Since then, the magazine changed its optical appearance and now offers even more content on the characterization of particles, powders, and pores. What stays: the positive response we get from our readers!



Title page of the first "Partikelwelt"

Since 2006, Dr. Dietmar Klank is the managing shareholder of the company. Thanks to him, the company was able to further establish itself on the market as an owner-managed company and continues its growth course.

On behalf of the 3P Instruments team, I would like to take this opportunity to thank our CEO. And we hope you enjoy reading our Particle World 24!

*Dr. Denise Schneider  
 Head of Marketing*



CEO Dr. Dietmar Klank with a gift and a certificate on the occasion of this 25<sup>th</sup> company anniversary



## Review: company excursion and 25<sup>th</sup> company anniversary of our CEO Dr. Dietmar Klank



On a sunny summer day in June, the entire 3P team took part in the annual outing. We went to a hops experience farm in the Hallertau region, with 2400 km<sup>2</sup> the second largest hop-growing region in the world. We learned a lot about the plant itself and its uses (not only as beer!). Afterwards, we went to Scheyren monastery and had some nice afternoon refreshments.

The day after, we had a typical Bavarian breakfast with weisswurst and pretzels. The occasion was a special one: our CEO Dr. Dietmar Klank celebrated his 25<sup>th</sup> company anniversary. The 3P team presented him with a gift and a certificate to thank him for 25 years of commitment and stability as well as to wish him all the best for the future.



# Bettersizer product line: New small volume dispersion units for special particle size measurements

Dr. Christian Oetzel, christian.oetzel@3P-instruments.com



## Introduction

Laser diffraction is a very flexible optical method for particle size determination in terms of application. This is due to, among other things, the very short recording times of the measurement signals (scattering spectrum), but also to the almost free choice of the dispersing medium (water, air, organic solvents, etc.). This means that specific dispersion units can be designed for certain applications in terms of sample preparation, dispersion and conveying, which can then be flexibly connected to the main unit.

The Bettersizer series consists of three models, which offer different measuring ranges and size determination methods. An overview is given in Tab. 1 and on our homepage ([www.3p-instruments.com/analyzers/laser-diffraction/](http://www.3p-instruments.com/analyzers/laser-diffraction/)), showing that a suitable device setup with an optimal price-performance ratio is available for every application.

A special challenge in laser diffraction systems are dispersion units which are particularly suitable for very small sample volumes: they are interesting, for example, for research materials that are only available in very small quantities. Also in case of expensive products such as precious metals, diamond powders or – on the other hand – very toxic materials, the aim is to carry out a measurement that is as representative as possible with a minimum sample amount. In addition to the sample quantity, however, for materials that can only be measured in organic solvents due to their physicochemical properties, minimizing the amount of the dispersing medium for a measurement is also crucial in order to reduce the costs for purchase or disposal.

To meet these requirements, the laser diffraction measurement devices of the Bettersizer line offer various optional small-volume dispersion units.

**Table 1** Models of the Bettersizer series, their size range and basic application

Model	Size Determination		Size Range	Description/ Application
	Wet Method	Dry Method		
Bettersizer ST	✓		0.10 – 1000 µm	Robust entry level device for standard applications in water
Bettersizer 2600	✓	✓	0.02 – 2600 µm (wet) 0.10 – 2600 µm (dry)	Wet and dry laser diffraction device for a wide variety of samples, flexible switch between different dispersing modules
Bettersizer S3 Plus	✓		0.01 – 3500 µm	High end particle size and shape analyzer in wet systems, optimized for very small as well as coarse particles



## BT-80N Pro

This small-volume wet dispersion unit requires at least 80 ml of medium for operation and, in addition to water, is suitable for all organic solvents such as alcohols, ketones, toluene, gasoline, oils, NMP, etc. The unit can be used both, manually or fully automatically controlled by software, with the models Bettersizer 2600 and Bettersizer S3 Plus.

The dispersion unit is equipped with a variable speed centrifugal pump. The integrated ultrasound for particle dispersion is also adjustable between 0 and 50 W.



Figure 1 BT-80N Pro and its features

- **Liquid volume:** approx. 80 ml
- **Sample quantity:** from approx. 0.03 g
- **For samples, especially dispersed in organic solvents** (acetones, toluenes, oils, etc.)

In summary, the BT-80N Pro is ideal for all applications that cannot be carried out in water (e.g., due to solubility or chemical reaction of the sample in water), where little sample quantity is available and the particles tend to sediment (e.g., high density) or when dry measurement is not an option (e.g., very fine particles, high degree of agglomeration...).

## BT-804

This small volume stand measurement cell for wet measurements is designed for very small sample quantities (approx. 0.005 – 0.1 g). It can be used software-controlled with the Bettersizer 2600. The material can be dispersed in water or an organic solvent, the maximum liquid volume is 8 ml. The cell is equipped with a stirrer so that slower sedimenting samples can also be measured.



Figure 2 above: BT-804 installed in the Bettersizer 2600  
below: BT-804 individually

- **Liquid volume:** up to 8 ml
- **Sample quantity:** approx. 0.005 – 0.1 g
- **For samples in water or organic solvent**

The BT-804 is intended, for example, for pharmaceutical products or applications in the biochemical field, i.e., substances that have a low density, therefore do not tend to sediment quickly and are only available or should be used in very small quantities.



### BT-903

The BT-903 is a fully automatic small-volume dry measuring cell developed for the Bettersizer 2600. The minimum amount of available powder is about 20 mg. The sample is placed in a test tube, quantitatively aspirated from the glass by vacuum and passed through a Venturi nozzle through the measuring cell for data acquisition.



Figure 3 above: BT-903 connected to the dry measurement cell of the Bettersizer 2600  
below: BT-903 individually

- For very small amounts of dry powder from about 20 mg
- Sample feeding by means of compressed air via Venturi nozzle

The BT-903 can be used for all materials that are only available in very limited quantities as well as samples that can be measured by dry dispersion only when wet measurement is not an option, e.g., due to solubility of the sample or chemical reaction.

### Summary

In summary, the Bettersizer series with the various instruments and dispersion modules offer a suitable solution for almost all applications. In particular, when it comes to applications where material is only available or should be measured in small quantities, the Bettersizer S3 Plus and Bettersizer 2600 models with the newly available modules fulfil almost all requests. A summary for all available dispersing modules for these two models is given in Tab. 2.

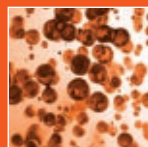


Table 2 Available dispersion modules for Bettersizer 2600 and S3 Plus

Dispersion Module	Medium	Instrument models	Sample amount	Automation
BT-802	Wet, water and alcohols	Bettersizer 2600	600 ml volume	Fully automated
BT-803	Wet, water and alcohols	Bettersizer S3 Plus	600 ml volume	Fully automated
BT-902	Dry, air	Bettersizer 2600	0.2 – 10 g	Fully automated
BT-903	Dry, air	Bettersizer 2600	0.02 – 1 g	Fully automated
BT-80N Pro	Wet, water, polar and non-polar organic solvents	Bettersizer 2600 Bettersizer S3 Plus	80 ml volume	Fully automated
BT-804	Wet, water, some organic solvents	Bettersizer 2600	8 ml volume	Semi-automated

# BeNano series for particle analysis: New Autotitrator and DLS Microrheology Option

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## Introduction

The BeNano series is the latest generation of powerful optical measuring devices for comprehensive nanoparticle characterization from Bettersize Instruments Ltd. The flagship of the equipment series, the BeNano 180 Zeta Pro, combines the methods of dynamic light scattering (DLS) for particle size measurement, electrophoretic light scattering (ELS) for zeta potential determination and static light scattering (SLS) for molecular weight determination in one system. Depending on the user, the series also offers device configurations that include only a selection of the features of the BeNano 180 Zeta Pro, i.e., the capabilities of the measuring device can be customized individually by the purchaser. Two avalanche photodetectors (APD) are available for DLS at 90°, alternatively at 173°. For the backscatter detector type, an intelligent routine ensures the optimal adjustment of the detector position. Multiple scattering is avoided which has the advantage that even concentrated systems can be measured regarding particle size distribution. For ELS measurement, the BeNano series relies on the innovative PALS (Phase Analysis Light Scattering) technique: Here, the applied

*BeNano 180 Zeta Pro in new design with autotitrator BAT-1*

electric field for the electrophoretic movement of the particles is permanently reversed and the electrophoretic mobility is determined by a phase analysis. The advantage of this method compared to conventional ELS is that even weakly mobile particles (e.g., organic dispersions) can be measured very accurately.

For the first time, the BeNano line was presented in the Particle World Edition 22 in September 2021 [1]. A very good summary of the three methods DLS, ELS and SLS, implemented in the BeNano 180 Zeta Pro, can be found in Particle World Edition 23 (September 2022) [2].

As Bettersize continues to develop and improve its products both by hardware and software, this article introduces the latest features "Autotitrator BAT-1" and "DLS Microrheology", which are now available on the recently redesigned instruments of the BeNano series.

## Titration experiments with the autotitrator BAT-1

Titration experiments in zeta potential measurements on aqueous dispersions are primarily performed to investigate the pH dependence of this colloidal parameter. In oxide materials such as silica, alumina or titanium dioxide, the zeta potential is positive at low pH values (strongly acidic range) and passes through a zero value, the so-called "isoelectric point" (IEP), when the pH is increased. In the more alkaline range, the material usually shows negative values. The IEP value is often the focus of many experiments: If the zeta potential is (near) zero in terms of magnitude, the dispersed particles tend to agglomeration or flocculation – at least in electrostatically or electro-sterically stabilized systems – and the dispersion is unstable. In most cases the aim is to keep the system stable, i.e., to set the zeta potential as high as possible. However, in certain applications, e.g., precipitation reactions, the aim is the opposite, i.e., a zeta potential as close as possible to the isoelectric point.

The autotitrator BAT-1 – in conjunction with the suitable devices of the BeNano series – has been developed especially for such titration applications: it is equipped with an integrated pH electrode and three automatic burette units, which can be controlled via the software using SOP, the minimum titration quantity is 0.28  $\mu$ l. Through the third burette, acid or bases can be added in different concentrations in an experiment in order to meet the IEP more precisely, for example. A detailed image of the system as well as a flowchart of the titration experiment BAT-1 + BeNano Zeta 180 Pro is shown in Fig. 1.

To set the target pH value, the appropriate titrants are added to the sample container

under software control until it is reached. The homogenization of the sample is ensured in the sample container by the integrated magnetic stirrer, while at the same time the sample pump ensures an adjustment of the pH value in the overall system through the measuring cell.

The pH titration of an aqueous BSA suspension (BSA = Bovine Serum Albumin, protein) serves as an example application: BSA is widely used in protein research and the dependence of the protein structure on the medium properties, e.g., pH value, is of great interest. The present sample was a 1 wt% BSA suspension, dispersed by magnetic stirrer in distilled, filtered (0.2  $\mu$ m) water. The pH value was 6.89

(almost neutral) and the zeta potential value determined by BeNano 180 Zeta Pro was -29.8 mV. In addition, the electric conductivity of the sample in the instrument was also determined: The initial value was 0.45 mS/cm. For titration into the acidic range for the determination of the IEP, two acidic titrants, 0.1 M and 0.5 M HCl, were used in order to optimally meet the predefined pH values within the framework of the granted tolerance (here 0.2).

The result of the measurement is shown in Tab. 1 and Fig. 2.

The automatically determined IEP (via software) after data acquisition was pH 4.74 (literature value 4.70).

