

# PARTICLE WORLD

Technical Papers  
of 3P Instruments  
EDITION 20  
SEPTEMBER 2019

**Interview** with the CEO of 3P Instruments  
about the latest developments

**Fast determination of stability  
and packing in inkjet inks**  
Examination of different pigments

**Overview contract analyses – LabSPA**  
(Lab for Scientific Particle Analysis)

## **Particle Size Analysis:**

From Gustav Mie to the latest generation  
of laser diffraction

Rheology  
Gas Adsorption  
Particle Size  
Specific Surface Area  
Contract Analysis  
Particle Shape

Chemisorption

Breakthrough Curves  
Dynamic Image Analysis  
Zeta Potential

TURBISCAN Principle

The logo consists of the letters '3P' in a bold, orange, sans-serif font. The '3' and 'P' are connected at the top. Below the letters is a thin horizontal line.

INSTRUMENTS

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3P Instruments, Adobe Stock

On the occasion of the upcoming 30th anniversary of 3P Instruments, our CEO and president Dr. Dietmar Klank will inform you about the latest developments in the field of characterization of particles, powders and pores. The interview was carried out by Elke Peter, info@elke-peter-werbung.de:

**Dr. Klank, your company will celebrate its 30th anniversary next year. What comes to mind when you look back at the company's history?**

Especially after the recent changes, which we will certainly talk about later, we should take a moment to look back at our company's history with pride. For many of our employees, 30 years means that they have spent an essential part of their professional life with and within the company. In the end, when one hears about restructuring from friends and family, the stability of the company's own development is valued. Equally, I appreciate the loyalty and continuous commitment as well as the know-how of our employees.

**In the beginning of the 1990s, the company had been able to establish itself relatively quickly in the particle measurement market with only few employees. What were the main reasons for this rapid initial success?**

Even though I have not helped to shape this period myself, I like to point out two essential factors for our success. First of all, the founder of the company secured the distribution rights for Cilas instruments. Cilas was the company that introduced commercial laser diffraction into the area of particle size analysis worldwide in 1968. Our company founder, Karl-Jürgen Rath, has already been active in selling these analysis instruments in 1990. Especially due to the Cilas laser granulometers for particle size analysis, a new sales company in the field of particle measurement technology had been established within a few years.

Secondly, from the very beginning Mr. Rath had focused on professional customer service. This strictly customer-oriented service policy is having a positive effect on our business development to this day. An enormous number of customers appreciate the technical service and application-oriented "after-sales support". Experienced scientists

perform the installation and instruction after the equipment is sold and are also available for clarifying scientific-applicative questions afterwards.

**Was it possible to continue the initial success?**

At the end of the 1990s, it became apparent that the company had reached a maximum turnover. Due to a lack of innovation in Cilas equipment, the French manufacturer lost market share, which was only partially prevented by our good sales and service work. Through the implementation of the analytical instruments of Dispersion Technology, USA, into our portfolio, the equipment offer in the area of particle size and zeta potential was extended. The novel possibility of investigating originally concentrated dispersions generated an additional demand. Nevertheless, two other reasons were vital for the next growth phase. A sales reorganization resulted in customers benefiting even more from the high scientific-applicative qualifications of the sales staff. In addition, marketing was raised to a significantly higher level. The Particle World, with its first issue published in September 2002, is an example of this.

**Are there other factors which influenced this growth phase of the former Quantachrome GmbH?**

This phase also included the acquisition of distribution rights for the French manufacturer Formulaction in 2005 and the further development of our scientific application laboratory LabSPA (Lab for Scientific Particle Analysis). We are very pleased to be working with Formulaction, a market leader in the stability of emulsions area, and have been doing so very successfully in recent years. With Formulaction we have a partner who strongly supports us with professional device development as well as in the fields of application and marketing.

**The company's history began 30 years ago with the distribution rights for Quantachrome and Cilas. Both manufacturers can no longer be found in your current product portfolio. How did this development take place?**

As already indicated, the company Cilas had neglected investments in new products in the field of particle size analysis for a long



time. The worldwide market share of Cilas had been estimated to be less than 3 %, but the market share was much higher in our sales area. In the midyear 2017, Cilas informed us that they were going to leave this market. Ironically, this happened exactly in the 50th anniversary year of the worldwide introduction of commercial laser diffraction by Cilas.

For us, this news was of course surprising, even though we had seen the technological standstill for a long time and had also addressed it towards the manufacturer. On the other hand, the stagnation phase had led to us being prepared to look for a new, forward-thinking partner. Still, the partnership with the innovative company Bettersize has exceeded our technological expectations, and we are very proud to have their high-tech devices in our portfolio.

#### **For your customers this certainly resulted in various problems...**

■ Yes, of course a lot of customers have been affected. We immediately reacted to the uncertain new situation with multiple customer information letters and clarified that we would continue to offer professional

maintenance and repair service and that all maintenance contracts would remain valid. Thus, it was and still is ensured that all former Cilas customers receive professional service from 3P Instruments. Our eight service technicians have almost 100 years of practical experience combined with Cilas equipment. We also offer international Cilas service for all models and spare parts, which is why many of our customers remain loyal to us.

#### **Would it be advantageous for your Cilas customers to consider purchasing a new particle sizer?**

■ We have a lot of users whose tasks have not changed in terms of measuring ranges for many years. Cilas instruments have always been known for their extremely long average life span. Our service policy, and I am happy to repeat its origins in the company's foundation 30 years ago, is outstanding, i.e., we also support Cilas instrument versions that have not been produced for more than 20 years. So why should the users of these devices not continue to fulfil their unchanged daily tasks with their still fully operating Cilas analyzer?

The situation is different if a new particle size analyser should be purchased. We recommend every user of the instrument to take a critical look at things and, of course, to take a look at the technological future, because there has been continuous development in recent years. Compared to a Cilas 920 or Cilas 1064, there are now particle size analyzers that use a significantly higher number of detectors, more backscattering and side-ways detectors, or double lens technology. In addition, a laser diffraction device can be equipped with integrated cameras to meet the ISO 13322-2 for particle shape and the detection of oversized particles in a finely divided sample. So why not think about the next technological generation of particle measurement technology for the next 20 years? →

**The story concerning Quantachrome is probably similarly exciting. What happened that led to the change of the company name last year?**

■ We were informed by email last year that the company Quantachrome Instruments, USA, had been sold with immediate effect. Anyone who is told the end of a successful cooperation, which had lasted for decades, in such an impersonal way will understand how big the disappointment of our employees was about the way this change had taken place. Regardless of that, immediate actions were necessary...

**...this can mean a lot of things. You still owned the distribution rights for the Quantachrome products...**

■ Of course, and we developed customer-friendly options for a transition. However, the termination of our distribution rights by the new owner immediately showed what we

had to do: design a new company name, acquire new equipment suppliers, and come up with a service policy both for our new customers and for our existing Quantachrome customers. It all came down to keeping the jobs of our committed employees, since we lost two out of four equipment suppliers within a short time.

By now, we also have a whole range of new 3P analyzers to offer in the field of gas adsorption. The service is similar to that of the particle size analyzers: our eight service technicians together have such immense experience with the Quantachrome analyzers we supply, that many of our customers appreciate this and still let the equipment we sold be maintained and repaired by us. We continue to offer accessories and consumables for Cilas and Quantachrome instrument users, and this internationally as well: measuring cuvettes, standard and special measuring cells, liquid nitrogen Dewars and many other accessories and consumables

are still available from us. If you are interested, you can contact us directly at [info@3P-instruments.com](mailto:info@3P-instruments.com) as well as our European partners in France, Italy, UK, Spain, Poland, Hungary, Russia and other European countries. "3P Europe" is one of our new concepts to combine the international acquisition of new customers with the support of existing customers.

**You are talking about new device manufacturers that you are working with. The company Bettersize has already been mentioned. Which other manufacturers and measurement methods are now part of 3P Instruments?**

■ There are some positive developments to be mentioned. Let me start with A for Altamira, a US manufacturer of analyzers and measuring systems for the characterization of catalysts. We are very pleased to act as European headquarters for Altamira and to be able to offer high-tech equipment for



temperature-programmed reactions in the field of catalyst characterisation in direct cooperation with the manufacturer. Another supplier is the US company Porous Materials, Inc. (PMI), a market leader in the characterization of filter and membrane materials, i.e. continuous pore systems. We have also taken over sales and offer instrument calibration and service for the devices of this long-established company.

Another focus in our instrument portfolio is on analytical instruments for gas sorption measurements. With the mixSorb (formerly dynaSorb), we offer our very own commercial measuring system for mixed gas and vapor sorption on the market. Additionally, in cooperation with a new partner, we provide a complete range of 3P sorption instruments in the field of classic (single-component) gas and vapor sorption, namely the 3P surface, 3P micro, 3P sync and 3P vapor. BET surface, pore analysis, and gas adsorption are still part of our key competences. If, by the way, a reader has expertise and special skills for the development of new sorption devices and is interested in a position, please contact us at info@3P-instruments.com...

**A lot has happened in a short time!  
How has this been managed?  
Surely there have also been difficulties?**

■ Of course. For example, we are still looking for good sales partners in some European countries. Perhaps an interested Scandinavian is reading this? As an innovative company, we have more good ideas than we are able to realize by ourselves or through our partners within the framework of research and development. A small example is our cryoTune and the concept of advanced scientific research in the field of the determination of specific surfaces. According to ISO 9277 and IUPAC nomenclature, the determination of BET surfaces with argon at the boiling temperature of liquid argon (87 K) is scientifically more correct for many materials than the determination with nitrogen at 77 K. With the cryoTune, we offer an option for BET instruments of different manufacturers which allows such argon measurements without liquid argon, i.e., only when using the readily available liquid nitrogen. The scientific support by interlaboratory tests of different material types takes a very long time in our busy scientific application laboratory, but we are working on it.

**I'm wishing 3P Instruments all the best for the future! One last question: Where is 3P heading in its 30th anniversary year?**

■ We have a whole series of projects that require our attention and time. We hope to complete our ISO 9001 company certification soon and to become even more professional with this step in all our sales, service, laboratory, and administration processes. Regarding equipment and methods training, our aim is to improve the experience exchange with our equipment users in addition to our annual training seminars.

The Bettersizer S3 Plus had an excellent start and we have just successfully participated in an interlaboratory comparison by the Federal Institute for Materials Research and Testing (BAM). Three different samples were tested and of a total of nine key figures, all nine were correctly determined in our laboratory, i.e. 100% of the conditions were fulfilled. We are certain that many laboratories will be equipped with the new Bettersizer S3 Plus in the coming years. This requires additional personnel for our sales department.

But also in the sorption area, the "Adsorption Week 2020" in Leipzig is a highlight in the anniversary year. We cordially invite you to this event!



## Adsorption Week 2020

■ **11<sup>th</sup> Mai 2020:**

Practical day at 3P Instruments: 3P gas adsorption, mixSorb adsorption of mixed gasses and analysis of particle size and shape with the Bettersizer S3 Plus

■ **12<sup>th</sup> May 2020:**

3P-Workshop „Gas sorption for characterizing surfaces and pore structures“

■ **13<sup>th</sup> May 2020:**

Symposium „Dynamic Sorption Methods“ of the Institute of Non-Classical Chemistry e.V., Leipzig, see also <https://www.dynamicsorption.com/>

■ **14<sup>th</sup> May 2020:**

Practical day at 3P Instruments: 3P gas adsorption, mixSorb adsorption of mixed gasses and analysis of particle size and shape with the Bettersizer S3 Plus

Those interested in adsorption have great opportunities with this adjustable programme of the two expert meetings (Workshop 3P and Symposium INC), to combine the expert lectures with flexible practical parts with the analysis equipment. We are looking forward to welcome many participants in Leipzig, and to our anniversary year 2020 with our partners.

# The Bettersizer S3 Plus for particle size analysis

## From Gustav Mie to the latest generation of laser diffraction devices

Dr. Dietmar Klank, Dr. Christian Oetzel, Dr. Frederik Schleife  
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Figure 1 Bettersizer S3 Plus

The basic principles of the application of light scattering for particle size determination have been known for a long time. This article is intended to outline the development of laser diffraction devices to date and to show why and to what extent there have been further developments in hardware and data evaluation. On the basis of the requirements of ISO 13320:2009 /1/, Mie evaluations are discussed and the historical achievement of Gustav Mie from the year 1908 /2/ is appreciated. Especially the characteristics of the Bettersizer S3 Plus (Fig. 1) show that new developments for an even better adaptation of the equipment technology to modern requirements of many tasks have taken place recently.

### Laser diffraction and Fraunhofer evaluation for particle size analysis

The term laser (acronym for **L**ight **A**mplification by **S**timulated **E**mission of **R**adiation) has given this method of particle size determination its name. Laser light is coherent and almost monochromatic, i.e. it consists of light of one wavelength. If it hits matter, then - depending on the size of this obstacle - different physical effects occur which are summarized under the term scattering.



These phenomena include, among others:

1. refraction as deflection of light when passing through a surface boundary
2. diffraction as deflection at an obstacle with a diameter significantly greater than the wavelength of the light and without interaction with the matter itself
3. Light scattering as the deflection of light at a particle in the size range of the wavelength or below, in which an interaction with matter, i.e. electrons, takes place

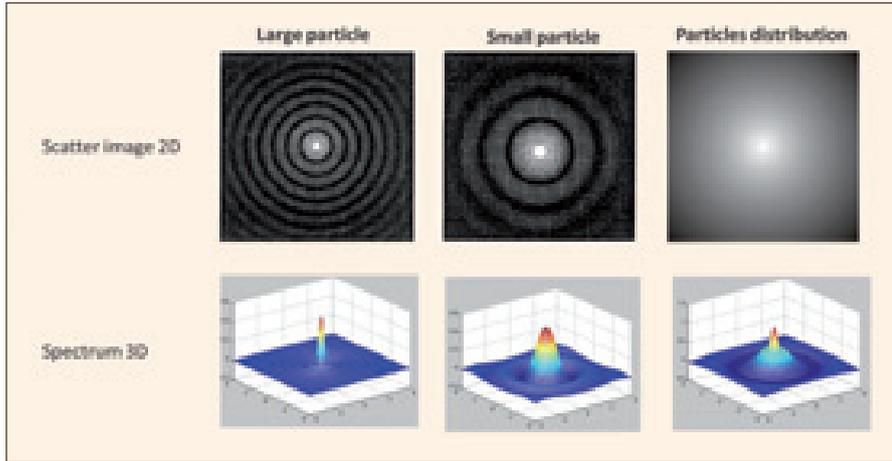
Laser diffraction as a particle size measurement method is therefore based on the deflection of light at particles that are significantly larger than the light's wavelength. If one visualizes the laser light diffraction at such an object in forward direction on a screen, a diffraction pattern with several intensity maxima and minima is created (Fig. 2). A particle with a larger diameter diffracts the laser beam less, i.e. at a small angle, than a smaller particle. Therefore, the light spectra of the small particles must be recorded by detectors at larger angles compared to the laser beam.



The Fraunhofer theory provides the suitable theoretical model for this type of light scattering experiment. In principle, this model has the advantage that no optical material parameters are required for evaluation, since it can only be used for particles that are significantly larger than the wavelength. The Fraunhofer evaluation is based on geometric optics and the Fresnel-Kirchhoff theory of light diffraction at the slit. At the obstacle itself (here: the particle) the light waves are faded out, at the edges they can pass. Due to the blanking, the passing light waves superimpose behind the particle in such a way that the characteristic diffraction patterns shown in Fig. 2 are created. The crucial finding of the Fraunhofer model is that the position of the light intensity minima (black rings) is a function of the particle size:

$$\sin \alpha_m = m \cdot 1,22 \frac{\lambda}{d}$$

$\alpha$  is the diffraction angle,  $\lambda$  the light wavelength,  $d$  the particle diameter and  $m = 1, 2, 3...$



**Figure 2** Diffraction images at different particles in 2D- and 3D-view, on the right the sum of the laser diffraction on multiple particles

With this theory, the diffraction patterns for a large and a small particle shown in Fig. 2 can be described very well and the particle size can be determined unambiguously by the diffraction angle and/or distance of the black circles.

If this model is now transferred to a monodisperse particle quantity, its diffraction intensity  $I$  depends on

- the particle-dependent light intensity  $I_p$
- the particle diameter  $d_p$
- the diffraction angle at which the light intensity is measured ( $\alpha$ ), and
- the particle volume ( $V_p$ )

$$I(\alpha) = f(V_p, I_p(\alpha, d_p))$$

For a mixture of particles of different diameters, the intensities measured by a detector at a certain angle must be weighted. This leads to a mathematic matrix algorithm which, based on the knowledge of the detector characteristics and the theoretical diffraction patterns of spherical particles, produces the desired particle size distribution. In this way, a particle size distribution can be calculated from a diffraction image as shown in Fig. 2 on the right.

In summary, the phenomenon of laser diffraction can be used for particle size analysis with the help of Fraunhofer theory under the following conditions:

- The particles are assumed to be opaque spherical particles (diffraction pattern corresponds to that of a thin, opaque two-dimensional disk).

