Certification Report

Certified Reference Material

BAM-P116

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

February 2020

Coordinator: Dr. F. Emmerling
Collaboration: C. Prinz, A. Zimathies
Bundesanstalt für Materialforschung und -prüfung (BAM)
Division 6.3
Richard-Willstätter-Str. 11
12489 Berlin, Germany
Phone: +49 30 8104 1133
Fax: +49 30 8104 71133
E-mail: Franziska.Emmerling@bam.de

Summary

This report describes the certification of the porous reference material BAM-P116. The certified value determined by nitrogen adsorption at 77.3 K according to the international standard ISO 9277 [1] is given in the table below.

Property	Value	U [a]	$2 \cdot s_x$ [b]	Unit
Specific Surface Area [c] A_{BET}	325	11	20	m^2/g

[a] Uncertainty $U = k \cdot u_c$ calculated according to ISO Guide 35 [2] and ISO/IEC Guide 98-3 [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 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).

[b] Standard deviation of the accepted data set mean value (twofold value).

[c] Specific surface area calculated in a relative adsorption pressure range of $0.08 \leq p/p_0 < 0.25$ as multi point BET model [4] with minimum of five points described in ISO 9277.

This report contains detailed information on the preparation of the CRM as well as on homogeneity investigation and on the analytical methods used for certification analysis.

The certified values are based on the results of 15 laboratories which participated in the certification inter-laboratory comparison.

Content

Page

List of abbreviations 5
List of Symbols 5
1. Introduction 6
2. Material 6
2.1 Selection and characterization of the candidate material 6
2.2 Specific surface area characterization 8
2.3 Homogenization and subdividing of the candidate material 10
3. Homogeneity 10
4. Stability 12
5. List of participating laboratories 15
6. Results of the inter-laboratory comparison and statistical uncertainty estimation 17
6.1 Experimental results 17
6.2 Statistical evaluation 20
7. Metrological traceability 21
8. Information on the proper use of the CRM 22
8.1 Recommended use 22
8.2 Transport, storage and handling 22
8.3 Shelf life 22
8.4 Safety information 22
8.5 Legal notice 22
9. Information on and purchase of the RM 23
10. References 24
11. Annexes 24
Annex 1: Calculation of uncertainty contribution of potential inhomogeneity 25
Annex 2: Measurement results of ILC-participants 26

List of abbreviations

(if not explained elsewhere)

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)
RM	reference material

List of Symbols

df	degrees of freedom
k	coverage factor
l	number of accepted data sets in the inter-laboratory comparison
M	mean square sum
n	number of observations
p	pressure of the adsorptive in equilibrium with the adsorbate
p_0	saturation vapor pressure of the adsorptive
s_{bb}	standard uncertainty due to between-bottle (in)homogeneity
s_i	standard deviation of single data set
s_r / s_w	Standard deviation of repeatability within the bottles
s_x	ILC standard deviation of a property value
U	expanded standard uncertainty of a property value
u_{bb}	estimated standard uncertainty due to within bottle (in)homogeneity
u_{char}	standard uncertainty due to characterization
u_c	combined standard uncertainty of a property value
u_{hom}	standard uncertainty due to (in) homogeneity
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

1. Introduction

The Certified Reference Material BAM-P116 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 of powders and porous solids.

The development of CRM serves to expand the offer of nanoporous reference materials with high specific surface areas. With this material, customer requests are addressed as materials with a specific surface area greater than 200 m^2/g were desired.

With this material it is possible to validate gas sorption instruments in test laboratories and to carry out monitoring that is required according to ISO/IEC 17025 [5].

The certification of this new CRM has been carried out based on BAM Guidelines for the Development and Production of BAM Reference Materials [6], ISO 17034 [7] and relevant ISO Guides [2], [8].

2. Material

2.1 Selection and characterization of the candidate material

A nanoscale titanium dioxide (TiO_2, also called titania) in the modification anatase was selected from several tested candidate materials.
The titania candidate material TP Hombikat (Lot 10588097-6) was delivered by Venator Germany GmbH. and consists of pure anatase according to the manufacturer's specifications.

Measurements with mercury porosimetry (Fig. 1) indicated a main pore size of approximately 350 nm, a pore volume of 1200 mm^3/g and a porosity of approximately 70%.
As a result of XRD measurements at BAM, Division 6.3, it could be confirmed that the crystal modification of TP Hombikat (Lot 10588097-6) is pure anatase (see Fig. 2). The particle size was determined to 25 µm, which is in accordance with the SEM data (Fig. 3).
Although anatase is metastable and 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 873 K. Therefore, the long-term stability of anatase modification is not affected in the temperature range between room temperature and the recommended degassing temperature of 453.15 K (see chapter 4. Stability).