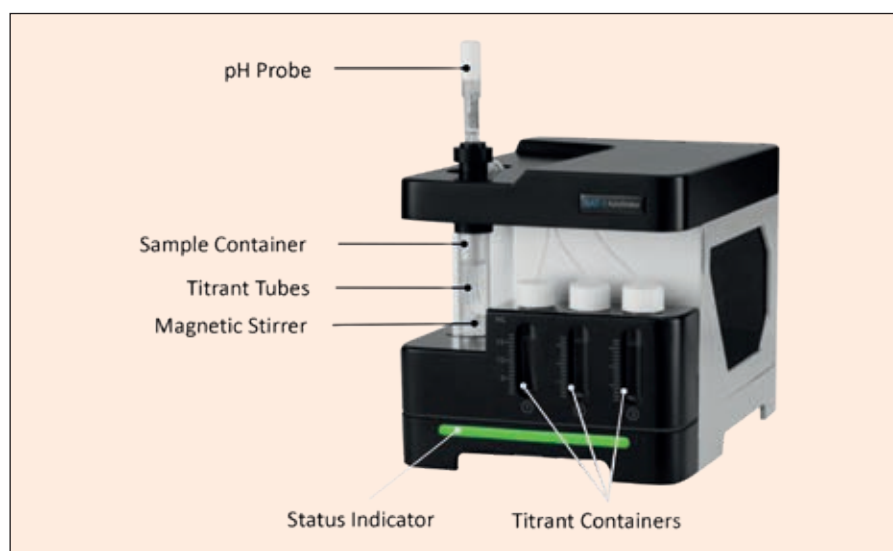


Figure 1a BAT-1

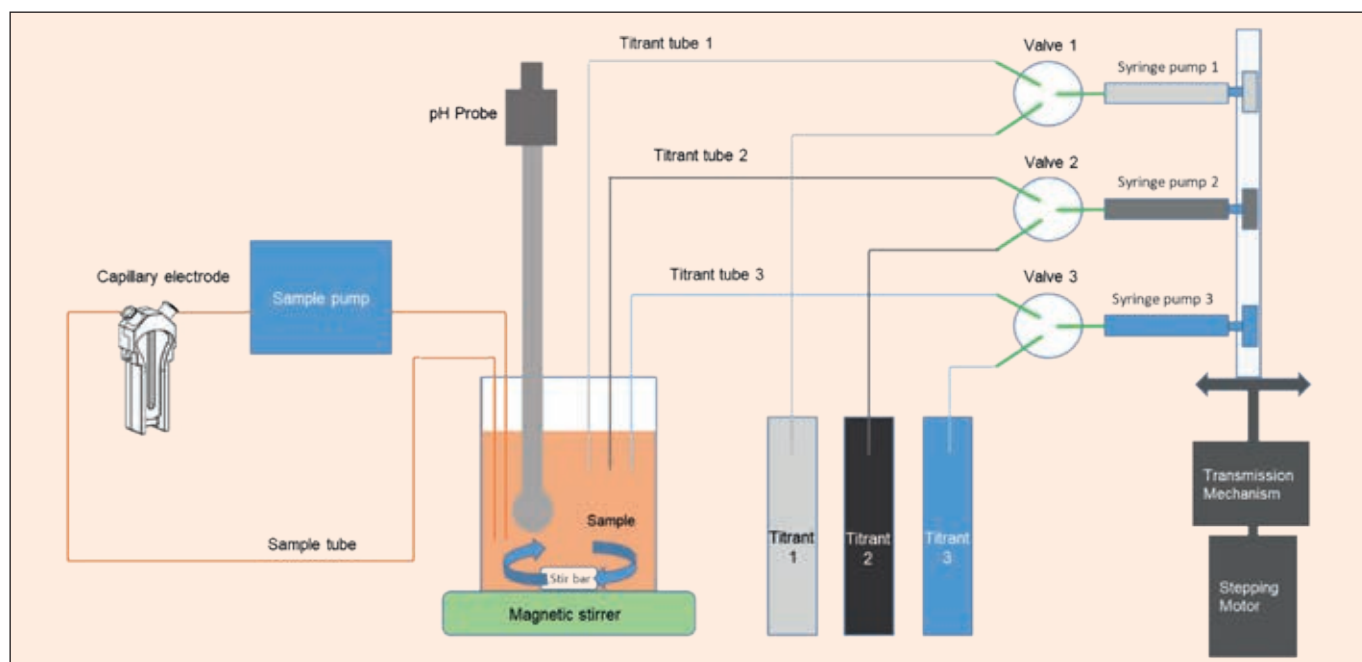
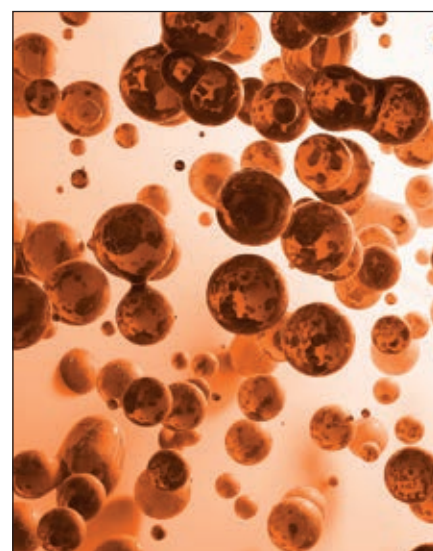


Figure 1b Flowchart for titration experiments with BeNano Zeta 180 Pro



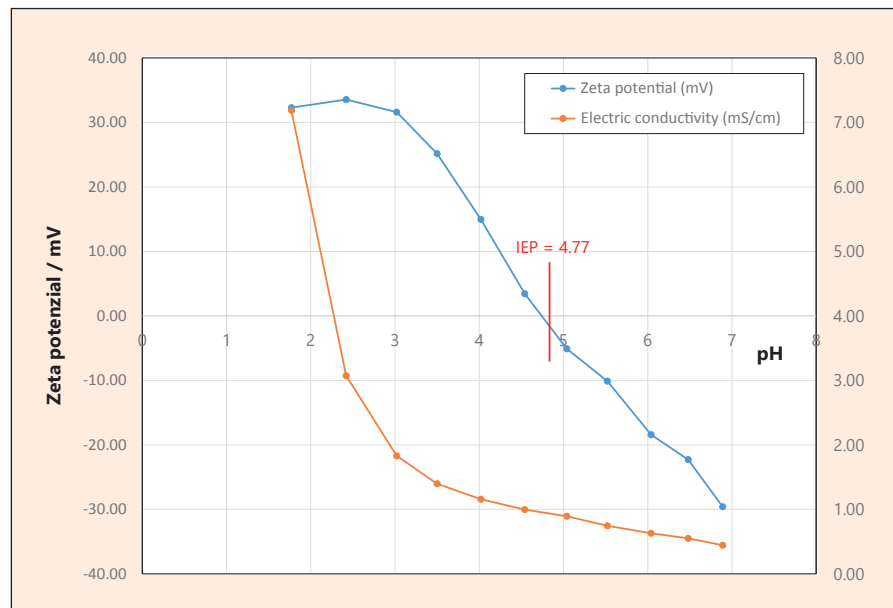
**Table 1** Results: zeta potential and electrical conductivity of BSA-in-water sample vs pH

pH	Zeta potential / mV	Electric Conductivity / mS/cm
6.89	-29.6	0.4439
6.48	-22.3	0.5500
6.04	-18.41	0.6281
5.52	-10.11	0.7459
5.04	-5.09	0.8927
4.54	3.43	0.9963
4.02	14.97	1.1569
3.50	25.16	1.3963
3.02	31.59	1.8286
2.42	33.55	3.0715
1.77	32.29	7.1874

## Dynamic light scattering microrheology

Microrheology is a field of rheology in which colloidal dispersions are investigated with regard to their viscoelastic behaviour with the help of flow tracers (usually particles on a micrometer scale) and the determination of their trajectory [3]. The method is used, for example, in rheological investigations of weakly structured polymers, protein solutions or gel structures, basically in liquid systems in which the tracers can diffuse particles over longer distances.

In the passive variant of microrheology (passive means no application of an external force or energy), the measurement is due to the displacement of the tracer particles caused by their thermal energy (= Brownian motion). The measurement



**Figure 2** Results: zeta potential and electrical conductivity of BSA-in-water sample vs pH

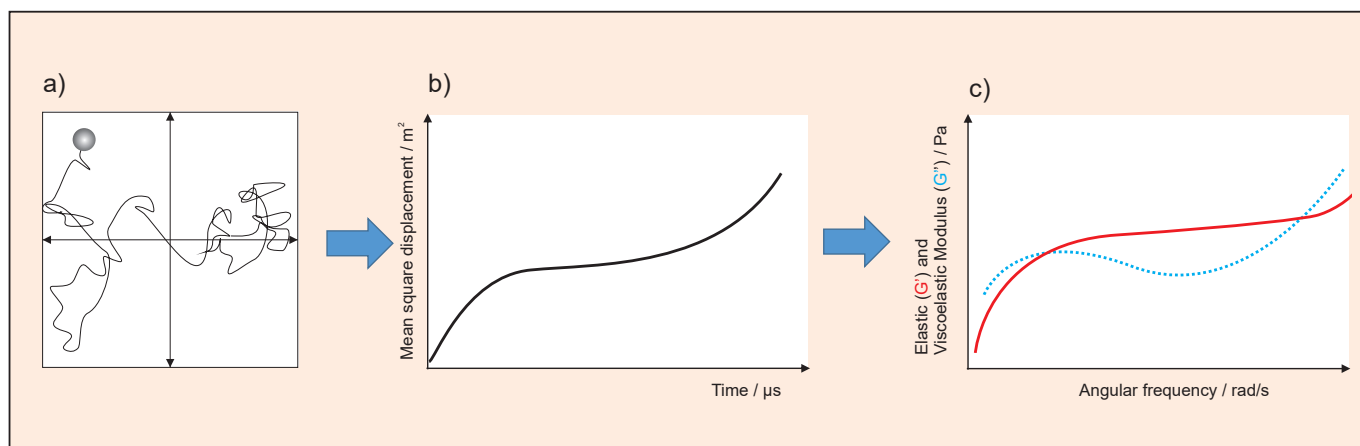
parameter is the so-called mean square displacement (MSD,  $\Delta r^2$ ), which is a measure of the volume that a particle migrates on average in a certain time period, if it performs a random motion.

The MSD is represented as a function of the decorrelation time, the MSD vs curve is directly related to the frequency-dependent complex modulus  $G^*(\omega)$  via the generalized Stokes-Einstein equation, which in turn contains the viscous and elastic components of the system. In easy words: when the particle moves in the medium, its velocity reflects the viscosity, and its displacement reflects the elasticity. The faster the particle diffuses, the lower the viscosity, the greater the displacement of the particle, the lower the elasticity of

the system. A scheme of the passive microrheology principle is shown in Fig. 3.

In Dynamic light scattering microrheology (DLS microrheology, DLS $\mu$ R) with the BeNano 180 Zeta Pro, the MSD curves ( $\Delta r^2(\tau)$ ) are determined from the measured autocorrelation function  $G_1(\tau)$  of the DLS experiment. Intensity measurement at 173° (Bettersize backscatter detection technology) is particularly suitable here, as – compared to conventional 90° detection – even significantly higher concentrated samples can be measured with very good precision.

With the BeNano 180 Zeta Pro, the DLS $\mu$ R comprises a total of 4 steps which are described below.



**Figure 3** Principle of the passive microrheology

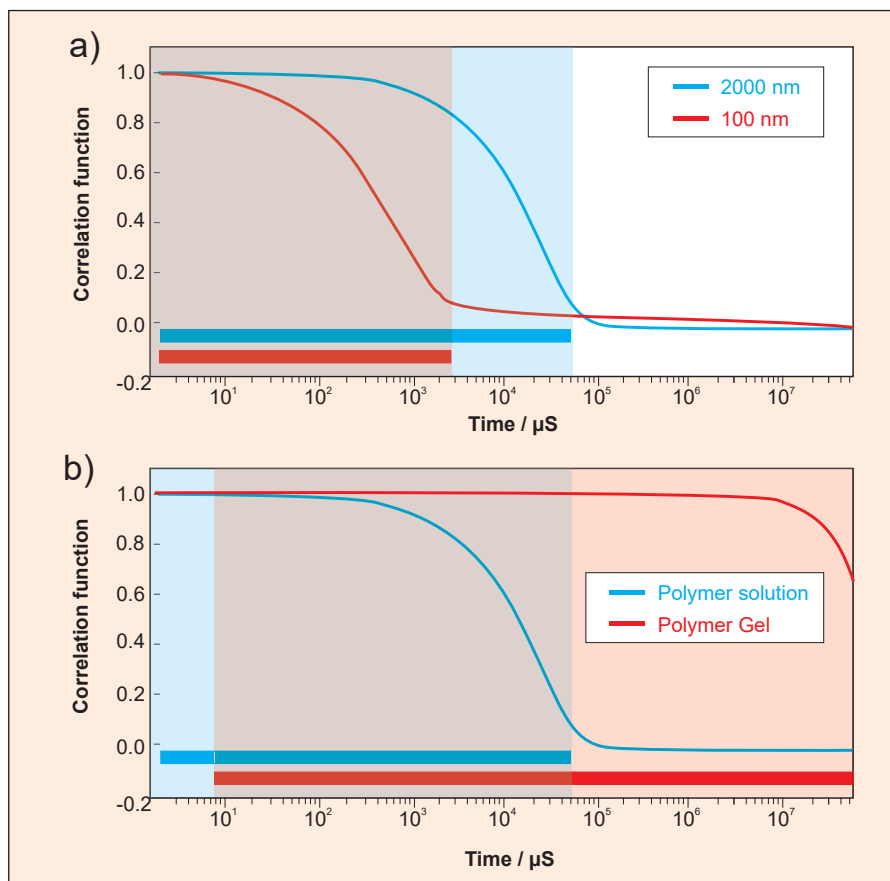
### 1) Addition of suitable tracer particles to the system to be characterized

The first step of DLS $\mu$ R is the addition or dispersion of the tracer particles into the substance to be measured. The particles should be in the submicron range (100 – 1000 nm) in terms of their particle diameter, and the particle radius must be known. In addition, the tracer particles must be chemically inert to the sample and, if possible, should not be prone to sedimentation in the system. A common tracer particle material for DLS $\mu$ R experiments is, for example, polystyrene.

### 2) Carrying out the DLS measurement

The DLS measurement is based on intensity fluctuation diagrams caused by the Brownian motion of the particles [4]. The autocorrelation function  $G_1(\tau)$  is then determined from the intensity fluctuation diagram: these represent curves decreasing from one to zero, which are used in classical DLS (with known viscosity of the medium) to determine the particle radius. Fig. 4a) shows as an example the correlation function of 100 nm and 2,000 nm particles of the same material in hyaluronic acid [5]. As expected, the drop to zero for the 100 nm particles is much faster as they move them much quicker as compared to the 2  $\mu$ m particles.

