BAM

Certification Report

Certified Reference Material BAM-P106

Porosity Properties of Nanoporous Titanium Dioxide

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Summary

This Report describes the certification of the porous reference material BAM-P106. The certified values determined by nitrogen adsorption at 77.3 K according to the international standards ISO 15901-2 and ISO 9277 are summarized in the Table below.

Property [a]		Value	Uncertainty [b]	Unit
Specific Surface Area [c]	A_{BET}	96.6	1.7	m^2/g
Specific pore volume [d]	$V_{p,0.99}$	0.2341	0.0024	cm^3/g
Hydraulic pore diameter	$4V_{p,0.99}/A_{BET}$	9.69	0.16	nm
Modal pore diameter	$D_{BJH,des}$ [e]	8.2	1.0	nm
Modal pore diameter	$D_{BJH,ads}$ [f]	11.5	0.9	nm

[a] Certified in accordance with the Guidelines for the Production of BAM Reference Materials [1]

[b] Uncertainty $U = k\ u_c$ calculated according to ISO Guide 35 [2] and ISO/IEC Guide 98 [3] with the coverage factor $k = 2$ (giving a level of confidence of approximately 95 %). The value of the combined standard uncertainty u_c of each certified property includes both an uncertainty contribution resulting from the interlaboratory testing and a second one taking into account possible inhomogeneities of the material

[c] Specific surface area calculated according to the BET model [4] as described in ISO 9277 [5]

[d] Single point total pore volume according to the Gurvich rule [6] determined from the adsorption branch of the isotherm at relative pressure $p/p_0 = 0.990$

[e] Pore size at maximum of the differential pore size distribution calculated from the desorption branch of the isotherm applying the BJH model [7] as described in ISO 15901-2 [8]

[f] Pore size at maximum of the differential pore size distribution calculated from the adsorption branch of the isotherm applying the BJH model [7] as described in ISO 15901-2 [8]

The listed value for the surface area and the values of the other pore size properties are method-defined (model dependent) parameters. Under the condition that the evaluation models used are applied as an integral part of the traceability statement, the certified values are traceable to the base units of the SI via calibrated measurements of the quantities pressure, volume, and mass.

A unit of the CRM BAM-P106 consists of a single bottle containing approximately 15 g of crystalline, nearly spherical titanium dioxide microparticles of about 85 µm in mean diameter.

The reference material is intended for performance checking of instruments used for the determination of BET specific surface area, specific pore volume, hydraulic pore diameter and BJH most frequent pore diameters from the desorption and the adsorption branch of the nitrogen isotherm determined by the static volumetric method.

The certificate of BAM-P106 is valid for two years from the date of shipment provided the reference material is stored under the recommended conditions.

List of abbreviations

(as far as not explained in particular sections of this Report)

ANOVA	analysis of variance
BET	Brunauer, Emmett, Teller (method)
BJH	Barrett, Joyner, Halenda (method)
CI	confidence interval
CRM	certified reference material
GUM	ISO guide to the expression of uncertainty in measurement
ILC	interlaboratory comparison (certification round robin)
MU	measurement uncertainty
RM	reference material
TI	tolerance interval

List of Symbols

k	coverage factor
l	number of accepted data sets in the interlaboratory comparison
n	number of observations
N	number of bottles selected for testing the homogeneity
s^2_{between}	variance between the bottles (homogeneity testing)
s^2_{within}	variance within one bottle (homogeneity testing)
s_x	ILC standard deviation of a property value
U	expanded standard uncertainty of a property value
u_{bb}	standard uncertainty due to between-bottle (in)homogeneity
u_{char}	standard uncertainty due to characterization
u_{c}	combined standard uncertainty of a property value
u_{lts}	standard uncertainty due to long-term (in)stability
x	property value of a candidate material
x_{cert}	certified property value of a CRM
x_{i}	result of a single measurement in the experiment

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1. Intention of the certification project

Today, pore size analysis by means of gas adsorption (together with mercury porosimetry) has still remained one of the most frequently applied methods for the characterization of nanoporous materials. Particularly for the pore size determination of a number of innovative porous materials with small nanopores (such as micro- and mesoporous zeolites and metal organic frameworks which are of growing importance for gas storage or low energy gas separation technologies) gas adsorption is indispensable for porosity characterization because pores below 4 nm cannot be detected by mercury porosimetry and possible alternative methods such as small angle X-ray scattering (SAXS) have been far from the status of a widely used standardized routine method up to now.
Therefore, in 1996 BAM has developed the very first two porous reference materials for the gas adsorption method with certified pore size and pore volume in addition to the BET surface area. In the meantime, all units of these two CRMs are sold out (BAM-PM-103 since summer 2008 and BAM-PM-104 since summer 2011). The successor material for CRM BAM-PM-103 was BAM-P105 (a nanoporous glass) certified in 2009. The high number of inquiries after a new porous CRM with similar porosity properties as those of BAM-PM-104 was the motivation for the current project to develop and certify an appropriate successor material intended for nitrogen adsorption.
The certification of this new CRM has been carried out on the basis of BAM Guidelines for the Development of Reference Materials [1] and relevant ISO Guides [2], [3], [9], [10].

2. Description of the material

2.1 Selection and source of the candidate material

In contrast to the predecessor material BAM-PM-104, which was an aluminium oxide (alumina), for the successor material a mesoporous titanium dioxide (TiO_2, also called titania) was selected from a number of tested candidate materials. The titania candidate material Sachtopore® NP 8060 was manufactured and delivered by Sachtleben GmbH Duisburg (Germany). According to the specifications by the producer, Sachtopore® NP 8060 is a novel spherically shaped sorbent for liquid chromatography on the basis of porous titanium dioxide. The special feature of the Sachtopore® adsorbents is their character as porous solids in spherical shape in spite of their 100 % crystalline structure. The spherical and porous Sachtopore® particles are shaped using special particle-forming and sintering steps. These lead to three-dimensional networks of intermingling crystallites which give the ceramic Sachtopore® particles their surface texture and porosity. The tertiary structure of the bridged crystallites offers high specific surface areas to enable adsorption processes for effective chromatographic separations.
Careful control of the production process leads to extremely narrow pore size distributions and hinders the generation of micropores. In addition to the high mechanical stability of the crystalline Sachtopore® particles, the material has also a remarkable chemical stability. As a refractory and temperature stable ceramic oxide, TiO_2 is practically insoluble in acids (up to concentrations of approximately 5 mol L^{-1}) and bases (also up to about 5 mol L^{-1}). Sachtopore® is therefore much more resistant than silica, which dissolves under basic conditions exceeding pH

8, and also much more resistant than aluminium oxide, which is amphoteric and hence dissolves in acids and bases.

As a result of XRD measurements at BAM, Division 1.3, it could be confirmed that the crystal modification of Sachtopore® 8060 is pure anatase. Although anatase is metastable i.e. thermodynamically less stable than rutile (the other main modification of TiO_2), the phase conversion rate of anatase into rutile is virtually zero at temperatures up to about 600 °C. Therefore, the long term stability of anatase is not affected in the temperature range between room temperature and the recommended degassing temperature of 180 °C (see 2.2).

One important advantage of the porous titania material Sachtopore® NP 8060 for the purpose of a porous reference material is the nearly ideally shaped nitrogen isotherm of Type IV with a H1 hysteresis according to IUPAC nomenclature [11]. The isotherm type H1 is often associated with porous materials known, from other evidence, to consist of agglomerates or compacts of approximately uniform spheres in fairly regular array, and hence to have narrow distributions of pore size.

Compared with the predecessor material BAM-PM-104 (amorphous alumina type 60), BAM-P106 exhibits a pronounced plateau in the upper part of the isotherm (see Fig. 3) which enables a better application of the Gurvich rule for the determination of the total mesopore volume [6].