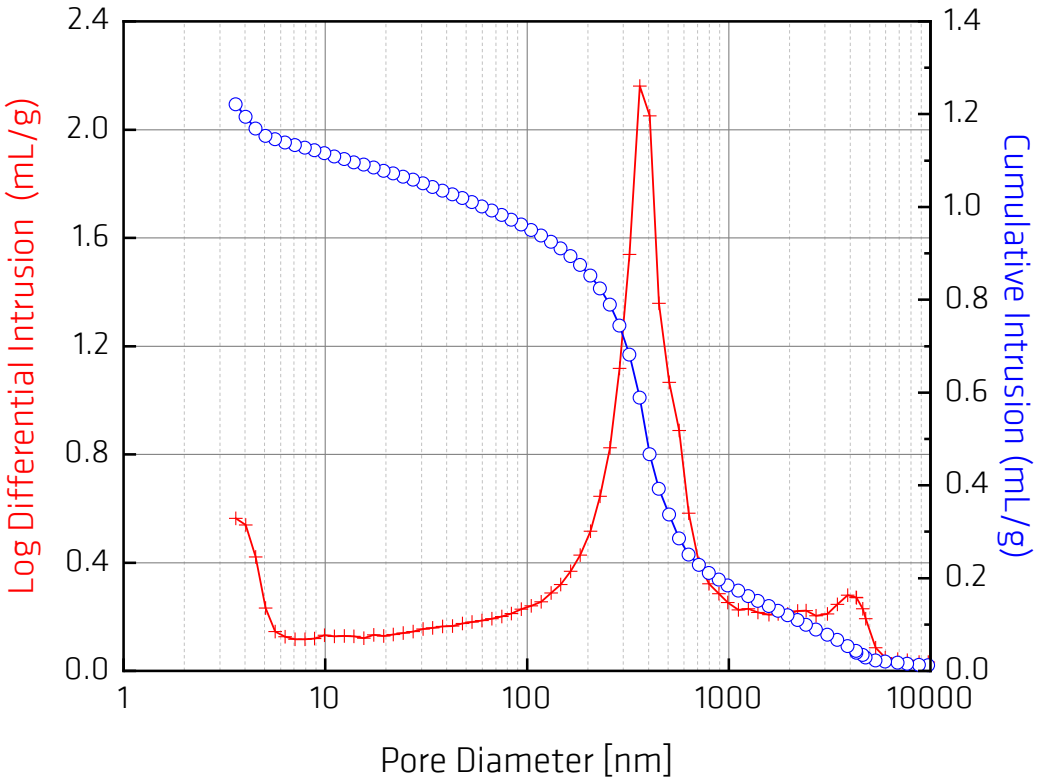

Fig. 1: Determination of pore size, pore volume and porosity by mercury porosimetry of the candidate material**.**

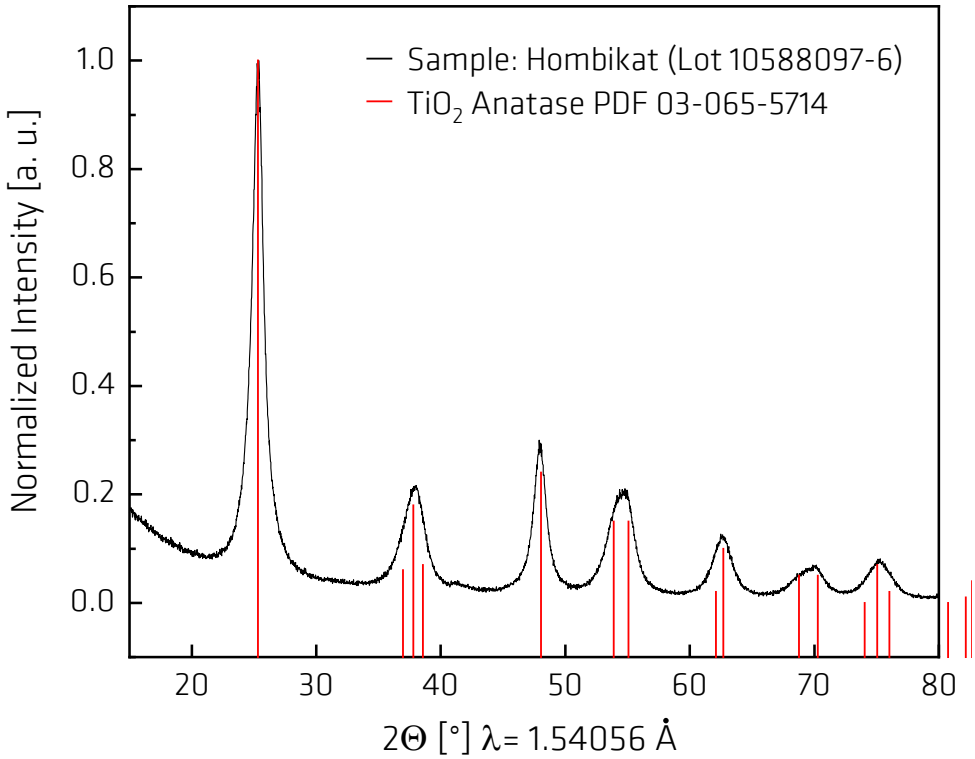

Fig. 2: X-ray powder diffraction pattern of the candidate material and comparison to the powder diffraction file (pdf) database entry [9] of titanium dioxide (anatase).

