PARTICLE WORLD

Technical Papers of 3P Instruments
EDITION 21
SEPTEMBER 2020

Determination of particle size and shape using sand as example

When is a material "nano"? - Nano-material test according to EU definition

Studies on adsorptive CO_2 removal

30th company anniversary - participate in the raffle now!

Contents

Imprint

Editor:
3P Instruments GmbH & Co. KG
Rudolf-Diesel-Straße 12
85235 Odelzhausen | Germany
Tel. +49 8134 9324 0
info@3P-instruments.de
www.3P-instruments.de

Editorial staff:
Dr. Denise Schneider

Illustrations:
3P Instruments, Adobe Stock, unsplash

Dear Readers,

This edition of Particle World 21 provides an update on news in the field of the characterization of powders, particles and pores. This year, 3P Instruments celebrates its 30th anniversary. Back in 1990, our company was founded as Quantachrome GmbH, has been independent for a long time and was renamed 3P Instruments two years ago. We appreciate the uncounted good wishes for our anniversary, such as from our cooperation partner INC e.V., with whom we have been involved in intensive project work for years; or from Altamira Instruments, our partner in the field of chemisorption, or Bettersize Instruments, the innovator in the field of particle size and particle shape. Enjoy reading technical articles from these and other areas that exemplify the range of different 3P application solutions:

- using a recognized method, our LabSPA (Lab for Scientific Particle Analysis) has been identifying the nanomaterials of many companies in accordance with the EU definition 2011/696EU for years;
- the mixSorb instrument series supported 3P Instruments to become a global player in the field of gas and vapor mixture adsorption enabling the investigation of CO_2 reduction under real conditions, including globally relevant separation and purification applications;
- with acoustic spectroscopy from Dispersion Technology and the Turbiscan technology from Formulaction, dispersions (emulsions and suspensions) are characterized in their original concentration; the Bettersizer S3 Plus with its combination of laser diffraction and dynamic image analysis enables particle analysis much closer to reality than was previously possible;
- in the field of gas adsorption, 3P Instruments offers new possibilities for the investigation of materials with different surface properties with the cryoTune and 3P sorption instrument series.

Our 30th company anniversary is a time to reflect on many successful years, during which numerous customers attested an excellent service to us. This service comprises high-quality technical service, expert laboratory measurements with detailed result reports as well as friendly and competent administrative support. Our company's name change and restructuring, the successful cooperation launch with device manufacturers Bettersize, JWGB and Altamira as well as a strengthened focus on our customer relationships have been our main priorities in the past few years. I am very grateful to both our entire 3P team and our customers, who have remained loyal to us with almost no exception throughout these challenging times. We will continue to win our equipment users and laboratory customers with innovative solutions and high-quality service.

Enjoy reading Particle World 21! Let me wish you all the best, especially health and success!

Dr. Dietmar Klank

Crossword puzzle for the 3P company anniversary

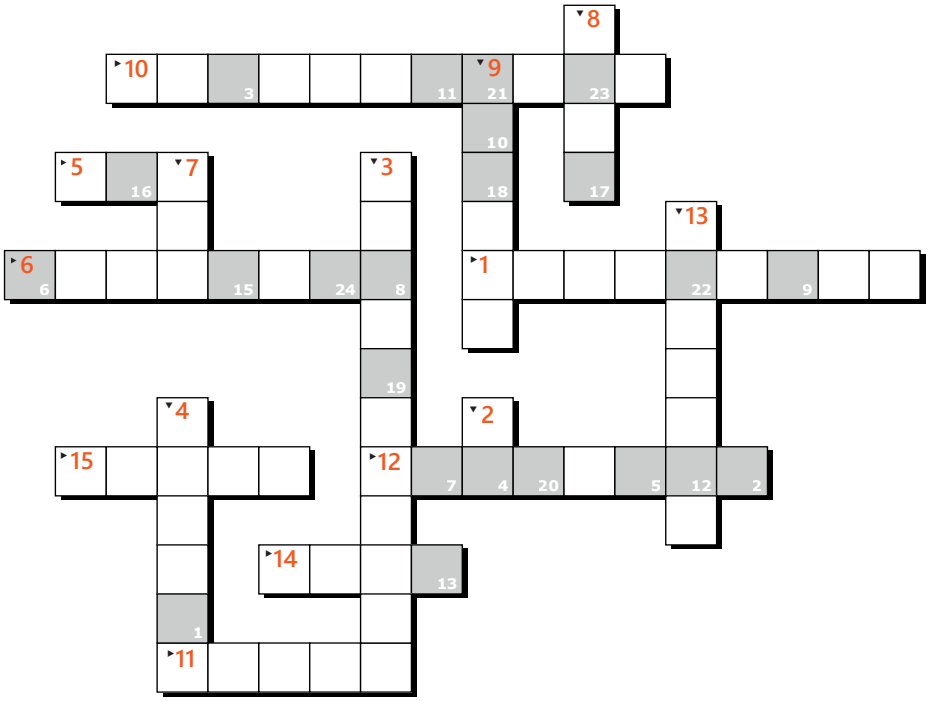
Celebrate with us and win great prizes!

Celebrate with us and win great prizes! Simply send the solution word by e-mail to **info@3P-instruments.com.** We will draw ten winners among the correct entries for the following prizes:

- **Voucher for**
  - a free participation in the 3P training seminar (German language) on the characterization of dispersions and powders and/or powders and porous materials, November 2021)
  - a free participation in the 3P Adsorption Week (English) on 12th April and/or 13th April 2021 in Leipzig (https://www.3p-instruments.com/adsorption-week/)
- **Voucher of 250 €** for contract analyses in the 3P contract laboratory (https://www.3p-instruments.com/contract-analyses/)
- **Free standard material according to 3P-list** (value approx. 250 Euro)
- **Book prices, available are:**
  - „Adsorption by Powders and Porous Solids – Principles, Methodology and Applications" (Françoise Rouquerol, Jean Rouquerol and Kenneth Sing)
  - „Characterization of Liquids, Dispersions, Emulsions, and Porous Materials Using Ultrasound" (Andrei S. Dukhin, Philip J. Goetz)
  - A book voucher of 100 Euro

By the way, you will find all the answers to the questions in this Particle World. The deadline is the **31th December 2020**. The ten winners will be notified by email, can then **choose one of the prizes** and specify the delivery address. The prizes will be sent free of charge by mail to the address provided by the winner. *

* The organizer points out that all personal data of the participants will not be given to third parties. Legal recourse is excluded.



Solution

1	2	3	4	5	6	7	8	9	10	11	12	13	C	15	16	17	18	19	20	21	22	23	24

1. Technology for the characterization of formulations
2. Abbreviation of "Dispersion Technology"
3. Location (town) of the headquarters of 3P Instruments
4. Abbreviation of the 3P contract laboratory "Laboratory for Scientific Particle Analysis"
5. Short form of measuring method for determining specific surfaces
6. Tempering option for sorption measurements in the range 82-323 K
7. Number of CCD cameras in the "Bettersizer S3 Plus"
8. Number of steps in the characterization of formulations
9. Which birthday does 3P Instruments celebrate in 2020?
10. Term for the science of mixing different components with the purpose of achieving desired properties or specifications of a product
11. Which noble gas is recommended for adsorption measurements at 87 K?
12. Manufacturer of chemisorption analyzers
13. Instrument family for adsorption of gas mixtures and breakthrough curve measurements
14. Abbreviation for "Volume Specific Surface Area"
15. Last name of the CEO of 3P Instruments

Service of analyzers of the manufacturers Cilas, Quantachrome and Altamira

As the former Quantachrome GmbH, we continue to look after the analytical instruments from the manufacturers Cilas and Quantachrome supplied by us as well as the old AMI instruments (for chemisorption experiments and temperature-programmed reactions) of our new partner Altamira.

Our experienced service technicians will continue to service the following analytical instruments supplied by 3P Instruments (formerly Quantachrome GmbH):

- Cilas 920, 930, 990, 1064, 1180, 1090, 1190
- Quantachrome devices, e.g., Monosorb, NOVA, Autosorb, gas pycnometers and much more

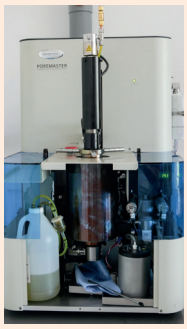
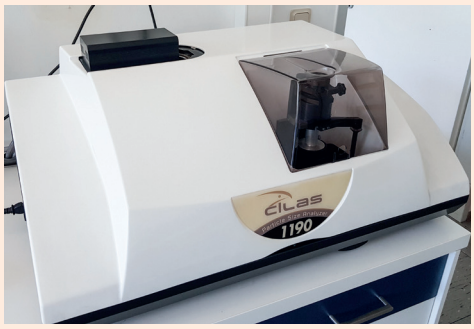
Before assuming that your older Cilas or Quantachrome device is beyond repair, be sure to contact **service@3P-instruments.com** for a free consultation.

3P Instruments still offers service and maintenance contracts, as well as spare parts, accessories and consumables (measuring cells, filling rods, heating jackets, dewars, etc.) for Cilas and Quantachrome instruments! You can also request standard materials and spare parts catalogues for the devices supplied by us.

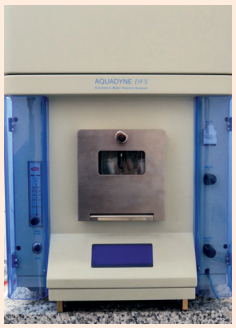
In addition, the purchase of Cilas and Quantachrome used equipment through our customer-friendly 3P service can still be worthwhile. Here are a few examples from our second hand instruments list:

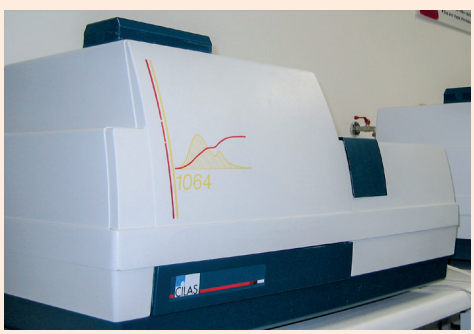
- Autosorb-1-MP for 15.000 Euro
- Cilas 920 or Cilas 930 for 12.000 Euro
- Bettersize Nanoptic (DLS device for nanoparticles) for 14.000 Euro

Our service offers and used equipment are both economically and ecologically reasonable: Check with 3P Instruments whether the further operation of your laser granulometer or gas sorption device is worthwhile! Save resources and save yourself a possibly unnecessary change of equipment in the laboratory.

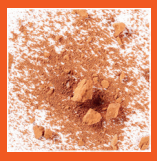







Investigation of different sands with the Bettersizer S3 Plus regarding their suitability for concrete production

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


Introduction

Sand is an essential raw material for the production of concrete in the construction industry. According to a study by the UNEP /1/ (United Nations Environment Programme), more than 30 billion tons of building sand are currently consumed each year to produce concrete. The sand used is mainly sea sand, partly river sand, which creates long-term problems for the environment and wildlife such as destruction of animal habitats, land shortage etc. when mined. For this reason, alternatives have been sought for a long time.

One possibility is the recycling of demolition waste and the resulting raw materials, e.g. brick dust. In addition, desert sand seems to be an almost unlimited resource. However, investigations by the Federal Institute for Geosciences in Hannover/Germany have shown that desert sand is not suitable as building sand due to the lack of certain size fractions such as coarse and medium grain size /1/.

For the ultimate suitability of a sand as a concrete raw material, the following main criteria apply:

1. Profitability (production costs) and sustainability (environmental compatibility)
2. Morphology of the sand grains (size distribution, particle shape)

For the examination of point 2., i.e. the powder morphology, two physical measuring methods are particularly suitable for sands, static light scattering /2/ and dynamic image analysis /3/. The Bettersizer S3 Plus combines both methods in a unique way and is therefore perfectly suitable for this task.

The Bettersizer S3 Plus

The schematic measurement setup of the Bettersizer S3 Plus is shown in Fig.1: During the measurement, the particles dispersed in a liquid medium are pumped through a double cell system. Laser light (532 nm) hits the particles in the first cell and is scattered characteristically depending on the size distribution. The scattered light is reliably detected over the range of 0.02 – 165°. This extremely large measuring range is realized using the DLOIOS system, a patented single-laser technique with double lens system and oblique light incidence.

In the second cuvette, the particles are continuously photographed, evaluated and statistically classified by the image analysis system, consisting of two high-speed CCD cameras and high-precision telecentric lenses, at a rate of up to 10,000 particles/minute in real time. The cameras have a 15-(0.5X lens) and 300-fold (10X lens) magnification. They can be used individually or combined and cover a particle size range from 1 – 3,500 µm. In summary, the Bettersizer S3 Plus with its unique design allows

- the exact particle size measurement of very small particles from 10 nm (DLOIOS technique)
- real number and volume distributions with suitable equivalent size diameters (CCD camera technology)
- higher accuracy in the coarse range than conventional static light scattering devices (combination method DLOIOS and CCD camera technology)
- Detection of individual oversized grains, agglomerates, air bubbles (CCD camera technology)
- Shape analysis with more than 20 specific shape parameters

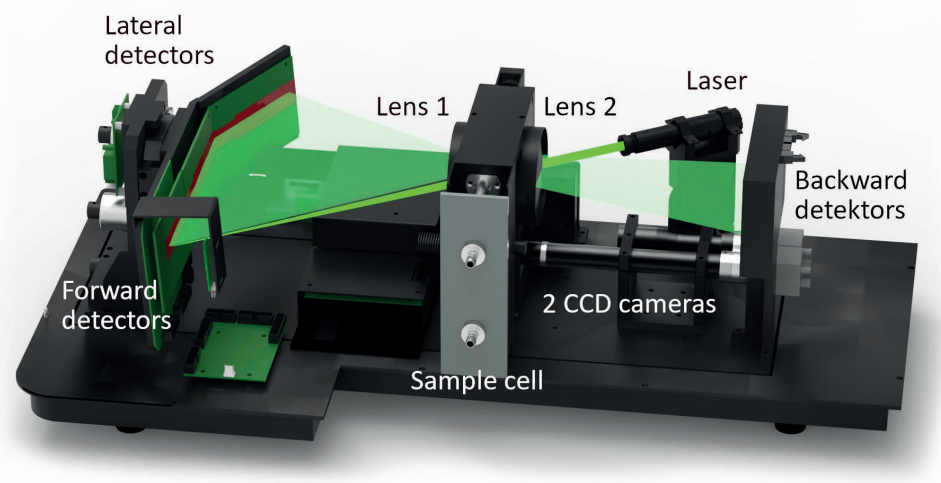


Figure 1
Schematic measurement setup of the Bettersizer S3 Plus (double cuvette system with DLOIOS technology and CCD camera unit)

Experimental and results

Materials, sample preparation and experiments

A standard sand (CEN standard sand DIN EN 196-1) commercially available in the construction industry was used as reference for the investigations. Accordingly, it meets the requirements for the processing properties of the liquid cement paste and the mechanical properties of the finished concrete.

As test sands, two crushed brick sands and a desert sand (untreated and "mechanically roughened") were used. All samples were riffled in advance over several stages until the required representative test quantity (approx. 2 g) was obtained. Tab. 1 gives an overview of all samples.

In each case, a representative sample of sand was added to the dispersing bath of a Bettersizer S3 Plus. After a two-minute exposure to the internal ultrasonic dispersing system (50 W), the sample was measured using static light scattering, dynamic image analysis and the combined method /4/. All measurements were performed on at least two different samples to test the reproducibility.

Results

It was found that all measurements were reproducible. In addition, image analysis using the two CCD cameras 0.5X and 10X in combination proved to be the most suitable for particle size measurement.

Fig. 2 shows the particle size distribution of the five sands measured by dynamic image analysis of the Bettersizer S3 Plus /4/. The CE area equivalent diameter was used as the size parameter and the volume distribution as the measure of the distribution. Tab. 2 gives an overview of the most important diameter values of the curves shown in Fig. 2.

Compared to the standard sand, all test sands have different distribution characteristics: The standard sand is polymodal with different maxima at about 200, 300, 800 and 1500 µm. The desert sands on the other hand show an almost monomodal distribution with a maximum at about 350 – 450 µm. It can also be stated that the treatment of the desert sand has led to a lowering of the maximum and to the formation of a small fine

Table 1 *Overview of the measured sands*

Designation	Description
Standard sand (CEN standard sand DIN EN 196-1)	Standard sand used as concrete sand
Crushed brick sand 1	Common ground crushed brick sand
Crushed brick sand 2	Common ground crushed brick sand
Desert sand untreated	Untreated desert sand
Desert sand treated	Desert sand roughened by mechanical processing DS 1

Table 2 *Important diameter values of all sands in µm (CE-equivalent area diameter)*

Designation	D3	D10	D16	D25	D50	D84	D90	D99
Standard sand (CEN standard sand DIN EN 196-1)	150.90	216.80	298.60	461.40	958.90	1678	1828	2422
Crushed brick sand 1	14.50	24.91	37.25	78.17	227.00	854.40	1129	1974
Crushed brick sand 2	10.95	16.48	20.93	28.74	83.24	364.90	569.70	1164
Desert sand untreated	145.90	223.10	263.10	316.80	433.60	656.90	740.80	1544
Desert sand treated	80.78	138.20	178.40	227.60	335.60	516.20	576.20	743.70

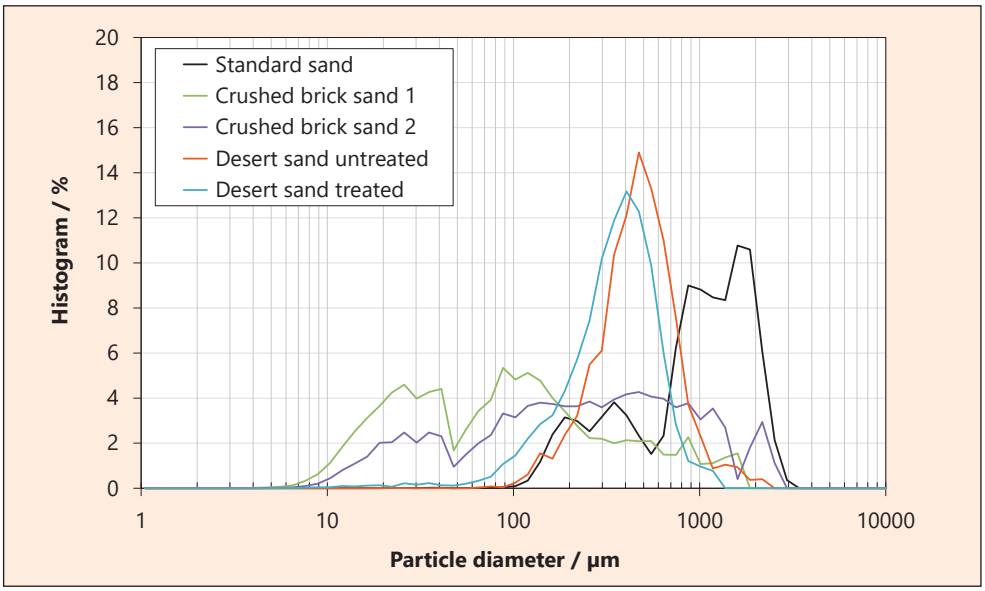


Figure 2
Particle size distribution of the sands, measured with the Bettersizer S3 Plus and using the combination method of static light scattering and dynamic image analysis

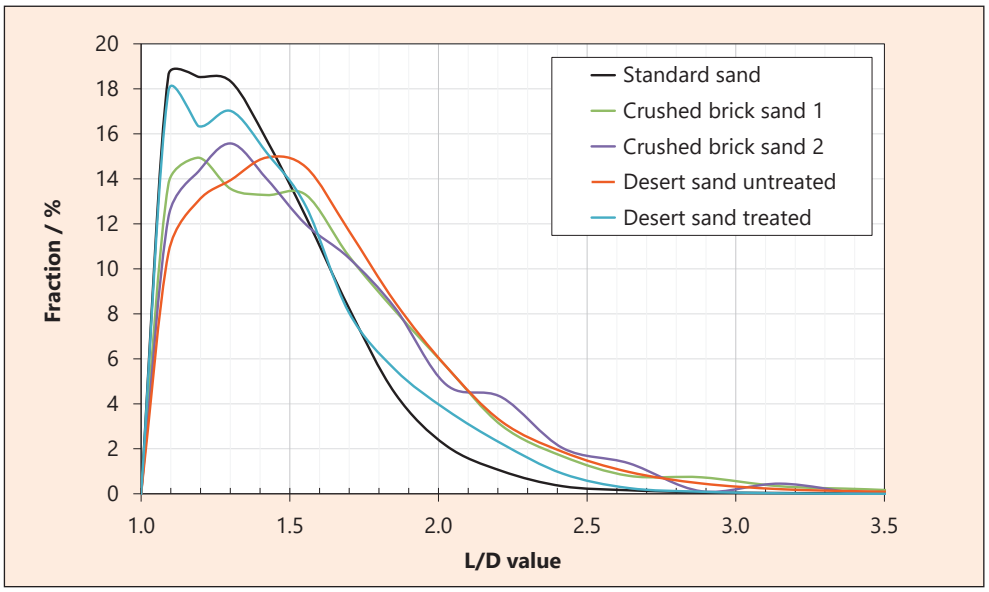


Figure 3
L/D value distribution of the five sands (dynamic image analysis)

fraction (< 100 µm), which previously (in the untreated state) did not exist. The crushed brick sands are very broadly distributed between about 10 µm and 2 – 3 mm and have by far the highest fine fraction (< 100 µm) of all sands.