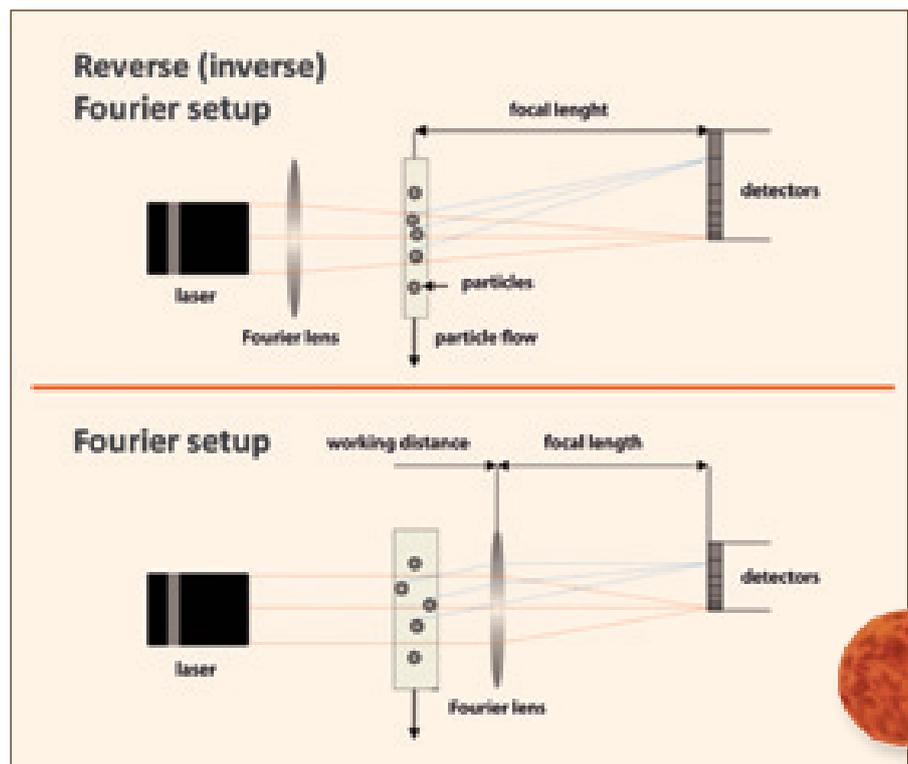
- The particles are clearly larger than the wavelength (with an assumed laser wavelength of 830 nm larger than about 5  $\mu\text{m}$ ). Only under this assumption, the optical material constants (refractive index  $n$ , absorption coefficient  $k$ ) do not play a role.
- Only forward scattering is considered.

The first commercial application of laser diffraction for particle analysis originated in 1966, when the French company Compagnie Industrielle des Lasers (Cilas) was founded to deal with various applications of laser techno-

logy. The first laser granulometer for particle size analysis was patented by Cilas in 1967 and was designed specifically for the cement industry. In the following years, the focus was placed on the extension of the measuring range, especially on the finer micro range. In 1979, the best known Cilas laser granulometer, the Model 715 with a measuring range from 1  $\mu\text{m}$  to 192  $\mu\text{m}$ , was introduced for the first time. With detectors arranged up to 45°, consistent measurement results were obtained in the medium  $\mu\text{m}$  particle size range with Fraunhofer evaluation and were the starting point for the triumphal march of laser diffraction in particle measurement technology. At the end of 2017, Cilas withdrew from this field /3/.

### ISO 13320:2009 and the importance of Mie theory

ISO 13320:2009 /1/ focuses on the two possible optical arrangements after introduction, definition of various parameters and justification for the need to revise the old ISO standard of 1999: the Fourier and the inverse Fourier setup (Fig. 3). The advantage of the Fourier setup is its variability with regard to focal length and lenses and the associated good resolution for coarser particles. However, the improved resolution is bound to a rather limited measuring range.



**Figure 3** Fourier and inverse Fourier arrangement as general possibilities of the optical platform for laser diffraction devices

In the inverse Fourier setup, on the other hand, the lack of a collecting lens behind the scattering particles causes the technical problem of recording the scattering spectrum in good resolution over a wide angular range. For this reason, a multi-laser technique is usually used in this setup.

However, the inverse Fourier design offers fundamental advantages when capturing very small particles, because - in contrast to the Fourier variant - signals are captured or quantified at larger scattering angles.

In addition, there are other differences. With the Fourier arrangement, parallel laser beams hit the particles so that they do not have to be in an optical plane in the measuring cell. This is not the case with the inverse Fourier design, where a convergent light beam approaches the particles, so that the particles should lie in one plane due to the uniform focal length. This is of course not the case in reality, especially for particles with a broad size distribution.

ISO 13320 also shows some ways in which instrument manufacturers can reduce certain disadvantages of a measurement setup, e. g., as mentioned above, by using several lasers, by the variability of the detectors or by alternative angles of laser light incidence.

Appendix A of ISO 13320:2009 presents the theoretical background of laser diffraction and static light scattering and summarizes the two common evaluation models, the Fraunhofer model described above and the Mie theory. The relevant optical effects can be seen in Fig. 4.

The Fraunhofer method only considers effects in which the interaction of light with matter does not play a role, i.e. the phenomenon of diffraction at the particle edges. Absorption as well as scattering as interaction of light with particle matter is not taken into account. This implies the limitation of the theory to larger particle diameters and the renunciation of the optical material parameters.

With particles of the order of the wavelength or smaller, however, this scattered light component can no longer be neglected and therefore this model cannot be applied.

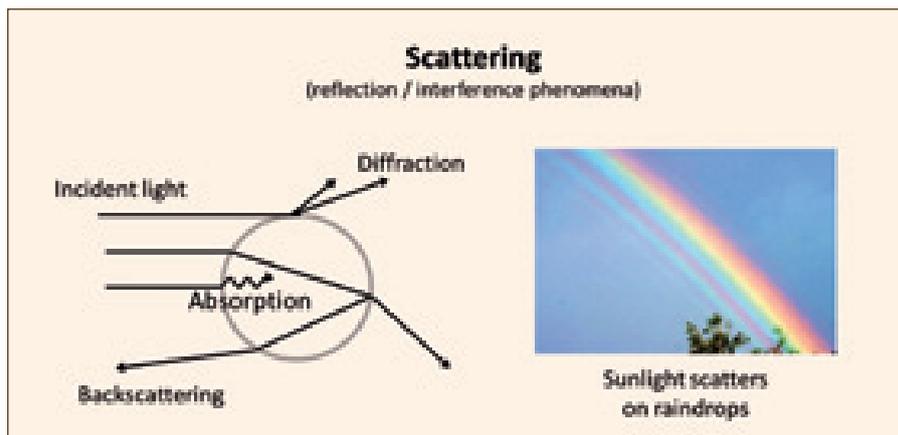


Figure 4 Optical effects of the interaction of light and particles, on the right a rainbow as an example of the scattering of sunlight by raindrops

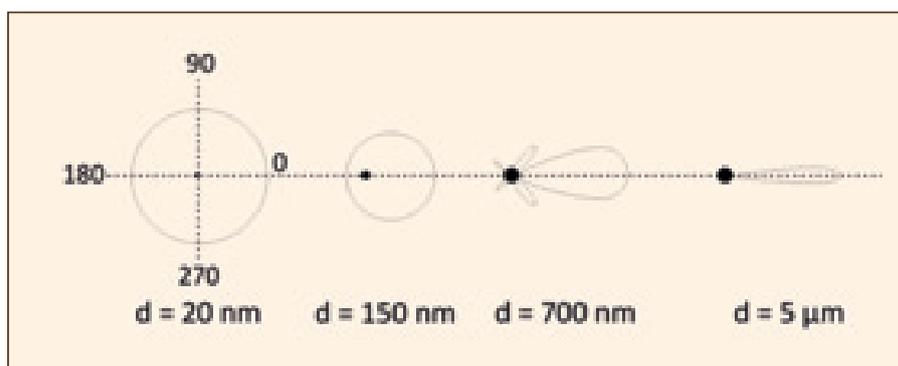


Figure 5 Scattering of laser light ( $\lambda = 633 \text{ nm}$ ) on particles of different sizes (polar diagrams)

The Mie theory, on the other hand, implements all the processes shown in Fig. 4, i.e. diffraction, absorption, emission and refraction, and has established itself as the standard for the evaluation of laser diffraction spectra in the meantime. Figs. 5 and 6 schematically illustrate the effect of particle size on scattering behavior in so-called polar diagrams: Fig. 5 shows this generally on particles of different sizes, Fig. 6 especially for gold colloids.

It appears that

- the smaller the particles are, the lower is the scattered light intensity
- the smaller the particles, the less scattering takes place in the forward direction, and
- for particles with a diameter  $< 100 \text{ nm}$ , scattering in all directions is almost identical

According to Mie theory, scattering diagrams in a medium (air, water, etc.) can be described exactly when they are spherical and quasi-translucent scattering centers and the optical properties, i.e. the refractive index of the scattering center and the surround-

ing medium, and the absorption coefficient of the scattering material, are known. If the scattering spectrum of a monodisperse quantity of particles is also used here, their scattering intensity

$$I(\alpha) = f(I_0, \lambda, x, R, k, \sigma)$$

within the framework of Mie theory depends on

- the initial light intensity  $I_0$
- the wavelength  $\lambda$
- the ratio  $x$  of particle circumference ( $2\pi r$ ) to wavelength  $\lambda$
- the complex refractive index  $k$  (with a real part and absorption coefficients as imaginary part)
- the distance  $R$  from the spherical center

Analogous to the application of the Fraunhofer theory, this description can be transferred to particle quantities with different diameters, and the size distribution function can be calculated accordingly.

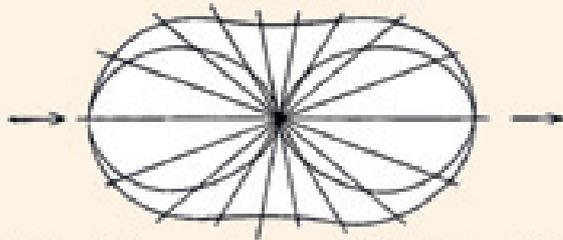


Fig. 17. Strahlungsdiagramm eines unendlich kleinen Goldkugelhens.

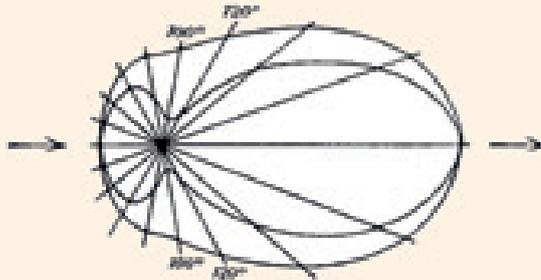


Fig. 18. Strahlungsdiagramm eines Goldkugelhens von 160  $\mu\mu$  Durchm.

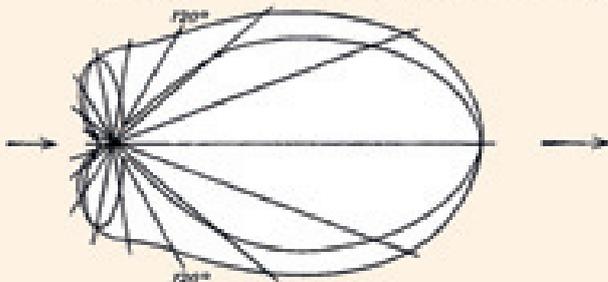


Fig. 19. Strahlungsdiagramm eines Goldkugelhens von 180  $\mu\mu$  Durchm.

Figure 6 Radiation diagrams for gold particles from top to bottom for infinitely small gold beads, for 160 nm and for 180 nm gold beads, from the original work by Gustav Mie /2/. (Note:  $\mu\mu$  corresponded at that time to the nanometer)

1908.

N<sup>o</sup> 3.

## ANNALEN DER PHYSIK.

VIERTE FOLGE. BAND 25.

### 1. Beiträge zur Optik trüber Medien, speziell kolloidaler Metallösungen; von Gustav Mie.

1. Die mannigfachen Färbungen der Metalle im kolloidalen Zustand haben im Laufe der Zeiten recht verschiedenartige Deutungen erfahren. Früher neigte man sehr zu der Meinung, daß die betreffenden Metalle (besonders das Silber) in mehreren verschieden gefärbten Modifikationen aufträten. Später ist die Meinung aufgekommen, daß die Farben auf optischer Resonanz

By implementing the Mie Theory as an evaluation model for measured light scattering spectra, the method of laser diffraction could for the first time also be used sensibly for particles with small diameters and thus be made accessible to a much larger field of application. For this reason, the scientist Gustav Mie will be honored and vital parts of his work will be presented in the following.

### Gustav Mie - memory and appreciation

Gustav Adolf Feodor Wilhelm Ludwig Mie was born on September 29 in 1868 in Rostock, Germany. In 1886, Gustav Mie began his studies of mathematics and physics at the University of Rostock, continued his studies at the University of Heidelberg in 1889 and received his doctorate there in 1891 with the dissertation "On the fundamental existence theorem of integrals of partial differential equations". In 1897, Mie habilitated at the Karlsruhe Institute of Technology (KIT) in theoretical physics. Five years later, Gustav Mie became an associate professor at the University of Greifswald, where he worked for fifteen years and, among other things, wrote the well-known work "Contributions to optics via media, especially colloidal metal solutions". In 1908 it was published in the "Annalen der Physik" in Leipzig (/2/, Fig. 7).

The theory developed by Mie is based on the solution of Maxwell's equations under certain conditions. In the end, he did not continue the work on his optical theory for three reasons:

1. The work appeared to be finished, all available experimental findings were completely explained mathematically by the developed optical theory.
2. The extension to ellipsoidal particles mentioned by Gustav Mie himself (Fig. 8) required an enormous amount of computational effort, so that such calculations were only tackled decades later.
3. Potential applications, such as the use of Mie theory for particle size analysis in many areas of research and development as well as quality control, were unthinkable at the time of publication. Gustav Mie and his fellow scientists had no idea of the possibility of mass use of laser technology, nor of the breakthrough of computer technology for calculating particle size distributions based on Mie theory within seconds.

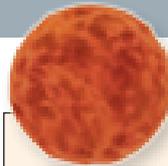
Figure 7 The original work by Gustav Mie from 1908 /2/

The discovery of the later on called Mie-effect was the first exact, complete, linear solution and numerical evaluation of the electromagnetic problem of any sphere in a monochromatic, plane, and electromagnetic field. The original Mie theory contains numerous restrictive assumptions and conditions, while the "modified Mie theory", which has been developed in the meantime, has gained outstanding importance today as a quantitative descriptive theory and rightly represents the basis of nano optics /4/.

In 1912/1913 Gustav Mie (Fig. 9) accomplished another enormous achievement by developing his theory of matter. From a "world function" /8/ with the field sizes he derived Maxwell's electrodynamics. His aim was to set up the world function in such a way that matter itself could be calculated as a solution to the variation equation. He also tried to include gravity and was thus a competitor of Einstein and the famous mathematician David Hilbert in the development of an extended theory of gravity /7/. In the



**Figure 9** Gustav Mie /9/, about 1905 in Greifswald. During this time, he worked on his publication on light scattering effects



*Beiträge zur Optik trüber Medien.* 445

gelb. Später steigt das Strahlungsmaximum besonders hoch im Rotgelb. Wollte man von Resonanz sprechen, so müßte man schon von einer Resonanz der Goldatome auf Gelb sprechen, die sich über der an farblosen leitenden Partikelchen zu erwartenden Erscheinung überlagert.

9. Schon unendlich feine Trübungen durch Goldpartikelchen zeigen (im schärfsten Kontrast zu dem, was man von vollkommen leitenden Teilchen zu erwarten hätte) eine charakteristische Absorption, die nur von der Menge des suspendierten Metalls (der Konzentration), nicht aber von dem Feinheitsgrad der Verteilung abhängt. Es wäre interessant experimentell zu untersuchen, wie sich das schließlich bei äußerst feinen Teilchen, die nur noch einige Atome enthalten, ändern mag.

10. Allgemein hängt die Absorption der kolloidalen Goldlösungen von zwei Eigenschaften des metallischen Goldes ab: dem Absorptionsvermögen und dem Reflexionsvermögen. Lösungen, in denen die diffuse Reflexion zurücktritt gegen die eigentliche Absorption, zeigen das Absorptionsmaximum der Goldteilchen, das im Grün liegt, sie sind daher rubinrot. Lösungen, die starke diffuse Reflexion zeigen, sind dagegen blau-durchsichtig, weil Gold hauptsächlich das rotgelbe Licht reflektiert.

11. Für die Vollständigkeit der Theorie ist es unbedingt erforderlich, auch noch das Verhalten ellipsoidischer Teilchen zu untersuchen.

**Greifswald, Physikalisches Institut.**  
(Eingegangen 7. Januar 1908.)

**Figure 8** Last page of the original work by Gustav Mie /2/ on optical diffraction phenomena with presentation of the limits of the theory for non-spherical particles: "11. For the completeness of the theory it is absolutely necessary to investigate the behavior of ellipsoidal particles".

years 1917 to 1919, Gustav Mie exchanged letters with Albert Einstein about field theories, mass and gravitation as well as relativity theories and reference systems. During this time, Mie was a university professor in Halle (from 1917 to 1924) before accepting a professorship at the University of Freiburg, where he formally retired in 1935. Gustav Mie became 88 years old and died on February 13 in 1957.

The importance of Gustav Mie's original work and the Mie theory developed from it for the description and use of many optical phenomena cannot be overestimated. Although his publication deals with optical effects of small gold particles, today's studies of electromagnetic scattering effects and radiation transmissions in the atmosphere and ocean are based on Mie theory, as is the use of optical effects to characterize particulate

surfaces /5/. Both Gustav Mie, during his lifetime, and his contemporaries had underestimated the importance of his work for the development of optical theory. The value of this rather dry, abstract, mathematical treatise - 69 pages long with 102 equations - has only been revealed by the developments in the last decades of the last century.

In summary, measured scattering spectra can be applied to particle size analysis with the help of Mie theory under the following conditions:

- The particles are spherical and are regarded as a translucent cluster of scattering centres.
- The complex refractive index of the particle and the liquid phase are known.
- A homogeneous material is used.

ISO 13320:2009 describes the topic of the complex refractive index as an essential basis of the Mie-evaluation in great detail. Appendix D of the ISO standard contains typical values as well as ranges for refractive indices of different materials. Ranges, i. e., no fixed values, result from the fact that most (mineral) compounds are of natural origin. In addition, most of the solids listed are anisotropic, i. e., their optical properties are directional. For many materials, both effects lead to a range of values instead of a fixed refractive index.

In the imaginary part of the refractive index, additional surface roughness of the real particles plays a role. If particles are scratched off a transparent glass plate, the scratching points are no longer transparent. The same applies to the scratched glass powder, which also does not appear transparent. The glass plate before and after scraping and the resulting glass powder are three objects of the same composition, but have different optical properties. The ISO standard therefore rightly points out that the values given therein apply without surface structure effects, as they are normal for real particles.

