Certification Report

Certified Reference Material BAM-P110

BET Specific Surface Area of Titanium Dioxide (Anatase) calculated from the nitrogen adsorption isotherm at 77.3 K

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Summary

This report describes the certification of the porous reference material BAM-P110. The certified value determined by nitrogen adsorption at 77.3 K according to the international standards ISO 15901-2 and ISO 9277 is given in the table below.

Specific Surface Area [a] A_{BET} in m^2/g	**Uncertainty** [b] U in m^2/g
107.8	1.6

[a] Specific surface area calculated in a relative adsorption pressure range $0.05 \leq p/p_0 < 0.3$ as multi point BET model [1] with minimum of five points described in ISO 9277 [2]

[b] Uncertainty $U = k \cdot u_c$ calculated according to ISO Guide 35 [3] and ISO/IEC Guide 98-3 [4] with the coverage factor $k = 2$ (giving a level of confidence of approximately 95 %). The value of the combined standard uncertainty u_c of the certified property includes both an uncertainty contribution resulting from the inter-laboratory characterization, the study of inhomogeneities, stability of the material and the uncertainty contribution due to the measurement result variations of the single instruments (mean data set precision).

The listed value for the surface area is a method-defined (model dependent) parameter. 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-P110 consists of a single glass bottle containing approximately 10 g of crystalline, pure anatase (99.5 %) titanium dioxide powder with a pore width of about 10-25 nm in mean diameter.

The reference material is intended for performance testing of instruments used for the determination of multi point BET specific surface area from the adsorption branch in a relative pressure range $0.05 \leq p/p_0 < 0.3$ of the nitrogen isotherm determined by the static volumetric method.

The certificate of BAM-P110 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)
CRM	certified reference material
GUM	ISO guide to the expression of uncertainty in measurement
ILC	inter-laboratory comparison (certification round robin)
MU	measurement uncertainty
RM	reference material

List of Symbols

df	degrees of freedom
k	coverage factor
l	number of accepted data sets in the inter-laboratory comparison
MS	Mean Square sum
n	number of observations
p	pressure of the adsorptive in equilibrium with the adsorbate
p_0	saturation vapour pressure of the adsorptive
s_i	standard deviation of single data set
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

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1. Intention of the certification project

The Certified Reference Material BAM-P110 is a porous titanium dioxide (Anatase) nanomaterial. This CRM is intended for use in the calibration and performance testing of gas sorption instruments used for determining the Brunauer-Emmet-Teller (BET) specific surface area [1] of powders and porous solids.

The certification of this new CRM has been carried out on the basis of BAM Guidelines for the Development and Production of BAM Reference Materials [5] and relevant ISO Guides [3], [4], [6], [7].

The development of the CRM was part of work package 5 of the FP7 Project "Development of reference methods for hazard identification, risk assessment and LCA of engineered nanomaterials", NanoValid (NMP4-SL-2011-263147). The BET specific surface area can be used for the calculation of the specific surface area by volume (SSAV), which itself is a proxy to identify a potential nanomaterial as proposed in ref. [8]. Compliance with the European Commission's recommendation of 18 October 2011 on the definition of nanomaterial (2011/696/EU) can be tested when it is "technically feasible and requested in specific legislation" [9]. Within the framework of the NanoValid project, the material was chosen, since titanium dioxide nanomaterials are often used in recent technologies, as for instance as pigments in coatings, are released in the environment and are of relevance for human- and eco-toxicological testing. Well characterized nanoparticles are necessary to underpin the development and use of standardized operation procedures (SOP) for testing the potential health, safety and environmental risks in relation to nanomaterials (cf. ref. [10]) and to enable valid human and eco toxicological testing.

2. Description of the material

2.1 Selection and source of the candidate material

A nanoscale titanium dioxide (TiO_2, also called titania) in the modification anatase was selected from a number of tested candidate materials.
The titania candidate material (NO-0058-HP) was delivered by IOLITEC nanomaterials (Germany). According to the specifications by the producer, NO-0058-HP consists of pure anatase. The provider indicated a pore size of 10-25 nm and a surface area between 50-150 m^2/g.

As a result of XRD measurements at BAM, Division 1.3, it could be confirmed that the crystal modification of NO-0058-HP is pure anatase (see Fig. 1). The crystallite size was determined to 22 nm, which is in accordance with the SEM data (Fig. 2). 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).

