

PARTICLE WORLD

TECHNICAL PAPERS of
QUANTACHROME
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Macroscopic powder characterization:
fully automated analysis of physical
powder properties

From the idea to the technology behind
the gas and vapour separation process:
dynaSorb BT is gearing up!

CryoSync™: Small option making a
substantial difference in gas adsorption

**“The next generation”
in particle measurement:**
the combination of static light scattering and
dynamic image analysis with the BETTERSIZER S3 Plus

Better Size
Better Shape
BETTERSIZER S3 Plus
Better Result
Better Value



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On the occasion of his 25th anniversary in his career, our CEO Dr. Dietmar Klank talks about the latest developments and news at QUANTACHROME GmbH & Co. KG. The interview was conducted by Elke Peter, info@elke-peter-werbung.de:

Dr. Klank, you recently celebrated your 25th anniversary in your career. Congratulations on that achievement! How do you feel?

From today’s perspective, I am very satisfied with my personal development and professional career. As a young graduate, you are hardly able to anticipate your business career. As of today, I have been working in this demanding position at QUANTACHROME GmbH & Co. KG since more than 10 years, and I am very pleased about the current status that is indeed very positive. QUANTACHROME is known for its permanent development. The current business year indicates the strongest growth in turnover in the company’s history. We are now involved in projects we would not have dared to dream about a few years ago.

How did you gain a foothold in the interesting field of particle size technology? After you earned your university degree, you changed to this business. Being a chemist, why did you embark on this career?

As you know, I have my roots in central Germany, studied Chemistry at Leipzig University. Back in 1992, I obtained my docto-

rate in the field of micropore characterization of activated carbons. It was a time of upheaval in the North-Eastern part of Germany. On the one hand, tens of thousands people in the traditional chemical triangle Bitterfeld-Wolfen/Buna/Leuna were laid off. On the other hand, university laboratories and similar facilities benefited from major investments in state-of-the-art technology. While I still wrote my dissertation using a data base originating from manually operated adsorption devices that I built on my own, we already received an automatic sorption analyzer in 1992. This was basically my career starting point in the distribution of such analyzers. Only then, I got involved in sales and distribution, accepted the position and became in charge for the instrument distribution in the North-Eastern part of Germany.

Being a newcomer in the field of sales and distribution at that time, how were the initial years?

This time was distinctive for me and my customers. Professional distribution was rather new to us, and the term “distribution” had a rather negative connotation, especially in the North-Eastern region. However, you could play your cards right when you remained authentically and actually offered solutions. With that in mind, I was very successful, especially in the distribution of adsorption instruments. My work clearly benefited from the expertise gained in the dissertation. Additionally, these sales activi-

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ties were very interesting from the first day on. I got in touch with numerous other business fields, as some analyzers are used for a broad range of applications. It is with a smiling face that I remember some stories. For example, I remember not having a phone for some weeks back in 1994. Accordingly, I had to use a public phone box to contact my customers. One or the other professor may have found it somewhat odd when the call was suddenly interrupted, as I ran out of cash money...

As far as I know, you did not start your sales career at QUANTACHROME. How was your professional career?

Back in 1992, I started as Account Manager for MICROMERITICS. End of 1998, I moved to QUANTACHROME. I considerably extended my knowledge base with a wide range of products, as -for example- particle size and zeta potential measuring devices played a more important role. As it is common in small companies, I held multiple functions: I was regional sales representative at QUANTACHROME for acoustic and electroacoustic spectrometers and later became Marketing Director in parallel.

Back to the 90s: after 6 years at MICROMERITICS, you changed to QUANTACHROME, a company working in the same business field. Are you in the position to name reasons for your decision, and which feedback did you receive from your customers?

Changing from MICROMERITICS to QUANTACHROME was one of the hardest career decisions, and I did not take it from one day to the other. At that time, MICROMERITICS GmbH had 7 employees. Since then, they became even less. In contrast, QUANTACHROME recruited a number of employees at that time. With the corresponding decisions of the company's senior management, QUANTACHROME could potentially set up a test laboratory using the known CILAS laser granulometers. While we at MICROMERITICS had to send our specimens to our parent company in the U.S. and wait for the results up to 8 weeks, more and more clients decided for a QUANTACHROME measuring device. Unfortunately, MICROMERITICS did not reasonably respond to this development, although it took me 2 years of useless discussions to finally draw my conclusions. In retrospect, my general opinion about this

situation was confirmed when my two former sales colleagues decided to leave the company after 4 and 8 years too.

Of course, some of my customers did not understand my decision, felt abandoned and missed my expert advice. Anyway, the development since then is clear proof that QUANTACHROME has a much faster pace. When I started at QUANTACHROME, we already counted 15 employees; now, we are more than 30. The main reason for my decision back then was the missing test laboratory being the base for fast customer support, and MICROMERITICS GmbH is still lacking it today. In contrast, our QUANTACHROME laboratory - we are now calling it LabSPA (Lab for Scientific Particle Analyses) - has permanently developed; it now employs 4 female and 1 male colleagues. It does not even include our development laboratory in Leipzig, where scientific employees work on customer-specific solutions. This development is proof of the fact QUANTACHROME never run into stagnation, but 20 years of substantial development. In that light, and especially from today's perspective, my decision was absolutely right.

How did your professional career develop at QUANTACHROME?

In parallel to my sales activities, and driven by my experience gained in changing companies as well as vocational uncertainty, I took up studies in economics at Distance-Learning University Hagen. In addition and as mentioned earlier, I became Acoustics (particle size analysis) and Electro-Acoustics (zeta potential) expert. Later on, I became gas adsorption product specialist, and assumed the responsibility for the marketing in 2002. Further, I have worked in the German Norm (DIN) committee for surface and pore analysis. Those were extremely busy years helping me to profoundly understand sales, the work as product specialist, but also marketing and economics. Assuming the marketing responsibility was a major milestone in my professional career and the company's history.

Can you explain that? Didn't your company have any marketing prior to that? Can you please illustrate this development step?

To put it short: it is easily explained with the sales figures. Let me point out one major

Read more on page 26 >>>



“The next generation” in particle measurement: the combination of static light scattering and dynamic image analysis: BETTERSIZER S3 Plus

Dr.-Ing. Christian Oetzel, christian.oetzel@quantachrome.de

Introduction

Since the 1970s, static light scattering and laser diffraction have become one of the most important and widely accepted methods for the determination of particle size distribution. Reasons for this development include deficiencies of previous standard methods such as sieving: long measurement duration, limited measuring range especially in the fine range ($< 10 \mu\text{m}$), but also lower distribution resolution and partially poor reproducibility. These aspects are the main advantages of static light scattering. In addition, this method can be easily automated with a suitable and very user-friendly instrument setup.

However, as any other method available on the market, laser diffraction also carries disadvantages that are mainly attributable to the tendency of manufacturers to considerably increase the up and downwards measuring range. Static light scattering includes an optical fitting method: the light scattering spectrum is fitted based on a theory (MIE or FRAUENHOFER), and the particle size distribution is calculated accordingly. However, the method does not provide information on whether the calculated distribution corresponds to reality and whether other circumstances such as agglomeration or a particle shape deviating from the ideal sphere have a major impact on the results. Especially in case of a wide distribution, coarse material is hardly or imprecisely found, as the majority of small particles dominate the statistics. Since coarse particles (especially $>100 \mu\text{m}$) are scattered in forward direction only, the resolution of the spread spectrum becomes increasingly difficult; especially in case very small particles are to be included.

This issue can be solved in the upper measuring range by combining static light scattering and dynamic image analysis. Image analysis allows an exact coarse particle size determination and further provides detailed information on the individual particles of the particle agglomerates: oversized particles and agglomerates can be directly measured. The images recorded provide essential information on the particle shape. However, the implementation of a measuring technology combination is quite challenging, as it requires a high-performant optical bench, an ultra-speed and high-resolution camera system as well as a very capable software to directly process all information online.

BETTERSIZER S3 Plus (Fig. 1) is the first instrument on the market that successfully combines these features offering unique and comprehensive particle size and shape characterization possibilities in the nanometer to millimeter range.

Figure 1
BETTERSIZER S3 Plus



BETTERSIZER S3 Plus – Instrument technology

Fig. 2 depicts the basic setup of BETTERSIZER S3 Plus: the base platform carries a wet measuring cell. A laser diode (green, 532 nm), the CCD camera system (2 cameras, X0.5 and X10) and a back-scattering detector are located at the right side of the measurement cell. A Fourier lens is placed directly in front of the measuring cell.

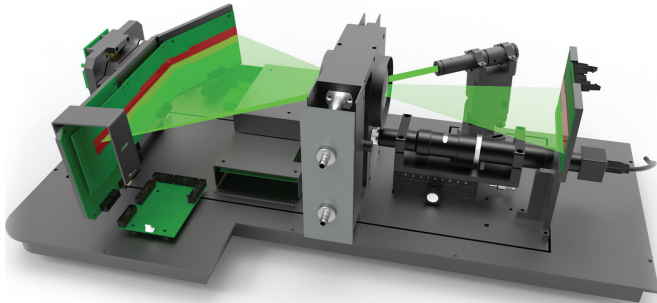


Figure 2
Setup of BETTERSIZER S3 Plus

Left to the measurement cell is a second Fourier lens and the detector system for the determination of forward and sideward scattering (two Fourier lenses = dual lens technology).

This specific setup allows

1. The exact measurement of very small particles (starting at 10 nm) using the dual lens technology (static light scattering)
2. Highest-possible measurement precision for very coarse particles (up to 3.5 mm) using a 0.5 X CCD camera (static light scattering combined with dynamic image analysis)
3. Particle shape determination, oversized particle analysis and agglomerate check using the 0.5 X and 10 X CCD camera (dynamic image analysis)

1. Static light scattering with innovative dual lens technology (DLOIS)

The diagram in Fig. 3 outlines the details of the specific **DLOIS** technology setup (**D**ual Lenses & **O**blique Incidence Optical **S**ystem).

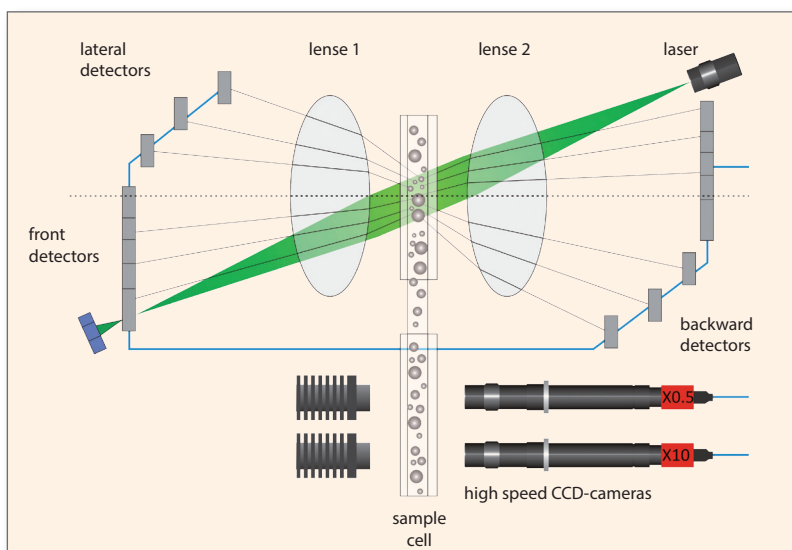


Figure 3 Schematic overview of the DLOIS technology deployed in BETTERSIZER S3 Plus and CCD camera technology (X 0.5 and X 10)

The laser (wave length 532 nm) is positioned in an oblique position towards the measuring cuvette ensuring the widest-possible scattering angle range of the lateral front detectors. Lens 2 produces an exactly parallel laser beam hitting the sample. According to the Fourier method, lens 1 focuses the scattered light in the detector plane. Therefore, the scattered particles in the cuvette do not necessarily have to be in one plane, which is a major disadvantage of the common inverse Fourier setup. Lens 2 provides for the focusing and collection of the back-scattering again at a very wide-angle range (0.02 – 165°) ensuring excellent detector resolution compared to other systems available on the market. A good scattering light resolution in the back-scattering area (> 90°) is decisive especially for the exact detection of very fine particles (< approx. 500 nm) (see Fig. 4).

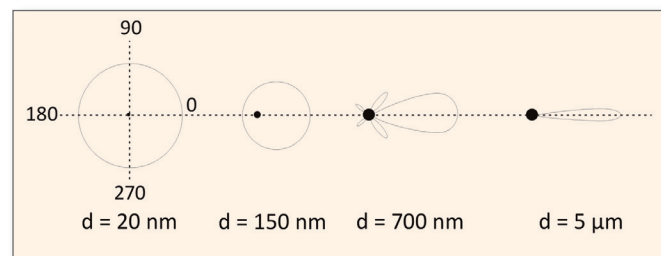


Figure 4 Laser light diffraction example ($\lambda = 633 \text{ nm}$) at various-sized particles (polar diagrams)

Further to that, a very wide angle offers the advantage that a second shorter-waved laser becomes unnecessary: Accordingly, no spread spectra of mixed wave lengths are measured, as it is strictly speaking prohibited to evaluate them using the common methods (FRAUNHOFER and MIE).

2. Static light scattering combined with dynamic image analysis

As already mentioned, an exact detection of coarse particles using static light scattering is challenging especially with a broad size distribution. Therefore, it is particularly useful to combine static light scattering (fine particles) with dynamic image analysis (coarse particles) to benefit from the advantages of both methods.

The high-speed CCD camera (X 0.5) integrated in BETTERSIZER S3 records images of coarse particles and statistically evaluates the results. Fig. 3 shows the measurement setup: during the measurement, the particles to be measured move through the measurement cell and cause the recorded light scattering spectrum (DLOIS), after that they pass the camera cuvette – which implies that the data collection (static light scattering, image analysis) is done simultaneously. During the measurement, the live CCD camera picture can be switched on online helping the user to directly evaluate dispersion and particle shape (spheres, agglomerates and possibly air bubbles, see Fig. 5)

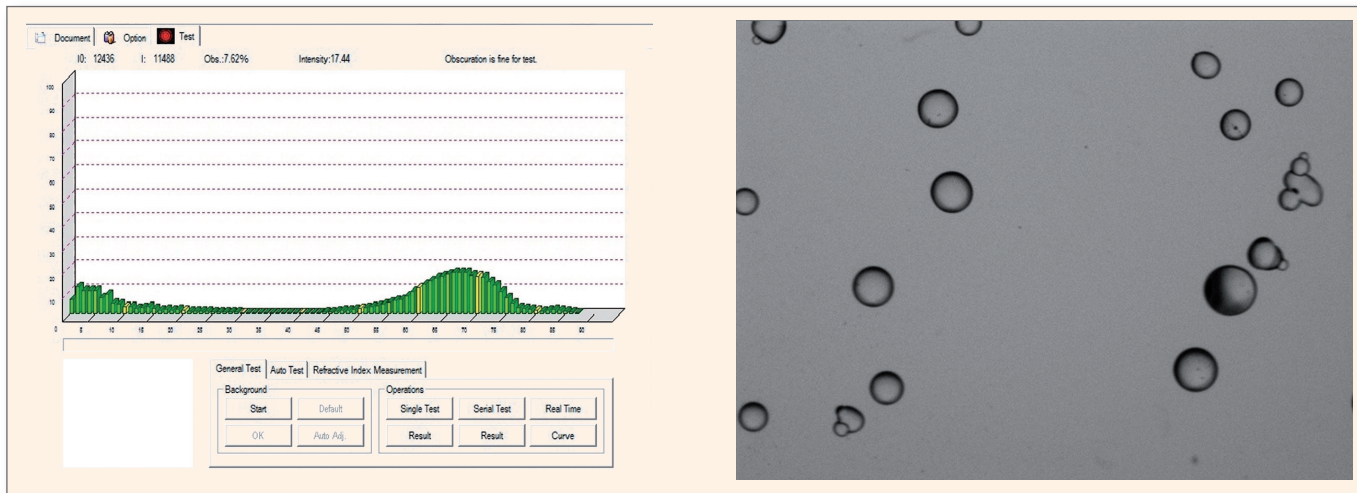


Figure 5 BETTERSIZER software with live CCD camera picture during a measurement

A smart routine combines the results of static light scattering and dynamic image analysis by weighting based on the concentration determination of both methods. To summarize, the combined use of DLOIS technology and dynamic image analysis allows for an accurate measurement of distributed systems from 0.01 to 3500 μm including a virtual evaluation of the analysis carried out.

3. Dynamic image analysis for the examination of particle shapes

BETTERSIZER S3 Plus offers the use of two high-speed CCD camera options with a recording speed of approx. 10000 particles per minute for the particle shape analysis:

- a) X 0.5-fold magnification for coarse particles (approx. 30 μm – 3500 μm)
- b) X 10-fold magnification for fine particles (approx. 4 μm – 100 μm).

Each individual particle is recorded, saved as image and statistically evaluated. Beside various equivalent diameters (surface, perimeter, maximum (L) and minimum (D) Feret etc.), aspect ratio (aspect ratio, length L/width D), circularity, roundness and perimeter are calculated.

In addition to the optimized determination of the particle size distribution, BETTERSIZER S3 Plus offers the optional use of important shape parameters for the extra characterization and classification of particles. This is a distinctive advantage compared to classic “pure” laser diffraction that assumes spherical particles in the evaluation process. Further, the system agglomeration degree can be evaluated, and oversized particles can be analyzed. The determination of various equivalent diameters furthermore provides users with a valuable comparison with other particle size analyzers such as sieving to verify the test results

Example: particle size and shape of sieved glass spheres

In this experiment, commercially available glass spheres (sieved between 400 μm and 800 μm) were dispersed in water using the standard wet dispersion unit of a BETTERSIZER S3 Plus, and the particle size distribution was determined. The evaluation was done using the combined method (static light scattering according to Fraunhofer and dynamic image analysis). The measurement result is shown in Figure 6.

