

PARTICLE WORLD

TECHNICAL PAPERS of
3P INSTRUMENTS
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3P

INSTRUMENTS

Characterization of
particles • powders • pores

Quantochrome

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QUANTACHROME GmbH & Co. KG has recently renamed its company name to 3P INSTRUMENTS. The General Manager of 3P INSTRUMENTS, Dr. Dietmar Klank, talks about the news. The interview was conducted by Elke Peter, info@elke-peter-werbung.de:

Dr. Klank, this year would be your 20th anniversary with QUANTACHROME, how have you experienced recent developments?

Since February, 9th of 2018, QUANTACHROME USA has a new owner. I myself received these news on that very day by email. It has been a great disappointment to me to learn of the immediate takeover over the internet rather than getting those informations from our partner of more than 25 years directly. All of a sudden our company with its employees and its excellent customer relationships was at stake, because it meant we had to perform a rather quick restructuring of our portfolio.

How did the situation develop after the takeover of QUANTACHROME USA?

There were three companies with the name QUANTACHROME, one in USA, one in UK and one in Germany. The German QUANTACHROME GmbH & Co KG was founded in 1990 and became 100% independent in 2006. This meant, we could announce that the takeover of QUANTACHROME USA did not affect us directly in the short term and that we would naturally try everything to

resolve all open questions on behalf of our customers with all parties involved. However, it also meant, that the new owner of QUANTACHROME USA would use his own network of agents and companies. So we began developing a strategic plan, that, once executed, will ensure the continued existence of our company for the future. The basis for this will be our current virtues such as professional competence, the highest level of services provided, great flexibility and the much appreciated customer friendliness.

Immediately after the takeover of QUANTACHROME USA, we started brainstorming in our company and we included every employee in this. Of course, no every idea can be realized and some ideas are mutually exclusive. But this is exactly what it comes down to – to stand together as a team and develop a harmonic concept from a large variety from ideas. In practice, this would mean, that we will keep collaborating with both new and current partners to complement our spread of analytical methods, but also to expand these collaborations for R&D purposes while at the same time take on more responsible on the European market.

Our company has been in constant development, especially within the last few years. It is now time to introduce a new era of the international development. 3P INSTRUMENTS stands for the applications our current virtues on a much larger and more international market.

How would this bigger internationality look in practice?

We have already been supporting more than the current QUANTACHROME analytical instruments. For some years we have good success with the market leaders FORMULACTION in the field of stability of dispersions and with DISPERSION TECHNOLOGY with acoustic spectrometers for particle size and zeta potential. And, besides being distributor for some instrument producers we have begun producing our very own instruments in the field of mixed gas sorption. In principle, we offer a large spread of analytical methods for the characterization of particles, powders, pores – and our new company name 3P INSTRUMENTS is derived from that.

Europe is a challenging field for marketing, sales and service due to the wide variety of languages. How will you address and resolve these challenges?

With regards to sales, we already have a lot of experience on which we can rely and expand upon. We have been the European distributor for Dispersion Technology (www.dispersion.com) and provide their services in the field of particle size and zeta potential measurements of original concentrated dispersions. From these experiences we have learned, partners we can use for collaborations in other countries and how to further develop our LabSPA (Lab for Scientific Particle Analysis) for test measurements and contract analyses. This means also, that the specific marketing becomes more efficient. Let us take our journal PARTICLE WORLD as an example: A few years back, we asked the CEOs of both CILAS France and QUANTACHROME USA, if the PARTICLE WORLD could be expanded with reports and articles from both companies for the European market. The idea was rejected by both companies. However, we are no longer in business with these two particular companies. So, let's think that idea again to create an optimized educational basis for the European customers, based on experiences of our R&D group, of our other specialists and of our LabSPA (Lab for Scientific Particle Analysis).

Another example would be our own development of analytical instruments for the determination of breakthrough curves of gas and vapor mixtures, which will be handled by us world-wide in the future. As of now, this brand of instruments will be

called mixSorb, which stands for dynamic gas sorption analyzer. We have compiled publications and informations on the field of dynamic sorption methods on the homepage www.dynamicsorption.com for downloading and we have also planned two international events for May 2019 in Leipzig:

- **14th May, 2019, in Leipzig:** Symposium on Dynamic Sorption Methods
- **15th May, 2019, same place in Leipzig:** Workshop on New Developments in Gas Sorption Methods for Characterization of MOFs and other synthesized porous materials.

Welcome to Leipzig in May 2019, forms for registration and informations can be found at www.dynamicsorption.com and also on www.3P-instruments.com

Could you sum up for your readers, what we can expect from 3P INSTRUMENTS in the future?

We are constantly striving to be the best possible partners for our customers in the field of particles-powders-pores. This is especially true for the users of analytical instruments from CILAS France and QUANTACHROME USA. We are the most experienced partner for professional maintenance and service for these instruments, many customers started with new maintenance contracts during the last few months, to save our experience for them and for good customer relationship in future.

In this issue of PARTICLE WORLD, you will also find more answers to this and further questions. Additionally, news can be found twice a month on our homepage www.3P-instruments.com. In the coming weeks, you will find information regarding:

- new capillary flow porometer and liquid-liquid-porometer for filter and membrane characterization
- new gas adsorption and pore characterization instruments
- the international Top-News for the characterization of metal organic frameworks (MOFs): the new mixSorb S for the measurement of mixed gas adsorption and breakthrough curves for MOFs and other small sample amounts of synthesized porous materials
- new particle sizer models for characterization of particles from nanometer up to millimeter scale
- new applications for acoustic measurements (www.dispersion.com) and of stability analyses (www.formulaction.com) of concentrated dispersions and emulsions.

I would also like to take this opportunity to extend our heartfelt thanks to our customers for their loyalty and cooperation. We will remain your partner in the future with our experiences and our services! And, I would also like to thank our employees, who can be very proud on their achievements for our customers and the future of 3P INSTRUMENTS.



“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@3P-instruments.com

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 FRAUNHOFER), 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 backscattering detector are located at the right side of the measurement cell. A Fourier lens is placed directly in front of the measuring cell.

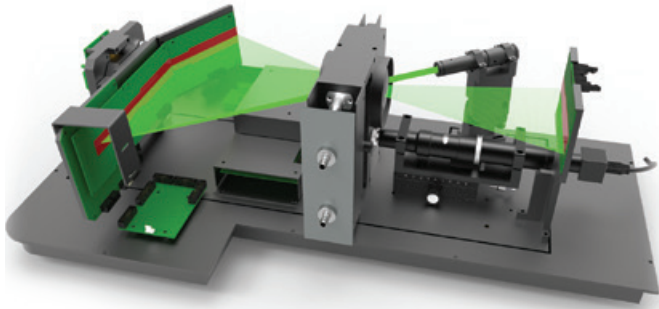


Figure 2
Setup of BETTERSIZER S3 Plus

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).

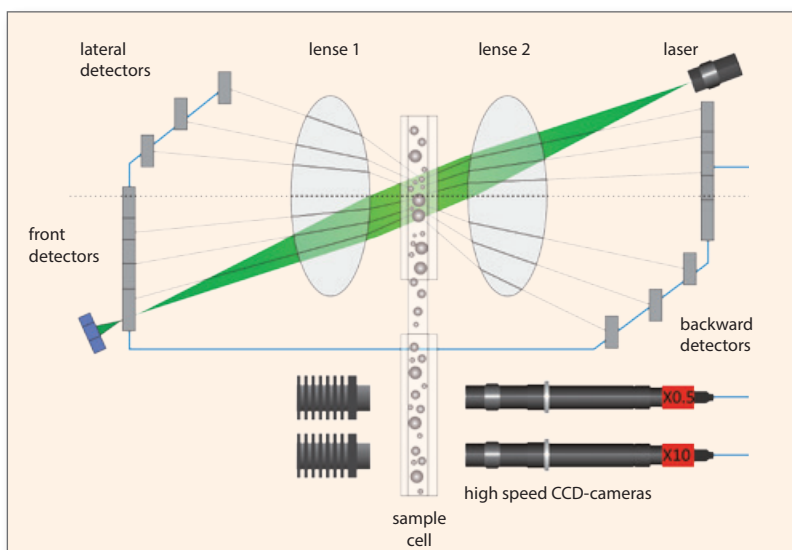


Figure 3 Schematic overview of the DLOIS technology deployed in BETTERSIZER S3 Plus and CCD camera technology (X 0.5 and X 10)

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 backscattering 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).

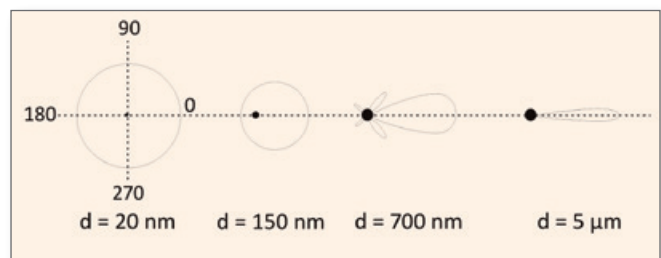


Figure 4 Laser light diffraction example ($\lambda = 633 \text{ nm}$) at various-sized particles (polar diagrams)

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)

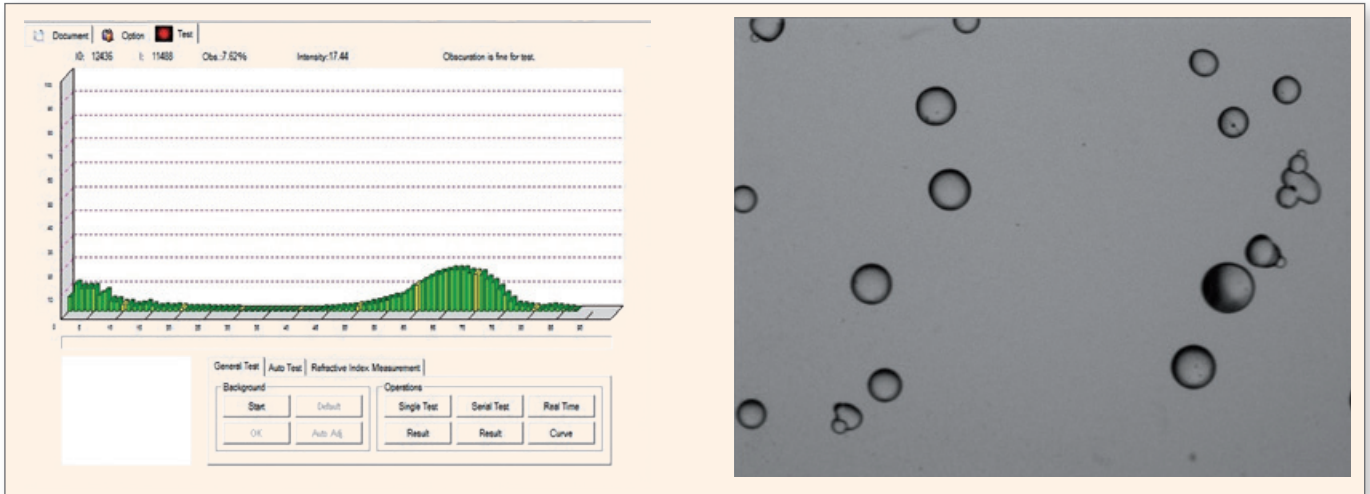


Figure 5 BETTERSIZER software with live CCD camera picture during a measurement

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.

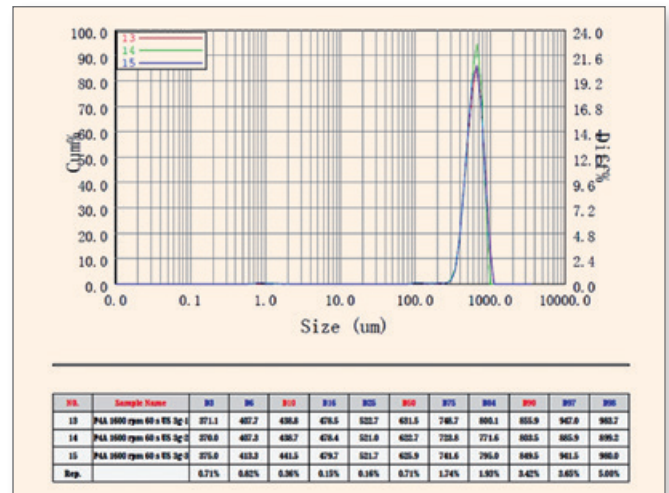


Figure 6 Sieved glass spheres measured with static light scattering combined with dynamic image analysis (BETTERSIZER S3 Plus)

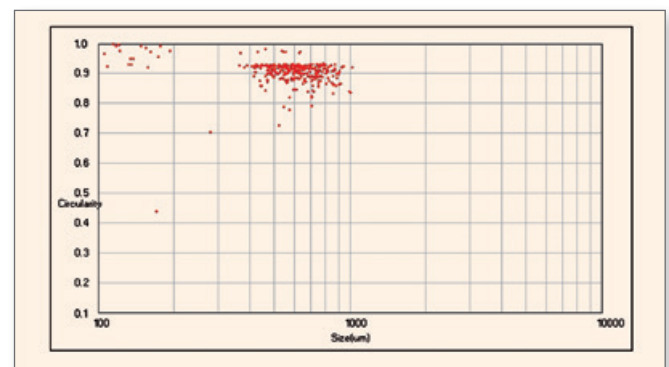



Figure 7 Trend diagram circularity vs. equivalent diameter of the glass sphere specimen

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 circular and therefore deviate from the requested quality of a spherical shape.

