

PARTICLE WORLD

Technical Papers
of 3P Instruments

EDITION 22

SEPTEMBER 2021

Studies on **particle size analysis**
of pharmaceuticals

Single and multi-component isotherms
with **dynamic methods**

Two premieres:

- The new **Bettersize BeNano** nanoparticle analyzers
- The **3P graviSorb** for water vapor adsorption analysis



3P graviSorb



Bettersize BeNano

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Imprint

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Dear Readers,

I am pleased to present our latest developments in Particle World 22 – as always, from the field of characterization of powders, particles and pores. In this issue, you will not only find articles on the practical application of analytical methods and corresponding measurement technology, but also on theoretical findings. In this context, I would like to refer to the article on adsorption studies with CO₂ and the fact (apparently still unknown to many users of gas sorption instruments) that it is not possible to characterize micropores smaller than 0.5 nm with nitrogen at 77 K! Appropriate solutions for the investigation of the entire micropore range can be found from page 17. The CO₂ sorption described here allows estimations for climate relevant CO₂ studies of adsorbents like MOFs, COFs, activated carbons, zeolites or other molecular sieves. In addition, we present news using the dynamic sorption analyzers mixSorb S and mixSorb SHP: it is now possible to record both single component isotherms up to a pressure of 8 bar (mixSorb S) / 50 bar (mixSorb SHP) and multi-component isotherms using one instrument!

New developments at 3P Instruments include also the characterization of powders and dispersions. The according articles illustrate why the Bettersizer and other 3P analyzers are becoming more and more widespread. The article "Particle characterization of active pharmaceutical ingredients and the proper dispersion of organic substances" shows that the coaxial Venturi structure of the Bettersizer 2600 is ideal for the characterization of fragile, organic substances. The article "Use of acoustic methods and current flow measurement in battery research" uses DT measurement technology to illustrate how practical the solution of industrial tasks can be for our equipment users, but also in the context of contract measurements in our application laboratory.

Furthermore, 3P Instruments is proud to present new analytical instruments. These include the BeNano series for the determination of particle size distribution, zeta potential and molecular weight of nanodispersions and the 3P graviSorb for the simultaneous recording of 11 water vapor sorption isotherms for research and quality control. Both measurement systems are implemented in our LabSPA (Lab for Scientific Particle Analysis) for test and contract measurements and thus enable additional solution options for complex tasks. In addition to the available analysis methods in the LabSPA, its internationalization is based above all on the direct customer contact of our highly qualified and experienced employees in terms of finding solutions for many application tasks.

I hope you enjoy the Particle World 22!

Dr. Dietmar Klank and the 3P Instruments team

News on the characterization of particles, powders, and pores

+++ Our instruments passed successfully round robin tests +++

Round robin tests are external interlaboratory tests with reference samples that are measured in different laboratories all over the world and the results are statistically evaluated. The aim of such tests is to ensure internal quality assurance and to demonstrate the performance of the equipment.

We are proud to announce that the DT-300 passed the round robin test for the determination of zeta potential with reference materials of the "National Institute of Standards and Technology" (NIST). In addition, the sorption analyzer 3P meso 222 has successfully passed the round-robin test "Pore size parameters of nanoporous titanium dioxide" of the "Federal Institute for Materials Research and Testing" (BAM). Furthermore, the Bettersizer S3 Plus successfully passed the BAM test „Particle size determination of ceramic powders by means of laser scattered light“.

More information in our blog articles:

<https://www.3p-instruments.com/dt-300-passes-nist-round-robin/>

<https://www.3p-instruments.com/3p-meso-222-passed-round-robin-test/>

<https://www.3p-instruments.com/bettersizer-s3-passes-interlaboratory-test/>

+++ We are hiring: Account Manager/Sales Representative (m/f/d) +++

For our department "Dispersions", we are looking for an Account Manager/Sales Representative (m/f/d) in the chemical-technical field for our Southern sales area (home office Southern Germany or on site in Odelzhausen).

More information: <https://bit.ly/3Dan6M7>



+++ New autosampler for Bettersizer particle size analyzers +++

The autosampler doses fully automatically up to 60 samples no matter if they are dry powders or pre-dispersed liquid dispersions. The included barcode printer ensures that the results are recorded for the corresponding sample. The sampler is cleaned by ultrasound to avoid contamination. It can be used with the Bettersizer S3 series and the Bettersizer 2600.

- Suitable for powders and dispersions
- Sampling volume: 0,5 – 5 ml
- Capacity sample vial: 10 ml

Watch the autosampler in action:

<https://vimeo.com/501794586/b10d5cc82a>



+++ New products for Pressure and Vacuum Swing Adsorption from L&C Science and Technology +++

We will soon offer devices for Pressure and Vacuum Swing Adsorption studies and the according humidity generators. The new series of PSA-1000 systems provides flexible and complete dual-bed laboratory testing apparatus for Pressure and Vacuum Swing Adsorption studies. All levels of gas separation R&D can be accomplished for adsorbate bed volumes ranging from 150 cm³ to 3,500 cm³. The Model PSA-300LC is a low-capacity, Pressure Swing Adsorption testing instrument designed for research studies where only extremely small sample volumes are available. All forms of gas separation R&D are possible, including use of the PSA-300LC for single-bed testing.

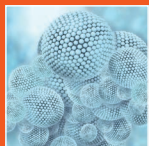
More information:

<http://www.landscience.com/products/>



The new nanoparticle analyzer series BeNano

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



Introduction

We proudly present a powerful tool for nanoparticle analysis: the BeNano series! With this, we start a new era of particle size analysis enabled by a new generation of capabilities. The new family member of Bettersize meets all your needs:

- Nano particle size analysis via dynamic light scattering (DLS)
- Molecular weight determination by static light scattering (SLS)
- Zeta potential measurement using electrophoretic light scattering (ELS)

The application fields are broad and reach from pharmaceuticals, drug delivery, bioscience & biopharmaceuticals to paints, inks and coatings.

Three methods in one device:
the BeNano series – watch the product video here:

<https://www.youtube.com/watch?v=LcelhYu0ECg>.

Features

- Wide Measuring Range: 0.3 nm - 15 µm
- High-performance Hardware
- Research Level Software
- Versatile Accessories



Table 1 The different models of the BeNano series

	BeNano 90	BeNano Zeta	BeNano 90 Zeta
Particle Size	■	—	■
Zeta Potential	—	■	■
Molecular Weight	■	—	■

Benefits

High resolution

The resolution of the DLS technology depends on the algorithm. Usually for two narrowly sized-distributed components with size difference of over 3:1, the algorithm discerns two individual peaks by adjusting the resolution to a higher level. The BeNano series provides several algorithms with different resolutions to meet the high-resolution requirements of different applications. Fig. 1 is the result of a 60 nm and a 200 nm latex mixture.

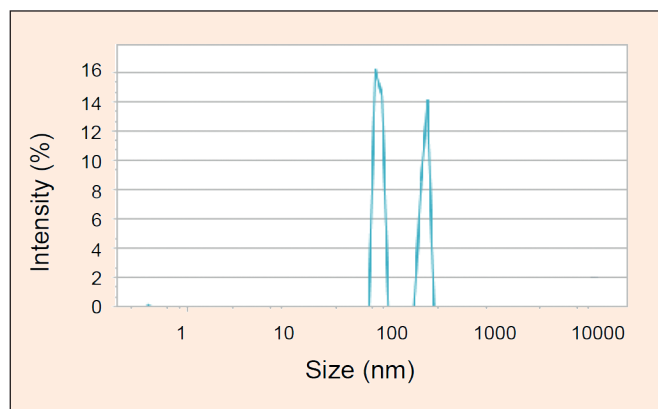


Figure 1
Particle size distribution of a 60 nm and a 200 nm polystyrene latex mixture

Very good repeatability

The optical system is robust and stable. It has an automatic intensity adjustment and intelligent signal judgment system to ensure high stability and repeatability of the measurements. Fig. 2 depicts the measurement repeatability of the 60 nm polystyrene latex. As shown, the system provides excellent repeatability with a relative standard deviation less than 1 %.

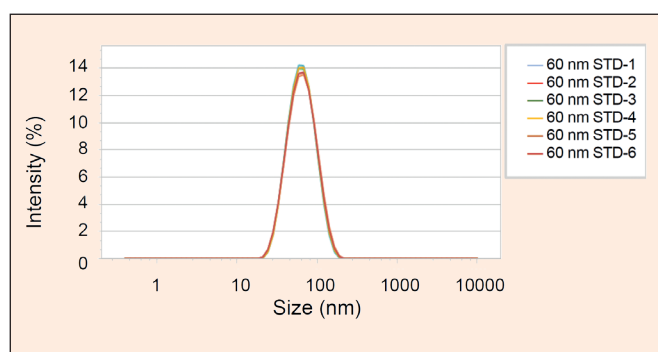


Figure 2 Particle size distribution of a 60 nm polystyrene latex



Precise measurement of...

■ ...small particles

The BeNano series is equipped with a 10 mW He-Ne laser, a high-sensitivity Avalanche photodiode detector (APD) and single-mode fibers, which provides unprecedented sensitivity and accurate measurement for extremely small particles with fast diffusion speeds. Even for molecules smaller than 1 nm such as vitamin B1 under very diluted conditions (as shown in Fig. 3), the BeNano series can effectively detect its scattering intensity and fast decay signals to obtain the particle size and size distribution.

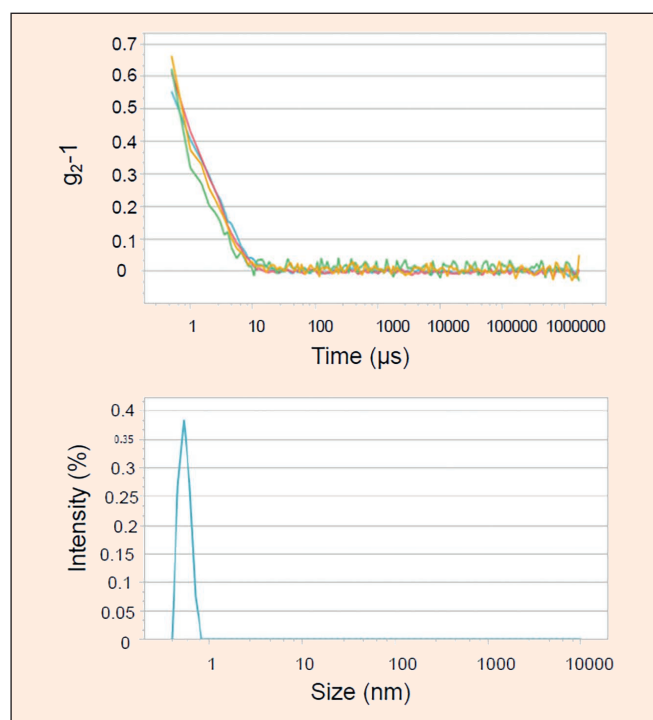


Figure 3 Measurement result and particle size distribution of vitamin B1

■ ...large particles

Large particles diffuse slowly and are likely to sediment. Applying DLS technology for large particles requires the intelligent adjustment of the scattering intensity and ensures enough correlation time for the slow decay. The highly effective detection system of the BeNano series can offer enough correlation time providing accurate calculation of slow decay signals. Fig. 4 is the measurement result of a 5 μm polystyrene latex.

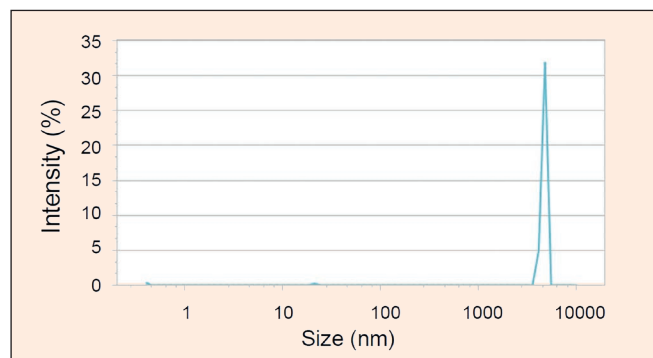
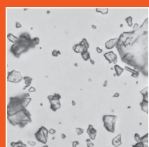


Figure 4 Measurement result of a 5 μm polystyrene latex

Particle characterization of active pharmaceutical ingredients and the proper dispersion of organic substances

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



Introduction

The comprehensive analysis of the chemical and physical properties of active pharmaceutical ingredients (APIs) and excipients forms the decisive basis for their application-specific development and formulation for tailor-made setting of the final product or drug properties. Their characterization must therefore not only play a central role in product development, but especially in quality assurance along the production chain.

The particle size (and its distribution) of powdery substances is one of the most important parameters that determine the final product performance and must therefore be precisely set in the development process or continuously monitored during production. The reason for this is the direct relationship between the solubility, and thus the bioavailability of a powdery substance and its particle size distribution. The large surface of very finely divided powders ensures greater solubility in, e.g., a carrier medium for application or in the body itself. Otherwise, powders with a very small particle size tend to dust which in turn makes safe handling during production, filling and medical use more difficult.

The primary particle size is also more than decisive for application in tablet form. Small grain sizes of the starting substances allow a high degree of compactability and thus final tablet strength, but prevent effective and rapid diffusion of liquid due to the small interparticle porosity and thus reduce the rate of active ingredient release.

Knowledge of the particle sizes of the individual substances is essential for processing powder mixtures, e.g., active ingredients and auxiliaries. Only a particle size distribution of the powder mixture that is as homogeneous as possible effectively prevents the individual components from separating during individual production steps and thus guarantees consistent quality with regard to the composition and active ingredient concentration in the final drug.



The sample preparation determines the analysis result

The widely used and most frequently used method for particle size analysis of powdery substances is laser diffraction (also static laser light scattering). Not least because of the wide particle size range (from a few nano- up to millimeters) that can be covered with this method, maximum reproducibility (deviations between repeated measurements of < 0.5 % when using modern measuring devices), shortest measurement duration (single measurement < 10 seconds) and the simplest application, thanks to SOP-supported and thus fully automatic measurement. Even if the requirements for particle size analyzers are precisely defined in numerous standards (e.g., ISO 13320:2020, USP <429>) and are therefore strictly regulated, the exact execution of measurements and, above all, sample preparation, depending on the application-specific requirements, is the responsibility of the user. Since it must be guaranteed that the scattered light signals detected during the measurement follow in any case the laws of so-called single light scattering, the particles to be analyzed must be fed to the measuring unit individually and in a suitable concentration and cross the beam path of the laser.