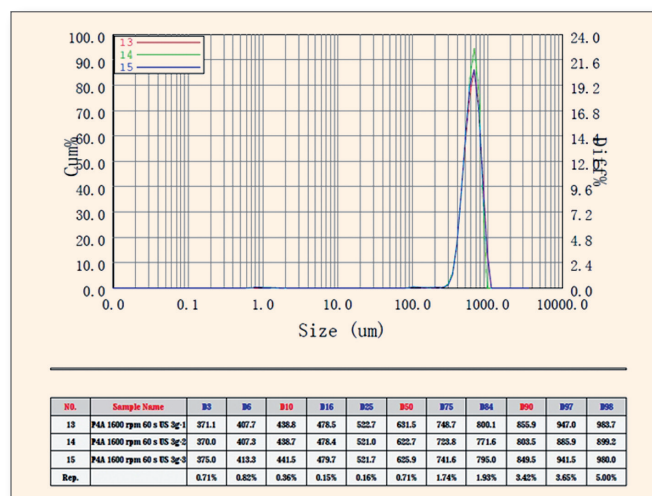


Figure 6 Sieved glass spheres measured with static light scattering combined with dynamic image analysis (BETTERSIZER S3 Plus)

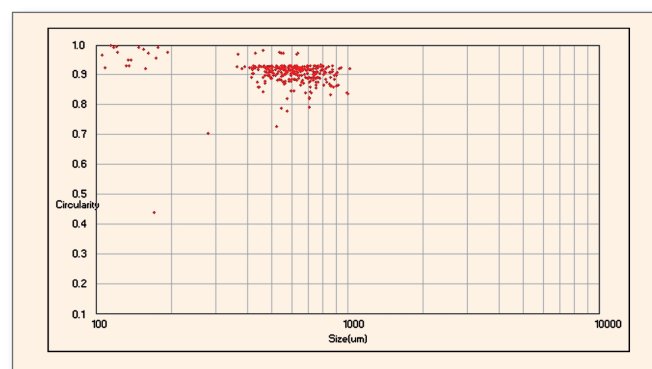



Figure 7 Trend diagram circularity vs. equivalent diameter of the glass sphere specimen

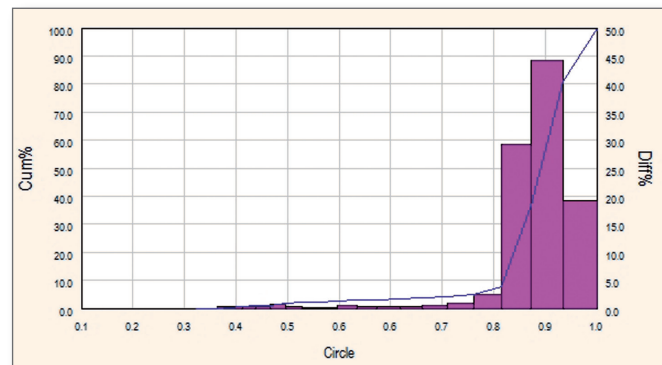
Table 1 Summary of details information table of the individual glass spheres

Nr.	Area [μm^2]	CE-Diameter [μm]	Feret max L [μm]	Feret min D [μm]	L/D	Circularity	Graph
1	819450	1021	1163	926.5	1.255	0.919	
2	797400	1007	1348	777.5	1.734	0.835	
5	680400	930.7	1013	892.5	1.135	0.92	
11	626850	893.3	1110	765	1.45	0.901	
17	597825	872.4	1105	709.1	1.559	0.93	
18	586350	864	1144	750.6	1.525	0.862	
19	581625	860.5	1215	615.7	1.974	0.832	
31	528525	820.3	1028	698.1	1.473	0.921	
36	508500	804.6	1151	570.8	2.017	0.866	
37	504000	801	947.8	662.4	1.43	0.928	
38	501075	798.7	1005	630	1.595	0.917	
39	500400	798.2	812.7	789.4	1.029	0.929	
46	472275	775.4	940.9	740.3	1.27	0.889	
49	462150	767	1049	540	1.944	0.891	

For coarse particles, the result slightly exceed the maximum size of 800 μm expected with the sieving method. For the fine particle size range, it is slightly below the expected values. Table 1 and the images of selected glass spheres illustrate the reasons for the particle size differences determined with sieving and combined measurement using static light scattering/dynamic image analysis: the majority of glass spheres seems to substantially differ from the ideal spherical shape.

Fig. 7 shows the trend diagram of the glass sphere specimen with the circularity put in relation to area equivalent diameter. Again, it becomes obvious that the majority of glass particles (circle = 1.0) deviates from the ideal sphere.

Even if circularity $C > 0.9$ (table 1, particle no. 11) is broadly defined and based on the sum curve of this value (Fig. 8), more than 50 % of the particles are not completely round and therefore deviate from the requested quality of a spherical shape.


Figure 8 Circularity sum curve: more than 50 % of the particles have a circularity of < 0.9

Summary

BETTERSIZER S3 Plus is an innovative particle size analyzer convincing with scientific and technical know-how, but also an unmatched price-performance ratio. Further information on BETTERSIZER S3 Plus is available at http://www.quantachrome.de/en/analysegeraete/bettersizer_s3_plus/. Please inquire details on contract and test analyses as well as instrument presentations at info@quantachrome.de.



Macroscopic powder characterization: fully automated analysis of physical powder properties

Dr. Frederik Schleife, frederik.schleife@quantachrome.de

Macroscopic and physical properties of powder bulks are the main characteristics of powder materials. The knowledge of these characteristics is crucial for the production, processing, packing, transport, storage and use of powders. For example, repose and collapsing angle need to be considered for the construction of a conical storage silo. Tap and bulk density are key figures in the dimensioning of packaging bags or barrels and in the manufacturing process of pills made from powder raw materials. Flowability and floodability indices are of importance when powdery raw materials or products are to be transported in pipeline airstreams. Although the macroscopic powder properties play a crucial role for their evaluation, there are only few analysis options available to quantify these parameters. Most measuring instruments are lacking accuracy and reproducibility making them suitable for a purposeful powder engineering to a limited extent only.

PowderPro A1 allows users to run comprehensive, fast and accurate tests on above physical key characteristics. This innovative physical test device incorporates state-of-the-art technology such as computer- or tablet PC-based control via Wi-Fi connection, a fully automated, digital image processing technology or 3D electro-magnetic material conditioning. PowderPro A1 is used to **determine 13 parameters of metallic and non-metallic powder specimen in accordance with ASTM D6393:**

- Repose and collapsing angle
- Difference angle, *flat-plate angle*
- Tap and bulk density
- Compressibility and dispersibility
- Uniformity and cohesion
- Powder porosity as well as flowability and floodability indices.

The key features of PowderPro A1 include:

Angle measurement using CCD camera and image processing routine

High-resolution CCD imaging technology is used to record an image of the pressed powder created under standard conditions. The unique image recognition and processing technology gathers parameters including bulk, collapsing and flat-plate angles etc. in a quick and simple and highly precise manner as well as with good reproducibility.

Automatic control technology

A fully automated computer or tablet PC control ensures ease of use and simple handling. Highly accurate and reproducible test results are ensured by the use of standardized measuring procedures (SOPs).

Data communication

An electronic scale can be connected to PowderPro A1 that automatically and directly transmits weighing data to the system. No further steps or manual input are necessary to use this information for data processing and results calculation.

Innovative technology to determine the tap density

Tap density is determined with PowderPro A1 by using the perfect combination of variable frequency and rotating vibration technology. Vibration frequencies can be continuously adjusted between 50 and 300 min⁻¹. Further, you can select between two different amplitudes (tapping height; 3 or 14 mm). Accordingly, the measuring cylinder is exposed to a uniform rotation movement throughout the entire vibrating time, which serves to creating a smooth surface and therefore exact readability.

Summary

PowderPro A1 is a easy to operate and exact measuring system for the comprehensive determination of physical characteristics of powders in accordance with a variety of

international standards making it an indispensable tool for understanding and exploring powders.

Specifications	
Measuring technology	Fully automated using CCD camera
Parameters	8 (measured) + 5 (calculated)
Powder types	metallic and non-metallic
ASTM conformity	ASTM D6393-08/D6393-14
ISO conformity	ISO 3953: 1993
USP conformity	USP32-NF27<616>
EP conformity	EP7.0 07/2010: 20934E
Reproducibility	≤ 3 %
Drop height tap density	3 or 14 mm
Vibration frequencies	50 – 300 times per minute (continuously adjustable)
Control	Tablet PC (incl.), smartphone or PC
Communication	Wi-Fi
Dimensions	600 x 350 x 730 mm (L x W x H)
Weight	42 kg
Power supply	AC 220 V, 50/60 Hz, 230 W

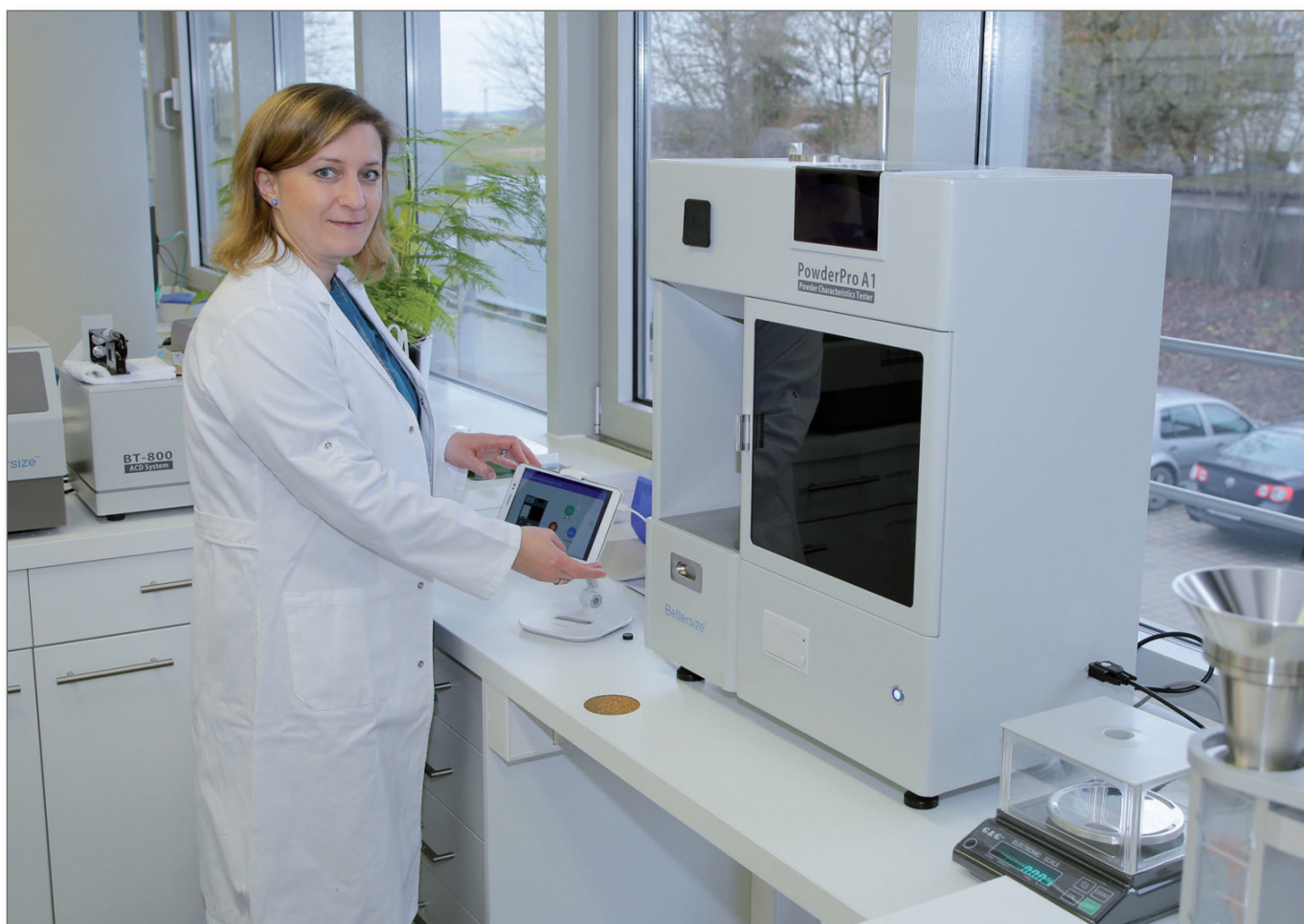


Figure 1 Our laboratory employee K. Eikelmann working with PowderPro A1 in the dispersion section of our LabSPA (Lab for Scientific Particle Analysis)

Particle size and shape measurement of granulates, dry powders and dispersions using dynamic image analysis

Dr.-Ing. Christian Oetzel, christian.oetzel@quantachrome.de

There is one key advantage of image analysis systems to determine the size distribution of a material in comparison to alternative methods like static light scattering, sedimentation or sieving: Every particle is photographed individually! This fact results in several important advantages:

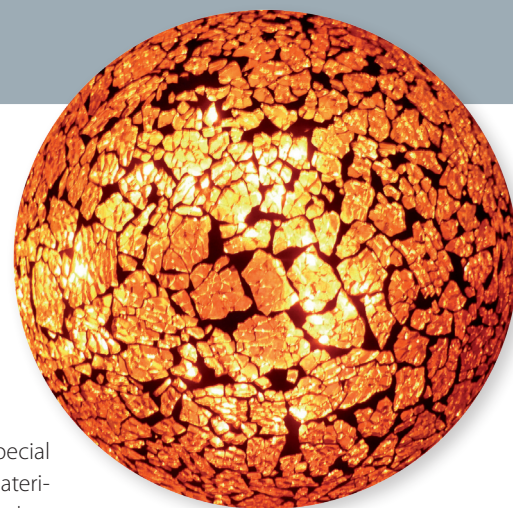
- Realistic share values especially at the outer parts of the size distribution, i.e. detection of oversized-particles and fine content
- Visual assessment of the state of dispersion of a sample (quality of dispersion, are agglomerates present)
- Calculation of reasonable size parameters depending of the application (e.g. geodetic length or Feret diameter for fibres)
- Choice of the distribution type depending on the topic (number, volume)

Furthermore it's possible to calculate special shape parameters to distinguish the materials additionally thanks to the individual photographs of the particles. For example the shape anisotropy of the particles (the deviation of the shape of an ideal sphere) is important for the processing of the material like transportation or compaction of powders, influence on the rheological properties in dispersions etc.

The new BeVision D1 – dynamic image analysis for dry- and wet dispersion

BeVision D1 is a microscopic image particle size and shape analysis instrument. The system is equipped by default with a dry dispersion unit, which mainly applies to coarser and granular material. The optional wet dispersion unit aims at micron range powder materials and dispersions.

The high-speed CCD camera enables a frame rate of 120 images per second to avoid trailing phenomenon in moving particles. Further the optical system is equipped with a high light LED array light source and a little phrase difference telecentric lens.



The dry sampler uses an electromagnetic vibration feeder with a software-controlled height adjustable feed funnel and gravity (free fall) to disperse the particles (figure 1). During the free fall process, images are taken in real time and the software identifies and analyses particles regarding size and shape immediately. Agglomerated particles are recognized automatically to achieve accurate results. Beside the equivalent particle diameter, shape parameters like aspect ratio, circularity and radius-thickness ratio are calculated.

The (optional) wet dispersion unit consists of a measurement cell and an external circulation dispersion system equipped with an ultrasonic bath and a centrifugal pump. It can be easily installed by sliding the cell in the provided bracket of the instrument.

Table 1 gives an overview about the most important size- and shape parameters, which are provided in real time by the BeVision D1.

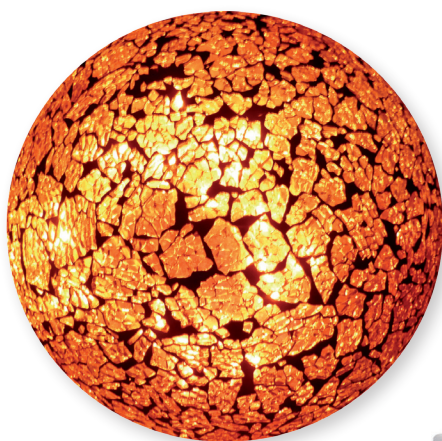


Figure 1 BeVision D1

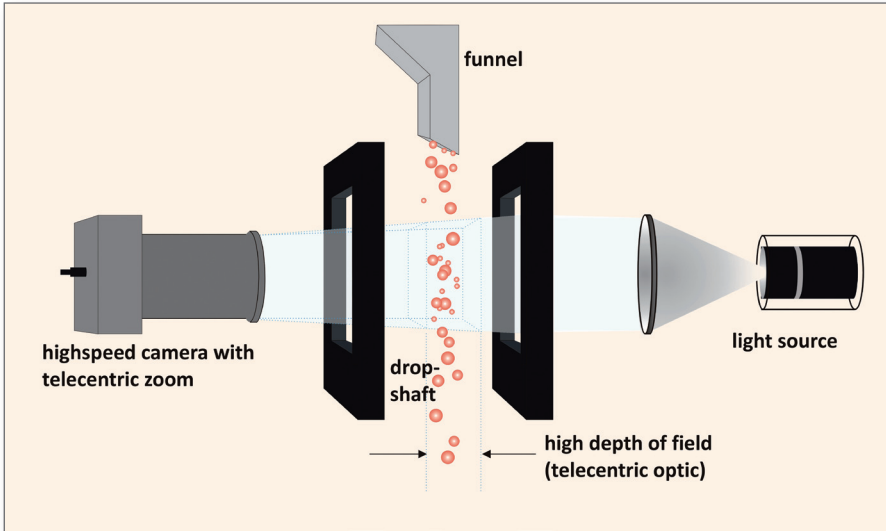


Figure 2 dry dispersion system of the BeVision D1

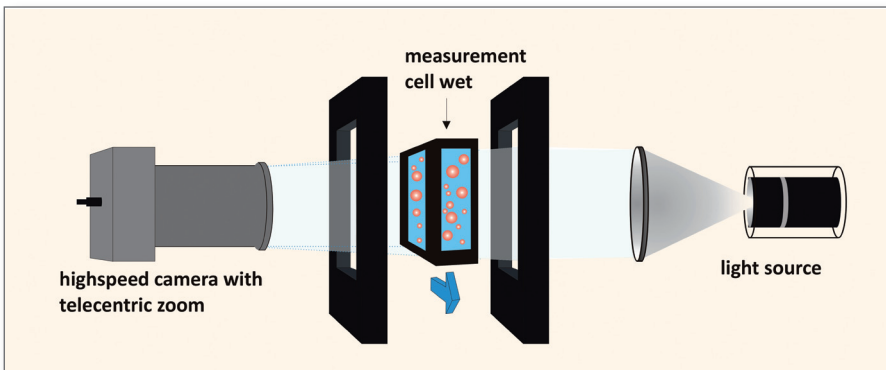


Figure 3 wet dispersion system of the BeVision D1

Summary of the benefits of the BeVision D1

- robust and sample adaptable dry feeding system – size range 30 μm – 10000 μm
- easy to adjust wet measurement unit equipped with a ultrasound disperser - size range 2 μm – 3500 μm
- stable and reliable optical camera system with high speed CCD camera (120 frames/s) – easy to calibrate with an adapted ruler with calibration scale
- real time image recording and analysing
- intelligent software to identify over 10000 particles per minute, automatic filtering of recognized connected or agglomerated particles to achieve stable and reliable results
- Calculation of different size (area equivalent diameter, Feret max and min etc.) and shape parameters (aspect ratio, circularity perimeter)
- Compliance with CE, FDA 21 CFR Part 11 and ISO 9001-2008 certification

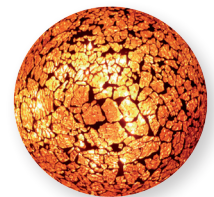


Table 1 BeVision D1 – Overview about the most important size- and shape parameters

Parameter and description	Draft
<p>CE-equivalent diameter D_{eq}</p> <p>D_{eq} is the diameter of a particle, which correspond to the diameter of the circle with the same area A of the 2D projection of the particle.</p>	
<p>FERET max L and FERET min D</p> <p>A FERET diameter is a measure of an object size along a specified direction. In general, it can be defined as the distance between the two parallel planes restricting the object perpendicular to that direction. L is the biggest, D is the smallest FERET diameter of a particle.</p>	
<p>ISO circularity (shape factor) C</p> <p>C of a given particle is the ratio of the perimeter of a circle with the same area A like the particle divided by the real perimeter P of the particle. Thus this value is a deviation of the ideal circle</p>	<p>$L/D=0, C = 1$</p>
<p>Aspect ratio L/D</p> <p>L/D is the ratio of the size of a particle of the longer side (Feret max L) to its shorter side (Feret min D)</p>	<p>$L/D=0,82, C=0,47$</p>



Heat resistance of lipid based ointments

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Introduction

Ointments are made of a mixture of fatty compounds, such as waxes, oils, and vegetal butters (e.g. shea or cocoa butter). The final texture should be soft enough while forming a strong network of wax crystals to enclose perfumes, active principles, and other agents during storage over a wide range of temperature (10-35 °C). With RHEOLASER CRYSTAL, we have characterized ointments in two ways:

1. Heating ramp analysis
2. Heating-cooling cycles analysis to evaluate thermal stability.

Experimental results

A 100% lipid-based ointment was used, which was composed mainly of shea butter (30 %), vegetable oils and waxes. Sample 1 showed the formation of crystals after some weeks of storage (see Figure 2). It deteriorated significantly the aspect and gave it an unwanted granular feeling on the skin.