Sample impurities also have an influence. The fixed values in the ISO standard table in Appendix D are therefore primarily intended for comparing the results of laboratories. In an interlaboratory test or other laboratory comparisons, materials should be as pure as possible and the same refractive index should be used and documented for the evaluations. This does not mean that the own samples, which are natural or partially contaminated, have exactly the same refractive index as smooth spheres of the pure material.

To complete the description, the standard notes that the refractive index depends on the wavelength of the light. In the table values of Appendix D of the standard, the corresponding wavelengths are given, but they do not necessarily apply to the specific analyzer available.

For the overall problem of refractive index and evaluation model, the ISO 13320:2009 notes that the theoretical model with the optical properties used can be tested by comparing the calculated with the actual solid's concentration. Large deviations indicate that either the optical model or the refractive index may not be correct. This solution for the concentration-based determination of the refractive index will be described later in this article.

## The Bettersizer S3 Plus: Hardware Technology „state-of-the-ISO 13320:2009“

The Mie theory is now used in modern laser diffraction instruments, such as the Bettersizer S3 Plus. As already mentioned, however, the following cases are particularly challenging for an evaluation of the scattered light spectra under consideration of the objective to obtain realistic particle size distributions representing the sample:

- Exact measurements of small particles down to the sub- $\mu\text{m}$  and nanometer range
- Realistic detection of large particles down to the lower mm range
- Characterization of non-spherical particles with pronounced shape anisotropy
- Characterization of particles with unknown optical properties or unknown complex refractive index

ISO 13320:2009 already lists these challenging borderline cases and offers some recommendations on how to take them into account. The state-of-the-art particle size measuring instrument Bettersizer S3 Plus provides the user with patented technologies, which enable to overcome the above mentioned four challenges on the basis of ISO 13320 and thus combine solutions for exactly these in only one measuring instrument.

### 1. The innovative Dual Lenses & Oblique Incidence Optical System (DLOIOS) of the Bettersizer S3 Plus

The general set-up of the optical bench of the Bettersizer S3 Plus is shown in Fig. 10. The schematic illustration explains in detail the special setup of the DLOIOS technology (Dual Lenses & Oblique Incidence Optical System). On the base platform on the right side of the wet measuring cell, a laser diode (green, 532 nm), backscatter detectors and a Fourier lens (Lens 2) are located directly in front of the measuring cell. Another Fourier lens (Lens 1) and the forward detectors are located to the left of the measuring cell. Lens 1 focuses the scattered light in the forward direction into the detector plane according to the classical Fourier design. On the one hand, Lens 2 generates an exactly parallel laser beam, which hits the sample, and, on the other hand, it acts as a collecting lens



and focuses the scattered light backwards towards the backscattering detectors. This indicates that the DLOIOS design is based on the conventional Fourier arrangement (both lenses act as converging lenses that focus the scattered light onto the detectors), so that the scattering particles in the cuvette do not necessarily have to be in one plane (as compared to the inverse Fourier arrangement). The challenge of precisely measuring small particles using the Fourier setup is overcome by adding the second Fourier lens (Lens 2) and thus allowing the backscattered light to be detected. In combination with the laser arranged obliquely to the measuring cuvette, this leads to a detection of the scattered light over a very large angular range ( $0.02^\circ - 165^\circ$ ) with excellent detector resolution. The diagonal incidence of light causes the scattering angle range at the lateral front detectors to widen.

The very wide angle coverage also has the advantage that there is no need for a second, shorter-wavelength laser and therefore no scattering spectra of mixed wavelengths are measured, which, strictly speaking, cannot be evaluated with the Mie model due to the wavelength dependence of the refractive index.

Due to the patented DLOIOS technology in combination with a high-resolution detector system, the Bettersizer S3 Plus compensates for a decisive disadvantage of the conventional Fourier setup and even increases the precision compared to small particles in comparison to the inverse Fourier setup.



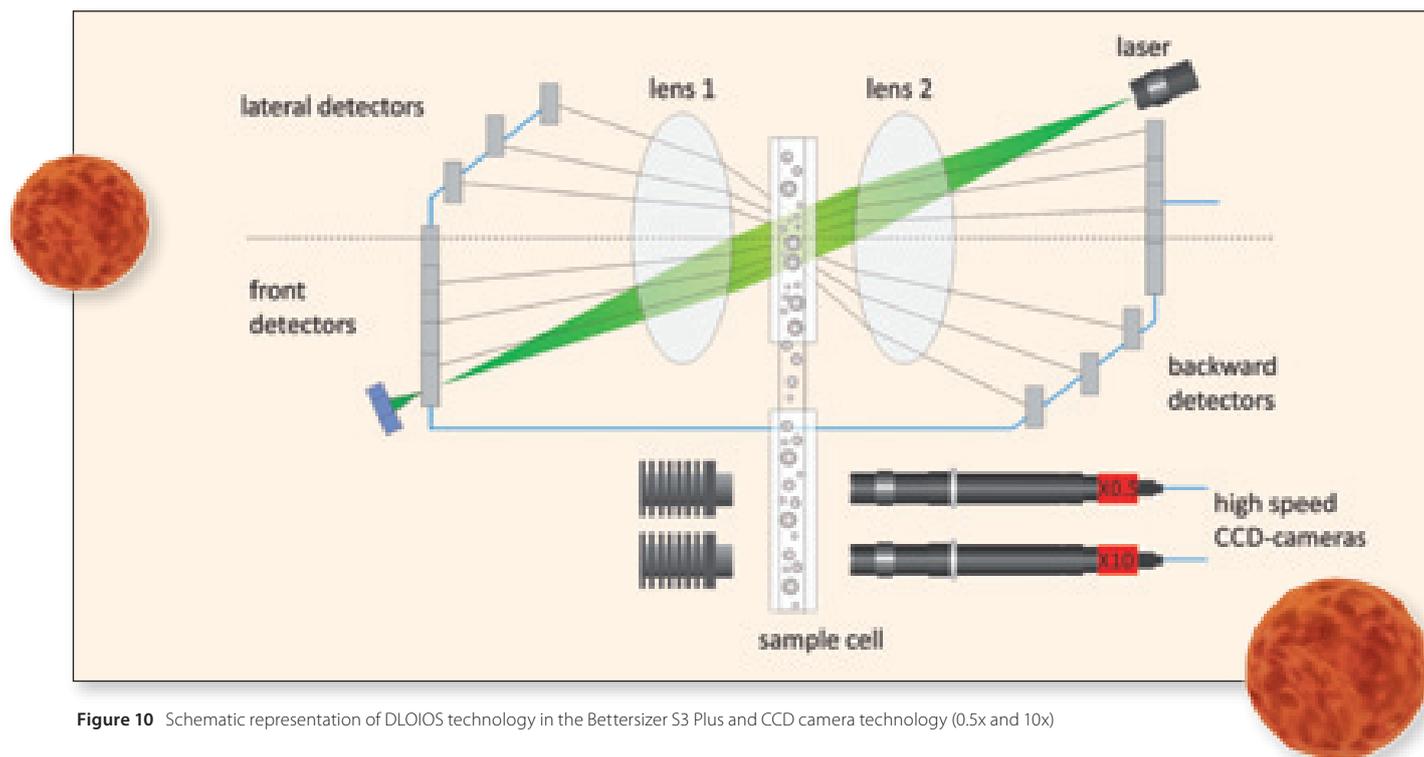


Figure 10 Schematic representation of DLOIOS technology in the Bettersizer S3 Plus and CCD camera technology (0.5x and 10x)

## 2. The double camera system of the Bettersizer S3 Plus

A closer look at the optical bench structure of the Bettersizer S3 Plus (Fig. 10, right) reveals that, in addition to the classical components for performing the light scattering experiment (lasers, lenses, detectors), a camera system is implemented. These are two high-speed CCD cameras (up to 70 fps) which enable sharp detection of moving particles at different magnifications and thus, an additional evaluation by means of dynamic image analysis. This can be used in two ways.

### I. Highest measuring precision for very coarse particles by a combination of measurement techniques

Especially in the case of expansive particle size distributions, small proportions in the particle coarse range are hardly to be found, but often play an important role in practice, e. g., if coarse proportions in fine products must be avoided at all costs. In detail, two phenomena make the reliable detection of the coarse fraction more difficult:

- on the one hand, coarse particles (especially > 100 µm) scatter (or diffract) the light exclusively in the forward direction, which makes it difficult to differentiate between or classify them with only minor differences in size

- on the other hand, in widely distributed particle collectives, the coarse particles are statistically underrepresented, which in turn makes their detection more difficult in the presence of a large number of smaller particles

ISO 13320:2009 notes in Appendix E that a microscopic inspection of the sample can be helpful to obtain information on particle size and shape. In the meantime, excellent possibilities to combine microscopic sample inspection (dynamic image analysis according to ISO 13322-2) with the actual particle size measurement (laser diffraction) have been developed. The image analysis provides an exact size determination of coarse particles and provides detailed information about the individual particles of the particle collective: oversized particles or agglomerates are visualized. However, a metrological implementation of this combination of methods is a challenge, because it requires a powerful optical bench, an ultra-fast and high-resolution camera system as well as a compelling software to process all information directly online.

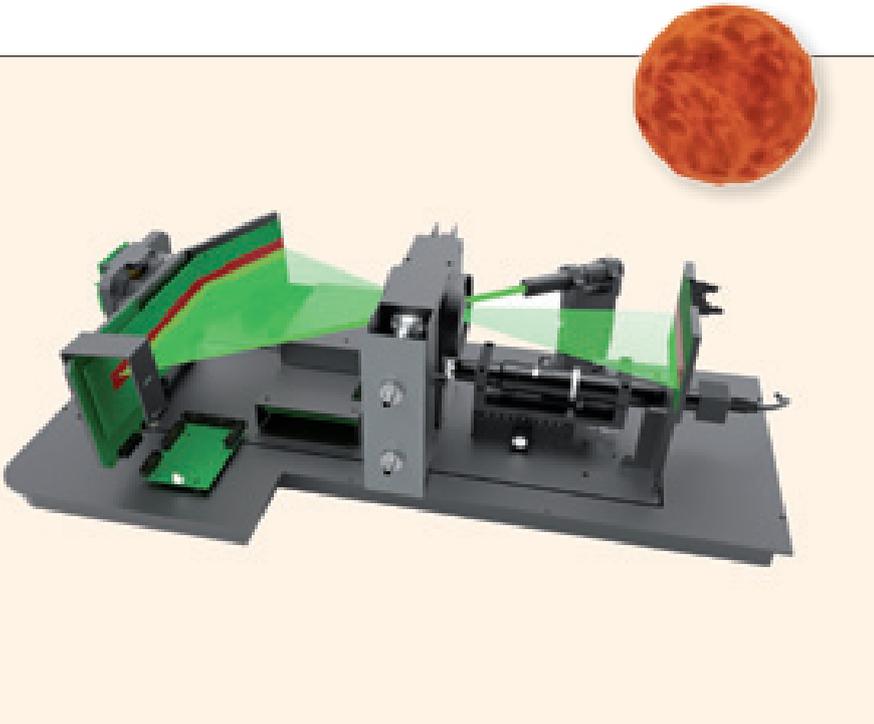
The Bettersizer S3 Plus uses one of the two integrated high-speed CCD cameras (0.5x) to photograph and statistically evaluate coarse particles. During the measurement, the particles to be examined move through the measuring cell for recording the light scattering spectrum (DLOIOS setup) and through a second camera cuvette. The data acquisition

of the scattered light signals for the classical laser diffraction experiment and the data collection of the single particle images for the image analysis are done synchronously. The live CCD camera image can be switched on during the measurement so that the instrument user can directly evaluate dispersion and particle shape (spheres, agglomerates, air bubbles).

The results from laser diffraction and dynamic image analysis are combined in an intelligent routine by weighting based on the concentration determination of both methods. The combined measurement results obtained in this way can then be separated from each other and the influence of the measurement method combination compared to pure laser diffraction or pure image analysis can be worked out. To summarize, the combined use of DLOIOS technology and dynamic image analysis allows a precise measurement of widely distributed systems from 0.01 - 3,500 µm as well as a visual evaluation of the performed analysis.

### II. dynamic image analysis for particle shape analysis

In addition to the combined use of dynamic image analysis and laser diffraction, the Bettersizer S3 Plus camera system also offers the ability to perform dynamic image analysis only. The intuitive and powerful software allows to obtain essential information about the particle shape from the captured images.



For particle shape analysis, the Bettersizer S3 Plus optionally offers two high-speed CCD cameras with a recording speed of about 10,000 particles/minute:

- a) camera with 0.5x lens for coarse particles (approx. 70  $\mu\text{m}$  - 3,500  $\mu\text{m}$ )
- b) camera with 10x lens for small particles (approximately 4  $\mu\text{m}$  - 100  $\mu\text{m}$ ).

Both cameras can be used individually for image analysis of particle size and shape or in combination in the case of very widely distributed samples. Each single particle is captured, stored as an image, numbered and statistically evaluated. Different equivalent diameters (area, circumference, maximum (L) and minimum (D) Feret etc.) as well as L/D and aspect ratio (D/L), circularity (roundness) and circumference (perimeter) are calculated.

In addition to the optimized determination of the particle size distribution, the Bettersizer S3 Plus can use essential shape parameters for the additional characterization or classification of particles. Especially for strongly form-anisotropic particles such as fibers or flakes, this is an advantage over classical laser diffraction, which is based on the evaluation of spherical particles. The determination of different equivalent diameters also offers the possibility to compare the results with other methods for size determination, e. g., sieving, and to verify their measurement results.

With the Bettersizer S3 Plus, the implementation of a double camera system into a high-tech laser diffraction device has thus been achieved. This analysis device opens up a unique characterization possibility with regard to particle size and particle shape from the nano to the millimeter range.

### 3. The concentration-based determination of the refractive index of unknown samples with the Bettersizer S3 Plus

For particle size measurements and their evaluation according to Mie theory, the refractive indices of more than 300 pure substances are available in the material database of the Bettersizer software. These can be extended by any number of materials. The evaluation of scattered light spectra is extremely demanding in the following cases:

- sample with completely unknown complex refractive index, e. g., newly synthesized materials
- sample with heterogeneous chemical composition, e. g., samples with impurities or other mixtures of substances
- sample with significantly different particulate optical properties compared to the bulk material as tabulated in the literature, e. g., due to different crystal structure or additional reflection of laser light at irregularly shaped particle interfaces

- sample having a distinctly strong optical dispersion (small Abbe number), which may cause its refractive index to differ significantly from the tabulated value if a significantly different wavelength referenced to the refractive index determination is used for particle size analysis

In order to solve these problems for the corresponding samples, a self-sufficient determination of the complex refractive index of the sample to be analyzed was developed for the Bettersizer laser diffraction analyzers. Especially in the scientific field, this function is used to significantly increase the accuracy and reliability of particle size measurements. The Bettersizer software does not only use an iterative adjustment of the refractive index up to a maximum fit quality. Instead, the following steps are performed on the basis of the ISO standard, Mie theory and the Lambert-Beer law:

1. Measurement of the angle-dependent scattered light intensity distribution and shading of the light intensity of the laser primary beam (obscuration)
2. Calculation of (theoretical) particle size distributions for 864 different, complex refractive indices (real part from 1.4 to 3.6; imaginary part each from 0.0001 to 3.0)
3. Calculation of the volume concentration using the measured laser shading for each of the 864 complex refractive indices, where Mie theory and the Lambert-Beer law result in a direct relationship between absorbance, volume concentration and particle size. Thus, (mathematically) possible complex refractive indices are calculated, which follow the mentioned laws or fit best to the measured scattered light intensity distribution and light shading.
4. Evaluation of the determined complex refractive indices with regard to the following criteria:
  - a) Comparison of the theoretically calculated with the measured scattered light intensity (at the same volume concentration)
  - b) Comparison of the angle dependence of the theoretically calculated scattered light signal with the actually measured scattered light signal.
5. Evaluation of reliability on the basis of the calculations that were carried out

The software then outputs the (up to) five complex refractive indices with the highest agreement to the scientific theory, whereby the one with the highest "credibility" is the recommended one for the analyzed sample (Fig. 11). Table 1 lists the complex refractive indices determined by the Bettersizer software compared to the literature values of some selected pure substances. It can be seen that the values partly correspond, while in other cases there are clear differences in the complex refractive index between pure material (literature value) and real sample due to the above-mentioned phenomena.

### Conclusion

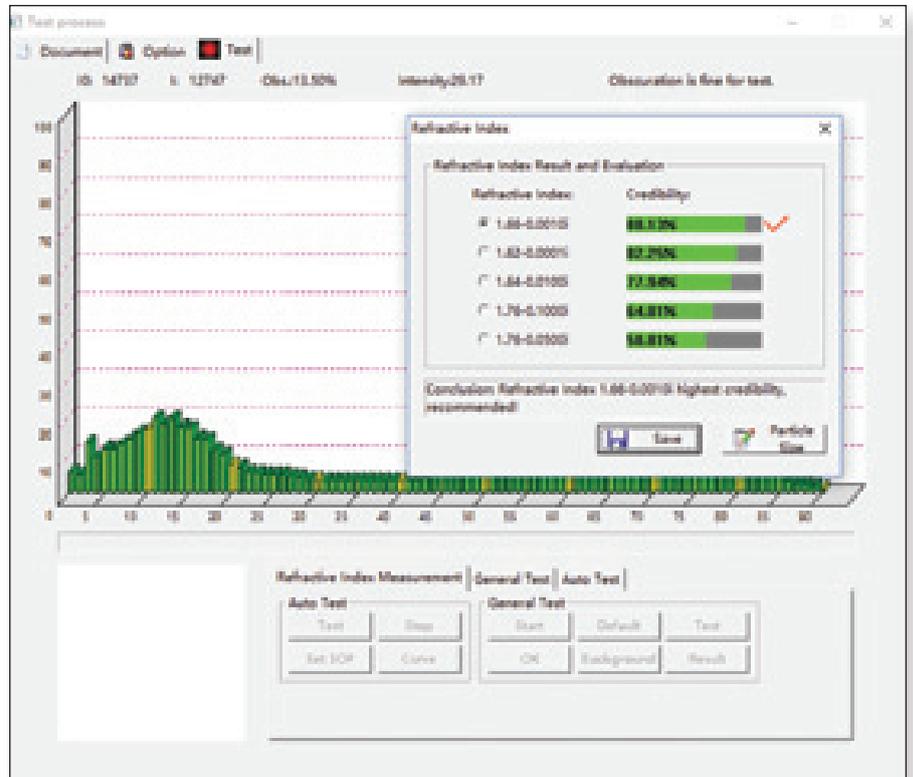
In recent years, Mie theory has established itself as the standard method for particle size analysis using laser diffraction. The associated possibilities and problems are described in ISO 13320:2009 and are innovatively implemented in the Bettersizer S3 Plus:

1. The challenges and limits of both Fourier and inverse Fourier technology are overcome in the Bettersizer S3 Plus by the innovative double lens technology (DLOIOS).
2. The additionally implemented double camera technology in the Bettersizer S3 Plus allows, in addition to visualizing and evaluating particles in general:
  - a high measuring precision for very coarse particles using the 0.5x CCD camera (particularly advantageous for the detection of "oversized" particles)
  - a detailed particle shape determination with oversize particle analysis and agglomerate check, optionally with the 0.5x-, the 10x- or with both CCD cameras combined (dynamic image analysis according to ISO 13322-2)
3. The concentration-based determination of the refractive index of unknown samples in the Bettersizer S3 Plus includes a measurement and calculation procedure for the complex refractive index and offers new possibilities, especially for research. These include testing the influence of the real and imaginary parts of the refractive index on the result and testing result plausibilities on the basis of particle concentration.