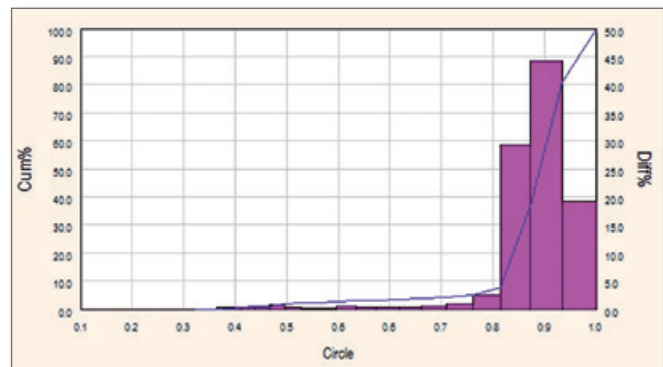
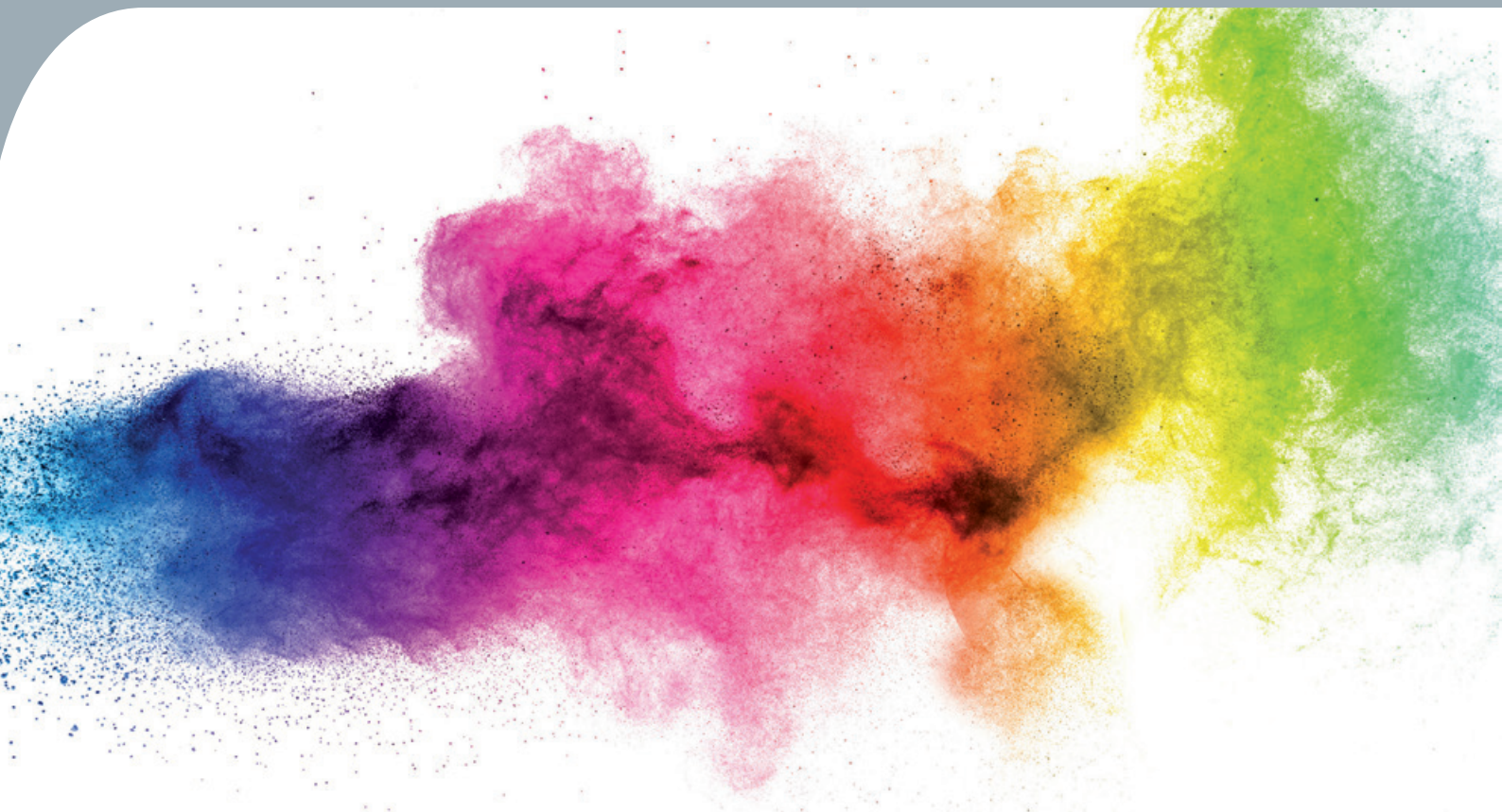


Figure 8 Circularity sum curve: more than 50 % of the particles have a circularity of < 0.9

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 www.3P-instruments.com/analyzers/bettersizer_s3_plus/. Please inquire details on contract and test analyses as well as instrument presentations at info@3P-Instruments.de.



Macroscopic powder characterization: fully automated analysis of physical powder properties

Dr. Frederik Schleife, frederik.schleife@3P-instruments.com

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 an 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

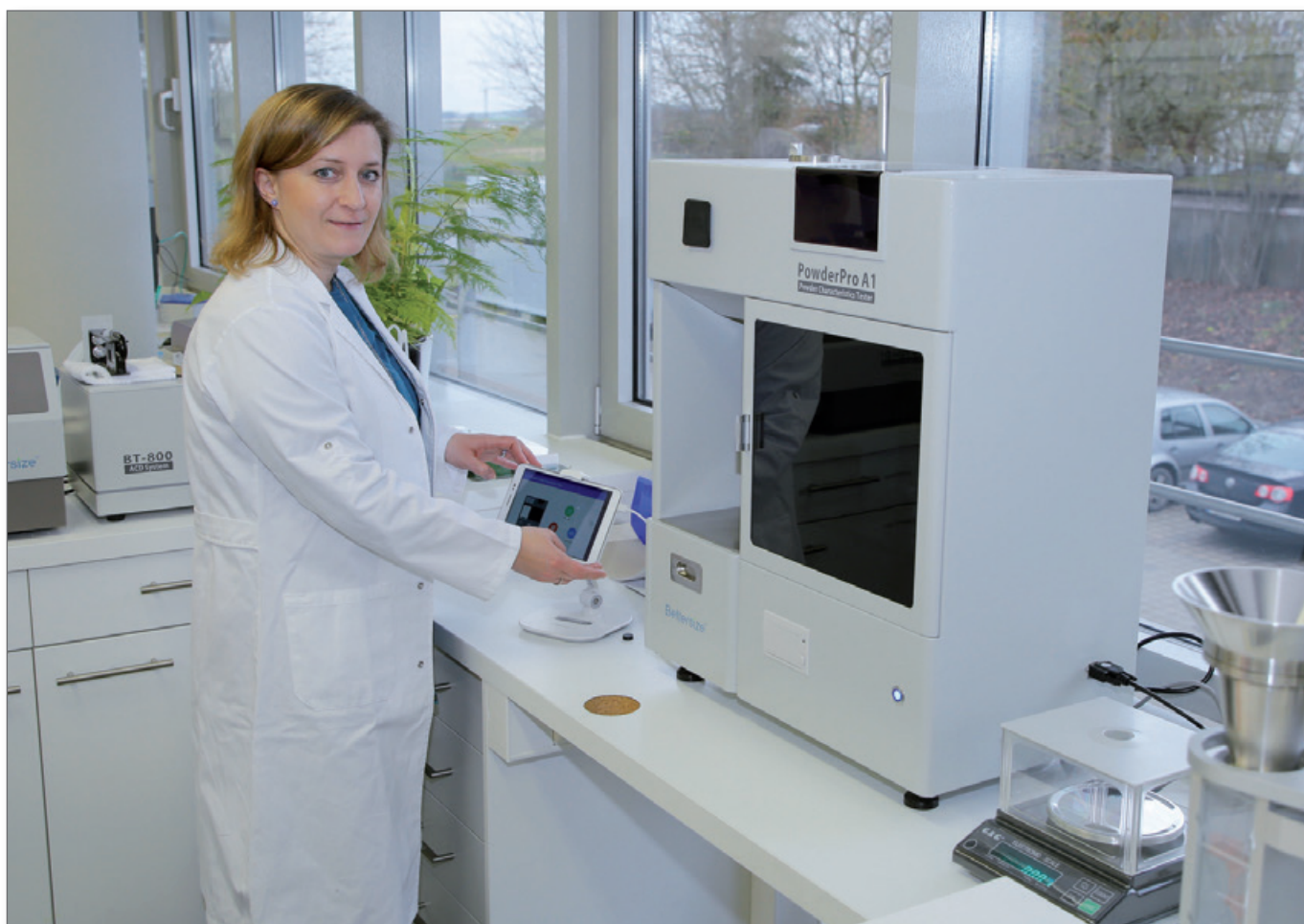
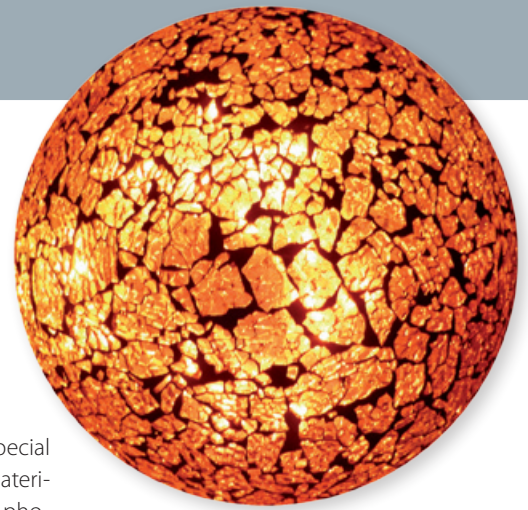


Figure 1 Our laboratory employee K. Eikelmann working with PowderPro A1 in the dispersion section of our LabSPA (Lab for Scientific Particle Analysis)

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

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



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.

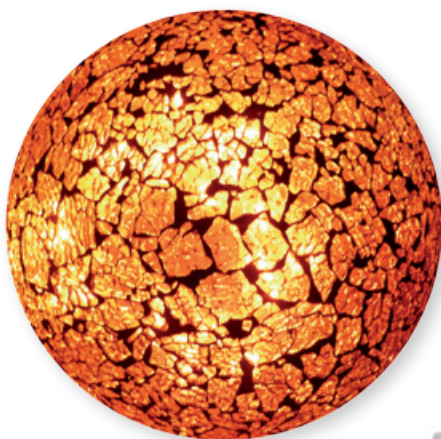


Figure 1 BeVision D1

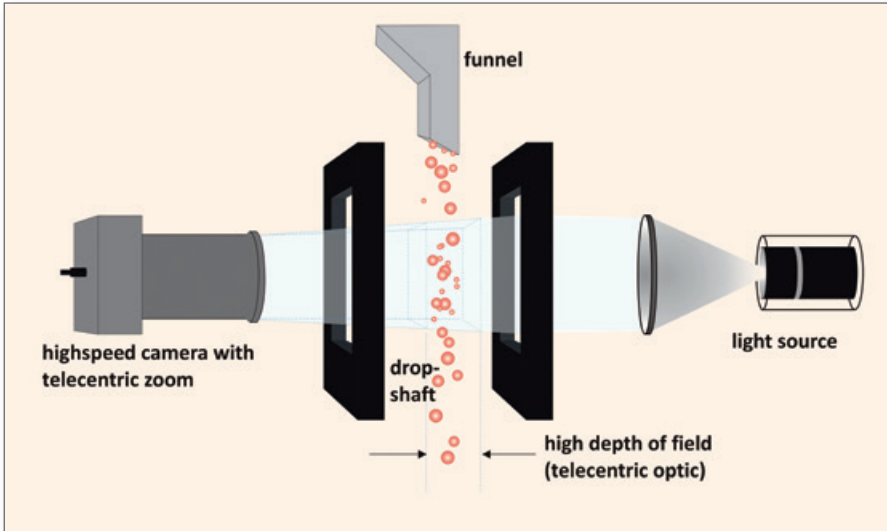


Figure 2 dry dispersion system of the BeVision D1

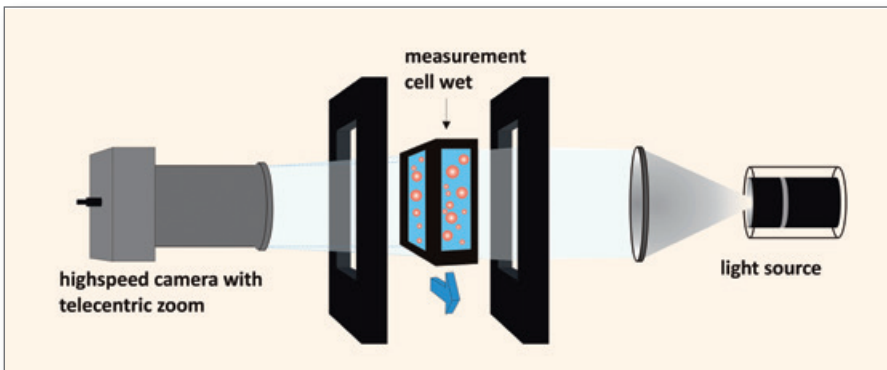


Figure 3 wet dispersion system of the BeVision D1

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

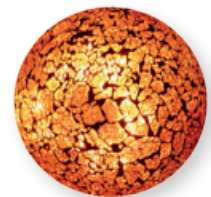
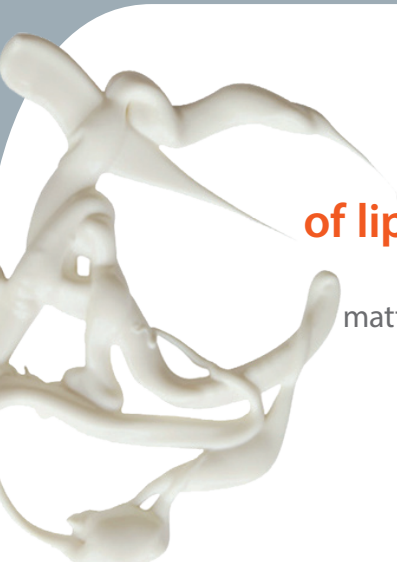


Table 1 BeVision D1 – Overview about the most important size- and shape parameters

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>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>	



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.

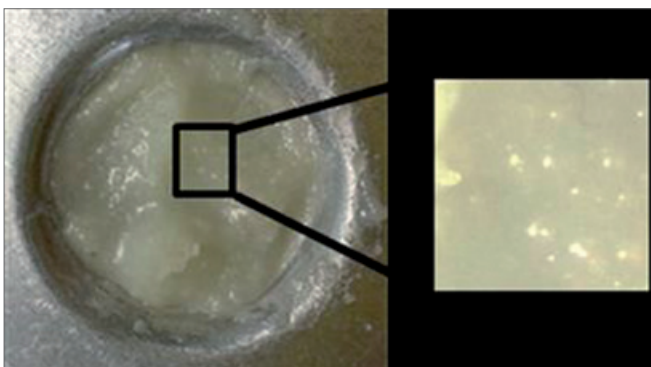


Figure 2 Photo of the Sample 1 where crystals are visible to the naked eye

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 an 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.

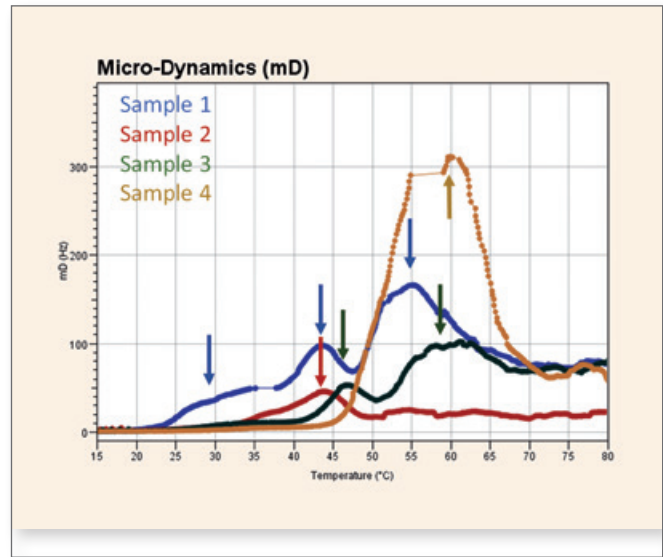


Figure 3 Micro-Dynamics as a function of temperature for the 4 samples

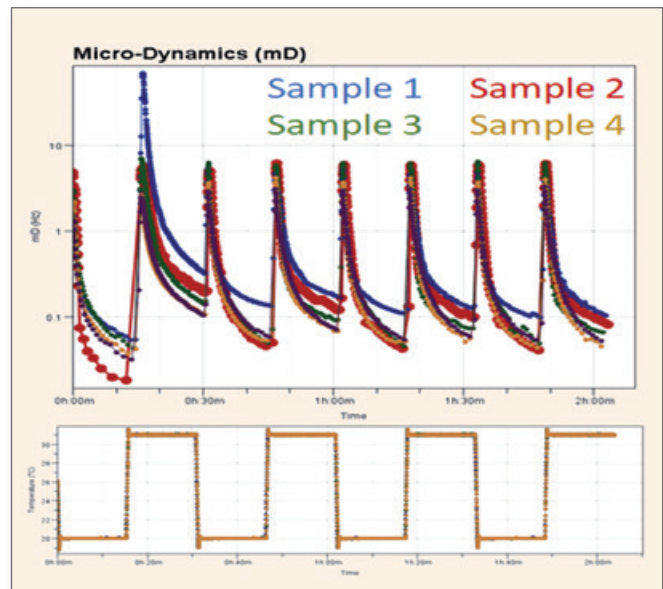


Figure 4 Micro-Dynamics as a function of 4 heating/cooling cycles for the 4 samples

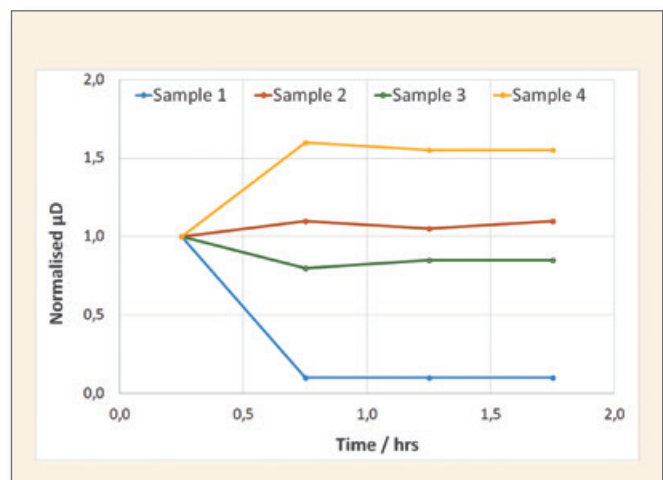


Figure 5 Micro-dynamics peak heights (first peak normalised) at heating for all the samples



Why use a microfluidic rheometer?