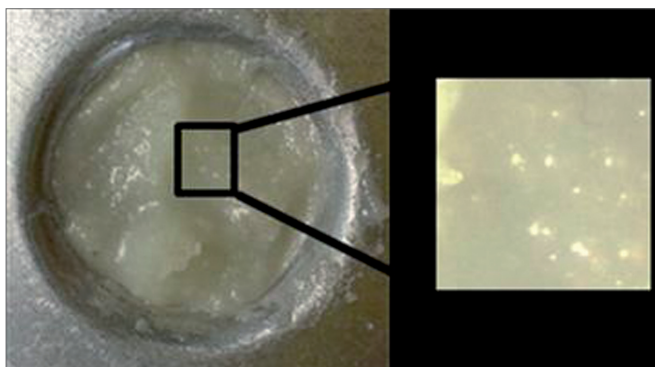


Figure 2 Photo of the Sample 1 where crystals are visible to the naked eye

To prevent this phenomenon, the formulator applied three different strategies:

- Sample 2: Product was recrystallized;
- Sample 3: Cetyl alcohol was added;
- Sample 4: Compritol 888® was added.



Figure 1
RHEOLASER CRYSTAL

Part 1 – Heating ramp analysis

The four different ointments were tested by using a heating ramp from 10 to 80 °C. During heating, fat crystals can undergo polymorphic and/or melting transitions. These transitions are accompanied by microstructural changes and therefore, by an increase of the Micro-Dynamics. Peaks can be observed and assigned to phase transitions.

In Figure 3, the four ointments have different signatures. The sample 1 has three different characteristic peaks, of which the first starts at 20 °C. This is the oil phase, which is not correctly entrapped by the wax/shear butter network. The second peak (44 °C) is attributed to the shea butter crystals, and the last peak (50-55 °C) indicates melting of the wax phase. In sample 2, only one peak can be observed, meaning that the product is a perfect eutectic (crystallized at the same temperature).

The phase transition starts at higher temperatures (>30 °C), so the oils are retained in a better and more efficient way. Sample 3 and sample 4 show melting at higher temperatures. However, cetyl alcohol did not induce a eutectic product as two clearly separated peaks can still be identified. Sample 4 shows one big melting peak at 50-60 °C. This ointment can be considered as eutectic with probably high stability. However, the end use properties were not satisfying as the ointment was not comfortable to spread on the skin.

Part 2 – Heating/Cooling cycles analysis

As shown in the part 1, the formation of crystals in shea butter may be due to a processing problem, and it can be also induced by environment conditions such as temperature changes during the storage and transports. It can be simulated by heating/cooling stress tests as following: heating at 31 °C for 15 minutes, and then cooling at 20 °C for 15 minutes, and so on.

Figure 4 shows the Micro-Dynamics during 4 heating and cooling cycles for all the samples. Sample 1 shows an important increase of μD during the first heating to 31 °C, as oils and soft fatty compounds start to melt and the oils are less retained. The heating has a significant impact on the material.

To quantify the restructuring capacity after heating and cooling, the μD levels are compared in term of the height of peaks at heating and the results are displayed in figure 4 (first peaks were normalized). The lower the variation of this parameter, the lower is the impact of temperature on the product.

In detail, the second heating peak in sample 1 showed a large decrease compared to the first peak, which means that the structural recovery is very poor because of the first destructive heating. Sample 4 with Compritol showed an intermediary behaviour. The recrystallised sample 2 and cetyl alcohol doped sample 3 have only small changes, indicating that the structural recovery is very good after heating and cooling cycles.

Conclusion

The original non-eutectic product with the shea butter crystals did not reach anymore the original properties in the thermal tests, indicating a very poor heat resistance. recrystallisation or the addition of high melting lipid excipients (long chain fatty alcohols or fatty esters) can both improve the temperature resistance by reinforcing the crystal network.

RHEOLASER CRYSTAL is a useful tool in the evaluation of cosmetic products heat resistance. Heating ramps can clearly identify the nature of quality problems, such as low melting or crystal phase segregation. Heating/Cooling stress test allow the evaluation of the products long-term stability against changing environment conditions.

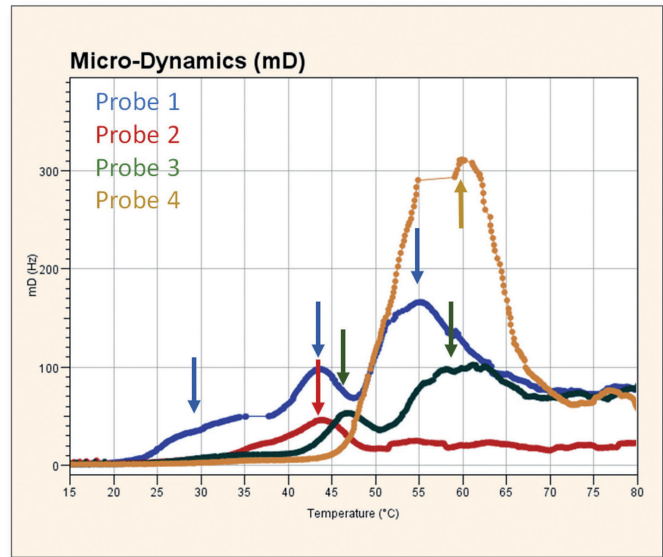


Figure 3 Micro-Dynamics as a function of temperature for the 4 samples

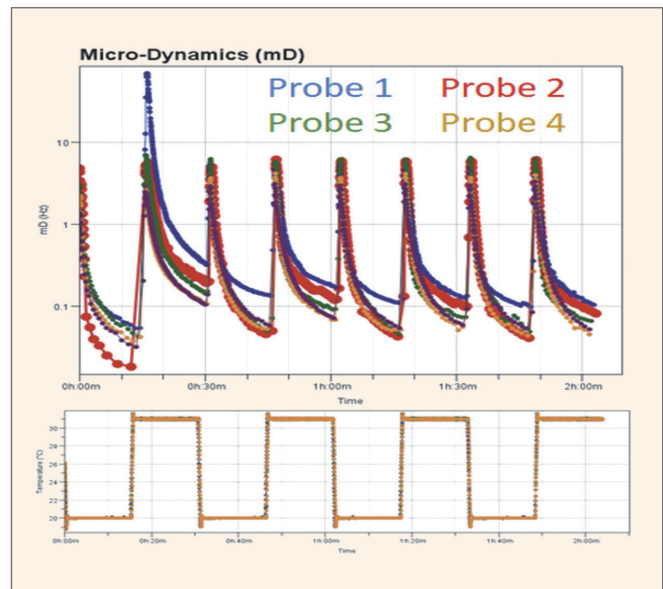


Figure 4 Micro-Dynamics as a function of 4 heating/cooling cycles for the 4 samples

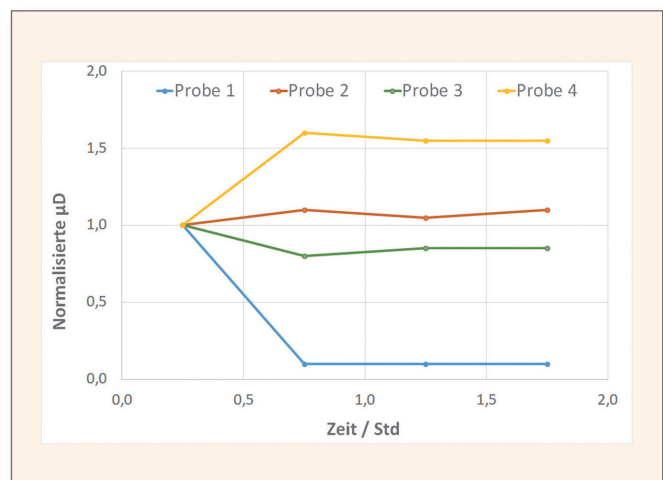


Figure 5 Micro-dynamics peak heights (first peak normalised) at heating for all the samples



Why use a microfluidic rheometer?

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Figure1
FLUIDICAM RHEO

Introduction

Multiple techniques have been developed over the years to assess rheological behaviour of complex fluids from water-like solutions to more pasty and thicker materials. The most commonly used instruments are based on a measure of the resistance to rotation of a spindle in contact with the sample. These instruments present multiple limitations, especially for liquid solutions: high sample volume is required, high shear rates are difficult to achieve and often hydrodynamic instabilities or interfacial artifacts affect the quality of the measurement.

In recent years, the use of microfluidics has increased to overcome these limitations. Microfluidic is the science dedicated to studying the flow behaviour in systems with at

least one dimension on the micron scale. Our technology uses a Y shaped flow comparator to measure viscosity.

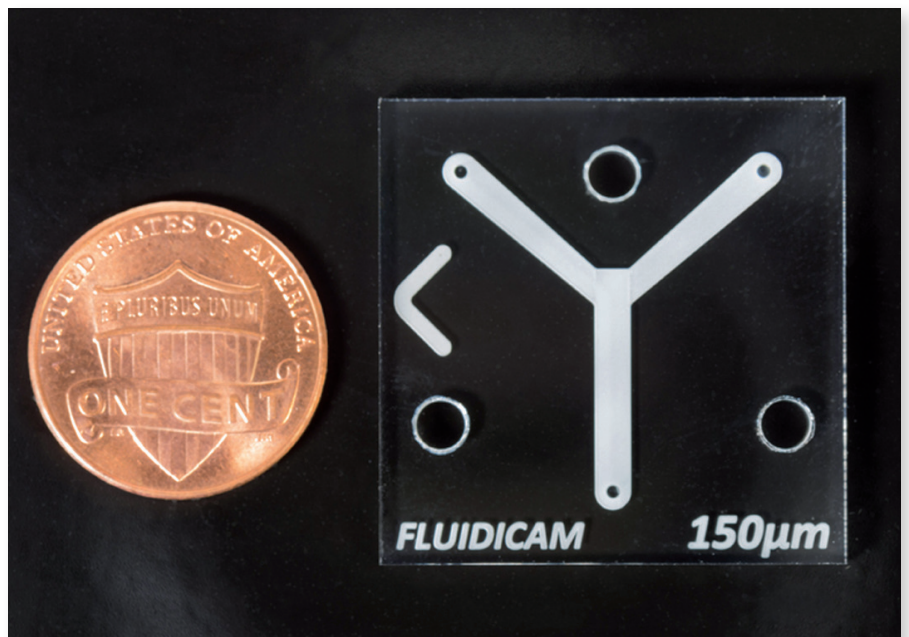


Figure 2 Dimensions of Microfluidics

Reminder on the technique

FLUIDICAM RHEO is based on a co-flow microfluidic principle to measure viscosity. Sample and viscosity standard are pushed together simultaneously into the microfluidic channel (typically 2.2 mm x 150 μm) under controlled flow rates. This results in a laminar flow, interface position between sample and reference relates the viscosity ratio between the two to the flow rates.

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

Interface centering

The instrument calculates the viscosity based on the interface position. At equal flow rates, the interface position will shift from the center, the more viscous fluid takes up more volume in the channel. However, the accuracy is the highest at the center of the channel, as the wall effect is minimized and the flow quality is optimized. Thus, the software uses smart algorithms to automatically adjust the flow rates to maintain demanded shear rate and the interface in a measurement area in the center of the channel.

Once the interface is centered, the wall interactions are negligible and viscosity can be measured in optimal conditions. The interface position is detected and images acquired.

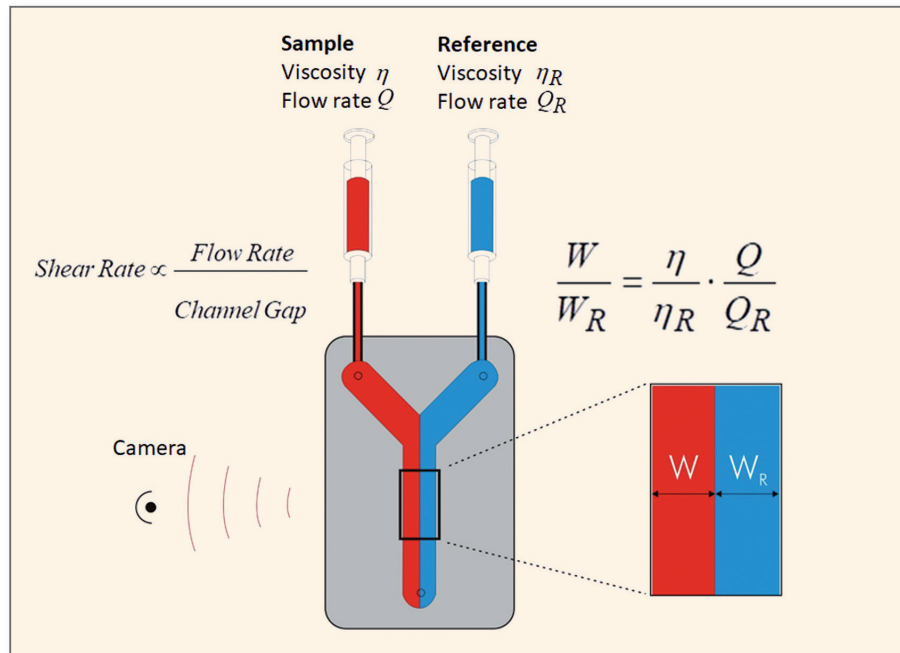


Figure 3 FLUIDICAM RHEO measuring principle

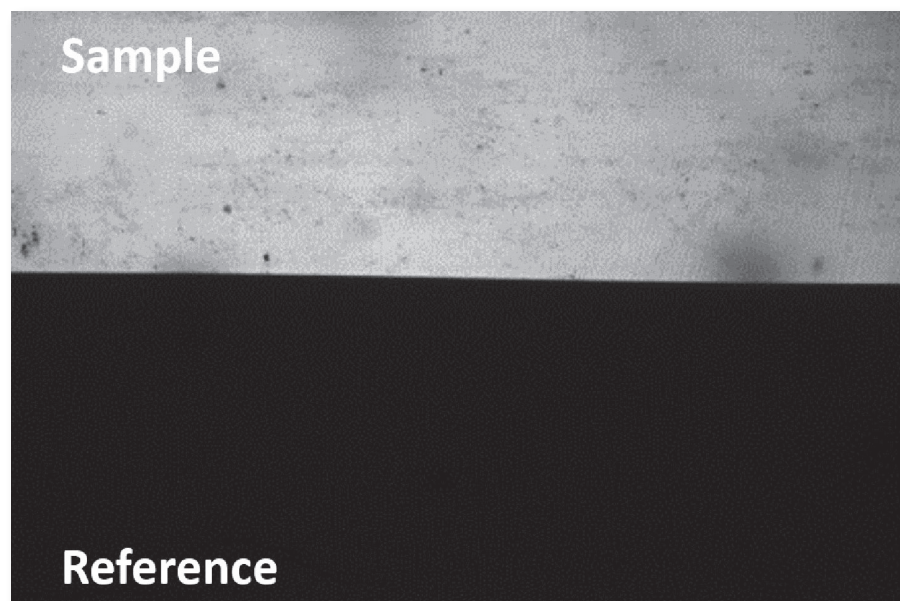
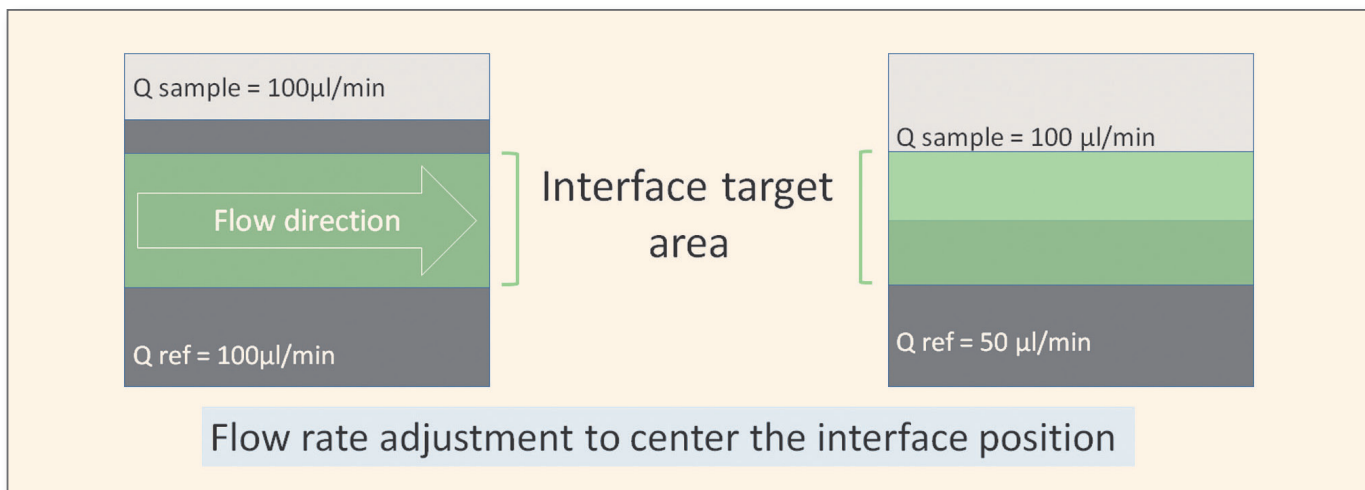


Figure 4 picture of interface

Figure 5 Interface centering



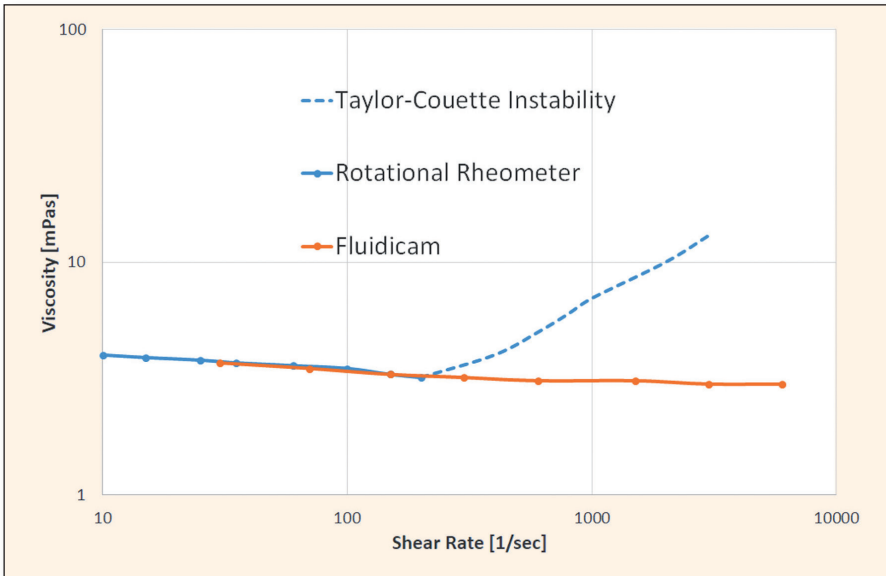


Figure 6 Viscosity of BSA solution (200 mg/mL at 25 °C) with FLUIDICAM RHEO and Rotational rheometer

Benefits of working with FLUIDICAM RHEO

1. Laminar conditions – stable flow

Measuring the viscosity of water-like solutions over a wide shear rate range is a challenging task with traditional techniques. Either inertial flow instabilities or low torque measurement limit the possibilities for precise data. By working with microfluidics these difficulties are overcome. FLUIDICAM RHEO always works in laminar flow conditions ($Re < 2300$) so no Taylor instabilities are to be expected and high flow rates prevent crossway diffusion.