A distinction is essentially made between the wet and dry dispersion options of the sample. Wet dispersion is generally characterized by effective particle separation, precise sample dosing and targeted application adaptation. The large number of freely selectable parameters for wet dispersion enable tailor-made sample preparation for particle size measurement: type of dispersion medium (water, polar solvents or non-polar solvents of all kinds), addition of dispersing additives (e.g., surfactants, polymers) as well as type, duration and strength of the mechanical particle separation (only stirring or additional ultrasonic disper-

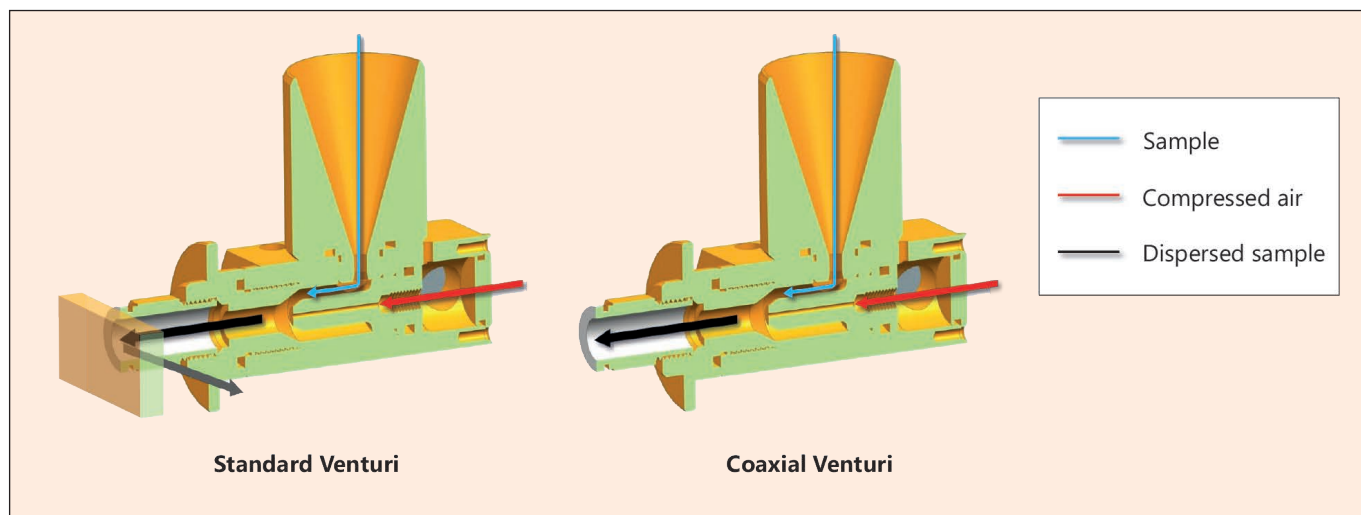


Figure 1 Design of dispersion units in particle size analyzers: standard Venturi structure (left) and coaxial Venturi structure (right)

sion with freely selectable power). Otherwise, this multitude of influencing factors on the sample preparation harbor the risk of inconsistent dispersion and thus poorer reproducibility of the measurements due to smallest deviations. Particularly for substances with high water solubility (pharmaceutical active ingredients but also auxiliaries such as sugar or salts), the requirements for the purity or absence of water of the dispersing medium are the highest priority.

Precisely for this reason, dry dispersion with compressed air is ideally suited for the particle size analysis of water-soluble powders in quality control.

For reproducible sample preparation and conveying by means of dry dispersion, it is necessary to ensure constant compressed air quality in terms of pressure and purity. However, thanks to integrated, digital pressure regulators and upstream air filters, this does not pose any challenge for modern systems (such as the Bettersizer 2600).

Dry dispersion is not just dry dispersion

However, there are differences in the choice of design and construction of the dry dispersion unit. Three mechanisms are described for particle separation by means of compressed air:

1. Shear – deagglomeration through rotational forces that act on the particles in the air flow;
2. Particle-particle impact – deagglomeration through collision of agglomerates with high kinetic energy;
3. Particle-wall impact – deagglomeration through collision of the agglomerates with the walls of the dispersing system.

The latter mechanism is characterized by the highest level of effectiveness and is used in a large number of commercially available dispersing systems in the form of a standard Venturi structure (Fig. 1, left). Unfortunately, it is precisely this high effectiveness of particle separation that harbors the risk of additional changes in the primary particle structure. Particularly in the case of crystalline, organic and thus soft substances, this can lead to a breakdown of the primary particles. The result of the subsequent particle size measurement suggests an incorrect high

proportion of fines and no longer reflects the particulate properties of the original sample. Since this must be avoided under all circumstances for a representative particle size measurement when choosing the dry dispersion unit, attention must be paid to the design of the Venturi system that is suitable for the type of sample.

An alternative to the standard Venturi structure with a baffle plate is the so-called coaxial Venturi structure (without a baffle plate; Fig. 1, right).

Evaluation of a dry dispersion system

How to find out whether the dry dispersion system used is suitable for the samples to be measured? First of all, regardless of the geometry of the Venturi system, a certain mechanical stress on the particles is required for deagglomeration. This can be adjusted via the strength of the applied air pressure. Depending on the strength of the interparticle interactions and the resulting degree of agglomeration of a sample, a specific air pressure is required for complete deagglomeration. A further, step-by-step increase in the applied pressure should then deliver stable results since the sample is already completely deagglomerated for the measurement. If the sample continues to be refined, this is due to the breakage of the primary particles.

Choice of dispersion pressure without changing the primary particle structure

If it should be determined at which pressure the sample is to be dispersed for particle size measurements, a pressure titration experiment is recommended, i.e., measurements of the same sample at different dispersing pressures. Fig. 2 and 3 show such pressure titration curves for two different samples of the active ingredient domperidone (Fig. 4). One of the samples is untreated (non-micronized) while the other was micronized or adjusted to the desired particle size in a further production step. The measurements were also carried out in a pressure range between 0.5 and 4.0 bar with a gradual pressure increase of 0.5 bar. In both cases, the coaxial Venturi design was used.

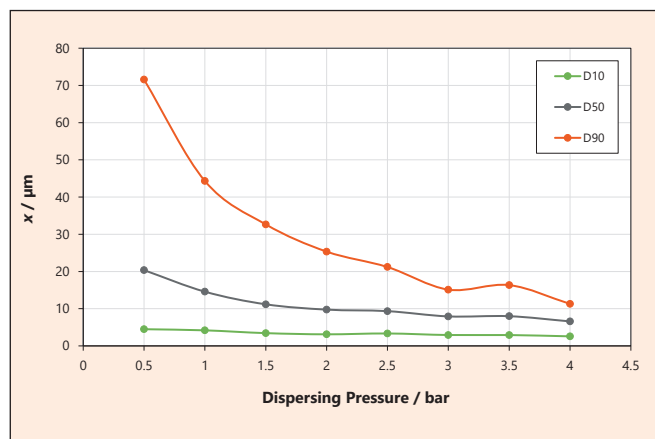


Figure 2 Particle size pressure titration data of non-micronized domperidone sample

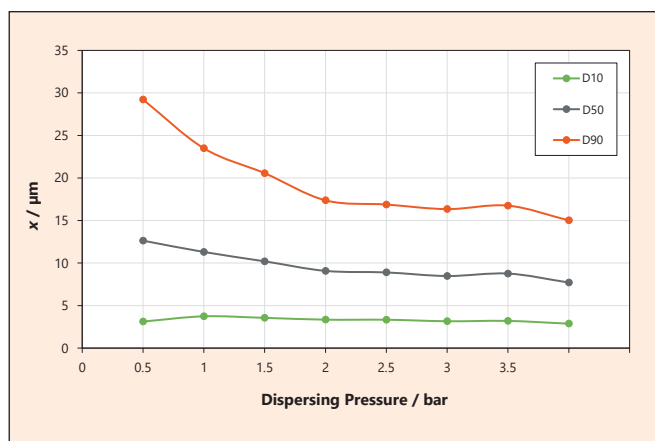


Figure 3 Particle size pressure titration data of micronized domperidone sample

Novel dispersion unit ideally suited for pharmaceutical use

The shown measurements were all carried out with the *Bettersizer 2600* particle size measuring device. Two different dry dispersion units are available for this particle sizer (Fig. 5). While the standard unit BT-902 is also suitable for large sample throughput, the small-volume drying unit BT-903 enables measurements with a few milligrams (depending on the sample, 50 – 200 mg). Both units use the coaxial Venturi structure and are therefore ideally suited for the characterization of fragile, organic substances. In particular, the *Bettersizer 2600* with the dry dispersing unit BT-903 can be unreservedly recommended for use in the pharmaceutical industry: it meets all the requirements of a modern particle size measuring device and is also characterized by its particularly gentle dispersion with minimal sample consumption.

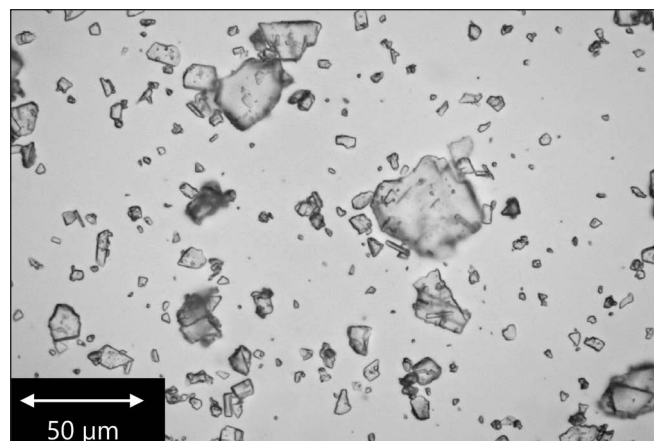


Figure 4 Light microscopic image of the crystalline, micronized domperidone sample

The particle size (especially the D90 value) decreases with increasing pressure for both samples. The rapid decrease at low pressure is due to deagglomeration. For the micronized sample, a stable plateau area between 2.0 and 3.5 bar is established in the titration curve which shows no further refinement. In the case of the non-micronized sample, this area cannot be clearly defined (especially in the D90 curve) which can be attributed to stronger interparticle interactions or to superimposed breakup of the fragile, larger particles. Nevertheless, the pressure range between 2.0 and 3.5 bar can be described as stable for both samples, especially when looking at the D50 values. Thanks to the coaxial Venturi structure, there is no change in the primary particle structure. This is only observed from a dispersion pressure > 4.0 bar. Accordingly, dry dispersion at 2.0 bar can be recommended for the particle size measurements of both domperidone samples, since the samples are largely deagglomerated but remain unchanged compared to the original state. Thus, the measurement results represent the particulate properties.

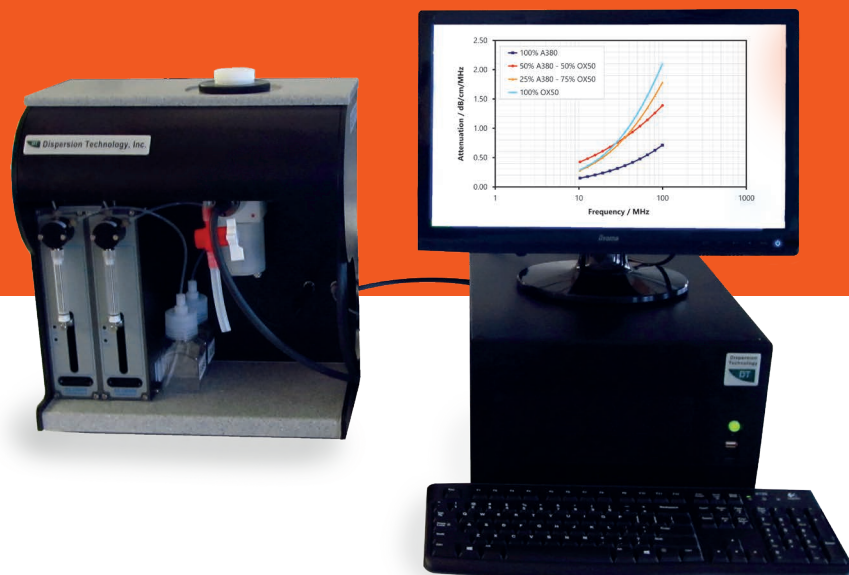
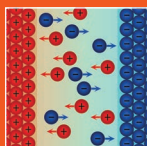
This shows that the use of a coaxial Venturi system (Fig. 1) is superior to the standard Venturi setup for the measurement of organic, pharmaceutical active ingredients and excipients. This is due to the fact that the described "milling effect" can be minimized or even completely excluded when using a coaxial Venturi system.



Figure 5 The dry dispersion units BT-902 and BT-903 for the *Bettersizer 2600* particle analyzer

Use of acoustic methods and current flow measurement in battery research

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Introduction

The development of rechargeable batteries (accumulators) with higher electrical power and service life as well as an increasing environmentally friendly production and disposal is one of the challenges of future technology. In addition, the manufacturing costs should be as low as possible in order to make end products, e.g. in the automotive sector, affordable for a wide range of customers.

With this goal in mind, there are different approaches in the research area, such as all-solid-state, lithium-air or lithium-sulphur batteries, all of which, however, are not yet ready for series production [1-3]. The most common system currently used in practice are the so-called lithium-ion NMC batteries (NMC: Nickel-Manganese-Cobalt). They are now used in key areas such as portable electronic devices (smartphones, tablets, notebooks) as well as in the entire electromobility sector (electric cars, hybrid vehicles, electric wheelchairs).