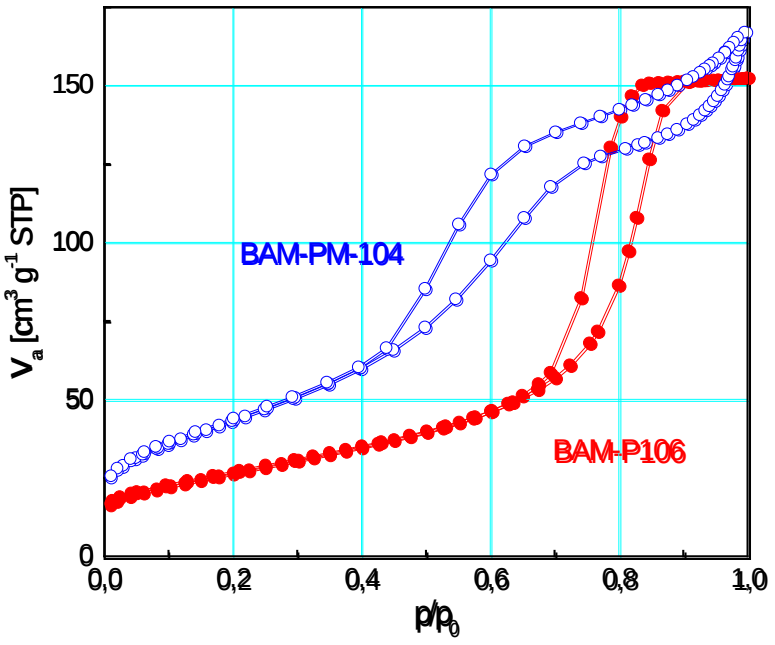


Fig. 1: Isotherms of porous CRMs BAM-PM-104 and BAM-P106

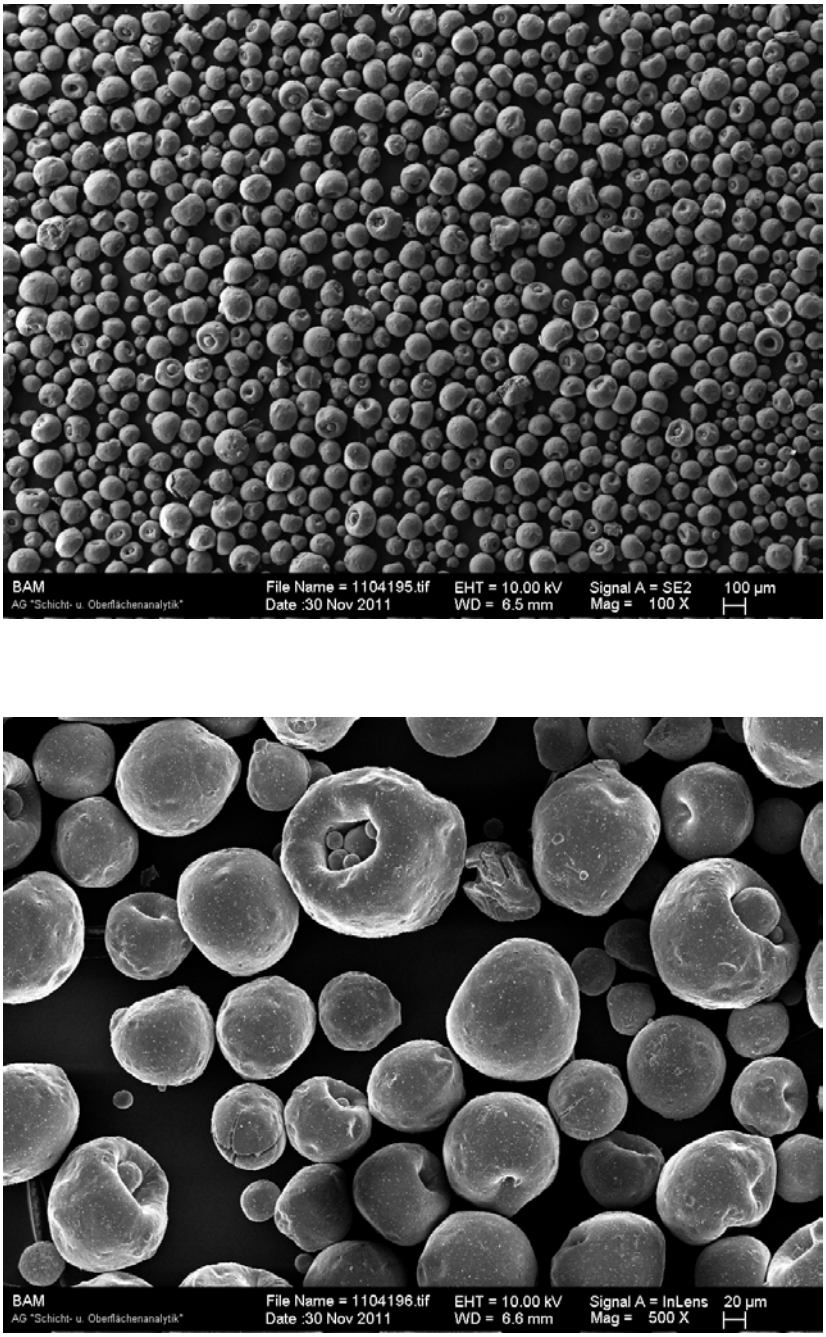
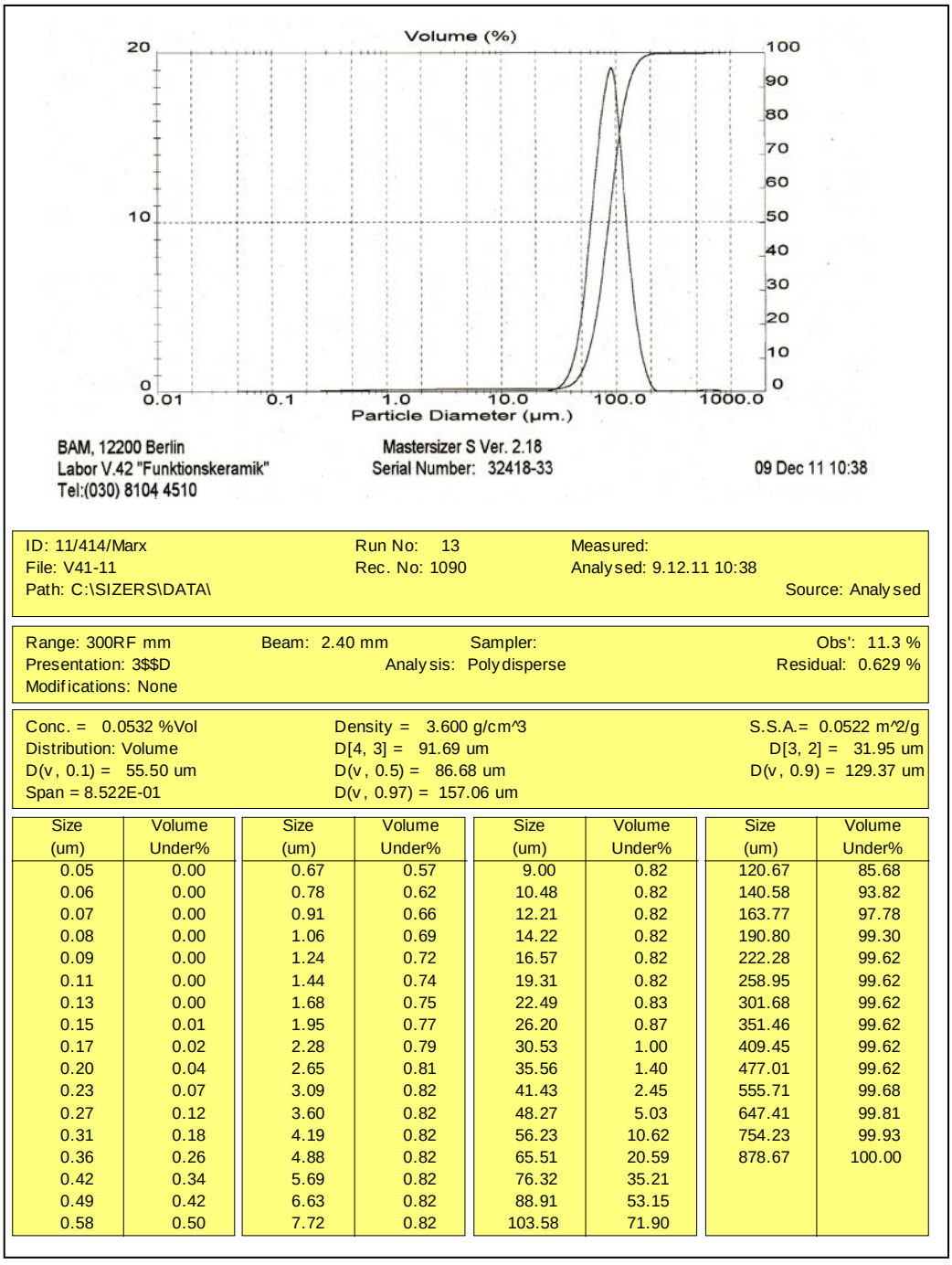


Fig. 2: Scanning electron micrographs of Sachtopore® NP 8060 at two different magnifications