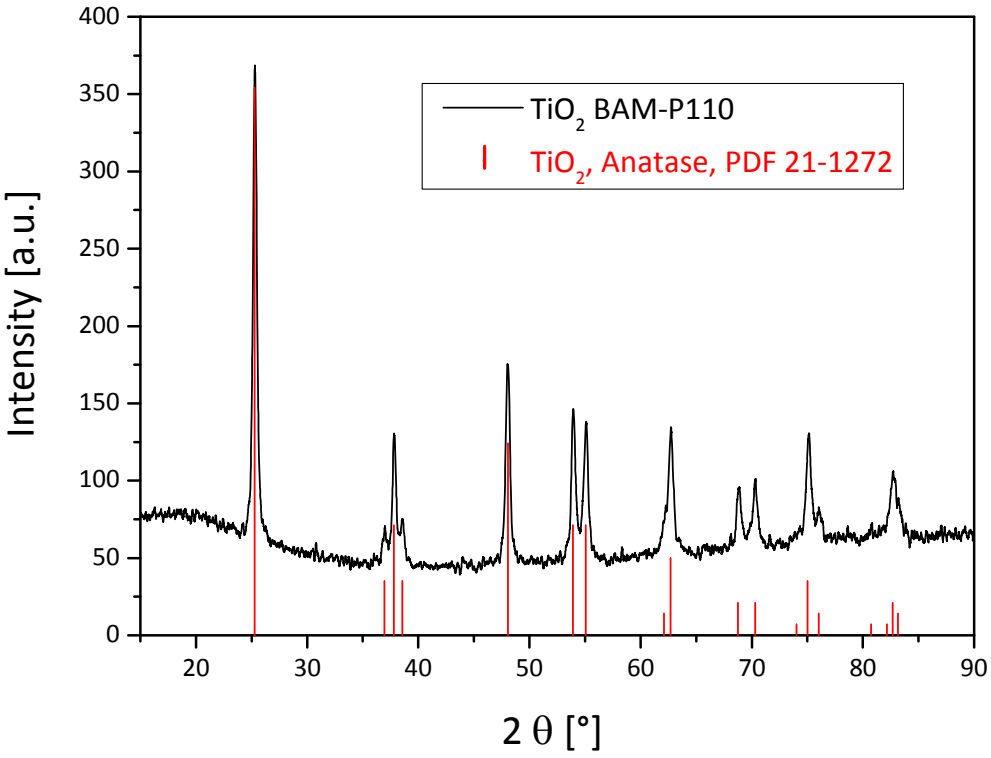

Fig. 1: X-ray powder diffraction pattern of the candidate material and comparison to the powder diffraction file (pdf) database entry [11] of titanium dioxide (anatase).