**Table 1** Comparison of the complex refractive indices calculated by the Bettersizer software with the literature values of some selected materials

Material	Refractive index (Literature)	Refractive index (measured)
CaCO <sub>3</sub>	(1.53-1.65)-0.1i	1.62-0.1i
BaSO <sub>4</sub>	1.65-0.1i	1.68-0.1i
ZnO	2.008-0.1i	2.02-0.1i
Carbon black	1.88-0.55i	2.00-1.0i
Al powder	1.4-3.9i	1.42-3.0i
SiO <sub>2</sub> - Quarz	1.54-0.00i	1.54-0.01i



**Figure 11** Schematic representation of DLOIOS technology in Bettersizer S3 Plus and CCD camera technology (0.5x and 10x)



### Literature

/1/ ISO 13320:2009  
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 /5/ M. I. Mishchenko and L. D. Travis. American Meteorological Society. December 2008. 1853-1861  
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 /8/ <https://de.wikipedia.org/wiki/Weltformel> (on 23/07/2019)  
 /9/ Helmut Horvath. J. of Quantitative Spectroscopy & Radiative Transfer. 110 (2009). 787-799

Further information and especially test measurements of the presented solutions of the Bettersizer S3 Plus can be requested at [info@3p-instruments.com](mailto:info@3p-instruments.com) or +49 8134 9324 0. Please visit our homepage at [www.3p-instruments.com/de/trade-fairs-and-seminars/](http://www.3p-instruments.com/de/trade-fairs-and-seminars/) and find out when the next workshop with Bettersize live demonstrations will take place. ■



### The new „Bettser S3 Plus“ successfully passes the BAM interlaboratory test "Particle size determination of ceramic powders by means of laser scattered light"

The new Bettser S3 Plus participated for the first time in an interlaboratory test of the Federal Institute for Materials Research and Testing (BAM) and passed the interlaboratory test RV BAM-5.5-2019 100 % successfully.

The objectives of the interlaboratory comparison were to guarantee internal quality assurance and to demonstrate the performance of the equipment. A total of 43 laboratories from 12 countries took part in the interlaboratory comparison "Particle size determination of ceramic powders by means of laser scattered light method" in 2019, of which

9 laboratories with less than 80 % of the criteria achieved failed the interlaboratory comparison.

The standard materials used were commercial products (glass beads,  $\text{Al}_2\text{O}_3$  powder and glass ballotini) with average particle sizes of 3, 6 and 35  $\mu\text{m}$ , respectively. The glass beads and the glass ballotini sample are characterized by a spherical particle shape, whereas the aluminum oxide has an irregular particle shape. The samples also differed in terms of particle size distribution and optical transparency: While the glass spheres and glass

ballotini are transparent particles with a narrow particle size distribution, the aluminum oxide to be characterized does not exhibit complete transparency and a broad size distribution.

The Bettser S3 Plus with its implemented double lens technology has met all criteria of the interlaboratory comparison within the permitted tolerances (z-Score according to DIN ISO 13528) (see table). 9 out of 9 sample/feature combinations were successfully tested, which corresponds to a result of 100 %. ■



**Table 2** Overview of the nominal values and the permissible tolerance range of the characteristic diameters of the particle size distributions as well as the measured values by the Bettser S3 Plus.

Material	$D_x$	Target value / $\mu\text{m}$	Tolerance range / $\mu\text{m}$ ( z-Score  $\leq 2$ )	Measured value / $\mu\text{m}$
Glass beads	$d_{10}$	2.775	1.755 – 3.796	2.658
Glass beads	$d_{50}$	6.299	5.197 – 7.402	6.299
Glass beads	$d_{90}$	12.764	10.879 – 14.649	12.923
Aluminum oxide	$d_{10}$	1.123	0.682 – 1.564	1.040
Aluminum oxide	$d_{50}$	3.112	2.693 – 3.532	3.209
Aluminum oxide	$d_{90}$	7.243	5.757 – 8.728	6.959
Glass ballotini	$d_{10}$	24.213	21.891 – 26.534	23.018
Glass ballotini	$d_{50}$	35.683	33.925 – 37.441	36.237
Glass ballotini	$d_{90}$	50.732	45.832 – 55.631	55.430

# Fast determination of stability and packing in inkjet inks

## Examination of different pigments

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### Introduction

Inkjet formulations include pigment particles that destabilize within their life cycle. This leads to destabilization phenomena such as particle sedimentation and so-called packing, which in turn can lead to aggregation of the particles as a sediment. These phenomena cause poor product performance or even the clogging of inkjet nozzles. In serious cases, this requires cleaning of the nozzles, which leads to an outage and the shutdown of the printing process.

By moving the nozzle head or shaking it manually, the ink can be transferred to its initial state, but aggregation phenomena normally cannot be reversed. Therefore, it is important to predict instabilities as described above to avoid defective products. In the following, the Turbiscan (Formulation) is used to quantify and predict instability phenomena.

### Method

Based on static multi light scattering, the Turbiscan emits light (880 nm) onto a sample and detects both the backscattered (BS) and transmitted (T) light over the entire height of the sample (see Fig. 1). By repeating this measurement over time in freely selectable frequencies, the Turbiscan allows the determination of physical stability. Via the Mie theory, the raw signal can be correlated directly with the particle concentration ( $\phi$ ) and the particle size ( $d$ ).

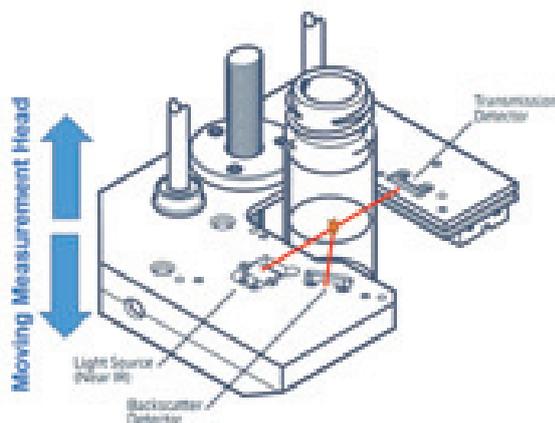


Figure 1 Setup of the Turbiscan measuring chamber

### Materials

Two inkjet samples, one with red pigment particles and the other with yellow pigment particles, were analyzed regarding stability differences based on the different particle types. Each sample was measured in 30 minutes intervals for 3 days in the Turbiscan to record destabilization profiles. In addition to sedimentation effects, packing and phase separation effects were also observed.

### Results

Figure 2 shows the raw data of the dispersions in the delta-depiction. For this, the first recorded scan is set to 0 % backscattering in order to be able to represent the subsequent variation of the sample more adequately. From the raw data it is already possible to identify occurring destabilization phenomena.

In the meniscus area of the sample (right-hand end of the graph in Fig. 2) a clear decrease of the backscattering intensity can be seen. This is due to a beginning elucidation, meaning particles migrate to the bottom of the sample.

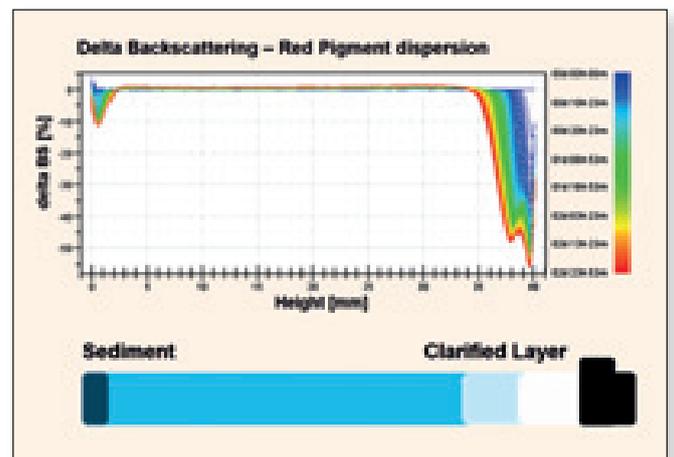


Figure 2 Red dispersion delta-backscattering data

At the lower end of the sample (left side of the graph), a negative development of the backscattering intensity is also observed. Typically, sedimentation can be observed in similar samples, which would be accompanied by an increase in the backscattering intensity. The detected decline in this case is due to diffusion of light due to very high particle concentration, and above all due to aggregation of the particles. In the sediment packing takes place.

Both samples show comparable raw data, so that the destabilization kinetics can be quantified very quickly and easily via the software Turbisoft.

### Kinetics of packing

The determination of the mean value of the backscattered light at the lower end of the sample (where packing could be observed) allows a determination of the packing kinetics of the two dispersions. This calculation provides the formulator of inkjet inks additional information to create formulations with desired properties.

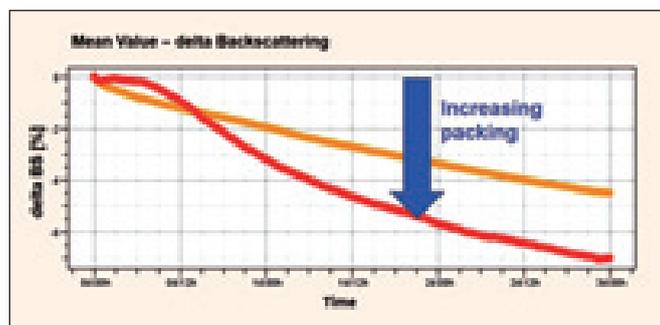


Figure 3 Packing kinetics of the two dispersions

In Figure 3, the kinetics of the two dispersions are compared regarding the packing phenomenon. The yellow pigment is characterized by linear kinetics, while the red pigment shows significantly more variation. This begins very slowly, but then overtakes the yellow dispersion after about 14 hours of measurement and shows more intense kinetics.

### Quantification of destabilization with the TSI

The TSI - Turbiscan Stability Index - is an algorithm-based computation in the software that compares all destabilization effects and combines them in one single number – for a simple one click ranking and easy sample comparison. The TSI considers all kinetics of sample destabilization and is always influenced by the dominant phenomenon.

Table 1 TSI values after different ageing times of the dispersions

Sample	TSI			
	2 hours	1 day	2 days	3 days
Yellow pigment	0.2	1.7	3.0	4.1
Red pigment	0.7	2.7	4.2	5.6

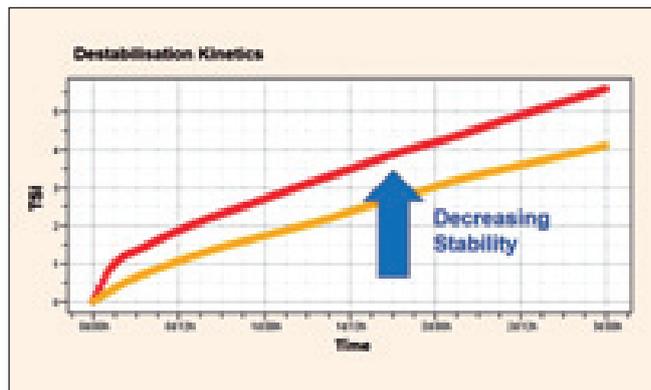


Figure 4 Turbiscan Stability Index (TSI) vs. time for both dispersions

Figure 4 shows the TSI plot of the two samples. It becomes clear that the red pigment leads to a much faster destabilization than the yellow one.

In this case, the TSI follows the already described trend above (packing is the predominant phenomenon). Within two hours, the TSI can provide information about the differences in the stability of the two formulations.

It should be noted that the TSI analyzes all phases of the sample and therefore recognizes the instability of the red sample over the yellow, regardless of the result of single kinetics.

More importantly, the trend due to the kinetics of packing (Figure 3) was only determined after several hours of analysis. The ability to quantify the stability of the dispersions with the TSI in a matter of hours provides added value to formulation scientists.

### Conclusion

Both samples show a very similar destabilization behavior. With the naked eye, it is very difficult to distinguish between the two samples. With the Turbiscan technique however, differences between formulations can be quantified:

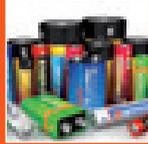
- Global stability with the TSI
  - Packing kinetics by observation of sedimentation and elucidation layers
- and all this in just a few hours!

Furthermore, an analysis of the particle size before and after storage could be made after the measurement. By shaking the resulting sediment, it is possible to carry out an analysis of the redispersibility with the Turbiscan in order to estimate the required energy input which is necessary to obtain the starting dispersion. ■

# Full characterization of rechargeable batteries

## Precise analysis of the viscosity of electrolyte solutions

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### Introduction

Lifetime and power capabilities of Li-ion batteries strongly depend on the electrolyte used. While developing new electrolytes, dielectric constant, viscosity and conductivity of the blend must be carefully considered. The latter two are known to be inter-dependent and linked with the Stokes model. Viscosity, that directly affects ionic conductivity, is a parameter which determines how fast a cell can be charged or discharged and must be carefully controlled.

Traditional solvent base for Li-ion batteries is a mixture of different solvents (EMC, DMC and EC). While EC has a high dielectric constant, improving the lithium salt dissociation, EMC and DMC possess lower viscosity and melting point: mixing them results in a good compromise between desirable electrochemical properties, a high dielectric constant ( $\epsilon$ ) and low viscosity ( $\eta$ ). Since battery electrolytes are a mixture of different solvents, viscosity measurements of these mixtures can reveal some difficulties regarding the low viscosity and the volatility of the products.

### Method description

The Fluidicam RHEO uses a co-flow microfluidic principle to measure viscosity. The sample and a reference solution are simultaneously introduced into the microfluidic

channel (typically 2.2 mm x 50  $\mu$ m) with controlled flow rates. This results in a laminar flow where the interface position between sample and reference relates to the viscosity ratio and flow rates (see Fig. 1).

Images acquired during the measurement enable the software to calculate the position of the interface and directly plot an interactive flow curve.

### Materials

- **DMC:** Dimethyl carbonate
- **EMC:** Ethyl methyl carbonate
- **EC:** Ethylene carbonate
- **LiClO<sub>4</sub>:** Lithium perchlorate

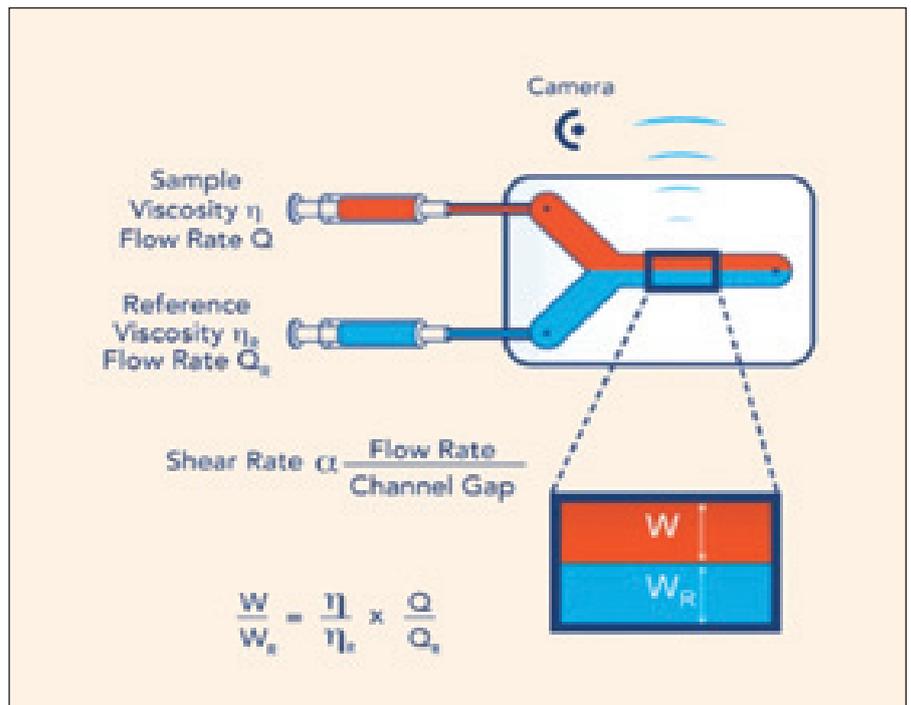


Figure 1 Fluidicam RHEO measuring principle

## Results

First, the viscosity of pure solvents and different mixtures of EMC : DMC : EC (different w/w EC ratios) were analyzed at different temperatures. Then, the viscosity of electrolyte solutions at different concentrations was studied. One single test is performed within 3 min analysis time and requires only 2 ml of sample for five repetitions.

### Temperature relation to the viscosity of the blends

Fig. 2 shows how the viscosity of analyzed mixtures of EMC : DMC, and EMC : DMC : EC decreases with temperature (range from 15 °C to 65 °C).