Size (um)	Volume Under%	Size (um)	Volume Under%	Size (um)	Volume Under%	Size (um)	Volume Under%
0.05	0.00	0.67	0.57	9.00	0.82	120.67	85.68
0.06	0.00	0.78	0.62	10.48	0.82	140.58	93.82
0.07	0.00	0.91	0.66	12.21	0.82	163.77	97.78
0.08	0.00	1.06	0.69	14.22	0.82	190.80	99.30
0.09	0.00	1.24	0.72	16.57	0.82	222.28	99.62
0.11	0.00	1.44	0.74	19.31	0.82	258.95	99.62
0.13	0.00	1.68	0.75	22.49	0.83	301.68	99.62
0.15	0.01	1.95	0.77	26.20	0.87	351.46	99.62
0.17	0.02	2.28	0.79	30.53	1.00	409.45	99.62
0.20	0.04	2.65	0.81	35.56	1.40	477.01	99.62
0.23	0.07	3.09	0.82	41.43	2.45	555.71	99.68
0.27	0.12	3.60	0.82	48.27	5.03	647.41	99.81
0.31	0.18	4.19	0.82	56.23	10.62	754.23	99.93
0.36	0.26	4.88	0.82	65.51	20.59	878.67	100.00
0.42	0.34	5.69	0.82	76.32	35.21		
0.49	0.42	6.63	0.82	88.91	53.15		
0.58	0.50	7.72	0.82	103.58	71.90		

Fig. 3: Particle size analysis of Sachtopore® NP 8060 by laser diffraction technique

2.2 Porosity characterization

After degassing the sample material in a vacuum (often carried out at elevated temperatures), the first step of pore size analysis using the gas adsorption method is the measurement of a low temperature physisorption isotherm (see Fig. 4). By means of appropriate models, a number of porosity parameters can be calculated from the isotherm data such as

- the specific surface area A_{BET} in m^2/g according to the BET model of Brunauer, Emmett, and Teller [4],
- the total mesopore volume $V_{p,0.99}$ according to the Gurvich rule [6],
- the hydraulic pore diameter $4V_{p,0.99}/A_{BET}$,
- the pore diameter $D_{BJH,des}$ according to the BJH method [7] of Barrett, Joyner and Halenda from the desorption branch of the isotherm (see Fig. 4 and 6),
- the pore diameter $D_{BJH,ads}$ from the adsorption branch of the isotherm (see Fig. 4 and 5).

The degassing of BAM-P106 has to be carried out in a vacuum. After heating the sample with a rate of about 5 K/min to 180 °C, further heating at this temperature for at least 3 hours is necessary. Afterwards, the sample is allowed to cool slowly back to ambient temperature. The final pressure should be < 0.1 Pa.

In the case that the very last part of the adsorption isotherm is influenced by the beginning macroscopic condensation outside the pore system (indicated by a steep increase of volume) it is recommended to determine the Gurvich single point total pore volume at a lower relative pressure ≥ 0.95 in the plateau of the isotherm.

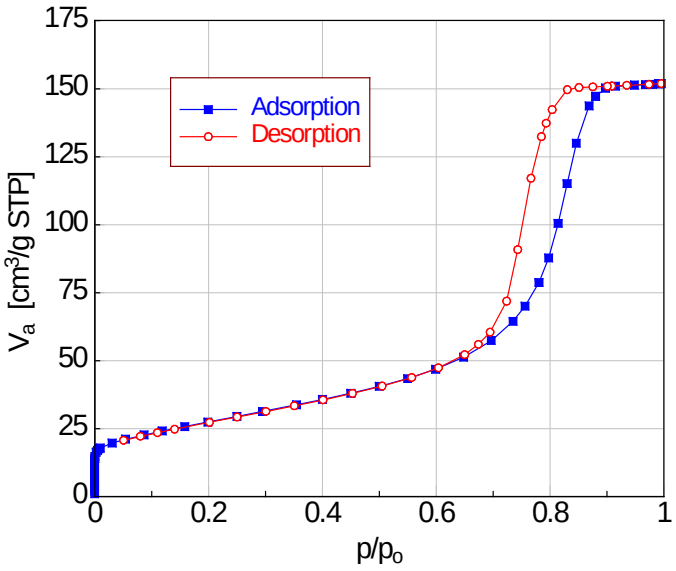


Fig. 4:
Complete N_2 isotherm of BAM-P106 at 77.3 K

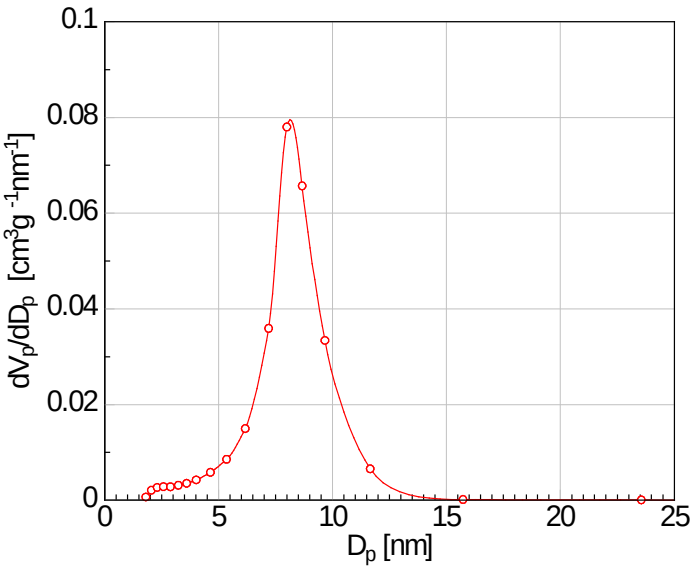


Fig. 5:

BJH pore volume distribution from the desorption branch of the N_2 isotherm

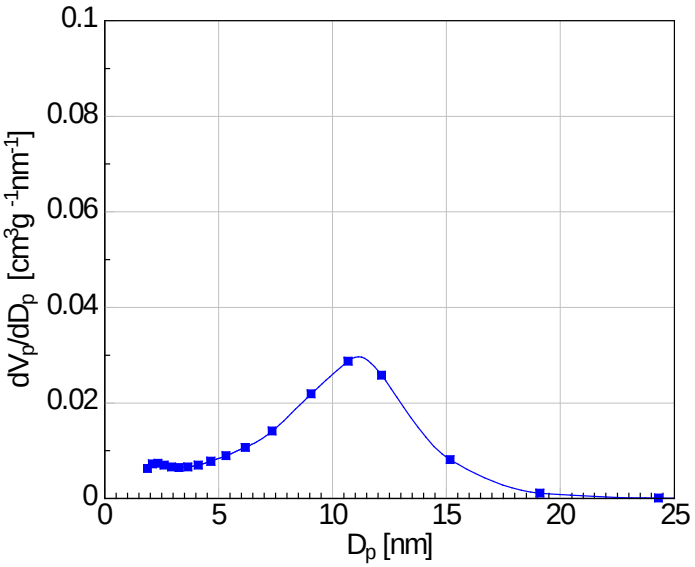


Fig. 6:

BJH pore volume distribution from the adsorption branch of the N_2 isotherm

3. Homogenization and subdividing of the candidate material

Homogenization and subdividing of the candidate material were carried out by means of a 8 port rotary sample divider PT 100 (Retsch, Germany) using the cross riffling scheme [12] seen in Fig. 7.

1	2	3	4	5	6	7	8		
⇓	⇓	⇓	⇓	⇓	⇓	⇓	⇓		
1-8	2-7	3-6	4-5	5-4	6-3	7-2	8-1	⇒	H
1-7	2-6	3-5	4-4	5-3	6-2	7-1	8-8	⇒	G
1-6	2-5	3-4	4-3	5-2	6-1	7-8	8-7	⇒	F
1-5	2-4	3-3	4-2	5-1	6-8	7-7	8-6	⇒	E
1-4	2-3	3-2	4-1	5-8	6-7	7-6	8-5	⇒	D
1-3	2-2	3-1	4-8	5-7	6-6	7-5	8-4	⇒	C
1-2	2-1	3-8	4-7	5-6	6-5	7-4	8-3	⇒	B
1-1	2-8	3-7	4-6	5-5	6-4	7-3	8-2	⇒	A

Fig. 7 Cross riffling scheme

The initial amount of Sachtopore® 8060 was subdivided into single units of at least 15 g packaged in glass bottles of 30 mL volume. The total number of units was 312, 28 units of them have been used for testing the homogeneity and stability and for the interlaboratory comparison as well.

4. Homogeneity and stability testing

4.1 Homogeneity

For testing the homogeneity, 12 individual units of BAM-P106 were randomly selected. Two replicate measurements per bottle were carried out under repeatability conditions. To detect the within-bottle standard deviation, 5 replicates from one additional, also randomly selected bottle were measured. The test results are summarized in Tables 1 and 2.