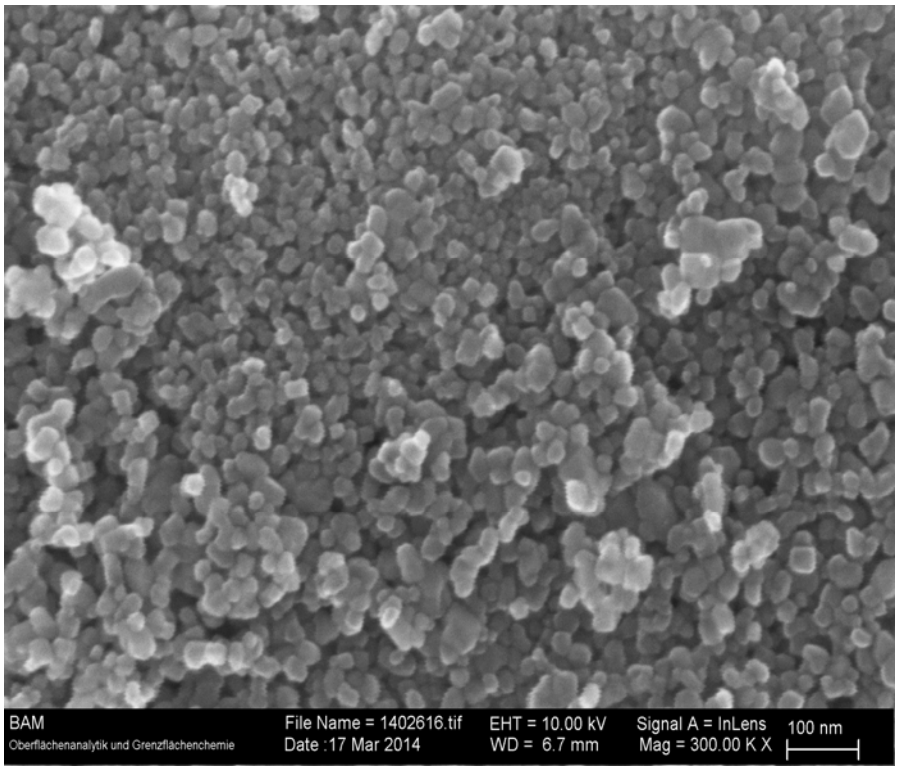

Fig. 2: SEM image of a sample of the candidate material. Agglomerates with smallest identified pore width of approximately 20 nm.

2.2 Specific surface area characterization

Prior to the measurement, outgassing of the sample is necessary. Outgassing has to be carried out in a vacuum. Heat the sample for degassing in a vacuum with a rate of about 5 K/min to 180 °C, then hold temperature at 180 °C for at least 3 hours. Afterwards, allow the sample to cool slowly back to ambient temperature.

After the sample material preparation the first step of specific surface area analysis is using the gas adsorption method for the measurement of a low temperature physisorption isotherm (see Fig. 3).

The certified values of specific surface area is calculated for multi-point (MP) BET data analysis by using the linear form (see Fig. 4) with a minimum of five adsorption points in a relative pressure range $0.05 \leq p/p_0 < 0.3$ according to the BET model [1] as described in ISO 9277 [2]. For the cross sectional area of nitrogen the value 0.162 nm^2 is used.

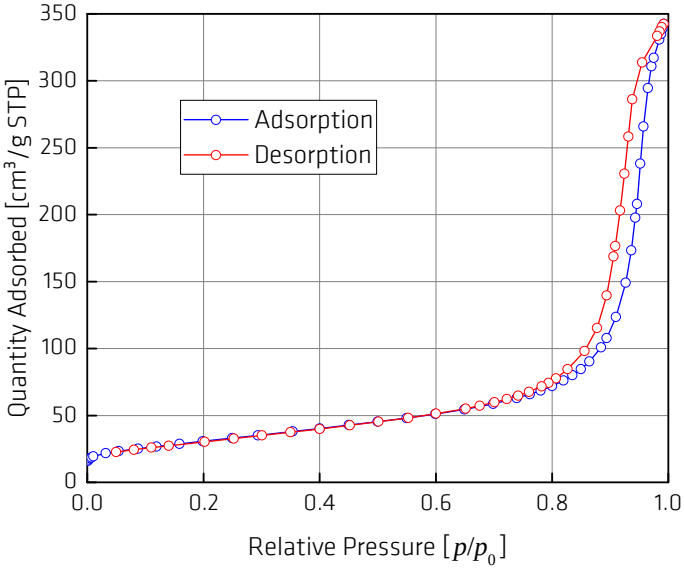

Fig. 3:

N_2 adsorption Isotherm of BAM-P110 at 77.3 K

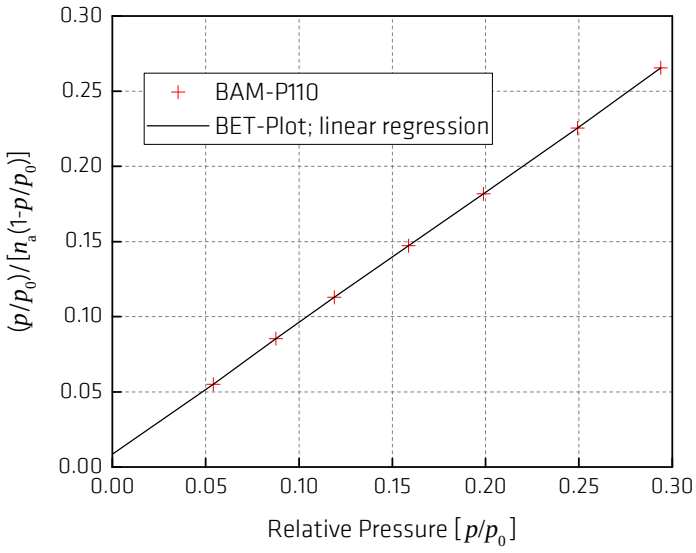

Fig. 4:

BET – Plot of BAM-P110

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. 5.