The two blends behave differently regarding temperature change. First, the presence of EC in the blend significantly increases the viscosity values. But the mixture viscosity is decreasing more compared to EMC : DMC. Tab. 1 contains the viscosity values for the two mixtures and associated standard deviation for each temperature.

Since the temperature-dependent variation of electrolyte viscosity directly affects the battery performances, it is essential to control this factor. Finding the right balance between viscosity and conductivity at different temperatures is quite challenging for formulators, thus the need for highly sensitive and efficient tools.

### Effect of EC concentration on the blend viscosity

The viscosity of the solvent base EMC : DMC : EC was then measured at different EC concentrations (see Fig. 3). All values are given in Tab. 2.

The results show that the blend viscosity increases with higher EC concentration, proving the impact of smallest EC concentration change on viscosity. Higher viscosities of the electrolytes involve lower ion conductivity and therefore may inhibit battery performances.

Due to the high sensitivity of Fluidicam RHEO to smallest viscosity variations, the instrument offers a rapid solution to optimize the formulations to select those fulfilling the set requirements.

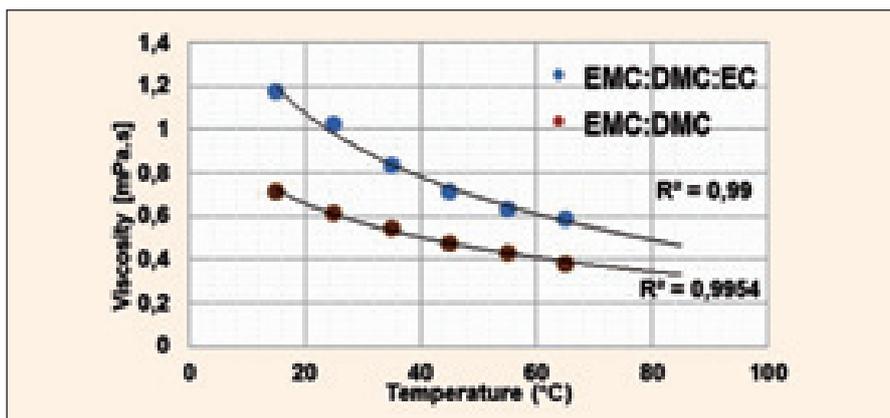


Figure 2 Viscosity-temperature dependence of the two solvents mixtures

Table 1 Viscosity values of the blends as a function of temperature

T / °C	EMC : DMC : EC = 1 : 1 : 0	EMC : DMC : EC = 1 : 1 : 1
	Viscosity / mPas	Viscosity / mPas
15	0.715 ± 0.001	1.178 ± 0.002
25	0.614 ± 0.002	1.021 ± 0.004
35	0.544 ± 0.002	0.832 ± 0.001
45	0.473 ± 0.004	0.714 ± 0.003
55	0.427 ± 0.001	0.592 ± 0.003
65	0.382 ± 0.002	0.590 ± 0.005

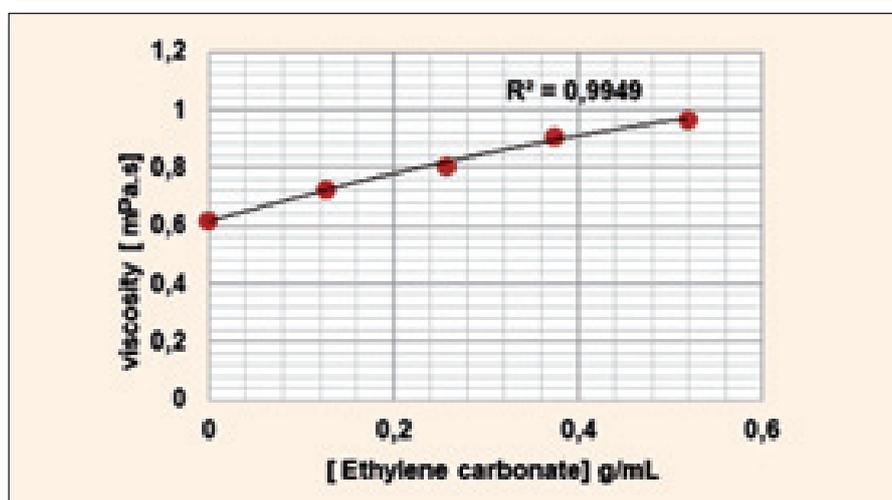


Figure 3 Viscosity as a function of EC concentration at 25 °C

Table 2 Viscosity as a function of EC concentration

EMC	DMC	EC	Viscosity / mPas
1	1	0	0.614 ± 0.007
1	1	0.245	0.726 ± 0.007
1	1	0.497	0.806 ± 0.001
1	1	0.724	0.908 ± 0.012
1	1	1	0.965 ± 0.008

### Electrolyte concentration and temperature influence on viscosity – the case of LiClO<sub>4</sub>

A model solution of EMC : DMC (weight ratio 1:1) was prepared and supplemented with different amounts of the dissolved lithium salt. Tab. 3 shows the blend viscosity at different temperatures, representative of the battery's range of application.

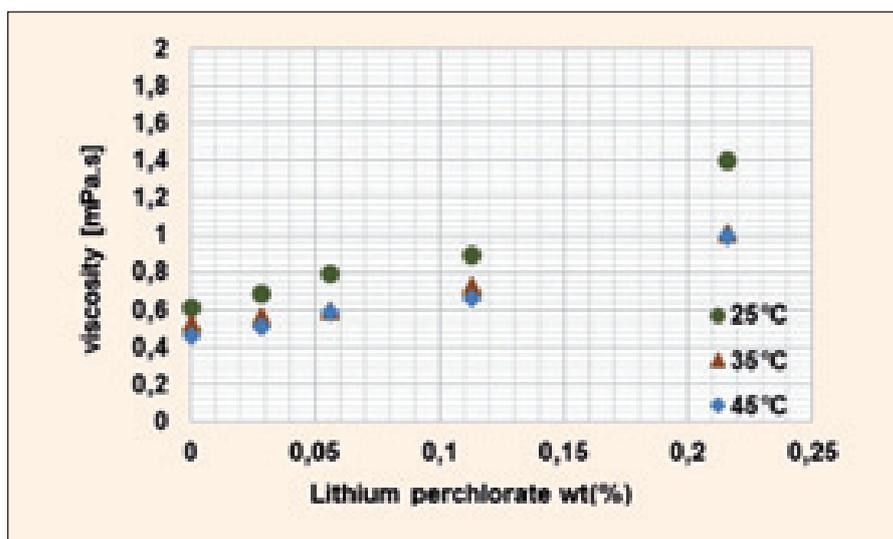
As presented, the viscosity of the electrolyte is related to the lithium salt concentration, but inversely related to temperature. As temperature increases, the viscosity of the electrolyte decreases.

On the other hand, the conductivity is proportional to salt concentration and inversely proportional to the viscosity of the electrolyte (Stokes Law for electrolyte conductivity). These tests were realized in a total analysis time of 1 hour and 20 min (for 17 tests) including sampling, whereas it would have taken about a day with a conventional capillary viscometer instead.

The Fluidicam RHEO is more suitable for viscosity measurements than conventional viscometers because of its confined microfluidic system avoids volatility and drying risks, which stem from the physical properties of solvents like low viscosity values and low boiling points.

**Table 3** Viscosity of blends at 25, 35, 45 °C

EMC : DMC : Li	Viscosity / mPas 25°C	Viscosity / mPas 35°C	Viscosity / mPas 45°C
1:1:0	0.614 ± 0.002	0.534 ± 0.002	0.461 ± 0.002
1:1:0.0286	0.684 ± 0.001	0.562 ± 0.004	0.512 ± 0.004
1:1:0.056	0.791 ± 0.006	0.598 ± 0.003	0.588 ± 0.003
1:1:0.113	0.893 ± 0.003	0.723 ± 0.001	0.662 ± 0.001
1:1:0.216	1.397 ± 0.008	1.005 ± 0.002	0.994 ± 0.002



**Figure 4** Viscosity as a function of Li<sup>+</sup> concentration and temperature

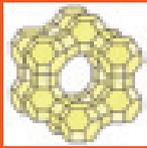


### Conclusion

The viscosity measurements obtained with Fluidicam RHEO are highly accurate and precise due to the high sensitivity of the instrument to small viscosity variations over the whole range of shear rate. Overall, Fluidicam RHEO has proven to be a reliable tool to characterize electrolyte viscosity. Its confined geometry helps working with volatile products. Intensive measurement requirements to identify optimum mixture parameters for best battery performances are fulfilled. ■

# The 3P surface DX for production and quality control of BET surface areas

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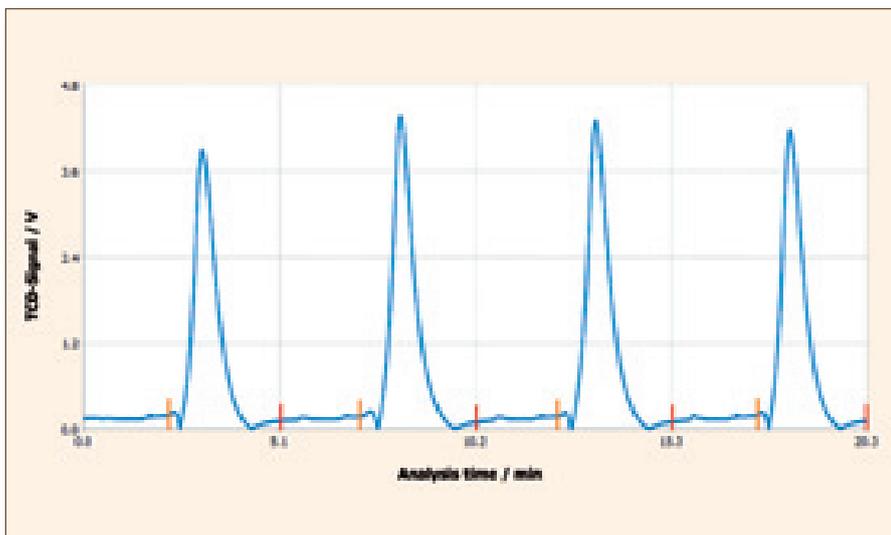
**Figure 1** The 3P surface DX with four measurement stations for fast and accurate BET measurements

The 3P surface DX (Figure 1) is a fully automated gas sorption instrument with four analysis stations to determine the specific surface area without the need of vacuum. The sample preparation (degassing) takes place in an external degassing station by means of adjustable inert gas flow, usually nitrogen. The analyzer operates based on the dynamic principle (flow method) and determines both single and multi-point BET surfaces. By default, the nitrogen and helium gases are connected to the analyzer. Internal high-precision mass flow controllers (MFCs) set the desired gas mixtures. Thus, different partial pressures (analogous relative pressures for static-volumetric systems) in the range from 0.05 to 0.3 are automatically usable.

## Measuring routine for single and multi-point BET measurements

After starting the measurement, all four measuring cells are rinsed with the respective gas mixture and the detector signal (thermal conductivity detector - TCD) is zeroed. Upon reaching a constant baseline, a sample loop of nitrogen is added to the helium carrier gas and fed to the TCD. The resulting peak area of the detector signal is assigned to the known sample loop volume,

i. e., the substance amount of the analysis gas (calibration peak). Subsequently, the Dewar filled with liquid nitrogen of analysis station 1 is lifted. As a result, the measuring cell dips into the liquid nitrogen and sample 1 adsorbs nitrogen from the flowing gas mixture while cooling. The adsorption equilibrium becomes recognizable by reaching the baseline again. From the resulting peak area, the adsorbed amount of substance is calculated using the calibration peak. In this repetitive measuring routine, the analysis stations 2 to 4 are then measured one after the other, afterwards - in a multi-point measurement - the gas mixture for the second measuring point is set, etc. A measurement run of four samples is illustrated in Fig. 2, one peak corresponds to one measuring point.



**Figure 2** Software screenshot of a measurement run to determine the specific surface area of three samples of material SRF-586 in reference mode - plot of analysis time (in min) against the TCD signal (in V) with color-coded integration limits

Fig. 3 shows the very good reproducibility on the basis of the BET line of 5-point BET measurements of one material in all four measuring stations (standard deviation  $\pm 0.019 \text{ m}^2/\text{g}$ ). The total analysis time depends on the number of samples, number of measuring points and the absolute surface in the measuring cell (sample weight). As a rule of thumb, this mode yields analysis times between five and seven minutes per measurement point. To further reduce the analysis time of multiple samples of the same material often used in production and quality control, the analysis system has a reference mode.

### Reference mode

The usage of the reference mode is suitable for samples of the same material (e. g., for different batches) and reduces the measuring time compared to normal mode. Assuming that for production control the measurement data should be available as quickly as possible in order to be able to readjust certain production conditions quickly, optimization in two directions is possible: a) decrease of sample preparation time by experience or testing, and b) optimization of measurement time. The reference mode works to reduce the measurement time by using the results of multi-point BET measurements as a reference for subsequent one-point measurements.

In reference mode, analysis station 1 is regarded as reference and is recalculated based on the peak areas of the analysis stations 2, 3 and 4 via the measured peak area with known specific surface area. In this case, a gas mixture with a partial pressure of nitrogen 0.3 (70% helium and 30% nitrogen) is used in a 1-point measurement. The measuring cell 1 is in each case equipped with a standard material with known BET surface area. Such a standard material will usually be an internal standard which has been characterized and specified several times by multi-point BET measurements.

Within the scope of this article, various measurements of different sample materials were carried out in reference mode. The selected samples include macroporous alumina, mesoporous silica and microporous activated carbon all of which's parameters are summarized in Table 1. All three materials act as internal standards, i. e., were measured several times on different BET devices.

### Reference mode with macroporous alumina

The alumina was measured six times with each measuring station. Fig. 4 shows the calculated mean value per measuring cell and the standard deviation of the six results. The maximum standard deviation of the three measuring stations is  $\pm 0.04 \text{ m}^2/\text{g}$ .

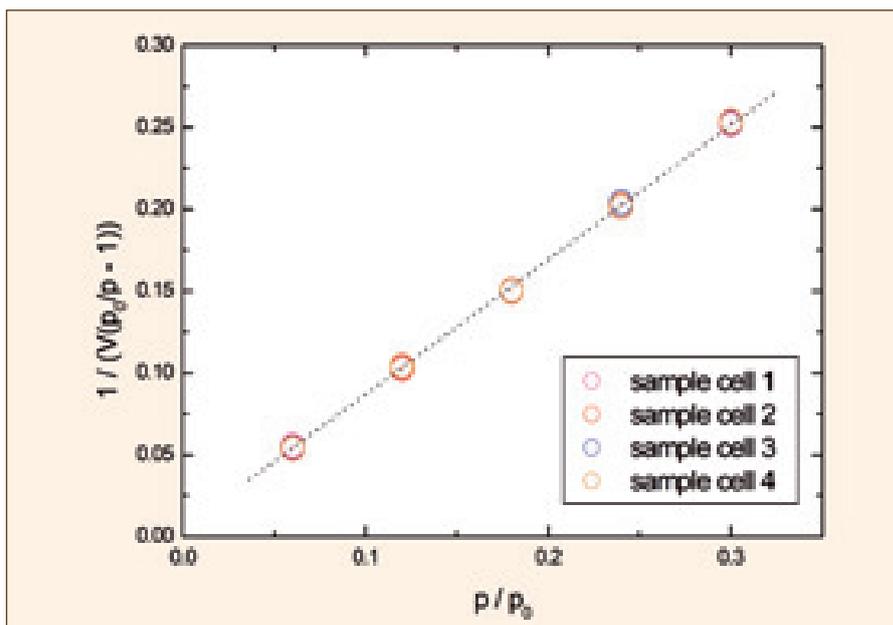


Figure 3 BET plots of 5-point BET measurements of one material in all four measurement stations

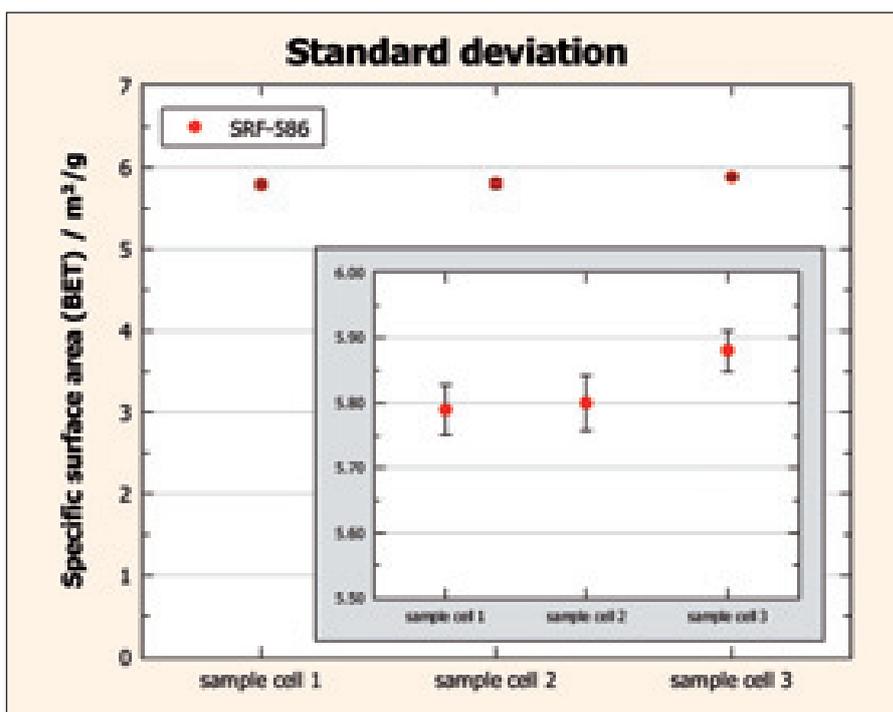


Figure 4 Plot of the calculated mean value per cell, including the standard deviation of six sample runs of sample SRF-586

Table 1 Sample overview of the materials used for reference mode tests

Sample type	Sample name	spezific BET surface area / m <sup>2</sup> /g	Sample amount / g	absolute surface area in measuring cell / m <sup>2</sup>	Preparation conditions
Alumina	3P SRF-586	5.86	5.50	32	1 h bei 350 °C
Silica	Silica	286	0.33	94	4 h bei 350 °C
Activated carbon	AK	1460	0.14	204	2 h bei 250 °C

## Reference mode with mesoporous silica

The mesoporous silica was measured seven times in succession. Fig. 5 shows the calculated mean value per measuring cell and the standard deviation of the seven analysis results. The maximum standard deviation of the three measuring stations is  $\pm 3.1 \text{ m}^2/\text{g}$ .