2. Closed system – no evaporation

The use of microfluidic chip which is an enclosed system provides additional advantages when measuring the viscosity of fluids and products that can easily evaporate (solvents: acetone or ethanol based products, glues, varnishes and paints for example).

3. Wide shear rate range – 2 configurations

The small gap inside the chip means that the system is highly confined. This enables easy access to elevated pressures within the channel. Thus, FLUIDICAM RHEO can cover a broad range of shear rates: $10^2 - 10^5 \text{ s}^{-1}$ with a single chip and allows the sample to be analyzed under real life conditions.

Figure 7 gives an estimation of accessible shear rates with plastic chips, glass provides more resistance to pressure and thus, modifies slightly the maximum shear rate for samples with viscosity above 10 mPa.s.

The values provided are to be considered as a guideline, it is important to remember that maximum available shear rate will not only depend on sample viscosity and other parameters are also to be taken into account.

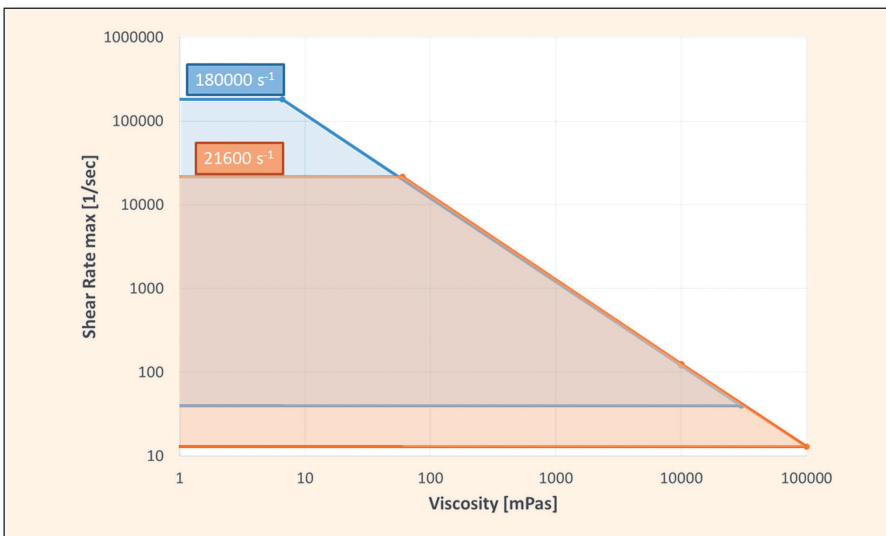


Figure 7 Accessible shear rate for 50 μm Chip (●) and in the 150 μm Chip (◐)

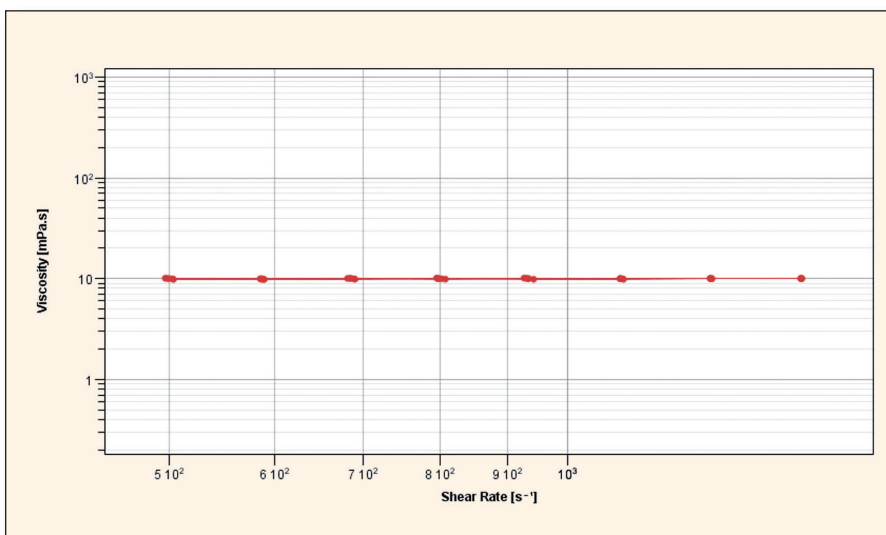


Figure 8 Viscosity of PEG 10 % solution at 4 °C (x5)

4. High accuracy – Continuous calibration

The constant comparison to a reference solution provides FLUIDICAM RHEO with remarkable precision. In fact, the instrument is calibration free depending only on the used viscosity standard. In addition, the software gives the user the possibility of choosing the reference - any Newtonian fluid can be used as a reference, as long as its viscosity is known (water, certified oil reference). Working with both, miscible and immiscible solutions is possible. The measured values are not only precise and repeatable but are also acquired in a shorter amount of time. FLUIDICAM RHEO can easily discriminate samples of similar viscosity. In the case of Natrosol LR 250 (HEC) solutions, the difference in viscosity was as small as 0.09 mPa.s.

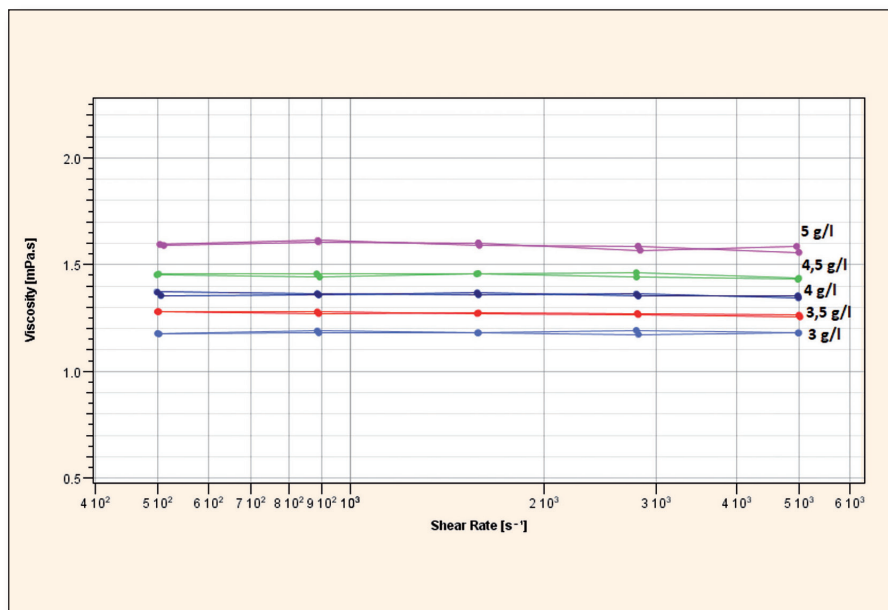


Figure 9 Viscosity of Natrosol diluted solutions at 5 concentrations from 3 to 5 g/L

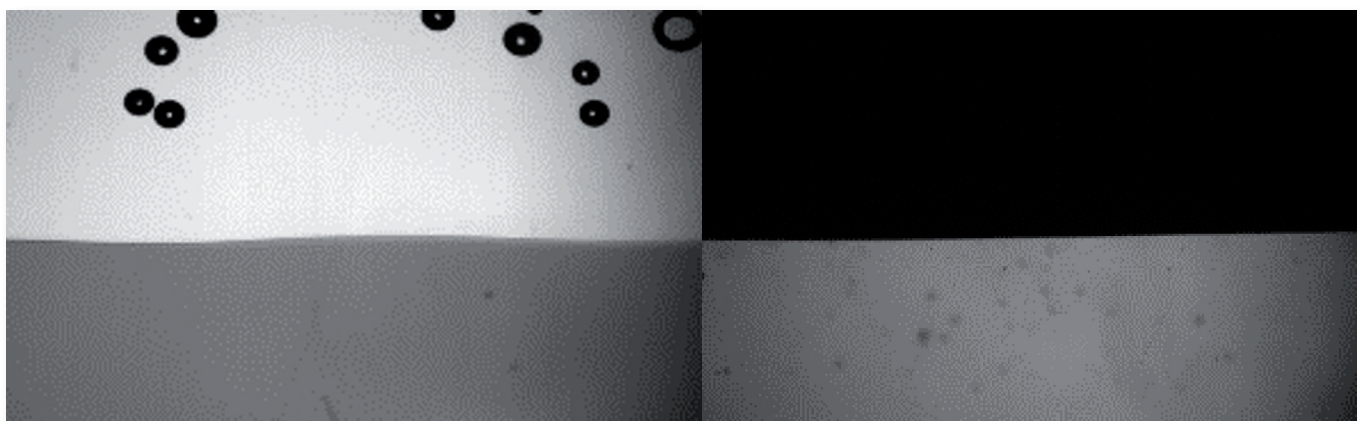


Figure 10 Pictures of interface in the FLUIDICAM RHEO

5. Visual concept

FORMULACTION's visual rheometer treats acquired images to determine sample viscosity. This measurement principle brings out an additional advantage to the technique – visual control data treatment. Therefore, it is possible to easily control and evaluate the quality of the data by reviewing the burst of the images: any perturbation of the flow can be noticed and incoherent values excluded making your data incomparably reliable. In addition, any sample heterogeneities can be observed.

Figure 10 on the left shows the presence of air bubbles in the sample that may explain some unexpected viscosity values, figure 10 on the right shows no sign of disturbed flow so it can be easily accepted.

6. Low volumes

The use of a small gap chip and viscosity determination based on adaptive algorithms minimizes the consumption of the sample. Which means, achieving high shear rate analysis is possible with less than 500 μL of the sample.

Conclusion

Using microfluidic principles offers unmatched possibilities in terms of accuracy. Taking advantage of laminar flow conditions FLUIDICAM RHEO can easily determine viscosity of the sample under shear using microvolumes of sample. This innovative optical technique is particularly suitable for high shear rheology of complex fluids. Even at low viscosities the measurement is extremely precise and reliable.

From the idea to the technology behind the separation process: **dynaSorb BT is gearing up!**

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In the light of a reasonable energy balance and the product purity obtained, adsorption-based separation processes of gas mixtures are considered highly efficient procedures for the separation of mixtures. In this technology, gas mixtures flow through an adsorber, which usually is adsorbent bed suitable for the separation process (such as activated carbon, zeolites, silica gel etc.). Separation is based on the preferential adsorption of one gas mixture component, different adsorption kinetics and/or molecular sieve effects.

The result of gas separation after flowing through the fixed bed adsorber is determined in a complex manner and by many sorption and transport characteristics (such as sorption kinetics, temperature, equilibria, inter- and intraparticle diffusion, co-adsorption and competition reactions). Accordingly, it is difficult to predict the influence of pressure, temperature, gas flow rate, particle size, gas composition and adsorber geometry on the anticipated separation process using equilibrium isotherms and adsorbent texture data. Consequently, it is that much more good news that with the introduction of dynaSorb BT, a high-performance experimental setup for applied research of industrial adsorbents and gas separation procedures has become available.

As technically relevant research usually considers the presence of humidity (e.g. separation of CO₂ from humid biogas), or as the separation process itself aims at separating/obtaining a vaporous component, it was just a matter of consequence to extend

dynaSorb BT with a powerful vapor option, so two configurations of the vapor option have become available. The resulting measurement capabilities and their relevance for practical applications are the subject of this article.

Vapor dosing options of dynaSorb BT

Option 1 – test gas

If the focus is put on vapor breakthrough at low concentrations (ppm range), it is recommended to use test gases. The test gas mixture (e.g. organic vapor, water or liquid gas such as in nitrogen or synthetic air) is directly connected to the gas input and led to the carrier gas via the corresponding mass flow controller. Using this approach, test gas can be diluted as needed, enabling the production of various vapor concentrations, even if just one test gas mixture is present.

Option 2 – one evaporator

One evaporator allows the production of vapor using a liquid supply. The liquid is fed via liquid mass flow controller to a heated mixing chamber where it is vaporized and mixed with the carrier gas. This evaporator concept offers major advantages compared to other solutions (e.g. washing bottle). The vapor needed can be precisely dosed using the liquid mass flow controller and is independent from pressure and temperature. A broad range of vapor concentrations can be covered by varying the ratio of carrier gas

flow and liquid added, both of which can be set independently. The liquid supply may also be filled with a liquid mixture enabling the simultaneous (but not independent) vaporization of several components. The results are vapor mixtures with constant compositions that can be led to the carrier gas in variable concentrations.

Option 3 – two evaporators

A configuration with two evaporators offers the highest-possible flexibility, as it is possible to independently modify the vapor concentration of two components. The separation of organic vapors from humid air can now be evaluated for a variety of combinations of relative humidity and vapor concentration.

This variety of configuration options (one or two evaporators), the possibility to vaporize liquid mixtures and to add low vapor concentrations as test gas open a wide range of experimental solutions for in-depth reproduction and evaluation of gas separation processes.

Following example demonstrates the operation of dynaSorb BT with vapor option (one evaporator) in studying the breakthrough behavior of propane in the presence of variable relative humidity. In addition to the integrated TCD, a mass spectrometer (Thermostar, Pfeiffer Vacuum) was used for the determination of the gas composition.

Breakthrough curves of propane in variable humidity

The measuring temperature was 25 °C, pressure 1 bar absolute and the volumetric flow rate 4000 mL min⁻¹ (standard flow rate) for all tests. The standard adsorber (inside diameter D = 3 cm, length L = 18 cm) was filled with approx. 55 g activated carbon for the tests. The sample was dried for at least 2 h at a temperature of 150 °C in a nitrogen flow.

Experiment 1: Propane breakthrough curve without humidity

The first experiment consisted of a single breakthrough curve measurement with 5 vol % propane in dry nitrogen carrier gas.

Experiment 2: Propane breakthrough curve at 30 % rel. humidity

The second experiment was a sequence of three breakthrough curves measured one after another. Conditioning the previously dried sample with humid nitrogen carrier gas and a relative humidity was the first breakthrough curve measurement. Immediately after that, the breakthrough curve of 5 vol% propane was measured with the presence of humidity (30% rel. humidity). After the complete breakthrough of propane, relative humidity was increased from 30% to 85%.

Experiment 3: Propane breakthrough curve at 85 % rel. humidity

The third experiment was a sequence of two breakthrough curves measured one after another. The previously dried sample was first conditioned for 8 h at a relative humidity of 85%. After this conditioning step, the breakthrough of 5 vol% propane was measured in the presence of humidity (85% rel. humidity).

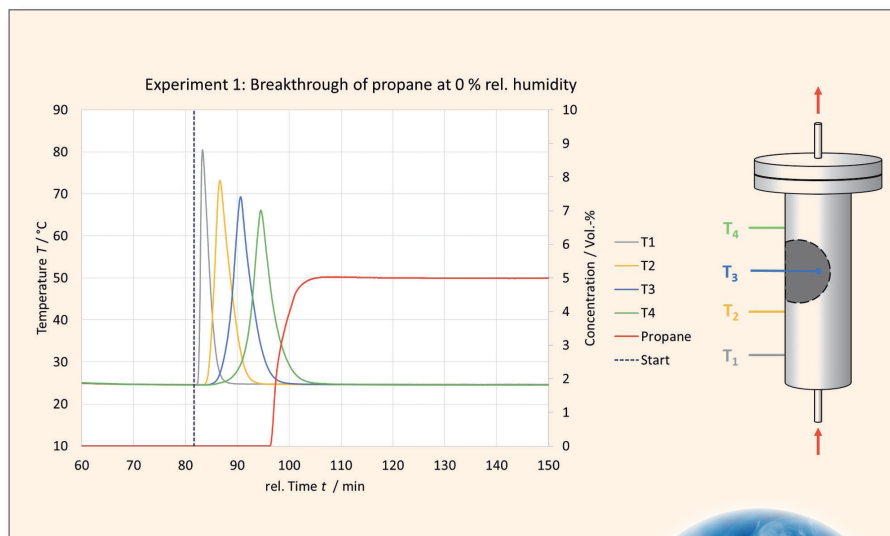


Figure 1 Breakthrough curve of 5 vol % propane in dry nitrogen carrier gas

Results

Experiment 1: Breakthrough curve of propane without humidity

Figure 1 depicts the breakthrough curve of propane. The red curve indicates the propane concentration measured at the adsorber outlet. The dashed line indicates the start of the breakthrough curve measurement. At that point in time, 200 mL min⁻¹ propane were added to the carrier gas (3800 mL min⁻¹ N₂). Only after approx. 15 min, propane could be detected at the adsorber outlet. A strong temperature increase in the adsorber bed was observed, which is attributable to the released adsorption heat. The temperature curves are depicted as grey, yellow, blue and green curve. For a better understanding of the temperature profiles, the right part of the figure includes a schematic drawing of the adsorber indicating the flow direction and the position of the individual temperature sensors T1 to T4. They are equidistantly distributed within the bed and measure the temperature along the adsorber column. In case of applying upstream flow direction, the changing entry gas composition reaches temperature sensor T1 first. Accordingly, propane adsorption first occurs in the section of T1. It records a bed temperature increase to 80 °C. The peak values of temperature curves later measured at T2 to T4 decrease in accordance with their position because of increased “blurring” of the entry propane concentration profile caused by dispersion in the adsorbers flow area. After approx. 30 minutes, the break-

through is completed; the fixed bed temperature has returned to 25 °C, and the outflow concentration is the same as the inflow concentration.

An integration of the breakthrough curve leads to an adsorbed material of 2.88 mmol g⁻¹. In Figure 2, this value is compared to a propane isotherm at 25 °C. The propane isotherm was measured with an iSorb HP using a volumetric method. For comparison purposes, the determined material adsorbed in the breakthrough curve experiment is depicted with the partial pressure of propane. In the present experiment setup, the pressure is 0.05 bar (5 vol % x 1 bar). In this case, both methods produce an excellent consistency – the load determined with the dynamic method integrates very well in the isotherm line. It can be assumed that in the propane adsorption in this activated carbon, almost no nitrogen is coadsorbed from the carrier gas, which would lead to a lower propane load compared to the pure isotherm. Further, it can be assumed that the gas flow speed was not set too high, i.e. the dwell time of the gas in the adsorber is sufficient for an adsorption balance to be obtained.