In the case of DLS $\mu$ R, on the other hand, the particle size must be known in order to determine the microrheological properties. Figure 4b) shows the correlation function of the 2,000 nm tracer particle in hyaluronic acid (polymer solution) compared to a polymer gel (5 % polyethylene glycol suspension). The decorrelation time in the gel is significantly longer, so the microrheological properties change accordingly. It is important to note here



**Figure 4** a) Comparison of the autocorrelation function of 100 nm and 2,000 nm particles, each dispersed in hyaluronic acid  
 b) Comparison of the autocorrelation function (2,000 nm particles) in a polymer solution (hyaluronic acid) and a polymer gel (5 % polyethylene glycol dispersion)

that the correlation function must drop in order to determine the microrheological properties.

### 3) Calculation of the MSD curve

The mean square displacement curve  $\Delta r^2(\tau)$  results from the autocorrelation function from the relationship equation

$$G_1(\tau) = A e^{-q^2(\Delta r^2(\tau))} \quad (1)$$

where  $q = 4\pi n \cdot \sin(\theta/2)/\lambda$  is the scattering vector.

### 4) Calculation of the frequency-dependent complex module and the (microrheology) parameters $G'$ , $G''$ and $\eta^*$

The complex modulus is depending on the MSD regarding the general Stokes Einstein equation over

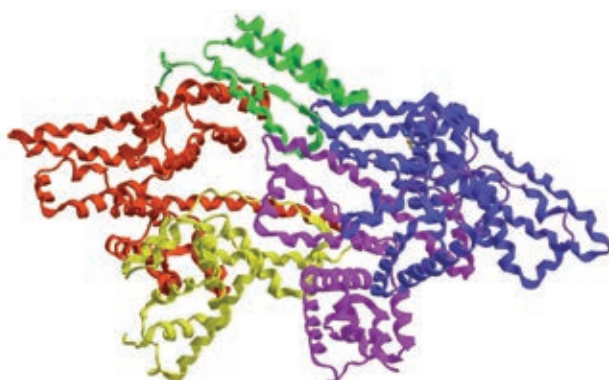
$$G^*(\omega) = \frac{k_B T}{\pi R i \langle \Delta r^2(i\omega) \rangle} = G'(\omega) + iG''(\omega) \quad (2)$$

Where  $k_B T$  is the thermal energy and  $R$  the particle radius.  $G'(\omega)$  is the elastic (storage) modulus and  $G''(\omega)$  is the viscous (loss) modulus. Thus  $G'$  and  $G''$  can be determined directly from the MSD curve. The complex viscosity  $\eta^*(\omega)$  can be derived from the relationship.

$$\eta^*(\omega) = \frac{G^*(\omega)}{\omega} \quad (3)$$

In addition to these parameters, the so-called "creep compliance"  $J(t)$  is of interest, which results directly from the mean shift over

$$J(t) = \frac{\pi \alpha}{k_B T} \quad (4)$$



## Example: Determination of the rheological behavior of sucrose solutions [6]

In the following experiment, sugar solutions in concentrations of 25, 40 and 50 wt.-% were examined regarding their micro-viscous properties using of the BeNano 180 Zeta Pro. The temperature of the samples was kept constant at 25°C, and polystyrene particles with a particle diameter of 400 nm were added as tracer particles. 10 µl of the polystyrene solution was added to 1 ml of sugar solution of all samples and examined by DLSµR.

Fig. 5 shows the correlation function of the three sugar solutions in comparison. Fig. 6 and 7 depict the respective  $G'$ ,  $G''$  and  $\eta^*$  diagrams as a function of angular frequency, Fig. 8 demonstrates the course of creep compliance as a function of time.

The delayed drop in the correlation curve with increasing sucrose concentration shows that the viscosity increases accordingly. This can be seen in Fig. 7; Tab. 2 shows the values of the complex viscosity in [Pa·s] at an angular frequency of 1044 rad/sm.

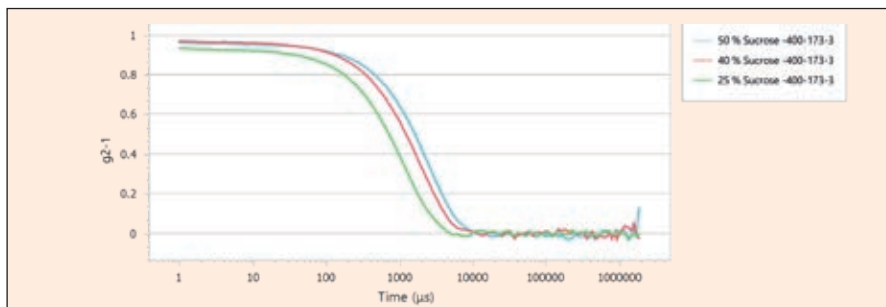
Fig. 6 shows that all samples have a high viscous modulus and that both viscous and elastic modulus increase with higher concentration. The complex viscosity (Fig. 7) shows little change up to a frequency of about 10,000 rad/s. A noticeable drop occurs only at very high frequencies, indicating a weak shear thinning effect.

**Table 2** The complex viscosity results of sucrose solutions with varying concentrations

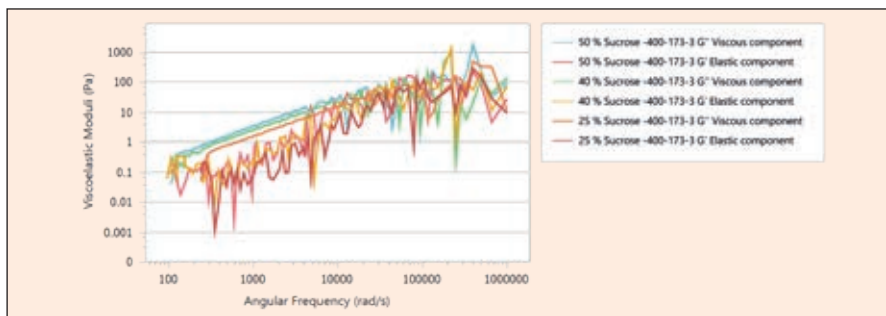
Sample Name	Complex viscosity at 1044 rad/sm [Pa·s]
25% Sucrose	1.53
40% Sucrose	2.55
50% Sucrose	3.56

## References

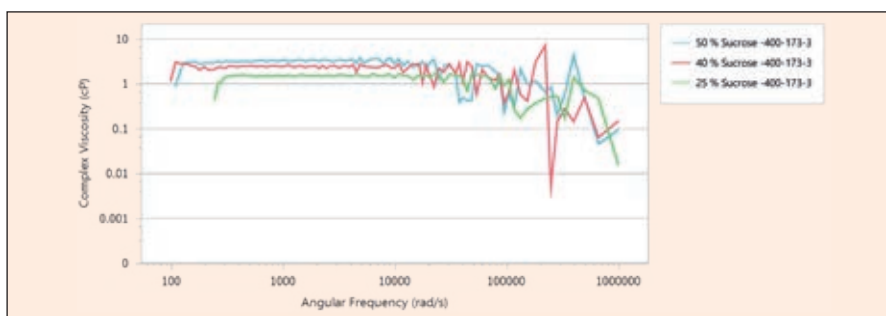
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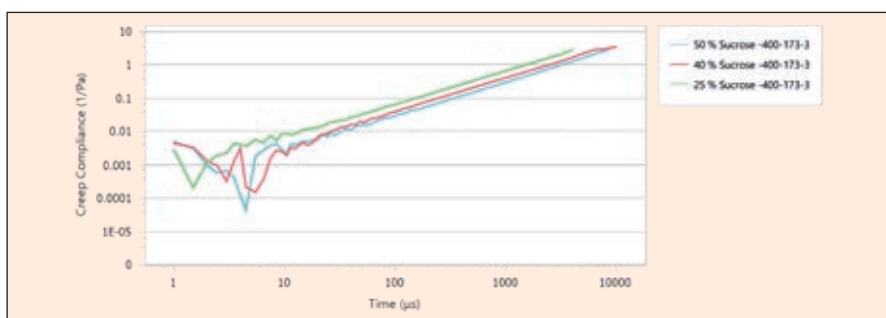
**Figure 5** Correlation functions of sucrose solutions with varying concentrations



**Figure 6** Viscoelastic modulus curves of sucrose solutions with varying concentrations



**Figure 7** Complex viscosity curves of sucrose solutions with varying concentrations

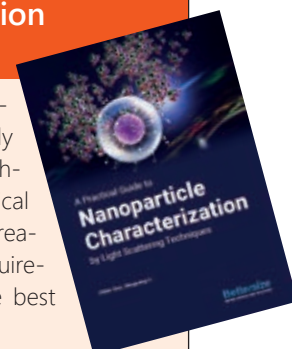


**Figure 8** Creep compliance curves of sucrose solutions with varying concentrations

## A Practical Guide to Nanoparticle Characterization by Light Scattering Techniques

Whether you are a beginner or an experienced researcher, this guidebook aims to provide a practical, easy-to-read guide on the seemingly daunting topic of nanoparticle characterization by light scattering techniques, the theory behind the measurements and highlights practical considerations for carrying out measurements. The goal is to equip readers with the necessary understanding to meet measurement requirements, and to come up with measurement solutions to reach the best practice in the characterization of nanoparticles.

Download now: <https://www.3p-instruments.com/a-practical-guide-to-nanoparticle-characterization-by-light-scattering-techniques/>





# Powder Characterization Analyzers

Dr. Carsten Blum, [carsten.blum@3P-instruments.com](mailto:carsten.blum@3P-instruments.com)



## Introduction

The macroscopic properties of powders are crucial for their evaluation for the production, processing and packaging of powders as well as for their transport, storage and application. For this purpose, corresponding parameters must be quantified. 3P Instruments offers a full range of instruments for the characterization of macroscopic powder properties in addition to its analytical instruments for particle size analysis of powders. Besides the Powder Pro A1 combination instrument, the device portfolio also includes instruments for determining density, bulk density and tapped density.

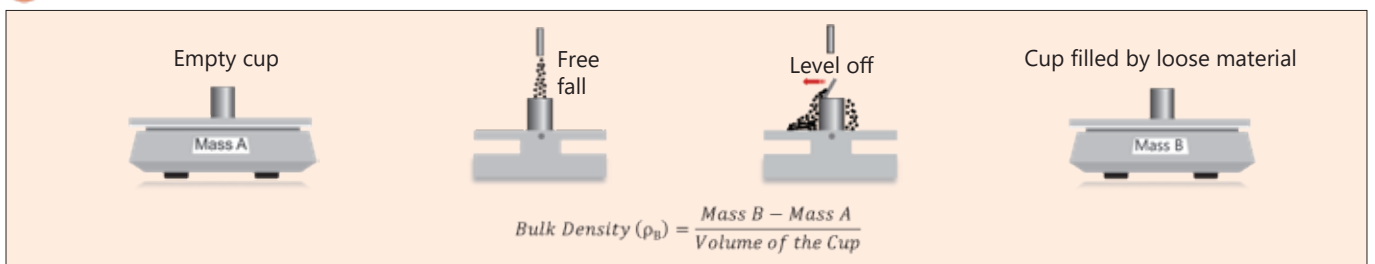
## Powder Characteristics Tester – PowderPro Series

The PowderPro A1 allows a comprehensive, fast and accurate characterization of powders with respect to macroscopic powder properties. This new type of physical test device combines many advanced technologies such as computer or tablet computer-based controlling via Wi-Fi connection, fully automatic digital image processing technology or a 3D electromagnetic material processing. With the PowderPro A1, 14 parameters of metallic and non-metallic powder samples can be determined according to ASTM D6393:

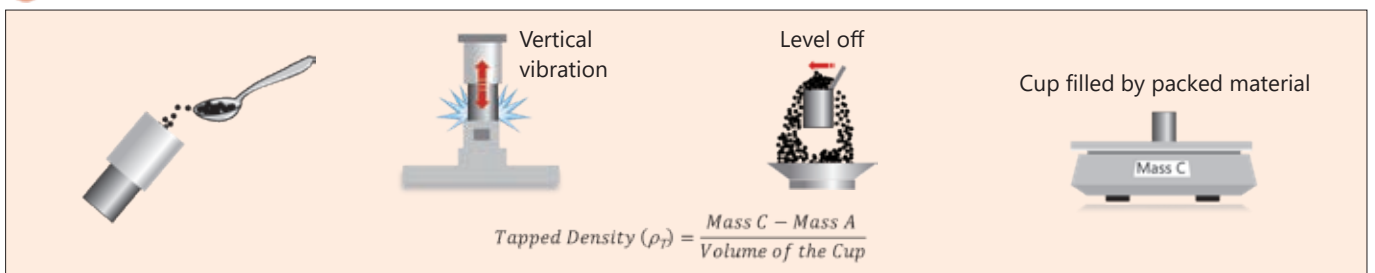
- Carr Angle of Repose
- Carr Angle of Collapse
- Carr Angle of Difference
- Carr Angle of Spatula
- Carr Packed Bulk Density
- Carr Loose Bulk Density
- Tapped Density
- Carr Compressibility
- Carr Dispersibility
- Carr Uniformity
- Carr Cohesion
- Voidage
- Flowability index
- Floodability index