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. 5: Cross riffling scheme used for subdividing the samples.

The initial amount of titanium dioxide powder (in its anatase polymorph form) was subdivided into single units of at least 10 g packaged in glass bottles of 30 mL volume. The total number of units was 448. 46 units of them have been used for testing the homogeneity and stability as well as for the inter-laboratory comparison also.

4. Homogeneity and stability testing

4.1 Homogeneity

For testing the homogeneity, 20 individual units of BAM-P110 were randomly selected. Two replicate measurements per bottle were carried out under repeatability conditions with the automated surface area and porosity analyzer ASAP 2020 (Micromeritics, Norcross USA). To detect the within-bottle standard deviation, 6 replicates from one additional 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}
		m^2/g
C06-05	ANA-H802.smp	110.1822
	ANA-H803.smp	109.4039
D05-02	ANA-H804.smp	110.0236
	ANA-H805.smp	109.7119
B04-01	ANA-H806.smp	110.0161
	ANA-H807.smp	109.3451
A02-03	ANA-H809.smp	110.2388
	ANA-H810.smp	110.1425
E03-06	ANA-H812.smp	110.2012
	ANA-H813.smp	109.7370
G08-07	ANA-H815.smp	109.2988
	ANA-H816.smp	109.5056
F08-04	ANA-H818.smp	110.0530
	ANA-H819.smp	110.0964
B01-03	ANA-H820.smp	109.5593
	ANA-H822.smp	109.8074
E07-02	ANA-H828.smp	109.3330
	ANA-H830.smp	109.5428
G06-05	ANA-H833.smp	109.9592
	ANA-H834.smp	108.0446
F05-01	ANA-H841.smp	109.2363
	ANA-H842.smp	109.6792
D02-04	ANA-H843.smp	108.3097
	ANA-H844.smp	109.7685
F04-01	ANA-H845.smp	108.4965
	ANA-H846.smp	109.5109
A07-01	ANA-H847.smp	110.1145
	ANA-H848.smp	109.8115
E06-08	ANA-H849.smp	108.6341
	ANA-H850.smp	109.9420
D04-08	ANA-H851.smp	108.5144
	ANA-H852.smp	109.7779
A05-07	ANA-H853.smp	110.1397
	ANA-H854.smp	107.9612
G04-02	ANA-H855.smp	109.8997
	ANA-H856.smp	109.9441
C01-05	ANA-H863.smp	109.2838
	ANA-H864.smp	109.7771
C04-03	ANA-H865.smp	109.2520
	ANA-H866.smp	109.6509

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

Bottle	Data file	A_{BET}
		m^2/g
B08-08	ANA-H857.smp	109.7498
	ANA-H858.smp	109.9620
	ANA-H859.smp	109.9195
	ANA-H860.smp	109.7302
	ANA-H861.smp	109.5444
	ANA-H862.smp	109.7741

To obtain the inhomogeneity contribution u_{bb}, a 1-way Analysis of Variances (ANOVA) was carried out with the experimental homogeneity data. The inhomogeneity contribution is included in the total uncertainty budget of the specific surface area [3]. The u_{bb} value for BAM-P110 (see Table 4) was calculated with the described equation (1) in the case of mean square between-unit is smaller than within-unit (see Table 3) [13].

Table 3: Analysis of variances calculated for specific surface area A_{BET} [14]

Source of Variation	Square sum	Degrees of freedom (df)	Mean Square sum (MS)	F	F-crit. 95%
Between Units	5.8000	20	0.2900	0.8372	2.0075
Within Units	8.6596	25	0.3464		

In case $MS_{between} < MS_{within}$ use:

$$u_{bb} = \sqrt{\frac{MS_{within}}{n}} \cdot \sqrt[4]{\frac{2}{df_{within}}} \qquad (1)$$

Table 4: Inhomogeneity contributions u_{bb} of BAM-P110

Property	u_{bb}	Unit
A_{BET}	0.22132842	m^2/g

The statistical evaluation of the homogeneity testing results indicated that no significant inhomogeneity for the specific surface area parameter of anatase titanium dioxide could be determined and therefore this candidate material is suitable for the certification as CRM BAM-P110.

From the homogeneity testing measurements a recommendation for the minimum sample intake of CRM BAM-P110 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-P110 also should be 0.8 g.