Table 1: Results of homogeneity testing between bottles (2 replicates for each bottle)

Bottle	Data file	A_{BET}	$V_{p,0.99}$	$4V_p/A_{BET}$	$D_{BJH(des)}$	$D_{BJH(ads)}$
		m^2/g	cm^3/g	nm	nm	nm
I01-05	TiO-H-66.smp	96.6595	0.234127	9.68872	9.13	12.10
	TiO-H-69.smp	97.2190	0.234648	9.65441	9.09	12.13
G01-07	TiO-H-72.smp	97.3690	0.234737	9.64318	8.13	12.11
	TiO-H-79.smp	97.2674	0.234726	9.65282	8.18	12.19
F04-01	TiO-H-85.smp	97.0016	0.233575	9.63179	8.14	12.21
	TiO-H-91.smp	97.7737	0.234912	9.61046	8.83	12.21
D01-05	TiO-H-101.smp	97.1728	0.234201	9.64061	8.14	12.09
	TiO-H-113.smp	96.2719	0.233934	9.71973	8.24	12.23
D04-02	TiO-H-104.smp	97.1759	0.234588	9.65622	8.12	12.09
	TiO-H-112.smp	96.9629	0.234145	9.65918	8.31	11.97
F01-07	TiO-H-107.smp	96.9406	0.233757	9.64536	8.19	12.07
	TiO-H-110.smp	97.0922	0.234398	9.65673	8.15	12.10
E02-08	TiO-H-115.smp	96.5343	0.233718	9.68434	8.30	11.98
	TiO-H-116.smp	96.7622	0.234225	9.68248	8.27	12.17
C04-03	TiO-H-118.smp	97.2970	0.234215	9.62887	8.29	12.00
	TiO-H-119.smp	97.1893	0.234408	9.64750	8.32	12.26
A02-06	TiO-H-121.smp	97.1147	0.234382	9.65381	8.27	12.12
	TiO-H-122.smp	97.0749	0.234085	9.64553	8.28	12.32
B03-07	TiO-H-123.smp	96.9652	0.234484	9.67290	8.23	12.06
	TiO-H-124.smp	97.4275	0.234329	9.62065	8.27	12.01
I06-02	TiO-H-126.smp	97.7113	0.234478	9.59881	8.29	12.24
	TiO-H-127.smp	97.6460	0.234675	9.61330	8.31	12.16
H04-05	TiO-H-129.smp	97.5283	0.233893	9.59282	8.35	12.10
	TiO-H-130.smp	97.5131	0.234757	9.62977	8.30	12.22

Table 2: Results of replicate measurements with samples from a single bottle

Bottle	Data file	A_{BET}	$V_{p,0.99}$	$4V_p/A_{BET}$	$D_{BJH(des)}$	$D_{BJH(ads)}$
		m^2/g	cm^3/g	nm	nm	nm
H01-04	TiO-H-81.smp	97.2351	0.233825	9.61895	8.09	12.22
	TiO-H-83.smp	96.8913	0.233326	9.63250	8.19	12.04
	TiO-H-89.smp	97.8869	0.235544	9.62516	8.11	12.04
	TiO-H-114.smp	97.2994	0.234029	9.62097	8.28	12.15
	TiO-H-117.smp	97.5293	0.234041	9.59881	8.28	12.16

To obtain the inhomogeneity contribution u_{bb} to be included into the total uncertainty budget of each porosity parameter, a 1-way Analysis of Variances (ANOVA) was carried out with the experimental homogeneity data. The u_{bb} values for BAM-P106 (see Table 3) were calculated according to ISO Guide 35 [2] as the maximum of the values obtained from the Equations (1) and (2).

$$u_{bb} = \sqrt{\frac{s^2_{between} - s^2_{within}}{n}} \quad (1)$$

$$u_{bb} = \frac{\sqrt{s^2_{within}}}{\sqrt{n}} \sqrt[4]{\frac{2}{N(n-1)}} \quad (2)$$

Table 3: Inhomogeneity contributions u_{bb} of BAM-P106

Property	u_{bb}	Unit
A_{BET}	0.2066554	m^2/g
$V_{p,0.99}$	0.0001774	cm^3/g
$4V_{p,0.99}/A_{BET}$	0.0189348	nm
$D_{BJH,des}$	0.2274371	nm
$D_{BJH,ads}$	0.0404815	nm

The statistical evaluation of the homogeneity testing results indicated that no significant inhomogeneity for the porosity parameters of Sachtopore® 8060 could be determined and therefore this candidate material has been suitable for the certification as CRM BAM-P106.

From the homogeneity testing measurements a recommendation for the minimum sample intake of CRM BAM-P106 can be derived because these measurements were carried out using sample masses of about 0.8 g. This means that the calculated value of u_{bb} is based on this sample mass and the recommended minimum sample intake for future usage of CRM BAM-P106 also should be 0.8 g.

4.2 Stability testing

The numerical results of the measurements to monitor the stability of the CRM BAM-P106 are listed in Table 4 for the period between April 2011 and October 2012. The stability measurements were carried out with the same automated surface area and porosity analyzer ASAP 2020 (Micromeritics, Norcross USA). The respective diagrams for each porosity property are depicted in Fig. 8 to 12.

Table 4: Numerical results of stability monitoring

Data file	Test date	A_{BET}	$V_{p,0.99}$	$4V_p/A_{BET}$	$D_{BJH(des)}$	$D_{BJH(ads)}$
		m^2/g	cm^3/g	nm	nm	nm
TiO2-022.smp	05.04.2011	97.04	0.2340	9.66	8.12	11.93
TiO2-023.smp	06.04.2011	97.35	0.2350	9.65	8.18	12.04
TiO2-030.smp	27.04.2011	97.00	0.2340	9.65	8.59	12.21
TiO-141.smp	10.10.2011	97.62	0.2341	9.59	8.29	12.13
TiO-143.smp	12.10.2011	97.45	0.2338	9.60	8.28	12.07
TiO-144.smp	13.10.2011	97.49	0.2344	9.62	8.28	12.08
TiO-145.smp	14.10.2011	96.78	0.2338	9.66	8.29	12.10
TiO-168.smp	25.11.2011	97.65	0.2348	9.61	8.31	11.88
TiO-182.smp	09.12.2011	98.06	0.2337	9.54	8.24	12.02
P106-192.smp	13.01.2012	97.11	0.2334	9.61	8.27	11.70
P106-236.smp	12.04.2012	97.53	0.2344	9.61	9.16	11.98
TiO-268.smp	22.06.2012	97.11	0.2351	9.69	8.28	12.53
TiO-299.smp	23.08.2012	98.20	0.2347	9.56	8.30	11.54
P106-326.smp	29.10.2012	97.80	0.2346	9.59	8.29	12.16
	$\bar{x}_{\text{Stab}}$ [a]	97.44	0.2343	9.62	8.35	12.03
	$\bar{x}_{\text{ILC}}$ [b]	96.60	0.2341	9.67	8.17	11.50
	$s_{x,\text{ILC}}$	2.08	0.0035	0.10	0.23	0.56
	$\bar{x}_{\text{Stab}} + 1 \cdot s_{x,\text{ILC}}$	99.22	0.2378	9.72	8.58	12.59
	$\bar{x}_{\text{Stab}} - 1 \cdot s_{x,\text{ILC}}$	95.06	0.2308	9.52	8.12	11.47

[a] Stab = stability monitoring, [b] ILC = interlaboratory comparison (certification round robin)

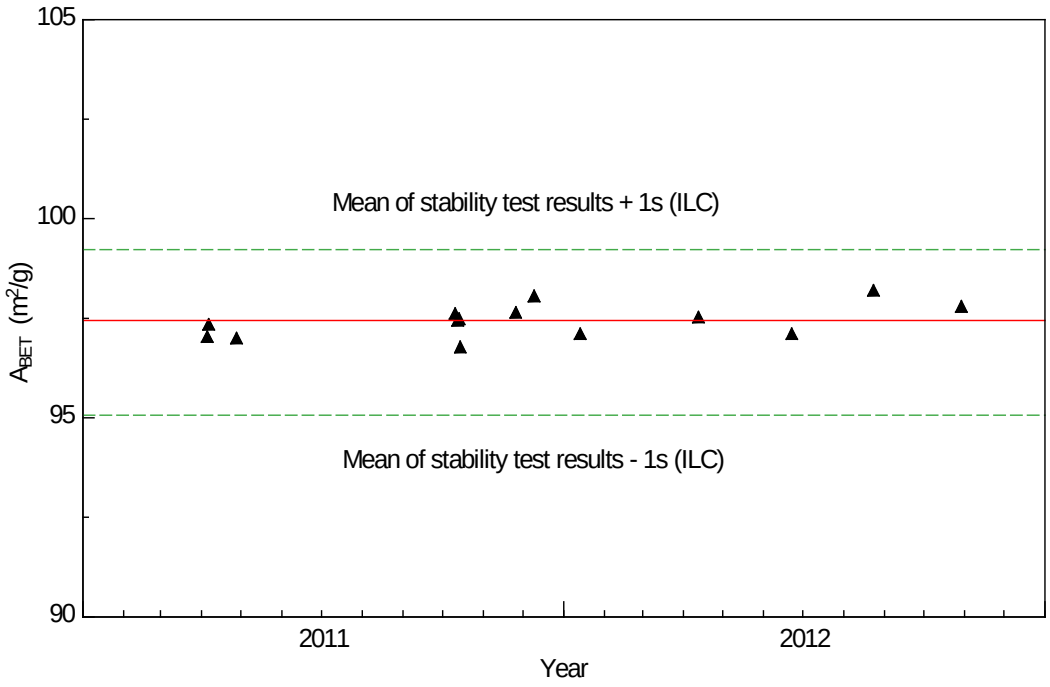


Fig. 8: Stability monitoring for the porosity property A_{BET} (BET specific surface area)