## Flowability Parameters

### ■ Bulk Density ( $\rho_B$ )



### ■ Tapped Density ( $\rho_T$ )



### ■ Compressibility ( $C_p$ )

$$\text{Compressibility } (C_p) = \frac{(\rho_T - \rho_B)}{\rho_T} \times 100\%$$

▲ Angle of Repose ( $\theta_R$ )

◐ Angle of Spatula ( $\theta_{Sp}$ )

$Angle\ of\ Spatula\ (\theta_{Sp}) = \frac{\theta_a + \theta_b}{2}$

◐ Cohesion ( $C_h$ )

$Cohesion\ (C_h) = (X \times 5\% + Y \times 3\% + Z \times 1\%) + 0.1\ g \times 100\%$

◐ Uniformity ( $U_f$ )

$Uniformity\ (U_f) = \frac{Particle\ size\ at\ the\ 60\ \% \ point\ of\ the\ cumulative,\ undersize\ PSD = D_{60}}{Particle\ size\ at\ the\ 10\ \% \ point\ of\ the\ cumulative,\ undersize\ PSD = D_{10}}$

## Floodability Parameters

▲ Angle of Fall ( $\theta_F$ )

◐ Angle of Difference ( $\Delta\theta$ )

$Angle\ of\ Difference\ (\Delta\theta) = Angle\ of\ Repose\ (\theta_R) - Angle\ of\ Fall\ (\theta_F)$

◐ Dispersibility ( $D_S$ )

$Dispersibility\ (D_S) = \frac{10.0\ g - (Mass\ D - Mass\ C)}{10.0\ g} \times 100\%$

## Gas Pycnometers – 3P densi Series

The 3P densi series is a compact and automated density analyzer for powders and solids as well as for the characterization of foamed materials for the determination of skeletal density. Sample preparation is performed in continuous or pulsed gas flow. Preparation, measurement and repeated measurement are carried out automatically. Repeated measurements are optionally affected either by pre-setting a user specified tolerance (Autostop) or a user specified number of runs. The sample volume of 3P densi 100L ranges from 10 cm<sup>3</sup> up to 100 cm<sup>3</sup>, the 3P densi 100S holds sample cylinders from 1 cm<sup>3</sup> up to 10 cm<sup>3</sup>. The instrument is easy to handle thanks to the 10-inch (25.4 cm) touch-screen.



## Tapped Density Analyzers – BeDensi T Pro Series

Tapped density is the ratio of the mass of particles to the total volume of powders that are filled into container after tapping under specific conditions. The total volume is the sum of true volume of particles, the pore volume of open and closed pores in powders, and interstitial volume between the packed particles after vibration. The tapped density of powdered, granular or flakey material is highly dependent on the manner in which the particles are packed together. During tapping, particles gradually pack more efficiently, the powder volume decreases and the

tapped density increases. Under controlled conditions of tapping rate, tap force and cylinder diameter, this condition of maximum packing efficiency is highly reproducible. Tapped density measurement (sometimes referred to as tapped bulk density, or just tap density) is formalized in a number of international standards to which BeDensi T Pro models are compliant. If a fixed number of taps for all analyses needs to be ensured, a special lockout feature is provided. This prevents unauthorized changes to the counter.



- Scott capacity instrument for the norm compliant determination of the bulk density of metal powders
- Compliant with ISO 3923-2 and ASTM B329-14



- Bulk density instrument for non-metallic powders, using natural deposition method
- Compliant with GB/T16913.3-1997-Part III



- Hall flowmeter for the norm compliant determination of the flowability of metal powders
- Compliant with ISO 4490 and ASTM B213-13

## Bulk Density and Flowability Instruments – BeDensi Series

Bulk density is the mass per unit volume of particles that is packed into a container without external force. The total volume is the sum of true volume of particles, the pore volume of open and closed pores in powders, and interstitial volume between the packed particles. Bulk density is also known as loose density, loose packing density or loose bulk density. Bulk density and flowability are the basic parameters of powder material characterization. Since these parameters significantly depend on the measurement conditions, their determination is defined in different norms depending on the material type. Accordingly, a defined performance of measurements or the use of instruments of defined and norm-compliant dimensions and designs is required.



# The influence of the sorption method sensitivity factor (SMSF) to gas sorption measurements

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In this article, we show a way to comprehensively describe the sensitivity of gas sorption measurements qualitatively and quantitatively. For this purpose, we introduce a sorption method sensitivity factor (SMSF) for the practical estimation of the sensitivity of an adsorptive-temperature-sorption method.

## Introduction

The word sensitivity can be defined as the quotient of the change in an indication of a measuring system and the corresponding change in a value of a quantity being measured. This must not be confused with the accuracy, which is depended on the temperature stability, the accurate pressure measurement, or the constant cold-warm zone over the complete measuring time. However, these additional accuracy factors are beyond the scope of this article and will be discussed elsewhere.

If the definition of sensitivity is referred to an adsorption device, the sensitivity can be described as the quotient of a pressure change in the manifold ( $\Delta p_1$ ) and the pressure change in the measuring cell ( $\Delta p_2$ ) after equilibration on the accessible surface of the adsorbent.

$$\text{Sensitivity} = \frac{\Delta p_1}{\Delta p_2} \quad (1)$$

A possible challenge occurs when the number of free gas molecules is much

larger than the number of adsorbed molecules after a dosing step, since this causes almost no pressure change in the manifold. This is the case, for example, when a very large void volume is present in combination with a very little sample amount. Samples with a very small surface area also cause such a phenomenon.

Tab. 1 summarizes typical situations for material characterization by use of manometric gas sorption.

**Table 1** Typical situations for material characterization by use of manometric gas sorption

Type of material	Available sample amount	Typical sample weight /g	Absolute surface available /m <sup>2</sup>	Potential solutions
microporous, SA = 1000 m <sup>2</sup> g <sup>-1</sup>	high	0.1 – 0.2	100	no problem with free space in the cell
microporous, SA = 1000 m <sup>2</sup> g <sup>-1</sup>	low	0.01 – 0.03	10	try to reduce free space in the cell
non-microporous, SA = 10 m <sup>2</sup> g <sup>-1</sup>	high	3 – 5	30	no special problem with free space in the cell
non-microporous SA = 10 m <sup>2</sup> g <sup>-1</sup>	low	< 1	< 10	try to minimize free space in the cell

By implication, this means that a reduction in the dead volume of the measuring arrangement leads to a higher sensitivity. The following possibilities are available in the laboratory to reduce the free space in the sample cell.

- Optimized sample cells, e.g., smaller bulb or no bulb
- Use of filling rods (remark: the use of a filler rod is only recommended when no micropore analysis is performed, because the thermal transpiration correction is based on the mean free path length of the measuring cell without a glass rod)
- Use of a small manifold (dosing volume)
- Separation of the dosing volume from the sample cell volume
- Minimizing the cold zone volume

The aim of this article is to give the user an idea or a feeling about the sensitivity of an experiment. For this purpose, it is obviously not advisable to include the pressure after the equilibration in such an estimation, since this is not known before the actual experiment. Therefore, we introduce a sorption method sensitivity factor (SMSF), which obtains the vapor pressure of the gas at the boiling point  $p_{0,bp}$  and the vapor pressure at the actual measurement temperature  $p_{0,mp}$ . Because  $p_{0,bp}$  is about the ambient pressure, we use equation 2 with

$$SMSF = \frac{p_{0,bp}}{p_{0,mp}} = \frac{101.3 \text{ kPa}}{p_{0,mp}} \quad (2)$$

and the SMSF of adsorptives at their boiling temperatures, like argon at 87.3 K or nitrogen at 77.35 K is defined as 1.0. However, there are scenarios where a higher sensitivity of the measurement is required. This is the case when physical tools, such as glass beads, cell type or filler rod do not help anymore to reduce the amount of free gas molecules in the cell to create a measurable effect. If the free space volume is optimized, a minimum 1 m<sup>2</sup> absolute sample surface shall be available in the cell for N<sub>2</sub>@77K or Ar@87K, independently that the measuring error at that limit can be already quite large. Typical samples with too low absolute surface area in a measuring cell can be porous thin films, many non-

porous samples, coarse powders, or simply any sample that is only limited available. For such cases, the additional method sensitivity plays an important role, defined by us as SMSF in equation 2.

### The principle to increase the SMSF by decrease of the measuring temperature

With the following hands-on example, the influence of  $p_0$  reduction by decreasing temperature is shown. Therefore, xenon was used in the range from its boiling point 165 K down to 140 K (Fig. 1).

Such a reduction in the measurement temperature as shown in Tab. 2 and Fig. 1 is not only the basis for the calculation of sorption enthalpies (isosteric heats of sorption) but also to reduce the  $p_0$  to allow characterization of smaller sample volumes. The SMSF for xenon at 140 K is

about 7, which is a significant improvement in sensitivity for small sample amounts.

According to this idea, Beebe et. al. [2] already studied the krypton adsorption of small surface areas at low temperatures about 80 years ago. An interesting detail is that already during this time, the authors considered the variable temperature of liquid nitrogen also for the krypton measurements. This seems to have been forgotten, because although Kr@77K has since been recommended for the analysis of small surfaces, neither ISO 9277 [3] nor IUPAC [4] refers to the variable temperature of liquid nitrogen in this context.

The boiling point of krypton is at 120 K, which means that a saturation pressure of 101.3 kPa in the cell can be reached. At 77.35 K in contrast, the saturation pressure cannot be measured since the temperature is below the triple point of this gas.

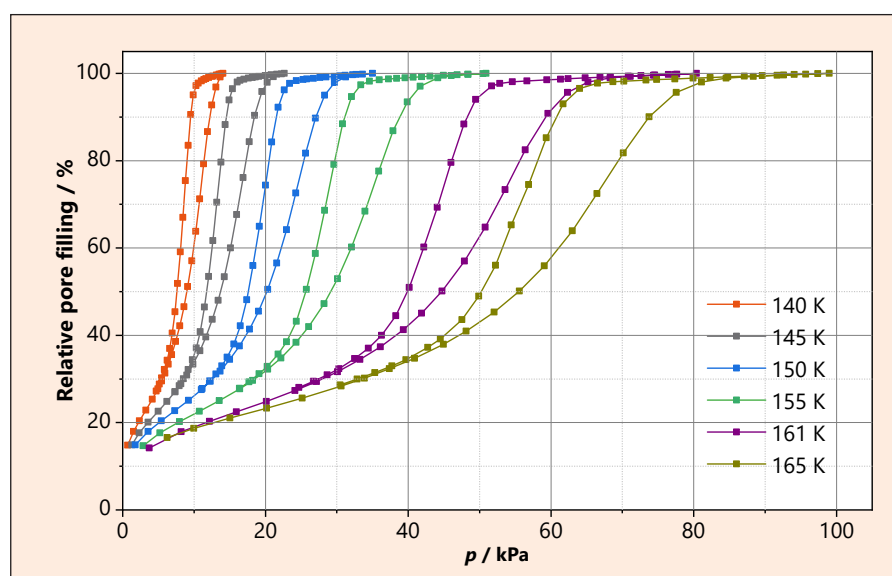


Figure 1 Example BAM P-115 standard material: relative pore filling of xenon at various temperatures vs. pressure.

Table 2 Change of SMSF with decrease of the temperature for xenon adsorption

Temperature / K	$p_0$ / kPa [1]	SMSF / -
165	101.3	1.0
161	81.8	1.2
155	54.9	1.8
150	37.1	2.7
145	24.5	4.1
140	15.7	6.5

However, the assumption of the existence of a liquid-like state on the surface of the material allows the adoption of the vapor pressure of the supercooled liquid, which accounts to 0.35 kPa. Due to this very low saturation pressure the number of free krypton molecules is drastically reduced. During the adsorption process in a volumetric manometric device the pressure change before dosing and after equilibrium is measured. If the initial pressure is low the relative change of that pressure due to adsorption is big, which allow the monitoring with a pressure sensor.

The SMSF for Kr@77.35 K accounts then to

$$PSF_{Kr,77.35K} = \frac{101.3 \text{ kPa}}{0.35 \text{ kPa}} = 289 \quad (3)$$

In contrast, the SMSF of N<sub>2</sub> at the same temperature is only 1. With other words, the sensitivity of a krypton adsorption is significantly more sensitive with respect to a N<sub>2</sub> adsorption experiment at 77.35 K. This can also be illustrated with a simple thought experiment. Let's assume a sample cell with a void volume of 20 cm<sup>3</sup> and a non-porous sample with only 1 m<sup>2</sup> of absolute surface in the measuring cell. At a relative pressure  $p/p_0$  of 0.2 the adsorbed volume for nitrogen and krypton is almost identical and accounts to  $V_{ads,N_2} = 0.287 \text{ cm}^3$  and  $V_{ads,Kr} = 0.222 \text{ cm}^3$  respectively. However, due to the higher saturation pressure of N<sub>2</sub> at 77.35 K with respect to Kr the volume of free gas molecules is significantly higher:

$$V_{free,N_2} = 20 \text{ cm}^3 - \frac{101.3 \text{ kPa} \cdot 0.2}{101.3 \text{ kPa}} \cdot \frac{273 \text{ K}}{77 \text{ K}} = 14.14 \text{ cm}^3 \quad (4)$$

$$V_{free,Kr} = 20 \text{ cm}^3 - \frac{0.35 \text{ kPa} \cdot 0.2}{101.3 \text{ kPa}} \cdot \frac{273 \text{ K}}{77 \text{ K}} = 0.046 \text{ cm}^3 \quad (5)$$



As a result, the dosed volume  $V_{dosed} = V_{adsorbed} + V_{free}$  for N<sub>2</sub> is around 300 times higher with respect to krypton. Finally, at the relative pressure of 0.2 at 77 K, around 98 % of N<sub>2</sub> and only 17 % of Krypton molecules remain un-adsorbed and that relatively large pressure change in case of krypton can be measured more accurately by a right low-pressure transducer.