## Reference mode with microporous activated carbon

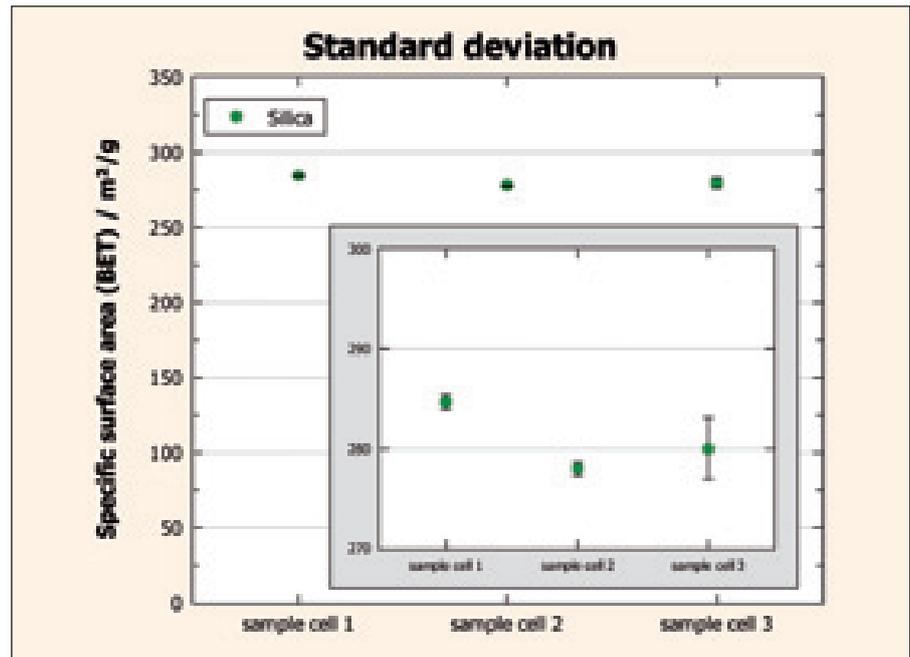
The activated carbon was measured five times with each measuring station. Fig. 6 shows the calculated mean value per measuring cell and the standard deviation of the five results. The maximum standard deviation of the three measuring stations is  $\pm 2.0 \text{ m}^2/\text{g}$ .

The reference mode is thus applicable to microporous materials as well, even though the internal standard has been specified in another relative pressure range. The reference mode thus offers a very significant reduction in measurement time in production and quality control. This time advantage is due to the fact that instead of a 5-point BET measurement, only a 1-point BET measurement is performed, as a kind of calibration measurement of the sample to be measured in regard to the internal standard. One measuring point instead of five measuring points, with corresponding optimization of the sample weight, results in a decrease of measurement time by up to 80 %.

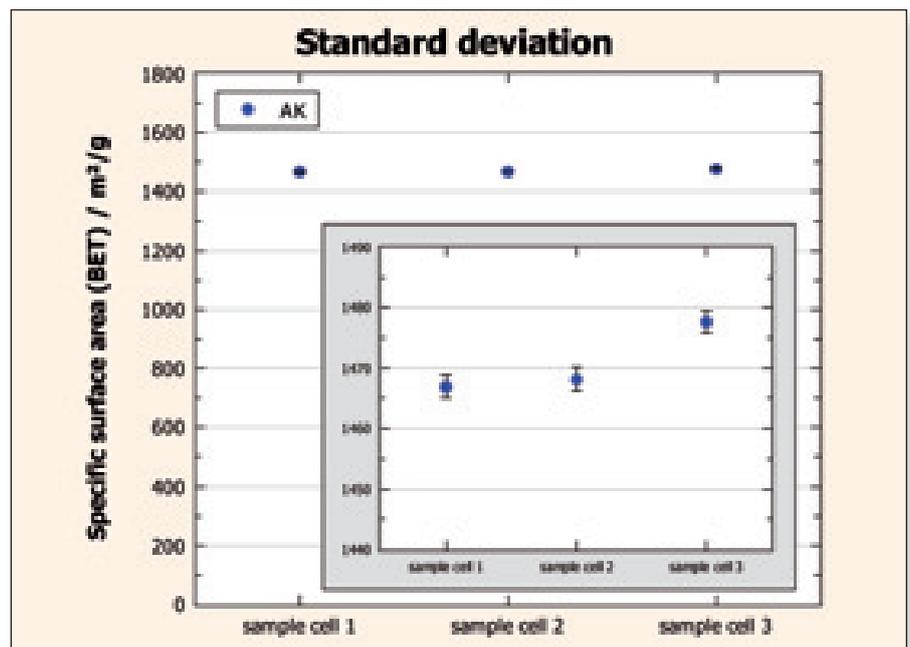
## Summary

The investigations show the outstanding suitability of the 3P surface DX for the determination of the specific surface area of various materials. The advantages of the analyzer and the available measurement routines are:

- fully automated single- or multi-point BET measurements according to ISO 9277 (DIN 66131)
- fully automated TCD calibration using a sample loop
- very good reproducibility of analysis results
- reference mode for brief analysis times, especially suited for production and quality control
- reference mode for all sample types
- easy device handling



**Figure 5** Plot of the calculated mean value per cell, including the standard deviation of seven sample runs of the silica sample



**Figure 6** Plot of the calculated mean value per measuring cell specifying the standard deviation of five measurement runs of sample AK

- extensive starter package with measuring cells, caps etc.
- clear and easy-to-use operating software including all modern functions
- very good price / performance ratio
- low running costs due to cheap consumables

The quality of the surface determination of the reference material in analysis station 1 is crucial for the illustrated reference mode. We

are happy to assist you in specifying your internal standards, i. e., we offer you special conditions for respective multi-measurements on request.

Let the 3P surface DX convince you personally. Device demonstrations or test measurements of your samples in our analytical laboratory (LabSPA - Laboratory for Scientific Particle Analysis) are part of our service. You can contact us at [info@3p-instruments.com](mailto:info@3p-instruments.com) or [+49 8134 9324 0](tel:+49813493240). ■

# The brand new 3P sync series

## Multi-station measurements at an optimal price/performance ratio

Dr. Martin Wickenheisser  
 martin.wickenheisser@3P-instruments.com



**Figure 1**  
 Sorption analyzer from the 3P sync series

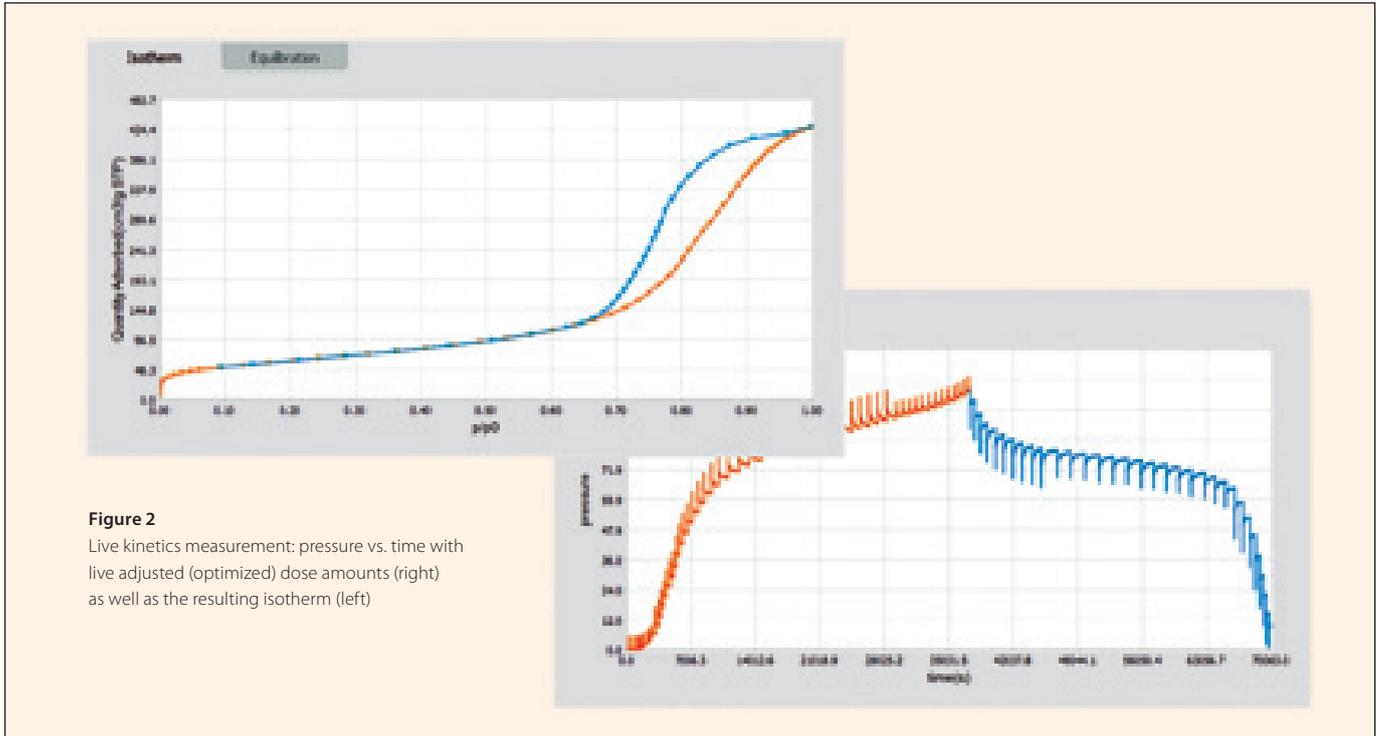
### Introduction

In Particle World 19, we presented our 3P micro and 3P meso series of gas sorption instruments with up to four measuring stations. A major advantage of this series is its measuring flexibility: each measuring station has its own gas inlet, separate internal lines, individual manifolds and a separate dewar for temperature control of the measuring cell. The 3P micro and 3P meso series are an excellent choice when high-resolution microporous isotherm measurements are required or different adsorptives should be measured at different measuring temperatures (e.g., N<sub>2</sub>@77K, Ar@87K, CO<sub>2</sub>@273 K etc.) in parallel without loss of time. Due to this arrangement, it is simple and straightforward to restart a measurement while other measurements are already running.

Even if this flexibility is not required - because the same adsorptive is often used or the laboratory space is limited - we offer you a suitable solution.

**Table 1** Model lines of the 3P sync series

Models	Sync 410	Sync 420	Sync 440	Sync 310	Sync 320	Sync 330	Sync 210	Sync 220	Sync 110
Number of measuring stations	4	4	4	3	3	3	2	2	1
Number of pressure transducers at the stations	1	2	4	1	2	3	1	2	1
P <sub>0</sub> pressure transducers	1	1	1	1	1	1	1	1	1
Pressure transducers at the manifold	1	1	1	1	1	1	1	1	1
Pressure transducers total	3	4	6	3	4	5	3	4	3

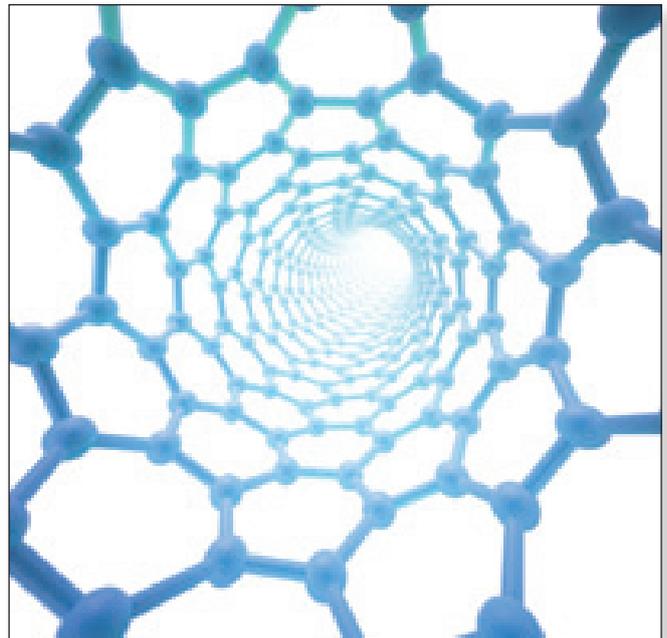
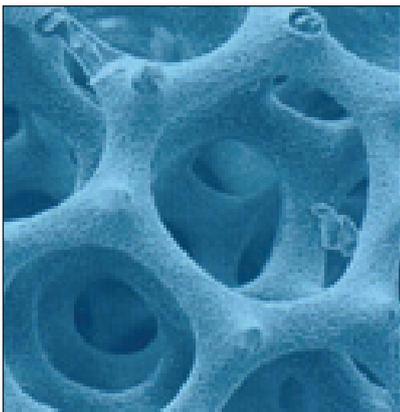


**Figure 2**

Live kinetics measurement: pressure vs. time with live adjusted (optimized) dose amounts (right) as well as the resulting isotherm (left)

### The new 3P sync-series

With the new 3P sync series, 3P Instruments now offers a new measuring instrument with up to four analysis stations and a separate  $P_0$  measuring cell for simultaneous measurement (in sync, name-giving for the series) of the saturation vapor pressure. The stations and measuring cell are temperature controlled by one single dewar vessel. Thus, the 3P sync enables the highest sample throughput with the smallest possible space requirement and minimum liquid nitrogen consumption. Depending on the sample volume, it can be constructed individually as a 1-, 2-, 3- or 4-station instrument. In addition, the number of pressure transducers can be configured at the measuring station. If the instrument is to be equipped with the fastest possible measuring configuration, a separate pressure sensor can be integrated in each of the four measuring stations. In case the measuring speed is not relevant (e.g., for measurements overnight), the measuring instrument can be equipped with only one pressure sensor for up to four measuring stations. In the most basic configuration, the 3P sync 110 has three 1000 Torr pressure transducers (measuring station, manifold and  $P_0$  cell) with only one measuring station and a maximum of six separate 1000 Torr pressure transducers (one per measuring station, manifold and  $P_0$  cell) with four measuring ports for minimum measuring time. Depending on the price/performance ratio, also less than six pressure sensors can be integrated, resulting in nine different 3P sync model series, as shown in Tab. 1.



Like the 3P meso and micro series, the instrument has a powerful software module for data acquisition, evaluation, and control. The intelligent dosing algorithm also displays kinetic data (pressure drop versus time, see Fig. 2) at the same time as the isotherm measurement. This allows to monitor the sorption process in real time or to interrupt the current measurement, e.g., to optimize dosing quantities, tolerance or equilibrium times.

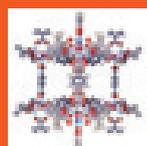
Would you like to test measurements or arrange a device demonstration? Please contact us: [info@3p-instruments.com](mailto:info@3p-instruments.com) or **+49 8134 9324 0**. ■

## The new mixSorb S series

# A perfect tool to investigate mixed gas / mixed vapor adsorption on a laboratory scale

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Industrial adsorbents such as active carbons, zeolites and silica gels are widely used in adsorptive separation processes on a multi-ton scale. After-treatment of exhaust gasses, removal of carbon dioxide in biogas plants, purification and fractionation of natural gas, air separation, respiratory protection and separation of isomers are just few examples where adsorptive separation is employed as the most efficient and economic separation technique. A complete understanding of the complex processes taking place in a fixed bed adsorber is the key to achieve the best separation performance.

Additionally, mixed gas adsorption on novel materials, like MOFs, COFs etc., have been in the focus of research in the last years. These materials exhibit high selectivities due to their extraordinary surface chemistry and should be investigated by mixed gas sorption for a deeper understanding of their sorption behavior. So far, they were mainly studied using the classic texture-descriptive analysis methods and in some cases, large BET surfaces were determined. In practice however, adsorbents are usually not used for the adsorption of nitrogen or argon adsorption at low temperatures (the conditions under which the classic textural analysis is carried out). Hence, the textural data acquired under these conditions are highly interesting, but hardly allow concrete

<p><b>mixSorb S &amp; SHP</b> Dynamic Sorption Analyzer</p>	<p><b>mixSorb L</b> Dynamic Sorption Analyzer</p>
<p>Small amounts of sample/powder (~ 1 ml) Basic research <b>For Institutes for basic research and R&amp;D of powders</b></p>	<p>Large amounts of sample/granulate (~ 130 ml) Application-oriented measurements <b>For companies/producers and institutes of applied sciences</b></p>

Figure 1 mixSorb L and mixSorb S / SHP

conclusions for practical applications. In industrial applications, gas and vapor mixtures have often to be separated into their single components, e.g. biogas into methane and carbon dioxide, or a certain noxious substance should be separated on a ppm scale from a gas mixture (gas purification). Hence, it should be predicted which component of the mixture can be removed by adsorp-

tion from a gas mixture and to which extent. However, these data cannot be delivered by textural analysis, such as BET surface area or pore size distribution, but by breakthrough experiments using the mixSorb series. 3P Instruments has now succeeded in completing a series of sorption instruments for the adsorption of gas and vapor mixtures:

The mixSorb S has recently been developed by 3P Instruments for the investigation of the adsorption of gas and vapor mixtures. This analyzer series allows experiments with very small sample amounts down to a few hundred milligrams (see Fig. 2). The mixSorb S provides unique capabilities to investigate novel materials, like MOFs, COFs etc., via mixed gas adsorption. In contrast to the mixSorb L, the mixSorb S is ideally designed for samples in powder form or only available in very small amounts. Especially R&D groups have now the possibility to measure freshly synthesized materials by complex dynamic sorption processes in a wide field of different gas- and gas/vapor-mixtures by changing different parameters like pressure, temperature gas velocity/dwell times, cycle tests and much more. These experiments allow to acquire data such as the effective adsorption performance, kinetics, co-adsorption phenomena or displacement effects, sorption selectivities, data of gas mixture adsorption and heat balance of the sorption process.