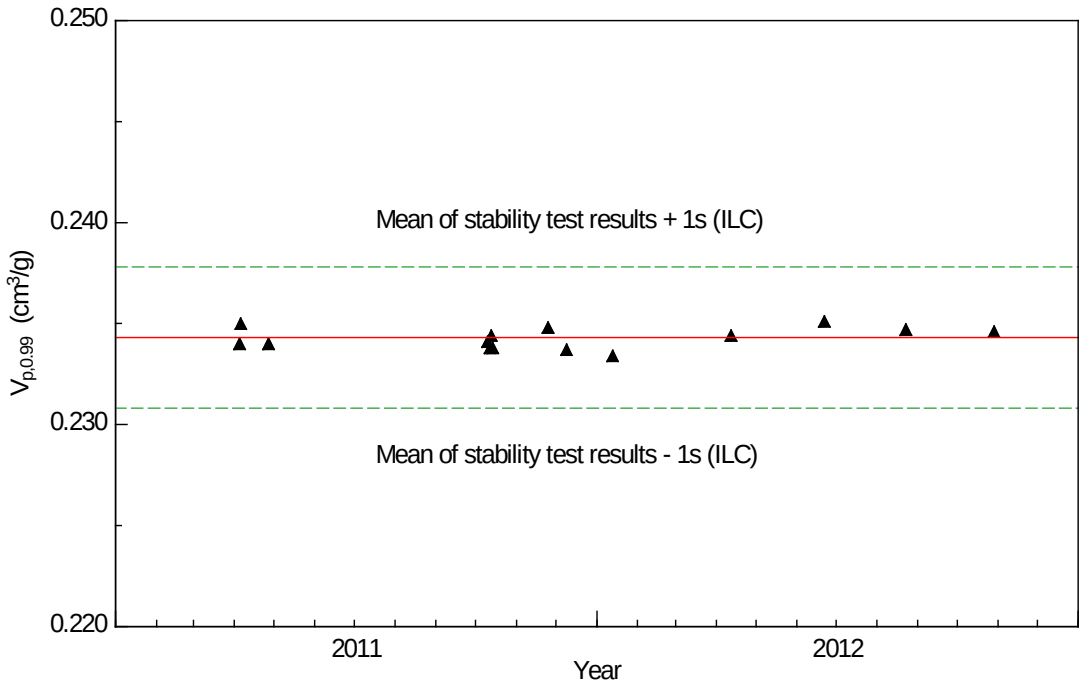


Fig. 9: Stability monitoring for the porosity property $V_{\mathrm{p},0.99}$ (specific pore volume)

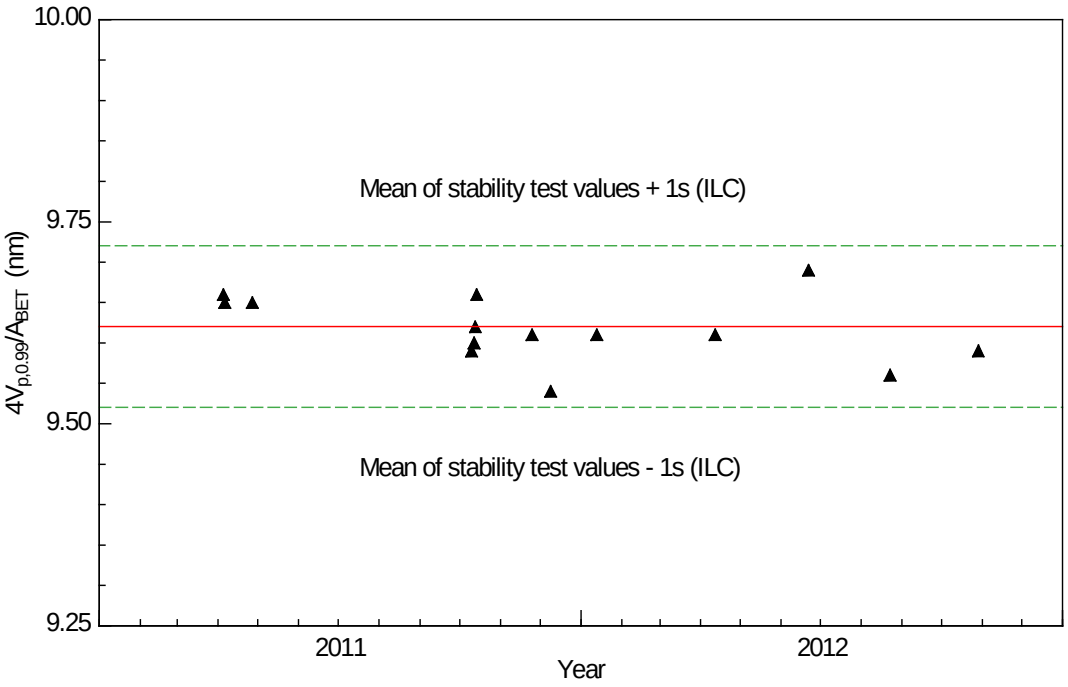


Fig. 10: Stability monitoring for the porosity property $4V_{p,0.99}/A_{BET}$ (hydraulic pore diameter)

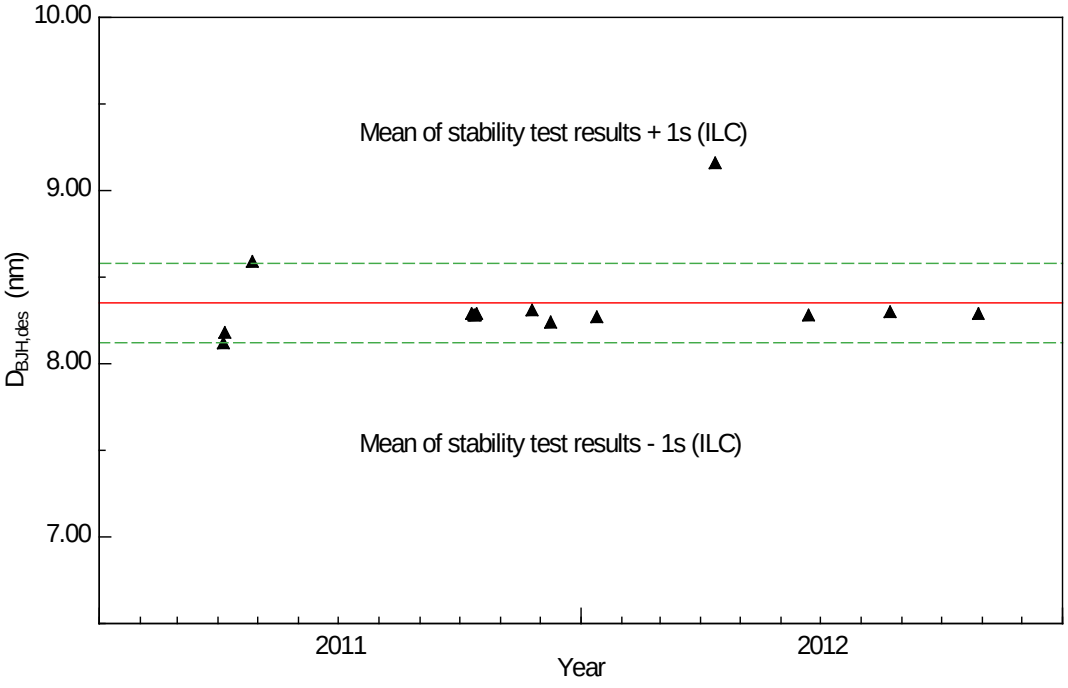


Fig. 11: Stability monitoring for the porosity property $D_{BJH(des)}$ (most frequent BJH pore diameter calculated from the desorption branch of the N_2 isotherm)