Experiment 2: Breakthrough curve of propane at 30 % rel. humidity

Figure 3 presents an overview of experiment 2. It is a sequence consisting of three subsequent breakthrough curve measurements. The vertical lines indicate the start of the individual measurements. Detailed results of experiment 2 are depicted in figures 4, 6 and 7.

The conditioning of activated carbon at a 30 % rel. humidity, as it was done in the experiment, is also a breakthrough curve measurement itself, as the activated carbon was previously completely dried in the nitrogen flow. After completion of the drying process at 150°C, the adsorber was cooled down to the analysis temperature of 25 °C in the nitrogen flow. Once the constant temperature was established, conditioning was started. 1.83 g h⁻¹ water was added via the evaporator to the carrier gas, which corresponds to a water concentration of 0.95 vol%. After approx. 15min, the breakthrough of water could be observed. The integration of the breakthrough curve results in a water load of 0.64 mmol g⁻¹. A comparison of this load with data measured in a water isotherm at 25 °C is available in Figure 5. Again, the results of breakthrough curve and isotherm measurement correspond very well.

The propane breakthrough at 30% rel. humidity was determined right after the conditioning (Figure 6).

The breakthrough time is comparable with the one in experiment 1. Additionally, the integration of the curve results in a similarly high propane load with 2.84 mmol g⁻¹ as it was the case at 0% rel. humidity. It can be stated that the adsorbed propane material amount does not differ substantially with rel. humidity between 0 and 30 % – an extremely valuable outcome for applied testing. It can be assumed that the water amount adsorbed in the conditioning is completely displaced by propane. This assumption can be confirmed and made visible in a unique manner with the temporary water concentration increase and the remarkable temperature profiles during the propane adsorption. The temperature profiles can be explained as follows: propane can be adsorbed with hardly any influence, as activated carbon at 30% rel. humidity is only slightly loaded with water (see Figure 5). The adsorption heat released in this process results in a quick heating of the fixed bed. The displace-

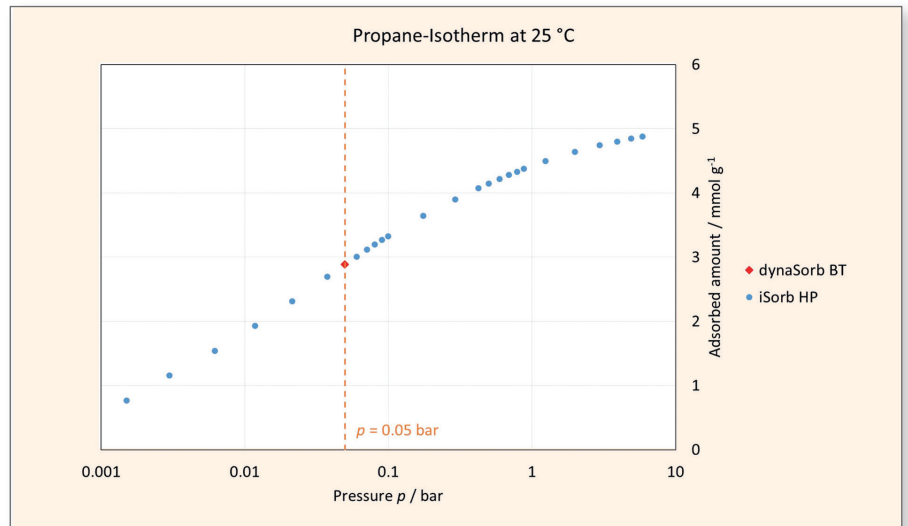


Figure 2 Comparison of load calculated by the integration of the breakthrough curve (experiment 1 with dynaSorb BT) with a propane isotherm determined with a volumetric method (iSorb HP)

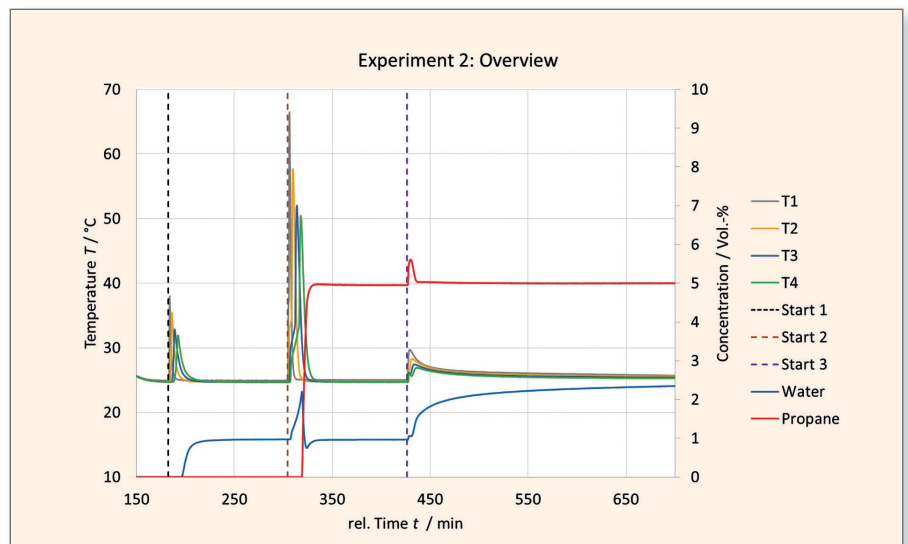


Figure 3 Temperature profile and concentration progression of water and propane of experiment 2 consisting of a sequence of three breakthrough curves. The dotted vertical lines indicate the start of the individual breakthrough measurements

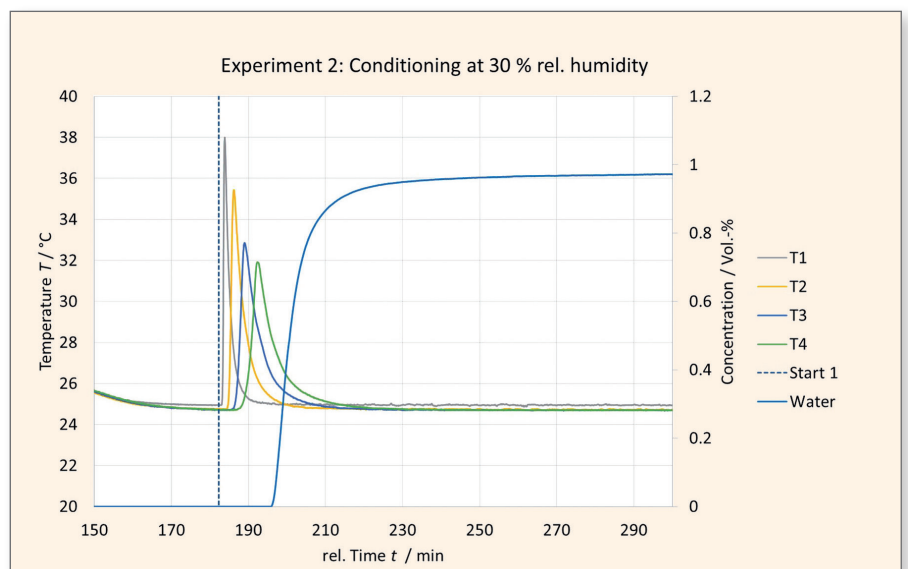


Figure 4 Detailed results of experiment 2 (temperature profile and concentration profile of water)

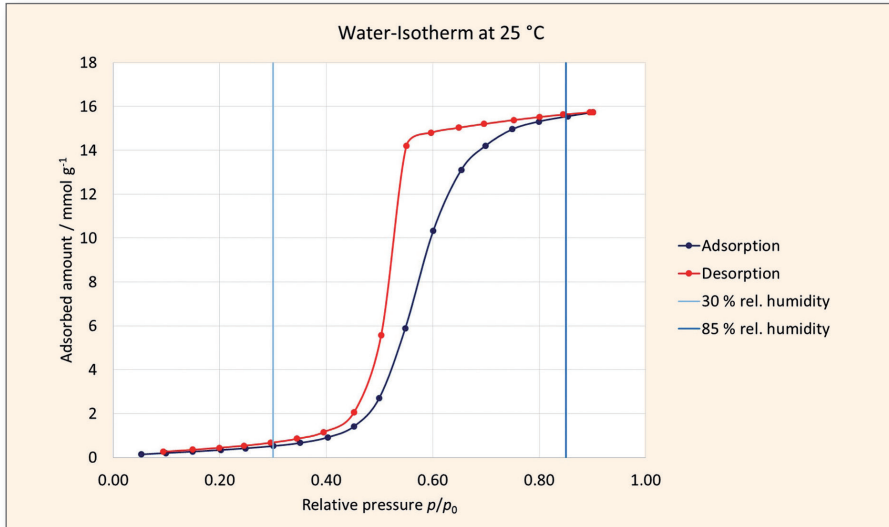


Figure 5 Water isotherms measured with AS-iQ, the vertical lines identify those isotherm sections that correspond to a rel. humidity of 30 % resp. 85 %

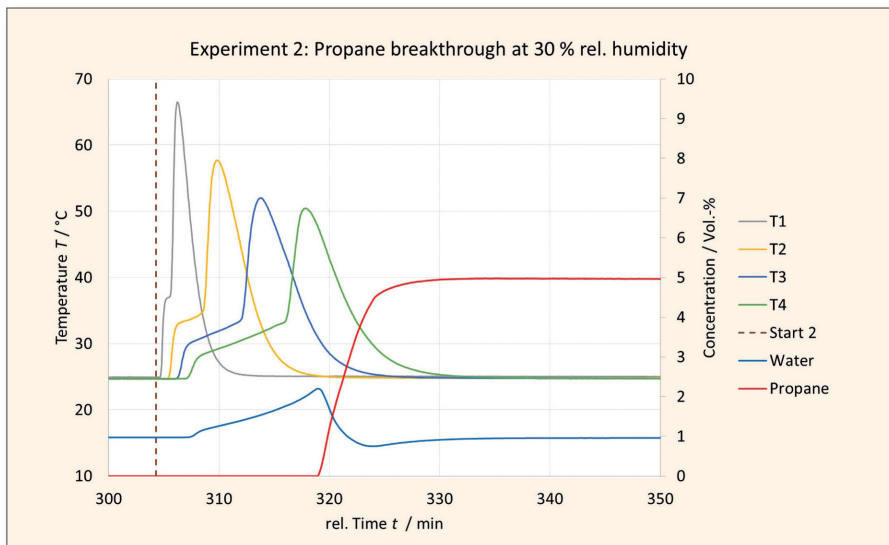


Figure 6 Details of experiment 2 (temperature profile and concentration profile of water and propane), adsorption of propane occurred while displacing previously adsorbed water

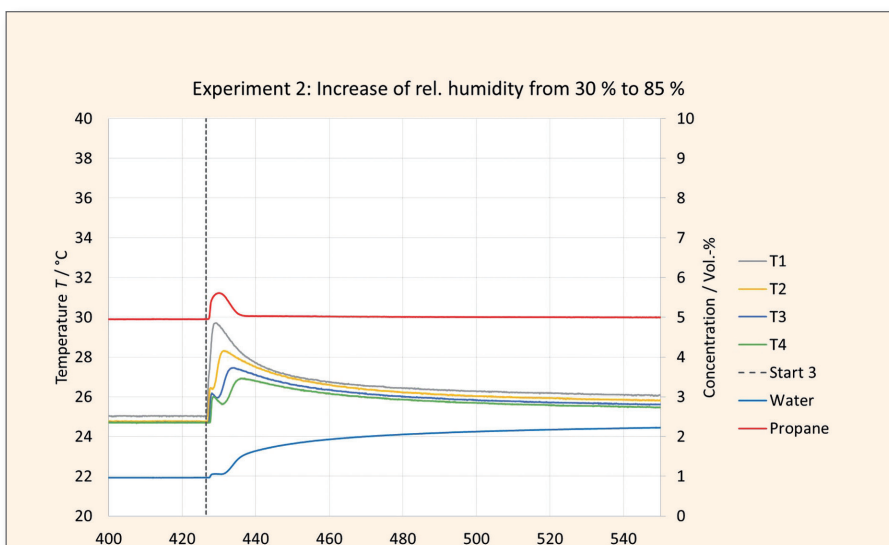


Figure 7 Details of experiment 2 (temperature and concentration profiles of water and propane), with the increase of rel. humidity from 30 % to 85 %, a sorption of water can be observed, previously adsorbed water is only slightly desorbed

ment of water (desorption) connected with the propane adsorption in an endothermic process causing the drop in the temperature increase. Once the water is completely displaced, temperature can quickly rise again. The water displaced in the section of sensor T1 is adsorbed in the next bed which causes an intermittent increase of the water load in these adsorber sections. During the subsequent adsorption of propane, higher water concentrations in these sections now need to be displaced, which causes a gradual extension of temperature profile drop from T1 to T4. An increased water concentration can only be observed at the adsorber outlet, when a temperature change can be noted in section T4.

After a complete propane breakthrough, the rel. humidity was set to 85% starting another breakthrough curve measurement: the breakthrough of 2.7 vol % water in the presence of 5 vol % propane in nitrogen and activated carbon previously loaded with 5 vol % propane at 30% rel. humidity. In the light of the propane isotherm in Figure 2, it is to be assumed that the sample is loaded with propane at approx. 50% of its maximum sorption capacity when the measurement is started. Further, a noteworthy pre-load with water can be excluded based on the previous findings.

The water breakthrough occurs in two steps: an immediate, but slight increase of water concentration accompanied by the desorption of a small amount of propane, followed by a continued increase of water concentration. Even after two hours, the water concentration still slightly increases, which is a clear indicator for the fact that the breakthrough is not completed yet. The integration of the incomplete breakthrough results in a water load of approx. 6 mmol g⁻¹. Considering the water and propane isotherms, a maximum value of 8 mmol g⁻¹ could be expected. This estimate is based on a maximum water load of activated carbon at 85% rel. humidity and humidity of approx. 16 mmol g⁻¹ (see figure 5), decreased by the pre-load of propane, which corresponds to approx. 50% of available pore volume to be filled (cf. figure 2).



Experiment 3: Propane breakthrough curve at 85 % rel. humidity

Experiment 3 (figure 8) studies the propane breakthrough behavior at 85 % rel. humidity. Prior to that, dried activated carbon was conditioned for a duration of 8 hours at 85 % rel. humidity.

It is evident that the conditioning scheduled for 8 hours at 85 % rel. humidity is insufficient to completely load the previously dried adsorber with water. On the one hand, the water concentration still increases after 8 hours. On the other hand, temperature sensor T4 (green curve) still indicates a temperature of approx. 27 °C. In contrast, temperatures at T1 to T3 have already decreased to 25 °C. This implies the bed at the adsorber output continues adsorbing water, while the bed is saturated in the section between input and T3. Using the temperature sensor positions, it can be estimated that the entire adsorber is saturated at approx. 60 – 70 % of the maximum water load. This implies that the duration of a complete conditioning would have to be increased to 12 – 14 hours. If the duration of a complete conditioning was derived only from the equilibrium isotherms and the inflowing vapor amount (cf. figure 5), it would be conclusive that

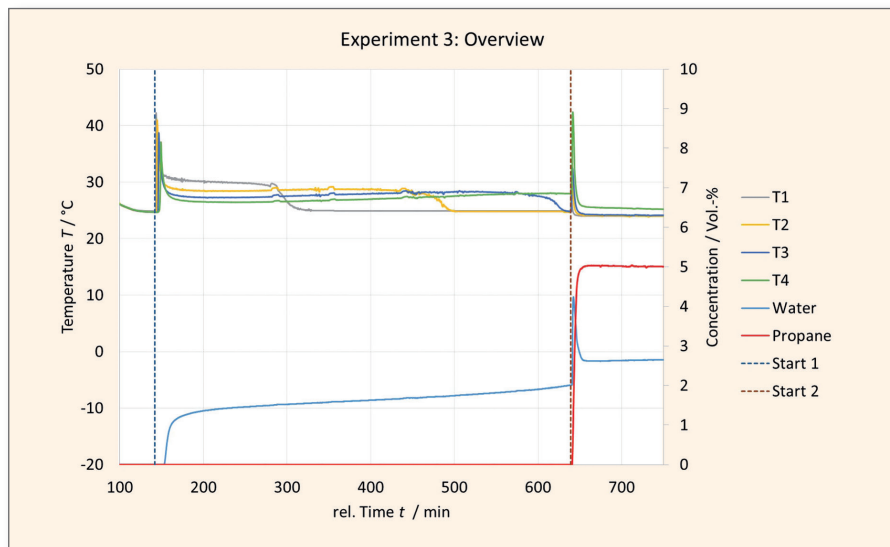
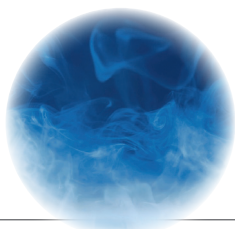


Figure 8 Temperature and concentration profiles of water and propane in experiment 3 consisting of one sequence of two breakthrough curves, the dotted vertical lines indicate the start of the individual breakthrough measurements

3 hours of conditioning were sufficient. This estimate considers the equilibrium load of activated carbon with water at 85% rel. humidity (16 mmol g⁻¹) multiplied by the weight of the sample examined. This enables the calculation of a time after which exactly this amount of water was added to the adsorber under the conditions specified herein. Using this approach, the calculated duration of 3 hours is estimated too short by a factor of four to five! This discrepancy can be explained with the isotherm form (figure 5) and the low sorption kinetics of the activated carbon pore filling with water. This isotherm form indicates that pores only start filling with water at a relative humidity

of 50%. In case of lower humidity, water adsorption at polar adsorption centers of activated carbon need to be considered. This contribution is just a small share of the overall capacity, but indicates rather high adsorption kinetics. This behavior is reflected in the breakthrough curve (figure 9): in the beginning, water concentration at the adsorber output is zero (adsorption at polar centers). It then quickly increases to a value of approx. 1.5 vol %, which corresponds to a relative humidity of 50%. Pores start filling with water in this humidity. This is the major aspect of water loading, although it is rather time-consuming. While the pores are filling, the initial concentration of water remains above approx. 1,5vol% and continues to slowly increase. The fixed bed temperature remains slightly increased, which is attributable to the released sorption and kinetics heat. Once the water sorption is completed in one bed, temperature again decreases to a bath temperature of 25°C.

The subsequent breakthrough measurement of propane is depicted in figure 10. Breakthrough time has shortened to 10 min. The propane amount calculated from the integration of the breakthrough curve is only 0.79 mmol g⁻¹. This corresponds to almost 30 % of the load determined in experiment 1 and 2.