Dipl.-Ing. Matthias Lesti, matthias.lesi@3P-instruments.com

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.

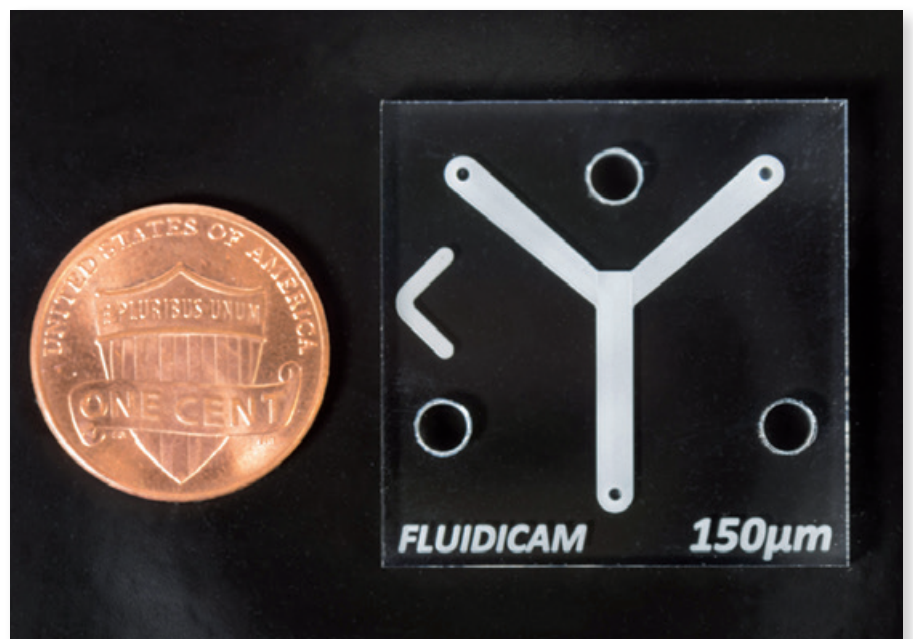


Figure 2 Dimensions of Microfluidics

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.

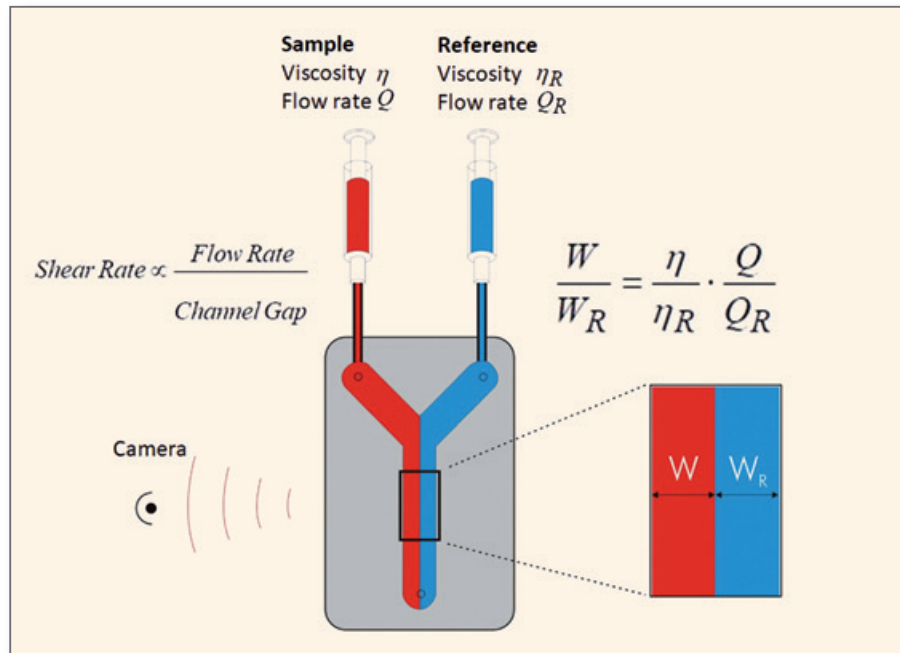


Figure 3 FLUIDICAM RHEO measuring principle

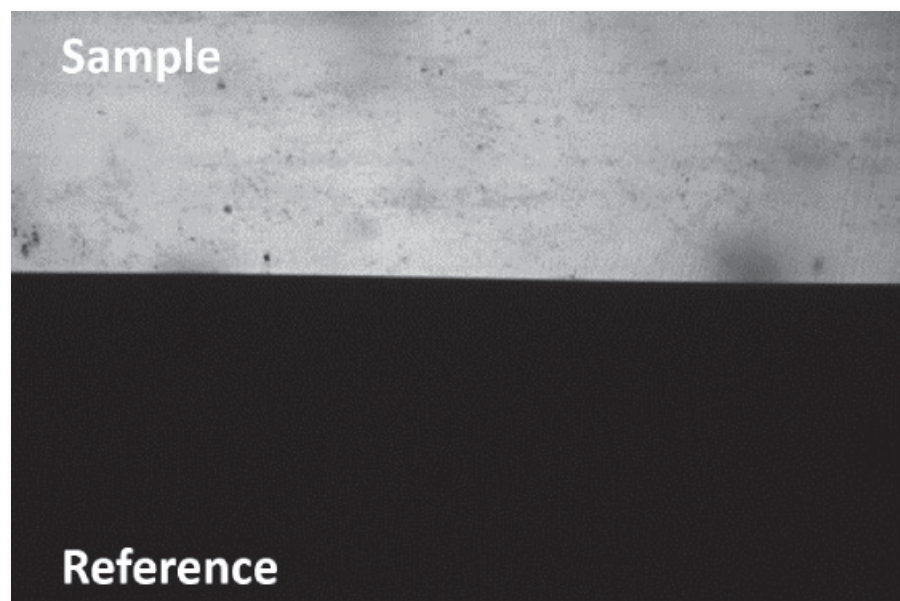
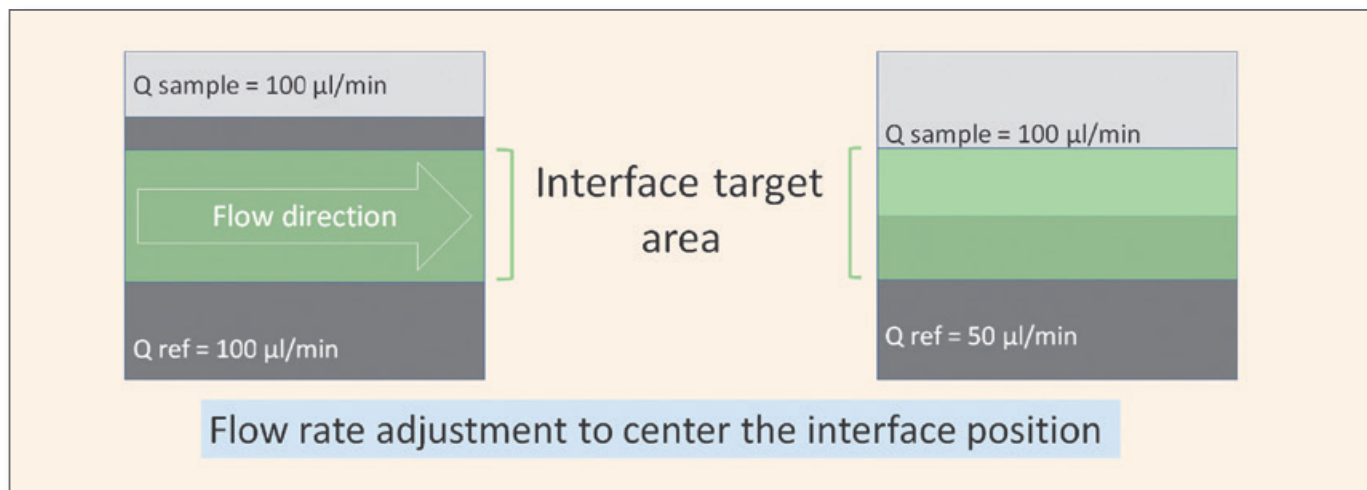


Figure 4 picture of interface

Figure 5 Interface centering



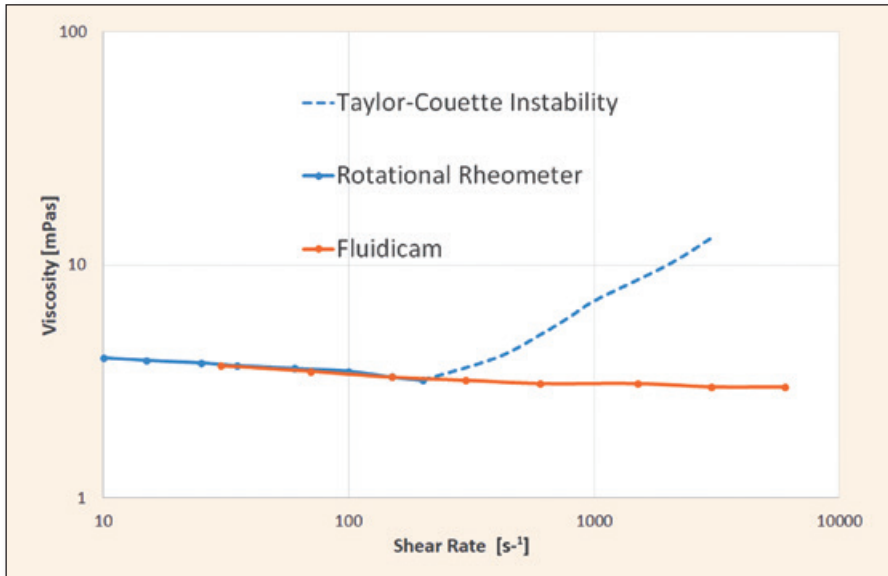


Figure 6 Viscosity of BSA solution (200 mg/mL at 25 °C) with FLUIDICAM RHEO and Rotational rheometer

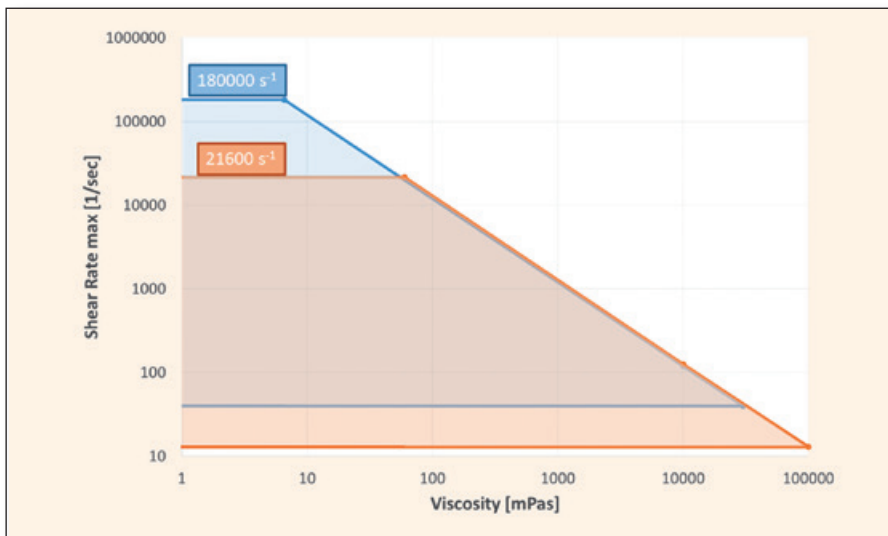


Figure 7 Accessible shear rate for 50 μm Chip (●) and in the 150 μm Chip (●)

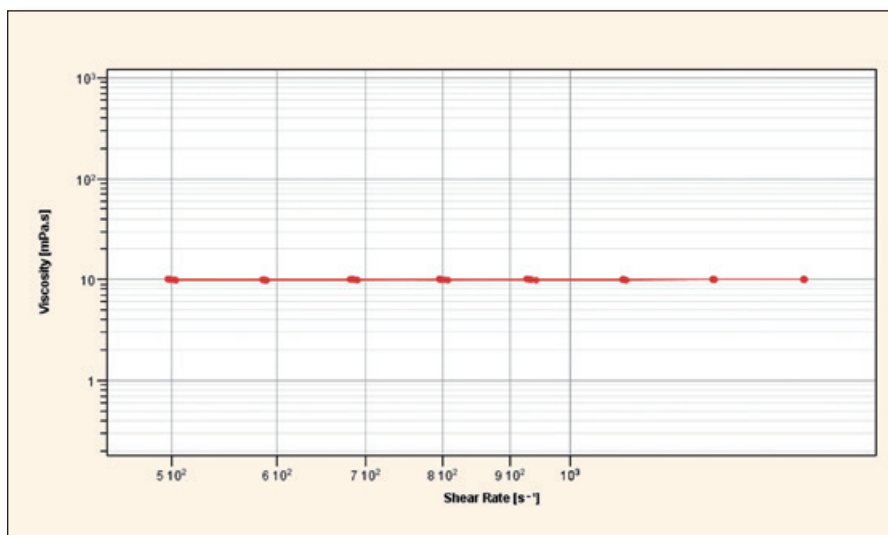


Figure 8 Viscosity of PEG 10 % solution at 4 °C (x5)

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.

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.