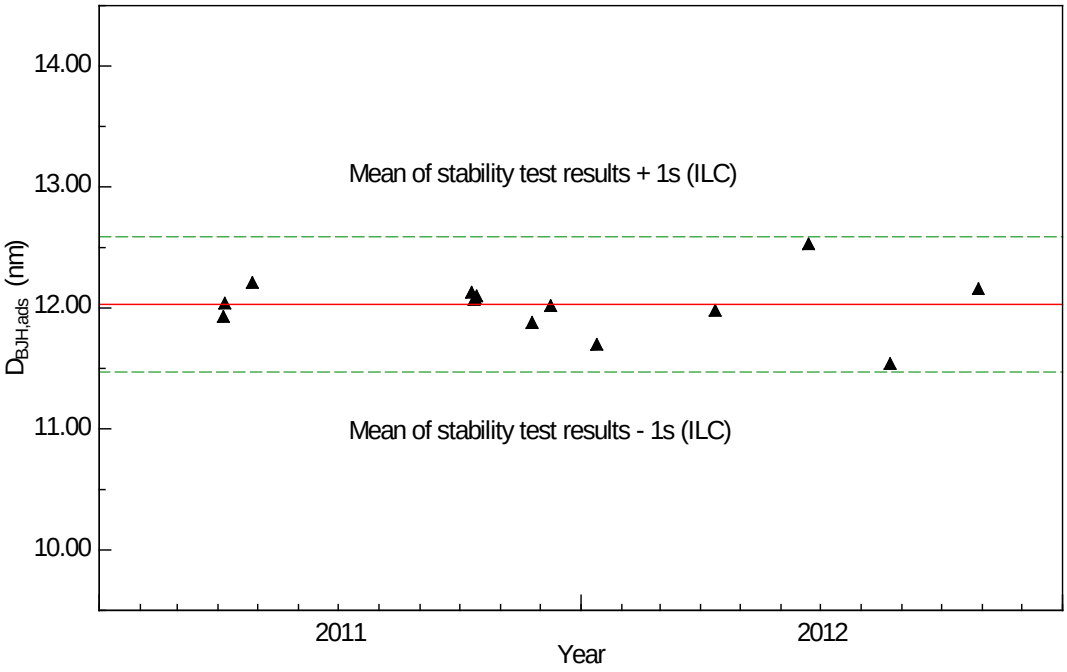


Fig. 12: Stability monitoring for the porosity property $D_{BJH(des)}$ (most frequent BJH pore diameter calculated from the adsorption branch of the N_2 isotherm)

The results of the statistical evaluation of the stability data (see Table 5) indicate that no instability could be detected for each porosity parameter but the contribution u_{lts} to the uncertainty of the certified values is not negligible and should be included in the final calculation of the combined uncertainty.

Table 5: Results of stability data evaluation according to ISO Guide 35

Property	intercept	slope	u(slope)	$u_{lts}(x)$	instability	negligible
A_{BET}	97.1520842	0.03581193	0.017307755	0.62307917	no	no
$V_{p,0.99}$	0.2340539	0.00002686	0.000024364	0.00087711	no	no
$4V_{p,0.99}/A_{BET}$	9.6386717	-0.00265805	0.001881466	0.06773276	no	no
$D_{BJH,des}$	8.2820656	0.00821111	0.012274471	0.44188094	no	no
$D_{BJH,ads}$	12.0470169	-0.00254192	0.011383081	0.40979093	no	no

The shelf life of CRM BAM-P106 estimated on the basis of the stability monitoring data is at least 36 month for a storage of the carefully closed bottle at temperatures below 30 °C under dry conditions.

5. List of participating laboratories

Aqura GmbH, Hanau (Germany)

BAM Federal Institute for Materials Research and Testing, Div. 1.3, Berlin (Germany)

BAM Federal Institute for Materials Research and Testing, Div. 5.6, Berlin (Germany)

Bayer Technology Services GmbH, Leverkusen (Germany)

Bayerisches Zentrum für Angewandte Energieforschung e.V., Würzburg (Germany)

BEL Japan Inc., Osaka (Japan)

Delft Solids Solutions, Delft (The Netherlands)

Fraunhofer-Institut für Keramische Technologien und Systeme, Hermsdorf (Germany)

Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Berlin (Germany)

Institute of Chemical and Engineering Sciences Ltd., Jurong Island (Singapore)

Instituto Pedro Nunes, Coimbra (Portugal)

Micromeritcs Instrument Corp., Norcross, GA (USA)

Micromeritics GmbH, Mönchengladbach (Germany)

POROTEC GmbH, Hofheim (Germany)

Quantachrome GmbH, Odelzhausen (Germany)

Quantachrome Instruments, Boynton Beach (USA)

Rubotherm - Präzisionsmesstechnik GmbH (Germany)

Sachtleben Chemie GmbH (Germany)

The Ural Research Institute for Metrology, Yekaterinburg (Russian Federation)

ThermoFisher Scientific, Milan (Italy)

University of Alicante (Spain)

The majority of the laboratories had already participated in previous interlaboratory comparisons in the field of gas adsorption measurements organized by BAM. Therefore, these laboratories had only to report their quality assurance measure performed to check the instrument performance. Three laboratories took part for the first time. These new participants had to pass a pre-qualification testing (three replicate measurements of an unknown porous material) before being accepted.

Table 6: Types of instruments used by the participants

Type of instrument	Number	Manufacturer
Surfer	2	ThermoFisher Scientific, Milan (Italy)
ASAP 2000	3	Micromeritics Instrument Corporation, Norcross, GA (USA)
ASAP 2010	1	
ASAP 2020	3	
ASAP 2420	3	
TriStar 3000	1	
TriStar 3020	1	
Autosorb-1	2	Quantachrome Instruments Corporation, Boynton Beach, FL (USA)
Autosorb-6	1	
Autosorb-iQ	1	
BELSORP-mini II	2	BEL Japan Inc., Osaka (Japan)
BELSORP-max	2	
non-branded (self made)	1	University of Alicante (Spain)
Total *	23	

* Two laboratories participated with two instruments each

6. Results of the interlaboratory testing and statistical uncertainty estimation

6.1 Experimental results

The interlaboratory comparison for the certification of BAM-P106 was performed on the basis of the Guidelines for the Production of BAM Reference Materials [1], data evaluation and statistical tests were carried out using the software package SoftCRM [13]. Each participating laboratory received a bottle containing about 8 g of the candidate material together with the instructions for running the tests and the data evaluation according to ISO standards 9277 [5] and 15901-2 [8]. The laboratories had to perform 5 replicate measurements with each participating instrument. The mean values for the porosity parameters gained by each instrument are shown in Table 7 and displayed graphically in Fig.13 to 17. The error bars at the data points for the data set means represent the standard deviation of the 5 certification measurements per data set.

Table 7: Data set means of the participants in the interlaboratory comparison (ILC)

Property x →	A_{BET}	$V_{p,0.99}$	$4V_{p,0.99}/A_{BET}$	$D_{BJH(des)}$	$D_{BJH(ads)}$
Data set no. ↓	m^2/g	cm^3/g	nm	nm	nm
01	99.28	0.2402	9.68	8.08	11.10
02	95.41	0.2331	9.77	8.22	11.29
03	96.95	0.2328	9.60	7.77	12.27
04	95.91	0.2307	9.62	7.77	12.27
05	101.11	0.2398	9.49	8.13	11.25
06	96.75	0.2374	9.82	8.34	11.16
07	94.97	0.2309	9.73	8.27	11.65
08	95.90	0.2296	9.57	8.19	11.62
09	103.44 [a]	0.2456 [a]	9.50	8.14	11.31
10	97.06	0.2334	9.62	8.26	12.10
11	94.96	0.2336	9.84	8.36	10.70
12	96.19	0.2323	9.66	8.44	12.21
13	96.34	0.2335	9.70	8.00	11.11
14	95.65	0.2325	9.72	8.65	12.04
15	96.38	0.2329	9.66	8.22	12.44
16	100.87	0.2395	9.54	7.86	11.21
17	96.42	0.2360	9.80	8.20	12.20
18	97.73	0.2341	9.58	8.29	11.17
19	95.97	0.2308	9.63	8.19	11.32
20	97.13	0.2339	9.63	7.41 [a]	10.66
21	97.08	0.2360	9.72	8.40	11.26
22	96.23	0.2402	9.98	7.78	10.74
23	90.81	0.2274	10.02	6.00 [a]	9.22 [a]
l	22	22	23	21	22
$\bar{x}$ [b]	96.60	0.2341	9.69	8.17	11.50
s_x [c]	2.08	0.0035	0.14	0.23	0.56
$\frac{s_x}{\sqrt{l}}$	0.44	0.0007	0.03	0.05	0.12
$\bar{x}+1\cdot s_x$	98.68	0.2376	9.83	8.40	12.06
$\bar{x}-1\cdot s_x$	94.52	0.2306	9.55	7.94	10.94
$\bar{x}+2\cdot s_x$	100.76	0.2411	9.97	8.63	12.62
$\bar{x}-2\cdot s_x$	92.44	0.2271	9.41	7.71	10.38

[a] insufficient data set mean for the particular property statistically detected as outlier and therefore have not been included in the evaluation

[b] average of the accepted data set means for the particular property on the basis of 5 single isotherm measurements each