From such a comparison between N<sub>2</sub> and Kr at 77.35 K, it can be deduced that the estimation of a sorption method sensitivity factor for defined adsorption measurement conditions could be an easy to use but also meaningful tool.

For all adsorptives at their boiling temperatures, a saturation vapor pressure near ambient pressure (1 atm = 1.013 bar = 101.3 kPa = 760 Torr = 14.7 psi) is present. In the same way that the SMSF for Kr at 77.35 K was calculated, the SMSF of Ar at 77.35 K can be determined using equation 2 and  $p_0$  value of the undercooled argon fluid.

$$PSF_{Ar,77.35K} = \frac{101.3 \text{ kPa}}{30.7 \text{ kPa}} = 3.3$$

Temperature not only affects the vapor pressure of the adsorptive but also on the number of gas molecules in the hot and

cold zones of the measuring cell. It was mentioned above that a small cold zone is preferable, as this reduces the dead volume. The physical reason for this is that density is temperature dependent and the gas molecules occupy a smaller volume in the cold. As an example, a warm zone volume of 20 cm<sup>3</sup> at 298 K and a cold zone volume of 5 cm<sup>3</sup> at 77.35 K is assumed. The total cell volume  $V_{cell} = V_{cold} + V_{warm}$  with  $V_{cold} = 5 \text{ cm}^3 \cdot 298 \text{ K} / 77 \text{ K} = 19.4 \text{ cm}^3$  therefore accounts to 39.4 cm<sup>3</sup>. If the measurement temperature and therefore the cold-zone temperature is increased to 273 K the total cell volume is only 25.5 cm<sup>3</sup> and therefore 35 % smaller. In other words: the temperature increase from 77.35 K to 273 K reduces the number of molecules in the cell by about one third. However, this advantage is small with respect to the reduction of  $p_0$  when the temperature is decreased.

As mentioned above, the accuracy and sensitivity of a sorption measurement depends on several factors and is not only related to the pore volume. As an example, the standard material BAM P-105 with a certified surface area of 197 m<sup>2</sup> g<sup>-1</sup> and an uncertainty of 4 m<sup>2</sup> g<sup>-1</sup> was measured with decreasing sample amount (Tab. 3) in order to reduce the available absolute

**Table 3** Example BAM P-105 standard material: N<sub>2</sub>@77K instrument test with 9 mm measuring cell diameter for small BET surface area

Type of measuring cell	Sample mass / g	BET surface area / m <sup>2</sup> g <sup>-1</sup>	Absolute BET surface in the measuring cell / m <sup>2</sup>
large bulb	0.2850	196.78	56.15
large bulb	0.0953	198.42	18.77
large bulb	0.0479	198.40	9.44
large bulb	0.0236	196.49	4.64
large bulb	0.0048	228.92	0.95
no bulb	0.0048	197.45	0.95



surface area. Down to an absolute surface area of about 4.5 m<sup>2</sup>, no influence of the large free space due to a large measuring cell could be detected. The threshold, however, is around 1 m<sup>2</sup> absolute surface area, as a reliable evaluation of the data is no longer possible due to the small pressure changes. However, by simply switching to an optimized measurement cell, accurate measurement and data reduction is possible as long as there is 1 m<sup>2</sup> of absolute surface area in the cell. If the cell contains less than 1 m<sup>2</sup>, Ar@77K may be fine to still measure reproducible BET surface areas, if there is even less absolute surface area in the cell, Kr@77K may be the right solution (Tab. 4).

However, a high SMSF is not the Holy Grail. Sometimes samples show a strong kinetic hindrance with conventional adsorptives due to surface effects or very narrow micropores. Such material properties can be responded to with the right choice of adsorptive and measurement temperature, which enables characterization. This is the case, for example, with CO<sub>2</sub>. Although a strong quadrupole moment is present, this molecule is used for the characterization of very small micropores, typically at 273 K. CO<sub>2</sub> has a p<sub>0</sub> of 3484 kPa (26142 mmHg) at this temperature, which according to equation 2 leads to a SMSF smaller than 1.

$$PSF_{CO_2,273K} = \frac{101.3 \text{ kPa}}{3484 \text{ kPa}} = 0.029 \quad (6)$$

**Table 4** Overview about challenges for samples with very low absolute surface area in a measuring cell, and their potential solution

Type of material	Measuring task	Potential solutions
coarse, non-porous powders, thin films or other material mixtures with very low pore content	determination of surface area	use of alternative measuring gases with low p <sub>0</sub> , e.g., Ar@77K, Kr@77K
coarse particles, thin films or other material mixtures with very low pore content	pore characterization	use of alternative adsorptives at temperatures with reduced p <sub>0</sub> value and liquid phase adsorbate for pore size distribution

**Table 5** Sorption method sensitivity factors (SMSF) of CO<sub>2</sub> measurements and maximum relative pressures p/p<sub>0</sub> for standard sorption instruments (101.3 kPa)

T / K	p <sub>0</sub> / kPa of undercooled CO <sub>2</sub> liquid	SMSF	Max. p / p <sub>0</sub> for 101.3 kPa devices
298	6421	0.016	0.02
273	3484	0.029	0.03
234	1036	0.100	0.10
195	188	0.540	0.54

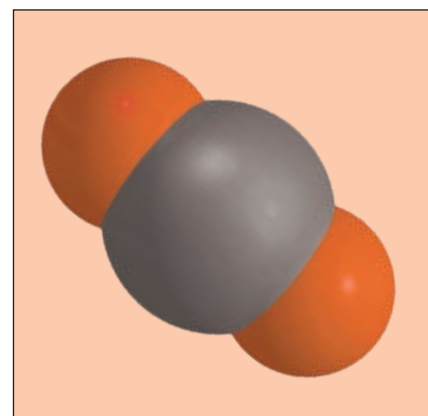
If the reciprocal is formed, it becomes apparent that a measurement of CO<sub>2</sub> at 273 K is 34 times less sensitive compared to a measurement of N<sub>2</sub> at 77.35 K. Additionally, a BET surface area evaluation is not possible, since a relative pressure of only 0.03 can be reached with a conventional adsorption device. As to see from Tab. 5, CO<sub>2</sub> might be alternatively measured at 234 K or 195 K to enable full data reduction possibilities.

### Summary

The sorption method sensitivity factor (SMSF) is an easy-to-use tool for the practical estimation of the sensitivity of an adsorptive-temperature-sorption method. If the SMSF increases significantly, as with Ar@77K, especially with Kr@77K, but also other adsorptives at relevant temperatures, such measurement can create the way to measure small surfaces areas in a reproducible way. On the other hand, small values may avoid problems of low temperatures near 77 K, as can be seen with the alternative CO<sub>2</sub>@195K or CO<sub>2</sub>@273K in case of kinetic hindrances with N<sub>2</sub>@77K or Ar@87K. Further 3P studies will deal with more alternative adsorptives to prevent some actual limitations of the standard adsorptives N<sub>2</sub>, Ar, or CO<sub>2</sub>.

### References

- [1] M. P. Freeman, G. D. Halsey, J. Phys. Chem., 60, 1119 (1956)
- [2] R.A. Beebe, J. B. Beckwith, J. M. Honig, J. Am. Chem. Soc. 1945, 67, 9, 1554-1558
- [3] ISO 9277:2010: Determination of the specific surface area of solids by gas adsorption – BET method
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# How isothermal is a sorption isotherm?

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## Introduction

If a solid surface is brought into contact with gas molecules, some of the gas molecules adsorb on the surface or in the pores (Fig. 1). The free molecules in the fluid phase are called adsorptive, but when the same molecules are adsorbed on the surface, it is called adsorbate, which is often assumed to be liquid-like.

Since this process is intensified with increasing relative pressure of the gas  $p/p_0$ , it is promoted by lowering the temperature and the adsorption process is determined by the difference in chemical potential  $\Delta\mu$  according to

$$\Delta\mu = (\mu_a - \mu_0) = RT \ln \frac{p}{p_0} \quad (1)$$

where  $\mu_a$  is the chemical potential of the adsorbate film and  $\mu_0$  the chemical potential of the bulk liquid. This potential difference is related to the ratio of the adsorptive pressure  $p$  and the saturation vapor pressure of the measuring gas  $p_0$ ,  $R$  is the universal gas constant and  $T$  the measuring temperature. The adsorbed amount is measured as function of  $T$ ,  $p$  and  $p_0$ . In this article, we have a look at the effects of the temperature parameter on the measurement results.

Nitrogen adsorption at the boiling point of liquid nitrogen,  $N_2@77K$ , has become the established method for quality control. However, scientific surface and pore investigations are increasingly being performed with different adsorptives at higher temperatures, such as  $Ar@87K$ ,  $CO_2@195K$  or  $CO_2@273K$ . One question for every measurement is the accuracy of the used measuring temperature. As example in technical articles, the specification of the experimental temperature with 77.35 K as the boiling temperature of

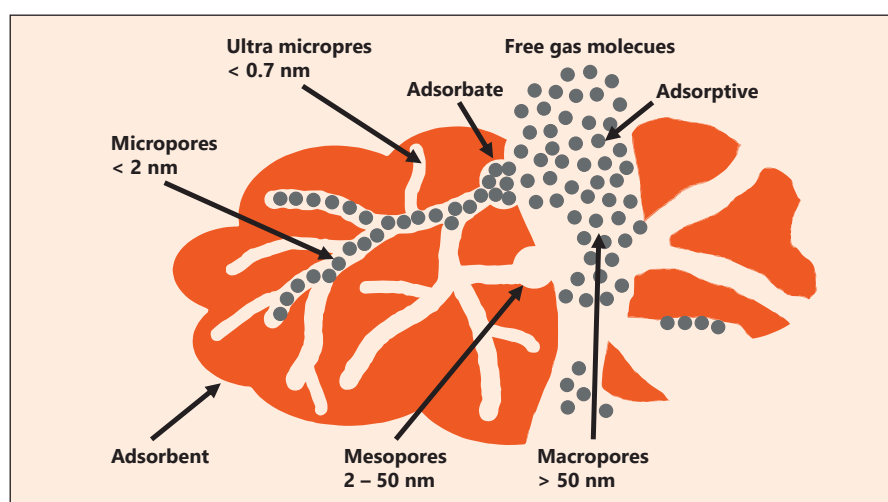


Figure 1 Schematic sorption process

liquid nitrogen suggests an unrealistic accuracy of two decimals if a standard liquid nitrogen dewar is applied. In scientific articles, however, the adsorption temperature of  $N_2$  measurements is often given as 77 K, 77.3 K, 77.4 K, 77.5 K or 78 K. Few users are aware that their reported temperature could very likely vary by as much as 0.5 K because of the dependence of the boiling temperature both from the purity of the liquid nitrogen, but mainly from the ambient pressure. Not only must the temperature dependence of the saturation vapor pressure be evaluated for very accurate results, but also the exact measuring temperature and its constancy must be known over the complete measuring time. So far, this is the state of the art for relating thermostats with temperature accuracies of 0.01 K close to room temperature and should be aimed at for other temperature ranges as well. The new developed cryoTune 77 option offers an easy-to-handle technical solution for such significant temperature stability improvement for accurate sorption studies.

## The inaccurate temperature of liquid nitrogen

The boiling temperature of a pure liquid, such as water or liquid nitrogen, depends on the ambient pressure. Due to that, the saturation pressure  $p_0$  must be measured in parallel with the actual standard  $N_2@77K$  measurement. This would not be necessarily in case of a constant measuring temperature. The literature boiling temperature of liquid nitrogen of 77.35 K is only right in case of standard ambient pressure of 101.325 kPa, which is rarely present. Frankly, a published temperature of 77.35 K for such measurements pretends an accuracy that is not true. Fig. 2 shows ambient air pressures in different locations in 2022, and only the ambient pressure fluctuations for our own laboratory in Leipzig/Germany in 2022 cause temperature swing in a pure liquid nitrogen bath between 77.15 and 77.58 K. In other words: if different worldwide laboratories measured the same sample on one day, they measure at different temperatures. Additionally, the measuring temperatures change, e.g.,

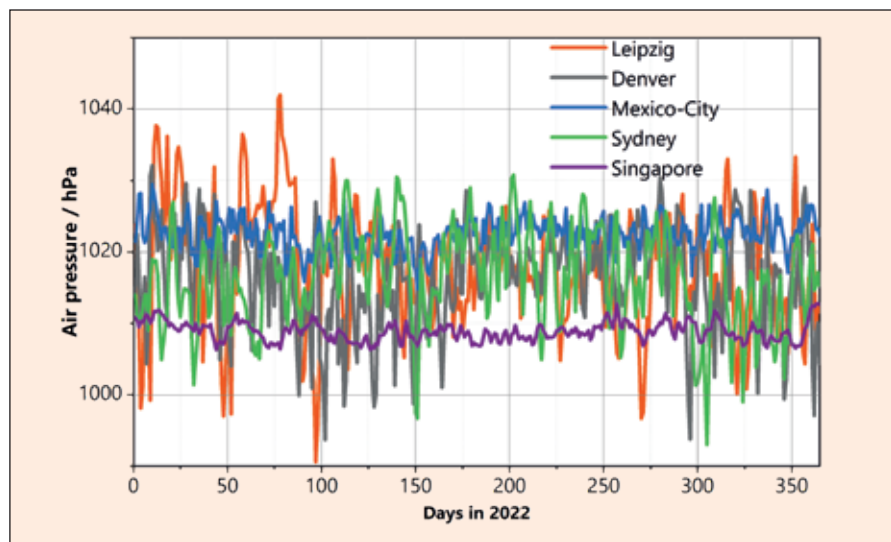


Figure 2 Ambient air pressures in different spots in 2022

during a 2-days micropore-mesopore measurement in one single lab because of the ambient pressure changes.