The manufacturing process of a modern accumulator is very complex and also includes numerous manufacturing steps in which organic solvents and generally liquid suspensions, i.e., hard material particles dispersed in a solvent, play an essential role. Particularly during processing, it is important that these systems are characterized in their original state with regard to properties such as particle size distribution, zeta potential or electrical conductivity in order to be able to assess the respective process step. It is precisely here that acoustic methods are available which in contrast to conventional optical methods such as static light scattering dynamic image analysis or electrophoresis can also be used in more concentrated dispersions [4].

In this article, the mentioned measurement methods are first briefly summarized. Subsequently, the functionality of an NMC battery cell is discussed, in order to discuss afterwards the areas of application of the methods in the production of such an accumulator.

Principle of measurement of acoustic methods and frequency-dependent current flow measurement – an overview

The methods "acoustic attenuation spectroscopy" for particle size determination and "electroacoustics" for determining zeta potential are predestined for many areas of application in battery development: Their great advantage is the possibility of measuring dispersions in their original state, i.e. without dilution or special preparation. Details on both methods can be found e.g. in [4-5] and a short summary is given below.



Acoustic attenuation spectroscopy for particle size measurement

The principle of acoustic attenuation spectroscopy for size measurement is shown in Fig. 1: A sound transducer transforms a high-frequency signal into an ultrasound wave. It is a short-wave package with a very constant amplitude and wavelength that will be launched into the dispersion to be characterized. To avoid overlap-effects, every individual "burst" is shorter than the time of transmission. During transmittance of the wave through the dispersion, it will be attenuated due to different loss interactions with the particles dispersed in the system [4-5].

The attenuated signal is detected by the sound receiving transducer and forwarded to the computer for signal-conditioning and analysis. Apart from the specific effects in the dispersion (I_0 to I), the attenuation is dependent on the gap L between sender and detector as well as on the soundwave frequency f :

$$\text{attenuation} \left[\frac{\text{dB}}{\text{cm}} \right] = \frac{10}{f[\text{MHz}]L[\text{cm}]} \log \frac{I_{\text{in}}[\text{dB}]}{I_{\text{out}}} \quad (1)$$

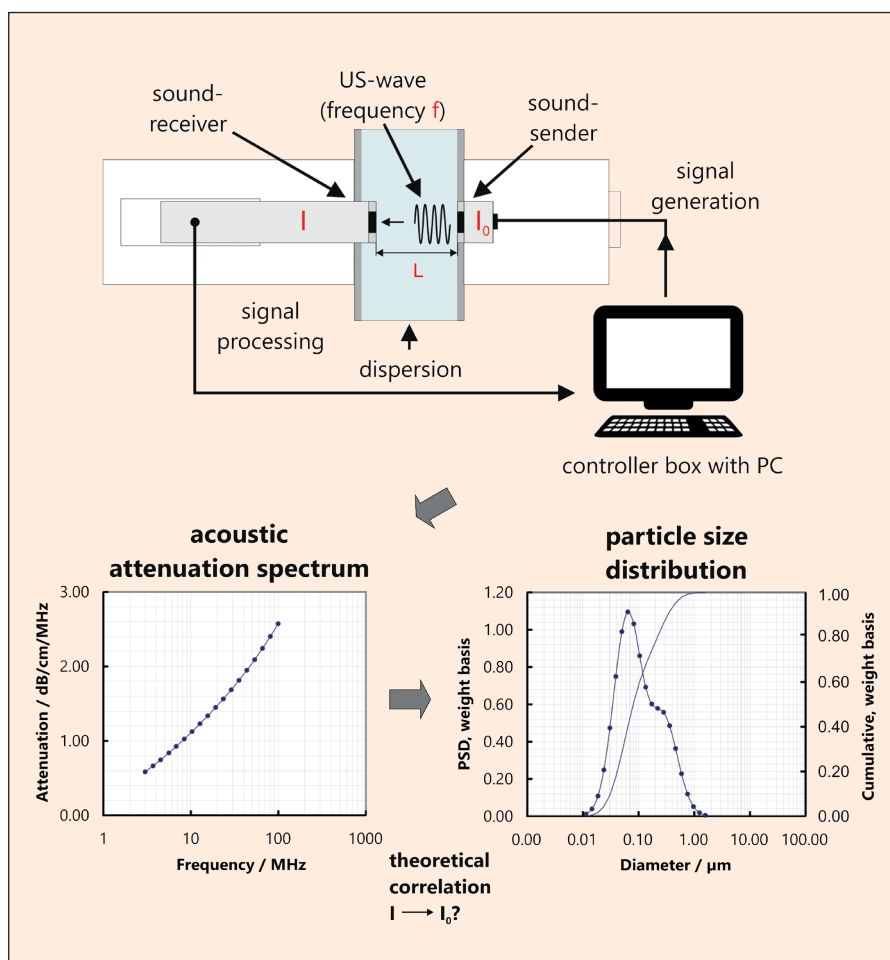


Figure 1 Measurement principle of acoustic attenuation for particle size measurement

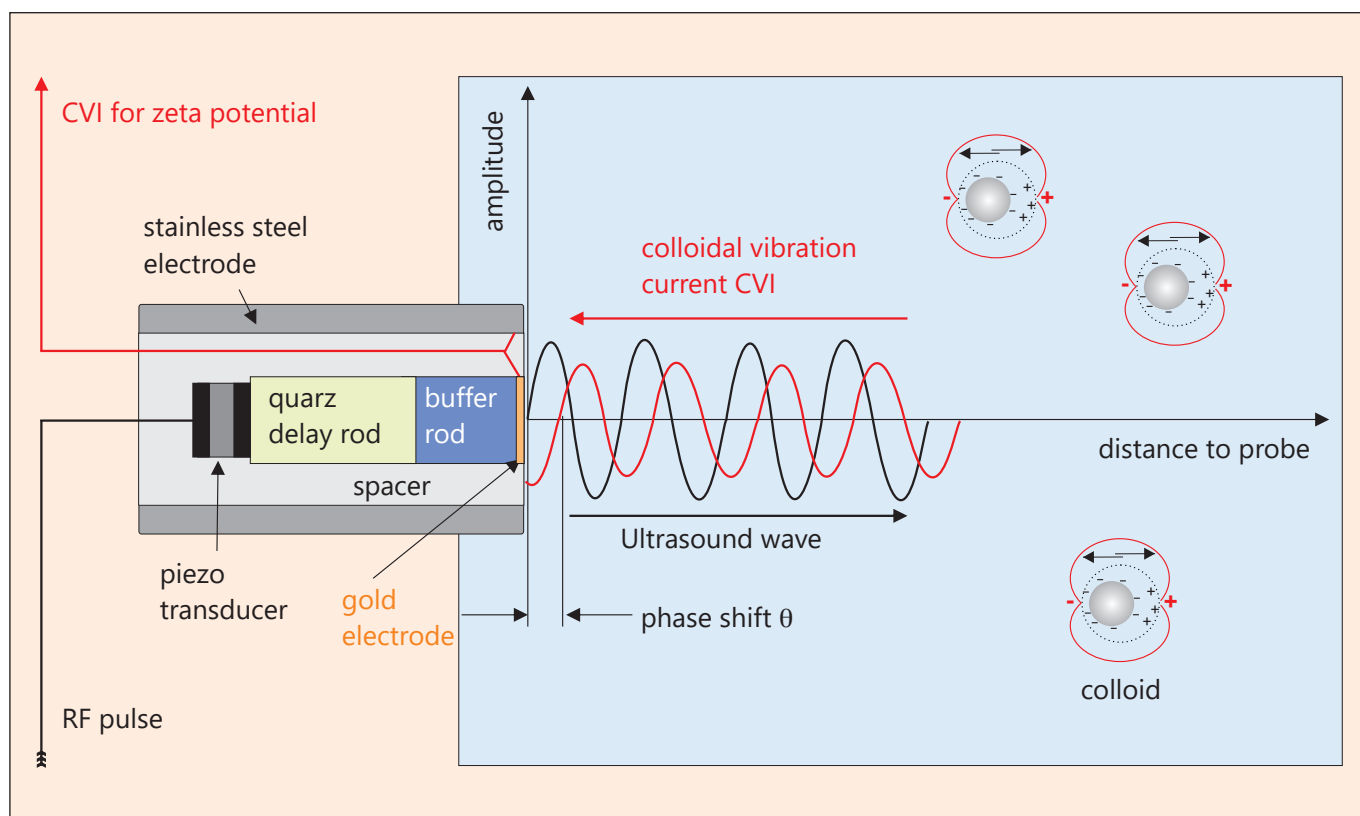


Figure 2 Measurement principle of electroacoustic for zeta potential measurement

The acoustic spectrometers from Dispersion Technology (DT) are using this method for particle sizing: The frequency range is 1 to 100 MHz and, due to the variable gap, a concentration range of 0.1 to 60 vol.-% can be realized. The measured spectrum will be fitted on the bases of the different theories describing the material specific attenuation mechanism [4-5].

Electroacoustic for zeta potential determination

A comprehensive description of this method for determining zeta potential can be found in [4-5]. Fig. 2 shows the measuring principle schematically.

A high frequency signal (RF-pulse) is transferred into an ultrasound wave by means of a piezo transducer. This wave passes a quartz delay rod for internal calibration, then a buffer rod and enters the dispersion as a short pulse with a narrow frequency distribution. The colloidal particles in the dispersion start a frequent motion relative to the surrounding liquid because of their mass inertia. Thus, the particles are shifted relative to their diffuse double layer: an oscillating electric field is generated which induces a measurable, alternating current – the colloidal vibration current (CVI). This is measured as a potential between two electrodes and can be used to determine the colloidal properties of the sample. The two important measurement parameters are the magnitude of the CVI signal which determines the absolute amount of the zeta potential and the phase shift θ between the ultrasound wave and CVI signal which determines the sign. The relation between the CVI and the zeta potential of the particles in the suspension in aqueous systems is normally described using the SDEL-theory [4]:

$$\mu_d = \frac{\epsilon_m \epsilon_0 K_S}{\eta K_m} \frac{(\rho_p - \rho_s) \rho_m}{(\rho_p - \rho_m) \rho_s} \quad (2)$$

Advanced theories for polar and non-polar systems are summarized in [6]. As with the acoustic attenuation method for size, the concentration range is 0.1 to 60 vol.-%. Furthermore, the system can be used for pumping or stirring systems and thus even for sedimenting particles.

All electroacoustic systems from DT are using this technique for zeta potential measurement.

Measurement of the electric conductivity in weak and non-polar organic solvents

A special measurement setup consisting of two coaxial stainless-steel electrodes and a guard electrode was used. The task of the latter is to eliminate leakage currents between the measuring electrodes. During a measurement, the instrument applies a sinusoidal voltage to the outer electrode and measures the current that flows through the sample to the inner electrode. The frequency of this applied voltage is changed depending on the measured conductivity in the range from 1 to 10 Hz.

The method is implemented in the DT-700 and a measurement range of 10^{-4} – 10^{-11} S/m can be realized.

Functional principle of an NMC battery cell

The setup and the functional principle of an NMC battery cell is shown in Fig. 3.

The anode (-) consists of an 8-18 μm thick copper foil coated with active material (graphite). The cathode (+) is a 15-25 μm thick aluminum foil coated with NMC active material. A microporous separator, which consists of a microporous polymer film normally coated with Al_2O_3 , AlOOH or SiO_2 , separates the two electrodes from one another. The whole system is immersed in an electrolyte liquid.

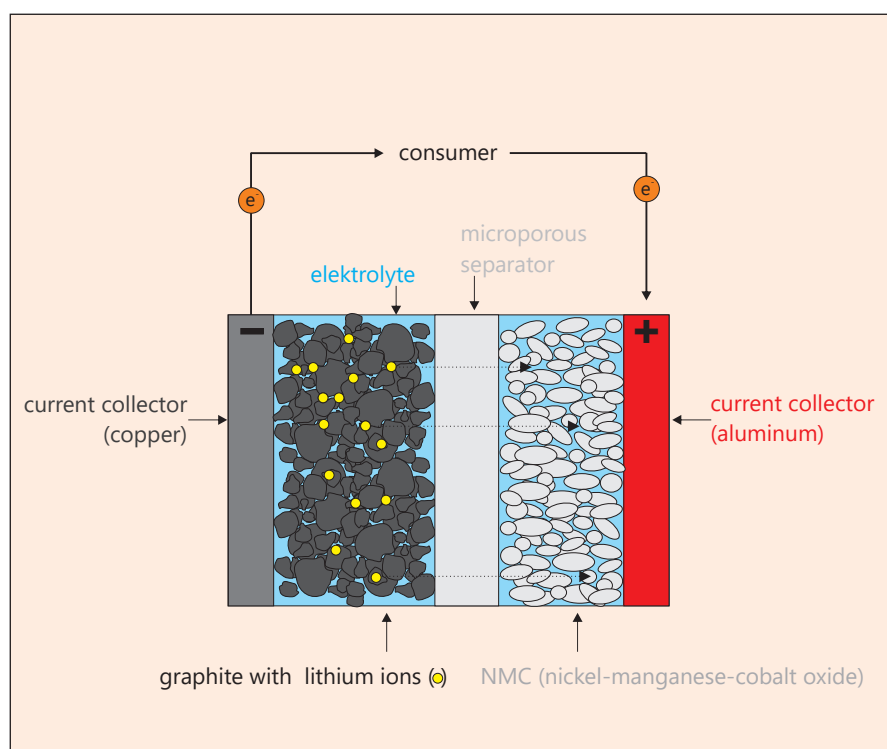


Figure 3 Setup and working principle of a NMR accumulator

During the discharge process, a current of electrons flows through the consumer. At the same time, positively charged lithium ions that are stored in the active material of the anode move through the separator to the cathode and are stored there in the NMC layer (charge equalization). During the charging process, the accumulator is connected to a power source and the process is reversed.

Suitable electrode-active materials for the Li-ion transfer as well as a good electrode wetting of the active materials are decisive for an optimal functionality. In addition, the ceramic coating ensures that the separator can be laminated and is thermally stable.

Suspensions and organic solvents play an essential role in the production of the cathode starting material NMC and the production of electrolytes. Furthermore, the coating process of the separator and the anode and cathode production are each carried out via a suspension route.