In summary, it can be said that none of the crushed brick or desert test sands show a particle size distribution that is approximately similar to that of the standard sand.

The so-called L/D value is used as a measure for the elongation of the sand grain particles: This represents the ratio of maximum (L) to minimum Feret diameter (D) /5/. The parameter varies between 1 and almost infinite. The higher this value becomes, the more elongated the particle is. An L/D value of 1 indicates an ideal spherical shape.

In order to be able to compare the sands well with each other, the L/D values from an equivalent diameter value of 300 µm were considered. Tab. 3 shows the 2-dimensional image, the equivalent diameter and the L/D value from the single particle lists of the samples of the standard sand, desert sand untreated and crushed brick sand 2. Fig. 3 shows the L/D-value distribution of the sands in comparison and Tab. 4 summarizes the characteristic percentages of these curves.

The untreated desert sand particles show the highest L/D values, i.e. these sand particles have the largest elongation and are on average more elliptical than spherical pronounced. The standard sand has the smallest elongation, i.e. it is rather compact and not elongated. Interestingly, the treated desert sand comes closest to the standard sand in terms of the L/D value. The crushed brick sands, on the other hand, are - just like the untreated desert sand - much more inhomogeneous with regard to the elongation of the particles.

Table 3 *Extract from the single particle list of standard sand, desert sand untreated and crushed brick sand 1 with 2-D image, equivalent diameter and L/D value*

	Standard sand		Desert sand untreated		Crushed brick sand 2	
						
Diameter / µm	2576	2320	1986	1872	1452	1405
L/D-value	1.537	1.255	2.554	1.662	1.757	1.499
						
Diameter / µm	1555	1543	1464	1312	1089	1186
L/D-value	1.197	1.470	2.130	1.518	1.214	1.544
						
Diameter / µm	1032	1028	994.3	988.2	889.5	796.4
L/D-value	1.014	1.034	1.463	1.849	1.482	1.050

Table 4 *Characteristic L/D values of standard sand, untreated desert sand and crushed brick*

	L/D 3	L/D 10	L/D 25	L/D 50	L/D 75	L/D 90	L/D 97	Average L/D	Number of particles > 300 µm	Total number of particles
Standard sand > 300 µm	1.014	1.049	1.126	1.270	1.463	1.667	1.918	1.322	25601	400000
Crushed brick sand 1 > 300 µm	1.020	1.066	1.167	1.372	1.638	1.929	2.306	1.440	3004	900000
Crushed brick sand 2 > 300 µm	1.022	1.074	1.181	1.369	1.648	1.963	2.308	1.453	886	900000
Desert sand untreated > 300 µm	1.025	1.085	1.202	1.401	1.650	1.933	2.294	1.470	81791	400000
Desert sand treated > 300 µm	1.015	1.030	1.135	1.294	1.511	1.776	2.067	1.359	17424	400000

Summary

The particle size and L/D value measurements with the Bettersizer S3 Plus show that the four test sands show significant differences in grain morphology compared to the polymodal standard sand. None of the test sands has a similar particle size distribution as the standard material. The desert sands are monomodally distributed, the main volume fraction of the particles is much finer. The crushed brick sands are polymodally distributed, but the coarse parts are missing considerably and they have a high volume fraction of fine particles < 100 µm, which is almost not present in standard sand.

In terms of grain expansion (L/D value), only the treated desert sand is similar to the standard sand, while the untreated desert sand and the crushed brick sands have a much larger expansion, i.e. are more elliptical than spherical pronounced.

The desert sands and crushed brick sands will therefore behave differently from the standard sand when used as concrete sand: The processing properties will be different and the mechanical properties of the solid building material will vary.

References

/1/ Press release BGR [available only in German]; https://www.bgr.bund.de/DE/Gemeinsames/Nachrichten/Aktuelles/2019/2019-08-06_wuestensand.html

/2/ ISO 13320 Particle size analysis - Laser diffraction methods

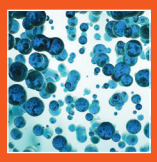
/3/ ISO 13322-2 Particle size analysis - Image analysis methods - Part 2: Dynamic image analysis method

/4/ Particle World Edition 19, June 2018, p. 4-8, 3P Instruments (https://www.3p-instruments.com/wp-content/uploads/2018/05/PARTICLE-WORLD-19.pdf)

/5/ ISO 9276-6 Representation of results of particle size analysis - Part 6: Descriptive and quantitative representation of particle shape and morphology

Nanomaterial identification in accordance with EU definition (2011/696/EU)

Dr. Marion Ferner, marion.ferner@3P-instruments.com




Nanomaterials – Chances and challenges

Nanomaterials frequently differ in their physical-chemical characteristics from their macroscopic characteristics of larger particles of the same material. Therefore, nano technology forms the basis for the development of numerous new and innovative products in a variety of industries (such as medicine/pharmaceutical, cosmetics, food products, dyes, electronics) and has recently experienced rapid growth /1/. However, the question has long been raised whether nanomaterials have negative effects on the environment and thus possibly pose a risk to human and animal health. Manufacturers from various industries are aware of this risk. Identification, characterization and risk assessment of nanomaterials is regulated in numerous ordinances and involve major challenges for the producers of such systems.

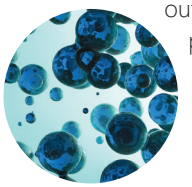
The EU Commission published a recommendation 2011/696/EU on October 18, 2011 on whether a material should actually be considered as nanomaterial /2/ (EU NM definition):

" 'Nanomaterial' means a natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50 % or more of the particles in the number size distribution, one or more external dimensions is in the size range 1 nm-100 nm."

To date, there is no generally valid measurement method available for classifying a material as nanomaterial or non-nanomaterial. Many cases require a combination of different measurement methods /3/. The difficulty of this definition lies in the following requirements:

Dispersion requirement

Many analytical measurement methods such as the particle size measurement from static or dynamic light scattering require the transformation of dry powders into stabilized dispersions without changing the basic material structure (single particles, aggregate or agglomerate). This demands the introduction of material-specific dispersion regulations.

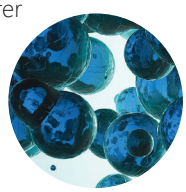


Particle number distribution requirement

There is no measurement method capable of measuring the particle number distribution of particle collections over a broad measuring range, with the necessary statistics and within a reasonable time frame and resolution.

Macroscopic fitting methods such as static light scattering, acoustic spectroscopy that determine a certain physical size of a dispersion and fit this result in the determination of the size distribution, mainly provide volume distributions. The conversion into a number distribution is difficult due to lacking precision for individual particles in the marginal areas of the size distribution.

Counting methods such as image analysis either do not offer the required measuring range for small particle sizes, or the statistics are not very meaningful.



Statistics requirements

Powders with a wide size distribution are a challenge for various methods with high-quality statistics. Most measuring methods are optimized for idealized samples or are limited to a defined size range. Accordingly, small particles (< 100 nm) can hardly be indicated in the presence of large particles (> 500 nm) using dynamic light scattering, as their signal is superimposed. Therefore, the detection of polydisperse samples is difficult.

Dimension requirement

Standard analysis methods do not detect platelets or nanorods/fibres with an external dimension resp. one or two external dimensions in the range of 1 nm to 100 nm correctly. Many measurement methods deliver equivalent diameters as result, which causes an overestimation of the minimal external diameter in platelets and nanorods/fibres resulting in misinterpretations.

LabSPA – Identification of nanomaterials

Depending on the sample to be analyzed (powder or dispersion), the 3P Instruments "LabSPA" (Laboratory for Scientific Particle Analysis) offers two different methods for the classification of a material as nanomaterial or non-nanomaterial:

- **LabSPA nano test:**
  method specifically designed by 3P Instruments to identify particles in dispersions, also suitable for widely spread samples
- **VSSA nano screening** for powder samples

Fig. 1 provides an overview. Both methods are described in detail below.

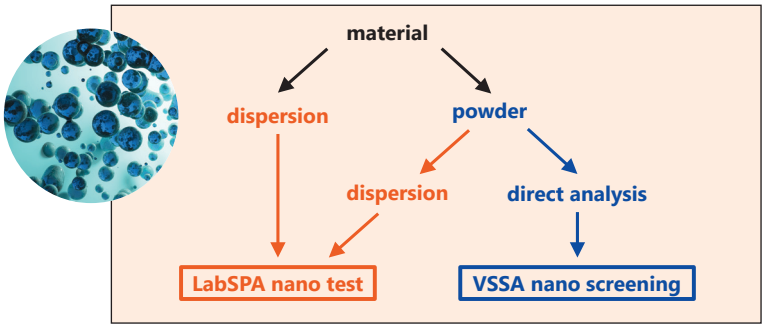


Figure 1 *LabSPA nanomaterial identification*

LabSPA nano test

LabSPA nano test is used to determine the number distribution and follows the requirements of EU NM definition (see Fig. 2).

1. Requirement: particle in dispersion

The LabSPA nano test is limited to particles in liquid dispersions. Therefore, powder samples require optimal, material-specific dispersing conditions. Again, the LabSPA is the ideal contact for application-based tasks. The following parameters are in focus when preparing a dispersion specification:

- Selection of a suitable dispersion medium (+ stabilizing additive, if necessary)
- Optimum solid content
- De-agglomeration through energy input (e.g. by ultrasound and/or high speed dissolver)
- Dispersion stability

If possible, dispersion should be carried out without the use of longer-chain additives, as these can change the particle diameter under certain circumstances. Therefore, electrostatic stabilization is preferable.

2. Sample separation into different size fractions

Standard analysis methods frequently detect particles in the submicron range, especially < 200 nm, incorrectly when large

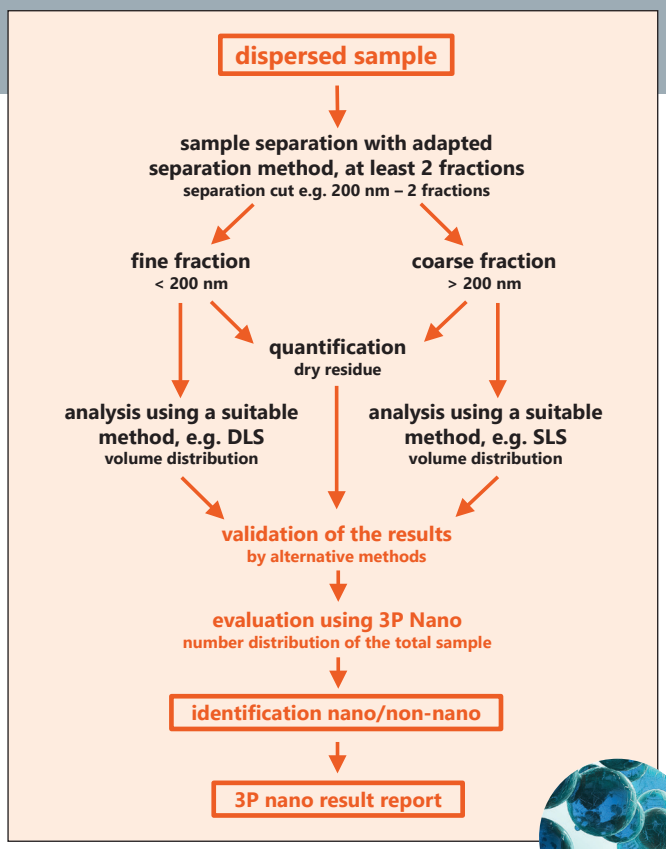


Figure 2 *LabSPA nano test*

particles are present. Therefore, the LabSPA nano test carries out a quantitative separation of the dispersed sample into at least two size fractions (e.g. coarse and fine fraction) using a suitable separation technique (e.g. centrifugation). Subsequently, the fractions are separately analyzed for their particle size distribution (see below). In this way, signal superposition by large particles (especially with widely distributed samples) and thus the problem of statistically recording small particles can be avoided. A separation cut is made near but above 100 nm (e.g. 200 nm). When using a centrifuge as a separation method, its adjustment (rotational speed and duration) is based on a modified Stokes' equation. The separation of the fine fraction (e.g. < 200 nm) from the coarse fraction (e.g. >200 nm) is achieved by separating the supernatant from the sediment.

3. Determination of particle size distributions (volume distributions) of individual fractions

The LabSPA nano test analyzes the separated fractions obtained with the sample separation regarding their particle size distribution: Suitable measuring methods are used for the respective sample type and preferably include dynamic light scattering (DLS) and acoustic attenuation spectroscopy for submicron and nanoscale particles as well as static light scattering (SLS) for microscale particles.

4. Quantitative determination of the individual fractions (dry residue)

The determination of the quantitative proportions of the different fractions is absolutely necessary for the evaluation of the obtained particle size distributions in the LabSPA nano test. This is done by evaporation and subsequent mass determination.

5. Particle count using special software "3P Nano" and report

According to the EU NM definition, a material tested in the LabSPA nano test is classified as nanomaterial, if the particle number $d_{< 100\ nm}$ is larger than particle number $d_{> 100\ nm}$, in accordance with following ratio:

$$d_{< 100\ nm} > d_{> 100\ nm}\ (supernatant) + d_{> 100\ nm}\ (sediment)\ (1)$$

In order to meet this number-based requirement for the identification of nanomaterials, 3P Instruments has developed a special software (3P Nano) that enables the conversion of volume-based distributions into number distributions, even from different analysis methods. Taking into account the determined weight proportions of the various fractions, 3P Nano provides the number distribution of the total sample by combining the distribution curves as a result and, consequently, a clear identification of whether the material examined in the LabSPA nano test is a nanomaterial according to the EU NM definition or not. The 3P Nano result report summarizes the results of the LabSPA nano test (Fig. 5).