We can conclude that a conventional  $N_2@77K$  isotherm is rather not strictly isothermal, but that effect can be compensated for  $N_2@77K$  with parallel measurements or calculations of the  $p_0$ -value from the real temperature in the coolant.

### Temperature dependent differences in sorption results

Accurate control of the adsorption temperature is particularly important when the vapor pressure of the corresponding adsorptive cannot be measured. In the following, we will give two examples where the actual  $p_0$  cannot be measured, namely  $Kr@77K$  and  $H_2@77K$ .

Hydrogen is known to be supercritical above 34 K, which is why no  $p_0$  exists or can be measured. This means that any ambient pressure and/or temperature fluctuations of the liquid nitrogen between individual measurements cannot be controlled and, if necessary, compensated for. It is therefore important to be able to control the temperature reproducibly. The influence of a temperature difference of 0.5 K on the measurement can be seen in Fig. 3. Here,  $H_2$  adsorption was performed on Zeolite 5A at 77.50 K and 78.00 K by use of a cryoTune 77 option (remark: we give the two temperature decimals for the cases of constant temperatures better than 0.01 K). The uptake difference is only  $2.5\text{ cm}^3\text{ g}^{-1}$  or 2 % respectively, in this spe-

cific case. This may seem negligible at first, but this is a random and especially avoidable error, which makes a comparison between different materials measured in different labs with a standard liquid nitrogen coolant difficult.

In addition, we also collected an isotherm at 90 K, also shown in Fig. 3. By increasing the adsorption temperature by 12 K, the total uptake is reduced by  $35\text{ cm}^3\text{ g}^{-1}$  with respect to the measurement at 78 K. This further highlights the great impact of the adsorption temperature on the adsorption behavior of porous materials.

Another example is  $Kr@77K$ . Such a measurement is performed when the sensitivity of a "normal"  $N_2@77K$  measurement is not sufficient to perform a complete material characterization (see also article

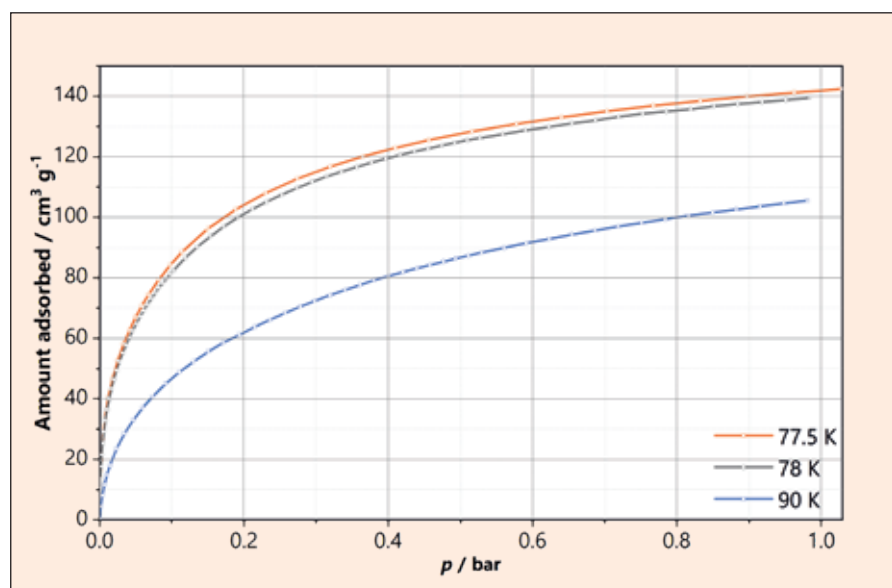


Figure 3 Accurate  $H_2$  sorption measurements at 77.50 K, 78.00 K and 90 K on Zeolite 5A

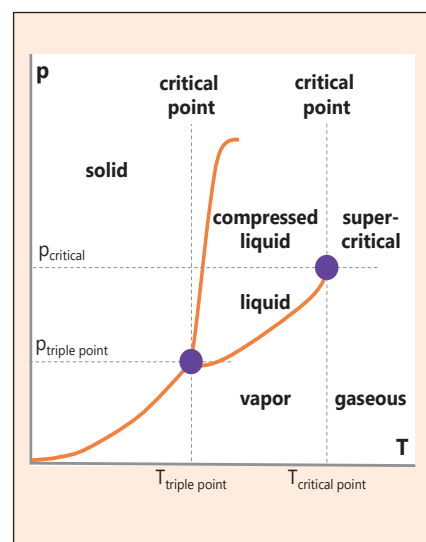


Figure 4 Schematic phase diagram of a substance

"The influence of the sorption method sensitivity factor (SMSF) to gas sorption measurements" on page 15). If a measurement is conducted with krypton around 77 K, the measurement will be well below the triple point of the gas. This means that physically there is no longer a transition between the vapor and the liquid phase, but that the vapor becomes solid directly by resublimation as the pressure increases (Fig. 4).

If a measurement is carried out with krypton in liquid nitrogen, only the vapor pressure of krypton ice can be determined. However, the ISO 9277 norm recommends a  $p_0$ -value of the so-called undercooled krypton liquid phase at 77.35 K of  $p_0 = 0.35\text{ kPa}$  (2.63 Torr). But this phase is only present inside the pores, and there-



fore, a  $p_0$  measurement is not possible. Additionally, the value of 0.35 kPa is calculated and only valid for exactly 77.35 K. However, if a closer look is taken on Fig. 2, one can see that for example in Leipzig/Germany the air pressure fluctuates around 5 % only within two weeks. With other words also the boiling temperature of liquid nitrogen deviates between 77.15 and 77.58 K.

The influence of air pressure becomes even clearer when an isotherm that has been measured is evaluated fictitiously with different air pressures. For this purpose, the standard material BAM-101 was measured with krypton at a temperature of 78 K (Fig. 5) and the surface area was determined using the BET equation (Tab. 1). Subsequently, based on the air pressures, fictitious  $p_0$  values were used for the evaluation. The results show that solely due to the fluctuation of the air pressure an error of about 5 % occurs in the evaluation of the data. This clearly shows that a control of the temperature, especially for measurements where the vapor pressure cannot be determined experimentally, is essential for a reproducible and reliable measurement. 3P Instruments has therefore extended its cryoTune portfolio to reliably control the measurement environment near the boiling point of liquid nitrogen (Fig. 6).

## Conclusions from truly isothermal sorption measurements for further scientific studies

To optimize the accuracy of scientific sorption measurements, a thermostatic system at constant temperature over the complete measuring time of an isotherm should be used. For exact scientific sorption studies, a measuring system with precise temperature control over the entire measuring time of an isotherm is necessary. In this way, both the measurement temperature and the saturation vapor pressure of the adsorptive are constant over the entire measurement time. A temperature constancy of better than 0.01 K has an influence on the accurate calculation of further texture parameters based on temperature-dependent material data. Tab. 2 lists such temperature-dependent parameters for precise data evaluation.

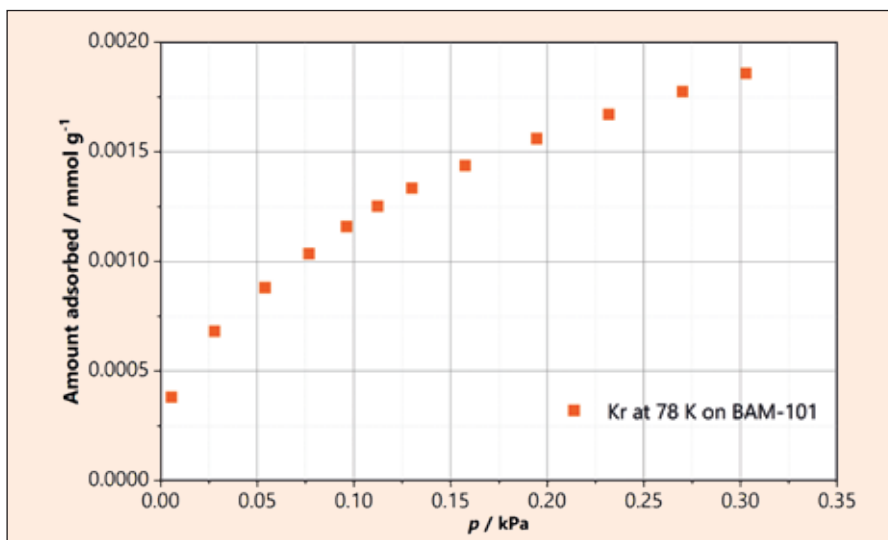


Figure 5 Krypton isotherm at 78 K on BAM-101

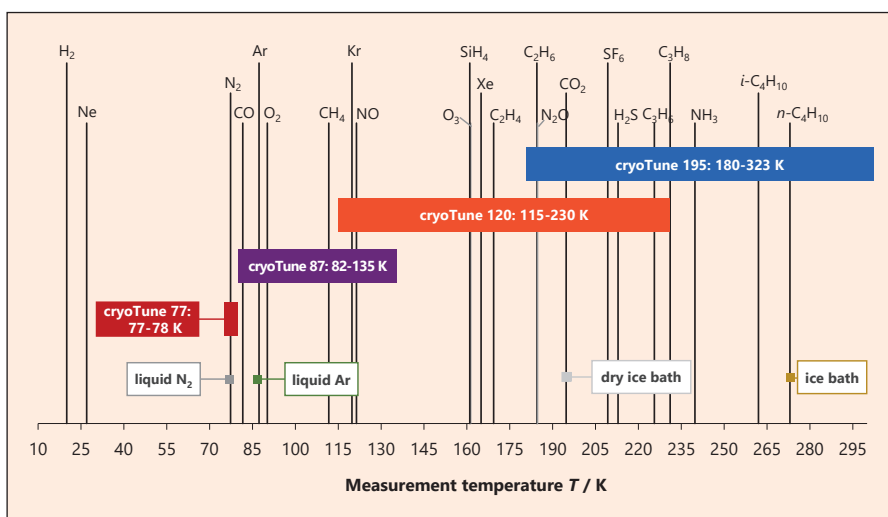


Figure 6 Boiling points and possible measuring temperatures of various adsorptives including the typical measurement ranges of the cryoTune models

Table 1 Temperature and pressure fluctuations and resulting surface areas of BAM-101

Air pressure / hPa	$T_{LN_2}$ / K	$P_{0,Kr}^*$ / kPa	$SA_{BET}$ / $m^2 g^{-1}$
1042	77.58	0.371	0.173
990.6	77.15	0.335	0.164
1016.7	77.38	0.355	0.169
irrelevant	78	0.4053	0.177

Table 2 Temperature dependent parameters for sorption data reduction

Parameters	Use of the parameter
$p_0$ -saturation pressure	calculation of $p/p_0$ dependent parameters such as BET surface area or BJH pore size distribution
Non-ideality factor	calculation of the accurate dosing volumes as basis to calculate accurate volumes adsorbed
Cross sectional areas	surface calculations such as BET method
Liquid density	calculation of pore volumes and of cross-sectional areas as basis of surface area calculations

# 3P Instruments starts new collaboration with Rubolab GmbH

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## Introduction

We are very pleased to announce that 3P Instruments just started a sales and service collaboration with the Rubolab GmbH. The company, founded in 2014, is specialized in high pressure adsorption techniques, including dynamic, volumetric and gravimetric measuring instruments. In combination with our existing instrument portfolio in the field of physi-, vapor- and chemisorption, it adds unique measuring capabilities for researchers who are also working on even highest pressure gas storage/ gas separation processes. From now on even up to 700 bar! In this news, we present two important instrument series.

## Magnetic Suspension Balance

The magnetic suspension balance technology allows high resolution mass determination under extreme conditions. An industrial microbalance is located outside the cell. Thanks to contactless magnetic suspension coupling, mass changes within the pressurized cell can be determined. When performing a measurement, the sample whose mass change is being measured is attached to a permanent magnet. The actual position is detected and controlled via a high-performance PID controller. In order to establish a free levitation position for permanent magnet and measurement object, voltage is applied to an electromagnet outside of the measurement cell. This allows the sample mass to be measured contact free under extreme conditions. Load decoupling allows the object weight being measured to be subtracted for taring or calibrating the measurement signal. In this case, only the permanent magnet remains in levitation position (zero-point position). When the measuring point is selected, the measurement object is lifted and corresponding weight is detected by the microbalance. The measurement objects can be a crucible, containing sample material, for example being used to measure adsorption isotherms or catalytic reactions. In addition, the measurement object could also be sinker with calibrated volume for high accurate density measurement of the sinker surrounding fluid. The RuboSORP Magnetic Suspension Balance is an advanced technology for measuring the mass of two measurement objects at the same time.