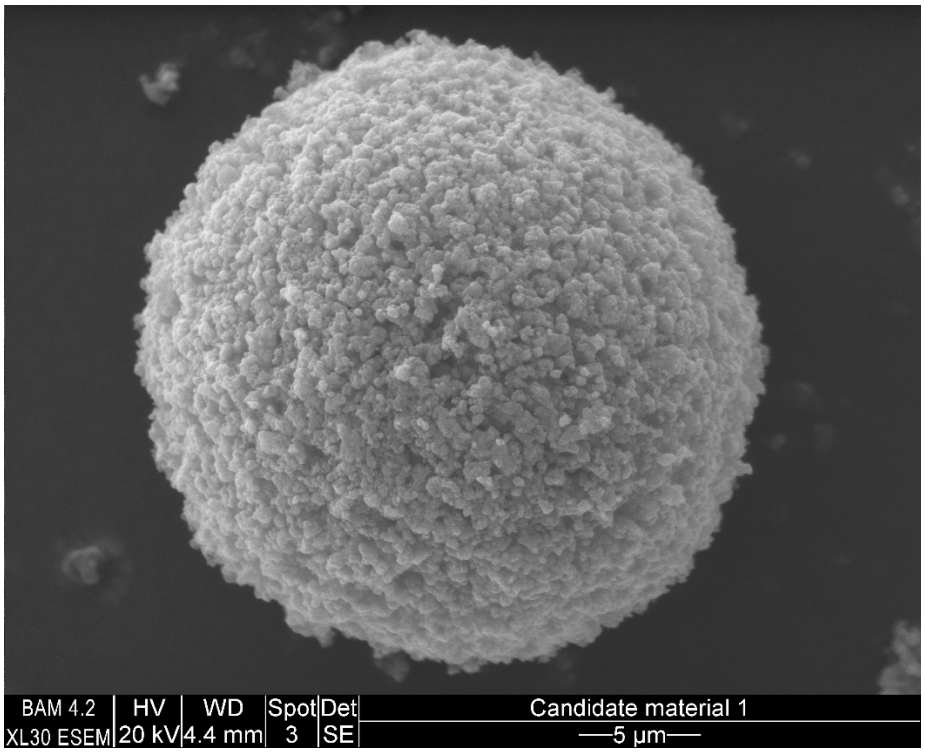

Fig. 3: SEM image of a sample of the candidate material (CRM BAM-P116) with a particle size of 25 µm.

2.2 Specific surface area characterization

Prior to measurement a sample preparation is necessary, according to the following steps: Heat the sample in vacuum with a rate of about 5 K/min to 453.15 K, then hold temperature at 453.15 K for at least 3 hours. Afterwards, allow the sample to cool slowly back to ambient temperature.

After the sample preparation, the first step of specific surface area determination is using the gas adsorption method for the measurement of a low temperature physisorption isotherm (see Fig. 4, Fig. 5).

The certified value of specific surface area is calculated for multi-point (MP) BET data analysis by using the linear form (see Fig. 6) with a minimum of five adsorption points in a relative pressure range of $0.08 \leq p/p_0 < 0.25$ according to the BET model as described in ISO 9277. The value used for cross-sectional area of nitrogen was 0.162 nm^2.

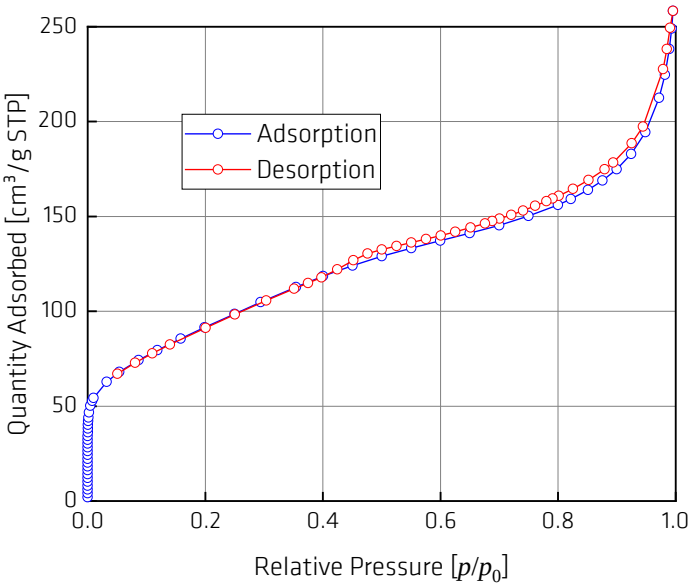

Fig. 4:

Linear plot of

N_2 isotherm of BAM-P116 at 77.3 K

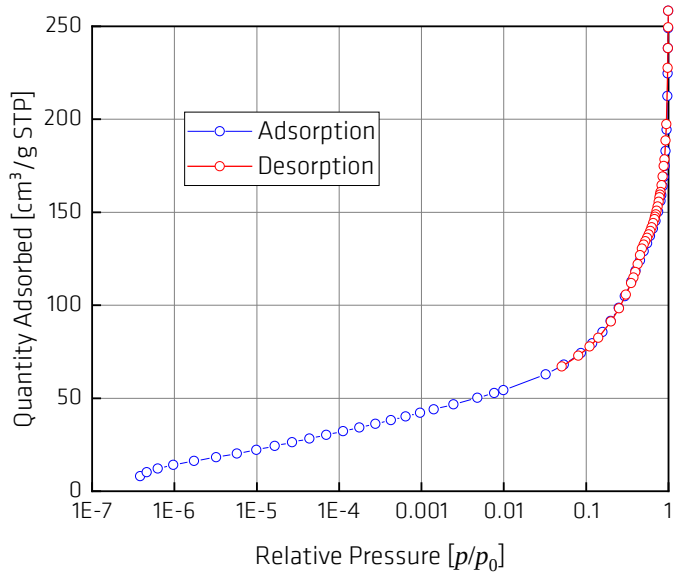

Fig. 5:

Logarithmic plot of

N_2 isotherm of BAM-P116 at 77.3 K

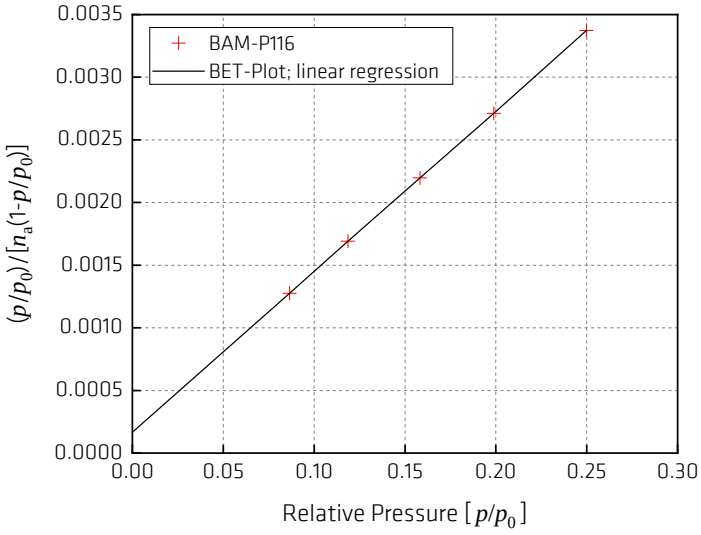

Fig. 6:

BET – Plot of BAM-P116

2.3 Homogenization and bottling of the candidate material

Homogenization and subdividing of the sample material were carried out by means of an eight-port rotary sample divider PT 100 (Retsch, Germany) using the cross-riffling scheme [10] shown in Fig. 7.

Fig. 7: Cross riffling scheme used for subdividing the samples.

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

The initial amount of titanium dioxide powder (in its anatase polymorph form) was subdivided into single units of at least 8 g packaged in glass bottles of 30 mL volume. The total number of units was 512. 25 units thereof have been used for testing the homogeneity and stability as well as for the interlaboratory comparison.

3. Homogeneity

For testing the homogeneity, 10 individual units of BAM-P116 were randomly selected. Three 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 standard deviation between and within the bottles. The test results are summarized in Table 1 and the homogeneity contribution to the total uncertainty was calculated using a 1-way-ANOVA (see Annex 1).

The estimation of analyte-specific inhomogeneity contribution u_{hom} to be included into the total uncertainty budget was calculated from the maximum uncertainty using Equation (1) to Equation (3) according to ISO Guide 35:

$$s_{bb} = \sqrt{\frac{M_{between} - M_{within}}{n}} \qquad (1)$$

$$u_{bb} = \sqrt{\frac{M_{within}}{n}} \sqrt[4]{\frac{2}{N(n-1)}} \qquad (2)$$

$$s_w = s_r = \sqrt{M_{within}} \qquad (3)$$

with

$M_{between}$	mean of squared deviations between bottles (from 1-way ANOVA)
M_{within}	mean of squared deviations within one bottle (from 1-way ANOVA)
n	number of replicate measurements per bottle
N	number of bottles selected for homogeneity study

In cases, where $M_{within} > M_{between}$ the inhomogeneity contribution to the combined uncertainty would be set to zero. This was not the case in this study.