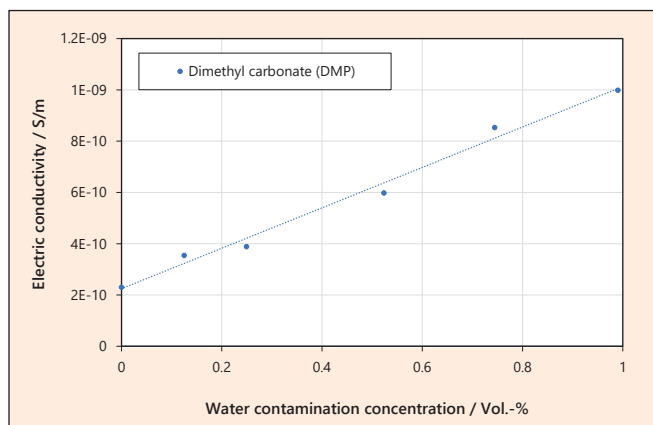


Figure 4 Electric conductivity in dependence of water contamination concentration, measured by means of a DT-700

Possible uses of acoustic methods and electric conductivity measurement for the manufacturing of NMC batteries

The main application of the acoustic methods is in the field of separator production as well as cathode and anode manufacturing, conductivity measurements are particularly useful for electrolyte production and cathode production.

Manufacturing of the liquid electrolyte

The electrolyte of the NMC battery cell consists of a conductive salt and an organic solvent or solvent mixture. In addition, certain additives that improve the long-term stability of the unit are used. Lithium hexafluorophosphate (LiPF_6) is used as the conductive salt, possible solvents include dimethyl carbonate (DMC) or ethylene carbonate (EC). Vinylene carbonate (VC), for example, is used as an additive. All components are mixed together in a reactor.

It is necessary that the liquid electrolyte is as free of water as possible, as this results in a decomposition reaction of the conductive salt. Fig. 4 shows an example of electric conductivity measurements on a pure DMC solvent in dependence of water contamination concentration.

Even small amounts of water-contamination lead to an increase in electric conductivity, measured using the DT-700. Thus, this method/parameter is ideal for checking the quality of the liquid electrolyte.

Manufacturing of the separator

The separator consists of a porous polymer membrane which is usually produced by a wet chemical melting process from a polymer-additive mixture using temperature, pressure and a subsequent rolling process step.

To increase the thermal stability in high-temperature applications, separators are coated with ceramic particles (e.g. Al_2O_3 , AlOOH , SiO_2) in a subsequent step: This is done using a suitable suspension and a gravure roller. The decisive process parameters for the coating process include the particle size distribution of the ceramic particles in the suspension and their stability against agglomeration. At this point, the acoustic methods "acoustic attenuation spectroscopy" (particle size distribution) and "electroacoustic" (zeta potential measurement) are particularly suitable because, in contrast to optical methods, the suspension can be measured in its original state, i.e., without dilution or other preparation steps.

For coating with Al_2O_3 particles e.g. aqueous suspensions are used. The maximum agglomerate size should be around 2-3 μm . Fig. 5 shows the dependence of the particle size of such an alumina suspension (12 wt.-% Al_2O_3 in water) on the pH value, in Fig. 6 the associated zeta potential vs pH measurement curve can be seen. Obviously, due to the high zeta potential, the suspension shows a monomodal size distribution with maximum diameters of about 1 μm in the weak acidic range (pH = 5), whereas in the weak basic range (pH = 9) with a zeta potential close to 0 a clear tendency towards agglomeration can be seen (agglomerate diameter up to 10 μm).

Thus, the pH should be set < pH 7 for a good working coating process with this type of suspension or, alternatively, suitable stabilizers should be used.

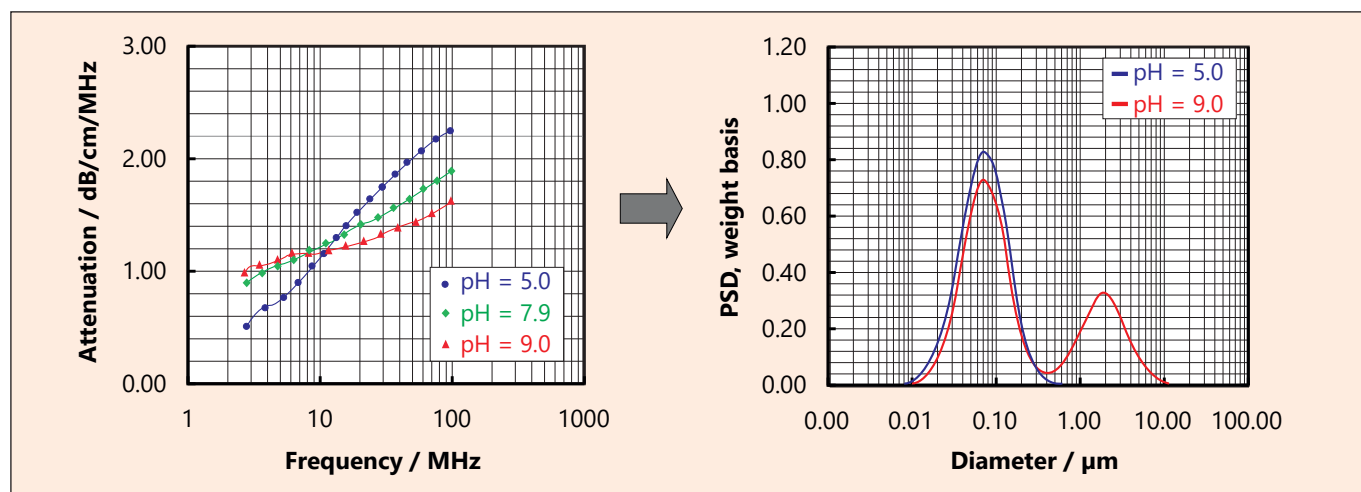


Figure 5 Particle size distribution of an aqueous, 12 wt.-% Al_2O_3 suspension in dependence of pH (measured using a DT-1202)

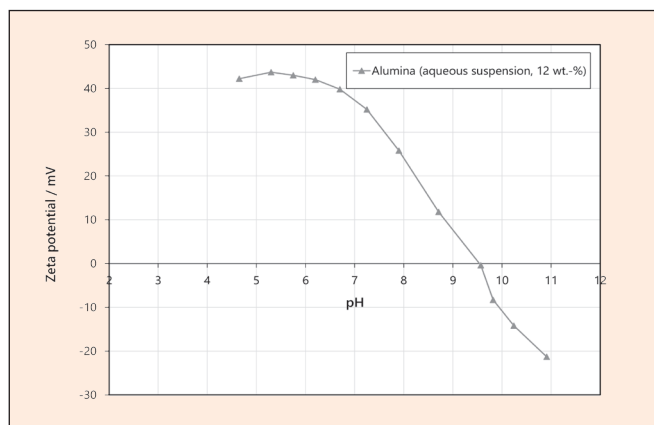


Figure 6 Zeta potential vs. pH of the 12 wt.-% Al_2O_3 suspension in Fig. 5 (measured with DT-1202)

Electrode production

Both the anode and cathode manufacturing of a lithium-ion NMC battery works suspension-based by coating the electrode material (copper or aluminum foil) using special application tool (e.g. lot nozzle or anilox roller).

At the cathode, the aluminum foil is coated with a $\text{Li}(\text{NiMnCo})\text{O}_2$ -in-NMP-suspension (N-methyl-2-pyrrolidone), which also contains carbon black and a binder (PVDF). An aqueous graphite-carbon black suspension is used for the anode (copper foil), which also contains a binder (carboxymethyl cellulose, CMC) and an additive (styrene-butadiene rubber, SBR). In this process step, the suspension properties of course will influence the quality of the coated electrodes, such as layer thickness accuracy or adhesion between substrate and layer.

The following example shows the possibilities of acoustic attenuation spectroscopy (particle size measurement) for electrode production: An aqueous, approximately 30 wt.-% graphite-carbon black CMC paste was measured with the aid of a DT-1202 regarding particle size distribution. The carbon black had a mean particle size of about 400 nm, the graphite of about 3.8 μm . Fig. 7 shows the measured attenuation spectrum and particle size distribution of the final produced paste.

For the calculation the Rouse-Bueche-Zimm model for structural losses was taken into account [4].



Conclusion

In this article, the possible uses of the three methods "acoustic attenuation spectroscopy for particle size", "electroacoustic for zeta potential" and "electric current measurement for electric conductivity in organic solvents" for NMR battery production process were investigated.

The acoustic methods are in particular ideal to characterize the suspensions used for electrode manufacturing and separator coating due to their possibility to measure in original concentrated systems.

The electric current measurement on the other hand is predestined to check the liquid electrolyte regarding water contamination. Thus, all systems can play an important role both in cell development and later in quality checks during battery production.

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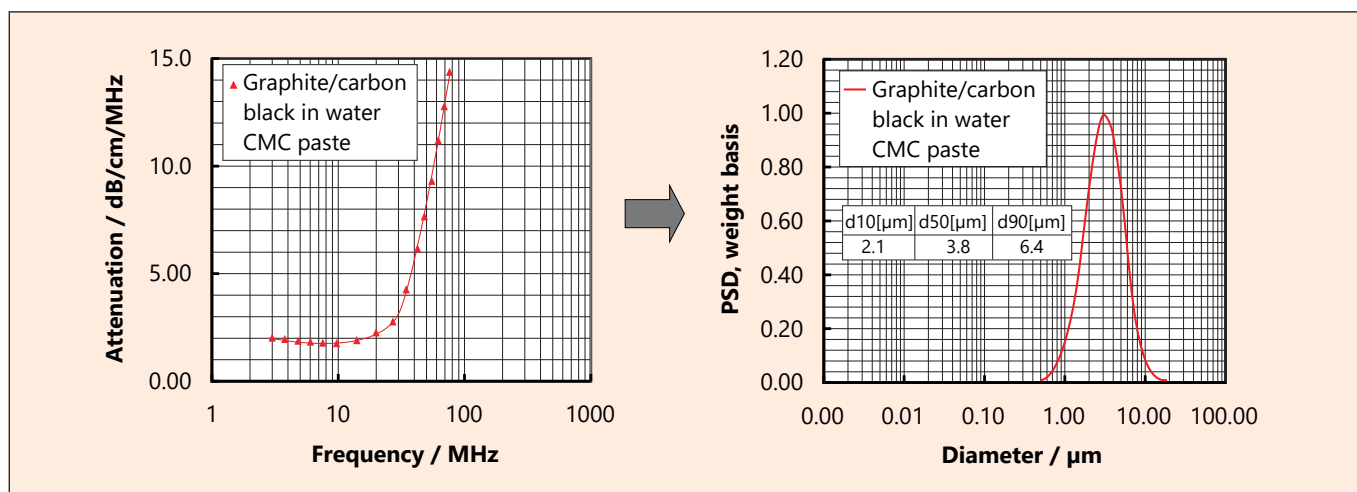


Figure 7 Particle size distribution of an aqueous, 30 wt.-% graphite-carbon black-CMC paste (measured by means of the DT-1202)

The brand new 3P graviSorb for water vapor adsorption analysis

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



Introduction

Water vapor adsorption plays an important role for the product development and quality assurance in many application fields. Typical examples are pharmaceutical products, shelf life of food, ceramic components (i.e. hydrophobicity/hydrophilicity), coatings, building materials and much more. With the new 3P graviSorb, we present our latest product of the 3P Instruments family, a fully automated gravimetric water sorption analyzer. It measures adsorption and desorption isotherms of water vapor both accurately and sensitively (see examples in Fig. 1), including sorption kinetics (Fig. 2), with minimal operator involvement. The weight of up to 12 samples is monitored and recorded as the relative humidity is automatically varied by the blending of dry carrier gas with a saturated gas stream. The carousel balance design of the 3P graviSorb allows increased analysis throughput by simultaneous investigation of up to 12 different samples, or 11 + 1 if one station is running an empty sample chamber or even a reference material for direct comparison (Fig. 3). The 3P graviSorb is an ideal solution for the determination of water uptakes for research and quality assurance. The complete automatic measuring process together with the precise balance, broad climate range and the user-friendly software make it the ideal instrument for high sample throughput with a minimum of costs and maintenance.