The mixSorb SHP series (high pressure) was designed especially for applications in the natural gas sector as well as gas storage studies on new materials under high system pressures (up to 68 bar). In order to reflect the technically relevant system parameters for the investigation of new materials, for the purification of natural gas for the separation of higher hydrocarbons, for drying, and for further investigations, higher pressures are necessary. On one hand the reversibility (loading and unloading of an adsorptive gas storage) are required in the field of gas storage studies. On the other hand, possible undesirable enrichment of impurities of the to be stored gas is required. For adsorptive methane storage, pressure ranges up to approx. 40 bar are frequently investigated. Another application is the adsorptive purification of reforming gas for hydrogen production. Technically, these processes are carried out at system pressures of about 30 – 40 bar. In this case, novel materials for this application should be examined in the mentioned pressure range (see Fig. 3).

For further information, please visit [www.dynamicsorption.com](http://www.dynamicsorption.com) or contact us directly under [info@3p-instruments.com](mailto:info@3p-instruments.com), +49 8134 9324 0. ■

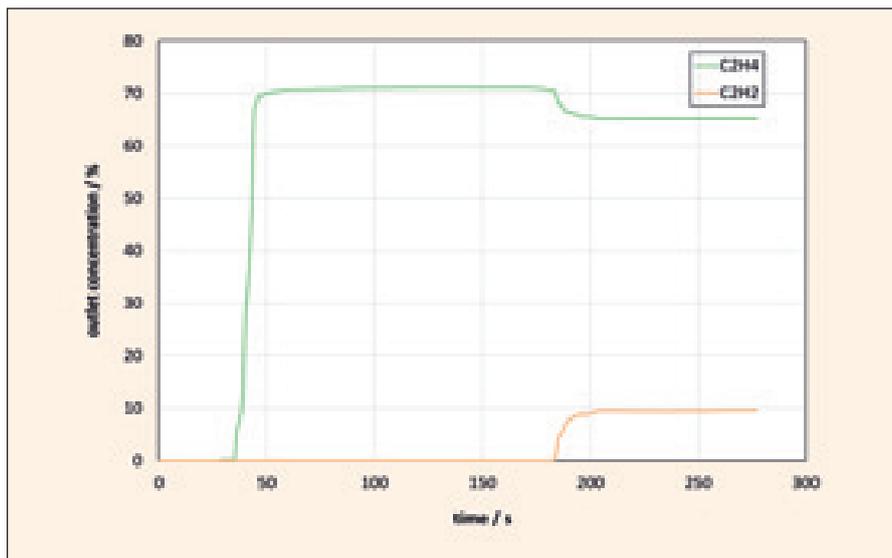


Figure 2 Example breakthrough experiment of a mixture of 65 % ethylene / 10 % acetylene in helium

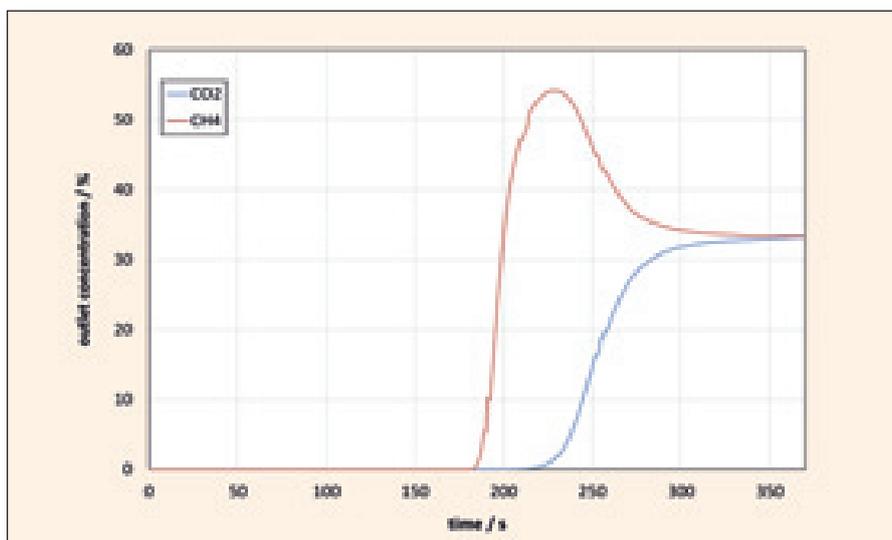


Figure 3 Example of a breakthrough experiment of a mixture consisting of CO<sub>2</sub>/CH<sub>4</sub>/He on activated carbon, 10 mL/min. each compound (total pressure: 10 bar)

## Invitation to Leipzig

### 3P Workshop on Adsorption

Tuesday 12<sup>th</sup> May 2020

### Practical days

May 11<sup>th</sup> / 14<sup>th</sup> 2020 at 3P Instruments and the Institute of Non-Classical Chemistry (INC)



### Leipzig Symposium

Wednesday 13<sup>th</sup> May 2020

### Registration & Information:

[info@3p-instruments.com](mailto:info@3p-instruments.com)

[www.3p-instruments.com/de/trade-fairs-and-seminars/](http://www.3p-instruments.com/de/trade-fairs-and-seminars/)

## Altamira is back!

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### Introduction

Attentive followers of 3P Instruments news surely already acknowledged that we have expanded our product portfolio in the field of catalyst characterization as well as customized reactor systems. With Altamira Instruments, based in Pittsburgh, USA, we found a powerful partner with unmatched expertise in this field of instrument development. Already in the 1990s Altamira developed fully automated laboratory instruments for flow-chemisorption and temperature programmed reactions for the examination of catalysts like TPR, TPD, and TPO. Altamira was founded by catalysis researchers and thus the analyzers have been (and still are) developed according to the demands of catalysis researchers, so they met the conditions of the industry from the beginning. Founded in 1984, Altamira Instruments is a manufacturer and supplier of chemisorption instrumentation as well as bench-scale micro-reactor systems for industrial and research use. Instruments manufactured by Altamira have been delivered to more than 300 sites around the world. These sites include leading laboratories, influential catalysis research groups, and major chemical research centers. The reliability of Altamira is clearly visible in the way that their instruments are still in operation after more than 20 years. This is the reason we still receive requests for purchasing a new AMI-90 or AMI-200, even though these analyzer versions are not being produced any longer and have been replaced by the AMI 300 device family.

This contribution gives a first overview of the range of product capabilities. Please do not hesitate to contact us if there is any question. There are almost unlimited possibilities for customized solutions.

By now, the AMI-300 is the flagship of Altamira Instruments (see Fig. 1) and serves as the basis for a series of analyzer versions. For example, the AMI-300 is available in standard and high-pressure variants, multi-station versions for higher sample throughput, with optional mass spectrometer, as AMI-300 IR with FTIR detector, or as sulfur resistant system AMI-300S.



Figure 1 AMI-300

### The Altamira-family of catalyst characterization instruments:

■ **AMI-300:**

The "flagship" of the AMI 300 family. It is a single station instrument with stand-alone computer and LabVIEW-based control software. It forms the technological basis for all other AMI models.

■ **AMI-300lite:**

entry-level version which sheds some features of the AMI-300 like the saturator and gas blending as a concession to pricing. However, the AMI-300lite still operates on fully automated and performs all TPR/TPO/TPD and pulse chemisorption functions.

■ **AMI-X300 und AMI-X300lite:**

Multiple workstation units of 300 and 300lite, where X stands for the number of analysis ports - which can run two up to eight independent experiments simultaneously.

■ **AMI-300IR:**

Instrument version for in-situ observation of adsorbed species to determine type and mode of adsorption. It uses a heated IR transmission cell coupled with an FTIR detector to gather real-time-information on the processes occurring on the surface of a catalyst.

■ **AMI-300R:**

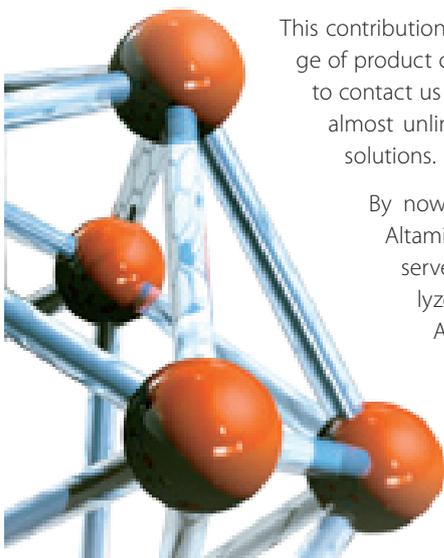
Reactor-version of the AMI-300 which is equipped with additional gas feeds and HPLC pump(s) with vaporizer(s) to facilitate reaction studies. The AMI-300R is also equipped with an auxiliary vent to route reactant gases directly into a secondary detection device (e.g., GC or MS).

■ **AMI-300RHP:**

Custom high-pressure version of the AMI-300R. It is equipped to provide up to 100 bar of operating pressure during a reaction experiment.

■ **AMI-300S:**

A sulfur tolerant version of the AMI-300. Enables experiments in the presence of H<sub>2</sub>S or SO<sub>2</sub> due to sulfur resistant coatings, valves and detectors.



With systems of the reactor series like the  $\mu$ BenchCAT or the customer specified BenchCAT installations, complex investigations of catalysts under different conditions are possible. Common applications are Diesel catalyst studies, fuel cell catalytic membrane studies, Fischer-Tropsch reactions, biofuel applications or hydrocarbon dehydrogenation studies, and many more.

#### ■ $\mu$ BenchCAT:

The  $\mu$ BenchCAT represents a complete, bench-top reactor (fixed-bed / PFR operation) for catalytic studies. All components are either in the gas or liquid phase and are contained in a fully automated compact package. A variety of options makes the  $\mu$ BenchCAT suitable for a wide range of studies. The system is perfect for kinetic and activity studies.

#### ■ BenchCAT:

The BenchCAT family of instruments are custom-designed micro-reactors which are fully automated and designed for unattended operation. These systems are generally designed for fixed-bed / packed-bed / plug flow (PFR) reactor operation (differential or integral mode), trickle-bed reactor operation, or batch (stirred) reactor operation. In addition, BenchCATs can also be built for CSTRs and even stationary or spinning catalyst basket-type reactor systems.

All BenchCAT systems can be configured individually according to the following parameters: number of gas inlets, number of liquid pumps, flow rates, pressure and temperature maxima, reactor material, preference of control software, and future upgrade possibilities. BenchCAT microreactors can be designed to conduct isothermal or temperature-programmed experiments and to analyze the effluent with a mass spectrometer, gas chromatograph, FTIR, or your choice of detector. Single or multi-station instruments are available.

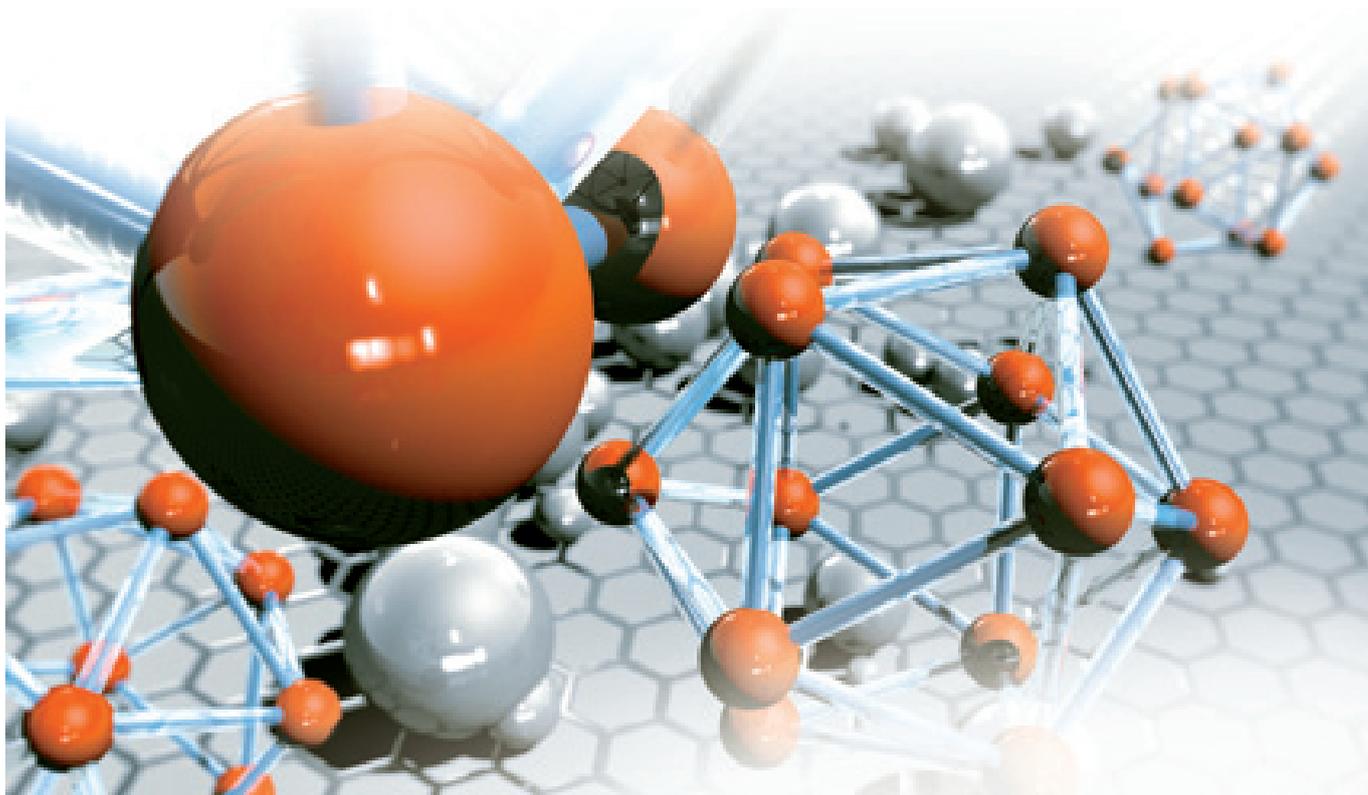
If you are interested or have further questions about an Altamira system, feel free to contact us at [info@3P-instruments.com](mailto:info@3P-instruments.com) or **+49 8134 9324 0**. ■



Figure 2:  $\mu$ BenchCAT



Figure 3: BenchCAT



# Characterization of through-pore systems with PMI-Porometers

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The application of membrane technology has seen a steady increase over the last decades. From the use in medical applications [1] such as dialysis over the development of separator sheets in battery and fuel cell technology [2] to the use of advanced filtration materials [3], membranes and other permeable materials have become part of our everyday life. Key to their development and research is the determination of the material's respective pore size distributions, with a special focus on analyzing all pores connecting from one side of the material to the other. These pores are called "through-pores".

While the analysis of any and all open pores of a substance can be achieved with other methods such as physisorption up to a pore size of 400 nm and mercury intrusion methods up to pore sizes of roughly 1 mm, it stands to note that these techniques do not differentiate between through-pores and terminal pores which end within the material. In order to characterize only the pores actually traversing the material completely, the two analytical methods required are permeametry and porometry (often called capillary flow porometry).

In this article, we highlight the capabilities and features of the porometers manufactured by our partner Porous Materials, Inc. (PMI). All porometers are able to perform basic analytical operations in both permeametry and porometry. Generally speaking, the instrument setup always includes a sample holder, in which a porous material (membranes, filter systems or textile samples) is fixed. The instrument then generates a programmable build-up of pressure in order to determine the amount of gas flowing

through the pore system of the sample. This is achieved by a combination of both pressure regulators and flow meters. Consistent calibration of all components yields precise analytical results over the complete instrument lifetime. Of the two methods applied, permeametry is the simpler one. Permeabilities are usually determined by applying pure gas pressure on one side of the material and measuring the gas flow on the other side of it. For specific filtration or isolation purposes, this is usually done with specific pure substances such as oxygen, carbon dioxide or

nitrogen. Special options on the instrument allow for the use of liquids such as water or ethanol as well, while a number of different sample holders allow for special applications, for example the ASTM compliant determination of the Frazier number [4].

Permeability measurements can be either conducted over a pressure range (spanning from 0 to 500 psi) in order to show sample behavior towards increasing stress, or at constant pressures over set amounts of time (see Fig. 1).