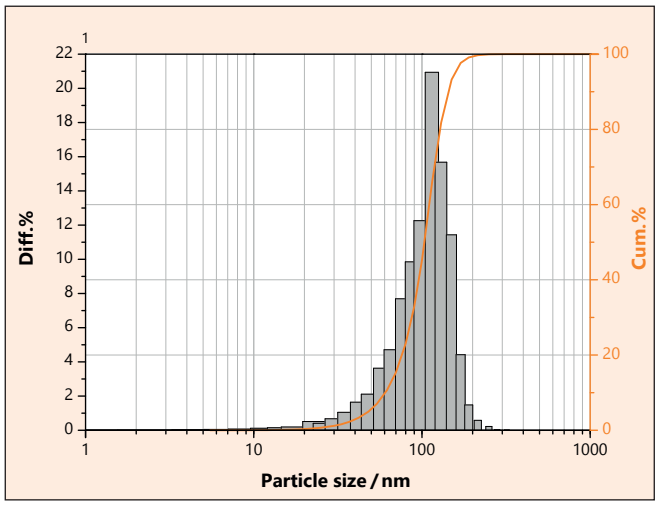


Figure 3 LabSPA nano test with separation into two fractions – volume distribution of the fine fraction < 200 nm of a widely distributed sample (dynamic light scattering, Bettersize Nanoptic 90)

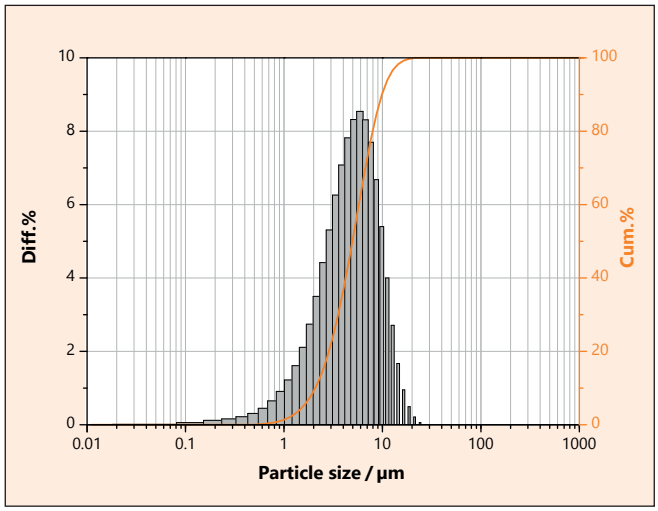
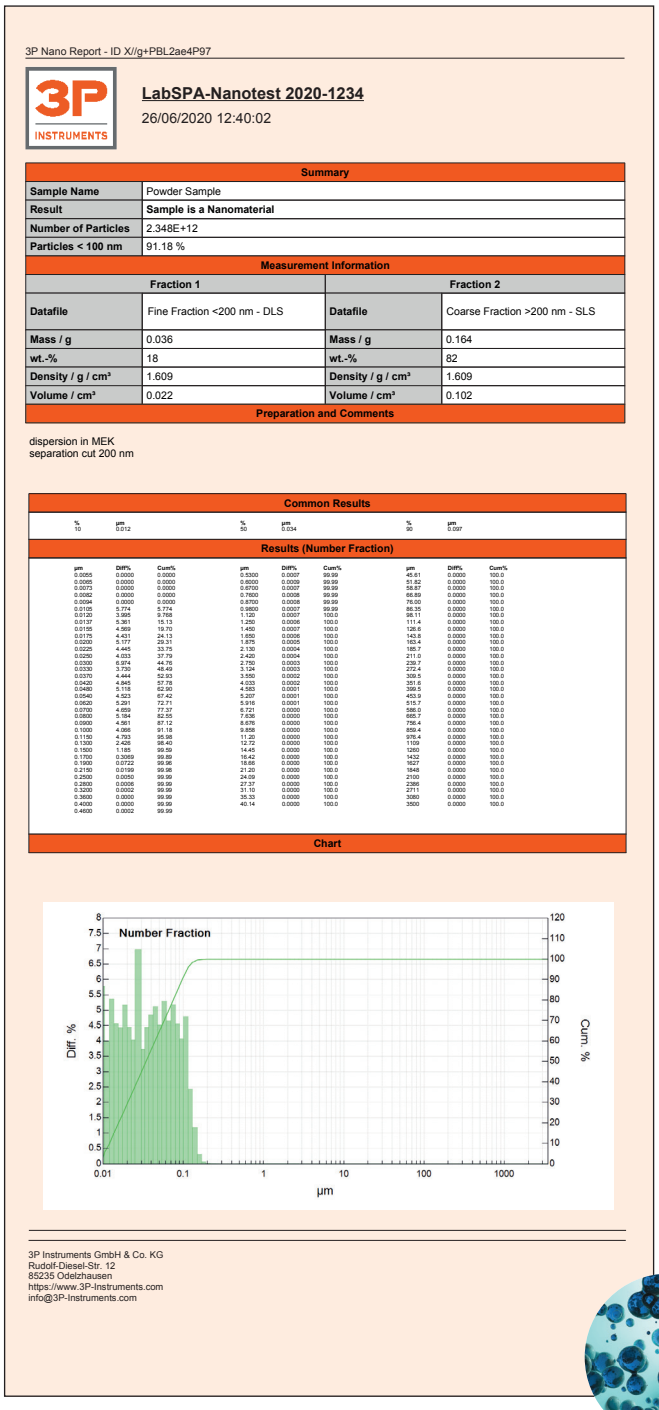


Figure 4 LabSPA nano test with separation into two fractions – volume distribution of the coarse fraction > 200 nm of a widely distributed sample (static light scattering, Bettersizer S3 Plus)

LabSPA nano test on the example of a widely distributed powder sample

A widely distributed powder sample was dispersed in dispersion medium after establishing a suitable dispersing rule. This sample was analyzed in the LabSPA nano test. Samples were separately analyzed and quantified, after they were separated into fine and coarse fractions by centrifugation at a separation cut of 200 nm (Fig. 3 and 4). The 3P Nano software analyzed the results. With the help of 3P Nano, both volume distributions are combined and transferred into a number distribution, taking into account the corresponding mass fractions (Fig. 5).



3P Nano Report - ID X//g+PBL2ae4P97

LabSPA-Nanotest 2020-1234

26/06/2020 12:40:02

Summary	
Sample Name	Powder Sample
Result	Sample is a Nanomaterial
Number of Particles	2.348E+12
Particles < 100 nm	91.18 %

Measurement Information			
Fraction 1		Fraction 2	
Datafile	Fine Fraction <200 nm - DLS	Datafile	Coarse Fraction >200 nm - SLS
Mass / g	0.036	Mass / g	0.164
wt.-%	18	wt.-%	82
Density / g / cm³	1.609	Density / g / cm³	1.609
Volume / cm³	0.022	Volume / cm³	0.102

Preparation and Comments

dispersion in MEK
separation cut 200 nm

Common Results

Results (Number Fraction)

Chart

3P Instruments GmbH & Co. KG
Rudolf-Diesel-Str. 12
85235 Odelzhausen
https://www.3P-Instruments.com
info@3P-Instruments.com

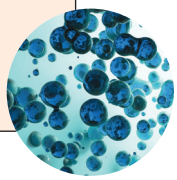


Figure 5 LabSPA nano with separation into two fractions - 3P Nano report after LabSPA nano test of a widely distributed powder sample

VSSA nano screening

The LabSPA nano test is limited to dispersions. However, often there is no suitable dispersion method available for a powder or the direct analysis of a powder is mandatory. In this case, VSSA (Volume Specific Surface Area) nano-screening by determining the BET surface area and density offers a solution. An overview on VSSA nano screening is presented in Fig. 6.

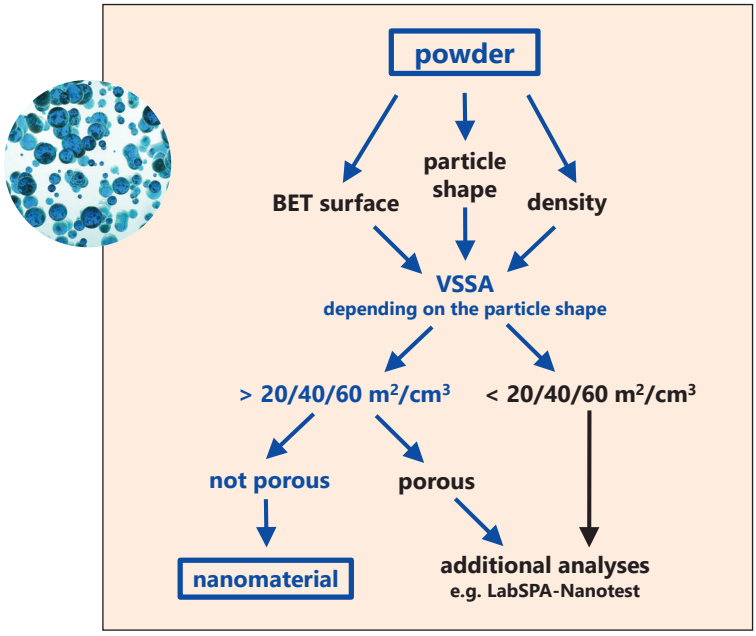


Figure 6 VSSA nano screening

Alternative EU NM identification for powder samples

VSSA nano screening is limited to dry powder and is an alternative method for classifying a material as a nanomaterial according to EU NM definition /2/:

"Where technically feasible and requested in specific legislation, compliance with the definition … may be determined … on the basis of the specific surface area by volume. A material should be considered as falling under the definition … where the specific surface area by volume of the material is greater than 60 m^2/cm^3.

However, a material which, based on its number size distribution, is a nanomaterial should be considered as complying with the definition … even if the material has a specific surface area lower than 60 m^2/cm^3."

According to this definition, and taking into account equation 2, a material is a nanomaterial, if the specific surface/volume (= VSSA) is larger than 60 m^2/cm^3

$$VSSA = SSA \cdot \rho \qquad (2)$$

with: VSSA…Volume Specific Surface Area, surface/volume / m^2/cm^3
SSA…Surface Specific Area, BET surface / m^2/g
ρ…Density / g/cm^3

However, the specific surface must not be used to prove that a material is not a nanomaterial. Especially fibers or platelets with only two or one dimensions between 1 and 100 nm produce false negative results. If VSSA < 60 m^2/cm^3, additional examinations, e.g. image analysis using electron microscopy, are necessary /3/.

VSSA depending on the particle shape

Image analysis methods provide important information on the particle shape. An adaptation of the VSSA method to non-spherical particles is absolutely necessary /4/, as it is also recommended by the EU Commission /3/. To classify a material as nano or non-nano material, the particle shape in equation 3 is considered when determining the VSSA limit:

$$VSSA_{cutoff} = 60\ m^2/cm^3 \cdot \frac{D}{3} \qquad (3)$$

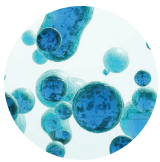
with: $VSSA_{cutoff}$… lower limit for the classification of a material as nanomaterial
D…number of dimensions 1-100 nm (D = 3 for spherical particles, D = 2 for fibres/nanorods, D = 1 for platelets)

Thus, taking into account the particle shape, a material is a nanomaterial if:

- Spherical particle: VSSA > 60 m^2/cm^3
- Fibres/nanorods: VSSA > 40 m^2/cm^3
- Platelets: VSSA > 20 m^2/cm^3

The above limits are only valid for non-porous materials. The VSSA method is not suitable for porous materials. Due to the additional surface area of the pores in porous materials, the VSSA method produces false positive results. The BET measurement method, which is the basis for determining the SSA, cannot distinguish between pore surface and outer surface. If the limit values are exceeded, either the porosity of the examined material must be excluded or the internal surface of the pores must be subtracted from the BET surface by suitable measuring methods in order to apply the VSSA method for nanomaterial identification.

If the values fall below the above-mentioned limits, the conclusion that the material under investigation is not a nanomaterial is inadmissible /3/. The VSSA screening is critically evaluated for nanomaterial identification /3/. In case of doubt, the LabSPA nanotest for number-based NM identification should be preferred.



References

/1/ https://nanodata.echa.europa.eu/index.php?r=product%2Foverview

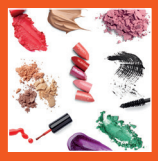
/2/ European Commission, Commission Recommendation of 18 October 2011 on the definition of nanomaterial, Off. J. Eur. Union L 275, p. 38–40, 2011.

/3/ H. Rauscher, A. Mech, N. Gibson, D. Gilliland, A. Held, V. Kestens, R. Koeber, T.P.J. Linsinger, E.A. Stefaniak: Identification of nanomaterials through measurements, JRC Science for Policy Report EUR 29942 EN (2019)

/4/ W. Wohlleben, J. Mielke, A. Bianchin, A. Ghanem, H. Freiberger, H. Rauscher, M. Gemeinert, V. Hodoroaba, Reliable nanoparticle classification of powders using the volume-specific surface area method, Journal of Nanoparticle Research (2017) 19: 61

Complete characterization of formulations in 4 steps – an overview

Dipl.-Ing. Matthias Lesti,
matthias.lesti@3p-instruments.com



Formulating is the science of mixing different components together to achieve desired properties or specification. The ingredients are often not compatible and they must be mixed following a specific strict procedure in order to obtain a uniform and durable structure. This task is even more challenging when formulating with natural ingredients. The constant need to create new formulations or reformulate existing formulations requires thorough monitoring of formulation properties.

Stability

«Is it stable?»

«What is the shelf life?»

«Does it pass my stability criteria?»

Dispersibility

«How to disperse my phases?»

«Which solvent?»

«Which type of surfactant and concentration?»

Redispersion

»Can it be re-homogenized?»

»Is manual stirring enough?»

Size

»How large are the particles?»

»Do they agglomerate in the original concentration?"

»Are they nano?»

The composition of a formulation can be summarized as following:

- **Liquid continuous phase:** water is the most commonly used solvent but not limited to water only.
- **Dispersed phase:** can be liquid, solid or air. The particularity of this phase is that it is non-compatible with the continuous phase. The particle/droplet size can vary from few nanometers up to visible particles and the concentration ranges from ppm up to 95 %. This phase is the one that provides the desired end-user properties to the formulation (e. g. moisturizer, coating properties, drugs, nutrition).
- **Stabilizers:** are one of the key components of the formulation. Stabilizers are essential to control the dispersion, achieve the desired particle size and maintain a "stable" formulation. Nowadays, the number of possibilities is very large and depends on the application. Surfactants have been, and remain, the most commonly used stabilizers. They are either coming from chemical synthesis or from natural, renewable resources. Recent studies push towards using polymers and biopolymers, proteins and even other particles as stabilizers.
- **Additives:** are added to adjust side properties nevertheless essential for the user appreciation, for example: viscosity, scent, colour, texture. The additive can have affinity with either the continuous phase, the dispersed phase or the interface.

Formulations can contain over 50 different ingredients and the fine adjustment of the compositions is the key to a perfect formulation. During the formulation study, it is of high importance to also consider process, packaging and dispensing, storage conditions and usage conditions. The formula needs to be adapted to all these external parameters.

Formulation characterization steps

Whether you are formulating paints, electronic slurries, cosmetics, food or pharmaceutical suspensions, there are four crucial steps to be considered for a full and complete characterization of your formula:

Dispersibility

Dispersibility is the ability to "suspend particles" (either solid, liquid or gas) in the continuous phase in a way that allows them to be equally distributed in the whole volume and preserve their original size. It can be considered as the foundation stone of the formulation process.

It is affected by:

- Solvent affinity with the particles
- Interactions between the continuous phase and stabilizer
- Interactions between the stabilizers and particles
- Stabilizer coverage of the interface
- Preparation process: mixing tool used, time and speed of mixing

A poor dispersibility will have a significant impact on final product specification as the particle/droplet size and homogeneity will affect overall stability and so the durability in time of colours for inks, polishing efficiency for CMP slurries (Chemical Mechanical Planarization), and taste for flavored food emulsions, ...

Monitoring the dispersibility will save time in formulation development and decision making. The dispersibility ratio (DR) is the most appropriate parameter to evaluate if the particle size in suspension corresponds to the so-called "primary" particle size.

Particle size

Once the particles are well dispersed, it is essential to be able to characterize their size. Recent studies (ISO norms, Formulaction application notes) show the importance of measuring particle size in the real sample (i.e., without dilution or mechanical stress) to understand the behavior of the particle in presence of other ingredients and upon the process used.

The ability to characterize the particle size without sample dilution is of great importance especially when working with nanoparticles where dilution can have huge impact on the size (it can trigger agglomeration for example).

Stability and Shelf Life

Well dispersed particles within the required size range must remain in that state for time of use of the formulation. Thus, stability is the next important parameter to consider. Indeed, stability is the capacity to remain unchanged with respect to predefined criteria over a given time under conditions of storage and use. Most of formed dispersions are thermodynamically unstable and with time, and destabilization is to be expected.

There are various destabilization phenomena and they have different origins. They can be classified in two main categories

- Size growth: Agglomeration-aggregation, coalescence, Ostwald ripening
- Particle/droplet migration: Sedimentation, creaming, phase separation, demixing

Thermodynamically speaking, a "stable" formulation does not exist (except for microemulsions). However, a certain degree of destabilization (usually not visually observed) over a given period is accepted for emulsions. Thus, the need to quantify the magnitude of occurring phenomena. This can be done using the so-called Turbiscan Stability Index (TSI) that can quantify and rank formulations according to their destabilization at a given time. This acceptable amount of variation and "period" is defined depending on the final application of the formulation and can vary from minutes (inhaler, vaccines) up to several years (cosmetics, paints).

Redispersion – the "shake before use" strategy

For some applications, destabilizations are inevitable but reversible. Paints, injectable drugs, dairy drinks are just few examples of such formulations and required to be shaken before use.

- Would the manual shaking be enough to well redisperse the formulation?
- How long should it be shaken for?
- What method to use: stirring, shaking, mixing, ultrasonic bath?
- Can the formulation retrieve its initial dispersion state?

All these questions must be considered, and the recommendations must be made to the user. Once the sample redispersion is achieved, the formulation is renewed and parameters like size, stability and re-redispersion can be studied again and again. It is of great interest to understand if the formulation can retrieve its original state and properties. How many of these "life cycles" can the formulation support before destabilization is irreversible (and under which storage conditions)?

Turbiscan: The global approach

The Turbiscan® technology is the most complete tool for formulation characterization: from dispersibility, average particle size, stability quantifying and monitoring, to redispersion studies. Dispersibility and particle size are measured with a single measurement (less than 30 seconds), without dilution or sample preparation. Stability is characterized up to 200 times faster than naked eye and provides full understanding of the destabilization mechanism and stability ranking of the formulation.

The Turbiscan technology is a unique tool providing full characterization of your formulation with an extremely wide range of applications:

- Electronics
- Polymers
- Raw Materials
- Pharmaceuticals
- Home and Personal Care
- Food and Beverages
- Agrochemicals
- Paint and Inks

You have a question about the characterization of formulations? You are welcome to write your question to **info@3P-instruments.com**, we will contact you immediately!

The acoustic spectrometer DT-1210 for particle size and zeta potential measurements of very small amounts of concentrated dispersions

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

Introduction

Zeta potential and particle size distribution of liquid suspensions and emulsions are important parameters for the evaluation of dispersion quality. Many methods available on the market require the sample to be diluted and specially prepared to determine these quantities, which almost always changes the actual properties of the suspension or emulsion. In contrast, when using acoustic methods, in most cases a measurement on the original concentrated sample is possible.

The acoustic spectrometers of the DT series in the DT-1200, DT-1201 and DT-1202 versions have been established for many years in various industries such as the ceramics and building materials industry. The systems are designed to determine the zeta potential and particle size distribution of dispersions within a very wide concentration range (0.1 - 60 vol %): Even paste-like or sedimenting slurries can be measured.

Until now, a limiting circumstance for particle size measurement was the required minimum sample size of about 30 ml. For this reason, Dispersion Technology has recently developed the DT-1210, which is based on the same technology as the current standard device DT-1202, but requires considerably less sample volume (> 3 ml). This article introduces the instrument and its measuring possibilities.