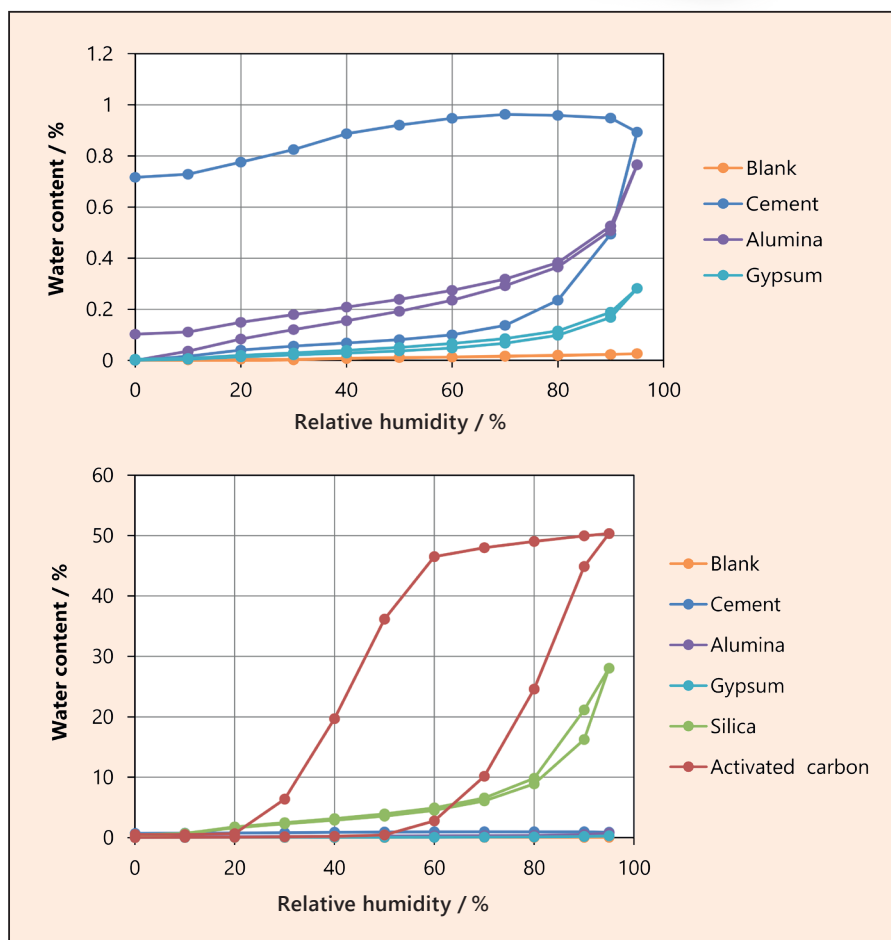


Figure 1 Water sorption isotherms of a wide range of materials with different water sorption capacity

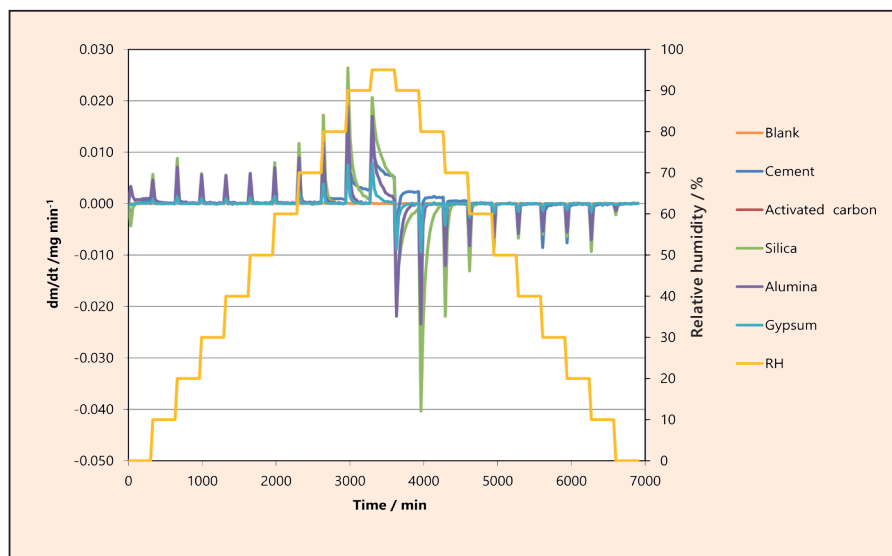


Figure 2 Ad- and desorption kinetics of selected types of materials

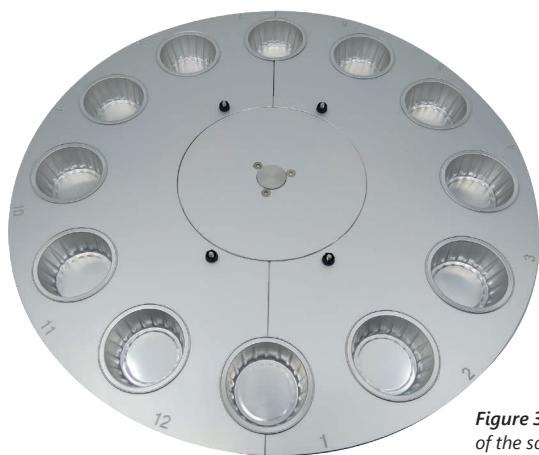


Figure 3 Carousel design of the sample holder

Measurement Capabilities

- **Isotherms:**
Mass change as a function of changing relative humidity (RH), increasing mass during adsorption (increasing RH), decreasing mass during subsequent desorption (decreasing RH).
- **Kinetics:**
Time-dependent sorption studies give the rate of ad- and desorption.
- **Effect of Temperature:**
Isotherms and kinetics change as a function of temperature. Can be used to yield sorption enthalpies

Features

- Complete automated system: automatic weighing & changing of climate according to settings of the user
- Easy-to-use, with a minimum of maintenance
- User-friendly, powerful software with advanced Excel export
- Results storage in database with back-up function
- High sample weight capacity, up to 125 g (up to 250 g as an option)
- High resolution & precision by using a 0.01 mg resolution balance
- 12 (11+1) samples can be measured simultaneously (Fig. 3)

Applications



Building Materials



Pharma



Paper & Wood



Polymers



Food



Textiles

Invitation to the 3P Instruments Online Adsorption Meeting (November 9th and 10th 2021)

The program includes talks by the following external speakers:

- Prof. Dr. Pascal Van Der Voort (Ghent University, Belgium)
- Prof. Dr. Nicola Hüsing (University of Salzburg, Austria)
- Prof. Dr. Maksim S. Mel'gunov (Boreskov Institute of Catalysis, Novosibirsk, Russia)
- Dr. Sven Elbert (Heidelberg University)
- Dr. Denys Grekov (IMT Atlantique, Nantes, France)
- Dr. Jens Möllmer (Institute of non-classical chemistry (INC), Leipzig, Germany)

In addition to the invited talks, there will be two flash sessions in the afternoon of both event days. If you would like to contribute a short presentation (15-20 min), please send your abstract to Dr. Sebastian Ehrling (sebastian.ehrling@3p-instruments.com) until October 17th 2021.

The participation for academic attendees is free!

For more information and registration,
visit <https://www.3p-instruments.com/trade-fairs-and-seminars/>.

The next Adsorption Week (online and on-site presence options)
will take place on **May 17th to 19th 2022 in Leipzig**. Stay tuned for more information –
visit <https://www.3p-instruments.com/trade-fairs-and-seminars/>!

You are not sure if you should participate? Our 4th (online) Adsorption Week on April 13th to 15th 2021 was a great success: a total of 17 speakers presented their topics to a broad audience from industry and research from 22 countries.

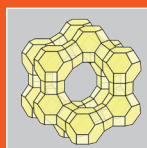
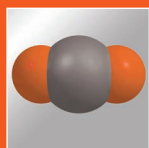
The participants rated all events with **4.26 out of possible 5 points**, and they particularly liked the variety of topics. Here are a few excerpts of the ratings – make sure you register for 2022!



Adsorption studies with CO₂ for climate research and surface characterization

And related studies to characterize smallest ultramicropores

Dr. Dietmar Klank, dietmar.klank@3P-instruments.com



Introduction

Sorption studies with carbon dioxide are becoming more and more important due to the relevance for climate issues. They are, however, also very helpful for the characterization of surfaces of fine and porous materials. The practical purpose of CO₂ adsorption from gas mixtures is studied preferably on breakthrough curves [1,2], which are explained more in detail at www.dynamicsorption.com.

CO₂ pure gas isotherms can also be determined manometrically, for example to get a first overview about the CO₂ sorption capacity of new synthesized materials. Unfortunately, scientific articles publish deviations in material data [3-8] due to the fact that CO₂ is not forming a liquid phase under the normed conditions for these analysis types. Within our work, we will show some easy ways to conduct CO₂ sorption studies by applying the correct adsorbate parameters, and to find the logical interpretation of the resulting material data.

The use of a so-called cryoTune 195 option offers completely new possibilities for the use of standard gas sorption analyzers of various manufacturers for the study of CO₂ sorption in a broad temperature range. And, in combination with a cryoTune 87 upgrade, it offers a unique configuration for the application of noble gas adsorptives such as Ar and Kr, of non-polar molecules such as CH₄, and also of non-spherical molecules such as O₂, CO₂, or n-butane – all these measurements are straightforwardly done at their boiling points (Fig. 1).

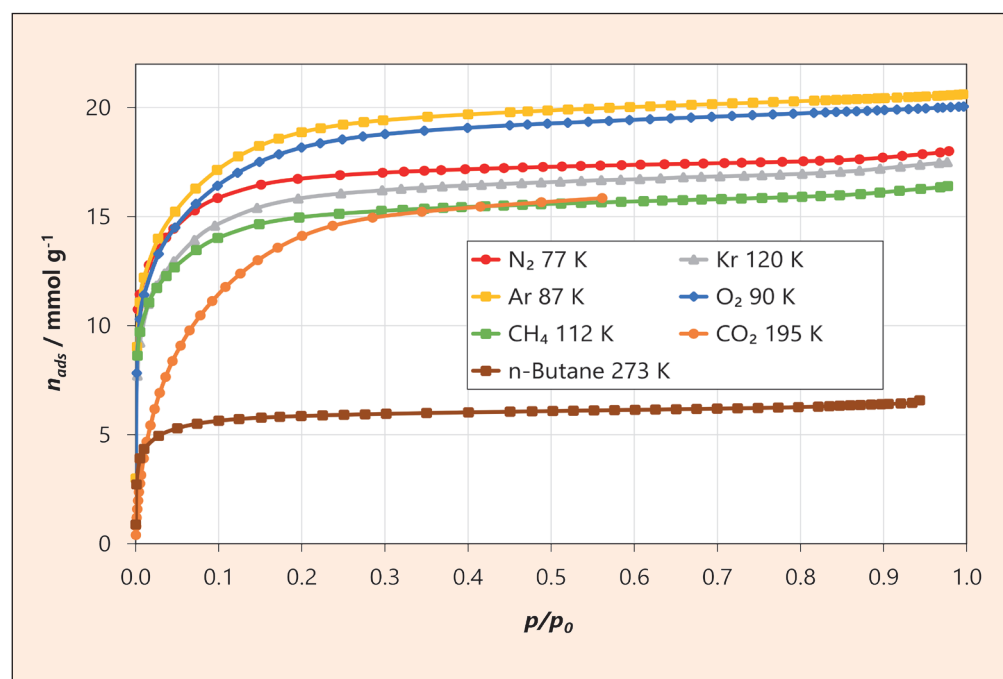
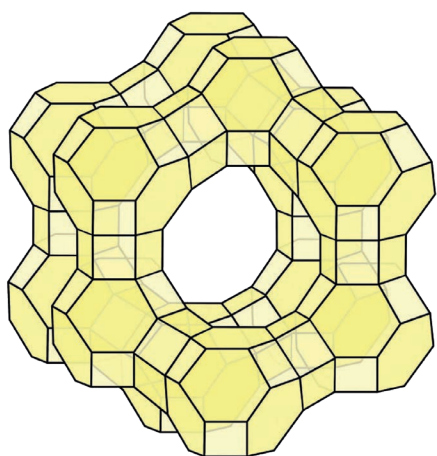


Figure 1
Adsorption isotherms using various adsorptives (at their boiling temperatures, for CO₂ at its sublimation temperature) on an activated carbon sample



In accordance with ISO 9277 [9] and the IUPAC-recommendation of 2015 [10], it is shown that particularly Ar 87 K is scientifically more suitable for measuring specific surface areas and micropores as compared to frequently used N_2 77 K. Finally, the measurements with CO_2 at 195 K by use of the cryoTune 195 offer a feasible way to compare the results of Ar 87 K (non-polar adsorptive) with N_2 77 K (medium quadrupole moment), and with CO_2 195 K (large quadrupole moment) to characterize special material surfaces by use of such different adsorptives.

Recommendations of ISO 9277 and IUPAC for the characterization of surfaces and micropores

The ISO 9277 [9] mentions: "Very often, argon at liquid argon temperature [...] is a good alternative for specific surface determination [...] because it is chemically inert monoatomic gas with symmetrical electron shell configuration quite different from that of nitrogen." In addition, Annex A lists some recommended cross-sectional areas of adsorbate atoms and molecules with the following comments: "In the case of graphitized carbon and hydroxylated oxide surfaces, the orientation of the nitrogen quadrupole is dependent on the surface density of hydroxyl groups, because the nitrogen molecules tend to interact vertically with surface hydroxyl groups. This leads to a reduced value of cross-sectional area of nitrogen. It is recommended to use Ar at the temperature of liquid Ar (87.3 K) for the determination of the BET area of such surfaces." Furthermore, the ISO 9277 explains that Ar adsorption at liquid nitrogen temperature (77.3 K) is no suitable alternative to the Ar adsorption at 87.3 K.

The IUPAC recommendation [10] lists a further limitation of the N_2 method and it is surprising that many scientific users of the sorption method still overlook that fact: "Because of kinetic restrictions at cryogenic temperatures (87 K, 77 K) argon and nitrogen adsorption is of limited value for the characterization of very narrow micropores." We come back to that fact later and summarize the three limitations of the N_2 method in gas sorption for surface and pore characterization:

- I. Nitrogen has a so-called quadrupole moment which influences the interaction with polar groups of the material.
- II. As ellipsoidal molecule, nitrogen has no defined adsorption position on the surfaces, but its unknown position, respectively even different positions at different locations on one material surface, influences the calculated BET surface area and other results.
- III. Micropores smaller than 0.5 nm cannot be detected by use of N_2 77 K adsorption and this refers not only to the pore size distribution of these ultramicropores but also to the determination of surface area and micropore volume.

The clear statement of the ISO norm 9277 [9] and the IUPAC recommendation [10] have stipulated a fundamental goal for the scientific use of the gas adsorption technique to describe surface and pore phenomena: the use of Ar at 87 K for many materials. While we can avoid the disadvantages I and II by using argon adsorption at 87 K, we need other alternatives to solve problem III, which will be discussed later in more detail.

The use of argon as adsorptive for surface and micropore characterization

First of all, the differences between nitrogen and argon adsorption for microporous materials should be considered. Fig. 2 shows that the nitrogen isotherms of a zeolite and an activated carbon is shifted to lower relative pressures, and the difference between Ar and N_2 is larger for the zeolite as compared to the activated carbon. That means, only a special part of the shift is caused by the temperature difference of 77 K and 87 K. The main part of the shift, and that is especially the case for the zeolite, is due to the specific quadrupole interactions between the N_2 molecule and the polar surface of the solid.

Additionally, the shift of the nitrogen isotherms to lower relative pressures causes another disadvantage of the N_2 measurements: the larger equilibration time at lower temperature and lower relative pressures increase the measuring time for N_2 measurements significantly, sometimes to a factor of two. Therefore, Ar sorption measurements at 87 K are more accurate from scientific point of view because the spherical Ar atom has no quadrupole moment. In addition, they are more precise because Ar measurements can be conducted in the optimal pressure range in a shorter analysis time.