4.2 Stability

The numerical results of the measurements to monitor the stability of the CRM BAM-P110 are listed in Table 5 for the period between June 2014 and December 2015. The stability measurements were carried out with the same automated surface area and porosity analyzer ASAP 2020 (Micromeritics, Norcross USA). The respective diagram for the specific surface area is depicted in Fig. 6.

Table 5: Numerical results of stability monitoring

Data file	Test date	A_{BET}
		m^2/g
ANA-749.smp	18.06.2014	109.5159
ANA-795.smp	06.10.2014	108.5045
ANA-796.smp	07.10.2014	109.6604
ANA-H866.smp	16.12.2014	109.6509
ANAT-893.smp	18.03.2015	109.3205
ANAT-894.smp	19.03.2015	108.5821
ANAT-896.smp	23.03.2015	108.4488
ANAT-897.smp	24.03.2015	109.4408
ANAT-898.smp	25.03.2015	109.5600
ANAT-899.smp	26.03.2015	109.6170
ANA-918.smp	20.05.2015	109.6804
ANA-941.smp	13.07.2015	109.6961
ANA-955.smp	14.08.2015	108.5292
ANA-989.smp	12.10.2015	110.1027
ANA-1032.smp	14.12.2015	109.5585
	$\bar{x}_{\text{Stab}}$ [a]	109.3245
	$\bar{x}_{\text{ILC}}$ [b]	107.7641
	$s_{x,\text{ILC}}$	2.0004
	$\bar{x}_{\text{Stab}} + 2 \cdot s_{x,\text{ILC}}$	113.3253
	$\bar{x}_{\text{Stab}} - 2 \cdot s_{x,\text{ILC}}$	105.3237

[a] Stab = stability monitoring

[b] ILC = inter-laboratory comparison (certification study)

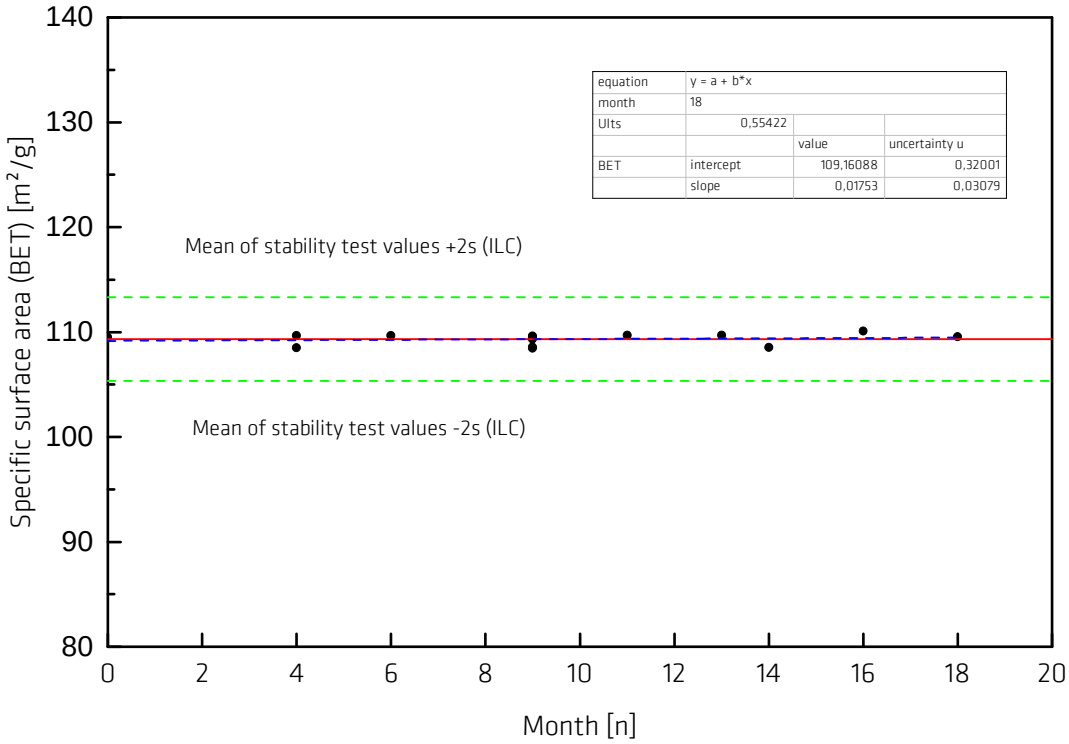

Fig. 6: Stability monitoring for the specific surface area A_{BET}

The results of the statistical evaluation of the stability data (see Table 6) indicate that no instability could be detected for the specific surface area but the contribution of u_{lts} to the uncertainty of the certified value is not negligible and should be included in the final calculation of the combined uncertainty.