Table 1: Results of replicate measurements with samples from a single bottle

Bottle	Data file	A_{BET} [m²/g]	Data file	A_{BET} [m²/g]	Data file	A_{BET} [m²/g]
	Result no. 1		Result no.2		Result no. 3	
A1(04)	Hom-1000.smp	337.2947	Hom-1002.smp	333.2455	Hom-1004.smp	334.7688
B4(01)	Hom-1006.smp	338.6953	Hom-1007.smp	332.4716	Hom-1008.smp	334.4214
C7(06)	Hom-1009.smp	329.7679	Hom-1010.smp	333.3437	Hom-1011.smp	331.7291
D4(01)	Hom-1013.smp	333.9599	Hom-1014.smp	332.5378	Hom-1015.smp	323.0227
D7(05)	Hom-1016.smp	332.4456	Hom-1017.smp	332.0870	Hom-1018.smp	333.3264
E5(01)	Hom-1019.smp	317.1313	Hom-1020.smp	333.1363	Hom-1021.smp	329.3459
F1(06)	Hom-1022.smp	332.6906	Hom-1024.smp	332.0462	Hom-1025.smp	330.4263
G3(08)	Hom-1026.smp	333.8005	Hom-1027.smp	332.6249	Hom-1028.smp	334.2173
G6(04)	Hom-1030.smp	334.3538	Hom-1031.smp	332.8885	Hom-1032.smp	330.1888
H8(05)	Hom-1033.smp	334.0929	Hom-1034.smp	324.4428	Hom-1035.smp	333.1360

Table 2: Analysis of variances calculated for specific surface area A_{BET}

Source of variation	Square sum	Degrees of freedom (df)	Mean square sum (M)	F	F-crit. 95%
Between Units	178.7918	9	19.8658	1.2571	2.3928
Within Units	316.0457	20	15.8023		

Table 3: Results to determine the maximum inhomogeneity contribution u_{hom} of BAM-P116

$\bar{x}_{hom}$	331.92132	
$M_{between}$	19.8658	
M_{within}	15.8023	
	Inhomogeneity contribution	Relative
s_r	3.9752	0.011976
s_{bb}	1.16383	0.003506
u_{bb}	1.2906	0.003888

Table 4: Inhomogeneity contribution u_{hom} of s_r

Property	$u_{hom}(s_r)$	$u_{hom\ rel.}(s_r)$	Unit
A_{BET}	3.9752	0.011976	m^2/g

4. Stability

The numerical results of the measurements to monitor the stability of the CRM BAM-P116 are listed in Table 5 for the period between November 2018 and December 2019. The stability measurements were carried out with the same sample preparation and automated surface area and porosity analyser ASAP 2020 (Micromeritics, Norcross, USA). The respective diagram for the specific surface area is depicted in Fig. 8.

Table 5: Numerical results of stability monitoring

Data file	Test date	A_{BET}
		m^2/g
Hom-1502.smp	19.11.2018	329.0182
Hom-1519.smp	03.12.2018	331.5698
Hom-1534.smp	17.12.2018	329.9524
Hom-1571.smp	18.02.2019	319.0015
Hom-1598.smp	04.04.2019	326.8427
Hom-1610.smp	30.04.2019	330.2429
Hom-1617.smp	23.05.2019	331.5733
Hom-1627.smp	12.06.2019	330.1371
CM1-1639.smp	02.07.2019	329.9562
Hom-1683.smp	05.08.2019	328.2619
Hom-1696.smp	18.09.2019	327.0951
Hom-1719.smp	15.10.2019	328.2152
116-1730.smp	21.11.2019	328.6635
116-1747.smp	16.12.2019	328.6874
	$\bar{x}_{\text{Stab}}$ [a]	328.5155
	$\bar{x}_{\text{ILC}}$ [b]	324.6171
	$s_{x,\text{ILC}}$	9.5012
	$\bar{x}_{\text{Stab}} + 2 \cdot s_{x,\text{ILC}}$	347.5179
	$\bar{x}_{\text{Stab}} - 2 \cdot s_{x,\text{ILC}}$	309.5131