DT-1210

Particle size measurement with acoustic attenuation spectroscopy

The measuring principle of acoustic attenuation spectroscopy for particle size measurement, which forms the basis for the DT-1210, can be seen in Fig. 1: It is a transmission method, i.e. transmitter and detector are located on opposite sides of the dispersion to be measured. The sample is placed in the sample chamber in its original condition. Short ultrasonic pulses (bursts, intensity I_0) with a precisely defined frequency and amplitude are coupled directly into the dispersion at the start of the measurement and are weakened when passing through the sample (attenuation, intensity I). The attenuated pulses are detected in 180°, and a complete frequency range (f = 1 – 100 MHz) is measured. Following applies to the acoustic attenuation A (dB/cm MHz):

$$A\left(\mathrm{dB}/\mathrm{cm}/\mathrm{MHz}\right) = \frac{10}{fL}\log\left(\frac{I_0}{I}\right) \quad (1)$$

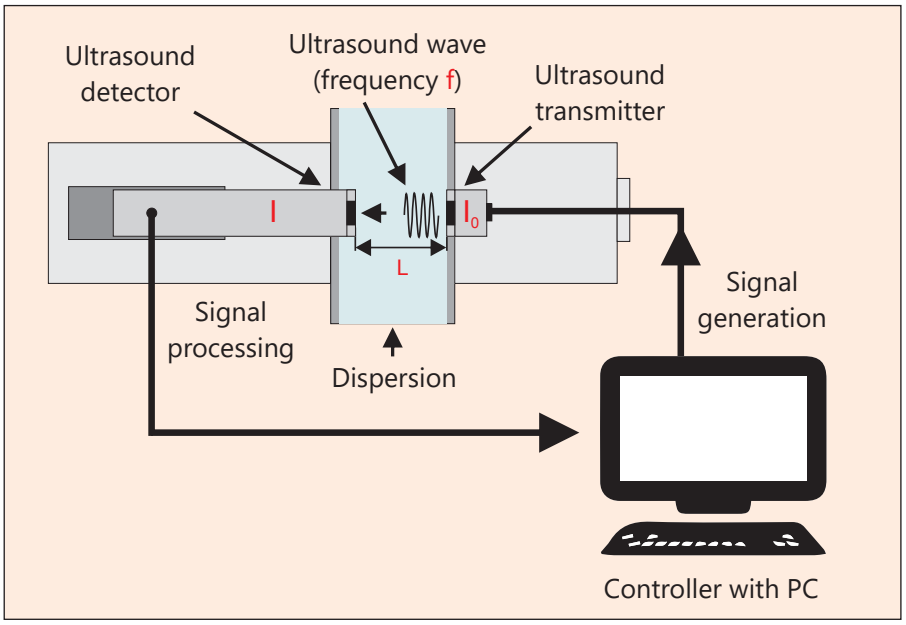


Figure 1 *Measuring principle of acoustic attenuation spectroscopy for particle size determination (DT-1210)*

f is the frequency, L the distance between transmitter and detector, I0 the intensity of the output wave and I the intensity of the attenuated wave.

The wide concentration application range (0.1 – 60 vol%) results from the unique gap technology: each frequency spectrum is determined at multiple transmitter-detector distances to achieve an optimal signal-to-noise ratio for low and high particle concentrations.

The particle size distribution is calculated from the frequency dependence of the acoustic attenuation using a suitable mathematical fit procedure. Effects such as viscous friction, sound scattering, thermal losses and structural effects are taken into account. Details are described in /1/ and /2/.

Fig. 2 shows the hardware implementation in the DT-1210. The small standing cell is about 25 cm wide and 15 cm high. The flexible silicone measuring cell is simply clamped between the ultrasonic transmitter and detector. The sample is added from above, the system is especially suitable for pasty systems and very easy to clean because it is openly accessible. A prerequisite for the measurement of very small sample volumes is the non-sedimentation of the sample during the measurement (8-12 min). We recommend using the DT-1202 in conjunction with a peristaltic pump (minimum sample volume approx. 40 ml) for non-stable samples.

Some application examples for particle size measurement with the DT-1210 can be found in the application section.

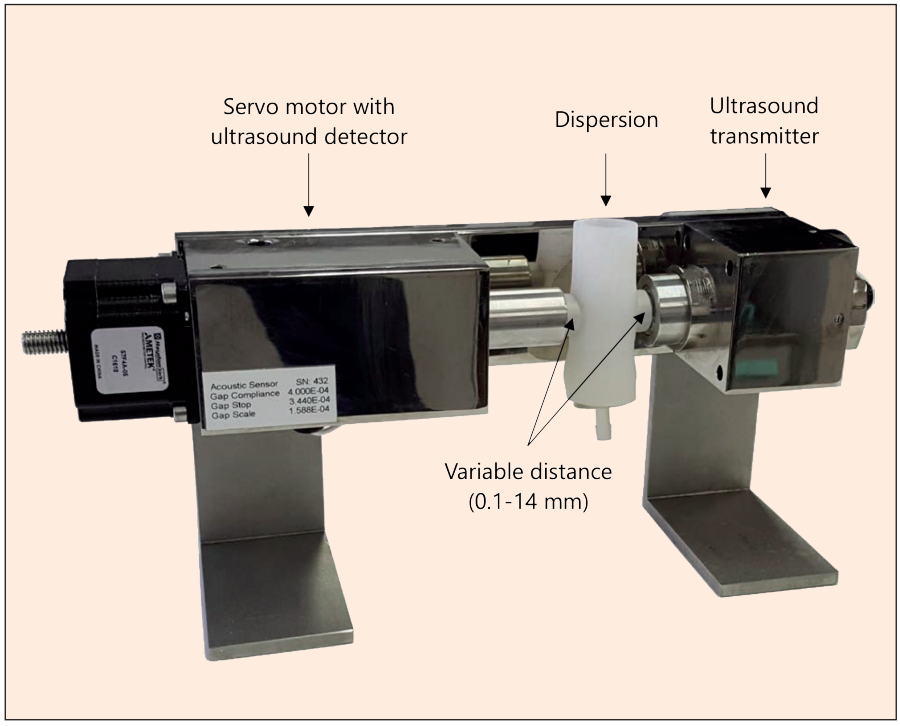


Figure 2 *DT-1210 Hardware*

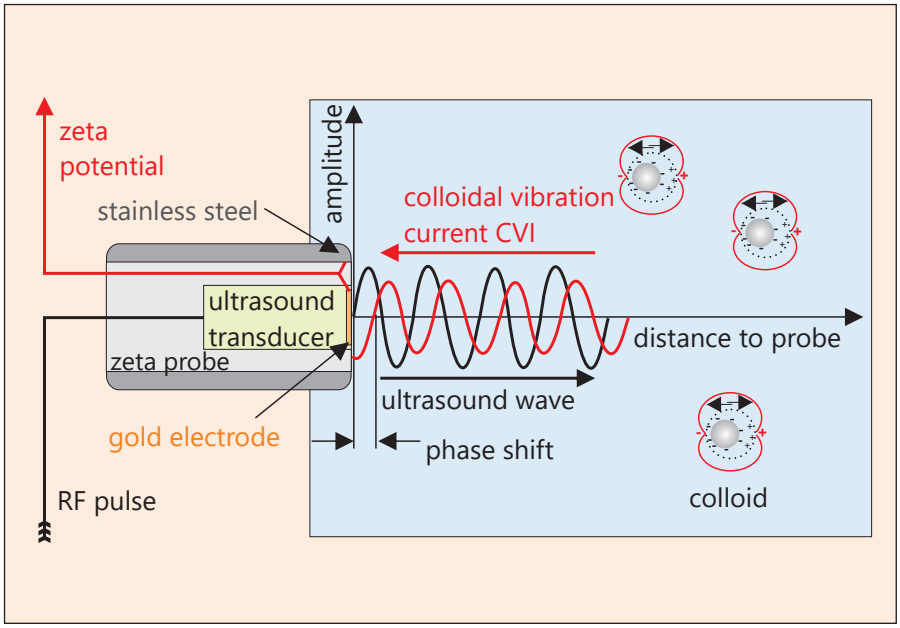


Figure 3 *Measurement principle of electro-acoustic in zeta potential measurement (DT-1210)*

Zeta potential measurement with electro-acoustic technology

In contrast to acoustic attenuation spectroscopy, the electro-acoustic method is a pulse-echo method at a certain frequency. Fig. 3 shows the measurement principle: The electro-acoustic sensor uses a piezo crystal to generate an ultrasonic wave of discrete frequency via a high-frequency signal (RF pulse), which is coupled into the dispersion to be examined. This causes the colloidal particles in the liquid medium to move at high frequency and thus to shift them towards their diffusely bound charge carriers.

Short-term dipoles are formed which generate a measurable alternating current - the colloidal vibration current. It is measured as the potential between the two electrodes of the zeta probe (stainless steel and gold). It is a pulse-echo method. The zeta potential ζ of the particles in the dispersion can be determined directly from the signal using the following equation:

$$CVI = A\phi \frac{\varepsilon_0 \varepsilon_m \zeta K_s}{\eta K_m} \frac{\rho_P - \rho_S}{\rho_S} \qquad (2)$$

with ζ being the zeta potential, ε_m relative permittivity of liquid, ε_0 the dielectric constant, φ the volume fraction of the particles, K_S the electrical conductivity of the dispersion, K_m the electric conductivity of the liquid, $\rho_{P;S}$ the corresponding particles and dispersion density, η is the dynamic viscosity of the liquid and A is a calibration constant. Further details on the procedure are described in /1/ and /2/.

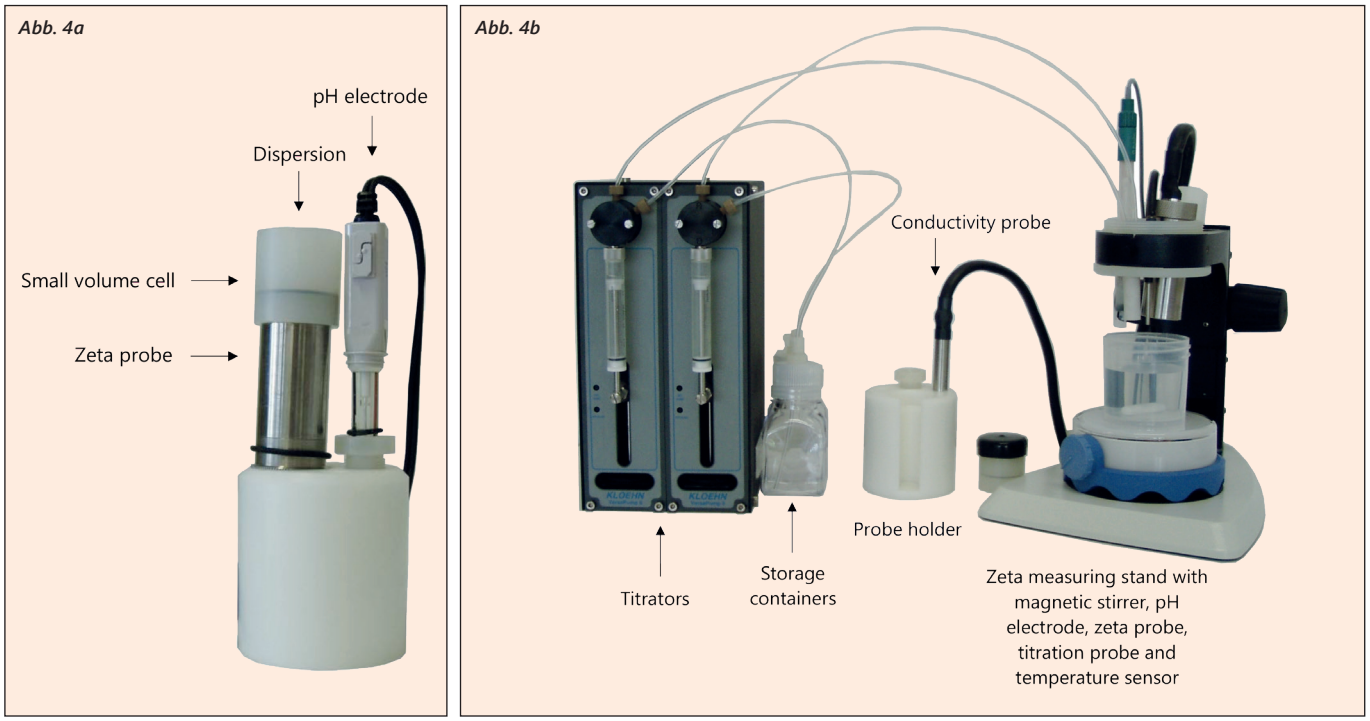


Figure 4 *left: setup zeta potential measurement of very small amounts; right: measuring station for titration experiments (DT-1210)*

Table 1 *DT-1210 device specifications*

	DT-1210, particle size measurement and zeta potential
Measured and calculated parameters	
Particle size / µm	0.001 – 1000
Zeta potential / mV	± (0.5% + 0.1)
pH	0.5 – 13.5 ± 0.1
Electrical conductivity / S/m	10^{-11} – 10^{1} ± 1% OP
Temperature / °C	0 – 100 ± 0.1%
Sound velocity / m/sec	500 – 3000 ± 0.1%
Frequency range / MHz	1 – 100
Measuring time	
Particle size / min	1 – 10
Zeta potential / min	0.5 (water); 0.5-10 (other solvents)
Sample requirements	
Sample volume range / ml	3 – 40
Concentration range / vol.-%	0.1 – 60
Temperature	7 – 50
Viscosity of the medium, colloid / cp	up to 20000

Fig. 4 shows zeta potential measuring probe with small volume attachment (> 0.1 ml, left), on the right the measuring station for titration experiments in DT-1210 (> approx. 40 ml).

Tab. 1 provides a summary of the DT-1210 device specifications.

Application example – DT-1210

One example for the use of carbon or platinum-carbon dispersions is the automotive catalyst technology. When processing the slurry or paste, the dispersion state of the particles in the system is essential for the quality of the resulting product. Particle size distribution and zeta potential - measured in the original, unmodified system - are important parameters with which the quality of such dispersions can be assessed. In the field of research, often only small sample quantities are available: This is exactly where the DT-1210 comes into play, as sample volumes of less than 5 ml are sufficient for particle size measurement. In addition, filling and cleaning the measuring cell after measurement is very easy thanks to the easily removable silicone measuring cell (Fig. 2).

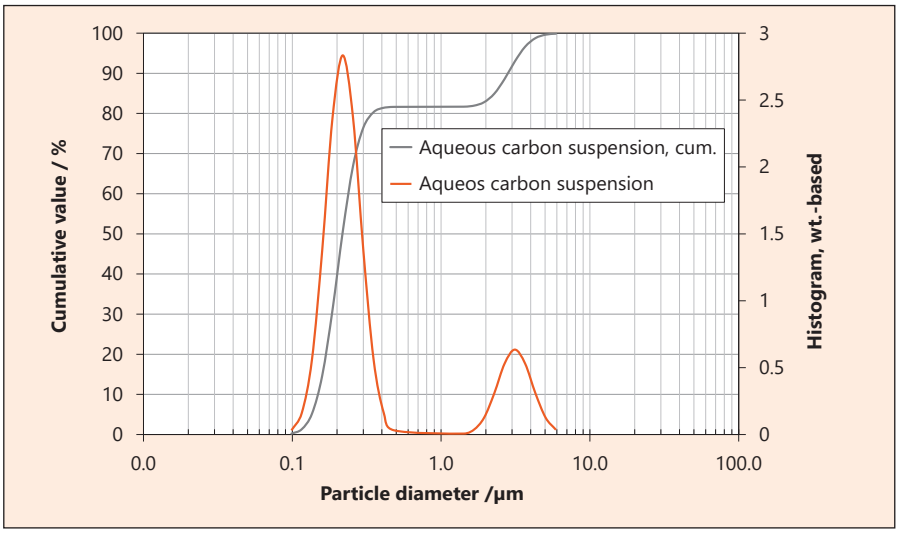


Figure 5 *Particle size distribution of the carbon particles in the aqueous 10 wt.% suspension*

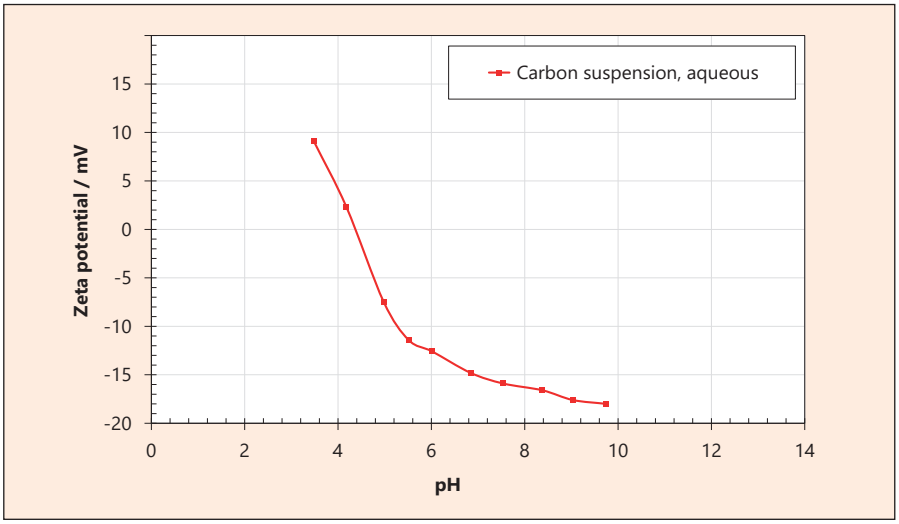


Figure 6 *Zeta potential vs. pH value of the 10 wt. % carbon suspension*

In the first application, the particle size distribution and the dependence of the zeta potential on the pH value of an aqueous 10 wt.% carbon suspension was investigated. DT-1210 was used: the particle size distribution was determined in the measuring cell shown in Fig. 2. The zeta potential was automatically measured in a small volume external beaker (see Fig. 4b). To adjust the pH value, 1-molar formic acid or caustic soda lye was used. The result of the particle size distribution is shown in Fig. 5 and Tab. 2. The titration curve of the carbon dispersion is indicated in Fig. 6. The values are summarized in Tab. 3.

In another application, the particle size distribution of a 10 wt.-% platinum-carbon NMP (N-Methyl-2-pyrrolidone) paste was measured in DT-1210. For this purpose, the pure NMP liquid (without disperse phase) was first characterized with respect to acoustic attenuation and viscosity. The single measurement is required and is then saved in the database for later measurements in this medium. After determining the properties of the background liquid, the paste was measured. Fig. 7 (page 20) shows the attenuation spectra of the NMP liquid, the paste and the best fit function calculated by the software. Fig. 8 (page 20) shows the particle size distribution determined from the fit function. Tab. 4 (page 20) summarizes the most important measurement results.

Table 2 *Results of the particle size measurement of aqueous carbon dispersion*

Sample	D10 / µm	D50 / µm	D90 / µm	Most common value fine / µm	Most common value coarse / µm	Coarse fraction / %
Aqueous carbon suspension	0.11	0.22	0.39	0.22	3.13	18

Table 3 *Results of the zeta potential measurement of aqueous carbon dispersion*

Added amount acid/base / ml/l dispersion	pH value	Zeta potential / mV
1.80	9.75	-18
1.43	9.03	-17.6
1.17	8.38	-16.6
0.89	7.54	-15.9
0.56	6.84	-14.8
0.21	6.02	-12.6
0	5.51	-11.4
0.27	4.98	-7.5
0.91	4.18	2.3
5.74	3.48	9.1

Summary

With the removable silicone measuring cell, the DT-1210 introduces the possibility to characterize dispersions in their original concentration and even pastes with very small sample volumes regarding zeta potential and particle size distribution. This was shown on various carbon systems that play an important role in catalyst production.

You are interested in a device demonstration? Please contact us at **info@3P-instruments.com** or **+49 8134 93240**.