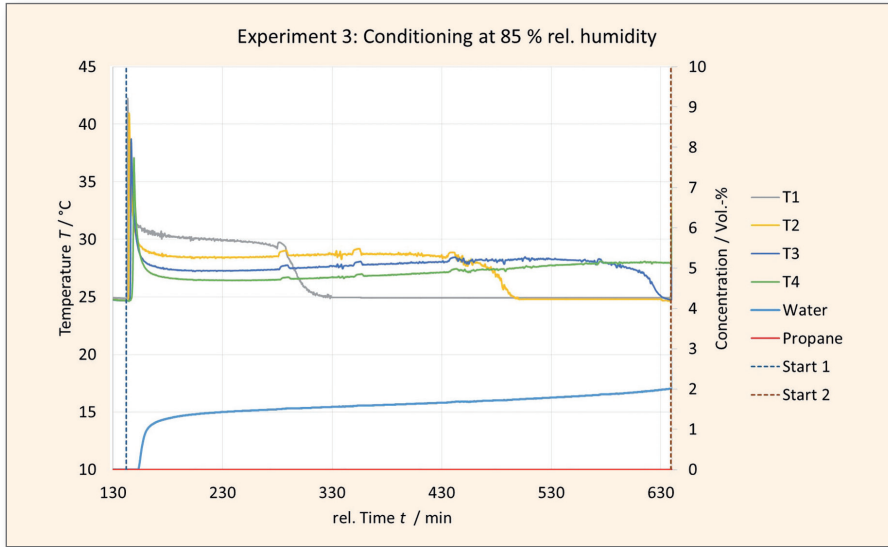


Figure 9 Details on experiment 3 (temperature and concentration profiles of water), after eight hours of conditioning at 85 % rel. humidity of the previously dried sample, the water breakthrough is still incomplete

With the breakthrough of propane, desorption of water can be observed. The results of experiment 2 suggest that desorption occurs in the part of the bed which was not fully loaded during the conditioning (adsorber outlet). As the adsorber was inhomogeneously loaded with water at the beginning of the breakthrough curve measurement, it is wrong to conclude that the propane load in the presence of 85 % rel. humidity corresponds to approx. 30% of the load measured at 0%. Following statement would be more conclusive: the propane load determined in experiment 3 is mainly attributable to the propane adsorption in the part of the fixed bed that was still not fully loaded after the conditioning. This part of the bed corresponds to approx. 30% of the entire bed height. It is further suggested by the fact that temperature sensor T4 records the highest temperature increase within the fixed bed. After a longer conditioning of 14 h, an immediate propane breakthrough would have to be expected, as the entire fixed bed would then be saturated with water. Such a spontaneous breakthrough does, however, not imply that no propane is adsorbed at all. A slow displacement of previously adsorbed water by propane would not only be conceivable, but even probable even with a pore system that is completely filled with water. However, it is impossible to develop a reasonable adsorption process removing propane from highly humid carrier gas. Accordingly, the technical relevance of these analyses compared to equilibrium-based data is to be emphasized.

Summary

Whether analysis focuses on dynamic sorption of vapors, sorption of gases in the presence of humidity or multi-component sorption - dynaSorb BT with integrated vapor option allows comprehensive characterization of industrial adsorbents and adsorptive separation processes. In this example, the sorption of propane in activated carbon was analyzed in variable rel. humidity. dynaSorb BT supported the analysis from sample preparation through defined sample conditioning up to the determination of breakthrough curves and the subsequent data evaluation. The analysis setup profoundly benefits from the fact that varying experiment conditions such as gas com-

position, temperature, pressure, gas flow rate and flow direction can be defined for each measuring sequence, which are then automatically processed. For example, experiment 2 is a sequence of three breakthrough curves measured one after another. Accordingly, even extremely complex experiments can be run in minimum amount of time and staffing. This analysis has shown that propane load did not differ substantially at rel. humidity between 0 and 30%. The load determined with the integration of breakthrough curves correspond very well with the volumetrically determined equilibrium data. Higher humidity produced major differences. Humidity increase after a propane breakthrough had only minor impact, while a substantial decrease in propane load was observed with previously wetted activated carbon. This implies that the order in which gas compositions are varied does have an impact on dynamic processes. Further, the influence of conditioning could be demonstrated. If the vaporization duration is too short, interpretation of breakthrough behavior may lead to wrong conclusions. Due to the large variety of data gathered by the instrument, users are protected against such misunderstandings. In this case, highly accurate temperature determinations within the fixed bed helped with the correct evaluation of the results.

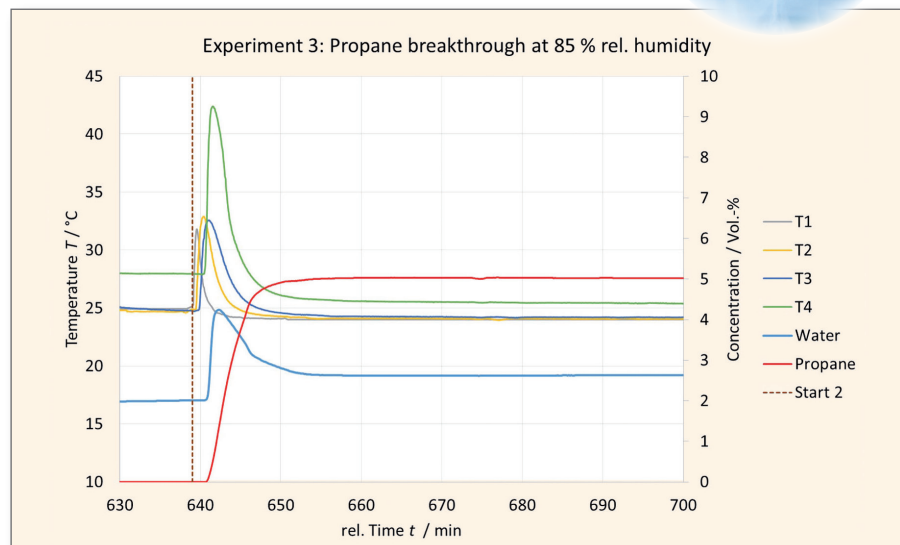
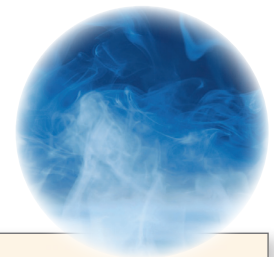


Figure 10 Details on experiment 3 (temperature and concentration profile of water and propane)

The new AUTOFLOW BET+: A Revival of the Flow Method

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Since the 90s static volumetric methods have slowly taken precedence over the earlier dynamic flow setups in the field of gas sorption analysis. This was in part due to the increased demands of research and development as well as quality insurance to establish more methods next to the classic 1-point BET such as multi-point BET analysis, or high-resolution pore analysis by means of physisorption. On the other hand the fully automated sequential analysis also offer a high degree of comfort and the advantages of simple dosing routines of pure gases and manometric determination of adsorbed amounts can also be fully appreciated. The very wide distribution of NOVA-, QUADRASORB- and AUTOSORB-series of instruments speaks for itself. However, the dynamic flow method is still very much in use, especially in areas, where fast analysis times and easy handling are of the essence. These fields such as quality control or where the static volumetric method does not supply valid analysis data for a variety of reasons employed the MONOSORB instrument successfully. Pharmaceutical products, raw materials for food or metal hydroxides and materials with crystal water inclusions are examples for the latter.

The new QUANTACHROME AUTOFLOW BET+ combines the advantages of the dynamic method with a high degree of automatization found in the volumetric method. Table 1 showcases the advantages over classic 1-point instruments and also over volumetric instruments.



The previous MONOSORB will be replaced by the AUTOFLOW BET+

Table 1 Advantages of the AUTOFLOW BET+

Advantages over single point BET-Instruments	Advantages over volumetric Instruments
Fully automated single and multi-point BET analysis	No vacuum pump required
STSA measurements possible, e.g. for carbon black applications	No need for time consuming void volume measurements
No calibration of the detector necessary, concentrations are measured directly	No need for void volume correction
Up to 3 parallel (simultaneous!) measurement stations for highest sample throughput	No cumulative errors, since each data point is independent of all other

The AUTOFLOW BET+ is arguably the highest throughput surface area analyzer available in the market today. The instrument includes a control module (with three independent degassing stations) and 1, 2 or 3 independent analysis stations. Single point BET surface areas can be evaluated in <5 min per sample. A three-station AUTOFLOW BET+ triples this output to as many as 36 sample analyses per hour, yielding an average of <2 min per sample. This translates to as many as 36 sample analyses per hour. This outstanding analysis throughput is equally extended to Multipoint BET determinations. For instance, 3-point BET analyses for single samples can be collected in <15 min per sample. A three-station AUTOFLOW BET+TM could thus yield 3 multipoint BET analyses in <15 min, or up to 12 multipoint BET analyses per hour. Such a high analysis throughput would of course need to be paralleled by high throughput sample preparation (degassing) capabilities. So each AUTOFLOW BET+TM includes three independent degassing ports (see Figures 1 and 2). Each degassing port has its own heating mantle and flow regulation valve, and can be independently programmed with up to six degassing steps (each step including target temperature, ramp rate and hold time). Standard degassing temperatures up to 350 °C are standard, but high temperature (HT) AUTOFLOW BET+TM models extend the upper limit to 450 °C using quartz heating mantles and glassware. The AUTOFLOW BET+TM is ideally suited to perform very fast, precise and high throughput BET surface area analyses of solid samples.

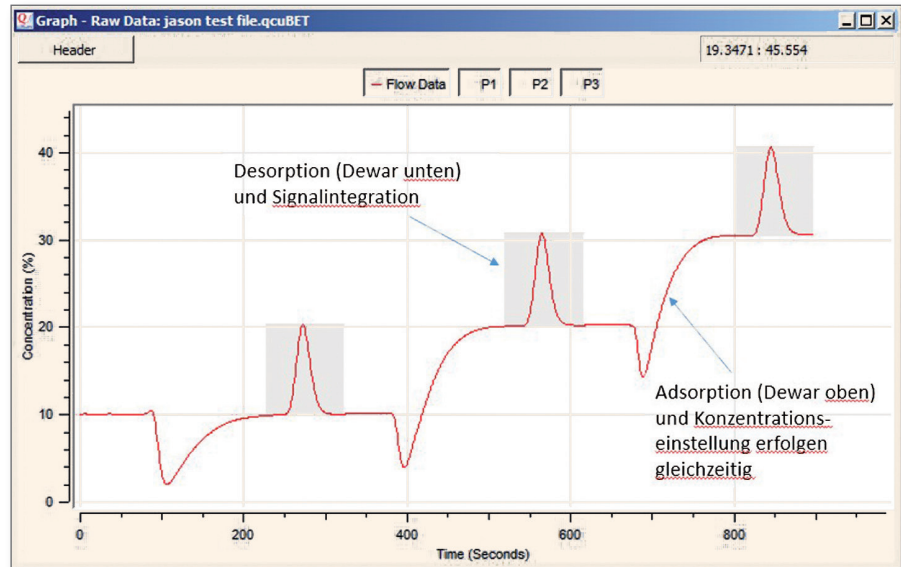


Figure 2 Full-automatic measurement with the AUTOFLOW: the next adjustment of the measuring gas is in parallel to the adsorption, after that the desorption follows with integration of the TCD-signal for the calculation of the gas volume adsorbed for the relevant measuring point

Abbildung 3 AUTOFLOW BET+ with control unit and three sample preparation stations (left) and maximum three measuring stations (right)



continuing from page 3

example: our company magazine "PARTIKEL-WELT" and "PARTICLE WORLD" in English that have been implemented in a Marketing concept since 2002. The following years indicated a distinctive correlation between a considerably enhanced marketing combined with the expertise of QUANTACHROME sales specialists. And when talking about marketing, I am always referring to expert marketing at QUANTACHROME. Some of the specialist articles are based on lab measurements that took weeks and support readers in getting familiar with the corresponding areas. Accordingly, we always appreciate customers asking for the next release of PARTICLE WORLD or downloading previous editions of PARTICLE WORLD from our homepage www.QUANTACHROME.nl.

In 2004, you were appointed as second CEO. End of 2006, when company founder Karl-Jürgen Rath retired, you became CEO of the company that was converted into a GmbH & Co. KG. Further to the marketing development since 2002, which other milestones do you identify in QUANTACHROME's history?

Of course, the company's growth is based on the foundation in 1990 by Karl-Jürgen Rath, its former CEO. That is the groundwork still supporting today's activities. Increased sales in the early 90s were mainly attributable to the traditionally used CILAS laser granulometers, a strong sales team and very distinct focus on the service from the first day on. I was already able to form the following milestones, including the DISPERSION TECHNOLOGY product groups in 1999 and FORMULACTION in 2005, the extension of our laboratory and the development of LabSPA, re-structuring of the sales department in 2012 as well as the implementation of an R&D department with in-house instrument engineering since 2014.

This sounds like a continuous success story. Did you ever face challenging times or even fractures in this company history?

Oh, of course we went through tough times! I am not only talking about certain times of stagnation, such as in the 90s, when it was unclear where our company is heading to, or times when employees left the company – a particular issue shortly prior to the turn of the millennium. The euphoria of the "new

economy bubble" was probably one of the reasons fluctuation increased to almost 30 % p.a. Thankfully, this situation quickly returned to normal, and the development since the beginning of 2014 is extremely positive: all employees remained "on board", except for two retirees. Or to put it differently: Since 2014, QUANTACHROME has hired nine university graduates. This figure is considerably higher than the total number of MICROMERITICS GmbH employees at the same time. The earthquakes QUANTACHROME went through since 1990 just helped us grow new ideas and innovation.

In 1990, QUANTACHROME started distributing measuring devices of QUANTACHROME Instruments/U.S.A. and CILAS/France. Now, CILAS has officially announced to stop engineering laser diffraction instruments in 2018. Do you mind asking how you see this development and what implications you see for QUANTACHROME GmbH & Co. KG?

In the beginning of the 90s, classic CILAS granulometers formed the lion's share of our company's turnover, as the cooperation between CILAS and company founder Karl-Jürgen Rath is dating back to the 70s. As you may know, CILAS first introduced the commercial laser diffraction in particle size analysis in the late 60s. The fact that this manufacturer is withdrawing from the market after almost 50 years almost appears as irony of history. Although this news came not as a total surprise to us, the concrete point in time was indeed a surprise. And it is no glorious chapter for CILAS how the company said farewell to long-term partners and especially customers.

So, what did we have to do when we got the information about CILAS' final decision? Of course, we regretted this decision, and we had to ask ourselves how to compensate this product range. We finally decided to continue offering the CILAS service including maintenance, spare and wearing parts to our CILAS customers. Accordingly, we quickly informed all CILAS customers about this imminent change. Our service specialists now support the oldest instrument versions and the latest CILAS laser granulometers, as the brand name will no longer be found on these analysis instruments by 2018. Thanks to our top service team, QUANTACHROME continues providing service and instrument maintenance for all CILAS instrument versions. However, we

needed an alternative for the sales and distribution of instruments...

What are QUANTACHROME's visions in the field of particle size using laser diffraction? Alternative plan sounds exciting ...

There might have been reasons for CILAS to withdraw from laser diffraction analysis; reasons that leave plenty of room for speculation. From our perspective, it has been clear for years that CILAS needed to develop a new generation of laser diffraction instruments to maintain their presence on the particle size market. Over many years, we have communicated this demand to CILAS. However, it seems the instruments manufacturer basically wanted to avoid the investment in a new instrument generation.

So, how did we derive "Plan B" from this situation in case CILAS really terminates the Particle Sizer production some time in the future? As we are well familiar with the market insights, we immediately contacted a company that has developed a high-tech Particle Sizer that can measure itself against any competing product. I am very glad to have found this partner, namely BETTERSIZER. Their high-tech Particle Sizer BETTERSIZER S3 Plus is just one of the instruments of the BETTERSIZER product range.

What is the innovative aspect of the BETTERSIZER?

That's easy to explain in direct comparison with the CILAS measuring instruments. By the way, CILAS instruments have been very reliable devices for standard applications. It's not without reason that we successfully distributed these instruments for decades. However, in various applications, we could no longer offer competitive solutions, as for instance, the measuring range did no longer meet the latest requirements. A traditional CILAS laser granulometer, which has been available until end of 2017 only, has a smaller measuring range, a narrower angle detection range, and no selection of sideways and backwards detectors for the smallest particles. Due to these disadvantages, we fell behind competitors in many business fields. BETTERSIZER S3 Plus now offers the capability of handling particle sizes from 0.01 up to 3500 µm, providing sideways and backwards detection up to 165° making it a top-range instrument. Other competitive instruments such as CILAS laser granulometers and similar ones do not feature dual-lens technology.

gy. So we directly compared BETTERSIZER S3 Plus with current market leading technology: is there any competitive instrument featuring dual-lens technology for extremely fine particles, a camera integrated in the analysis system for the detection of coarse particles and to visualize so-called oversize grains or agglomerates? BETTERSIZER S3 Plus even incorporates a second CCD camera for simultaneous particle form analysis! We now support these high-tech instruments with an outstanding cost-benefit ratio, an experienced consultant team and direct access to LabSPA offering test and third-party analytics. We mean what we say: whoever intends investing in a laser diffraction instrument definitely should consider testing the BETTERSIZER series ...

You are talking about BETTERSIZER being a new partner. How does the collaboration work?

When I first contacted BETTERSIZER, I received a very positive response. Since then, we have been filling our common goal with life. Three of our experts have visited the BETTERSIZER manufacturing and development facilities, and they were all very impressed about the excellent manufacturing quality. They were even more surprised about scientific developments that are already incorporated in the instruments, as I mentioned earlier. We can honestly state that we indeed hoped to meet a strong technology partner. However, learning that our expectations are even surpassed has been a real surprise to us. We now have all BETTERSIZER instruments available in our LabSPA and sincerely hope for a long-term partnership between BETTERSIZER and our company. We have already established a trustful partnership with market leader FORMULACTION and their TURBISCAN to analyze original emulsion stability. Further, QUANTACHROME is one of the market leaders in gas adsorption. Given the high-tech instrument features, why shouldn't we aim at a similar success story with BETTERSIZER laser diffraction analysis instruments?

Characterization of dispersions and powders seems to become a quite exciting subject... You also mentioned gas adsorption for pore analysis: what's the latest news at QUANTACHROME?

Last year, we introduced CryoSync being a complete innovation and presented the corresponding measuring data. This develop-

ment by QUANTACHROME Instruments follows the 2015 IUPAC recommendation that strictly focuses on argon adsorption at 87 K for certain surface and pore examinations. In order to produce a temperature of 87 K, we previously needed liquid argon which was either not available everywhere or which required additional storage tanks and continuous supply of liquid argon. This is all history with the new CryoSync. It only requires liquid nitrogen that is available anyway in laboratories that deploy such instruments. The highlight of CryoSync is the fact that it does not occupy additional space in the laboratory. Further, it does not produce compressor noise as the alternative Cryo-Cooler, which we only offer for specific measuring ranges, but no longer for standard measurements at 87 K. Beside its zero decibel noise -complete silence- CryoSync just consumes 30 Watts. A considerable number of research institutes have already upgraded to CryoSync and invested in sorption analysis instruments including CryoSync, as it is now state-of-the-art technology. This trend will gain further speed, as it is evident: if you are supposed to use argon 87 K for micropore analyses, as specific correlations between nitrogen and surface centres occur due to the so-called quadrupole moment, you will of course also have to question BET surface determination in general - at least in the scientific environment. We are currently running comprehensive tests in our LabSPA, and we appreciate working with other groups for further systematic investigation. Maybe, one or the other poster will already be presented during our events in spring, when QUANTACHROME GmbH & Co. KG will award three prizes for the posters at each event.