The unique technology ensures measurements within a pressure range of up to 700 bar and a maximum temperature of 400 °C. The measurement cell and all components in fluid contact are resistant to aggressive and toxic atmospheres. Due to this, a variety of different fluids can be used, e. g., inert gas, aggressive and toxic gases, supercritical fluids, flammable and explosive gases, gas mixtures and vapor.



Figure 1 RuboSorb MSB

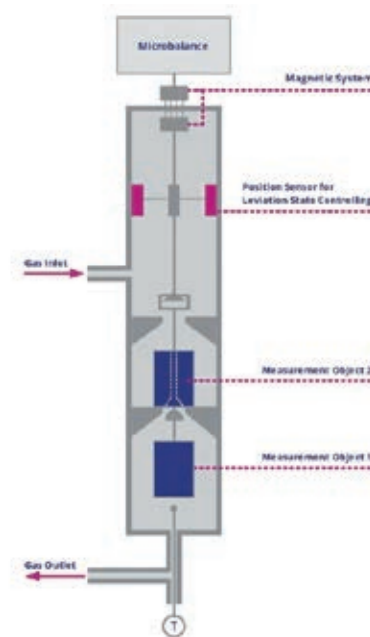


Figure 2 Experimental Setup

## Highlights of the Magnetic Suspension Balance

### ■ Simultaneous Measurement of two Samples

The magnetic suspension balance simultaneously measures two different sample materials or sinker (dual sample version).

### ■ Forced Flow Through Measurement Conditions

The magnetic suspension balance can be equipped with a forced flow through sample crucible which improves interaction between sample and surrounding fluid atmosphere.

### ■ Most Advanced Magnetic Suspension Balance Technology

The balance is equipped with unique features, e. g., a self-optimizing Magnetic Suspension Balance controller as well as a failsafe high speed ethernet interface.

### ■ Integrated Calculation of Measurement Uncertainty

The software which will be used for controlling RuboSORP Magnetic Suspension Balance contains an integrated calculation of measurement uncertainty according to GUM guidelines (guide to the expression of uncertainties in measurement). This allows a more holistic view of data and best level of scientific work.

## Volumetric High-Pressure Adsorption

The manometric method is a well-established technique to measure sorption isotherms. Major advantages of manometric instruments are short measurement times and a high grade of automation. The RuboSORP MPA series of manometric measuring instruments are specially designed for rapid characterization of multiple sample materials. There are three different versions, which differ in the number of sample ports: MPA-1 with only one sample, MPA-3 with three different sample ports and consequently the MPA-5 with 5 different sample ports. The max. possible pressure range is up to 200 bar. The temperature range of the RuboSORP MPA standard configuration is between 10 °C and 450 °C.

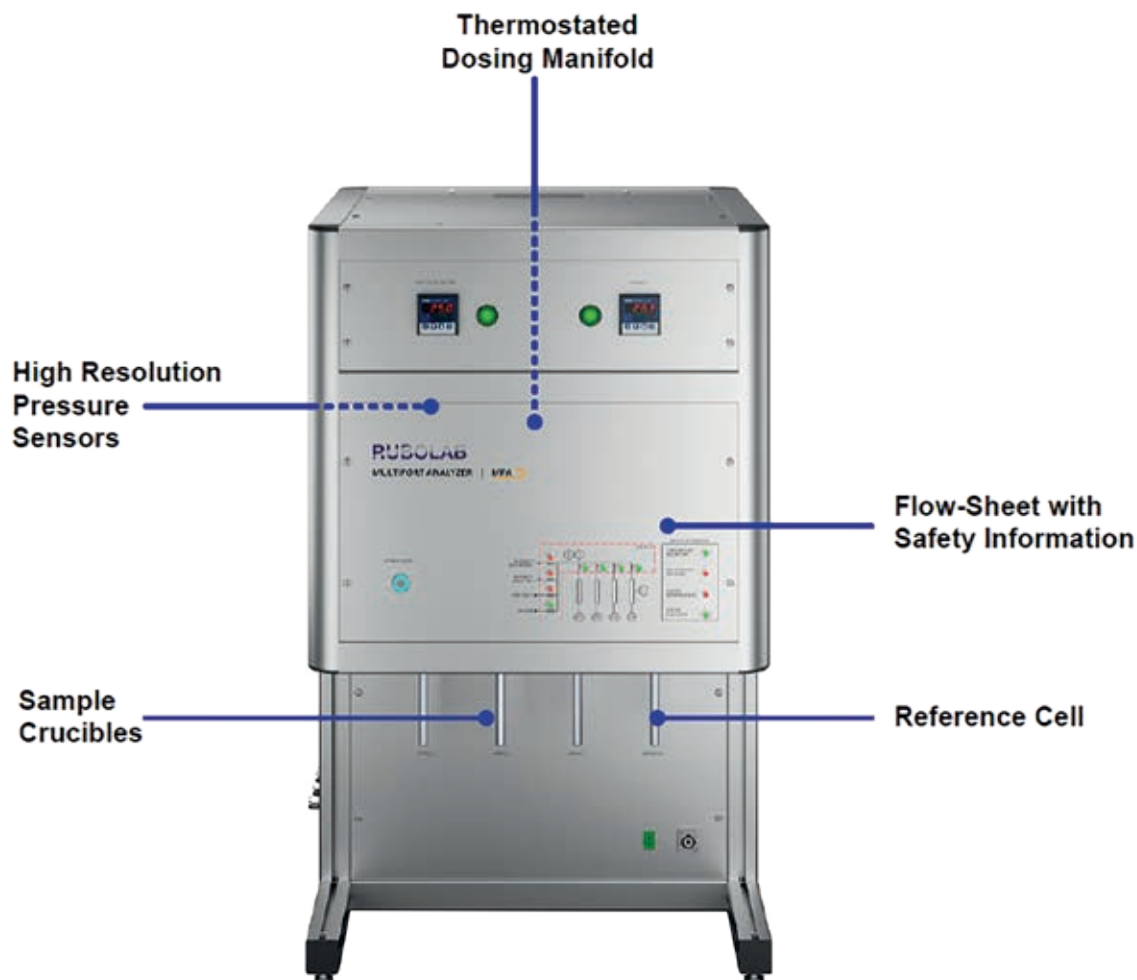


Figure 3 RuboSORP MPA

# New Altamira Series for Catalyst Characterization

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Founded in 1984, Altamira Instruments is a manufacturer and supplier of chemisorption and bench-scale micro-reactor systems for industrial and research applications. We are glad to introduce the next generation of Altamira's catalyst characterization family. The Altamira AMI-400 series are fully automatic catalyst characterization devices designed based on the concept of unattended operation, specifically for the needs and applications of catalyst researchers. It features highly reliable test control components, comprehensive data processing software, and can provide the necessary kinetic parameters for characterizing catalysts. The overall design of the AMI-400 is more compact, smaller in size, more economical, and provides rapid catalyst characterization capabilities at the same time. These instruments are designed for customers with limited budgets and conventional application requirements.

The basic AMI-400TPX provides all temperature programmed analysis techniques such as TPR/TPO/TPD. However, it can be upgraded with an injection loop to enable pulse chemisorption experiments as well as dynamic BET analysis. The AMI-400PRO adds the capability of automated gas blending and vapor experiments thanks to the build-in saturator.



Figure 1 Altamira History



## Highlights

- High-precision electronic mass flow controllers which ensure a stable baseline with changing temperatures and quality of data
- Use of 1/16" stainless steel tubing to minimize dead volume
- A clamshell furnace with adjustable mounting to ease insertion and removal of samples
- Capability of heating catalyst samples to 1,200 °C with linear temperature ramps from 1 °C to 50 °C per minute
- A sub-ambient temperature option which provides the capability to operate linearly, between -130 °C and 1,200 °C
- Automatic air-cooling of the furnace which is provided to reduce the time between experiments
- A universal temperature zone which controls the temperature of all valves and lines downstream of the reactor. The temperature of this zone is controlled by the software and serves to prevent both condensation and retention of the adsorbate in valves and lines upstream of the detector.
- A saturator is provided as an option to suffuse the treatment gas with liquid vapors.
- A highly linear thermal conductivity detector (TCD) is standard. The resolution of the TCD is operator defined and controlled by the software.
- A choice of TCD filaments is offered to maximize sensitivity and chemical compatibility of the instrument.



Figure 2 AMI-400TPX



Figure 3 AMI-400PRO

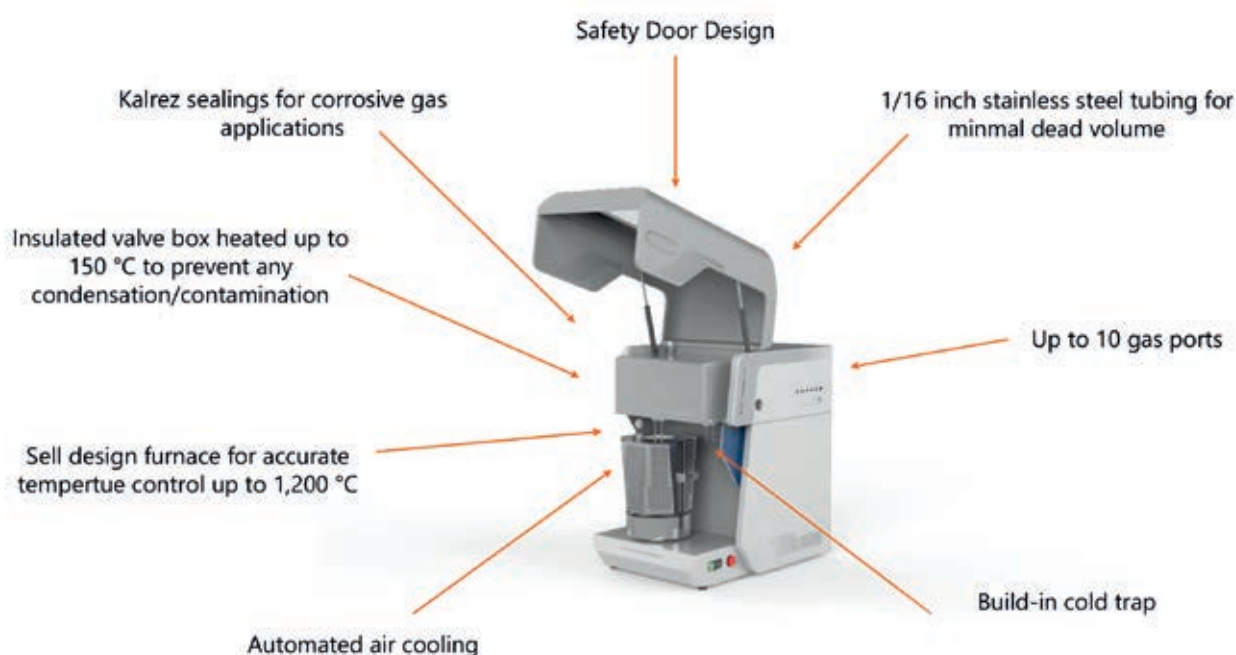


Figure 4 AMI-400TPX functions

## Invitation to the Adsorption event series and review of our Adsorption Week 2023

Dr. Denise Schneider, [denise.schneider@3P-instruments.com](mailto:denise.schneider@3P-instruments.com)

### Invitation to Adsorption Week 2024

Our next hybrid annual meeting on adsorption & characterization of porous materials will take place on 14<sup>th</sup> – 16<sup>th</sup> May 2024. Registrations for online participation or on site open from December 2023 at

[www.3P-instruments.com/events](http://www.3P-instruments.com/events)

Not sure what to expect?  
Read the review of 2023  
(see next page).



### Free webinars on Gas Adsorption - "Sorptions World"

The webinars are aimed at anyone interested in sorption worldwide, regardless of the analytical instrumentation. You can't attend?

No problem, you will receive the video recording afterwards!

- 19<sup>th</sup> September 2023      The limits of surface and pore volume characterization
- 22<sup>nd</sup> November 2023      Community Meeting with external talks
- January 2024              Aspects of accurate error analysis for gas sorption studies
- March 2024                Investigation of completely new possibilities of sorption measurements with alternative adsorptives

The overview and registration can be found at [www.3P-instruments.com/events](http://www.3P-instruments.com/events)



# Review of our conference "Adsorption Week" April 25<sup>th</sup> – 27<sup>th</sup> 2023

## Annual Conference on Adsorption & Characterization of Porous Materials

For the 6<sup>th</sup> time already, the Adsorption Week was organised by the Institute for Non-Classical Chemistry e.V. (INC) and 3P Instruments - again with complete success! We welcomed over 150 international guests from 22 countries to our two-day hybrid conference full of exciting, inspiring, and also scientifically challenging lectures.