[c] standard deviation of the data set means for the particular property

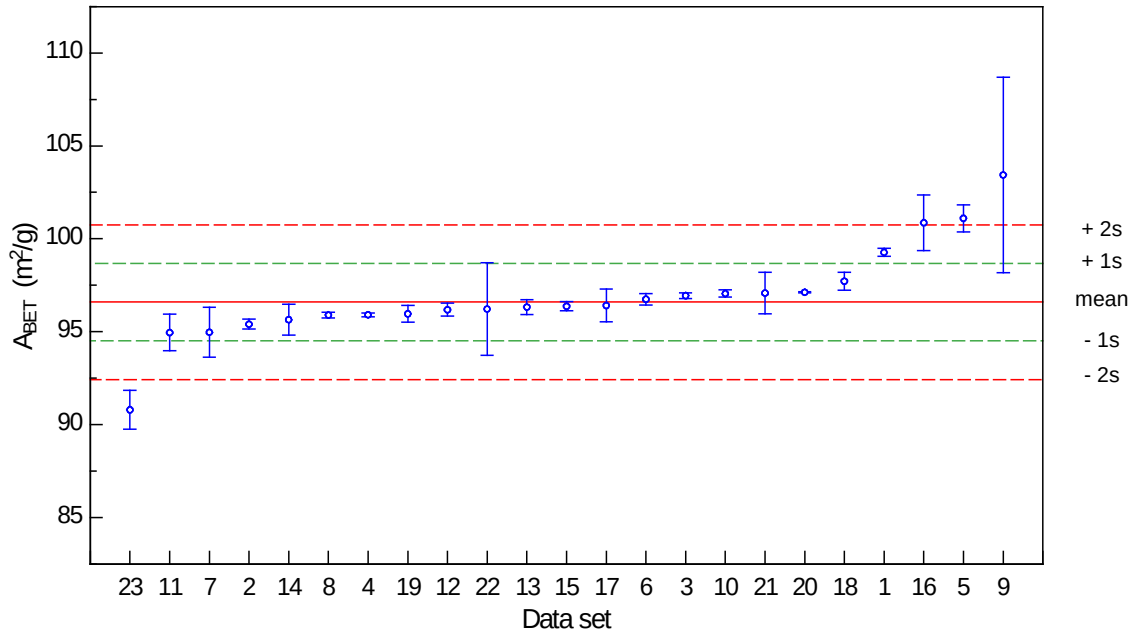


Fig. 13: Calculated data set means for A_{BET}

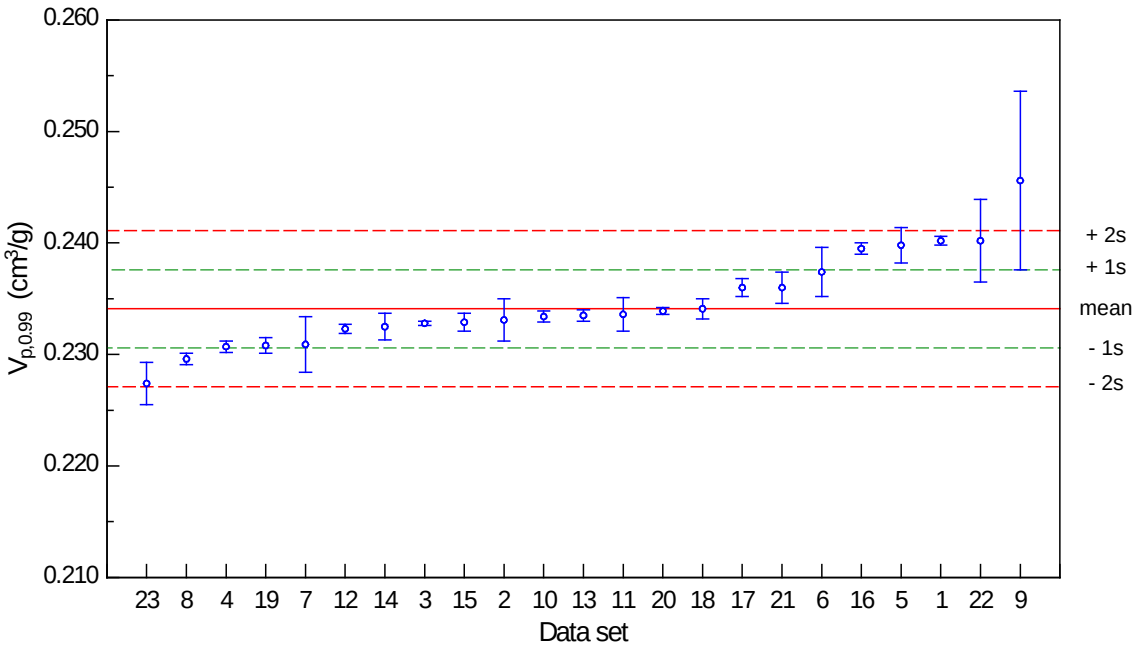


Fig. 14: Calculated instrument means for $V_{p,0.99}$

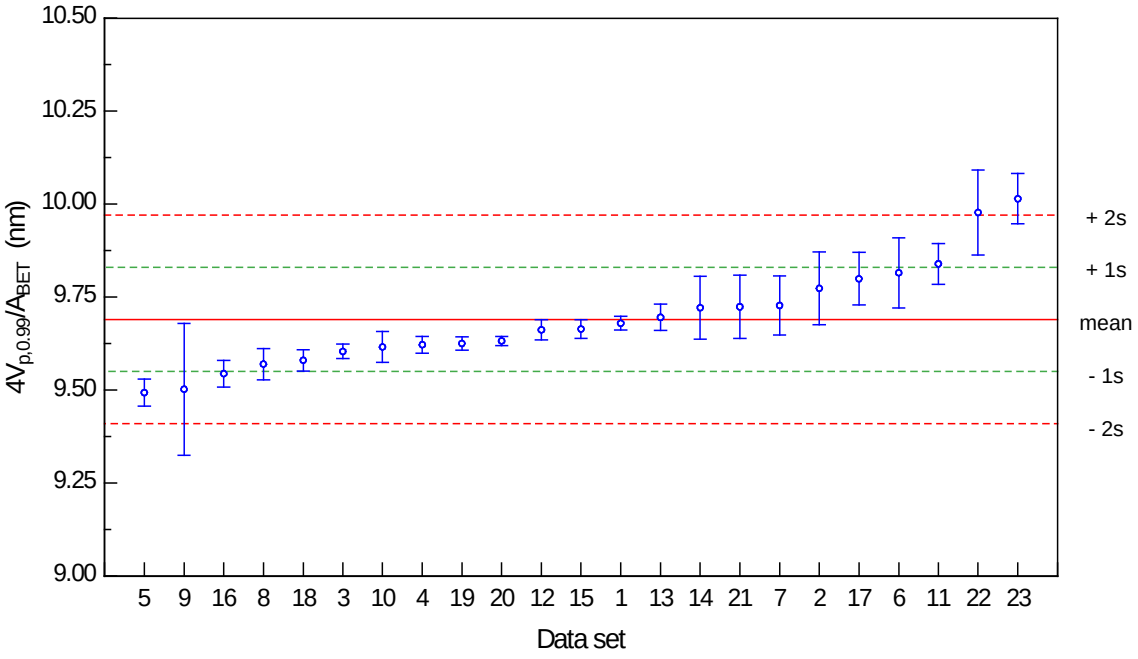


Fig. 15: Calculated data set means for $4V_{p,0.99}/A_{BET}$

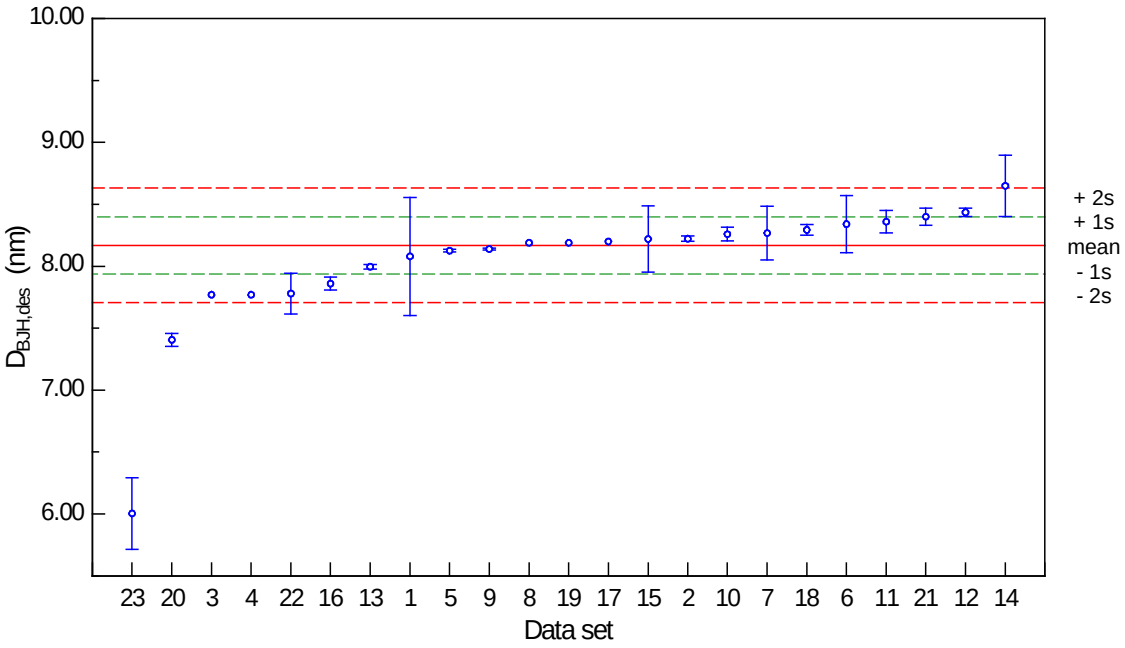


Fig. 16 Calculated data set means for $D_{BJH(des)}$

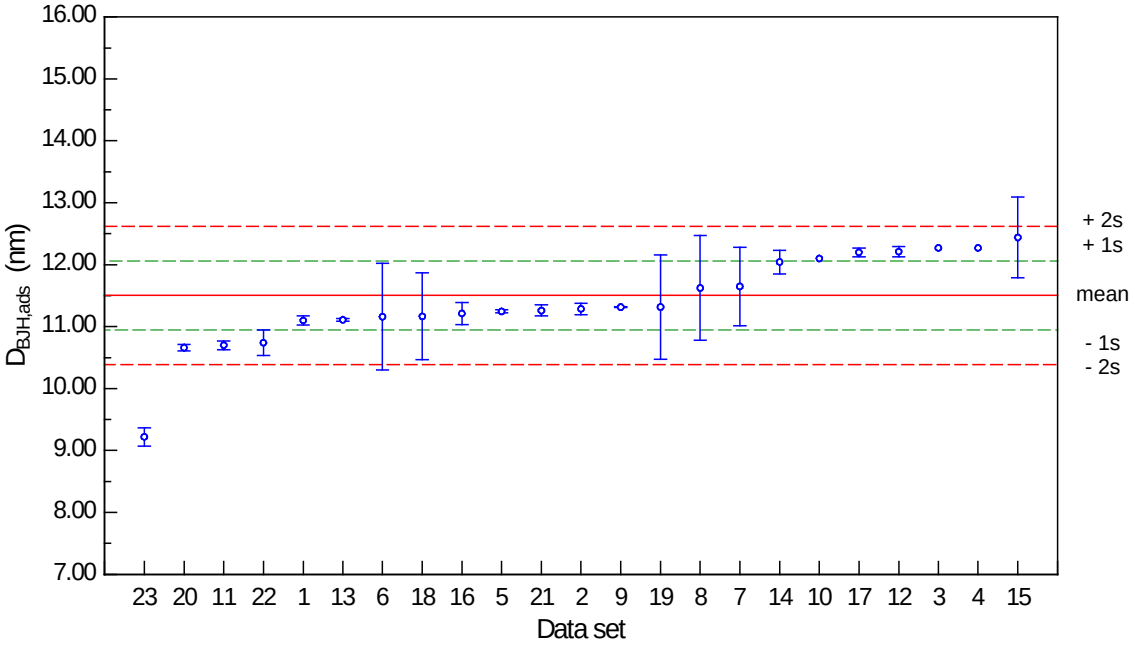


Fig. 17: Calculated data set means for $D_{BJH(ads)}$

6.2 Statistical evaluation

An important aspect for the statistical treatment of the experimental data according to ISO Guide 35 to obtain the uncertainties of the certified values was the fact that different instruments were used by the participating laboratories (see Table 6). Moreover, although all participants in the intercomparison followed the same standardized procedure, significant differences caused by different implementations in different laboratories were to be expected. This has been confirmed by the observation of very heterogeneous standard deviations indicating that the single experimental data did not belong to the same "mother distribution" and data pooling was not allowed. Therefore, the statistical treatment was performed using the laboratory mean values for each parameter to be certified.

The following statistical parameters were calculated:

- the mean of data set means
- the standard deviation of the distribution of laboratory means, and the standard deviation of the mean of laboratory means
- the confidence interval of the mean of laboratory means at the 0.05 significance level

The statistical tests carried out (at significance levels of 0.05 and 0.01) were:

- Cochran test for the identification of outliers with respect to laboratory variance
- Grubbs test for the identification of outliers with respect to the mean

- Dixon and Nalimov test for the verification of possible outlier indications
- Kolmogorov-Smirnov Test (Lilliefors version) for the normality test
- Test for skewness and kurtosis

As a result of the statistical analysis a small number of outliers was detected (for the parameters A_{BET} and V_p data set No. 9, for D_{BJH}(des.) data sets No. 20 and 23, for D_{BJH}(ads.) data set No. 23).

These instrument mean values were excluded from the calculations of the certified values and their uncertainties. The results of the calculations with the evaluation software SoftCRM [13] after deleting the outlying instrument means are presented in Table 8.

Table 8: Statistical evaluation of the ILC data using the software program SoftCRM

Property x	$\bar{x}$	s_x	u_{char}	CI	TI	Unit	Pooling	l
A_{BET}	96.5958	2.0812	0.4437	0.9227	5.6129	m^2/g	no	22