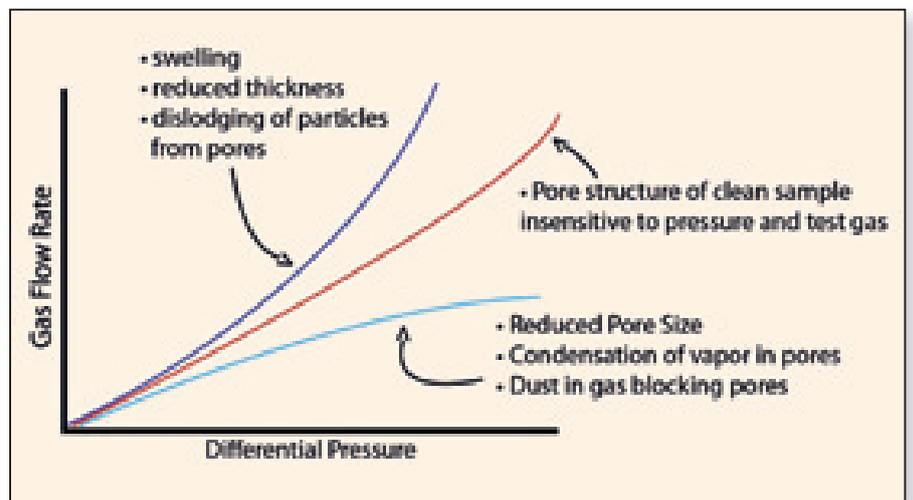


Figure 1 General shapes of permeability measurements by a porometer

While permeability is a more general technique, which focusses on a sample's behavior under set conditions or its suitability towards specific selectivity, capillary flow porometry allows for a more detail oriented study and characterization of a material's through-pore system. Capillary flow porometry is a two-step analysis based on liquid extrusion. During sample preparation, the material is soaked in an ideally wetting liquid with a contact angle close to 0°. The low contact angle means that the liquid will spontaneously fill all accessible pores and remain within these pores due to its surface tension alone. During the first analysis step, the instrument applies a set pressure on one side of the sample and increases the pressure over a user determined range. At the same time, the instrument measures the gas flow through the pore system, which should initially be 0 L/min as all through-pores are blocked by the wetting liquid. As pressure

increases, at some point the force exerted on the wetting liquid in the largest pores is high enough to push the liquid out of the pores and allows for the gas to flow through the sample. This point is called the "bubble point" and corresponds to the largest pore in the material. As pressure increases, smaller pores are cleared of the wetting liquid, resulting in an increase of flow through the sample. When all pores are emptied, the increase in flow is directly proportional to the increase in pressure and only depends on the materials characteristics determined during permeability measurements conducted in the same pressure range. This quasi-linear section (see Fig. 2) determines the end of the first step. The obtained curve is called the "wet curve". In the second step, the analysis is repeated without filling the sample pores by a wetting liquid. This results in another quasi-linear curve (called "dry curve"), which will intersect with the

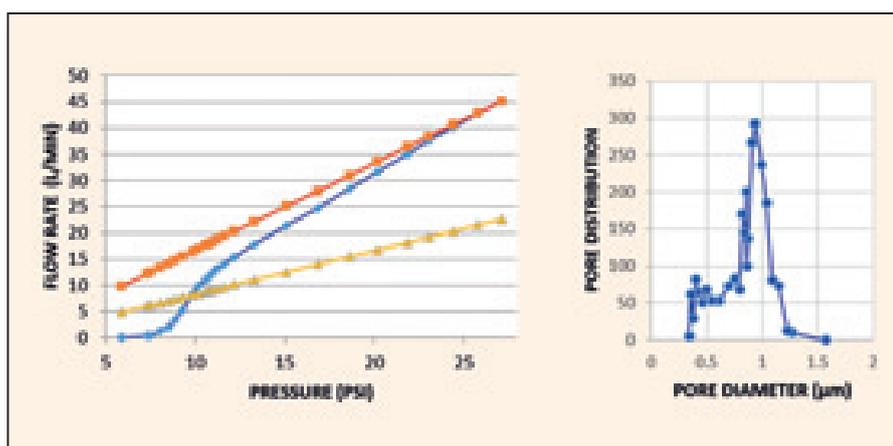
terminal section of the wet-curve under ideal circumstances. The point of intersection between the two curves marks the smallest pore size within the material. The "mean flow pore size" (MFP) is determined by halving all values of the dry curve and taking the pore size at the point of intersection between wet curve and half-dry curve (see Fig. 2). Based on the cumulative flow and the slope between two points, a pore size distribution can be calculated based on the surface tension of the wetting liquid and by applying the Young-Laplace-formula [5]:

$$P = \frac{4 \times \gamma \times \cos(\theta)}{D}$$

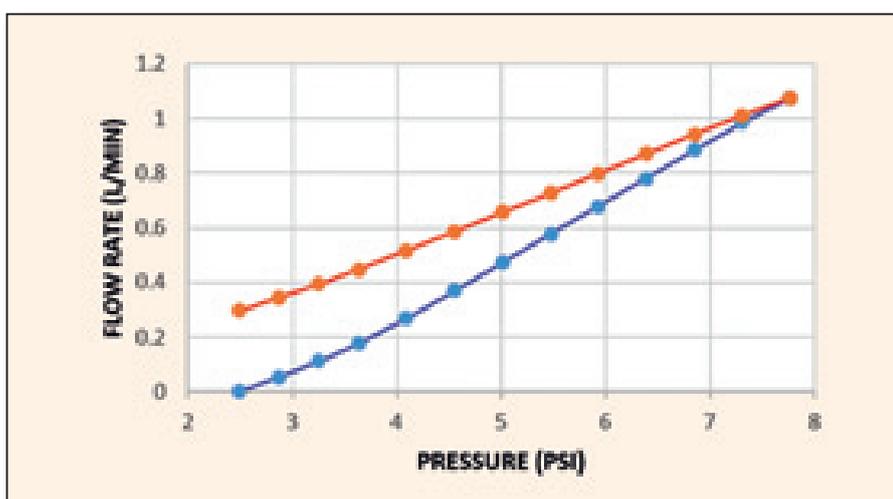
with P = pressure,  $\gamma$  = surface tension,  $\theta$  = contact angle and D = pore diameter

Depending on the type of application, samples may exhibit a low number of through-pores, which means that the maximum achievable flow through a given sample area can be too low for the lower resolution limit of the flow meters inside the instrument. There are options to use larger samples, such as holders for diameters of up to 47 mm or clamp-on holders which require no sample shape preparation prior to analysis, which increase the total available area of the sample and thus the amount of pore volume available. This increase leads to larger amounts of flows and allow a successful measurement of the more problematic samples. However, at times increasing the sample size is not an option, for example if a small filter component needs to be evaluated. In these cases, instruments can be fitted with a microflow option. This option consists of a pressure regulator, which is located on the "flow-side" of the sample. While the flow meter is too imprecise to determine flows lower than 1 % of the total volume of the meter, the pressure regulator gives a much more precise reading while only suitable for very low amounts of gas flow. This option allows for the detection of flows below 1 L/min. (see Fig. 3)

The development of composite membranes and membrane coated carrier substrates, which are in themselves unporous, poses a challenge to the characterization of through-pores. Since the gas cannot actually pass through the substrate and is only able to cross the material in a horizontal or



**Figure 2** Capillary flow porometry measurement of a 1 µm track etched membrane (left) with wet curve (blue), dry curve (red) and half-dry curve (yellow) and corresponding pore size distribution (right)



**Figure 3** Microflow capillary flow porometry showing wet curve (blue) and dry curve (red) of a lasered membrane with 3 mm diameter.

“in-plane” direction, a typical sample setup for pore size characterization is no longer viable. In these cases, a special in-plane sample holder is required. The sample is fitted in between two polymer gaskets and pressure is administered only on a small radial opening on top of the sample so the pressure propagates only in the sample plane itself. This allows for the analysis of combined materials by means of both capillary flow porometry as well as permeametry (see Fig. 4).

This method may also show differences in the interconnectivity between through-pores crossing the material in through-plane direction and channels interlinking these pores in in-plane direction.

With the use of the wetting liquids Galwick (surface tension = 15.9 dyn/cm) and Silwick (surface tension = 20.1 dyn/cm) and pressures up to 500 psi (~35 bar), pore sizes can be measured down to a minimum of ~15 nm. Measuring smaller pores would require the use of pressures of higher than 500 psi, which is not advisable regarding the physical strain these pressures would put on the internal valving and sensors of the instrument. Instead, it is possible to artificially decrease the surface tension of the wetting liquid in the pores by switching from pressurized air to a liquid-liquid approach. In this setup, a second liquid is put on the pressurized side of the sample after the sample has been saturated with the wetting liquid. In the case of using Galwick as a wetting liquid and bringing it in contact with isopropyl rather than compressed air, the surface tension on the interface between the two liquids decreases to 4,3 dyn/cm and allows for the characterization of pores from a maximum of 0,3 μm down to a minimum of ~3 nm (see Fig. 5).

## Conclusion

These examples highlight the flexibility of the PMI porometers, which can be adapted to face any analytical challenge with regards to through-pore characterization. This article showcases only some major features of the

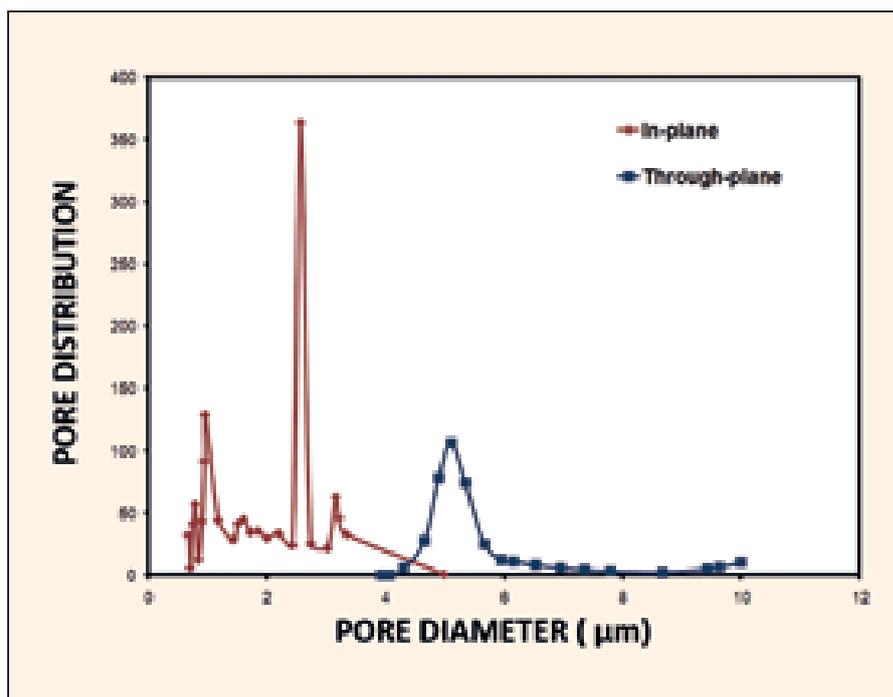
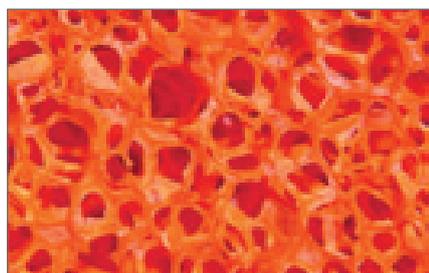


Figure 4 Comparison of pore size distribution in through-plane direction (blue) and in-plane direction (red) on a piece of cardboard sheet

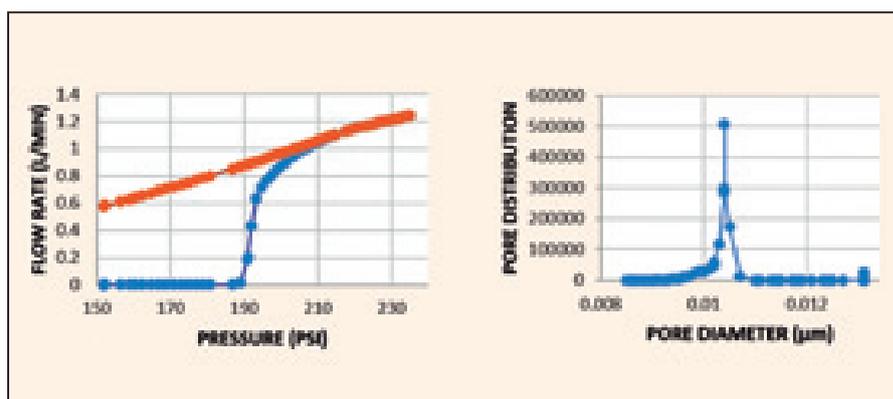


Figure 5 Microflow capillary flow porometry flow curves (left; blue = wet, red = dry) and corresponding pore size distribution (right) of a 10 nm polycarbonate-based membrane obtained by liquid-liquid-porometry with a combination of Galwick and isopropyl

instruments. A large variety of sample holders and adapters can further increase the spectrum of viable materials for this method, such as hollow-fiber kits, special sample holders (such as the Frazier module or an automated wetting function) and different wetting liquids for special applications. If you are interested or have further questions about the use of porometry and permeametry, feel free to contact us at [info@3P-instruments.com](mailto:info@3P-instruments.com) or +49 8134 9324 0. We are happy to help and are your partner in characterization of particles, powders and pores. ■

## Literature

- [1] S. P. Adiga, et al. Interdiscip Rev Nanomed Nanobio-technol. 2009 Sep-Oct; 1(5).
- [2] H. Lee, et al. Energy & Environmental Science 2014 7(12).
- [3] G. A. Gebreslase, J. Membr. Sci. Technol. 2018, 8 (2).
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- [5] R. Finn, Notices of the AMS 1999, 46 (7).

## LabSPA - contract analyses



Do you already know our scientific application laboratory LabSPA (Laboratory for Scientific Particle Analysis)? We offer a wide range of contract analyses for the characterization of dispersions, powders and porous materials. Individual analyses, on-demand orders for a large number of samples or comprehensive laboratory projects - everything is possible at LabSPA. On request, you can directly contact the laboratory staff responsible for your samples.



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

Order-No.	Parameter/ Methodology
140056	Particle size distribution/ Laser diffraction method - wet measurement
140057	Particle size distribution/ Laser diffraction method - dry measurement
140058	Particle size distribution/ Laser diffraction method in isopropanol
140059	Particle size distribution/ Laser diffraction method in other dispersion media
97388	Particle size analyses/ Method development laser diffraction
140060	Particle size distribution/ combined method laser diffraction and CCD-camera technique - wet
97381	Particle size and shape of dry powders and granulates, 30 µm - 10 mm
90006	Particle size distribution by acoustic spectroscopy, > 5 nm
97423	Particle size determination with DLS resp. PCS, 1 nm – 9.5 µm
140097	Particle size by sieve analysis
140061	Particle size distribution and image analysis/ laser diffraction and image analysis - wet measurement

### Zeta potential, electrical conductivity and permittivity

90007	Zeta potential/ Electroacoustic
90008	Zeta potential as function of the pH-value (titration)
90009	Dielectrical permittivity
97239	Electrical conductivity of non-liquid systems

### Viscosity of liquids and dispersions depended on temperature and shear rate

330001	Viscosity of liquids and dispersions, one-point measurement
330002	Viscosity of liquids and dispersions, in dependence of the shear rate
330003	Viscosity of liquids and dispersions, in dependence of the shear rate and the temperature

### Drying behavior of coatings and films

90013	Drying behavior short time characterization / Micro rheology
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### Melting behavior of foods and cosmetics products

97411	Melting behavior/ Micro rheology
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### Stability of liquid dispersions: emulsions, suspensions and foams

90010	Stability / multi light scattering
90012	Heavy fuel characterization

### Dispersion projects

97732	Formulation of dispersions
97734	Nano-material test according EU definition
97735	Dispersion project, individual

### Flowability, compressibility and further specific properties of powders

Order-No.	Parameter/ Methodology
140016	Angles of repose and collapse of powders
140017	Dispersibility, uniformity and cohesion of powders
140018	Flat plate angle (angle of spatula) of powders
140019	Compressibility of powders
140020	Porosity of powders
140021	Flowability and floodability Indices of powders

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

90021	Multipoint-BET with nitrogen
98030	Multipoint-BET with carbon dioxide
90022	1-point-BET with nitrogen
90023	Multipoint-BET with krypton (for small surfaces)
97425	STSA surface area for the characterization of carbon blacks
90024	Micropore surface / Micropore volume

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

90015	Pore size distribution / Pore volume
90020	Extended porosimetry
97436	Hg contact angle measurement

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

90025	BET-surface area, pore volume, average pore size
90026	Standard mesopore analysis (BJH-method)
90027	High resolution mesopore analysis
90028	Micropore analysis
97497	Micropore analysis of pore systems < 0.7 nm (probe molecule method)
90029	Micropore and mesopore analysis
97561	Pore analysis of thin porous layers (krypton 87 K-method)
96884	Micropore analysis of carbon materials
96885	Isotherm measurement in the normal pressure range
97562	Determination of adsorption enthalpy in normal- and high-pressure range
97499	High-pressure adsorption isotherm up to 200 bar, from 77 K up to 400 °C
90030	Evaluation of gas sorption analyses (from external data) acc. to state-of-the-art evaluation methods

### Characterization of through-pore-systems (pore size, bubble point, gas and

97395	Characterization of through-pore-systems, standard
97404	Characterization of through-pore-systems, special
97396	Gas permeability up to 35 bar
97397	Liquid permeability up to 14 bar

### Density, raw density, bulk- and tap density as well as porosity and average pore size (alternative to Hg-porosimetry and gas adsorption)

90088	Density (true density) of solids by gas pycnometry
97500	Density (true density) of solids
97501	Density of liquids
97502	Density of dispersions
90089	Stampfdichte
90114	Bulk density
90090	Raw density, gravimetric by mercury pycnometry
97503	Raw density by buoyancy weighing
97824	Raw density by powder covering

**Closed cell determination of foams and vacuole volume of milk powder**

Order-No.	Parameter/ Methodology
90091	Closed cell determination, uncorrected
97290	Closed cell determination, corrected
97291	Foam material characterization, compressibility
97507	Vacuole volume of milk powder

**Vapor sorption (DVS and volumetric sorption of water and other vapors)**

97274	Water vapor isotherm, adsorption and desorption, gravimetric
97390	Water vapor isotherm adsorption, desorption and sorption kinetics, gravimetric
90081	Water vapor isotherm, adsorption and desorption, static-volumetric
90082	Water vapor isotherm, adsorption
90083	High resolution water vapor isotherm, adsorption and desorption
90084	Water vapor isotherm, hysteresis behavior
90085	Water vapor isotherm incl. determination of the adsorption heat
97391	Vapor sorption, static-volumetric

**Chemisorption and temperature programmed reactions for the catalyst characterisation**

90086	Chemisorption analysis, static-volumetric
97405	Adsorption equalibration of gas mixtures
90087	Temperature programmed reactions (TPD/TPR/TPO a.o.)
97392	Temperature programmed reactions (TPD/TPR/TPO a.o.) with mass spectrometer

**Adsorption of gas mixtures and corrosive gases**

330020	Study of the regenerability of adsorbents
330009	Adsorption equalibration of gas mixtures
330010	IAST-calculations
330011	PRAST-calculations
330012	Kinetics - diffusion
330013	Uptake - kinetics

**Breakthrough curves of gases, vapores and gas/vapour mixtures**

330014	Breakthrough curves of pure gases or vapors through textiles
110781	Breakthrough curves of non-corrosive gases through packed adsorber column
110782	Breakthrough curves of gases and vapors
330017	Breakthrough curves of corrosive gases through packed adsorber column

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330026	Special studies of adsorption from components from water

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