Among others, we had the pleasure to welcome Prof. G. Maurin from Montpellier, Prof. J. Denayer from Brussels, Prof. M. Oschatz from Jena, Prof. S. Henke from Dortmund, Prof. G. Gor from New Jersey and Prof. S. Lucena from Cear  (remotely) to Leipzig. In addition, the program was rounded off by young researchers from all over Europe and representatives from Total, Shell, TLK Energy and Hitachi Zosen Inova, who spoke about current challenges in tackling the climate crisis. In the evening of the first day, some young scientists took the opportunity to discuss their current projects with an interested and stimulating

audience during a poster session. The outstanding posters were well received and many expert discussions flared up and networking points were created.

On the third day, Dr. Sebastian Ehrling and Dr. Denise Schneider (both 3P) had the opportunity to discuss with young scientists from Germany, Portugal, Norway and Great Britain about their current scientific tasks. In a workshop, ways to present scientific results in lectures were showed. In a flash talk karaoke session, all participants surpassed themselves and managed to present the project of another person in a 3-minute flash talk with only 30 minutes of preparation time. Hats off to that – we were very impressed!

Thanks to all lecturers, the hotel venue and all online and on-site participants! We really liked the good mood and the familiar atmosphere.

Here are some impressions:



# LabSPA - Excerpt from our list of contract analyses



## Particle size and shape of powders and dispersions: wet and dry

Order-No.	Parameter/ method	Description
140056	Particle size distribution / Laser diffraction method – wet measurement in water	Determination of particle size distribution according to ISO 13320-1 in water, measuring range 0.01 – 3500 µm, the specific experimental conditions (tap water or deionized water, ultra sound treatment, dispersion additives) are chosen after consultation
140057	Particle size distribution / Laser diffraction method – dry measurement in pressurized air	Determination of particle size distribution according to ISO 13320-1 by means of dry dispersion with pressurized air, measuring range 0.1 – 2600 µm
140058	Particle size distribution / Laser diffraction method – wet measurement in isopropanol	Determination of particle size distribution according to ISO 13320-1 in isopropanol, 0.01 – 3500 µm
140059	Particle size distribution / Laser diffraction method - other dispersion media	Determination of particle size distribution according to ISO 13320-1 in alternative liquids in consultation, measuring range 0.01 – 3500 µm
140258	Particle size analyses / Method development laser diffraction – wet or dry measurement	Optimized application of the laser diffraction to investigate the most suitable dispersion and measurement parameters for a certain material
140060	Particle size distribution/ Combined method laser diffraction and dynamic image analysis – wet measurement	Determination of particle size distribution in liquids, measurement range 0.01 – 3500 µm, beneficial especially for broad size distributions up to the mm range, the specific experimental conditions (dispersion medium, ultra sound treatment, dispersion additives) are chosen after consultation, incl. exemplary images
140259	Particle size distribution / dynamic image analysis - dry	Determination of particle size and shape analysis acc. to ISO 13322 dry; dispersing with vibratory feeder and free drop chute, measuring range 30 µm – 10 mm
90006	Particle size distribution / Acoustic spectroscopy – wet measurement, > 5 nm	Determination of particle size distribution by means of ISO 20998-1 in liquid medium, measurement in original sample concentration up to 50 Vol.-%, measurement range 5 nm – 1000 µm
140135	Particle size / Dynamic light scattering (DLS resp. PCS)	Determination of particle size according to ISO 22412 in liquid medium, measuring range 0.3 nm – 15.0 µm (dependent on sample)
140369	Particle size as function of temperature / Dynamic light scattering (DLS resp. PCS)	Determination of particle size according to ISO 22412 in liquid medium as function of temperature, measuring range 0.3 nm – 15.0 µm (dependent on sample)
140061	Particle size distribution and shape analysis/ Image analysis or/and laser – wet or dry measurement	Comprehensive particle size and shape analysis, determination in liquid or dry, maximum measurement range for particle size 0.01 – 10000 µm, 4 – 10000 µm for particle shape



## Zeta potential, electrical conductivity and permittivity of liquids and dispersions

Order-No.	Parameter/ method	Description
140370	Zeta potential / Electrophoretic Light Scattering (ELS)	Determination of the zeta potential of dispersions acc. to ISO 13099-3 in polar liquids, measuring of dispersions in original concentration up to ca. 50 Vol.-%
90007	Zeta potential / Electro acoustic	Determination of zeta potential according to ISO 13099-2 in liquid medium
140371	Zeta potential as function of temperature / Electrophoretic Light Scattering (ELS)	Determination of zeta potential according to ISO 13099-2 in liquid medium as function of temperature
140372	Zeta potential titration / Electrophoretic Light Scattering (ELS)	Determination of zeta potential according to ISO 13099-2 in liquid medium as a function of pH or amount of additive
90008	Zeta potential as function of the pH-value (titration)/ Electro acoustic	Determination of the zeta potential of dispersions acc. to ISO 13099-3 as function of the pH-value or of additives in polar liquids, evaluation of the isoelectric point, measuring of dispersions in original concentration up to ca. 50 Vol.-%
140373	Molecular weight / Static light scattering (SLS)	Determination of molecular weight in liquid medium using debye-plot, measuring range 342 Da – $2 \times 10^7$ Da (sample dependent)
90009	Dielectrical permittivity	Determination of the dielectric constant as measure of the permittivity of a dispersion or homogenous liquid to an electrical field
97239	Electrical conductivity of liquid systems	Determination of the electrical conductivity of non-polar and polar liquids and dispersions, $10^{-11}$ – $10^{-4}$ S/m

## Stability of liquid dispersions: emulsions, suspensions, foams

Order-No.	Parameter	Description
90010	Stability/ Multiple light scattering	Stability analysis of emulsions and suspensions acc. to ISO TR 13097, temperature range 4 – 80° C

## Dispersion projects

Order-No.	Parameter	Description
97732	Formulation of dispersions	Formulation/Deflocculation, Creation of a work instruction to stabilize or disperse a dispersion, optimization of additives and solids contents, and optimization of the dispersing conditions (deflocculation method like ultrasonic treatment, stirring etc.)
97734	Nano-material test regarding EU definition	Nano-material test regarding EU definition 2011/696/EU using the LabSPA-Nano-method
97747	Nano-material test regarding EU definition-routine	Nanomaterial test regarding EU definition 2011/696/EU using the LabSPA-Nano-method based on a developed SOP

## Flowability, compressibility and further specific properties of powders

Order-No.	Parameter	Description
140016	Angles of repose and collapse of powders	Determination of angles of repose and collapse of powders according to ASTM D 6393-08/D 6393-14
140017	Dispersibility, uniformity and cohesion of powders	Determination of dispersibility, uniformity and cohesion of powders according to ASTM D 6393-08/D 6393-14
140018	Flat plate angle (angle of spatula) of powders	Determination of flat plate angle of powders according to ASTM D 6393-08/D 6393-14
140019	Compressibility of powders	Determination on Powder analyzer acc. to ASTM D 6393-08/ D 6393-14 resp. ISO 3953:1993 Includes tap- and bulk density
140020	Voidage of powders	Determination of voidage of powders according to ASTM D 6393-08/D 6393-14
140344	Flowability of metal powders	flowability measurement of metal powders through a defined funnel geometry, 3 repeats, according to ISO 4490-2008
140021	Flowability and floodability indices of powders	Determination of flowability and floodability indices of powders according to ASTM D 639308/D 6393-14 Includes angles of repose, angle of collapse, dispersibility, uniformity, cohesion, flat plate angle, voidage, flowability and floatability indices of powders

## Specific surface area (BET-surface area) of powders and porous solids

Order-No.	Parameter	Description
170158	Multipoint-BET with nitrogen	Specific surface multipoint-BET-analysis by nitrogen adsorption at 77 K, acc. to ISO 9277 (volumetric method), standard is 5-point-measurement (alternative on demand), requires at least 1 m <sup>2</sup> absolute sample surface area in the sample cell
170271	Multipoint-BET with argon	Specific surface multipoint-BET-analysis by argon at 87 K, acc. to ISO 9277 (volumetric method), standard is 5-point-measurement (alternative on demand), requires at least 1 m <sup>2</sup> absolute sample surface area in the sample cell
170159	Multipoint-BET with carbon dioxide, 273 K	Specific surface multipoint-BET-analysis by carbon dioxide adsorption at 273 K, acc. to ISO 9277 (volumetric method), standard is 5-point-measurement (alternative on demand), requires at least 1 m <sup>2</sup> absolute sample surface area in the sample cell
170272	Multipoint-BET with carbon dioxide, 195 K	Specific surface multipoint-BET-analysis by carbon dioxide adsorption at 195 K, acc. to ISO 9277 (volumetric method), standard is 5-point-measurement (alternative on demand), requires at least 1 m <sup>2</sup> absolute sample surface area in the sample cell
170161	Multipoint-BET with krypton (for small surfaces)	Specific surface multipoint-BET-analysis with krypton adsorption at 77 K, acc. to ISO 9277 (volumetric method), standard is 5-point-measurement (alternative on demand), recommended method for absolute sample surface areas smaller than 1 m <sup>2</sup> in the sample cell
170162	STSA surface area for the characterization of carbon blacks	STSA surface area as specifically determined external surface of carbon black samples acc. to ASTM D 6556 (volumetric method), with additional determination of the BET surface area
170163	Micropore surface / Micropore volume	Micropore surface area and volume with nitrogen adsorption at 77 K, evaluation acc. to t-method or Dubinin-Radushkevich acc. to DIN 66135-3 (volumetric method) and BET surface area (ISO 9277)

### Pore volume, pore size, pore size distribution (Hg-Pososimetry)

Order-No.	Parameter	Description
90015	Pore size distribution / Pore volume	Hg-intrusion and extrusion: Measurement range ca. 1000 $\mu\text{m}$ – 0,0036 $\mu\text{m}$ pore diameter, pore volume and pore size distribution acc. to ISO 15901-1
90020	Extended porosimetry	Hg-intrusion and extrusion: Measurement range ca. 1000 $\mu\text{m}$ – 0,0036 $\mu\text{m}$ pore diameter, pore volume and pore size distribution acc. to ISO 15901-1, additional determination of raw density and porosity [%]

### Pore volume, pore size, pore size distribution (gas adsorption)

Order-No.	Parameter	Description
170165	Standard mesopore analysis, N <sub>2</sub> 77 K (BJH-method)	Determination by nitrogen adsorption at 77 K, 20 points adsorption plus 35 points desorption, max. detectable pore diameter ca. 0.4 $\mu\text{m}$ (limited by the method of gas sorption), BJH-pore size distribution (DIN 66134), alternative DFT-evaluation, pore volume, BET-surface area (ISO 9277)
170274	Standard mesopore analysis, Ar 87 K (BJH-method)	Determination by argon adsorption at 87 K, 20 points adsorption plus 35 points desorption, max. detectable pore diameter ca. 0.4 $\mu\text{m}$ (limited by the method of gas sorption), BJH-pore size distribution (DIN 66134), alternative DFT-evaluation, pore volume, BET-surface area (ISO 9277)
170166	High resolution mesopore analysis, N <sub>2</sub> 77 K	Determination by nitrogen adsorption at 77 K, 40 points adsorption plus 39 points desorption, max. detectable pore diameter ca. 0.4 $\mu\text{m}$ (limited by the method of gas sorption), BJH-pore size distribution (DIN 66134), alternative DFT-evaluation, pore volume, multipoint-BET-surface area (ISO 9277)
170275	High resolution mesopore analysis, Ar 87 K	Determination by argon adsorption at 87 K, 40 points adsorption plus 39 points desorption, max. detectable pore diameter ca. 0.4 $\mu\text{m}$ (limited by the method of gas sorption), BJH-pore size distribution (DIN 66134), alternative DFT-evaluation, pore volume, multipoint-BET-surface area (ISO 9277)
170167	Micropore analysis	Determination by nitrogen adsorption at 77 K or carbon dioxide at 273 K, BET (ISO 9277) and pore volume, depending on sample material and customer requirement the most suitable micropore evaluation is applied (DR, DA, HK, SF, DFT, GCMC), (DIN 66135, part 1 to 4)
170276	Micropore analysis, Ar	Determination by argon at 87 K or carbon dioxide at 195 K, BET (ISO 9277) and pore volume, depending on sample material and customer requirement the most suitable micropore evaluation is applied (DR, DA, HK, SF, DFT, GCMC), (DIN 66135, part 1 to 4)
170168	Micropore and mesopore analysis, N <sub>2</sub>	Determination by nitrogen sorption at 77 K, ca. 70 points adsorption plus ca. 20 points desorption, BET (ISO 9277), pore volume and mesopore distribution (DIN 66134), depending on sample material and customer requirement the most suitable micropore evaluation is applied (DR, DA, HK, SF, DFT, GCMC), (DIN 66135, part 1 to 4)
170278	Micropore and mesopore analysis, Ar	Determination by argon adsorption at 87 K, ca. 70 points adsorption plus ca. 20 points desorption, BET (ISO 9277), pore volume and mesopore distribution (DIN 66134), depending on sample material and customer requirement the most suitable micropore evaluation is applied (DR, DA, HK, SF, DFT, GCMC), (DIN 66135, part 1 to 4)

# Your partner in particle characterization


3P Instruments has over 30 years of profound expertise in the characterization of emulsions and dispersions, of particles and powders as well as surfaces and pores.



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