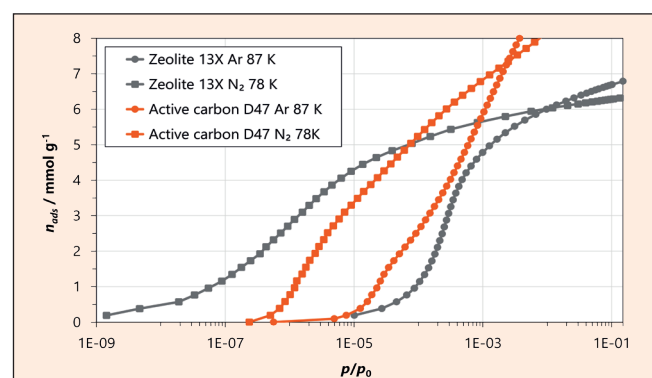


Figure 2 N_2 77 K and Ar 87 K isotherms of zeolite 13X (grey) and activated carbon D47 (orange), the N_2 77 K isotherms are shifted to the left (lower relative pressures)

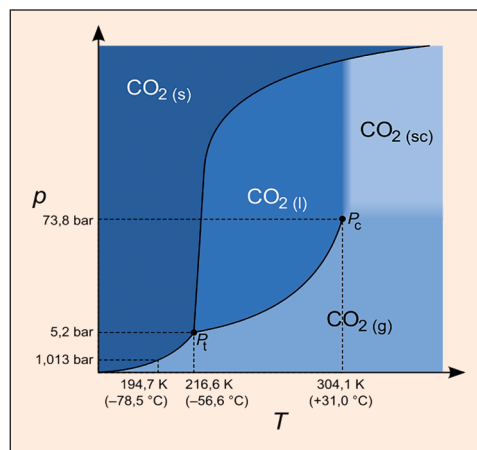


Figure 3 Phase diagram of carbon dioxide:
The liquid phase exists only at elevated pressure above the triple point

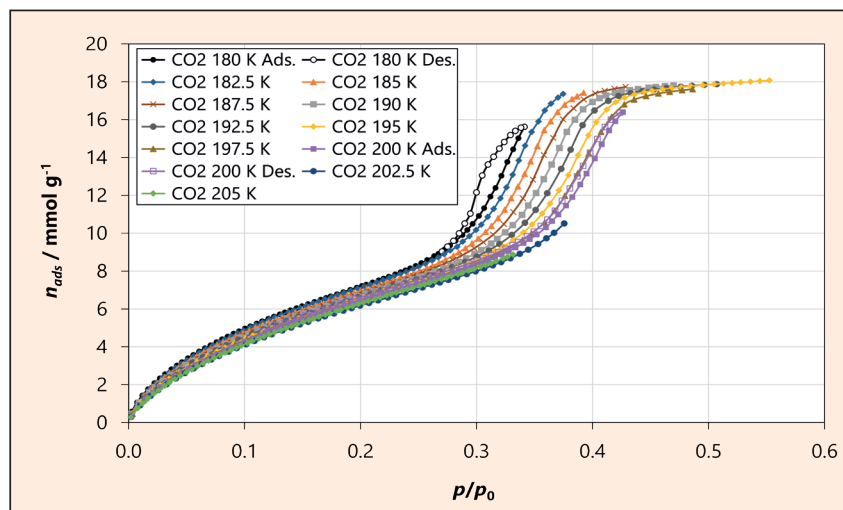


Figure 4 CO₂ isotherms in 2.5 K-steps; for clarity of vision, desorption curves are only shown for 180 K and 200 K – all other isotherms show similar hysteresis and are omitted [13]

Evidence for a liquid-like CO₂ adsorbate phase

Independent of the discussion about N₂ and Ar, the results of such standard measurements can only give a raw indication about the sorption behavior of CO₂ on a special material surface. In other words, the BET area or the calculated pore size distribution from an Ar 87 K isotherm cannot give an easy answer about the CO₂ adsorption behavior of that material. 3P Instruments offers simulation tools to estimate the sorption behavior for industrial purposes [15], but the users of classical sorption analyzers need direct CO₂ adsorption isotherms to estimate the CO₂ adsorption behavior of their materials.

CO₂ sorption analysis was performed in the temperature range from 180 K to 205 K (Fig. 4). Furthermore, Argon isotherms in the range from 87 K to 93 K were collected for comparison. These experiments were conducted on a 3P micro 300 with a cryoTune 87 module and a cryoTune 195 module for Argon and CO₂ analysis at a temperature stability of < 0.004 K.

When evaluating N₂ or Ar isotherms, one assumes a liquid-like adsorbate phase, e.g. saturation pressure of liquid adsorbate or density of liquid adsorbate to calculate pore volume by use of the Gurvitch rule. In comparison, the phase diagram of carbon dioxide (Fig. 3) shows a liquid phase which only exists at high pressures (between 5.2 and 73.8 bar) and above the triple point at 216.6 K. So what to do in the case of CO₂ adsorbate without a liquid phase under normal conditions?

In the literature, CO₂ isotherms are partially represented below the triple point of 216.6 K and in relation to the sublimation pressure of CO₂ [3 - 6]. For micropore calculations, other studies are using the vapor pressure of the undercooled liquid. The nature of the CO₂ adsorbate phase has significant relevance on the resulting material data for the calculations based on these CO₂ isotherms. We therefore investigated the pore filling of CO₂ in MCM-41 at different temperatures.

The analytical possibilities for CO₂ isotherms are a consequence from the vapor pressure of the dry-ice formation on the one hand and the maximum pressure of the analytical instrument applied on the other hand. The results in Fig. 4 showcase that the

MCM-41 pores are not fully filled below 185 K, as dry ice is formed by resublimation within the sample cell. Furthermore, the MCM-41 pores cannot be filled completely before reaching ambient pressures at temperature above 200 K. As the isotherms slope with following plateaus show, the adsorption data can be used for characterization of surface area and pores as well as CO₂ sorption capacity and isosteric heats of adsorption determination in a temperature range between 185 K and 200 K with good applicability.

While MCM-41 shows a complete filling of the 4.8 nm pores at 195 K (Fig. 4), literature shows that no mesopores > 5 nm can be filled at 195 K with CO₂ in a CMK-3 material [12]. It can therefore be concluded, that the limit for this method is at ~ 5 nm, meaning that larger pores cannot be characterized with CO₂ at 195 K, while smaller pores can be analyzed readily. Further, Fig. 4 shows the pore filling with CO₂ in the same relative pressure range as the corresponding Ar 87 K adsorption for MCM-41, which confirms the applicability of the saturation vapor pressure of the undercooled liquid CO₂.

The calculated volume of the MCM-41 pores < 5 nm is 0.64 cm³ g⁻¹ (Ar 87 K) and 0.63 cm³ g⁻¹, when assuming the adsorbate density of undercooled CO₂ liquid respectively (Tab. 1). If CO₂ would be adsorbed as resublimated dry ice, the calculated pore volume would be 20 % smaller which is however not correlating with the argon-based results.

Table 1 Calculated Pore volume of MCM-41 dependent on the adsorbate properties

Adsorbative	T / K	Pore volume / cm ³ g ⁻¹	Used adsorbate density from
Ar	87	0.64	Liquid argon
CO ₂	195	0.63	Undercooled CO ₂ liquid
CO ₂	195	0.51	CO ₂ ice

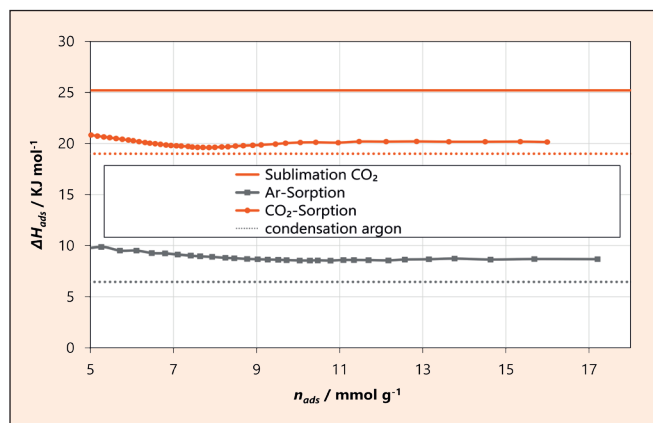


Figure 5 Isothermic heats of adsorption for MCM-41 in the pore filling range for CO₂ and Ar isotherms and compared to the heat of condensation and sublimation of CO₂

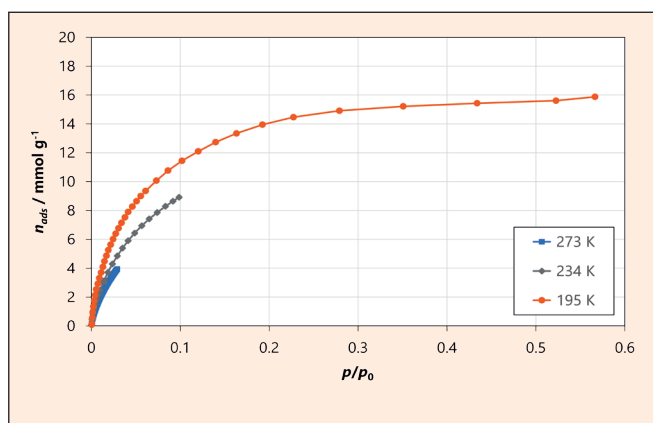


Figure 6 Active carbon CO₂ isotherms at 273 K, 234 K, and 195 K

The isosteric heats of adsorption for Ar and CO₂ calculated from their isotherms by using the Clausius-Clapeyron equation can be found in Fig. 5. These values are above the heats of condensation of the corresponding analysis gases which are 19 kJ mol⁻¹ for undercooled CO₂ and 6.4 kJ mol⁻¹ for argon. The heat of adsorption for CO₂ on MCM-41 is significantly lower than the heat of sublimation of 25.2 kJ mol⁻¹ of dry ice, and thus indicates a liquid-like adsorption phase as well.



Table 2 Active carbon results from the isotherms in Fig. 6 compared to Ar at 87 K

	CO ₂ 273 K	CO ₂ 234 K	CO ₂ 195 K	Ar 87 K
BET surface area / m ² g ⁻¹	1077	1092	1278	1458
Pore volume / cm ³ g ⁻¹	0.166	0.335	0.553	0.569

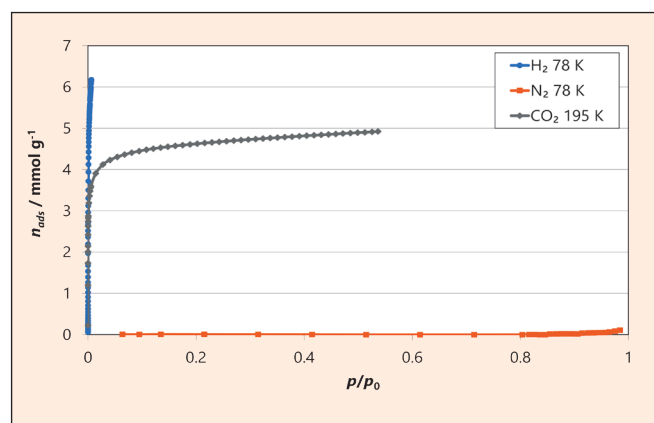


Figure 7 Effect of kinetic constraints on Zeolite 4A: N₂ does not fill the micropores because of the molecule size ratio to the low temperature of 77 K, H₂ fills the 0.4 nm micropores at 77 K because of smaller molecule size, but CO₂ at 195 K with similar molecule size to N₂ fills the 0.4 nm micropores because of the higher measuring temperature.

The ease of implementation and the advantages of CO₂ 195 K measurements

Fig. 6 and Tab. 2 demonstrate the main advantages of the CO₂ adsorption at 195 K in comparison to 273 K. Because of the temperature dependency of the saturation pressure p_0 and the limitation of classical gas sorption instruments to ambient pressure, the micropore filling with CO₂ at 273 K is not complete for many microporous materials at ambient pressure. The lower the temperature, the more micropores of the active carbon are filled. The 195 K isotherm not only reaches the isotherm plateau, but also covers the complete BET range up to the relative pressure of 0.6. Tab. 2 shows the differences in the results of the CO₂ isotherms at 273 K, 234 K, and 195 K as compared to Ar 87 K. The very small differences between the calculated pore volumes of the measurements using CO₂ at 195 K and Ar at 87 K can be explained with small uncertainties of the adsorbate densities. The deviation of 12 % between the BET areas between CO₂ 195 K and Ar 87 K is probably caused by the unclear position of the single CO₂ molecules on the solid surface. Molecules arranged flat have a different space requirement than molecules arranged edgewise on the solid surface.

It is therefore practicable to measure samples with Ar at 87 K if it is certain that no ultramicropores smaller than 0.5 nm are present. If the absence of such ultramicropores is not assured, respectively if N₂ or Ar results show unexpected low adsorbed volumes because of small ultramicropores (N₂ 77 K isotherm in Fig. 7), a CO₂ 195 K isotherm is the best solution for the determination of the micropore volume and the BET area.



Figure 8 3P micro 200 connected with two cryoTune 195

Fig. 8 gives an impression how easy the measurements at flexible temperatures can be done with the cryoTune 195. CO₂ or other adsorptives can be used in the range 180 K – 353 K, the dewar is filled with liquid nitrogen, and the cryo unit 195 is installed inside the dewar and is connected with the controller on the top or next to the analyzer. The short video how to install and use a cryoTune with a 3P analyzer or with an instrument from other manufacturers can be found at www.3p-instruments.com/de/analyzers/cryotune/.