Table 6: Results of stability data evaluation according to ISO Guide 35

Property	intercept	slope	u(slope)	$u_{\mathrm{lts}}(x)$	instability	negligible
A_{BET} in m²/g	109.16088	0.01753	0.03079	0.55422	no	no

The shelf life of CRM BAM-P110 estimated on the basis of the stability monitoring data is at least 10 years for a carefully closed bottle stored at temperatures below 30 °C under dry conditions.

5. List of participating laboratories

AQura GmbH, Hanau (Germany)

AQura GmbH, Marl (Germany)

Bundesanstalt für Materialforschung und –prüfung (BAM), Div. 1.3, Berlin (Germany)

Bayer Technology Services GmbH, Leverkusen (Germany)

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

BEL Japan Inc., Osaka (Japan)

Centro Ricerche Fiat, Torino (Italy)

Delft Solids Solutions, Delft (The Netherlands)

ECSIN-Veneto Nanotech, Padova (Italy)

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

Instituto Nacional de Metrologia Brasil, Duque de Caxias (Brasil)

Micromeritics Instrument Corp., Norcross, GA (USA)

Micromeritics GmbH, Mönchengladbach (Germany)

NanoLogica AB, Södertälje (Sweden)

Oerlikon Metco WOKA GmbH, Barchfeld-Immelborn (Germany)

POROTEC GmbH, Hofheim (Germany)

PTT Global Chemical Public Company Limited, Rayong (Thailand)

Quantachrome GmbH, Odelzhausen (Germany)

Quantachrome Instruments, Boynton Beach (USA)

ThermoFisher Scientific, Milan (Italy)

University of Alicante, Alicante (Spain)

UNIZAR, Zaragoza (Spain)

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

Table 7: Types of instruments used by the participants

Type of instrument	Number	Manufacturer
BELSORP-max	1	BEL Japan Inc., Osaka (Japan)
BELSORP-mini II	1	
ASAP 2010	2	Micromeritics Instrument Corporation, Norcross, GA (USA)
ASAP 2020	3	
ASAP 2020 Plus	1	
ASAP 2420	1	
Gemini 2360	1	
Tristar	1	
TriStar 3000	2	
TriStar II 3020	1	
TriStar II Plus	1	
Autosorb-1	1	Quantachrome Instruments Corporation, Boynton Beach, FL (USA)
Autosorb-1 MP	1	
Autosorb-6 B	1	
Autosorb-iQ	1	
Autosorb-iQ 2	1	
NOVA 2000e	1	
NOVA 3200e	1	
Surfer	2	ThermoFisher Scientific, Milan (Italy)
non-branded (self-made)	1	University of Alicante, Alicante (Spain)
Total *	25	

* Four laboratories participated with two instruments each

6. Results of the inter-laboratory comparison and statistical uncertainty estimation

6.1 Experimental results

The inter-laboratory comparison for the certification of BAM-P110 was performed according to the Guidelines for the Production of BAM Reference Materials [5]. Data evaluation and statistical tests were carried out using the software package SoftCRM [14]. Each participating laboratory received a bottle containing about 10 g of the candidate material together with the instructions for running the tests and the data evaluation according to ISO 9277 [2]. The laboratories had to perform 6 replicate measurements with each participating instrument. The mean values for the specific surface area gained by each instrument are shown in Table 8 and displayed graphically in Fig. 7. The error bars at the data points for the data set means represent the standard deviation of the 6 certification measurements per data set.