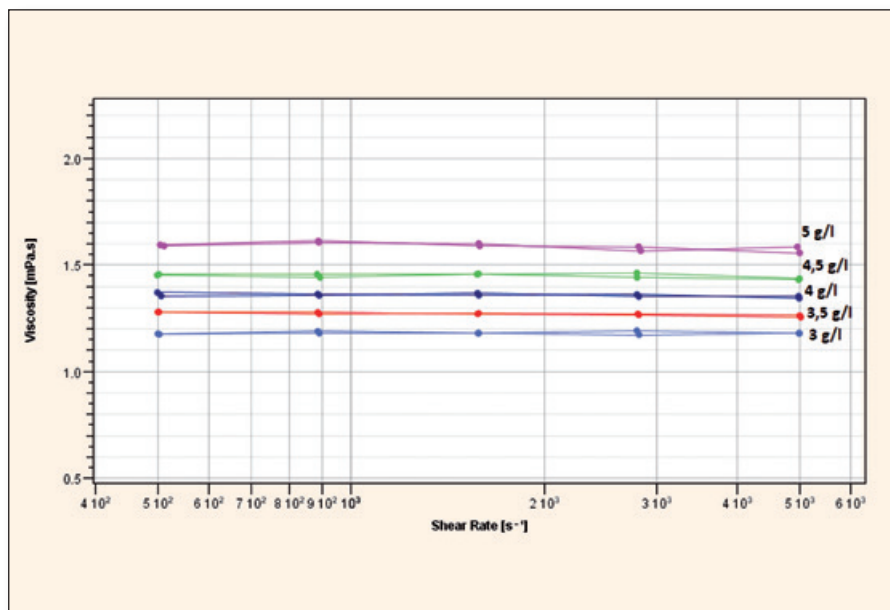


Figure 9 Viscosity of Natrosol diluted solutions at 5 concentrations from 3 to 5 g/L

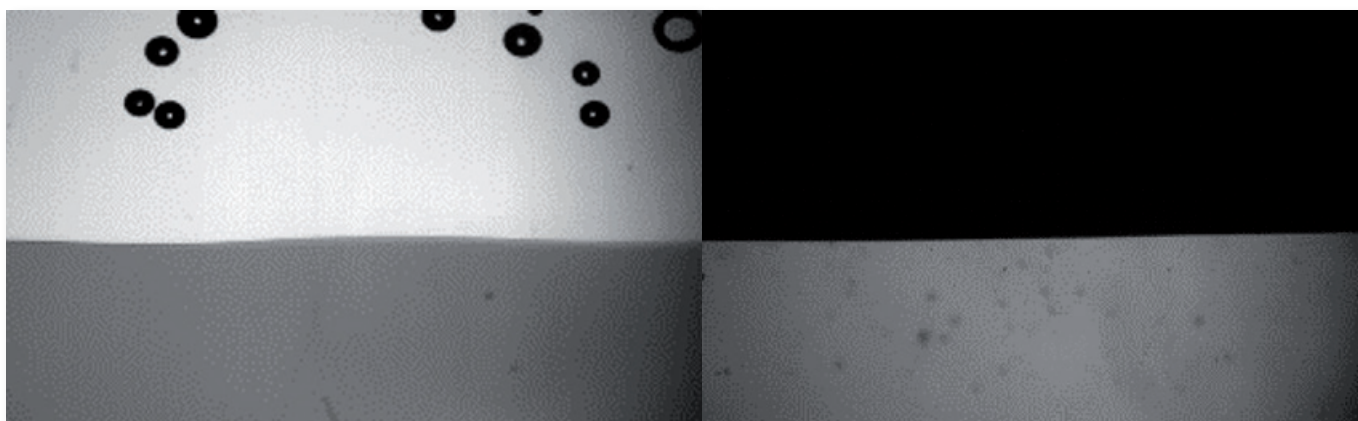


Figure 10 Pictures of interface in the FLUIDICAM RHEO

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.

Characterization of liquids, dispersions, emulsions, and porous materials using ultrasound

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

The title of our overview here is the same one as of the book of A. S. Dukhin and P. J. Goetz, which has become available with its third edition recently [1]. The new edition is not a simple copy of the former editions, but exceeds the second edition by 25%, mainly because of the new studies published especially in the completely new Chapter 14 in the book. Otherwise, there have been substantial additions made to the other application (Chapter 8-13) as well.

The particle size distribution and zeta potential of liquid dispersions are key parameters for estimating the dispersion quality. Therefore the choice of a suitable measuring method for the determination of those parameters plays an important role for the quality control and research and development. Especially in the field of highly concentrated dispersions a dilution of the sample, for instance, is leading to a significant change of the electrochemical properties, whereby the measured particle size and zeta potential are effected dramatically. For a representative characterization of such concentrated suspensions or emulsions, a measurement technique is needed, allowing a macroscopic analysis of the dispersions in original state. The acoustic spectroscopy (Figure 1) provides: the determination of particle size by measurement of the attenuation of ultrasound waves in concentrated dispersions from nanometer to the upper micrometer range. The zeta potential is calculated from so called Colloid Vibration Current (Figure 2).

One of the main advantages of ultrasound over other traditional characterization methods is that ultrasound eliminates the need for sample dilution, means that the methods are for use of the study of unchanged samples, to study the dispersions and emulsions in their original concentrations. There are currently four International Standards covering the described methods of ultrasound measurements for the characterization of dispersions: ISO 20998 Part 1 and 2 for acoustic particle sizing and ISO 13099 Parts 1 and 3 for electroacoustic zeta potential measurements.

We can give a very short overview here only, and want to demonstrate the practical importance of the acoustic and electroacoustic methods with the titles of the chapters 7 – 14 of the book [1]:

- Acoustic and Electroacoustic measurement techniques
- Applications for dispersions
- Applications for nanodispersions
- Applications for emulsions and other soft particles
- Titrations
- Applications for ions and molecules
- Applications for porous bodies
- Peculiar Applications of acoustics and electroacoustics for characterizing complex liquids

The DT-instruments as the DT-310 (Figure 3) in the following table are unique devices to solve complex applications and can be equipped with pH-Temperature option, with electric conductivity probes for aqueous and non-aqueous dispersions, with permittivity option, with a peristaltic pump, a non-aqueous option for the DT-system and with an automatic titration with two or only one burette.

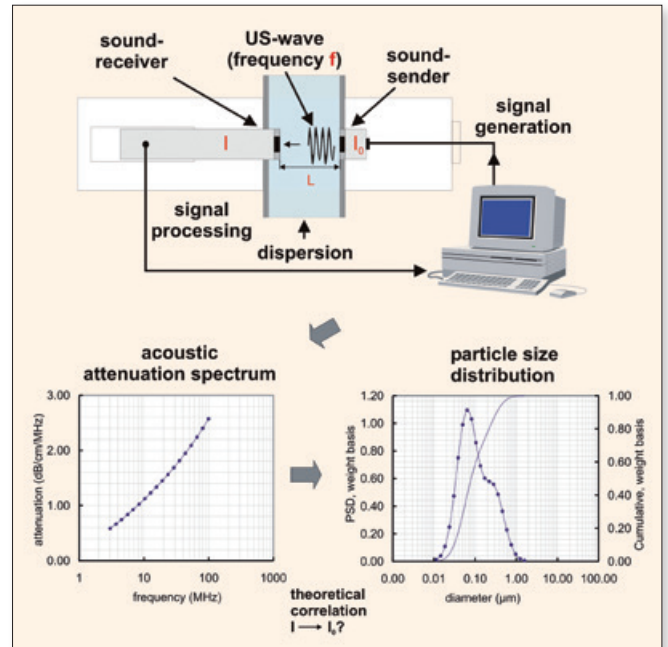


Figure 1 Principle of acoustic spectroscopy with the DT-1202 and DT-100 from DISPERSION TECHNOLOGY

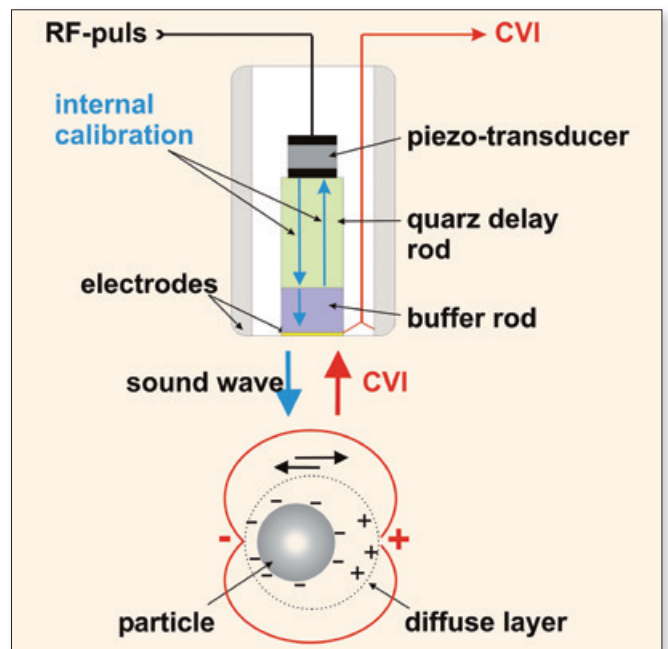


Figure 2 Principle of electroacoustic spectroscopy with the DT-310 and DT-1202 from DISPERSION TECHNOLOGY

Especially if you don't find another method to characterize your original samples to solve your special application, don't hesitate to contact us for some test. It is quite easy very often to send a test sample to our LabSPA (Lab for Scientific Particle Analysis) to get an idea if it is to solve with our set of particle characterization techniques: info@3P-instruments.com.

Table 1 Specifications of DT-Spectrometer

	DT-1202	DT-300/DT-310	DT-100	DT-600
	Particle size and Zeta potential	Zeta potential	Particle size	Rheology
Calculated parameter				
Mean size (µm)	0.005-1000	-	0.005-1000	-
Lognormal parameter	Yes	-	Yes	-
Bimodal parameter	Yes	-	Yes	-
Zeta potential (mV)	± (0.5% + 0.1)	± (0.5% + 0.1)	-	-
Longitudinal viscosity (cP)	optional	-	-	0.5-20000 ±3%
Bulk viscosity – Newtonian systems (cP)	optional	-	-	0.5-100 ±3%
Liquid compressibility 10 ⁴ /Pa ⁻¹	optional	-	-	1-30 ±3%
Newtonian test – MHz range	optional	-	-	any
Measured parameters				
Temperature (°C)	0 –100 ±0.1°C	0 –100 ±0.1°C	0 –100 ±0.1°C	0 –100 ±0.1°C
pH	0.5-13.5 ±0.1	0.5-13.5 ±0.1	0.5-13.5 ±0.1	0.5-13.5 ±0.1
Frequency range (MHz)	1-100	1-100	1-100	1-100
Acoustic attenuation (dB/cm MHz)	0-20 ±0.01	-	0-20 ±0.01	0-20 ±0.01
Sound speed (m/s)	500-3000 ±0.1	-	500-3000 ±0.1	500-3000 ±0.1
Electroacoustic signal	±1%	±1%	-	-
Electric conductivity (S/m)	10 ⁻⁴ -10 ¹ ±1%	10 ⁻⁴ -10 ¹ ±1%	10 ⁻⁴ -10 ¹ ±1%	-
Measurement time (min)				
Particle size	1-10	-	1-10	1-10
Zeta potential – aqueous systems	0.5	0.5	-	-
Zeta potential – non-aqueous systems	0.5-5	0.5-5	-	-
Sample requirements				
Sample amount (ml)	20-110	2-100	20-70	20-100
Volume fraction % ¹	0.1-50	0.1-50	0.1-50	no restrictions
Electric conductivity	no restrictions	no restrictions	no restrictions	no restrictions
pH	0.5-13.5	0.5-13.5	0.5-13.5	0.5-13.5
temperature (°C)	< 50	< 50	< 50	< 50
Viscosity medium (cP)	Up to 20000	Up to 20000	Up to 20000	Up to 20000
Micro-viscosity medium (cP) ²	Up to 100	Up to 100	Up to 100	not restricted
Viscosity colloid (cP)	Up to 20000	Up to 20000	Up to 20000	Up to 20000
Particle size (µm) ³	0.005-1000	0.005-100	0.005-1000	not restricted
Zeta potential (mV)	no restrictions	no restrictions	no restrictions	no restrictions


Figure 3 DT-310 instrument from DISPERSION TECHNOLOGY for zeta potential studies of complex suspensions in original concentrations

- 1 Measurement device can measure systems with a higher content than 50 vol.-%, but the theory for the determination of PSD and zeta potential is strictly applicable up to 50 vol.-%. In some systems with a low density contrast it is the lowest volume fraction 1 %.
- 2 The decisive viscosity for particle size- and zeta potential-measurements is the one, at which the particle expires, when it moves into the acoustic field. This „micro-viscosity“ can be – for gelatinous or structured systems e. g. – much smaller than the value measured by means of a conventional rheometer. In this case, the sphere of influence exceeds clearly the dimension of the particle.
- 3 Particle size measurement range for the zeta potential can depend on the density contrast.

References

- [1] A. S. Dukhin and P. J. Goetz, *Characterization of liquids, dispersions, emulsions, and porous materials using ultrasound*, Elsevier, third edition, 2017



mixSorb L

Dynamic Sorption Analyzer

From the idea to the technology behind the separation process: mixSorb L is gearing up!

Dr. Christian Reichenbach, christian.reichenbach@3P-instruments.com

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 mixSorb L, 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

mixSorb L 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 mixSorb L

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 mixSorb L 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).

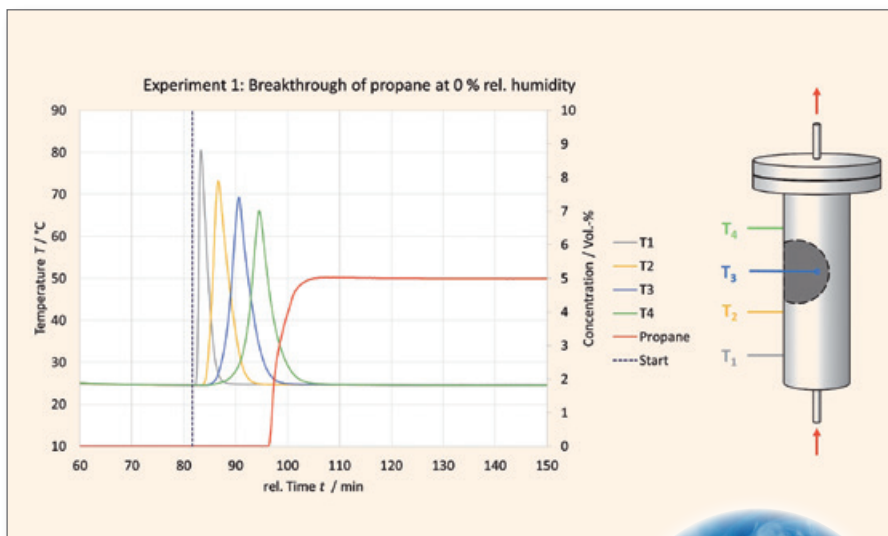


Figure 1 Breakthrough curve of 5 vol % propane in dry nitrogen carrier gas

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. 15 min, 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-

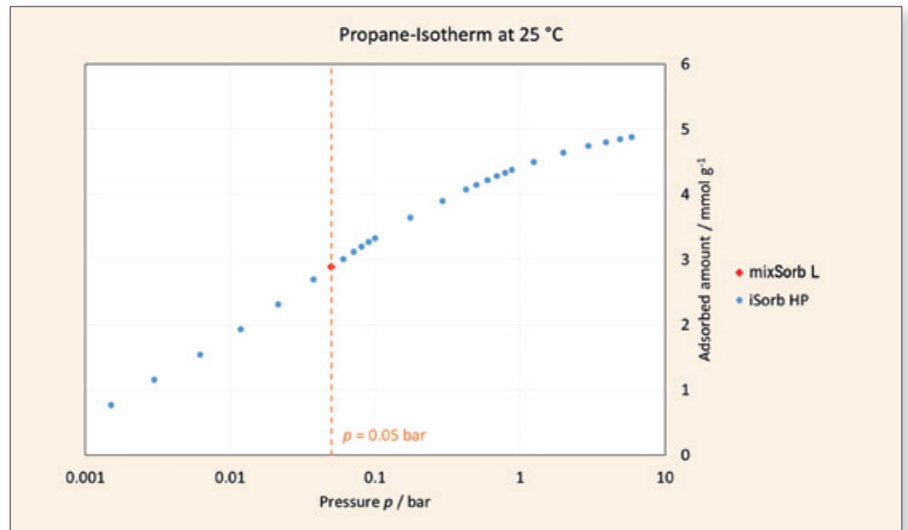


Figure 2 Comparison of load calculated by the integration of the breakthrough curve (experiment 1 with mixSorb L) with a propane isotherm determined with a volumetric method