References

/1/ Particle World, issue 8, December 2008, technical articles by Quantachrome

/2/ Andrei S. Dukhin, Philip J. Goetz, "Characterization of Liquids, Dispersions, Emulsions, and Porous Materials Using Ultrasound", 3rd edition, ISBN-13: 978-0444639080, 2017, Elsevier

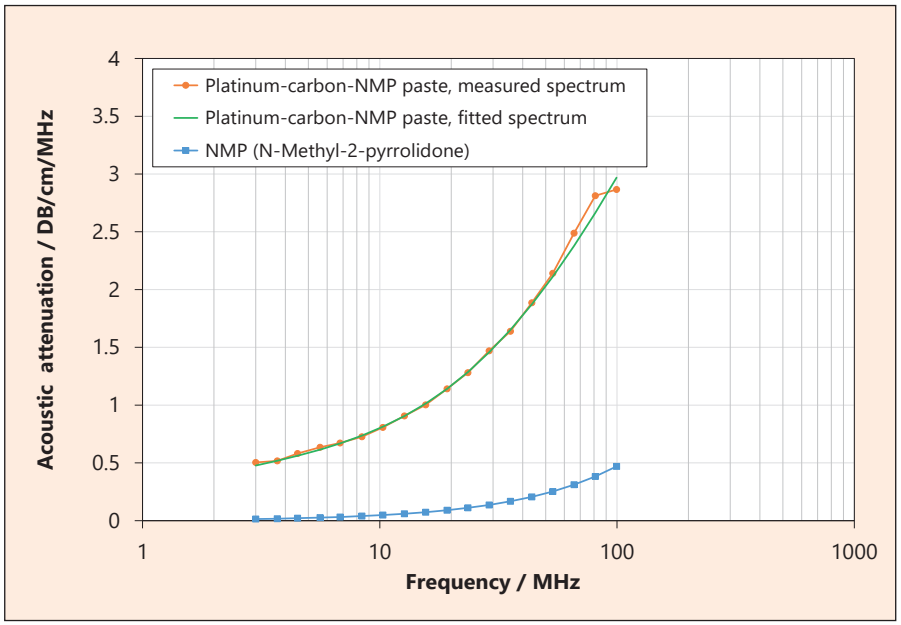


Figure 7 *Measured acoustic attenuation spectra of the background liquid NMP and the Platinum-carbon-NMP paste as well as calculated fit function*

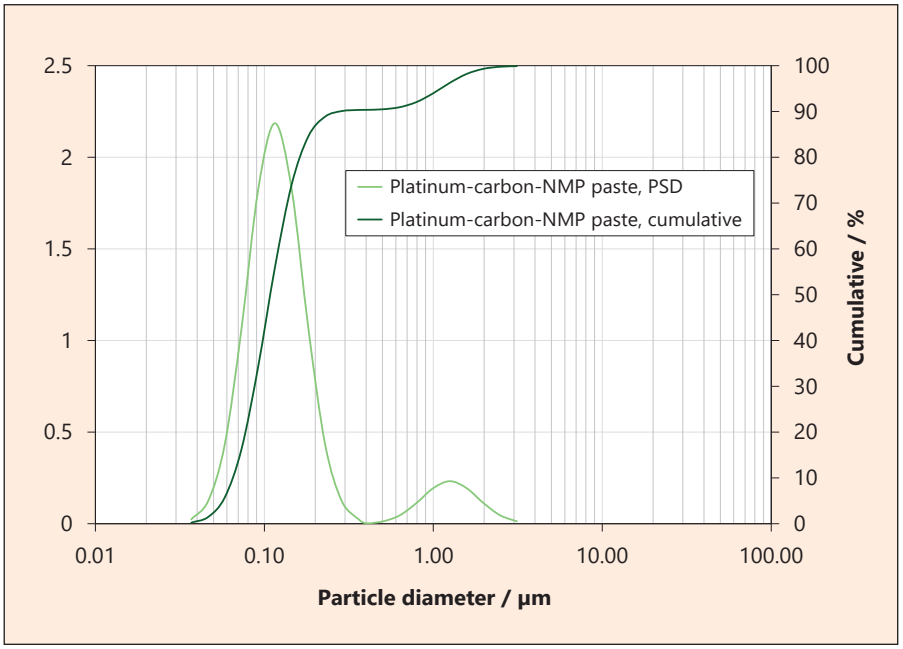


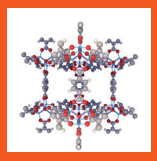
Figure 8 *Particle size distribution of the Platinum-carbon-NMP paste, determined from the fit function shown in Fig. 7*

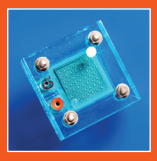
Table 4 *Results of the particle size measurement of Platinum-carbon-NMP paste using DT-1210*

Sample	D10 / µm	D50 / µm	D90 / µm	Most common value fine / µm	Most common value coarse / µm	Coarse fraction / %
Platinum-carbon pastes	0.06	0.11	0.283	0.12	1.25	10

Application of substance data for sorption analyses in adsorptives at various temperatures

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





Recent developments in adsorption measurements in a variety of substances increasingly lead to the application of different measurement gases in order to increase the quality of characterizing porous and nonporous surface structures. It turns out that users of sorption measurement technology often have insufficient parameters available for carrying out the measurement and the subsequent data analysis. Various publications provide contradictory or at least inexplicable substance data as a basis for sorption measurements and the subsequent data analysis. Even substance data in ISO standards are inconsistent due to missing explanations for the measurement data analysis. This article describes such examples and solution approaches and concludes with options on how to improve the comparability of measurement data in texture-describing sorption measurements.

Noble gases as adsorptives for surface and pore characterization

An increasing number of research teams expand their measurement capabilities for the application of noble gases for texture analyses, especially with argon adsorption at 87 K. Scientific articles describe the main questions of gas sorption measurements and the application of evaluation models /1-4/. Unlike nitrogen and other molecular adsorptives such as carbon dioxide, oxygen and *n*-butane, noble gases have the advantage that

- Spherical noble gas atoms cannot attach to different positions at solid substances.
- Therefore, the cross-sectional areas of a noble gas atom do not depend on its position.
- As noble gas atoms do not have a permanent dipole or quadrupole moment, they do not - unlike other dipole or quadrupole adsorptive molecules - align with solid surface groups in various ways.

If you consider the adsorption interaction of micro-, meso- and macroporous and nonporous surfaces, following mechanisms apply:

a) In case of low relative pressure, the adsorptives directly interact with the solid surface in the micropores, i.e. the quadrupole moment of the N_2 molecule has considerable impact on the measurement result. Therefore, argon at 87 K is recommended as adsorptive /5/.

b) If relative pressure is increased, especially in the BET range (p/p_0 = 0.05-0.30), the adsorptives directly interact with the solid surface in meso- and macropores as well as the external particle surface. This implies that the mentioned properties of the N_2-molecule have an impact on the accuracy of the results. Accordingly, argon at 87 K is recommended in ISO 9277 /1/.

c) If relative pressure continues to rise, a mono- or multimolecular adsorbate layer is formed on the solid surface in meso- and macropores as well as the external particle surface. This means that additional adsorptive molecules have no longer direct contact to the polar species of the solid surface. Accordingly, different adsorptives in mesopore analyses such as the BJH method should lead to almost the same results, as the solid substance polarity only affects the mono layer, but not the capillary condensation in mesopores and small macropores.

The cross-sectional area of adsorbates for the calculation of BET surface areas

Following section discusses the topic of unspecified substance data for the determination of specific surfaces (BET surface areas). For this purpose, measurements were carried out in a mesoporous standard substance with various adsorptives at their boiling temperatures (Fig. 1, /6/). The reference substance is non-microporous in order to eliminate potential micropore effects such as pore exclusion effects or kinetically inhibited diffusion in ultramicropores.

As the examined substance (adsorbent) does not have micropores, the direct contact surface of adsorbate and adsorbent is the only surface affected by the mono layer in the BET analysis range. Accordingly, Tab. 1 lists the BET surface area depending on adsorptive and measurement temperature as well as some adsorptive parameters.

The cross-sectional area of an adsorbate atom or molecule can be calculated using equation 1 /7/. The following equation was used for all adsorptives to calculate the BET surface areas in Tab. 1:

$$a_m = 1{,}091 \cdot \left(\frac{M}{N_A \cdot \rho_l}\right)^{2/3} \quad (1)$$

with a_m being the cross-sectional area of one adsorbate atom resp. molecule, M the molar mass, N_A the Avogadro's number and ρ_l the density of the liquid adsorbate phase.

The BET surface areas determined in Tab. 2 allow for following interpretation:

- The application of adsorbate cross-sectional area calculated from the liquid density in the N_2 77 K method leads to more than 30 % larger BET surface areas than all other adsorptives.
- This can result from a higher reduced measurement temperature (last column Tab. 1), the quadrupole moment or non-applicable cross-sectional area of the non-spherical N_2 molecule in the examined silica substance.
- The dropping BET surface areas in the noble gas row may be explained with the polarizability of these atoms. It remains to be examined whether further studies find this dependency also in different substances.

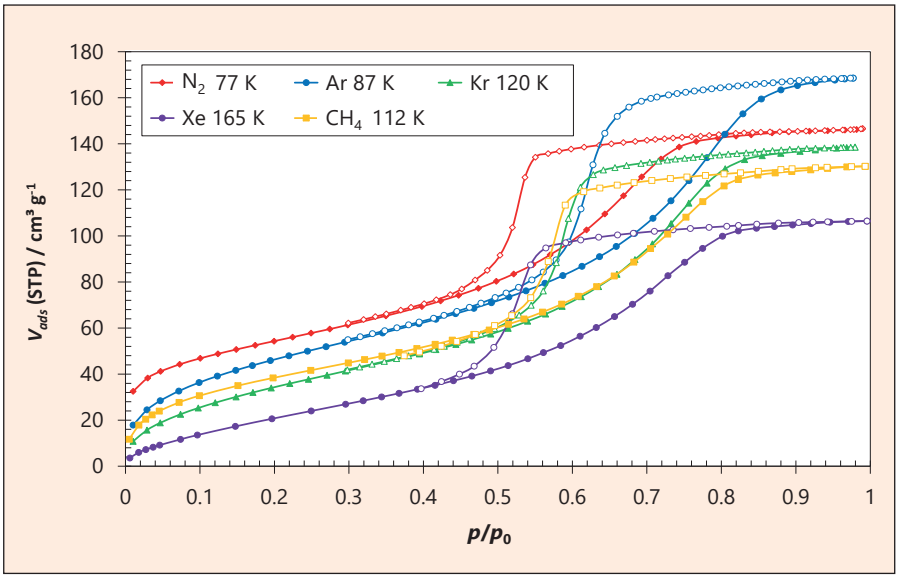


Figure 1 *Sorption isotherms of mesoporous standard substance (BAM P-105) of adsorptives at their boiling temperatures*

Table 1 *Measurement conditions, BET surface areas and adsorbate properties of the measurements from Fig. 1 using the mesoporous standard substance BAM P-105*

Adsorptive and temperature	A_{BET} / $m^2 g^{-1}$	a_m / nm^2	Polarizability α / 10^{-24} cm^3	Quadrupole moment / 10^{-40} C m^2	$T_{red} = T/T_{crit.}$
N_2 77 K	200	0.162	1.74	- 4.72	0.611
Ar 87 K	150	0.142	1.63	0	0.576
Kr 120 K	140	0.162	2.46	0	0.574
Xe 165 K	120	0.192	4.09	0	0.569
CH_4 112 K	150	0.174	2.59	0	0.586

with: A_{BET}...BET surface area; a_m...cross-sectional area of one adsorbate atom resp. molecule

Publications /1 – 3/ frequently refer to McClellan and Harnsberger /7/ regarding the cross-sectional area of adsorbates, who published a comprehensive comparison of measurement results and the corresponding recommendations in 1967 already. Based on the fact that the BET method was originally developed for characterizing catalysts only, their recommendations definitely were a major progress in the acceptance of the gas sorption method for characterizing other substance types at that time. However, McClellan and Harnsberger /7/ clearly describe their approach on the traditional application of N_2 at 77 K: "Most workers use 16.2 A^2, and we have chosen this as our working standard." Mainly for practical considerations (easily available N_2 measurement gas and liquid nitrogen for temperature control), the application of N_2 77 K as reference system imply that the main assumptions for other adsorptives are still based on the comparison with N_2 77 K measurements, i.e. on the adsorption of a non-spherical molecule with significant quadrupole moment. Just as McClellan and Harnsberger adhered to N_2 77 K as reference system in their comprehensive data analyses, this approach has been widely accepted throughout decades of adsorption publications and even include references in current standards. As an example, Lowell et. al. /3/ mention on the application of krypton adsorption at 77 K to determine small specific surfaces: "The cross-sectional area calculated from the density of the supercooled liquid krypton is 0.152 nm^2... but the higher cross-sectional area of 0.202 nm^2...is commonly used." Interestingly, Lowell et.al. /3/ and ISO standard 9277 /1/ as well as other authors adopted the cross-sectional area of 0.202 nm^2 for krypton at 77 K, although McClellan and

Table 2 *Comparison of adsorbate cross-sectional areas indicated in ISO 9277 /3/ compared to values of a commercial device software /5/ and consistent values from eq. 1*

Adsorptive	T / K	Cross-sectional area / nm²				
		Recommended in /1/	Values according to /2/	Values according to /3/	Values in /4/	Calculated from eq. 1
N_2	77	0.162	0.162	0.162	0.162	0.1626
Ar	77	0.138	0.138	0.138	0.1385	0.1411
Ar	87	0.142	n.a.	0.142	0.142	0.1433
Kr	77	0.202	0.202	0.202	0.205	0.1522
Kr	87	n.a.	n.a.	n.a.	0,205	0,1550
Kr	120	n.a.	n.a.	n.a.	n.a.	0,1577
Xe	77	0.168	0.170	0.168	n.a.	0.1694
Xe	165	n.a.	n.a.	n.a.	n.a.	0.1923
CO_2	195	0.195	0.210	0.195	n.a.	0.1636
CO_2	273	0.210	n.a.	0.210	0.210	0.2009
O_2	77	0.141	0.141	0.141	n.a.	0.1354
O_2	90	n.a.	n.a.	n.a.	n.a	0.1412

With T...temperature, A_{BET}...BET surface area

Harnsberger /7/ did not recommend this value for Kr 77 K, but for Kr at 195 K. The temperature dependency of adsorbate cross-sectional areas is thus negated, but should also be taken into consideration for the data evaluation of sorption isotherms at various temperatures. Common knowledge for decades is complemented with the latest computer simulations. Just to mention one example, /7/ such simulations are used to discuss the temperature dependency of the liquid density and with that the averaged cross-sectional area of the adsorbates. Especially if new studies confirm previously known assumptions such as temperature dependency of the adsorbate cross-sectional area, such findings should be incorporated in standards and recommendations, or the substance data should at least be explained. As is becomes obvious in Tab. 2, numerous publications include assumptions that are not further explained that lead to special regulations, e.g. for krypton 77 K and CO_2 195 K evaluations. As explained in Tab. 2, such inconsistencies were included in annex 1 of ISO 9277, where the xenon atom has an attributed cross-sectional area of 0.168 nm², while the smaller krypton atom is assigned with a considerable higher cross-sectional area of 0.202 nm².

Table 3 *BET surface area of aerated concrete depending on the adsorptive*

Adsorptive and temperature	A_{BET} / m² g⁻¹	Comparison A_{BET} vs. A_{BET} von Ar 87 K / %	Quadrupole moment / 10^{-40} C m²
Ar 87 K	42.0	0	0,00
O_2 90 K	49.4	+ 18	- 1.03
N_2 77 K	65.9	+ 57	- 4.72
CO_2 195 K	111.1	+ 165	- 13.40

In addition, the values for krypton indicated in Tab. 2 column 4 of the commercial software /4/ do not depend on the temperature as would make sense from the physical perspective, i.e. a constant value of 0.205 nm² is posted for the krypton cross-sectional area at 77 K and 87 K. The value of oxygen in Tab. 2 column 3 (ISO 9277) definitely does not accidentally correspond to the value of the last column for oxygen at 90 K. These are just a few examples of how discrepancies consistently appear in publications and the practical laboratory work making the evaluation of accurate sorption results and their comparison rather difficult.

There is a variety of measurement results making the application of N_2 77 K with a cross-sectional area of 0.162 nm² more than questionable from the scientific perspective. If you consider further adsorptive molecules with quadrupole moments, measurement results indicate a considerable influence of the quadrupole moment on BET surface areas resulting from Ar, O_2, N_2 and CO_2 measurements at the corresponding boiling temperatures, as summarized in Tab. 3. The test of aerated concrete indicates a considerable dependency of BET surface area from the adsorptives quadrupole moment.

Practical applications of various adsorptives and measurement temperatures

Relevant adsorptives for surface and pore characterization feature different boiling temperatures that require the corresponding measurement temperatures as indicated in Tab. 2. Recent technological developments of 3P Instruments increasingly facilitate the application of variable measurement temperatures in gas sorption measurements.

CryoTune (Fig. 2) is an external temperature controller that only requires liquid nitrogen for cooling covering a temperature range of 82 – 323 K for sorption measurements. In general, cryoTune can be used in combination with adsorption devices of any manufacturer. 3P Instruments has extensive experience, offers the corresponding connectors to own and third-party devices and provides support videos to cryoTune users. The cryoTune temperature calibration is very easy for the user and ensures a high service and maintenance friendliness.

Conclusions

The very complex work of McClellan and Harnsberger /7/ as well as today's high flexibility in the application of adsorptives and variable measurement temperatures require a new evaluation and critical review of statements and recommendations based on N_2 77 K. A scientifically more feasible basis of the nonspherical and quadrupolar N_2 77 K seems to be the spherical and nonpolar Ar 87 K that is frequently mentioned in publications /1 – 6/, although it is not consistently applied in texture characterizations. Surface polarities should increasingly be evaluated combining the use of nonpolar (Ar, Kr, Xe, CH_4) and quadrupolar (O_2, N_2, CO_2) adsorptives. The cryoTune series allows for such measurements and comparisons for (almost) any sorption analyzer user.

We recommend a consistent approach for the application of the adsorbate cross-sectional area. The determination of the cross-sectional area from liquid density was already the focus of the comprehensive work by McClellan and Harnsberger /7/ more than 50 years ago. If these values (Tab. 2, right column) are used consistently, differences in the determined BET surface areas can frequently be attributed to specific interactions between various adsorptives and solid substance, as it is obvious in Tab. 1 and 3. Additionally, these parameters are to be applied depending on the temperature, as indicated in Tab. 2 (right column), e.g. for krypton measurements at 77 K, 87 K and 120 K.

Beside the adsorbate cross-sectional area, data analysis requires further adsorptive parameters such as saturation vapor pressure, non-ideal coefficient and adsorbate density. Again, contradictions appear in their presentations in publications. Therefore, 3P Instruments will present new results and recommendations during the next adsorption workshop on April 13, 2021 in Leipzig. More information on the workshop and additional events during the 3P Adsorption Week 2021 is available at:

https://www.3p-instruments.com/adsorption-week/

If you are interested in an earlier exchange of experience in the application of alternative adsorptives and substance data, or if you would like to discuss your substance for projects, contract, test or comparative measurements, please feel free to contact us at **info@3P-instruments.com**!