[a] Stab = stability monitoring

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

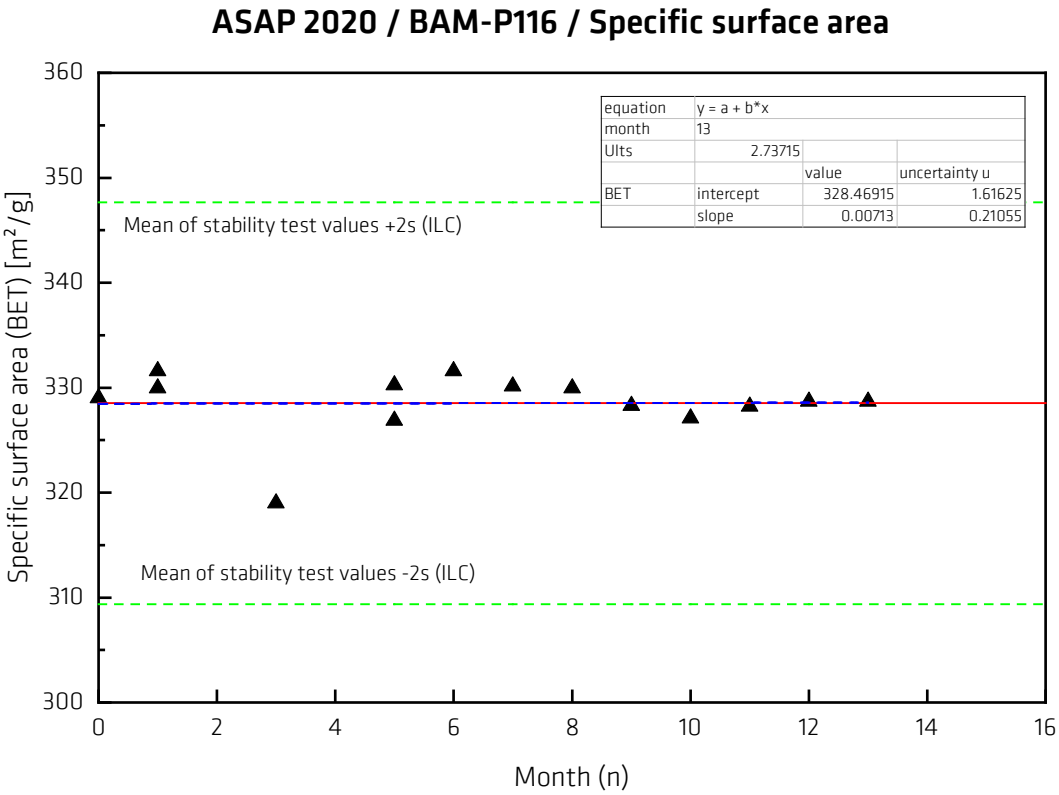

Fig. 8: Stability monitoring for the specific surface area A_{BET}

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. However, 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_{lts}(x)	$u_{lts\ rel.}$(x)	Instability	Negligible
A_{BET} in m²/g	328.46915	0.00713	0.21055	2.73715	0.00833	no	no

The shelf life of CRM BAM-P116 estimated based on the stability monitoring data is at least two years for a carefully closed bottle stored at temperatures below 30°C under dry conditions.

5. List of participating laboratories

3P INSTRUMENTS GmbH & Co. KG, Odelzhausen (Germany)
Anton Paar QuantaTec Inc., Boynton Beach (USA)
Bundesanstalt für Materialforschung und –prüfung (BAM), Div. 1.3, Berlin (Germany)
Bundesanstalt für Materialforschung und –prüfung (BAM), Div. 5.4, Berlin (Germany)
Evonik Technology & Infrastructure GmbH, Hanau-Wolfgang (Germany)
Evonik Technology & Infrastructure GmbH, Marl (Germany)
Forschungsinstitut für Anorganische Werkstoffe -Glas/Keramik- GmbH, Höhr-Grenzhausen (Germany)
Forschungszentrum Jülich GmbH, Jülich (Germany)
Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin (Germany)
Institute of Chemical and Engineering Sciences (ICES), Jurong Island (Singapore)
Instituto Nacional de Técnica Aeroespacial, Madrid (Spain)
Instituto Pedro Nunes, Coimbra (Portugal)
IPT - Instituto de Pesquisas Tecnológicas, São Paulo (Brazil)
Oerlikon Metco WOKA GmbH, Barchfeld-Immelborn (Germany)
Particle Testing Authority - Micromeritics GmbH, Unterschleißheim (Germany)
Particle Testing Authority - Micromeritics Instrument Corp., Norcross, GA (USA)
Universiti Teknologi PETRONAS, Seri Iskandar (Malaysia)
Ural Scientific Research Institute for Metrology (UNIIM), Yekaterinburg (Russian Federation)

28 laboratories were invited to the inter-laboratory comparison. 18 laboratories agreed to participate and submitted results. One laboratory participated with two instruments.

Most of the participating laboratories had already participated in previous inter-laboratory comparisons in the field of gas adsorption measurements. In addition, the laboratories confirmed that their quality management were in accordance with ISO/IEC 17025 or ISO 17034. The types of instruments used by the participants are listed in Table 7.

Table 7: Types of instruments used by the participants

Type of instrument	Number	Manufacturer
3P-Meso222	1	3P INSTRUMENTS GmbH & Co. KG
ASAP 2010	1	Micromeritics Instrument Corporation, Norcross, USA
ASAP 2020	4	
ASAP 2420	2	
Gemini V	1	
TriFlex	1	
TriStar 3000	1	
TriStar II Plus 3030	1	
TriStar II Plus	1	
Autosorb-iQ	2	Anton Paar QuantaTec Inc., Boynton Beach, USA
Autosorb-iQ 2	2	
NOVA 2000e	1	
NOVA 4000e	1	
Total *	19	

6. Results of the interlaboratory comparison and uncertainty estimation

6.1 Experimental results

The inter-laboratory comparison for the certification of BAM-P116 was performed according to the Guidelines for the Production of BAM Reference Materials [6]. Data evaluation and statistical tests were carried out using the software package SoftCRM [11].