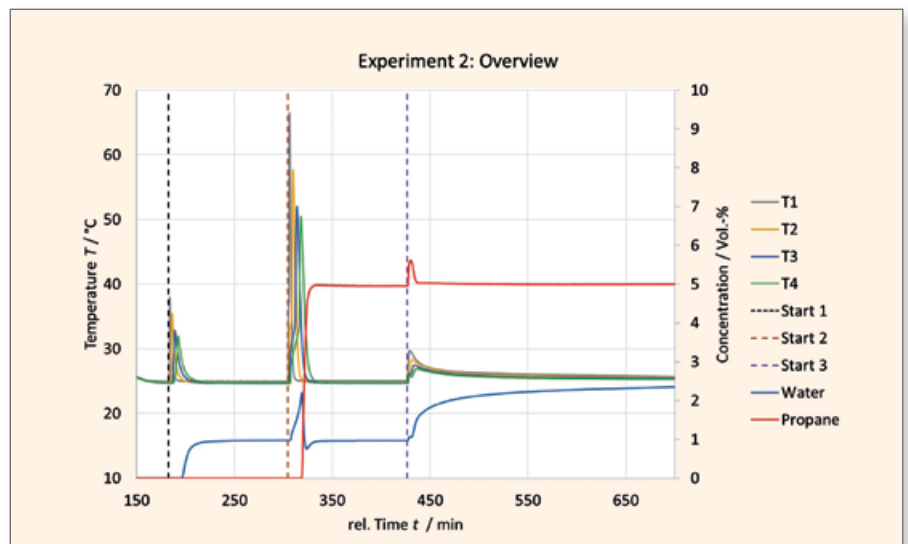


Figure 3 Temperature profile and concentration progression of water and propane of experiment 2 consisting of a sequence of three breakthrough curves. The dotted vertical lines indicate the start of the individual breakthrough measurements

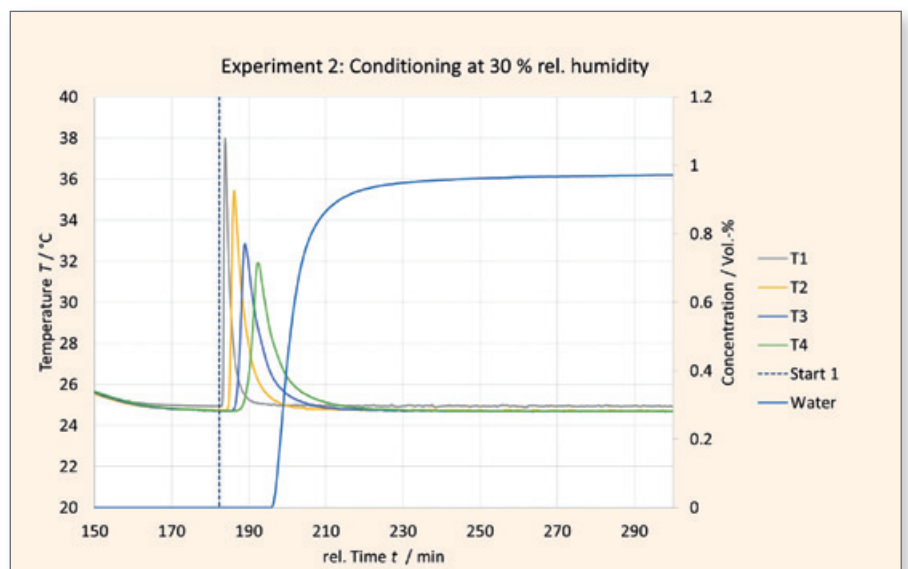


Figure 4 Detailed results of experiment 2 (temperature profile and concentration profile of water)

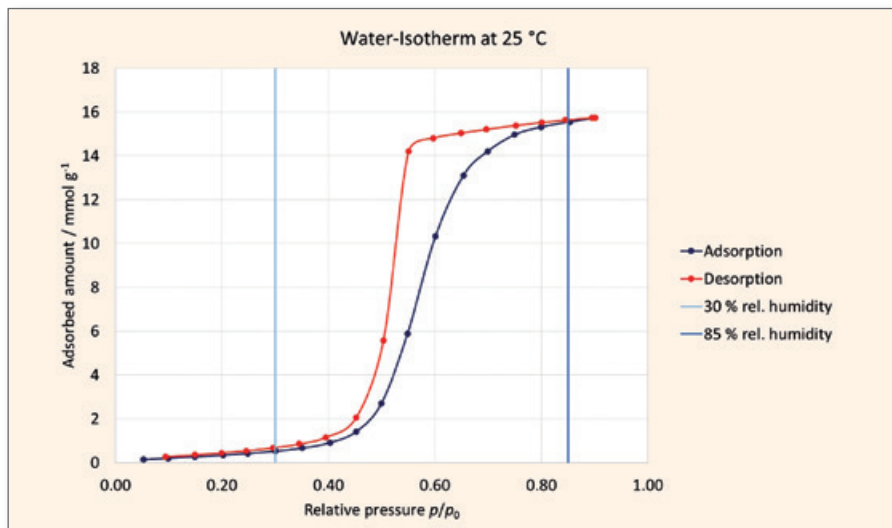


Figure 5 Water isotherms, the vertical lines identify those isotherm sections that correspond to a rel. humidity of 30 % resp. 85 %

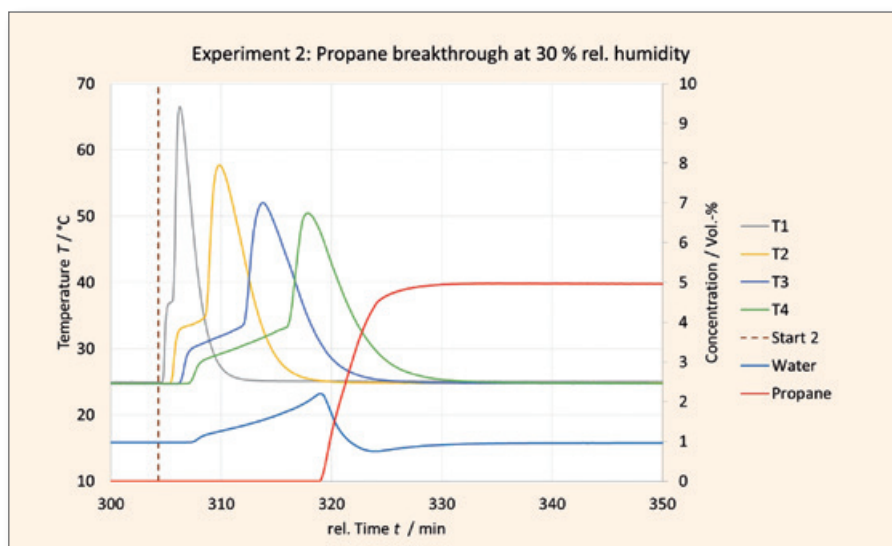


Figure 6 Details of experiment 2 (temperature profile and concentration profile of water and propane), adsorption of propane occurred while displacing previously adsorbed water

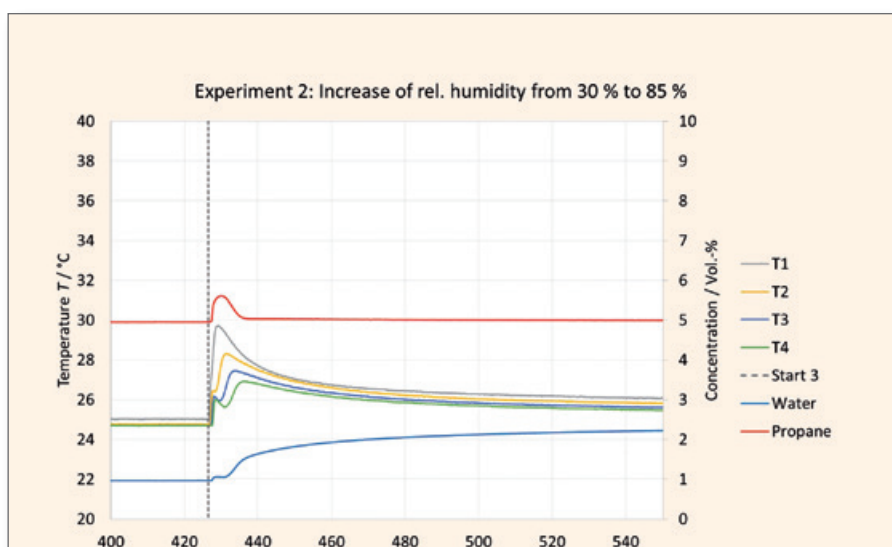


Figure 7 Details of experiment 2 (temperature and concentration profiles of water and propane), with the increase of rel. humidity from 30 % to 85 %, a sorption of water can be observed, previously adsorbed water is only slightly desorbed

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

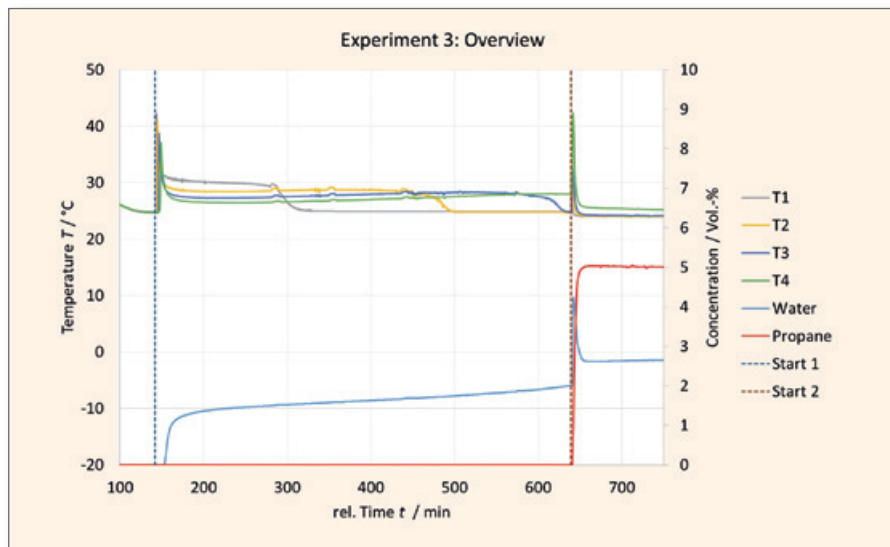


Figure 8 Temperature and concentration profiles of water and propane in experiment 3 consisting of one sequence of two breakthrough curves, the dotted vertical lines indicate the start of the individual breakthrough measurements

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. 1.5 vol% 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 mixSorb L

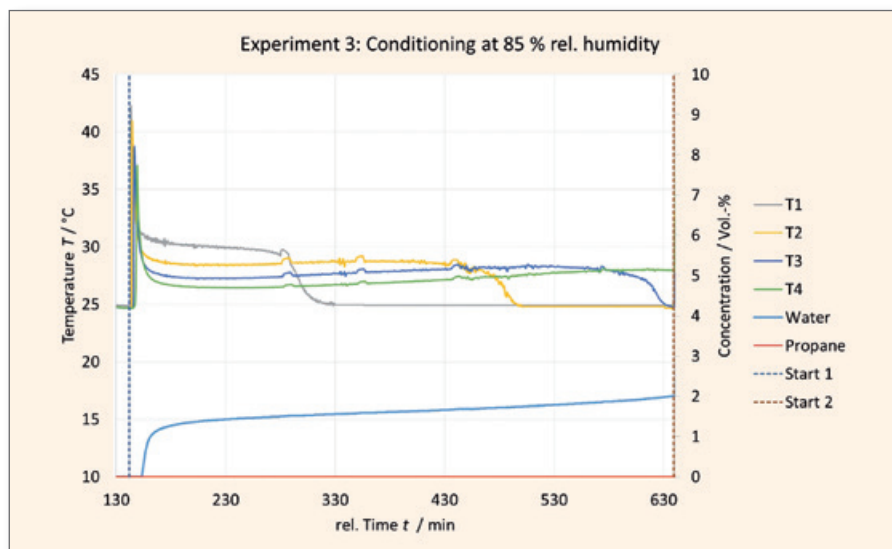


Figure 9 Details on experiment 3 (temperature and concentration profiles of water), after eight hours of conditioning at 85 % rel. humidity of the previously dried sample, the water breakthrough is still incomplete

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 - mixSorb L 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. mixSorb L 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 composition, temperature, pres-

sure, 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.

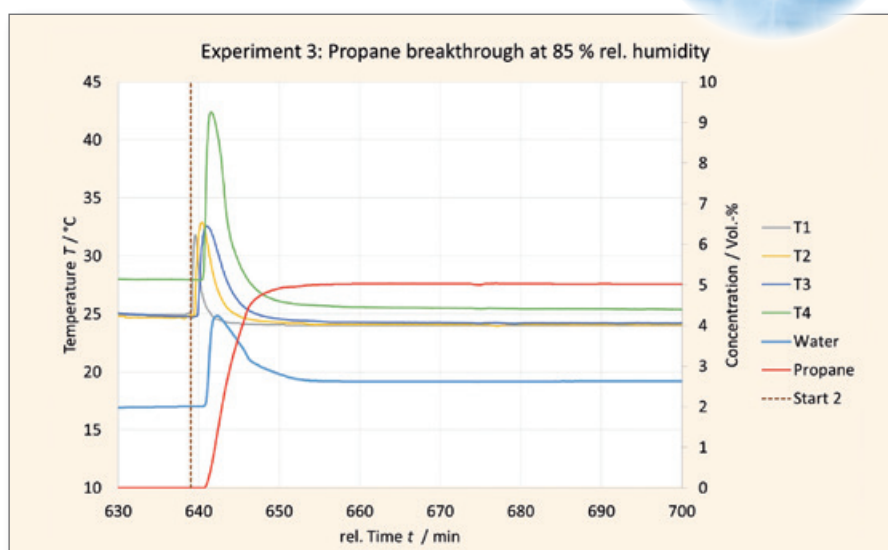
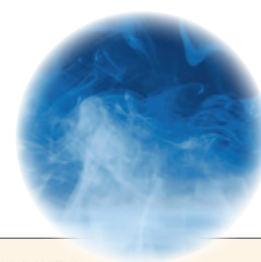
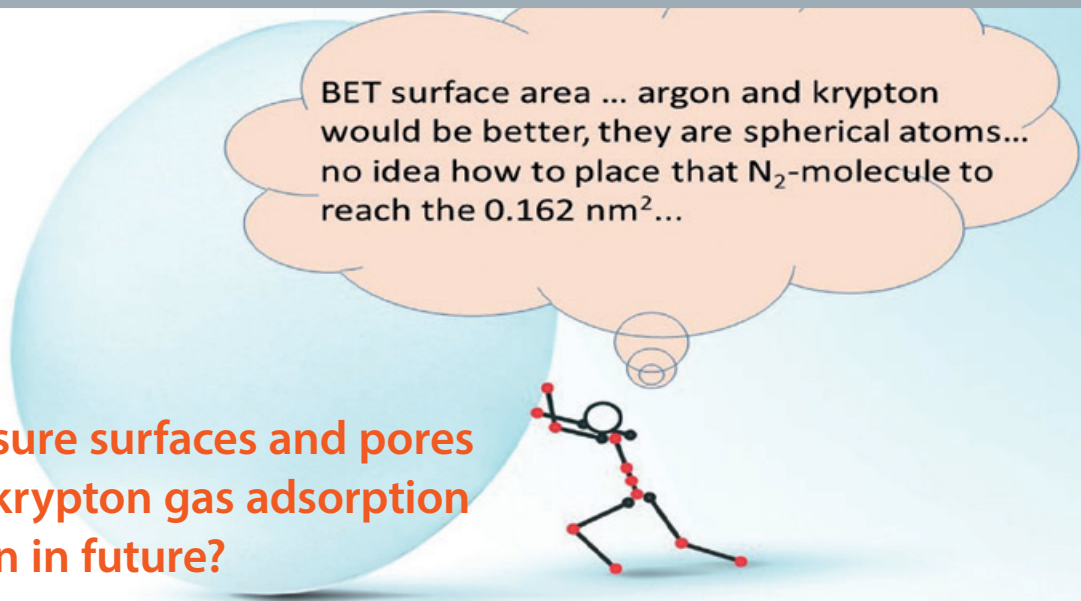


Figure 10 Details on experiment 3 (temperature and concentration profile of water and propane)



Why do we measure surfaces and pores with argon and krypton gas adsorption much more often in future?