$V_{p,0.99}$	0.2341	0.0035	0.0007	0.0016	0.0095	cm^3/g	no	22
$4V_{p,0.99}/A_{BET}$	9.6908	0.1345	0.0292	0.0582	0.3595	nm	no	23
$D_{BJH(des)}$	8.1691	0.2311	0.0504	0.1052	0.6293	nm	no	21
$D_{BJH(ads)}$	11.5034	0.5580	0.1190	0.2474	1.5049	nm	no	22

The plausibility of the obtained means of the instrument means has been checked by the comparison between the results of the homogeneity measurements, the stability study, and the ILC measurements (see Table 9).

Table 9: Plausibility comparison of the mean values obtained from different tests

Property x	Mean values from homogeneity test	Mean values from stability test	Mean values from ILC	Plausibility remark
A_{BET}	97.1460	97.1521	96.5958	ok
$V_{p,0.99}$	0.2343	0.2341	0.2341	ok
$4V_{p,0.99}/A_{BET}$	9.6454	9.6387	9.6908	ok
$D_{BJH(des)}$	8.3235	8.2821	8.1691	ok
$D_{BJH(ads)}$	12.1308	12.0470	11.5034	discrepant, but still within MU, therefore accepted

The combined uncertainty $u_c(x)$ for each certified value was calculated according to Equation (3) using the numerical values summarized in Table 10 as the combination of the standard uncertainty of the mean of the instrument means, the contribution of the variation between the bottles, the long term stability contribution, and the uncertainty contribution due to the measurement result variations of the single instruments (mean data set precision). The last contribution also serves as an estimate for possible inhomogeneities within the bottles.

$$u_c^2(x) = u_{char}^2 + u_{bb}^2 + u_{lts}^2 + \frac{1}{l^2}\sum_{i=1}^{l} s_i^2 \qquad \text{with} \qquad u_{char}^2 = \frac{s_x^2}{l} \tag{3}$$

Table 10: Values of the uncertainty components for the porosity parameters of BAM-P106

Property	$\bar{x}$	$u_{char}(x)$	$u_{bb}(x)$	$u_{lts}(x)$	$\frac{1}{l}\sqrt{\sum_{i=1}^{l} s_i^2}$	$u_c(x)$	$U(x)$	l	Unit
A_{BET}	96.5958	0.4437	0.2067	0.6231	0.1857	0.8138	1.6277	22	m^2/g
$V_{p,0.99}$	0.2341	0.0007	0.0002	0.0009	0.0003	0.0012	0.0024	22	cm^3/g
$4V_{p,0.99}/A_{BET}$	9.6908	0.0292	0.0190	0.0677	0.0143	0.0775	0.1549	23	nm
$D_{BJH(des)}$	8.1691	0.0504	0.2274	0.4419	0.0340	0.5007	1.0014	21	nm
$D_{BJH(ads)}$	11.5034	0.1190	0.0405	0.4098	0.0866	0.4373	0.8746	22	nm

The certified values of each porosity parameter with a reasonable number of digits and the respective expanded uncertainties (rounded according to DIN 1333 [14]) are summarized in Table 11.

Table 11: Final values for the certified porosity properties of BAM-P106

Property	Certified value x_{cert}	Expanded uncertainty $U = k \cdot u_c$ (with $k = 2$)	Unit
A_{BET}	96.6	1.7	m^2/g
$V_{p,0.99}$	0.2341	0.0024	cm^3/g
$4V_{p,0.99}/A_{BET}$	9.69	0.16	nm
$D_{BJH(des)}$	8.2	1.0	nm
$D_{BJH(ads)}$	11.5	0.9	nm

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