Table 8: Data set means of the participants in the inter-laboratory comparison (ILC)

Property x →	A_{BET}
Data set no. ↓	m^2/g
01	107.7747
02	109.4490
03	103.5734
04	109.1917
05	110.3383
06	109.2562
07	110.7337
08	105.3897
09	104.5342
10	106.8533
11	109.9802
12	109.1615
13	104.5333
14	108.2311
15	107.7000
16	105.4085
17	108.1683
18	107.8823
19	106.7254
20	110.6167
21	96.9844 [a]
22	108.1297
23	108.8100
24	106.9081
25	106.9880 [b]
l	24
$\bar{x}$ [c]	107.7641
s_x [d]	2.0004
$\frac{s_x}{\sqrt{l}}$	0.4083
$\bar{x}+1\cdot s_x$	109.7645
$\bar{x}-1\cdot s_x$	105.7636
$\bar{x}+2\cdot s_x$	111.7649
$\bar{x}-2\cdot s_x$	103.7633

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

[b] Insufficient data set. One outlier of 6 replicate measurements detected. Mean calculated from remaining 5 replicate measurements.

[c] Average of the accepted data set means

[d] Standard deviation of the data set means for the particular property

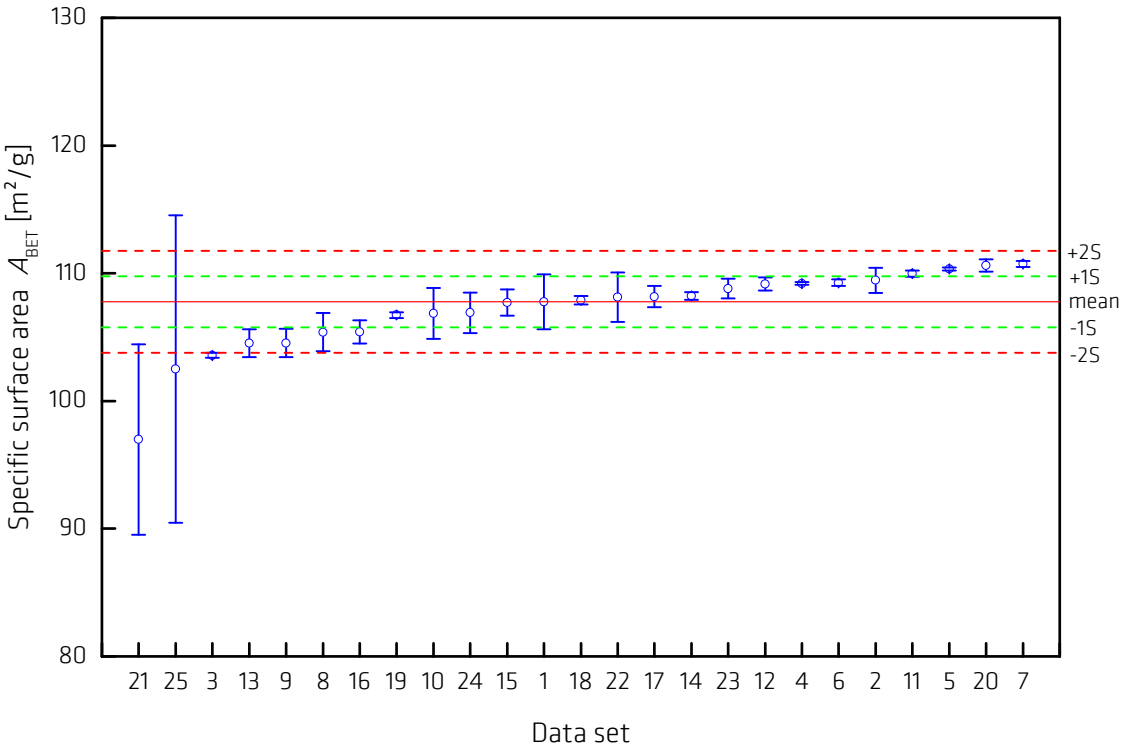

Fig. 7: Calculated data set means for A_{BET}

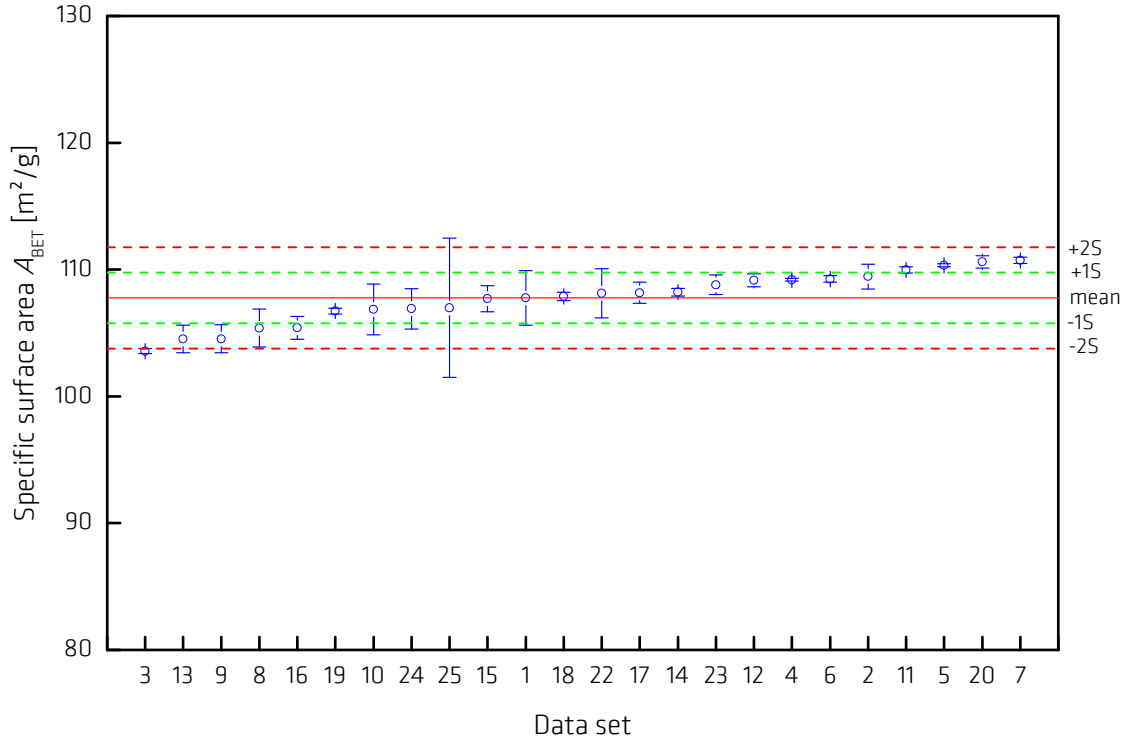

Fig. 8: Calculated data set means for A_{BET} without outlier

6.2 Statistical evaluation

An important aspect for the statistical treatment of the experimental data according to ISO Guide 35 to obtain the uncertainty of the certified value was the fact that different instruments were used by the participating laboratories (see Table 7). Furthermore, although all participants in the inter-laboratory comparison 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 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 value (see Table 8) for certified the specific surface area.

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 only very few outliers were detected for the parameter A_{BET}. These outliers were data set No. 21 and one replicate measurement in data set No. 25.