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Introduction

The fundamentally reviewed IUPAC report »*Physisorption 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 of isotherm data. "New recommendations" that have been the basis of applying our measurement 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). We have identified this advantage more than 20 years ago and realized the 87 K temperature by use of liquid argon for a long time. Recently we connected our instruments with a so-called CryoSync option, which has been specified from the producer with 82 – 100 K temperature range originally, but has been changed up to 115 K in the meantime on the basis of our recommendation. Our further research shows, that we can also reach the 120 K and that is a very interesting temperature, the boiling point of the krypton noble gas. This article describes these additional research options with a critical discussion of the nitrogen results as traditional basis not only for pore but also for surface determination.

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).

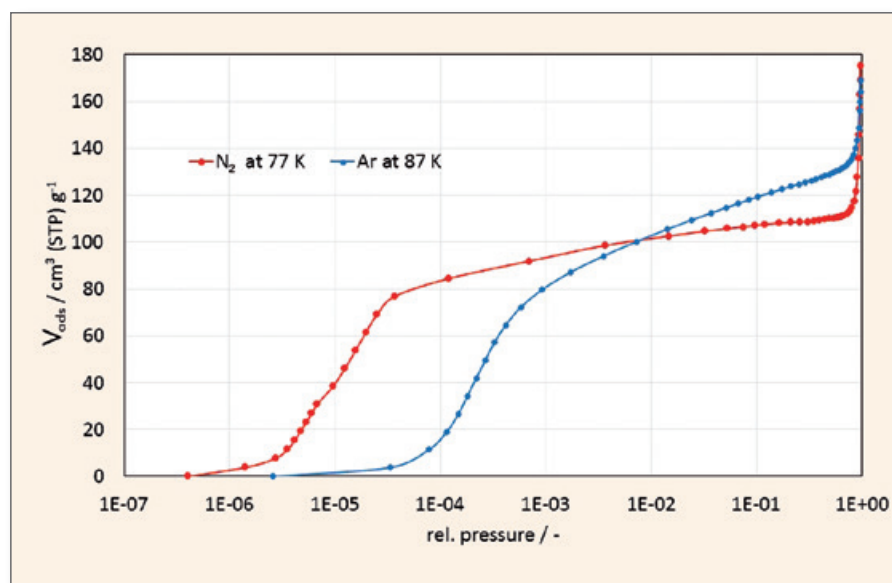


Figure 1 Ar-87 K and N₂-77 K isotherms in zeolite 13 X

The inventive idea was to make these advantages available to studies that have no liquid argon available. Because of the availability of technical solutions for liquid argon compensation, such ways of thermostates 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 was possible to realize for our studies.

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 gases 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 subcooled 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 [2,3,4]. 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 subcooled 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 [2]). In case of argon and krypton, calculation was based on the density of liquids subcooled 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 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

Table 1 Area occupation of N₂, Ar and Kr at 77 K (from [2])

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 [4])

Calculated with graphitized carbon black using p _o (subcooled liquid)	Calculated with oxides using p _o (liq.) (subcooled liquid)	Calculated with oxides using p _o (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

summarizes 3 different average area occupancies 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 studies clearly confirm the doubts expressed quite some time ago already [3]. 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.

Figure 2 Hg intrusion curves of macroporous alumina N5

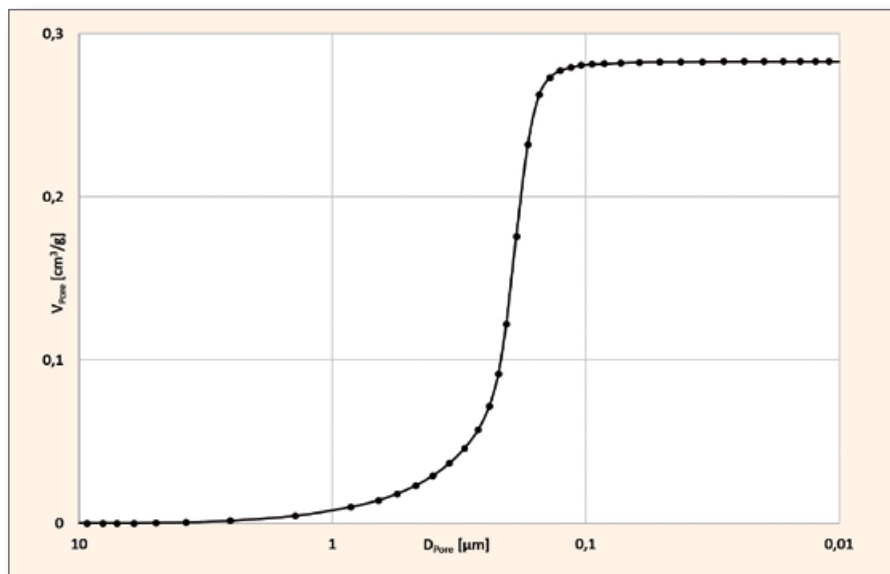


Table 3 Calculated BET surface area of alumina N5

Adsorptive	T [K]	Area occupation calculated from	Area occupation [nm²]	AS (BET) [m²/g]
N ₂	77	p _O (liquid)	0.162 nm²	5.42
Kr	77	adjusted to a _m (N ₂)	0.202 nm²	5.01
Ar	77	adjusted to a _m (N ₂) with p _O (liquid)	0.166 nm²	5.22
Ar	77	adjusted to a _m (N ₂) with p _O (solid)	0.180 nm²	5.24

Determination of the specific surface area of a macroporous alumina with selected adsorptives

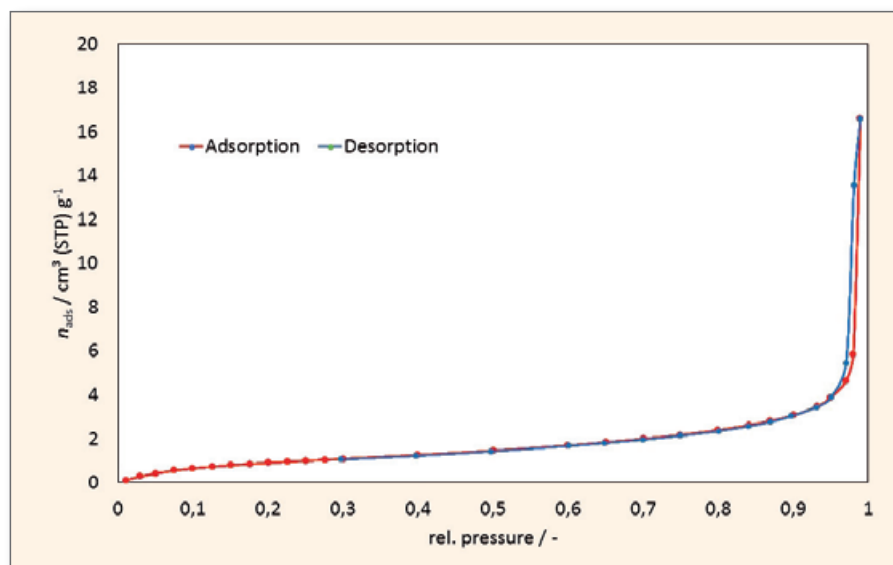
Using the example of macroporous alumina (N5), BET surface areas determined for different adsorptives and measurement temperatures are to be compared. The specimen is a granulate with a grain diameter between 1 and 2 mm. The BET surface area (N₂ at 77 K) is approx. 5 m²/g. The cumulative pore distribution determined with mercury intrusion is shown in Fig. 2 from which a total pore volume of about 0.28 cm³/g can be read. The pore size distribution reaches from approx. 0.1 to almost 10 µm. 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 multi-layer 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 alumina, 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 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 alumina 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 at their boiling temperatures (87 and 120 K). Thus, concerns resulting from the questionable nature of the adsorbate phase below the triple point temperature

Figure 3 Krypton sorption at 120 K in macroporous alumina N5**Table 4** BET surface areas of alumina N5 with area occupation of adsorbate molecules calculated from liquid densities

Adsorbative	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

can be removed. You have read correctly: with the temperature range of 82 – 120 K we can easily measure krypton isotherms at their boiling temperature of 120 K (see Fig. 3). Beside argon at 87 K, another noble gas turns out to be suitable for carrying out isotherm measurements at its boiling temperature, such a rare isotherm is shown in Fig. 3.

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 m²/g, the calculation with nitrogen produces a substantially higher value of more than 5 m²/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 evalua-

tion 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 alumina of 0.123 nm². This value nicely corresponds to the outcome of other studies [2] and suggest a reduction of the nitrogen area occupation to 0.13 nm².
2. The possibility of measuring krypton isotherms at 120 K opens innovative approaches for questioning considerably larger N₂ 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 adsorbative should produce the same specific surface area even with different measuring temperatures. Such options as the CryoSync now offers a quite simple

approach for measuring an entire isotherm family and interpreting the results for BET surface area, adsorbate density and area occupation between 87 K (p₀ of krypton approx. 12 Torr) and 120 K (p₀ of krypton approx. 760 Torr).

4. Our LabSPA (Lab for Scientific Particle Analysis) has such options available 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 adsorbative molecule without permanent electrical dipole or quadrupole moment [5]. Some of our further measurement programs will evaluate which deviations occur between the nitrogen to the argon and krypton BET-results in various organometallic (MOFs) and other meso and microporous pore structures.

We gladly keep you updated on further adsorbative application results. If you are interested in such temperature option as the CryoSync, please contact us directly. Such option is to use not only to use with the adsorption instruments of 3P INSTRUMENTS but with other gas adsorption instruments too, and we can help to find the right procedure.

The topic of the use of different adsorptives will be in the focus of our 3P European workshop 2019, which will be held in English on May 15, 2019, in the nice city Leipzig/Germany – in combination with the Symposium on Dynamic Sorption Methods at the same place on May 14, 2019. Please contact us for more information or use the link to www.dynamicsorption.com for further information and the form to register you early enough.

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- [2] F. Rouquerol, J. Rouquerol, K. Sing, *Adsorption by powders & porous solids*, p. 171 ff.
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The source to find experiences on dynamic sorption methods

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Welcome to www.dynamicsorption.com, this site collects and summarizes all the features, advantages, examples and knowledge of dynamic sorption (or flow sorption) methods. Feel free to browse through the pages about breakthrough curves, mixture adsorption and the commercial breakthrough analyzers of the mixSorb series, and our specialist literature for download under [Resources](#).

The dynamic sorption method is a unique technique to investigate a lot of valuable properties of adsorbent materials. From a practical point of view not only pure component isotherms should be known, also cycle stability, long time stability, competitive adsorption, and the kinetics are important properties for the choice of an optimal adsorbent. These properties are often difficult to access with static methods and in some cases the results cannot easily transferred to an industrial scale. Especially kinetic data from static experiments suffer from poor transmissibility to industrial separation processes, because of different macroscopic conditions (i.e. pressure, presence of other components).

Why is the determination of sorption characteristic with dynamic methods so important?

- Most industrial separation processes by adsorption work under dynamic conditions.
- Different kinetics of guest molecules can be play a key-role during separation.
- In industrial separation and purification tasks always gas mixtures are present.
- In most cases, the adsorbent is arranged as a fixed bed and a gas mixture is forced through it.

Based on this points it can be figured out, that the knowledge of selectivity, kinetics and the dynamic of heat generation and -release is very important for choice of an adsorbent and for process design.

In industrial gas separation or gas cleaning processes often the product requirements of the effluent gas is given in form of a required purity. Due to the interplay of macroscopic conditions like gas velocity, concentration of impurities or feed temperature and physical properties like co-adsorption, kinetics, and heat effects, an estimation of the usable sorption capacity based on pure component isotherms is not always possible. Usually, this sorption capacity is much lower than the equilibrium loading of the pure components. In such cases the determination of breakthrough curves under downscaled process conditions gives a valuable insight into the performance of the adsorbents. Considering these points, the dynamic sorption method is further beneficial for:

- Downscaling of industrial processes
- Investigation of adsorbents under relevant gas velocities
- Investigation of cycle stability of materials
- Determination of optimal regeneration conditions.

With our team of experts, we can offer you a large variety of analyses in the field of dynamic sorption. Together with our world-wide partners we will discuss your application with you.

- Breakthrough Curves with Gas and Vapor Mixtures
- Mixture Isotherm of Gases and Vapors
- Measurement of more complex Sequences of various Adsorption and Desorption Steps
- Cycle Stability Testing
- Emulation of a Pressure Swing Adsorption process.

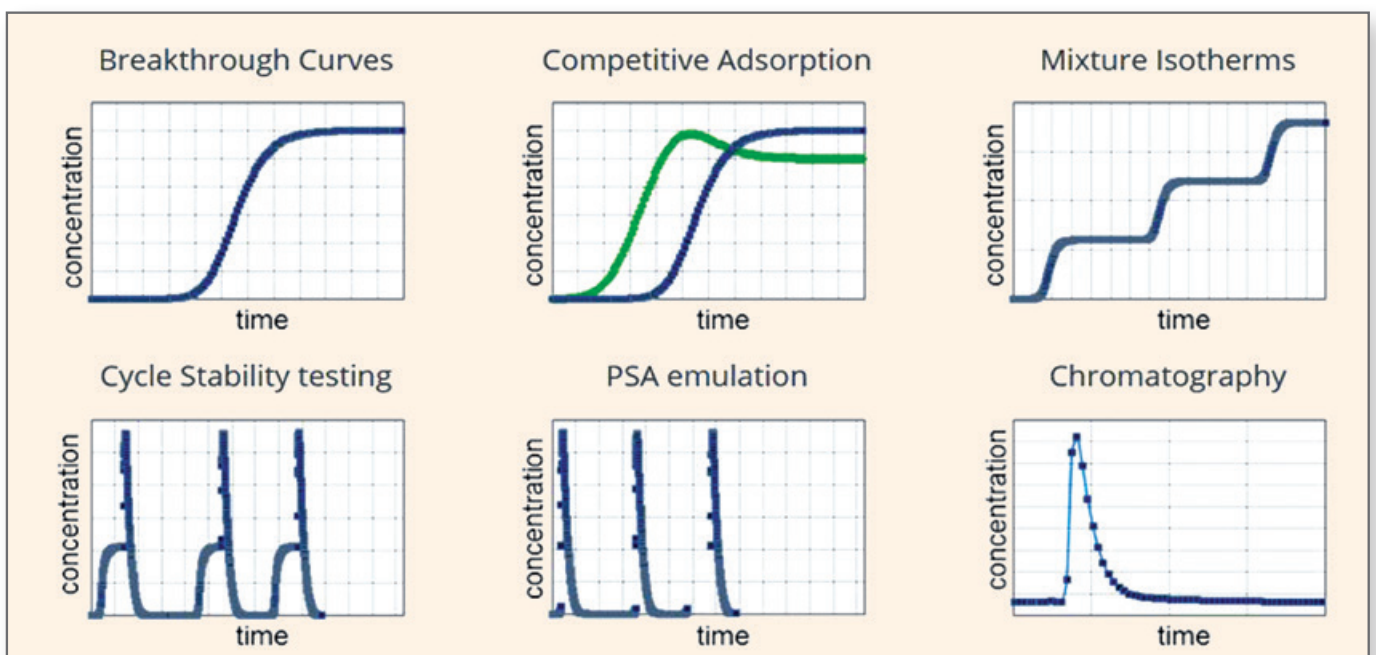


Figure 1 The mixSorb instrument series allows investigations in the six fields of investigations



Figure 2 The mixSorb L instrument offers flexible adsorber volumes, standard adsorber with 130 ml (left) and small adsorber with 5 ml volume (right), the mixSorb S is optimized for MOFs and similar materials, its adsorber cell is for samples below 1 ml bulk volume

The following gases and vapors are our standard testing gases/liquids, others are available on request.