The candidate material for the participants was prepared from 13 bottles of the entire charge (see section 2.3). These bottles were merged and divided by means of an eight-port micro rotary riffler (Quantachrome, Germany) to approximately 4.5 g sample mass. The reduction of the original sample quantity was carried out in order to provide the participants with an optimal sample quantity for the analyses. A sample quantity of 0.4 g was planned for an analysis.

Each participating laboratory received one bottle together with the instructions for sample preparation and instrumental analysis. The data was evaluated according to ISO 9277 in a relative pressure range of $0.08 \leq p/p_0 < 0.25$ and the value used for the cross-sectional area of nitrogen was 0.162 nm^2. The laboratories had to perform five 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. 9. The error bars at the data points for the data set means represent the standard deviation of the 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
C01	323.5382
C02	335.5118
C04	331.0994
C06	329.4746
C07	279.1672 [a]
C08	288.5212 [a]
C09	332.3300
C10	306.2448
C11	325.6660
C13	303.9440
C14	235.2667 [a]
C15	313.3392
C16	318.5712
C17	328.6232
C18	328.9886
C19	322.3763
C26	332.1161
C27	331.6699
C28	330.3799
l	16
$\bar{x}$ [b]	324.6171
s_x [c]	9.5012
$\frac{s_x}{\sqrt{l}}$	2.3753
$\bar{x}+1\cdot s_x$	334.1183
$\bar{x}-1\cdot s_x$	315.1159
$\bar{x}+2\cdot s_x$	343.6195
$\bar{x}-2\cdot s_x$	305.6147

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

[b] Average of the accepted data set means

[c] Standard deviation of the accepted data set mean value.

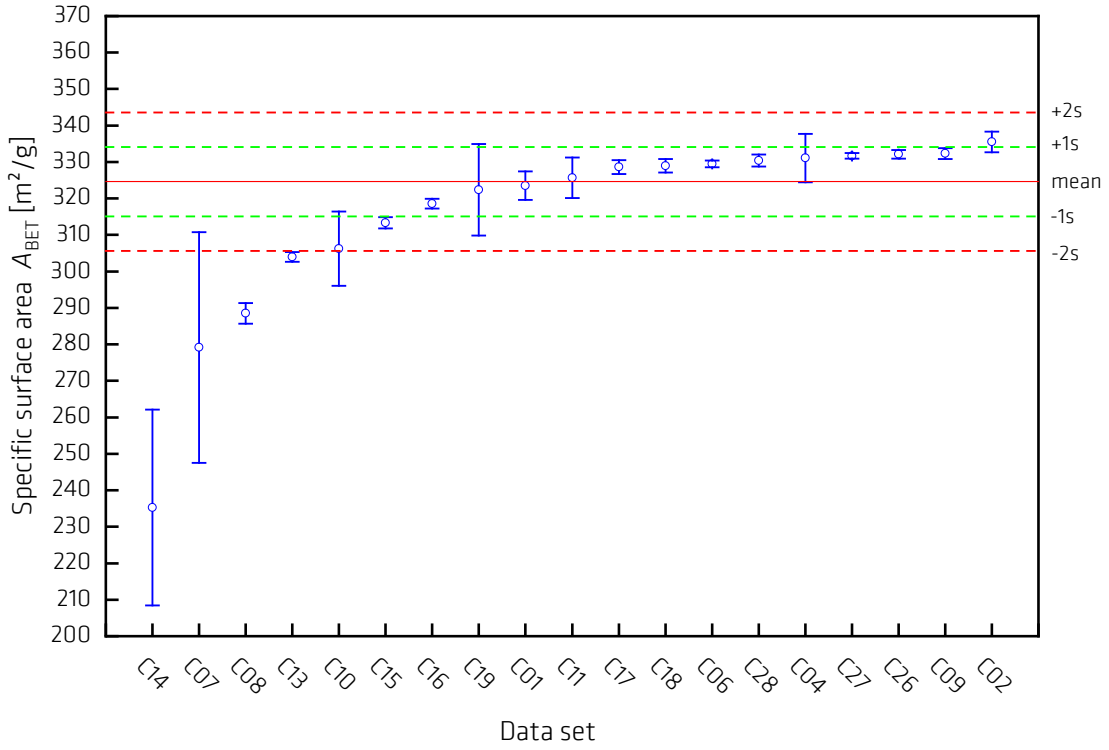

Fig. 9: Submitted results for A_{BET} with calculated data set means and standard deviations (l = 16)