Conclusion

1. The investigations proof that CO₂ below its triple point at 216.6 K shows the characteristics of a liquid phase adsorbate within pores smaller than 5 nm.
2. CO₂ sorption isotherms at 195 K can be described well with the saturation vapor pressure of undercooled liquid CO₂ and its corresponding density.
3. Classical sorption instruments (limited to about 1 bar) are capable of characterizing pores smaller than 5 nm by the use of CO₂ at 195 K, and therefore allow the study of the complete BET range as well as the micropore range compared to CO₂ sorption experiments at 273 K.
4. Due to its large quadrupole moment, CO₂ is suitable as a comparative adsorbate to Ar or N₂ for the study of surface polarities.
5. The higher analysis temperature of 195 K creates kinetic diffusion advantages when comparing CO₂ 195K to sorption studies with N₂ 77 K and Ar 87 K. This allows the analysis of ultramicropores with pore diameters below 0.5 nm in active carbons, molecular sieves or soil samples (clay or humic acids) with shorter analysis times and without kinetic hindrances.

6. The cryoTune series for easy and accurate thermostatic control between 82 K and 323 K enables new possibilities in CO₂ sorption studies of different material classes. Recommended parameters for CO₂ 195 K isotherm data reduction are:

- non-ideality coefficient: 0.000202 kPa⁻¹
- saturation pressure of undercooled liquid [11]: 188 kPa
- density of adsorbate phase: 1.258 g cm⁻³
- cross-sectional area of CO₂ adsorbate molecule [14]: 0.170 nm²

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Recording of single and multi-component isotherms using dynamic methods

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Introduction

The climate change is a widely discussed topic and therefore both scientific and industrial researchers are working in this field. Carbon dioxide plays a crucial role within this challenge, since CO₂ is mainly responsible for the blanket, trapping the heat in the atmosphere.

A simple literature research reveals that in the last 4 years around 18,000 different papers were published dealing with the topic of CO₂ adsorption. Often new materials are discussed highlighting the strong interest [1].

For the characterization or the suitability testing of new materials, single component isotherms are classically recorded. With the help of common adsorption models, such as the Ideal Adsorbed Solution (IAS) theory, the ideal separation behavior is then calculated [2]. The IAS theory is only applicable to "ideal adsorption processes", since the original theory is based on hypotheses, e.g., that the framework is thermodynamically inert [3]. Therefore, this theory has limitations for materials such as zeolites [4], MOFs [5] or carbon-based materials which mostly result in an over-evaluation of the material. A prediction of real competitive adsorption behavior based on only pure component isotherms is hard to realize, but highly desirable [6]. The alternative way for experimental characterization is to

include co-adsorption processes. However, this process can be very complicated since numerous parameters such as temperature, total pressure, and the composition of the gases, and thus the partial pressure, must be taken into account.

With the mixSorb S and the mixSorb SHP, it is now possible to record both single component isotherms up to a pressure of 8 bar (mixSorb S) / 50 bar (mixSorb SHP) and multi-component isotherms on one instrument.

In this article, different approaches are compared to prove the robustness of this method. For this purpose, isotherms of CO₂ and CH₄ were recorded using dynamic manometry, classical gravimetric adsorption and so-called step breakthroughs on a mixSorb SHP.

Material preparation

All following described experiments were conducted with the 3P reference material "AC-ref" which is an activated carbon from Blücher GmbH.

Prior the experiments the sample was heated at 150 °C under reduced pressure for 120 minutes to remove any residuals in the pores.

Device preparation

Up to now, the mixSorb device was used to determine breakthrough curves of gases or vapors on materials of interest. However, thanks to the modular design of the units, additional experiments can be carried out by making small technical changes to the equipment. Breakthrough curve experiments are conducted at a fixed pressure. Accordingly, it is of high interest to know the isothermal curve of the material over a wide pressure range in order to exploit the full potential of the material without having to perform numerous breakthrough experiments at different partial pressures. Based on this consideration, we were able to adapt the mixSorb S and SHP devices in such a way that it is now also possible to record the isotherm course of a material from 0.1 bar to 50 bar via dynamic experiments. To

Table 1 Summary of all conducted calibration experiments

#	Adsorber Filling	Gas	T / °C	Flow rate / mL min ⁻¹	Purpose
1	empty	He	25	20	<ul style="list-style-type: none"> ■ Determination of calibration factor He ■ Manifold volume
2	empty	He	50	20	
3	Cu beads	He	25	20	
4	empty	CH ₄	25	3	Conversion factor over the whole pressure range
5	empty	CO ₂	25	3	Conversion factor over the whole pressure range

perform such an analysis, the device must be equipped with a vacuum pump, which allows to evacuate parts of the device. In addition to this hardware extension, some minor calibration steps need to be performed (summarized in Tab. 1).

Firstly, three experiments are conducted to determine both, the calibration factor of helium and the manifold volume of the device. The first one is needed to determine the conversion factors of the used gases for experiments of interest. The conversion factor is needed since the used mass flow controllers are calibrated for nitrogen at a constant pressure. The manifold volume needs to be known since the sample volume can be calculated with this value.

The evaluation of these data is done with a special extension of the mixSorb Manager software.

Adsorption experiment - dynamic manometry

Basics

Once the conversion factor of CO₂ and CH₄ are known and the manifold volume is determined, the sample can be loaded in the adsorber. Firstly, the pressure rise curve of helium was recorded. Since the manifold volume of the device is known from the calibration, the sample volume can be determined by simple subtraction, because it can be assumed that no helium adsorbs on the activated carbon at 25 °C. This routine is comparable to a dead volume measurement of a static device. Subsequently, the pressure rise curve of each gas of which the conversion factor was previously determined can be measured with the same measuring routine. In this study, CO₂ and CH₄ were used because they are highly relevant in current research. Fig. 1A shows the pressure rise

curve of methane at 25 °C as an example. From this, the dosed quantity of gas can be calculated via the conversion factor and the density for STP conditions (Standard Temperature and Pressure). The detected amount is calculated from the gas density in the measuring cell, the gas density in the manifold and the free space volume of the measurement cell (accessible from the helium curve) (Fig. 1B). Finally, the difference between the dosed and detected amount is normalized to the sample mass and plotted against the corresponding pressure point to obtain an isotherm (Fig. 1C).

Temperature influence

One elegant feature of using the mixSorb SHP for recording high pressure isotherms is the easy temperature control. The experiments with CO₂ and CH₄ were conducted at four different temperatures, namely 0 °C, 25 °C, 50 °C and 70 °C. This would allow for example the determination of the heat of adsorption for any material and adsorptive.

As expected, the loading is increased at lower temperatures since the interactions of CO₂ or CH₄, respectively, with the activated carbon are increased.

One key point of this experiment is the flow rate. Adsorption processes are exothermal which means that heat is released during the adsorption of a gas on any surface. Therefore, the flow rate needs to be very low to allow heat transfer without changing the sample temperature. To evaluate the robustness of this method, gravimetric adsorption experiments with CH₄ at 0 °C as well as CO₂ at 0 °C and 70 °C were carried out on the same material. A high-pressure ultra-micro balance from Sartorius AG was used for this.

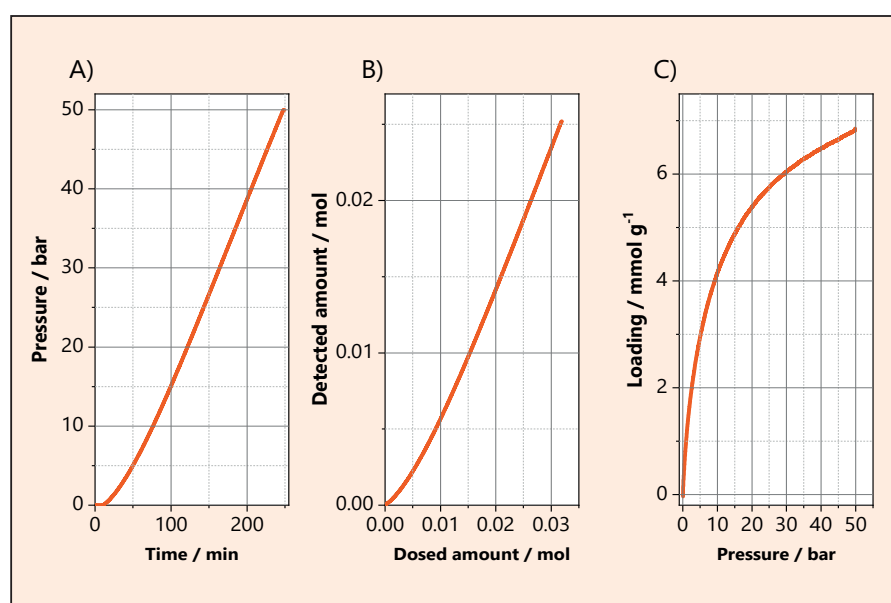


Figure 1 Evolution of measuring data from A) pressure rise curve over B) the detected amount vs dosed amount and C) the final isotherm

The direct comparison of both methods reveals that a very good match is observed especially in the pressure region between 1 and 10 bar. At elevated pressures, the dynamic isotherms are slightly deviating compared to the gravimetric method. This might be due to small differences in the measurement parameters, such as conversion factors or buoyancy correction parameters. However, technical processes such as pressure swing adsorption experiments are commonly performed between 10 and 40 bar [7] (partial pressure of the respective gas). The dynamic manometric method is therefore an easy and fast way to screen materials in this pressure range without the need for an additional high pressure gravimetric or manometric device.

Another interesting and noteworthy aspect is the measurement time, which is clearly depending on the used adsorbent, the used amount, the gas, the flow rate and the temperature. For example, the isotherm of CO₂ at 0 °C from 0.1 bar up to 30 bar was recorded in less than 5 hours, compared to ~20 hours using the gravimetric method. Additionally to that, one can get isotherms with very high number of data points with the dynamic method. This fact allows a good observation of the adsorbed amount in the pressure range of interest.

Step Uptakes for evaluation isotherms

Another possibility to record isotherms with the mixSorb device are the measurement of so-called step-uptakes. For that, a sequence of breakthrough experiments is recorded by continuously increasing the volume fraction of CO₂ or CH₄. Fig. 4A shows an example of this experiment for CH₄ in helium at 40 bar. In order to obtain individual pressure points and thus an isotherm, different volume fractions, namely 25, 40, 55, 70 and 85 %, of CH₄ were chosen. At a total pressure of 40 bar, this results in partial pressure points of 10, 16, 22, 28 and 34 bar. By integrating the area of each individual breakthrough experiment, the loading can be determined. Finally, the loadings are summed up and plotted against the partial pressure of CH₄ to obtain the isotherm (Fig. 4B). To get access to different pressure ranges, the MFC set-up of the used device might be customized.

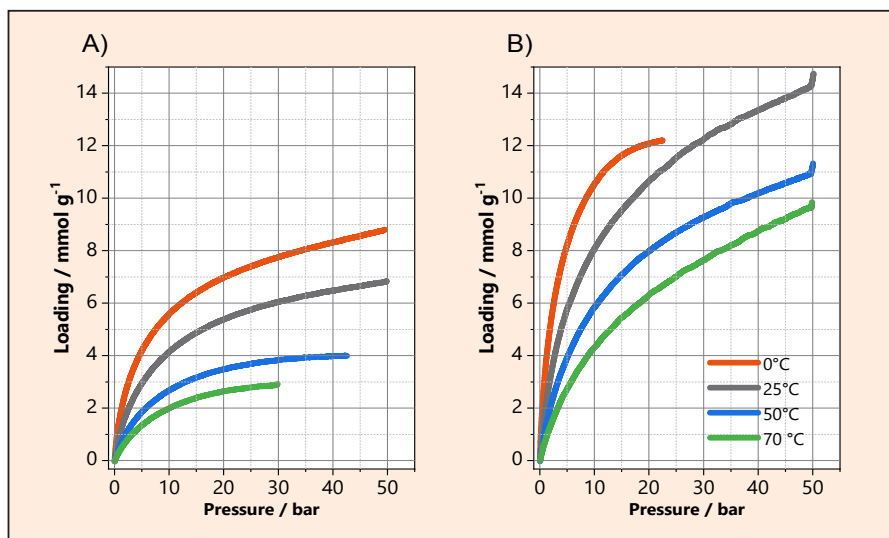


Figure 2 Isotherms of AC-ref at different temperatures with A) CH₄ and B) CO₂. The data were collected on a mixSorb SHP using the dynamic manometry method in a pressure range from 0.1 to 50 bar and a flow rate of 3 mL min⁻¹

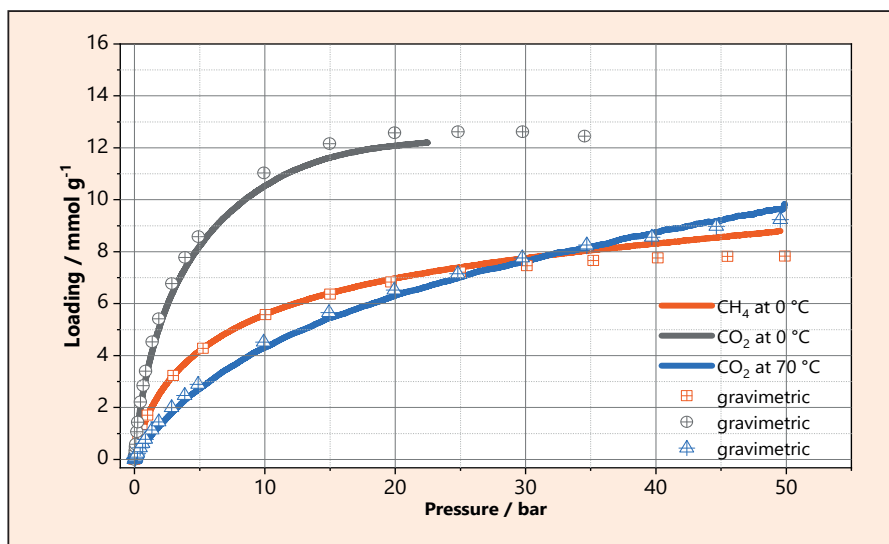


Figure 3 Comparison of sorption isotherms recorded on mixSorb SHP and gravimetric measured isotherms