- CO₂, CH₄, N₂, He, O₂, C₃H₈, NH₃
- H₂O, Toluene, 2-Propanol, Cyclohexane, 1,4-Dioxane

Contract analysis, method development and project work are an excellent possibility for many companies and institutes to profit from our services. Our scientific approach and good laboratory experience provide high quality analysis services. We are equally ready to discuss with you urgent analyses with short process times as well as rentals of analyzers, training of your staff, comparison measurements towards your analyses or project work. Additionally, dynamic simulations can be carried out and compared to your measurements in order to gain information about mass transfer properties. Our 1-dimensional model allows the determination of time constants with the "Linear Driving Force" approach. Beside the dynamic sorption experiments we can also provide the measurement of pure component isotherms, pore size analysis, the determination of density and specific surface area.

Scientific Support

We are ready to discuss your scientific questions with you.

- You want perform a separation process in presence of humidity and have only pure component data?
- You don't know the optimal regeneration conditions for your material?
- You want to get an idea about the cycle stability of your new adsorbent?
- How does the particle size influence the kinetics of your separation process?

You can download the most recent scientific presentation publications of our experts from <http://www.dynamicsorption.com/resources/> and the titles are:

- Flexible MOFs for Gas Separation – A Case Study Based on Static and Dynamic Sorption Experiments, R. Eschrich, May 2018
- Investigation of Mixed Gas Sorption in Lab-Scale, A. Möller, April 2018
- Adsorption of Polar and Nonpolar Vapors on Selected Adsorbents: Breakthrough Curves and their Simulation, R. Eschrich, April 2018
- Investigation of EtOH/Water Vapor Mixtures on Adsorbents with Different Surface and textural Properties, A. Möller et. al., March 2018

Summary and conclusions

1. A reliable statement of the useable sorption capacity under process relevant conditions is only possible by breakthrough experiments.
2. A breakthrough curve reflects the concentration profile in the adsorber column and is therefore useful for a realistic estimation of the performance of an adsorbent.
3. Mixture adsorption equilibria are easily accessible by the dynamic method. An automatic measurement of a mixture gas adsorption isotherm with variable partial pressures and a constant total pressure is possible. For high diluted mixtures the dynamic method would be the best choice.
4. The shape of breakthrough curves are mainly influenced by the mass transfer of adsorptive molecules into the adsorbent particles. Based on well-established models this relationship can be used for the determination of transport properties for the system under investigation.
5. Due to the possibility of automatization, dynamic sorption methods are one of the most time-saving methods for the determination of mixed gas adsorption equilibria.

Please contact us for further information, see our invitations on the next page, welcome to Leipzig in 2019!

We welcome you in Leipzig for two gas sorption events in 2019 !



Leipzig Symposium on Dynamic Sorption Methods: Advanced Sorbent Materials on the Way to Application, May 14, 2019

After great success with the Leipzig Symposium on Dynamic Sorption Methods in 2017 and 2018, we continue the collaboration and sponsoring of that event and its organizing Institute of Nonclassical Chemistry in Leipzig.

Characterization of Selectivities and Kinetics of Novel Materials is the focus of the Symposium 2019. The symposium will be held in English and will provide an overview of dynamic sorption processes with MOFs and other novel materials corresponding to the methodology of modern experimental technologies given by experts in the field. Well-known lecturers will introduce the current view on this topic from a material viewpoint to the state-of-the-art technology. To intensify the discussions, posters will be presented and discussed in a separate session.

Deadline for sending Symposium poster contributions:

31.03.2019

Please send the title of your poster and a short abstract to:

info@inc.uni-leipzig.de

The three best posters will be awarded again, please read more from the first circular at

<http://www.dynamicsorption.com/symposium/>

Leipzig Workshop on New Developments in Characterization of Surfaces and Pores by Sorption Methods, May 15, 2019

In combination with the Symposium on Dynamic Sorption Methods in 2017 and 2018, we invite to the Workshop on New Developments in Characterization of Surface and Pores. The tradition from the last two years is to hold that workshop at the same place in Leipzig, that combination makes it perfect to participate both adsorption events.

The historical city Leipzig Southern from Berlin is good to reach from all cardinal points, with the airport, intercity train station and the motorway junction nearby. Between the scientific lectures you should use some time to visit the historical center, which is only few minutes on foot: The market place with the impressive Old Town Hall, medieval St. Thomas's Church, where composer Johann Sebastian Bach worked, the oldest coffeehouse in Germany - the "Coffebaum" - from 1711, St. Nicholas's Church, where the peaceful political changes of 1989 started, and the unique passage and courtyard system including the legendary traditional restaurant "Auerbachs Keller".

Deadline for sending Workshop poster contributions:

31.03.2019

Please send the title of your poster and a short abstract to:

info@3P-instruments.com

The three best posters will be awarded, please read more from the first circular at www.3P-instruments.com



3P INSTRUMENTS – reliable service for CILAS and QUANTACHROME instruments in the past and in the future

High Quality of products and processes assured via Quality control systems as ISO 9000 needs regular checks of measurements and testing devices. We offer professional service not only for the state-of-the-art instruments but also for older CILAS and QUANTACHROME instruments as NOVA or AUTOSORB, QUADRASORB or ULTRAPYC, CILAS 920 or newer CILAS 1090, DT-1202 or TURBISCAN and many other instruments as you can find at our homepage www.3p-instruments.com. Our regular Maintenance and Calibrating service is based on the following conditions:

- 1) Maintenance is done once or twice a year by one of our experienced service engineers.
- 2) Maintenance includes a thorough control of your device's properties necessary for exact and precise measurements and controlled handling.
- 3) We offer you three types of maintenance contracts, ranging from the check of your measurement device once a year to a maintenance including the spare parts twice a year.
- 4) In appointing a time for the maintenance we will consider your suggestions as far as possible.

Maintenance contract types from 3P INSTRUMENTS for former CILAS and QUANTACHROME instruments:

Type E (Eco)

- Maintenance once a year executed by an experienced 3P INSTRUMENTS technician
- General check, adjustment and cleaning of the system incl. minor repair works
- Software maintenance
- Test-measurements with standard materials
- Certification of Maintenance incl. documentation of the measurement results

Spare parts for repair as well as driving- and travelling-costs are charged separately.

Type S (Standard)

- Maintenance once a year executed by an experienced 3P INSTRUMENTS technician
- General check, adjustment and cleaning of the system incl. all repair works
- Software maintenance and software-updates
- Test-measurements with standard materials
- Certification of Maintenance incl. documentation of the measurement results
- 10 % discount on spare parts and possible further necessary service visits

Spare parts for repair as well as driving- and travelling-costs are charged separately.

Type O (Opti)

- Maintenance twice a year executed by an experienced 3P INSTRUMENTS technician
- General check, adjustment and cleaning of the system incl. all repair works
- Software maintenance and software-updates
- Test-measurements with standard materials
- Certification of Maintenance incl. documentation of the measurement results
- 10 % discount on spare parts and possible further necessary service visits
- All spare parts needed for the maintenance works are included in the price for the maintenance.

Spare parts for repair as well as driving- and travelling-costs are charged separately.

Maintenance work will be done during regular working time at the time scheduled by the 3P INSTRUMENTS Service Department and the instrument user in advance.

Maintenance schedule for a CILAS Granulometer as example:

- Exchange of all silicone tubes within the measurement circuit
- Exchange of all drive- and sealing-rings
- Exchange of the blower filter
- Cleaning and lubrication of the stirrer bearing
- Check of the flexible tube pump-bearing and –drive
- Cleaning and check of the whole optical systems incl. the laser
- Check of the printed circuit boards
- Control of the electrical junctions and plug-in connectors
- Check and adjustment of the operating voltage
- Check and adjustment of the stirrer- and pump-speed
- Check of the software and software-update if necessary
- Measurement with standard samples (calibration)
- Issue of the examination-certificate
- Examination badge

There are some ways to reach us: [+49 8134 9324 0](tel:+49813493240) or info@3p-instruments.com or service@3p-instruments.com, don't hesitate to contact us for the most experienced service of former CILAS and QUANTACHROME instruments.



3P INSTRUMENTS as specialist in the field of adsorption

The specific surface area, pore size distribution and pore volume are important parameters for characterizing the surface properties of microporous and mesoporous materials. As 3P INSTRUMENTS will continue to offer solutions in the field of surface area and pore size analysis, this article gives a short overview. Different analytical instruments are available from 3P INSTRUMENTS and we call them according to the main applications:

- 3P surface** for BET surface area measurements
- 3P meso** for mesopore isotherms, micropore volume and BET surface area
- 3P micro** for micro- and mesopore isotherms, pore volumes and BET surface area

3P INSTRUMENTS offers a fully automated dynamic single- and multi-point sorption analyzer. 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 are such as quality control or where the static volumetric method does not supply valid analysis data for a variety of reasons. Pharmaceutical products, raw materials for food or metal hydroxides and materials with crystal water inclusions are examples for the latter. The new **3P surface** (Figure 1 and 2) can handle up to four samples and combines the advantages of the dynamic method with a high degree of automatization as found in the volumetric method.

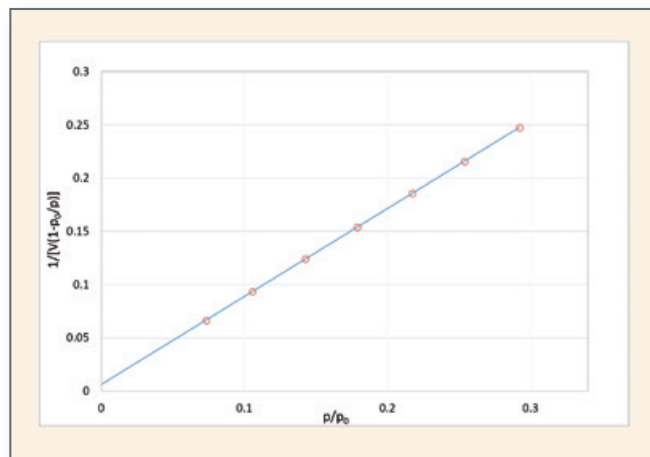


Figure 2 3P surface – a typical BET plot of an alumina sample



Figure 1 3P surface - four port automated flow BET analyzer

The most commonly used and most reliable method for measuring isotherms is the static volumetric method of gas adsorption. The **3P meso** series (Figure 3 and 4) follows the principle of independent analysis ports for determination of meso and macropores from 2 up to more than 100 nm. One, two and four port systems are available to meet optimal client demands. Designed for the field of quality assurance and/or production control, these analyzers provide an independent dosing manifold equipped with 1000 Torr transducers for each measurement port. Each of the measurement stations include the capability to degas the sample in-situ (up to 400 °C), this principle avoids sample contamination during sample transfer from separate degassers to the analysis port without making any further precautions. However, for materials where this effect are insignificant, external degassers are available as well.



Figure 5 3P micro 300 - three port surface area, mesopore and micropore analyzer



Figure 3 3P meso 400 - four port surface area and mesopore analyzer

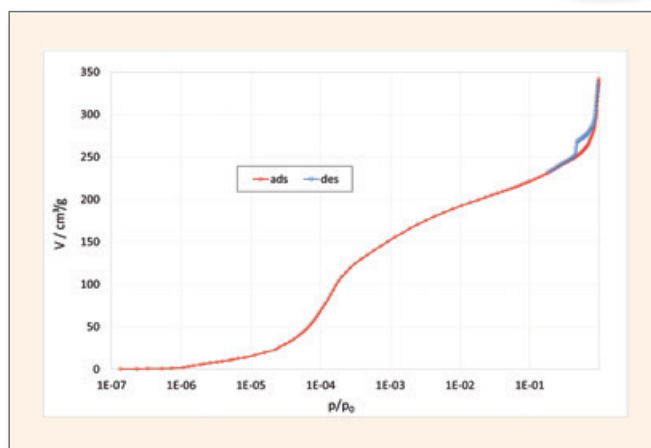


Figure 6 3P micro - a typical micropore isotherm of a micro- and mesoporous zeolite ZSM-5

To complete the set of adsorption analyzers, the **3P micro** series (Figure 5 and 6) offers high performance physical adsorption of microporous materials, such like activated carbon, zeolites, MOFs and similar materials. According to the different needs of sample throughput and analysis conditions, the instruments can be equipped with one, two or three completely independent analysis ports. Each port is equipped with an independent manifold, containing a set of 1000, 10 and 1 (or 0.1) Torr transducers, an independent p_0 transducer and a separate dewar or other coolant device. Imagine to carry out a parallel analysis of nitrogen, argon and carbon dioxide of the same material without any time loss! Or imagine to carry out an experiment of H_2 adsorption at three different temperatures at the same time, e.g. to calculate heats of adsorption values on a promising gas storage material. These are just some examples of the superior instrument design. As each analysis port acts completely independent, there is zero time loss, independent if one, two or three analyses are started at the same time or if another measurement is started while others are already running. In-situ degassing is possible as well by default to avoid sample contamination.

In case you want to test or compare **3P INSTRUMENT** performance with your own materials, our application team will be very pleased to assist you. Please don't hesitate to contact us at info@3P-instruments.com.