References

/1/ ISO 9277:2010: Determination of the specific surface area of solids by gas adsorption – BET method

/2/ F. Rouquerol, J. Rouquerol, K. Sing "Adsorption by powders & porous solids", Academic Press 1999

/3/ S. Lowell et. al "Characterization of porous solids and powders", Kluwer 2004

/4/ Quantachrome software, version ASiQwin 5.21, 2017

/5/ IUPAC recommendation, Pure Appl. Chem. 87(9-10), 2015, 1051-1069

/6/ S. Dantas et. al, Langmuir 2019, 35, 11291–11298

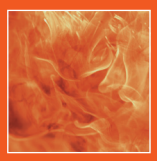
/7/ A. L. McClellan, F. Harnsberger, Journal of Colloid and Interface Science 23 (1967), 577-599

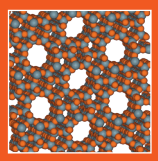
/8/ C. Reichenbach, D. Klank, Vortrag Fachgruppe Adsorption, Berchtesgaden 2020

Figure 2 *Space and energy saving as well as silent (no compressor): the cryoTune enables the realization of temperatures for sorption measurements in a temperature range of 82 – 323 K. In combination with the sorption analyzer 3P micro 300, it is possible to operate all three measurement stations with different measurement gases. For example, it is possible to simultaneously analyze one sample with Ar 87 K, N_2 77 K and CO_2 195 K.*

Studies on adsorptive CO_2 removal from nitrogen in variable humidity

Dr. Andreas Möller, Konrad Eisinger, Dr. Carsten Blum
andreas.moeller@3P-instruments.com





Introduction

Various strategies are being pursued to meet the EU and global climate objectives. In addition to a reduction in fossil fuels, the possibilities of actively removing CO_2 from air or exhaust gases by adsorption are also being investigated /1, 2/. These methods only make sense if acceptable separation rates can be achieved and if they are energy-efficient /3/. Such methods should be less sensitive towards contaminants that may appear with varying concentrations and offer good long-term stability. Water also plays a major role as an interfering component /4/.

This study investigates materials for their suitability in adsorptive systems to separate CO_2 from air. Such porous materials need to have a high sorption capacity, high selectivity for CO_2, fast sorption kinetics, good regenerability and high cycle stability. In addition, this study examines the influence of humidity in sorption capacities in zeolites 4A and 5A and an amine functionalized polymer. In order to obtain results transferable to the application, a dynamic measurement method was used, and the breakthrough curves obtained were evaluated for sorption capacities and sorption kinetics. In addition to the CO_2 breakthrough curves, breakthrough curves of water vapor and their temperature curves at 50 % relative humidity and 313 K at 1 bar were obtained.

Experimental design

Material and sample preparation

Two zeolites with narrow pores, i.e. 4A and 5A, and one amino functionalized macroporous polymer, Lewatit VP OC 1065, were selected. The zeolites have particle sizes of approx. 1.5 up to 2.5 mm; the polymer has smaller particles sized at approx. 0.5 mm. CO_2 with a purity of 99.995 % and N_2 with a purity of 99.999 % were used as fluids. In order to conduct tests in the presence of humidity, the evaporator integrated in the device was used in combination with distilled water. Both zeolites were heated up in situ after they were placed in a N_2 gas flow of 300 ml·min^{-1}. Material was heated with a ramp of 2 K·min^{-1}, and temperature was kept at a constant level of 673 K for 300 min. The polymer was heated at 10 K·min^{-1} to 383 K, and temperature was kept at this level for 5 hours. Again, a N_2 gas flow of 300 ml·min^{-1} was used as carrier gas.

Breakthrough curves

All breakthrough curves were measured in the breakthrough curve analyzer mixSorb L by 3P Instruments. The adsorber has a diameter of 3 cm and a height of 20 cm. It features four temperature sensors and is made of stainless steel. The gas phase composition at the adsorber outlet was analyzed with a thermal conductivity detector and additionally with a mass spectrometer. All evaluations were carried out using the mass spectrometer data set.

After the samples were prepared, the adsorber was fed with the carrier gas and thermostatically controlled at 313 K. When moisture free analysis was desired, nitrogen was used as the carrier gas. For sample runs where moisture was needed, nitrogen with a relative humidity of 50 % was used. Once the conditions were constant (temperature, analyzer signals etc.), carbon dioxide was added. During the measurements, the total gas flow was 5000 ml·min^{-1} (STP). This corresponds to an empty sample holder (adsorber bed) flow rate of 0.135 m·s^{-1}. Measurements were concluded once a steady-state condition was achieved. This

condition is characterized by constant fixed bed temperatures and a constant gas composition at the adsorber outlet. Once the breakthrough curves were determined with CO_2 from dry carrier gas, samples were re-heated to 523 K in the zeolite setup and 383 K in the polymer setup to desorb CO_2. The progress of the desorption process was analytically monitored. Subsequently, breakthrough curves of water vapor with a relative humidity of 50 %, at 313 K and 1 bar were measured as absolute values. After the equilibrium was achieved, the CO_2 breakthrough curve was again determined for each sample.

Results and discussion

Under dry conditions, zeolites are characterized by good sorption capacity and kinetics. The highest sorption capacity was achieved with zeolite 4A with 0.768 mmol·g^{-1}. The Lewatit sorption capacity is 0.605 mmol·g^{-1}, while a zeolite 5A capacity of 0.341 mmol·g^{-1} was determined. The lower absorbing capacity of zeolite 5A compared to zeolite 4A at low CO_2 partial pressure can be explained with larger pore width and consequently less interaction. The macroporous polymer's high capacity is not attributable to the pore system, but the amine functionalization of the surface and -accordingly- this group's affinity for CO_2. The breakthrough curves under dry conditions are indicated in Fig. 1. For better clarity, temperature is not included in this figure.

At first sight, a deviation between the load obtained and breakthrough times is obvious. Compared to the high polymer load, the area left of the breakthrough is rather small. This can be explained in regards to the adsorber volume. Due to the low bulk density, the polymer falls behind based on the volume. Zeolite 4A offers the best sorption capacity of all three materials with regard to volume. Such effects need to be considered in the design of industrial-scale systems. Another finding in Fig. 1 is the larger noise in the Lewatit curve. It can be explained with the large volume reduction caused by the drying process, which causes the adsorber not to be filled with the entire volume. Light particles cause a slight movement in the bed, i.e. strictly speaking it is no longer a fixed bed. Again, this fact needs to be taken into consideration for industrial-scale systems. The breakthrough curves allow conclusions on the sorption kinetics. Zeolite 5A features the best kinetics, as the breakthrough curve shows a sharp increase. The polymer and zeolite 4A produce a wide, slowly increasing breakthrough curve, which is an indicator for the limitations of these materials. In the case of zeolite 4A, slower kinetics are probably attributable to the tighter pore system. In addition, the binder might also have an impact. Zeolites typically involve transport limitations. A transport-limiting effect may be suspected in macroporous polymers in the amino functionalized surface. The kinetics in the polymer are another reason for a reduced load in dynamic experiments compared to equilibrium data described in publications /5/. This limitation needs to be considered in the scaling of industrial systems, as they frequently produce even higher empty flow rates /6/.

Fig. 2 to 4 show the breakthrough curves of water in nitrogen (50% RH) at 313 K and ambient pressure, as well as their temperature profile. These temperature curves are an additional indicator for the affinity of such materials for water. In order to facilitate the comparability of materials, all images are scaled equally.

Considering the breakthrough times and temperature curves, high sorption capacities and affinities for both zeolites can be assumed. Sorption heat produces temperature peaks of approx. 373 K in the bed. In contrast, the polymer produces only little temperature increases combined with rather low sorption capacity. It needs to be assumed that especially the primary amine groups interact with the water.

Breakthrough curves of CO_2 in the presence of humidity are indicated in Fig. 5. In order to increase clarity and because of constant water vapor concentration, lower CO_2 concentration and subsequently a reduced displacement effect during the test, water vapor signals are eliminated from the test. Spontaneous breakthroughs are detected for zeolites. The load is almost zero

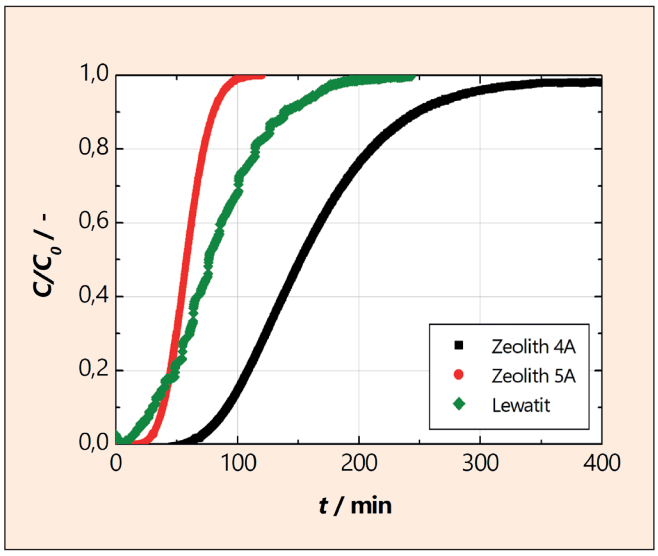


Figure 1 *Breakthrough curves of 2000 ppm CO_2 of dry nitrogen in zeolite 4A, 5A and Lewatit VP OC 1065 at 313 K, 1 bar, 5000 cm^3·min^{-1}*

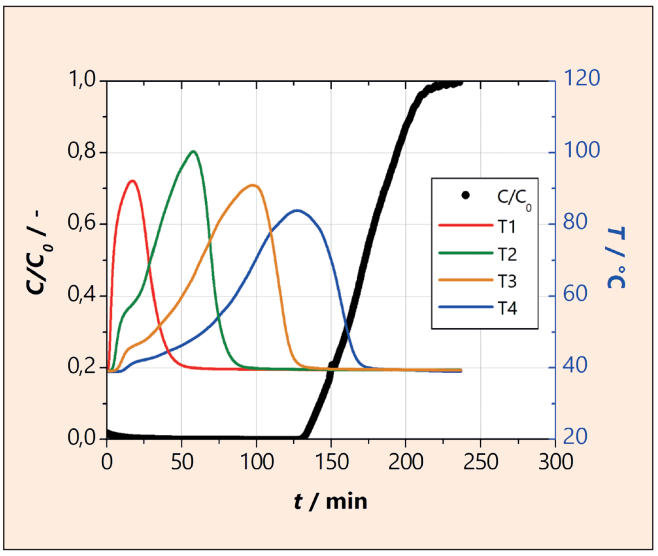


Figure 2 *Breakthrough curve of water in zeolite 4A at 313 K, 1 bar, 5000 cm^3·min^1, rel. humidity 50 %*

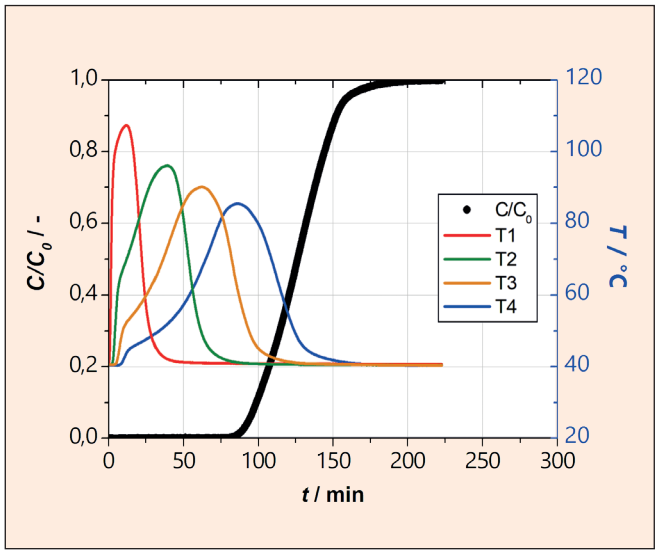


Figure 3 *Breakthrough curve of water in zeolite 5A at 313 K, 1 bar, 5000 cm³·min¹, rel. humidity 50 %*

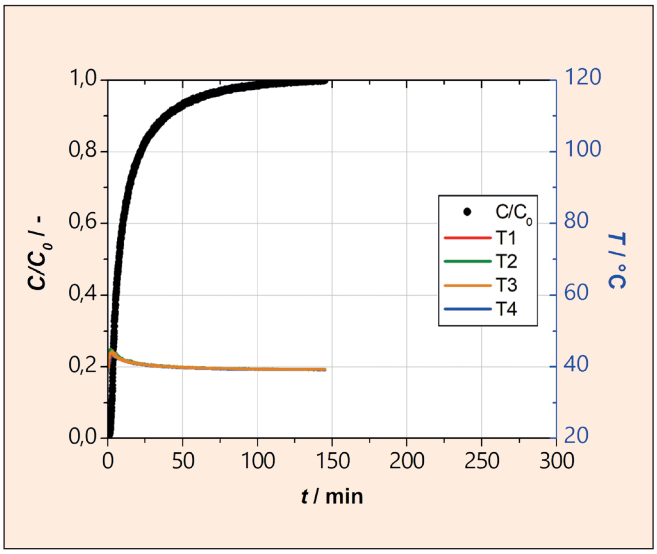
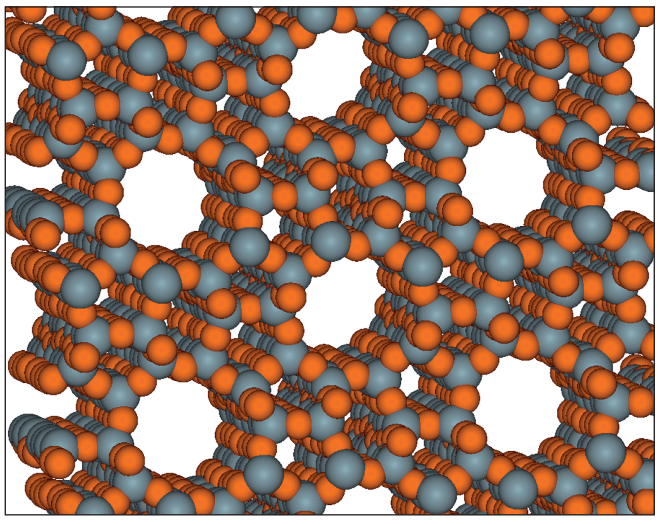


Figure 4 *Breakthrough curve of water in Lewatit VP OC 1065 at 313 K, 1 bar, 5000 cm³·min⁻¹, rel. humidity 50 %*

in both cases. Water is adsorbed in the zeolite pore system to such an extent that the displacement of CO_2 is insignificant.

Both zeolites are therefore rather unsuitable for CO_2 separation from wet gas flows, as it would be the case in Direct Air Capturing applications. However, there are advantages in the purification of dry gas flows due to improved kinetics. A sorption loading of 0.819 mmol·g^{-1} was obtained for the polymer. This adsorbent is the most suitable of all materials selected to adsorb CO_2 in low concentrations and with presence of humidity. Accordingly, it is ideal for Direct Air Capturing. All loadings obtained are summarized in Tab. 1.

Due to the slow kinetics, CO_2 was also detected at the adsorber outlet shortly after the start of the experiment using Lewatit. This is reflected in a quickly rising CO_2 concentration. Accordingly, the selected conditions only cause a reduction of CO_2 and not the complete removal from the gas mixture. Material development could focus on the enhancement of polymer kinetics. An interesting observation is the fact that the polymer breakthrough curve in the presence of humidity is less significant than in dry condi-



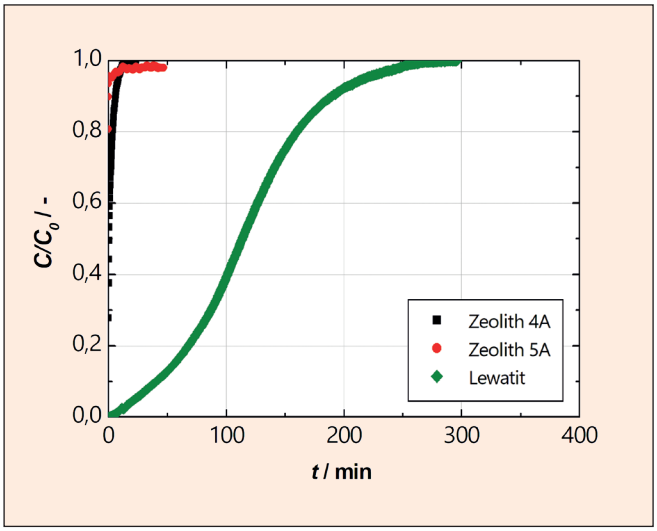


Figure 5 *Breakthrough curves 2000 ppm CO_2 from a wet nitrogen flow in zeolite 4A, 5A and Lewatit VP OC 1065 at 313 K, 50 % relative humidity, 1 bar and 5000 cm³·min⁻¹*

Table 1 *Loadings from breakthrough tests of 2000 ppm CO_2 from dry and wet (50 % RH) nitrogen at 313 K, 1 bar, volume flow 5000 cm³·min⁻¹*

Sample	CO_2 load of dry N_2	CO_2 load of moist N_2
Zeolite 4A	0.768 mmol·g^{-1}	< 0.010 mmol·g^{-1}
Zeolite 5A	0.341 mmol·g^{-1}	< 0.010 mmol·g^{-1}
Lewatit VP OC 1065	0.605 mmol·g^{-1}	0.819 mmol·g^{-1}

Summary

It was shown that zeolite 4A in the presence of humidity produced the best purification efficiency under the specified conditions. This is mainly attributable to the volume-based evaluation of results. Due to the lower bulk density, the Lewatit-filled adsorber achieves a lower purification performance, although the polymer mass loading is similarly high. These effects must be considered in the system design.

As to be expected, breakthrough curves of water vapor show a strong affinity for both zeolites resulting in significant temperature peaks up to approx. 373 K in the adsorber. Although the polymer also has a certain sorption capacity for water, it is connected to a much lower temperature profile. This observation leads to the conclusion that the affinity for water is less for the polymer. In addition, the sorption capacity for water is also lower.

A complete breakdown of sorption capacity for zeolites can be observed for breakthroughs of 2000 ppm CO_2 from a wet carrier gas flow in samples treated with water, while the sorption capacity of amine functionalized polymer even increases. Based on orienting and practice-oriented tests, Lewatit can be recommended for Direct Air Capturing. The experiments are a valuable indicator for the development of material that an improvement of the sorption kinetics of the polymer seems desirable.

Let us personally convince you of the efficiency of our mixSorb systems; larger sample amounts can be tested with mixSorb L, while mixSorb-S series are the recommended choice for very small sample amounts. Device demonstrations and sample tests in our analysis laboratory are part of our service. We are available at **info@3P-instruments.com** and **+49 8134 93240**.