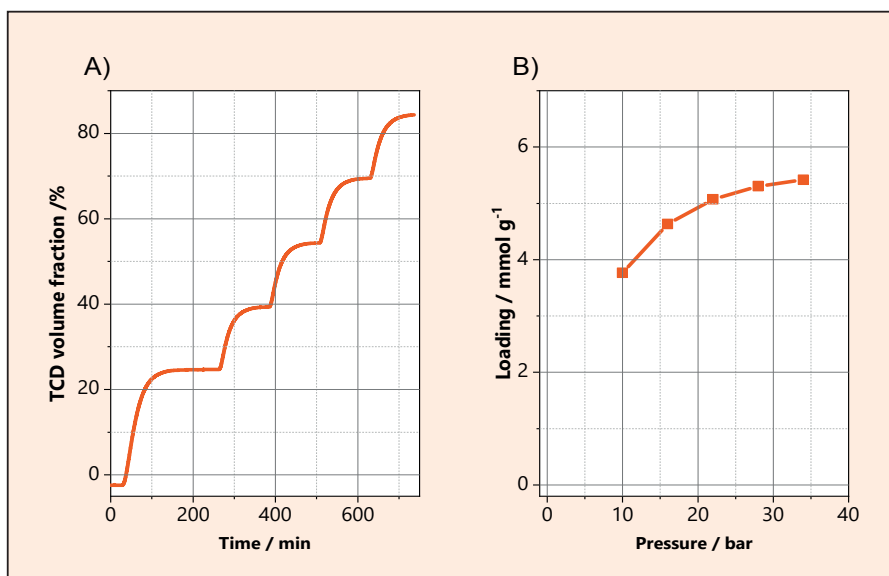


Figure 4 A) Sequence of 5 breakthrough experiments with 25, 40, 55, 70 and 85 % volume fraction of CH₄ in Helium at 40 bar with a total flow of 8 mL at 25 °C. B) The resulting isotherm

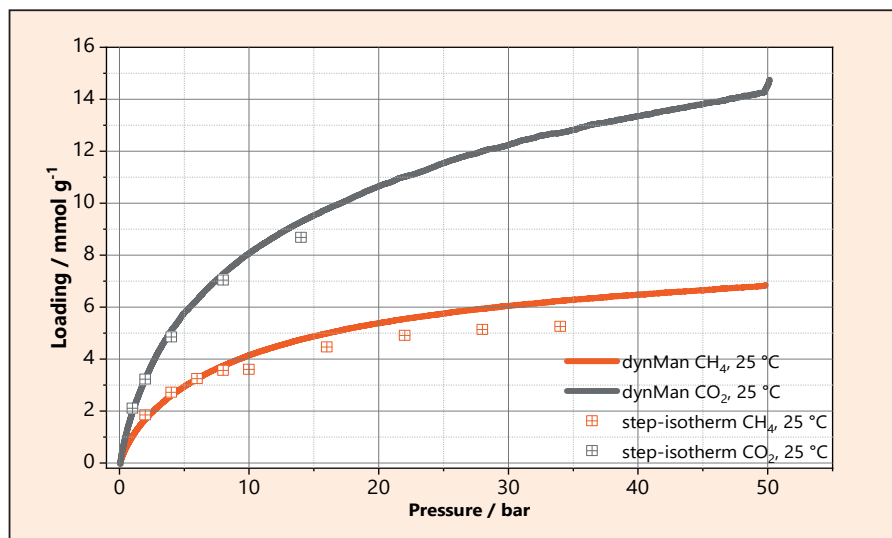


Figure 5 Comparison of isotherms from step-uptakes gained from sequential breakthrough experiments and dynamic manometry

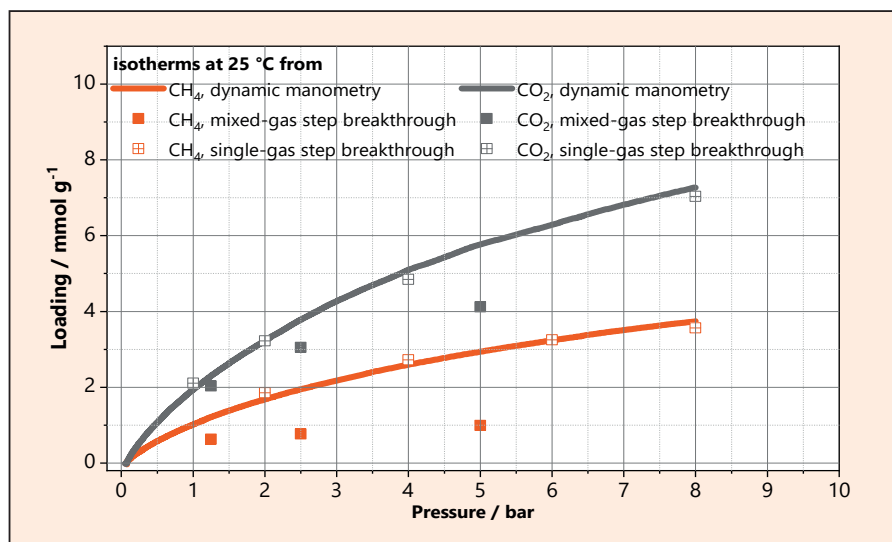


Figure 6 Comparison of all three methods

The advantage of step-uptakes is that a new adsorption step is only started when the TCD signal no longer changes, and therefore the sample is equilibrated. Fig. 5 shows the direct comparison of the dynamic manometry and the step isotherms for CH_4 and CO_2 . The pressure range below 10 bar for CH_4 and below 4 bar for CO_2 was covered by another sequential breakthrough experiment. It is noticeable that especially the pressure range below 10 bar shows a very good agreement with the dynamic manometry and accordingly also with the gravimetry. A possible

cause why the isotherms from step-uptakes slightly deviating at higher pressures could be a co-adsorption of helium [8] or mass transport limitations in the pores.

The issue with recording single-component isotherms is the fact that they are carried out without a carrier gas. However, real processes in technology always take place with a carrier gas. Although it is assumed that the carrier gas is inert to the materials, interactions occur that can influence the actual uptake behavior of the analyte.

Mixed gas adsorption

As mentioned at the beginning, the investigation of the simultaneous adsorption of two gases is of utmost importance. Often, the adsorption behavior of mixtures is only predicted from single isotherms, which then deviates strongly from the real adsorbed amounts in technical applications. With the presented method of sequential breakthroughs, it is also possible to investigate two or even three gases simultaneously. In this specific case, CH_4 and CO_2 were studied at three different partial pressures. The total pressure of the system was again 40 bar, but the partial pressures of the individual gases are limited by the MFC used, so that fractions of 3.125 % (1.25 bar), 6.25 % (2.5 bar) and 12.5 % (5 bar) were subject of this investigation.

As expected, all loadings of each component in the mixture are smaller than pure component equilibria, which indicates a sorptive competition of the fluids. This behavior must be taken into account by the design and dimensioning of technical sorption processes.

Calculation of mixed gas isotherms

Based on the single component experiments, it is possible to fit the data using the Toth equation, which is recommended for activated carbons [9].

Fig. 7A shows the comparison of the fitted isotherms of CH_4 and CO_2 in comparison with the experimental data collected at 25 °C. From this fitting, it is possible to calculate the single isotherms of a 50/50 mixture of CH_4 and CO_2 and the combined one (Fig. 7B).

The fitted isotherms show a very good agreement with the experimental ones (determination Coefficient $R^2 > 0.999$). More interestingly, the first two steps of the calculated mixed-gas isotherms match very well with the experiment, proving on the one hand the robustness of the method and on the other hand the applicability of the model used. At 10 bar, the model over-predicts the loading of both gases. At this point, a clear evaluation of the causes is not possible and needs to be tackled in further studies.



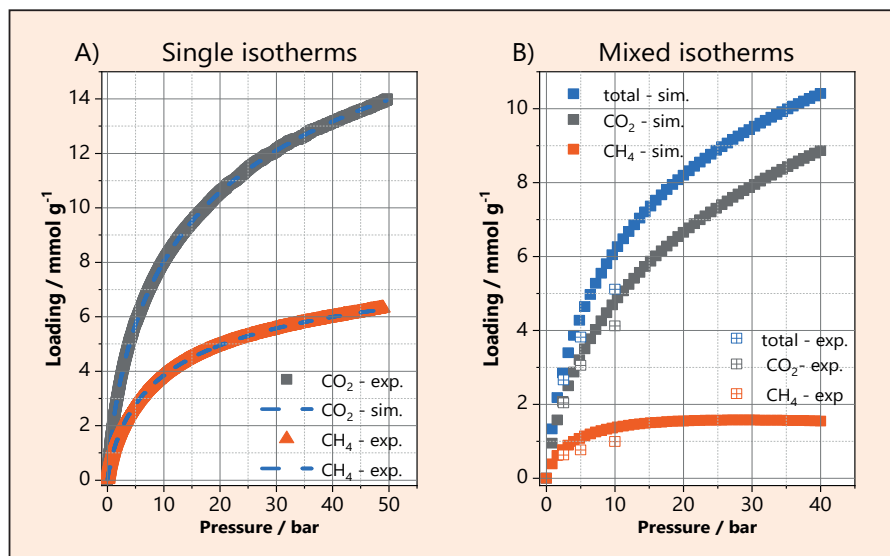


Figure 7 A) Comparison of fitted isotherms based on the Toth equation and the experimental isotherms from the dynamic manometry. B) Calculation of the mixed-gas isotherms of a 50/50 mixture of CH₄ and CO₂ in comparison to the experimental data measured with breakthrough experiments

Conclusion

In the present study, two different methods for recording high-pressure isotherms on the mixSorb SHP were compared with a gravimetric method. This showed that it is possible to record high-pressure pure component isotherms with the mixSorb SHP. This considerably minimizes the equipment costs, as it may no longer be necessary to purchase two devices for recording breakthrough curves and high-pressure isotherms. In addition to the financial savings, processes can be optimized and shortened. Rapid screening of new materials for application in separation, sensor technology or concentration can be enabled.

For future reliable studies on the adsorption or separation behavior of porous materials towards different gases, the measurement of breakthrough curves is essential. In our opinion, studies with mixed gas isotherms should also be confirmed to show the real behavior of a material towards adsorptives. First investigations on the mixSorb SHP showed that the theoretical approach overinterprets the adsorption behavior for the considered system. Furthermore, the measurement effort required to obtain calculated isotherms of mixtures is rather high compared to a mixture gas breakthrough curve. Through further investigations and optimizations, it will be possible in the future to obtain scientifically relevant and reliable results with this method in a short time and with a relatively manageable effort.

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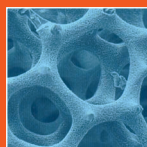
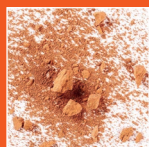
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From nanoparticles to oat drinks

A day in the particle laboratory of 3P Instruments

Dr. Denise Schneider, denise.schneider@3p-instruments.com



For more than 20 years, the 3P contract laboratory LabSPA (Laboratory for Scientific Particle Analysis) is offering analyses for the extended characterization of dispersions, powders and porous materials. Individual analyses, on-demand orders and comprehensive laboratory projects are on the agenda, as well as test and comparison measurements. On a laboratory area of 250 m², measuring instruments for more than 150 material parameters "all about particles" are available. The qualified employees with an accumulated laboratory experience of more than 100 years carry out several thousand measurements per year, evaluate them and provide assistance with application-related questions for customers who have problems with their equipment or measurements.

■ **Odelzhausen, Bavaria, Germany – 7:54 a.m.:** Barbara Danner unlocks the door to the 3P Instruments particle laboratory. The overnight measurements of adsorption isotherms for the determination of pore size distributions and specific surface areas are finished. The next samples are already waiting at the sample preparation station to be analyzed. Colleague Helmut Gronegger enters the lab shortly afterwards and takes over the evaluations and reweighing of further samples, while Ms. Danner carries out pending density determinations.

■ **8:17 a.m.:** Emails are processed and customer inquiries answered. The work continues straight away: incoming samples are screened so that express samples can be processed immediately, as they have to be completed within two working days. "In one week, express samples arrive three times on average," says Helmut Gronegger.

■ **10:23 a.m.:** Colleagues Dr. Marion Ferner, Kariene Eikermann and Bettina Deponte have been analyzing different materials for two hours. "Not only should the particle size be determined on various customer samples, but the particle shape should also be evaluated. Fortunately, we can realize both with the Bettersizer S3 Plus in a single device," says Bettina Deponte. Dr. Ferner points to a preliminary discussion in which a customer mentioned that his material might contain nanoparticles and that a nano classification according to the EU definition in the LabSPA nano test is necessary (see Particle World 21, p. 9). While Ms. Eikermann uses a Turbiscan TLab to analyze various oat drinks with regard to their foam stability, Dr. Ferner starts preparing protein solutions to identify aggregate formation using dynamic light scattering.

■ **1:00 p.m.:** Freshly strengthened by lunch and while measurements are running in the laboratory, it is now time for customer consultations and the writing of analysis reports. The 3P lab customers appreciate the detailed and meaningful result reports, which go far beyond simple instrument printouts and address the individual problems of the clients in detail.

LabSPA also receives samples from international partners, therefore the reports are prepared in either German or English. Yannice Ricci from the French partner Ribori Instruments judges the quality of the 3P reports: "Believe me from all reports that I receive from all suppliers I have, yours are complete and perfectly done!" The 3P employees are very proud of such evaluations.

■ **It never gets boring in the lab:** "I really like the mixture of practical work and evaluation or interpretation of the results. Surface and pore characterization by means of gas adsorption is very varied: we have recently started using many different adsorptives such as argon, krypton, hydrogen, xenon and carbon dioxide. In addition, the technical exchange with customers from a wide range of industries is an interesting enrichment - so every day is exciting all over again," says Helmut Gronegger.

"Especially the combination of our many available analytical methods enables us to accompany customers in projects both in research and development and in the optimization of processes. Here we are constantly challenged to learn about current topics in the pharmaceutical, cosmetics, agricultural and food industries. For me, this is what makes our LabSPA so appealing," enthuses Ms. Eikermann.

■ **Meanwhile, it is late afternoon, 5:00 p.m.:** The colleagues from the laboratory make sure that the overnight measurements are running properly - because new results are already being sent to the customers the next day.

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