Are you referring to your Leipzig Workshop that you already held last year?

Exactly. We will again hold our gas adsorption workshop in Leipzig on April 18, 2018, present new research results in surface and pore characterization and also run a CryoSync live demo. We especially invite doctoral students offering free-of-charge admission to the workshop. We at QUANTACHROME aim at supporting scientific training, as more than 10 of our employees started their professional career in the field of particle analysis right after they earned their university degree. However, we also warmly invite laboratory and research managers to the mutual exchange of experience. Our goal is

to further encourage expert discussions with one poster session and three awards for the best posters.

On April 17, i.e. one day earlier, the Institute for Nonclassical Chemistry (INC) Leipzig will hold this year's "Leipzig Symposium on Dynamic Sorption" (in English) at the same venue. Our company proudly sponsors this event. Last year, this INC symposium was successfully held for the first time and on the occasion of its 20th founding anniversary. We have provided a broad range of specific information including publications and presentations about the sub area of practical adsorption on our homepage www.dynamicsorption.com. You will further find the registration form for the 2018 event, not to forget about the three poster awards we sponsor to the Symposium on Dynamic Sorption 2018.

One last question: does QUANTACHROME have more surprises to offer in 2018? Will you be present at other events as well?

2018 will be filled with activities, and I am not only referring to the exhibitions Filtech, Analytica, Ceramitec and Achema, where we will be present with our highlights including BETTERSIZER S3 Plus. We will attend numerous conferences, e.g. the NCCC 2018 in The Netherlands or roadshows in Benelux and Switzerland.

Let me please close this interview with a few words of appreciation, as I never walked alone in those past 25 business years. I would like publicly thank our entire team working in administration and service, in the dispersion and pores sales teams, in our lab called LabSPA, and our R&D team in Leipzig. Almost 50% of them have been taking this road with me at QUANTACHROME since more than 10 years already. I would further like to address my appreciation to the younger colleagues whose ideas and dedication made the past years such a tremendous success. There are numerous business partners and companions, but especially customers who we are very grateful to. I would particularly like to express my gratitude to my wife and daughter for their loving understanding and support of my career, especially during the first years in business.



Small option making a substantial difference in gas adsorption: CryoSync™ for surface and pore analysis

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1. Introduction

Ever since and across industrial sectors, QUANTACHROME is a synonym for comprehensive characterization of dispersions, powders and porous solids. With innovative products and measurement procedures, QUANTACHROME is market-leading in the area of promoting and enhancing new scientific approaches in this field.

The unique combination of measuring methods, system specifications and customer support provided by application experts ensure state-of-the-art laboratory practice in compliance with the highest scientific standards, which has become obvious in the recent past:

The fundamentally reviewed IUPAC report »*Physiosorption of gasses, with special reference to the evaluation of surface area and pore size distribution*« was published in 2015 and is an up-to-date compendium for the characterization of porous materials using gas sorption /1/. Besides an extended isotherm classification, this updated release includes numerous recommendations for the measurement and interpretation von isotherm data. "New recommendations" that have been the basis of applying our measure-

ment methods since many years. A fact that becomes obvious in this central topic: the characterization of micropores using physisorption of argon at a temperature of 87 K (boiling temperature of argon). QUANTACHROME has identified this advantage more than 20 years ago and continued improving this method to perfection. This is particularly evident from the instrument design, powerful evaluation methods (DFT kernel) to collect texture data from argon isotherms and the latest introduction of CryoSync™. It is a cost-efficient and compact optional accessory to AUTOSORB-iQ for the reliable temperature control ranging between 82 – 120 K targeting working group customers who require the characterization of microporous material using argon adsorption at 87 K in conformity with IUPAC who have no liquid argon available for cooling the specimen. This main application of CryoSync™ - the adequate substitution of liquid argon as cryogen - was already presented and expanded on in Particle World 18. This article describes additional research options available with the temperature range covered by CryoSync™.

The advantages of argon isotherms at 87 K in micropore analysis

For the sake of completeness, the main advantages of argon adsorption at 87 K compared to N₂ isotherm measurements at 77 K are as follows:

- Unlike nitrogen, argon has no quadrupole moment which is the reason that no specific interaction between adsorptive and polar or ionic surface areas is to be expected.
- Accordingly, argon isotherms produce much more reliable texture data regardless of the solid surface's chemical properties.
- Compared to nitrogen sorption at 77 K, argon adsorption analysis at 87 K is considerably less time-consuming, because the filling of similar pores can occur much more readily at much higher relative pressures (see fig. 1).

The inventive idea of CryoSync™ was to make these advantages available to studies that have no liquid argon available. The fact that technology such as CryoSync™ is indeed an adequate alternative to specimen temperature control with liquid argon is indicated in figure 2. This study compares two argon isotherms in microporous zeolite (13 X) measured at 87 K. In one case, temperature was controlled using liquid argon, while the second used CryoSync™. No significant difference was noticed, which is the reason that such technical solutions are explicitly mentioned in the current IUPAC report.

The following section explains additional measurement possibilities arising from the use of CryoSync™, as the temperature range is not limited to 87 K. When filled with liquid nitrogen, a temperature range between 82–120 K is covered inviting you to discover a whole lot more: CryoSync™: going far beyond!

Measurement of a set of isotherms at various temperatures

CryoSync™ allows precise isothermal measurements within a temperature range that is rather difficult to achieve. It enables users to study the temperature dependency of various sorption mechanisms (micropore filling, multilayer adsorption, pore condensation, pore blocking, cavitation etc.) as well as the phase behavior of pore fluids and even sorption-induced structural changes such as gate opening and breathing of certain MOFs. How about an argon measurement at 83.8 K – which is exactly the triple point of argon? CryoSync™ handles any of these tests. Further, the availability of the temperature range facilitates the calculation of isosteric adsorption enthalpies.

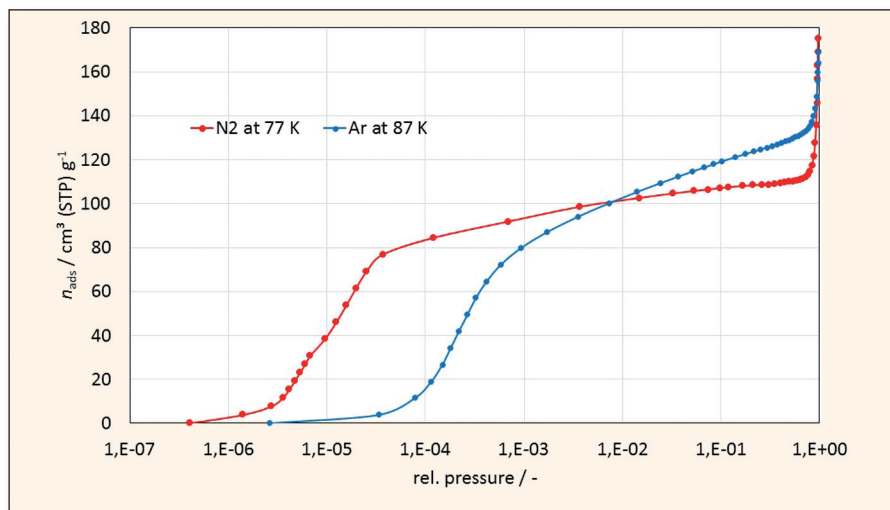


Figure 1 Ar-87 K and N2-77 K isotherms in zeolite 13 X measured with AUTOSORB-iQ-MP/CryoSync™

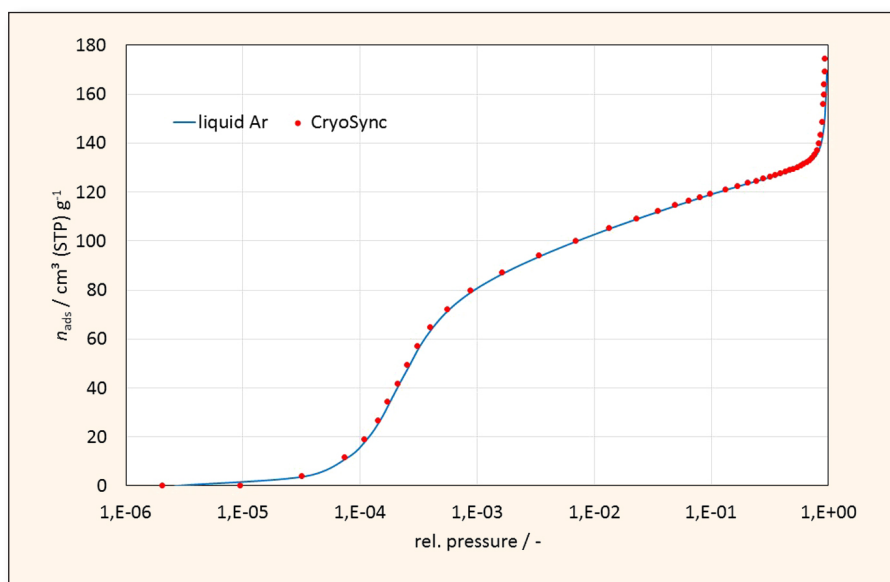


Figure 2 Comparison of argon isotherms measured at 87 K in zeolite 13 X (blue curve: temperature control with liquid argon; red dots: temperature control using CryoSync™)

Determination of BET surface areas with alternative adsorptives and the question for correct area occupation of adsorbate molecules

The determination of specific surface areas A_S is almost exclusively done with BET evaluation of nitrogen isotherms at 77 K. In general, it determines the number of adsorbate molecules forming a monolayer n_M on the solid surface which is then multiplied by the average area occupation a_m of the adsorbate molecules:

$$A_S = a_m n_M N_A \quad (\text{Eq. 1})$$

A value for the area occupation a_m can be calculated using the molar mass M and the density of the liquefied adsorptive ρ_L at the corresponding measuring temperature:

$$a_m = 1,091 \left(\frac{M}{\rho_L N_A} \right)^{2/3} \quad (\text{Eq. 2})$$

In case of nitrogen at 77 K, the area occupation is $a_m(\text{N}_2) = 0.162 \text{ nm}^2$. There are very pragmatic reasons for the fact that nitrogen has become the adsorptive for the determination of specific surface areas. This is mainly attributable to the cost-efficient availability of this chemical material as high-purity inert gas on the one hand and in liquid state for the cooling of specimen, which was

obviously the only choice in the 1930s and 1940s. Knowing that noble gas atoms have more favorable adsorption properties because of their spherical symmetry, scientists soon started using alternative gasses such as argon, krypton and xenon as adsorptives for the determination of specific surface areas. However, in most cases and due to lacking alternatives, a measurement temperature of 77 K was used. For all of the above-mentioned noble gasses, this temperature is below the triple point temperature. Accordingly, these substances re-sublimate with increasing pressure, which puts into question the unequivocal calculation of the area occupation of atoms adsorbed at the solid surface. The area occupation calculation of equation 2 requires the exact knowledge of the liquid density at the selected measurement temperature.

Of course, it was bound to happen: the BET surface areas determined with noble gasses considerably deviated from the values gathered with nitrogen, although the deviations were mostly explained with the undefined condition of the adsorbate phase below the triple point. In addition, there was disagreement about which saturated vapor pressure is to be used for the calculation of BET surface areas in this case: the saturated vapor pressure of the re-sublimated gas or of the sub-cooled liquid. To overcome these differences in the surfaces, area occupation for noble gasses was postulated there and then, which reproduced the values obtained with nitrogen using equation 1. Depending on the chemical properties of the evaluated surface, different values were constructed [4,5,6]. The argon example furthermore indicates that different area occupation values for adsorbed argon atoms were calculated even with one and the same measurement temperature and the same surface conditions, depending on whether the calculation of the BET surface area refers to the saturated vapor pressure of the sub-cooled liquid or the solid argon (see table 2).

Table 1 compiles the area occupation of nitrogen, argon and krypton at a temperature of 77 K resulting from the calculation based on equation 2 (from [4]). In case of argon and krypton, calculation was based on the density of liquids sub-cooled to 77 K. The standard area occupation is indicated for comparison purposes. It becomes obvious that the calculated area occupation of argon and nitrogen has prevailed. In contrast, there is a considerable difference between the

Table 1 Area occupation of N₂, Ar and Kr at 77 K (from [4])

Adsorptive	Area occupation [nm ²]	
	Calculated with eq. 2 from liquid density	Commonly used value
N ₂	0.162	0.162
Ar	0.138	0.138
Kr	0.152	0.202

Table 2 Area occupation of an argon atom [nm²] at 77 K (from [6])

Calculated with graphitized carbon black using p_0 (sub-cooled liquid)	Calculated with oxides using p_0 (liq.) (sub-cooled liquid)	Calculated with oxides using p_0 (solid) (solid material)
13.8	16.3	18.2
14.3	17.7	18.5
13.7	16.1	17.9
15.1	16.7	18.2
13.7	16.6	18.1
14.3	15.3	17.9
12.9	16.6	17.4
13.0	17.6	17.8
Average value: 13.85 ± 0,7	Average value: 16.65 ± 0,6	Average value: 18.0 ± 0,3

calculated and the commonly used area occupation requirement for krypton; a deviation caused by the alignment with the surface obtained with nitrogen, and which does not have a scientific basis. Table 2 is even clearer about this issue. It summarizes 3 different average area occupations for argon at 77 K obtained for surfaces determined with nitrogen and subsequent averaging. In this context, it is beyond comprehension why specifically argon atoms should require 20 – 30 % more area than in non-polar carbon surfaces, while the dumbbell-shaped nitrogen molecule with its additional quadrupole moment is allocated universal area. An arrangement that can only be explained with lacking technical alternatives back at that time.

From a scientific perspective, the questions remain why the use of different adsorptives usually leads to different BET surface areas of solid material and which adsorptive is the most suitable one for coming closest to the actual geometrical surface. As these questions are still not fully answered, there is still a lot of uncertainty about the BET method, and especially among critical users of it.

It seems questionable to us that deviating results of other adsorptives compared to N₂ 77 K BET calculations can be aligned simply by altering the area occupation. Recent stu-

dies clearly confirm the doubts expressed quite some time ago already [5]. The fact that the N₂ molecule is indeed a somewhat special and certainly not the ideal case, as it does not occur as atom (spherical symmetry) and as it has an interfering quadrupole moment. Time may have come to turn the scientific discussion upside down, as from scientific perspective, our following postulate seems to be worth a more profound research:

All texture-determinating sorption measurements based on molecule area occupation, in which the direct interaction between adsorptive atoms and solid surface play a significant role, should be carried out as noble gas adsorption at the noble gases boiling temperature, or it should at least be verified with such measurement.

Of course, this area occupation a_m is unable to consider the various positions of a nitrogen molecule in a solid surface area - the contrary is the case. Based on the BET calculations from noble gas isotherms, we critically evaluate the question whether the BET surface area determined with nitrogen is scientifically plausible, especially in the light of CryoSync™ offering ideal technical conditions for such examinations. So, let's use the available options and draw our own conclusions.

Determination of the specific surface area of a microporous aluminum oxide with selected adsorptives

Using the example of macroporous aluminum oxide (N5), BET surface areas determined for different adsorptives and measurement temperatures are to be compared. The specimen is a granulate with a grain diameter between 1 and 2 mm. The BET surface area (N_2 at 77 K) is approx. $5 \text{ m}^2/\text{g}$. The cumulative pore distribution determined with mercury intrusion is shown in figure 3 from which a total pore volume of about $0.28 \text{ cm}^3/\text{g}$ can be read. The pore size distribution reaches from approx. 0.1 to almost $10 \mu\text{m}$. This implies a distinctive macroporous material with a negligible share of larger mesopores; the presence of micropores can even be completely excluded. Therefore, this material is perfectly suitable for our purposes, as multilayer adsorption at the solid surface area is the only sorption mechanism suitable and meeting the requirements for the correct implementation of the BET method.

When using the adapted area occupation for krypton (tab. 1) and argon (tab. 2) for our aluminum oxide, following BET surface areas (see table 3) are the result of using the adsorptives at 77 K.

The results are impressive proof of the fact that rather similar surface areas can be calculated for different adsorptives, if you

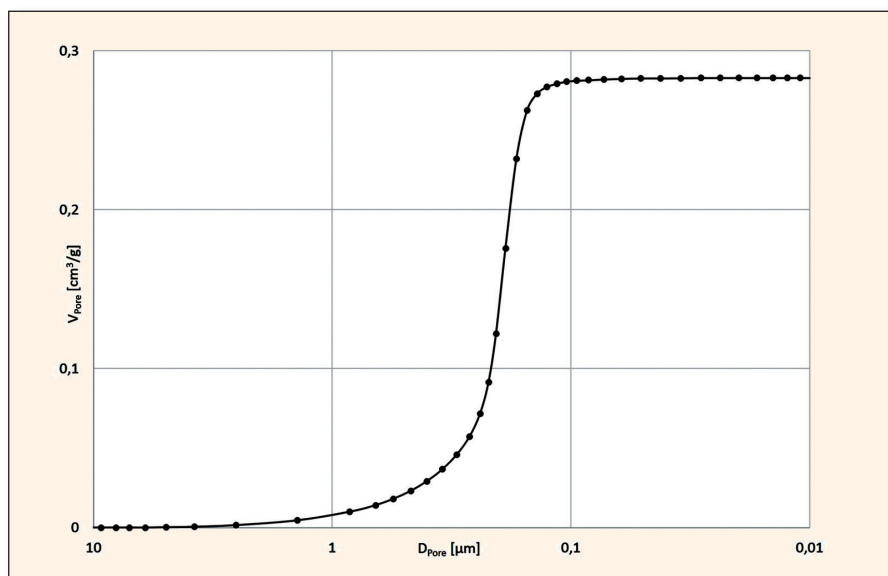


Figure 3 Hg intrusion curves of macroporous aluminum oxide N5, measured with POREMASTER 60 GT

adhere to certain conventions and use the “adapted” area occupations of noble gasses. If you remember the origin of the “adapted” area occupations, matching values are no surprise, while the deviations occurring with different oxides become clear when reviewing the values of columns 2 and 3 of table 2. The results for aluminum oxide N5 differ substantially, if the area occupation calculated from the liquid densities is used for the BET surface area calculations.

These results are summarized in table 4. Further, this table includes results from argon and krypton isotherms which could be measured with CryoSync™ at their boiling

temperatures (87 and 120 K). Thus, concerns resulting from the questionable nature of the adsorbate phase below the triple point temperature can be removed. You have read correctly: the temperature range of 82 – 120 K covered by CryoSync™ now makes it possible to easily measure krypton isotherms at their boiling temperature of 120 K (see Figure 4). Beside argon at 87 K, another noble gas turns out to be suitable for carrying out isotherm measurements at its boiling temperature, and it is a great pleasure to us presenting you such a rare isotherm as shown in figure 4.