References

/1/ C.H. Yu, C.H. Huang, C.S. Tan, Aerosol Air Qual. Res., 2012, 12, 745-769

/2/ T.C. Merkel, H. Lin, X. Wei, R. Baker, J. of Membrane Science, 2010, 359 (1-2), 126-139

/3/ A. Goeppert, H. Zhang, M. Czaun, R.B. May, G.K. Surya Prakash, G.A. Olah, S.R. Narayanan, ChemSusChem, 2014, 7 (5), 1386-1397

/4/ A. Kumar, D.G. Madden, M. Lusi,K.-J. Chen, E.A. Daniels, T. Curtin, J.J. Perry, M.J. Zaworotko, Angewandte Chemie, 2015, 54 (48), 14372-14377

/5/ W. Buijs, S de Flart, Ind. Eng. Chem. Res., 2017, 56, 12297-12304

/6/ H.W. Kajszika, Adsorptive Abluftreinigung und Lösungsmittelrückgewinnung durch Inertgasregenerierung, Herbert Utz-Verlag, München 1998.

/7/ M. Parvazinia, S. Garcia, M. Maroto-Valer, Chemical Engineering Journal, 2018, 331, 335–342

Highly selective materials for the solid phase extraction of precious metals from process and recycling water

Dr. Hans Uhlig, Institut für Nichtklassische Chemie e.V. (INC)
uhlig@inc.uni-leipzig.de

Issue and objective

The selective separation of precious metals from recycling solutions is gaining growing interest due to the steadily increasing raw material prices, the dropping metal content of the ores and the high added value. Precious metals such as platinum, palladium and ruthenium from catalysts or other sources, e.g., the corresponding recycling solutions contain only small percentages from the electronic industry. The reprocessing of such recycling solutions is therefore always accompanied by enrichment processes. In addition to the standard processes such as classification, electrolysis or precipitation as a poorly soluble compound, liquid-liquid extraction in particular is increasingly used to recover platinum metals from primary and secondary raw materials.

The separation of precious metals from aqueous solutions requires materials that have both high capacities and high selectivity. These properties can be achieved by introducing novel organic anchor groups. Complex-forming organic molecules allow the efficient separation of heavy metals from aqueous solutions with high selectivity. The anchor groups have special areas within the molecule which can only be occupied by metal ion with the appropriate size, valence, and / or coordination properties.

The goal of this work was to synthesize new, highly selective materials that can be used for separation of precious metals from process water. The studies were carried out in a joint project between the "Institut für Nichtklassische Chemie e.V." in Leipzig (INC) and the Institute for Inorganic Chemistry at the University of Potsdam, funded by the AiF (BMWi AiF-IGF 18743 BR).

Carrier materials based on silicate moldings

In this study, a porous silica gel (Millipore - PrepPak®-500/Silica) and costum-made porous glass materials with defined pore sizes were used as carrier materials. A connection of functional surface groups such as 3-chloropropyltrimethoxysilane succeeded with different loading capacities. In addition to the already established and used characterization techniques such as cryogenic nitrogen sorption, mercury porosimetry for texture analysis, particle size analysis and alternative techniques such as thermogravimetric mass spectrometry (TG-MS), ICP-OES, AAS or REM-EDX, an additional method specifically for the analysis of the modification was developed. This new technique is able to determine the freely accessible surface functionalities on the carrier material. All methods are used to determine a possible loading with the respective ligands depending on the pore size and surface of the carrier material.

Within the scope of the project, carrier materials were synthesized with a defined ratio of accessible surface to pore volume while maintaining a constant pore volume. The adjustable pore sizes are in the range from 4 to 30 nm. A further surface modification resulted in a selective group density of up to 2.5 mmol/g with still very good accessibility. Kinetic studies in liquid phase complemented the characterization.

Studies on the adsorption of selected precious metals and their recovery

Some of the costum-made surface-modified materials were examined with respect to their adsorption properties regarding precious metals such as platinum, palladium and ruthenium. Firstly, the maximum loading capacities for single metals in the liquid phase were determined (see Fig. 1). Subsequently, studies on mixtures of metal ions were carried out. For this purpose, a special set up with automatic sampling at the INC was used for the investigation of the dynamic sorption process of metal ions on functionalized material as stationary phase.

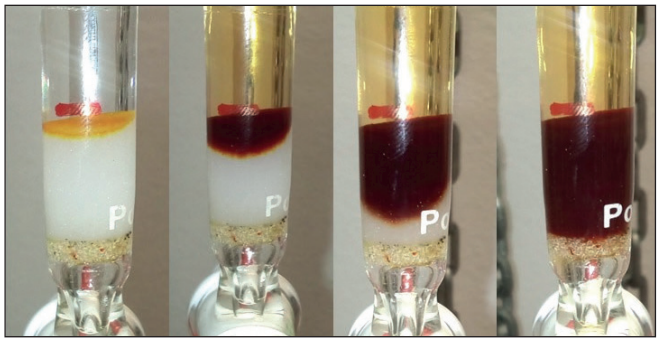


Figure 1 *Glass reactor filled with a stationary phase of functionalized material with different loadings*

In a first series of experiments, aqueous solutions were mixed with palladium and platinum salts and defined conditions regarding concentrations and pH-values were set. This mixture of substances was then passed through a bed with surface-immobilized solid phase in a continuous process (see Fig. 1). By detecting the concentration of palladium and platinum at the column outlet over time, a breakthrough characteristic can be observed for both components (see Fig. 2). It can be deducted that palladium is preferably adsorbed on the surface. In contrast, platinum shows an early breakthrough and reaches the inlet concentration of the injected solution faster than palladium. After completing the experiment, the stationary phase was removed and the concentration of the metals on the surface before and after sorption was determined using ICP-OES. The metals were successfully rinsed from the surface of the stationary phase using a hydrochloric acid thiourea solution. Repeating cycles of adsorbing the metals and rinsing from the surface were additionally carried out. The loadings of the respective metals based on the mass of the solid phase can be determined by means of a holistic mass material before and after the adsorption of the metals on the surface and after regeneration of the stationary phase.

After the loading step, the used stationary phase contained about 7.2 wt.% of palladium and 0.4 wt.% of platinum (see Fig. 3). Through regeneration, approx. 5.0 wt.% of palladium and 0.2 wt.% of platinum can be rinsed from the stationary phase. Cyclic tests already show a constant working stroke after the first adsorption-regeneration run. The residual loading on the surface remains constant after the first cycle. Palladium can be separated from platinum with a selectivity of 14.5, with an equal inlet concentration of both metal salts. Thus, it is possible to separate palladium from a solution containing palladium and platinum.

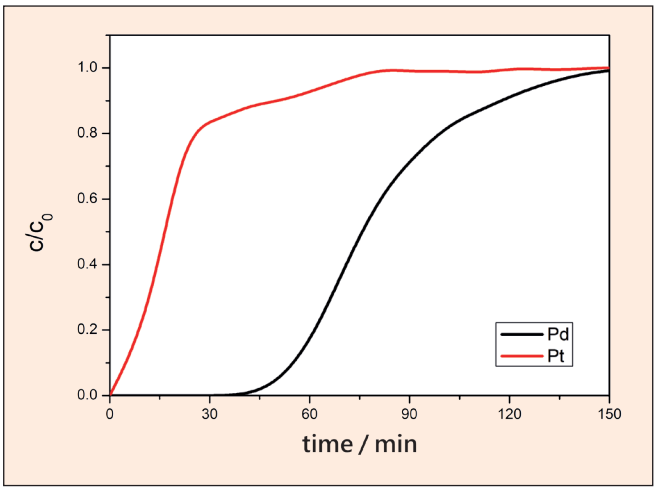


Figure 2 *Breakthrough characteristics for palladium and platinum from hydrochloric acid solution (pH = 1) at 25 °C on the stationary phase of functionalized silica gel*

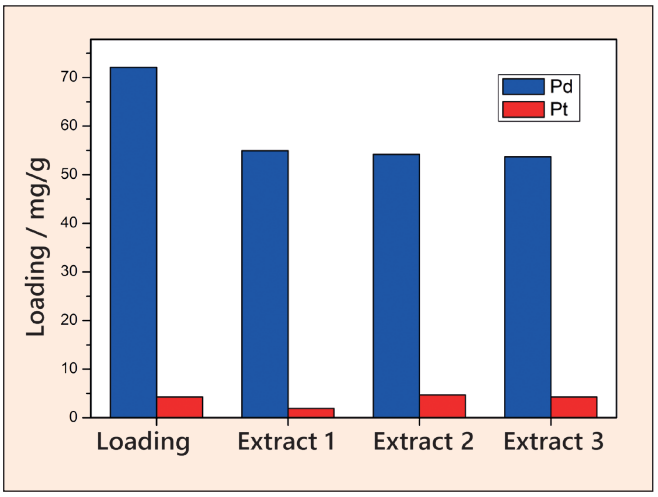


Figure 3 *Results of the loading of palladium and platinum (determined from ICP-OES measurements) of the extracted functionalized silica gel*

Conclusions

In this study, porous, highly selective materials based on silicate moldings or porous glasses were successfully synthesized and investigated regarding their use for the separation of precious metals from aqueous solutions. Some of the solid phase materials showed very good regeneration properties and were also convincing in cyclic operation.

The results demonstrate the successful development of a palladium separation technology that is already available at the INC.

If you are interested in the implementation of your idea from the material to the process, please feel free to contact us:

e-mail: **uhlig@inc.uni-leipzig.de**
office@inc.uni-leipzig.de
phone: **+49 341 235 2405**
homepage: **https://research.uni-leipzig.de/inc/**

The "Institut für Nichtklassische Chemie e.V." – your partner for application-oriented research and services

Dr. Jens Möllmer, moellmer@inc.uni-leipzig.de

The "Institut für Nichtklassische Chemie e.V." (INC), with its currently 20 scientists, is a competent project partner or service provider for application-oriented development in the field of chemistry and chemical process engineering since more than 20 years and is a member of the Deutsche Industrieforschungsgemeinschaft Konrad Zuse.

The main focus of the research and development work of the institute certified according to DIN ISO 9001 is:

- functionalized materials: new development and characterization of alloys, catalysts and adsorbents such as activated carbons, zeolites, silica gels, metal-organic frameworks;
- biogas and biomethane: studies on cleaning (especially desulphurization) of biogas and upgrading to biomethane; determination of chemical-physical parameters influencing biogas production such as digestion processes and process-inhibiting ingredients (ammonia);
- exhaust air, exhaust gas and wastewater treatment: development and testing of physical and chemical processes (adsorption, absorption, membrane separation, catalytic oxidation);
- inorganic monoliths and membranes: manufacture and characterization of porous glasses and ceramics;
- processing of petroleum fractions and residues by extractive processes with liquid gas and supercritical media;
- development of new analytical techniques and measuring methods for the characterization of processes and materials;
- construction and operation of pilot plants.

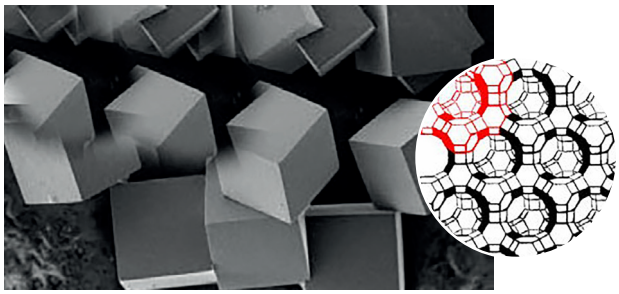
Our industrial partners are mainly small and medium-sized companies from Germany, which implement the research results obtained on technical processes. The scientists and employees of the INC thus significantly influence the state of the art through innovative process and product development.

For several years, there has been a close cooperation of the INC with 3P Instruments GmbH & Co KG. This resulted in the establishment of an annual joint adsorption week including a symposium on dynamic sorption processes. Recent projects have led to the establishment of the institute as a competence center for adsorption technology and the expansion of the 3P Instruments product portfolio.

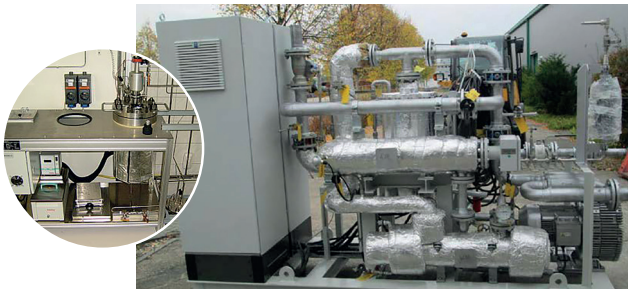
We thank 3P for the successful cooperation, look forward to the future and wish the managing director Dr. Dietmar Klank and his team from 3P-Instruments GmbH & Co. KG all the best for the 30th company anniversary!

Renewable Energies / Biomethane

Functionalized Materials



Scale-down, Scale-up, Piloting



Process Development

Methods

- Adsorption
- Catalysis
- Oxidation Technologies
- High Pressure Technology
- High Temperature Processes
- Non-Classic Energies

A new twist on chemisorption: Combining detectors for maximizing insight of your catalysts

Gary Deger, gdeger@altamirainstruments.com

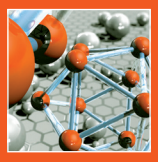


Figure 1 *AMI-300 fitted with customized IR transmission cell in an FTIR instrument*

Traditional chemisorption techniques for catalyst characterization include Temperature Programmed Desorption (TPD), Temperature Programmed Reduction/Oxidation (TPR/O) and Pulsed Chemisorption. The most common detectors utilized for analysis is the Thermal Conductivity Detector (TCD), or Mass Spectrometer when multiple compounds of interest are evolved. These techniques rely solely on the observation of evolved gases from a catalyst surface. The end results yield number and strengths of sites but not the nature of the sites, the type of adsorption, or whether there exist multiple types of sites.

To address the type of chemical bonding at these sites, an in-situ analysis would have to be performed. Fourier Transform Infrared (FTIR) spectroscopy is an ideal choice for such an analysis due to its speed of analysis and spectral discrimination to the different types of chemical bonding found between catalysts and the adsorbing gases. However, the use of FTIR has limited abilities in determining the strength of these sites and quantification results are limited, at best.

In order to combine the benefits of both, users typically had to purchase two separate instruments, along with data analysis software in two formats. However, Altamira has now developed the AMI-300IR which combines all the standard AMI techniques (TPD, TPR/O and Pulsed Chemisorption) with real-time observation of the catalyst surface by Fourier Transform Infrared (FTIR) spectroscopy and quantification of absorbing gases by TCD. This combination of techniques allows for the direct observation of the adsorbed species as well as quantifying catalyst uptake and desorption.

For the FTIR solution, a custom designed heated IR transmission cell is mounted into a commercial FTIR instrument which then fits into the furnace cavity of a standard AMI-300 (see Fig. 1).

A sample is prepared in the form of a thin, self-supported catalyst wafer by pressing approximately 100 mg of catalyst powder into a disk and then securing it in a proprietary catalyst holder within the IR cell. The IR beam can thus pass through the catalyst wafer. The wafer can be heated in the flow cell (up to 500 °C) with the temperature being monitored and ramped as desired. Fig. 2 shows a schematic of the cell.

The sample can then be subjected to all the standard chemisorption treatment, heating and desorption procedures, while monitoring the catalyst surface and the adsorbates via the IR spectrometer.

What follows are several examples of TPDs and Pulsed experiments utilizing both FTIR and TCD detectors.