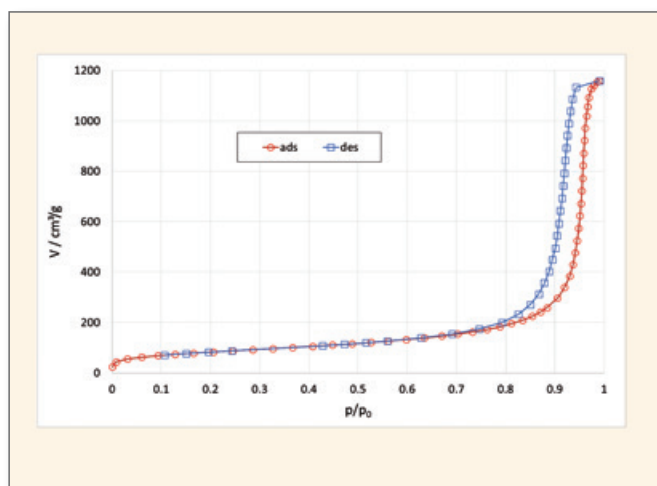


Figure 4 3P meso - a typical mesopore analysis of a porous glass sample

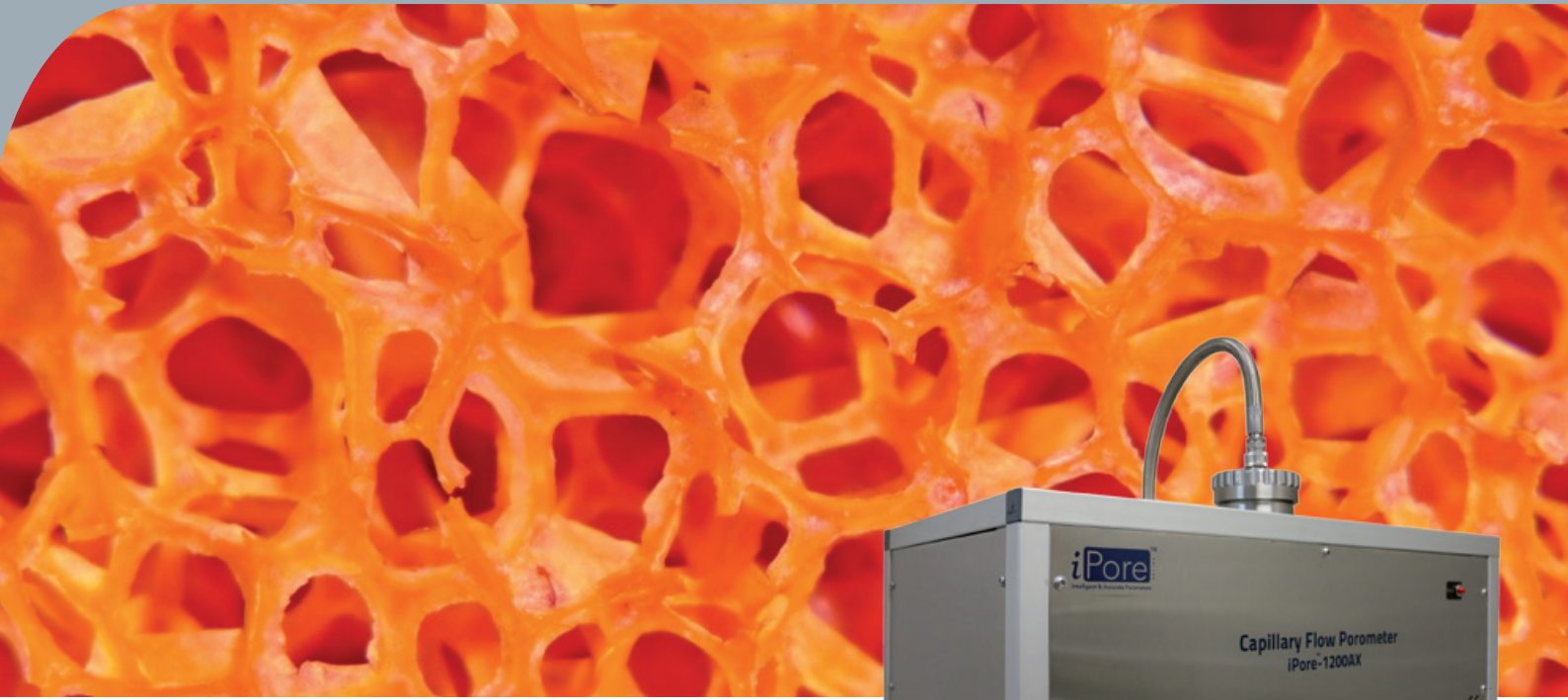


Figure 2 Universal capillary flow porometer iPore-1200AX, Porous Materials Incorporated (PMI)

Now Available: Liquid-Liquid-Porometry for materials with very small through-pores

Dr. Carsten Blum, carsten.blum@3P-instruments.com

The standard capillary flow porometry is well known and very useful to characterize the pore structure of materials such as membranes, filter media, ceramics, paper, textile and similar materials. A non-toxic liquid is allowed to spontaneously fill the pores in the sample and a non-reacting gas is allowed to displace the liquid from pores by increasing the gas pressure. First the larger pores will get emptied, as the pressure increases more and more smaller pores are progressively emptied. The pressure and flow rate of gas through the emptied pores provides the through pore distribution and the first detectable flow pressure defines the so called bubble point, which is related to the maximum pore size in a sample (Figure 1).

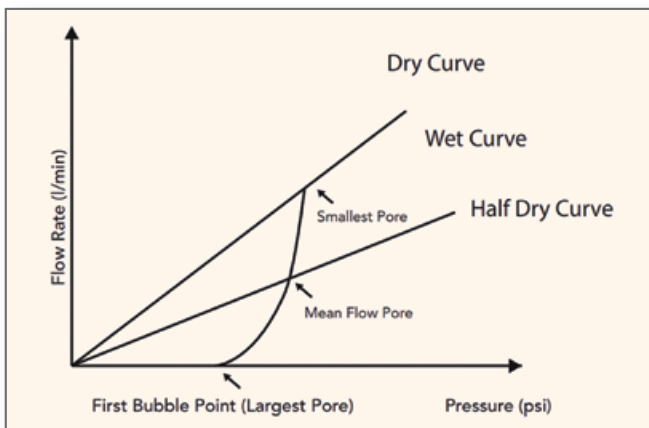


Figure 1 Parameters measured in capillary flow porometry



Figure 3 Liquid-Liquid Porometer of type LLP – 1100A, Porous Materials Incorporated (PMI)

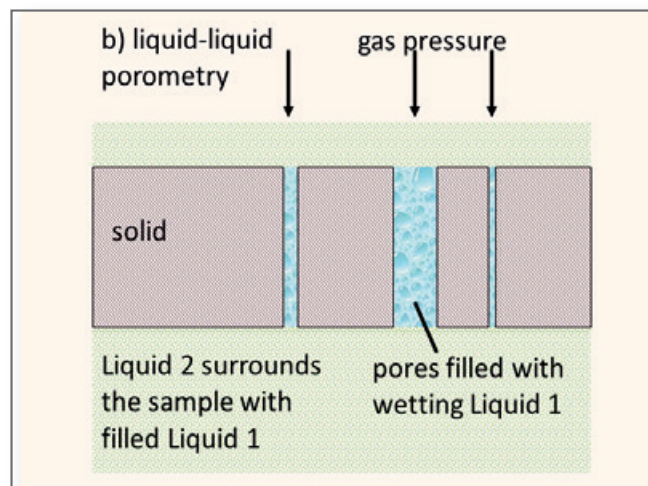
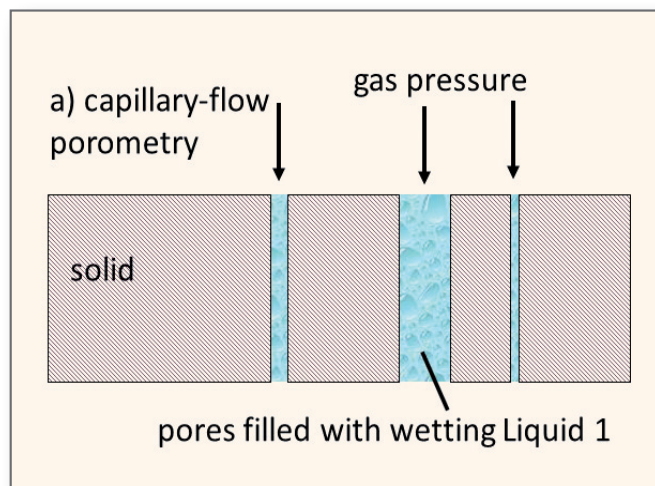


Figure 4a/4b Measuring principle of the conventional capillary flow porometry (a) in comparison to Liquid-Liquid Porometry method (b)

However for many materials having very small pores (< 20 nm) or for materials which doesn't withstand relatively high pressures, liquid-liquid porometry (LLP) might be the better choice. It is a valuable technique for measuring the pore structure characteristics of ultrafiltration membranes. Such membranes can act as barriers to particles, including bacteria, pollens, spores, or pesticides. Further LLP is capable of measuring pore diameters, pore size distribution and liquid flow rates of materials having very low permeability. Typical examples are reverse osmosis membranes, nanofiltration membranes, blood purification membranes or battery separators. Very low liquid permeability is measured fully automated for pore diameters down to 3 nanometers and the needed pressures are much less than those for capillary flow porometer. A typical benchtop capillary flow porometer is shown in Figure 2, Figure 3 shows the Liquid-Liquid-Porometer LLP-1100A, both from Porous Materials Inc. (PMI).

However for many materials having very small pores (< 20 nm) or for materials which doesn't withstand relatively high pressures, liquid-liquid porometry (LLP) might be the better choice. Further LLP is capable of measuring pore diameters, pore size distribution and liquid flow rates of materials having very low permeability. Typical examples are reverse osmosis membranes, nanofiltration membranes, blood purification membranes or battery separators. Very low liquid permeability is measured fully automated for pore diameters down to 3 nm and the needed pressures are much less than those for capillary flow porometer. A typical capillary flow porometer is shown in Figure 2, Figure 3 shows the Liquid-Liquid-Porometer.

Measurement Principle

A wetting liquid spontaneously fills the pores of the material. Figure 4 shows the main difference between the conventional capillary flow porometry (Fig. 4 a) and the liquid-liquid porometry (Fig. 4b). In case of LLP, two immiscible wetting liquids are selected. Liquid 1 with lower surface tension is used to fill the pores of the sample. Liquid 2 is surrounding the sample and Liquid 1 and is pressurized to displace the Liquid 1 from the pores and flow through the empty pores. The flow rate of Liquid 2 is also measured without wetting the sample with Liquid 1. The pore diameter is related to the surface

tension of the two liquids. The flow rates yield pore distribution and liquid permeability (Figure 4). The working Equation for the LLP-method is

$$D = 4 \gamma_1 \cos \theta_1 / p$$

with pore diameter D , interfacial surface tension of liquids γ_1 , cosine of contact angle of liquid 1 on pore surface $\cos \theta_1$, and the differential pressure p applied on the sample by liquid 2.

A good choice for the Liquid-Liquid porometers from PMI is to take the immiscible and saturated wetting liquids such as silwick and alcohol. The pores of the material are filled with silwick as Liquid 1, and alcohol as Liquid 2 is pressurized to displace the silwick and flow through the pores. The amount of liquid flowing out is measured in balance. Alcohol flow rate and differential pressure are measured. Because surface tension of silwick and alcohol are low, contact angles are taken as zero. Mean flow pore diameter and pore distribution are computed like standard capillary flow techniques.

The main advantage of the elegant technique Liquid-Liquid Porometry (LLP) is as follows: capillary flow porometry can provide pore size information by use of high test pressures not suited for measuring ultrafiltration membranes. Liquid-Liquid Porometry (LLP) by comparison can measure the required pore structure characteristics without distorting the pore structure or damaging the membranes. The pressures for LLP are about 10 times lower as with conventional gas-liquid porometry, means, if the study of some pore structure requests 20 bar pressure in case of gas-liquid porometry, only about 2 bar are necessary to characterize the same pores by use of LLP. This point is combined with another main advantage, lower pore sizes up to about 3 nm can be characterized by LLP method.

Don't hesitate to contact info@3P-instruments.com in case of interest, we have both the capillary flow porometry and the Liquid-Liquid porometry for your samples available.

Establishing LabSPA as laboratory service provider for the characterization of particles, powders and pores

With the pore laboratory renovation just finished in Odelzhausen and the current extension of our shared laboratory in Düsseldorf, 3P INSTRUMENTS 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 3P INSTRUMENTS 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 3P INSTRUMENTS are always carried out in our LabSPA (Lab for Scientific Particle Analysis). Complex characterizations of particles, 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 3P INSTRUMENTS. You receive a comprehensive test report within a short processing time. The measurement results provided by 3P INSTRUMENTS 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.

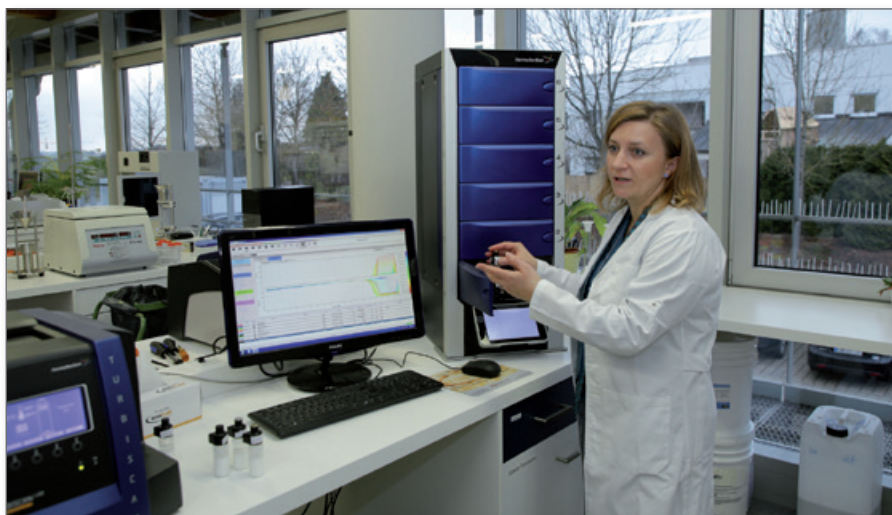


Figure 1 Our dispersion laboratory: Ms. Eikelmann explaining stability tests of original emulsions in TURBISCAN TOWER

Our specialists

3P INSTRUMENTS's specialists do what they are best at: sharing their expertise with you. 3P INSTRUMENTS 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 3P INSTRUMENTS's profound expertise. An increasing number of customers recognizes the difference between 3P INSTRUMENTS

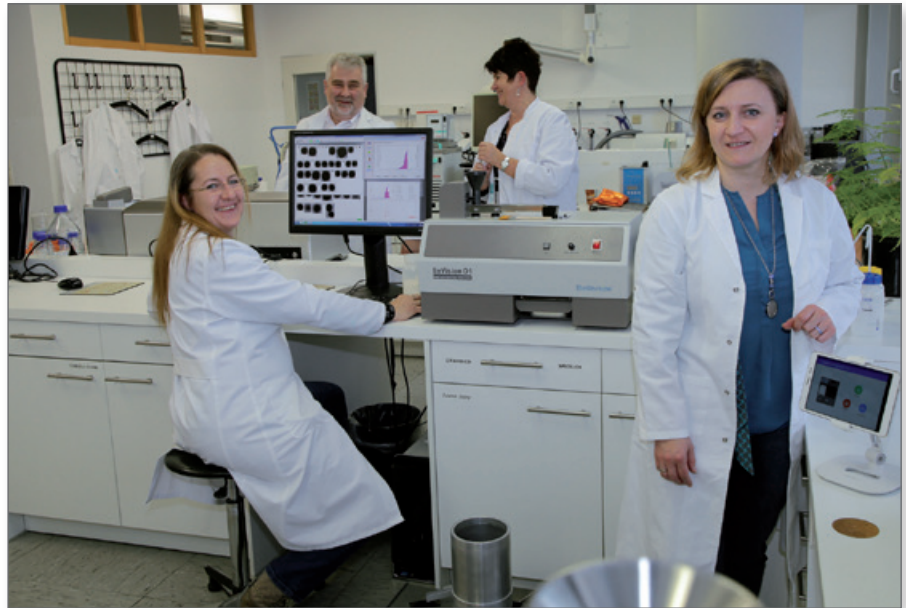


Figure 3 Our dispersion laboratory employees: B. Deponte, Dr. M. Ferner and K. Eikelmann (from left to right); When the general manager is in the lab, there is always a reason for a smile...

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.3P-instruments.com under "Contract Analysis", and the corresponding measuring methods are found at "Measurement methods".



Characterization of particles

- 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 pores

- 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



Characterization of
particles • powders • pores



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