The instrument mean value of data set No. 21 was excluded from the calculation of the certified value and the data set No. 25 was recalculated with five replicate measurements.
The result of the calculation with the evaluation software SoftCRM [14] after deleting the outliers is present in Table 9.

Table 9: Statistical evaluation of the ILC data using the software program SoftCRM

Property x	$\bar{x}$	s_x	u_{char}	Unit	Pooling	l
A_{BET} in m^2/g	107.7641	2.0004	0.4083	m^2/g	no	24

The plausibility of the obtained values 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 10).

Table 10: Plausibility comparison of the mean values obtained from different tests

Property x	Mean value from homogeneity test	Mean value from stability test	Mean value from ILC	Plausibility remark
A_{BET} in m^2/g	109.5587	109.16088	107.7641	ok

The combined uncertainty $u_c(x)$ was calculated according to Equation (3) using the numerical value summarized in Table 11. This equation is a 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).

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

Table 11: Values of the uncertainty components for the specific surface area of BAM-P110

Property	$\bar{x}$	u_{char}	u_{bb}	u_{lts}	$\frac{1}{l}\sqrt{\sum_{i=1}^{l} s_i^2}$	u_c	U	l	Unit
A_{BET} in m^2/g	107.7641	0.4083	0.2213	0.55422	0.3080	0.7859	1.5719	24	m^2/g

The certified value of the specific surface area with a reasonable number of digits and the respective expanded uncertainty (rounded according to DIN 1333 [15]) are summarized in Table 12.

Table 12: Final value for the certified specific surface area of BAM-P110

Property	Certified value x_{cert}	Expanded uncertainty $U = k \cdot u_c$ (with $k = 2$)	Unit
A_{BET}	107.8	1.6	m^2/g

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