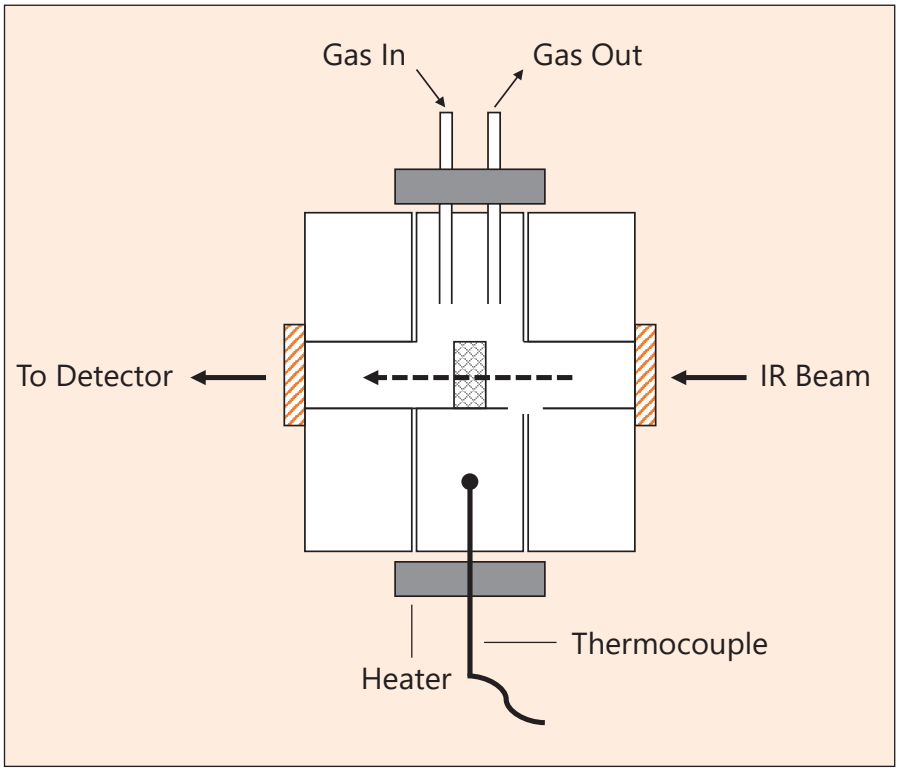


Figure 2 *Scheme of the IR cell and the measurement setup*

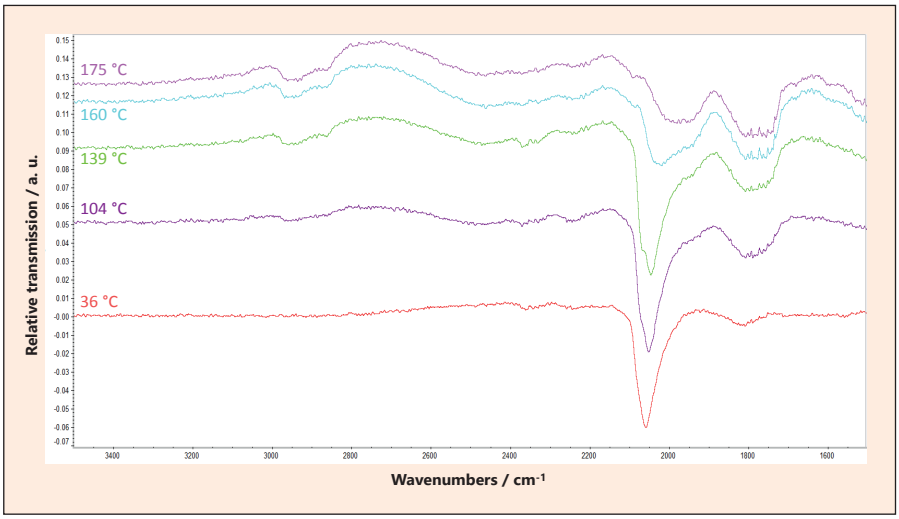


Figure 3 *CO signal as a function of temperature*

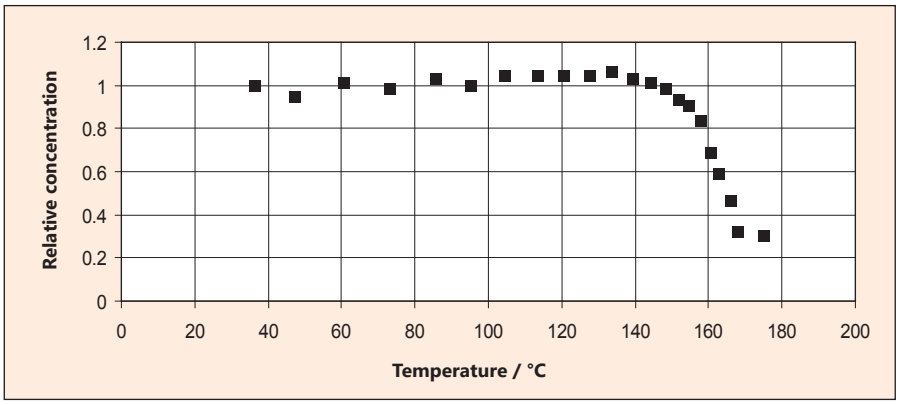


Figure 4 *Isobar of CO adsorbed on 1% Pt/Al_2O_3*

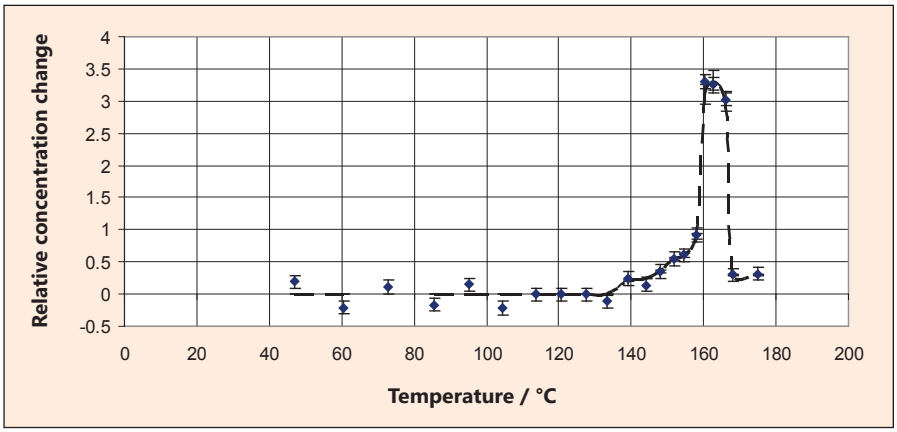
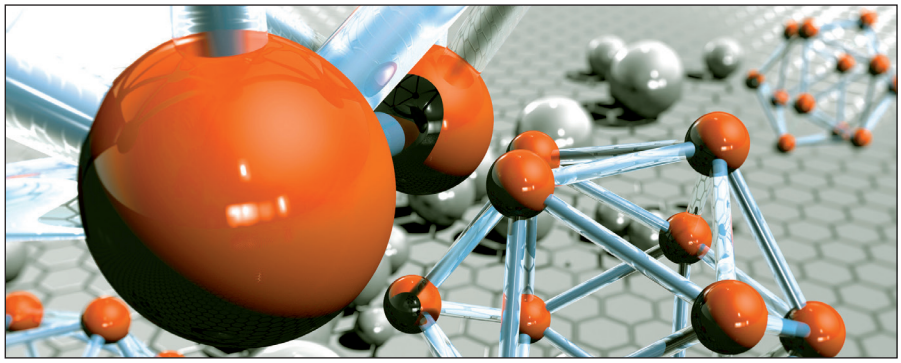
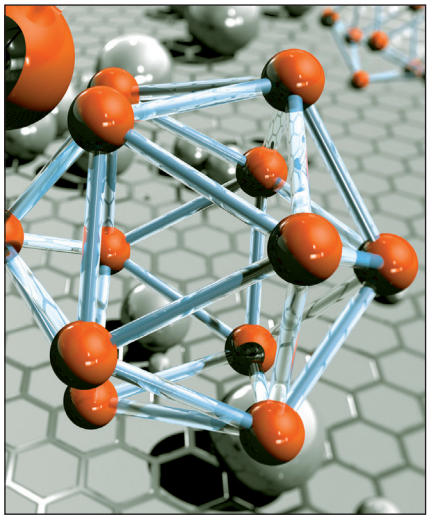


Figure 5 *Derived CO TPD*





Observation of CO adsorbed on a Pt catalyst

An example of the kind of information that can be obtained with Chemisorption-FTIR is the type of adsorption and desorption of CO on a platinum surface. A 1 % Pt/Al_2O_3 catalyst was pressed into a wafer and mounted in a transmission IR cell. The sample was reduced for several hours in flowing hydrogen at 200 °C, cooled to room temperature, treated with flowing CO and then flushed with inert gas for an hour in order to remove the gas-phase and any loosely held CO. The resulting IR spectrum (background subtracted) shows adsorption peaks at approximately 2060 cm^{-1} corresponding to linearly adsorbed CO (see Fig. 3). Using a TCD, you would only know that there was adsorption, but not if the mode of adsorption was linear or bridged.

As this sample was also heated, the CO band followed as a function of temperature (see Fig. 3). It can be seen that the transmission of the CO band decreased with increasing temperature. According to Beer's Law, absorbance is proportional to concentration so from these measurements it is possible to construct an isobar and from it obtain a derived TPD. These are shown in Fig. 4 and 5, respectively.

Differentiation between Brønsted and Lewis acid sites using ammonia chemisorption

Ammonia can be used as a probe molecule to determine the magnitude and type of acid sites in a catalyst. Fig. 6 below shows an example of ammonia adsorbed on a silica-alumina material. Three broad bands were identified as belonging to the adsorbed ammonia at approximately 1760, 1480, and 1380 cm^{-1}. The band at 1480 cm^{-1} can be assigned to ammonia adsorbed on Brønsted acid sites, the others to ammonia adsorbed on Lewis sites /1/. By carrying out a temperature programmed experiment and following the absorbance of the three bands as a function of temperature it is possible to measure the isobars for each type of adsorption and examine the strength of each particular adsorption. These isobars are shown in Fig. 7.

It can be seen from the data that the adsorption reflected in the 1380 cm^{-1} band is more strongly held than the other two perhaps indicating a stronger Lewis-type bond.

For additional information on catalyst uptake or desorption quantitation for the treatment gases, the user can now easily switch to the TCD detector by removing the FTIR and inserting the furnace. This is an easy 5-minute procedure for the AMI-300 since the standard Altamira Chemisorption instrument has a built-in TCD detector in the flow path exiting the reactor.

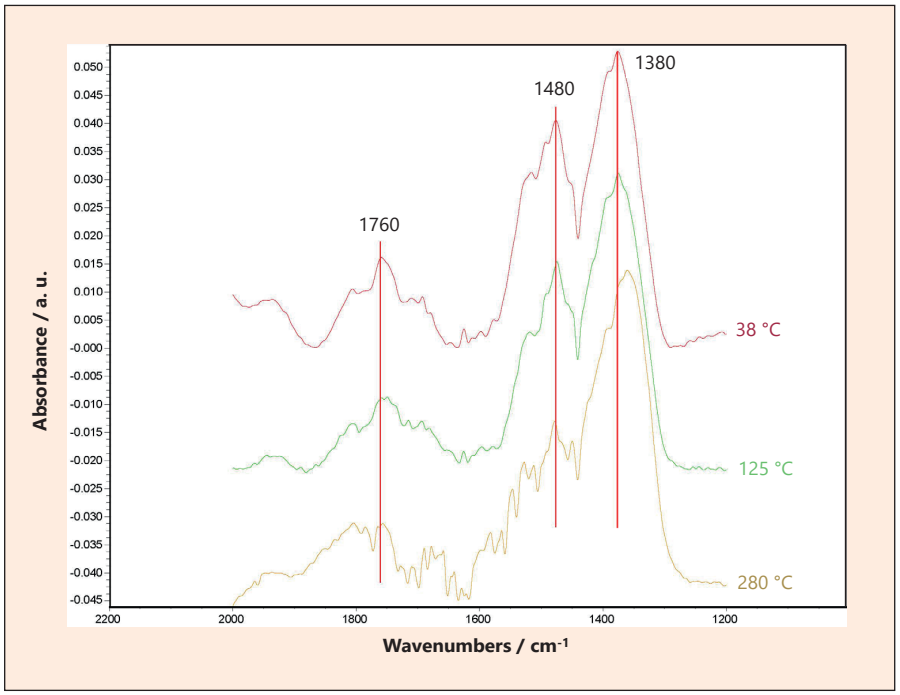


Figure 6 *Ammonia bands on silica-alumina shown at three different temperatures*

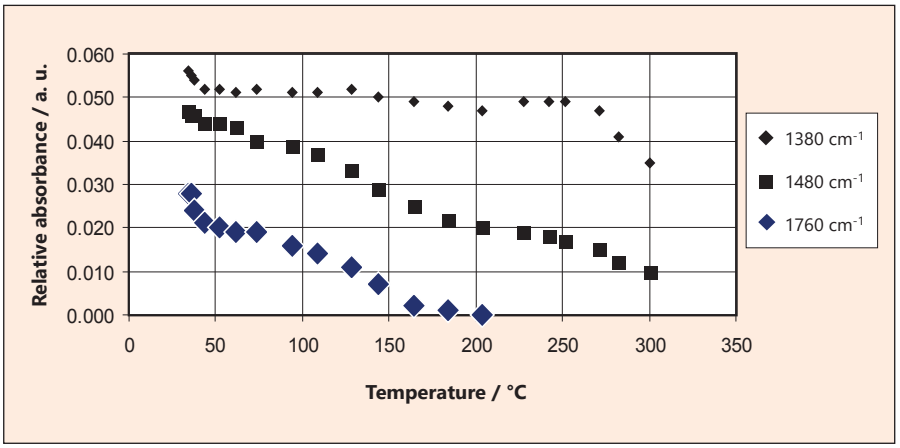
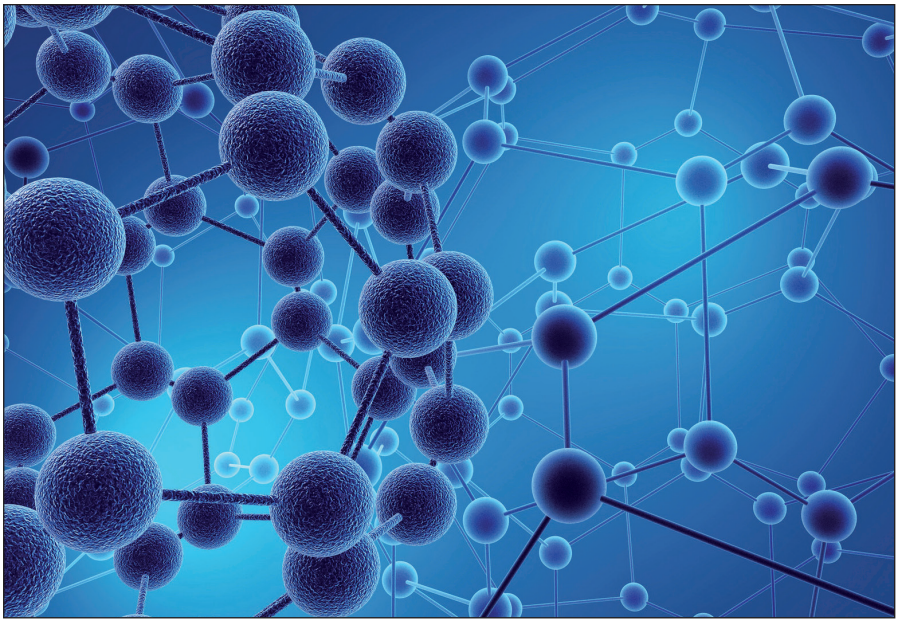


Figure 7 *Isobars for each of the three main ammonia bands on silica-alumina*

TPD experiment for NH_3 on a zeolite using a TCD

What follows is an example of a TPD that can calculate site specific adsorption, activation energies and basic desorption temperature profiles for a silica-alumina Zeolite (ZSM-5) /2/.

Ammonia desorption from ZSM-5 generates multiple peaks from ca. 100 to 500 °C /3/. Hence, determination of acid sites can be achieved by adsorbing ammonia at higher temperatures, thereby eliminating the physisorbed ammonia at lower temperature regimes. The current study uses this approach. Deconvolution of the TPD peaks provides the approximate ammonia uptake values.



Experimental

The catalyst used for this study had an aluminum content of 0.22 %, which approximates to 80 µmoles/gram of the catalyst.

TPD procedure

The sample was first treated with helium from room temperature to 600 °C. This was followed by adsorption of a 10 % ammonia in helium mixture at 30 °C. Then a stream of helium gas was passed over the sample to remove any loosely held ammonia. This was followed by the TPD step under a carrier stream of helium and linearly ramping from 30 to 600 °C.

A 500 µl sample loop was used to perform the pulse calibration procedure to determine the amount of ammonia adsorbed at the adsorption temperatures.

Results

Fig. 8 is the deconvoluted TCD signal of the TPD curve that was generated for the 30 °C ammonia adsorption experiment. You can see the overall peak (% TCD) and the deconvoluted peaks signals, 1, 2 and 3. Tab. 1 gives the summary of the integrated areas under each deconvoluted peak and the corresponding ammonia uptake that was calculated in µmoles/gram of the sample, using the built-in calibration loop. The highest temperature of each peak is also shown in the table.

Ammoniak-TPD-Diagramme von ZSM-5 Ammonia TPD patterns from ZSM-5 can exhibit multiple desorption peaks. The desorption signal observed below ca. 150 °C corresponds to physically adsorbed ammonia. Physisorption can occur not only on the catalyst surface but also on various components of the experimental system. It can be virtually eliminated by conducting the sorption at elevated temperatures above 100 °C. The other desorption signals correspond to ammonia adsorbed on surface acid sites with multiple signals being discerned between 200 and 500 °C. The nature of these signals, particularly the high temperature signals, can be directly related to the acidity of the catalyst.

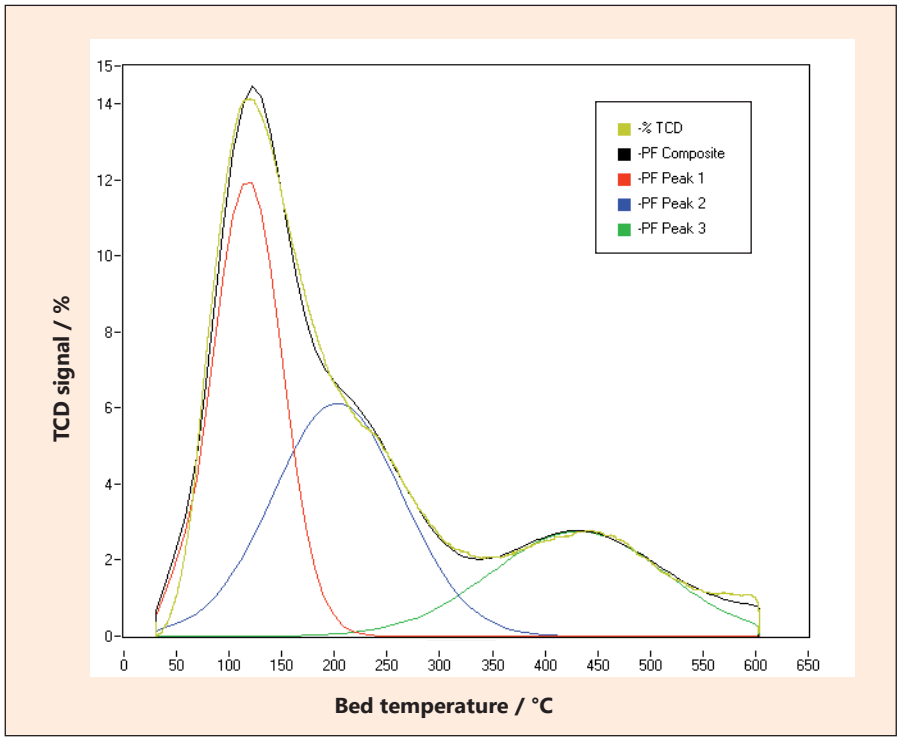


Figure 8 *Peak deconvolution curves of the ammonia TPD*

Table 1 *Summary of integrated results of the TPD curve from Fig. 8*

Peak Number	Integrated Area	Uptake / µmoles/g	Peak Temperature / °C
Peak 1	29,013	157	122
Peak 2	28,006	152	220
Peak 3	17,133	93	441

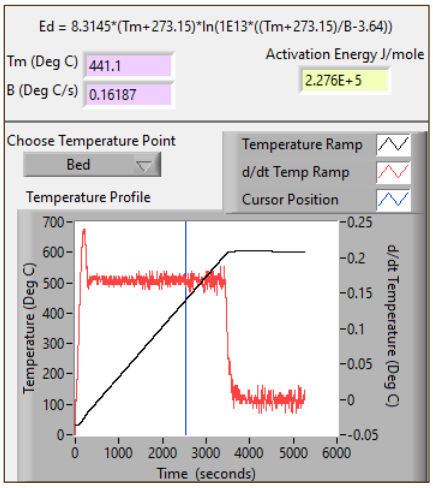


Figure 9 *Activation energy calculation and maximum temperature for peak 3*

Using the uptake numbers from Tab. 1 for the non-physisorbed peaks (2 and 3), we can calculate several additional values using the software in the AMI-300IR. As an example, the calculations for the activation energy at the maximum desorption temperature for peak 3 were carried out (Fig. 9).

Summary

The AMI-300IR presents an extension of our AMI catalyst characterization instruments which, in various forms, have been manufactured since 1984. The use of real-time FTIR, when combined with our other standard detectors, can now provide the catalyst researcher with not only the number and strengths of sites but also with the nature of the adsorption.

Are you interested in more information on the AMI-300IR series? Contact us at **info@3P-instruments.com** or **+49 8134 93240**.

References

/1/ M. Niwa et al., J. Phys. Chem. B, 110 (2006) p. 264

/2/ Altamira Application Note: Acid Site Determination on Zeolite Catalyst

/3/ S. B. Sharma et al., Applied Catalysis A: General, 102 (1993), 253-265

3P Instruments celebrates 30th company anniversary

3P Instruments GmbH & Co. KG
Rudolf-Diesel-Straße 12
85235 Odelzhausen | Germany
Tel. +49 8134 9324 0
info@3P-instruments.com

www.3P-instruments.com