Table 3 Calculated BET surface area of aluminum oxide N5

Adsorptive	T [K]	Area occupation calculated from	Area occupation [nm ²]	A _S (BET) [m ² /g]
N ₂	77	p_0 (liquid)	0.162 nm ²	5.42
Kr	77	adjusted $a_m(N_2)$	0.202 nm ²	5.01
Ar	77	adjusted to $a_m(N_2)$ mit p_0 (liquid)	0.166 nm ²	5.22
Ar	77	adjusted to $a_m(N_2)$ mit p_0 (solid)	0.180 nm ²	5.24

Table 4 BET surface areas of aluminum oxide N5 with area occupation of adsorbate molecules calculated from liquid densities

Adsorptive	T [K]	Calculated area occupation [nm ²]	BET surface area [m ² /g]
Krypton	77	0.152	3.84
Krypton	120	0.163	3.70
Argon p_0 (liquid)	77	0.138	4.35
Argon p_0 (solid)	77	0.138	4.03
Argon	87	0.143	4.11
Nitrogen	77	0.162	5.42

If using the area occupation calculated with equation 2 from liquid density, the BET surface area value determined from nitrogen now deviates considerably. If - regardless of minor deviations - the surface area values based on spherical adsorptives argon and krypton are rather similar at about $4\text{m}^2/\text{g}$, the calculation with nitrogen produces a substantially higher value of more than $5\text{m}^2/\text{g}$ - a considerable deviation by more than 25%.

This result lets us assume that the nitrogen molecules adsorbed in the first molecule layer can be oriented in close arrangement at a polar surface and that nitrogen molecules are oriented rather in upright position at the solid surface, and closer then at random orientation in liquid nitrogen. In this case, it would only be consequent for the evaluation of oxidic surface areas to use a modified, reduced area occupation for nitrogen.

Summary

1. The BET surface area quotient of argon and nitrogen used from Tab. 4 leads to an area occupation of nitrogen at aluminum oxide of 0.123nm^2 . This value nicely corresponds to the outcome of other studies [4] and suggest a reduction of the nitrogen area occupation to 0.13nm^2 .
2. The possibility of measuring krypton isotherms at 120 K opens innovative approaches for questioning considerably larger N_2 BET surface areas of oxidic materials.
3. Further investigations seem necessary to evaluate the relatively small difference in material parameters, e.g. between krypton measurements of 77 K and 120 K. In unporous, macroporous and mesoporous materials, the corresponding specific surface area generally have a fixed value, i.e. one adsorptive should produce the same specific surface area even with different measuring temperatures. CryoSync™ (Fig. 5) by QUANTACHROME now offers a simple approach for measuring an entire isotherm family and interpreting the results for BET surface area, adsorbate density and area occupation between 87 K (p_0 of krypton approx. 12 Torr) and 120 K (p_0 of krypton approx. 760 Torr).

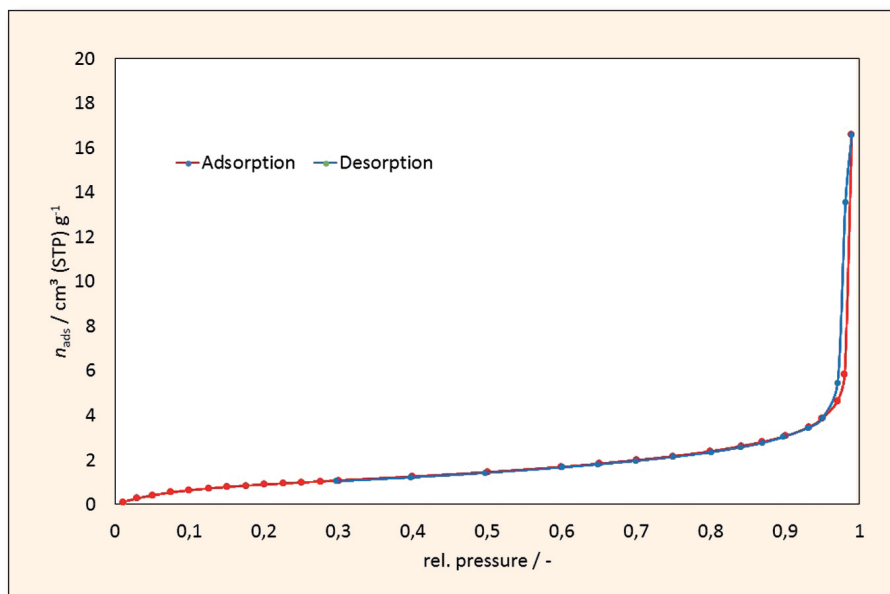


Figure 4 Krypton sorption at 120 K in macroporous aluminum oxide N5, measured with AUTOSORB-iQ-MP/CryoSync

4. Liquid nitrogen and CryoSync™ allow users to run simple measurements of following adsorptives at their corresponding boiling temperatures:

- Argon at 87 K
- Krypton at 120 K
- Methane at 112 K
- Nitrogen at 77 K
- Oxygen at 90 K

Argon and krypton are atomic adsorptives (noble gases) without permanent electrical dipole or quadrupole moments. Due to its tetrahedon-shaped molecule, methane is also of interest as symmetrical adsorptive molecule without permanent electrical dipole or quadrupole moment [7]. Further measurement programs in our LabSPA (Lab for Scientific Particle Analysis) will evaluate which deviations occur between the BET surface area of nitrogen, argon and krypton in various organometallic (MOFs) and other mesoporous and microporous pore structures.

The easy-to-achieve temperature range of 82 – 120 K of CryoSync™ offers new possibilities not only for determining the micropore distribution with measuring gasses at boiling temperatures, but also the correspon-

ding surface area determination. Further, it allows the determination of temperature dependencies from sorption isotherms. Such temperature-dependent isotherm families should not only enable the calculation of isosteric adsorption temperature, but also the temperature dependency termination of the area occupation of an adsorbate molecule.

We gladly keep you updated on further adsorptive application results. An initial workshop is scheduled on April 18, 2018 in Leipzig:

<http://www.quantachrome.de/en/messen-und-seminare/>

Literatur

- [1] Thommes et al., Pure Appl. Chem. 87(9-10), 1051-1069 (2015)
- [2] Partikelwelt 18, 31 – 34, <http://www.quantachrome.de/partikelwelt/>
- [3] Partikelwelt 15, 24 – 27, <http://www.quantachrome.de/partikelwelt/>
- [4] F. Rouquerol, J. Rouquerol, K. Sing, Adsorption by powders & porous solids, S. 171 ff.
- [5] A. L. McClellan, H. F. Harnsberger; Cross-sectional Areas of Molecules Adsorbed on Solid Surfaces; Journal of Colloid and Interface Science, 1967, 23, S. 577 – 599
- [6] S. J. Gregg, K. S. W. Sing; Adsorption, Surface Area and Porosity; Academic Press, London and New York, 1967; S. 75 – 93
- [7] C. Graham, J. Pierrus, R. E. Raab, Mol. Phys. 67 (1989) 929 – 955.



Figure 5
 AUTOSORB-iQ-MP with integrated CryoSync: CryoSync is located in the Dewar vessel, the small controller is visible to the right, and the temperature is controlled using a PC software, CryoSync basically does not require additional laboratory space, operates completely silently and has a power consumption of max. 30 watt

Establishing LabSPA as laboratory service provider for the characterization of dispersions, powders and porous materials

With the pore laboratory renovation just finished in Odelzhausen and the current extension of our shared laboratory in Düsseldorf, QUANTACHROME has taken yet another step towards a full-scale laboratory service provider. Customers benefit from our broad service range that includes contract analyses, method development and the implementation of laboratory projects, as they are hardly available from one hand.

The interaction between our LabSPA (Lab for Scientific Particle Analyses) with our experts, the R&D department and technical service result in a unique and ever-growing QUANTACHROME competence structure in the area of particle measurement. We invite you to discuss your tasks with our LabSPA, as we might be able to solve them right here:

- Development of methods and project handling
- SOP measurements including measurement routine enhancements in consultation with customer
- Individual samples, sample series, external quality assurance of your products
- Strict confidence is a matter of course
- Short processing times and professional test reports

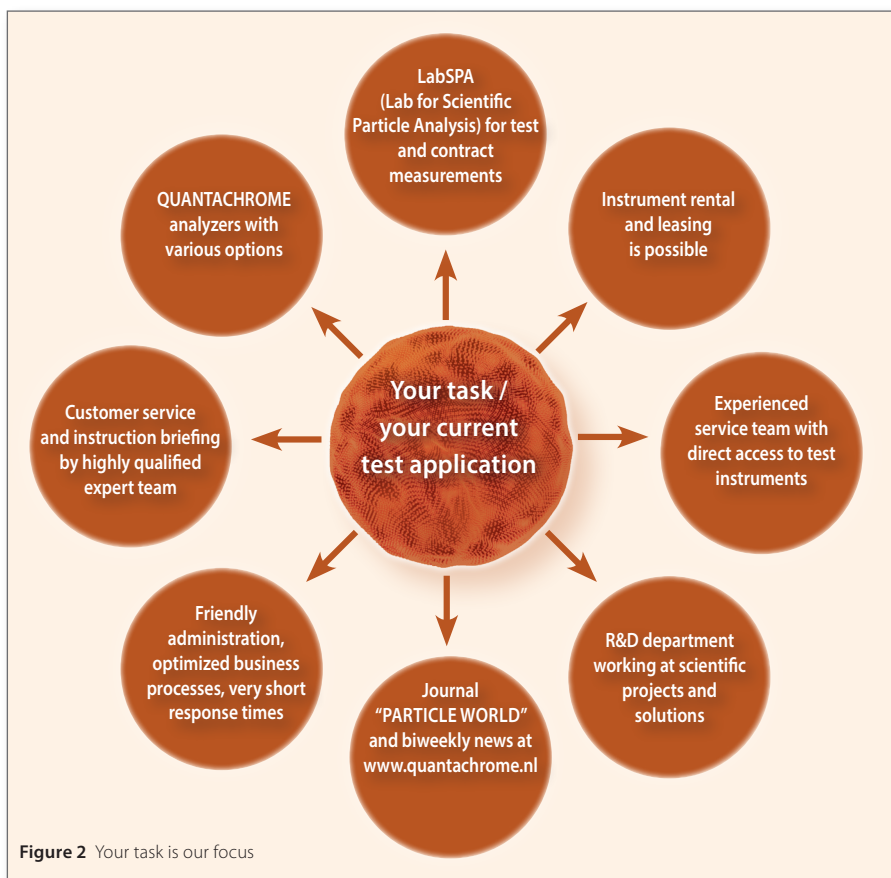


Figure 2 Your task is our focus

Test and contract analyses in the LabSPA

Test measurements at QUANTACHROME are always carried out in our LabSPA (Lab for Scientific Particle Analysis). Complex characterizations of dispersions, powders and

porous materials (Fig. 4) are our daily work, and short processing times are usually no problem, as long as test goal and the shipping of samples have been agreed in advance. With a laboratory area of approx. 500 m² and a total of about 40 test instruments located at three branch offices, we are capable of carrying out test measurements for you – yet another good reason to decide for QUANTACHROME. You receive a comprehensive test report within a short processing time. The measurement results provided by QUANTACHROME are a reliable basis prior to taking the investment decision for a new test instrument. Our application specialists are qualified to fit even the most individual needs and will gladly support you with valuable advice.

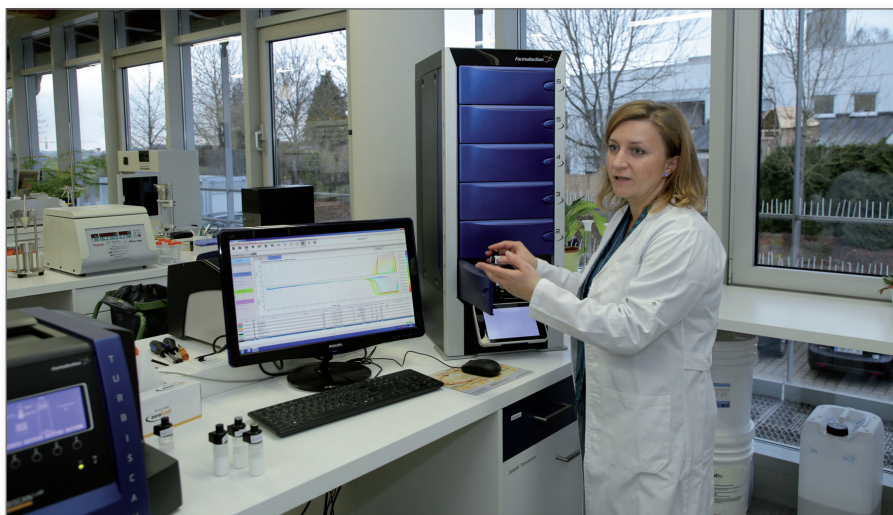


Figure 1 Our dispersion laboratory: Ms. Eikelmann explaining stability tests of original emulsions in TURBISCAN TOWER

Our specialists

QUANTACHROME's specialists do what they are best at: sharing their expertise with you. QUANTACHROME GmbH & Co. KG employs 10 natural scientists (inorganic chemistry, technical chemistry with the focus on adsorption and catalysis, physics, material science, biology) holding a doctoral degree and further specialists in the field of chemical engineering, construction chemistry and general laboratory work. They are not only in charge for the consultation prior to taking the investment decision for an instrument, but also the interpretation of test and contract analyses, system instruction and user training. You do not only get direct access to the expertise gained in the application laboratory, but also practical expert discussions and test measurements when receiving a system instruction prior to the purchase decision.

ISO, DIN and IUPAC recommendations, measurement implementation including the enhancement of measuring conditions, special tips and tricks as well as a comprehensive results evaluation let customers appreciate QUANTACHROME's profound expertise. An increasing number of customers recognizes the difference between QUANTACHROME

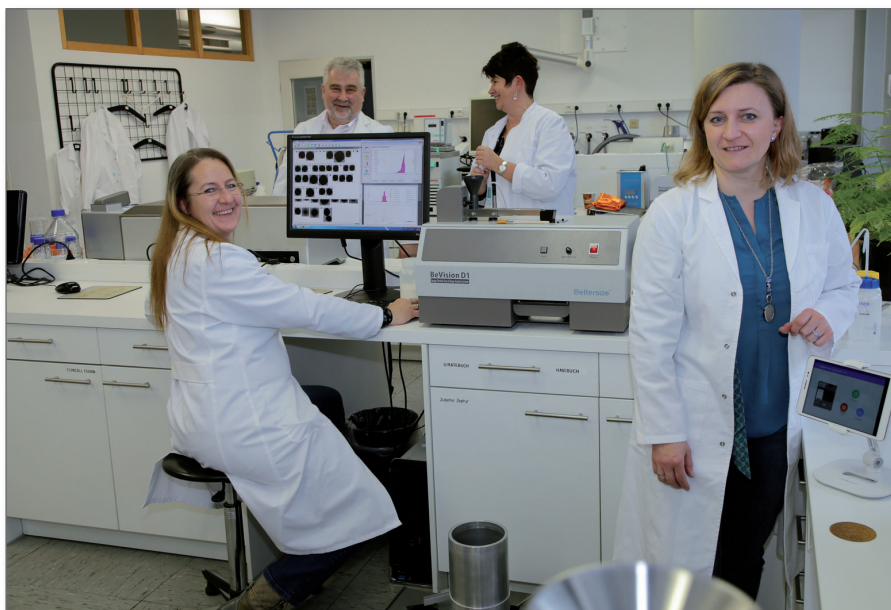
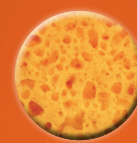
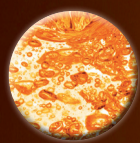


Figure 3 Our dispersion laboratory employees: B. Deponte, Dr. M. Ferner and K. Eikelmann (from left to right); When the general manager is in the lab, there is always a reason for a smile...

and other providers who do not offer practical customer service such as system trainings and whose remote application laboratories just issue results printouts instead of conclusive result reports. This quality difference is proof enough to continue with our LabSPA and the permanent enhancement of our quality management, as these factors

make LabSPA a reliable and trustful partner for contract analyses. Individual analysis options are available on our homepage www.quantachrome.de under "Contract Analysis", and the corresponding measuring methods are found at "Measurement methods".



Characterization of dispersions

- Particle size from nanometer to millimeter range and particle shape
- Stability of original emulsions, dispersions and foams
- Zeta potential and particle size of concentrated suspensions
- Viscosity depending on the shear rate of dispersions and liquids
- Rheology of emulsions and suspensions in stable state
- Drying behavior of films and coatings

Characterization of powders

- Particle size ranging from nanometers to millimeters, including particle shape
- Specific surface (BET surface area)
- Pore analysis (pore volume and pore size distribution)
- Density, raw density, bulk density, TAP density
- Water adsorption (dynamic vapor sorption)
- Repose angle, dispersity, flowability

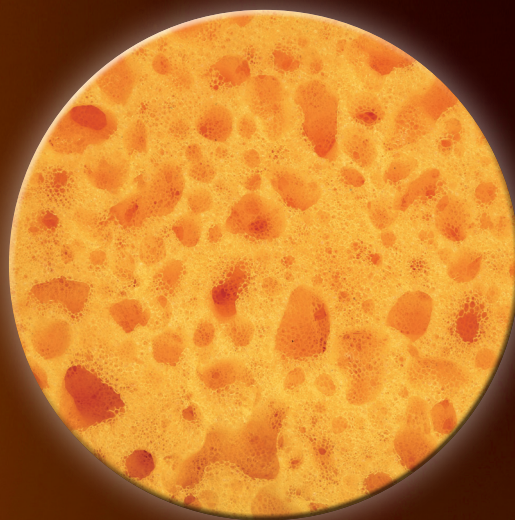
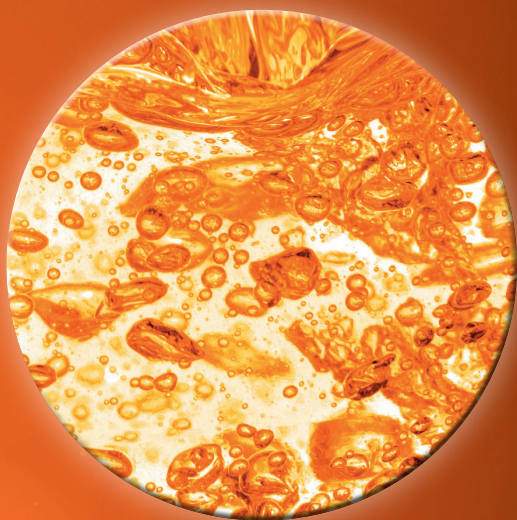
Characterization of porous material

- Specific surface (BET surface area), pore volume, density and raw density
- Pore size distribution from 0.3 nm up to approx. 1 mm
- Characterization of through-pore size (filter, membrane)
- Characterization of active catalyst surfaces
- Adsorption gases and vapors from low to high pressure range
- Breakthrough curves of gas and vapor mixtures

Figure 4 Analysis options in the LabSPA for the characterization of dispersions, powders and porous material

Your partner in particle characterization

QUANTACHROME offers profound expertise for the characterization of dispersions, powders and porous materials in Belgium, Croatia, Denmark, Hungary, Luxembourg, Netherlands, Slovenia, Serbia, Switzerland and some other European countries.



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