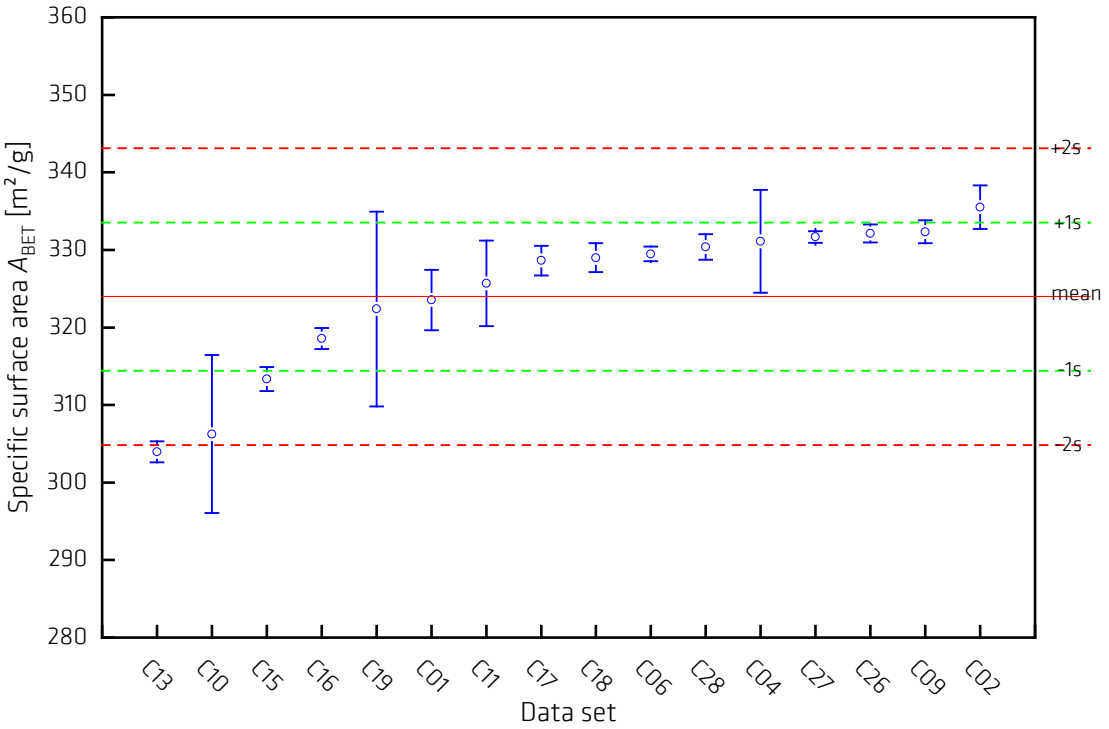

Fig. 10: Calculated data set means for A_{BET} without outlier

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) certification to certify 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 few outliers were detected for the parameter A_{BET}. These outliers were data sets C07, C08 and C14.
The results of the calculation with the evaluation software SoftCRM after deleting the outliers are presented in Table 9.

Table 9: Evaluation of the ILC data using the software program SoftCRM

Property x	$\overline{x}$	s_x	u_{char}	Unit	Pooling	l
A_{BET} in m^2/g	324.6171	9.5012	2.3753	m^2/g	no	16

Before the combined uncertainty is calculated, the calculated relative uncertainties from $u_{hom}(s_r)$ and $u_{lts}(x)$ are used to adapt the uncertainty budget for the homogeneity and stability for the accepted data set of the inter-laboratory comparison (ILC) participants.

Table 10: Adaptation of u_{hom} and u_{lts} to the ILC data set

Mean value from ILC	$u_{hom\ rel.}(s_r)$	u_{hom}	$u_{lts\ rel.}(x)$	u_{lts}
324.6171	0.011976	3.88761	0.00833	2.70406

The combined uncertainty $u_c(x)$ was calculated according to Equation (4) using the numerical values 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).

$$u_c^2(x) = u_{char}^2 + u_{hom}^2 + u_{lts}^2 + \frac{1}{l^2}\sum_{i=1}^{l} s_i^2 \quad \text{with} \quad u_{char}^2 = \frac{s_x^2}{l} \tag{4}$$

Table 11: Values of the uncertainty components for the specific surface area of BAM-P116

Property	$\bar{x}$	u_{char}	u_{hom}	u_{lts}	$\frac{1}{l}\sqrt{\sum_{i=1}^{l} s_i^2}$	u_c	U	l	Unit
A_{BET}	324.6171	2.3753	3.88761	2.70406	1.21814	5.43612	10.87224	16	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 [12]) are summarized in Table 12.

Table 12: Final value for the certified specific surface area of BAM-P116

Property	Certified value x_{cert}	Expanded uncertainty $U = k \cdot u_c$ (k = 2)	Unit
A_{BET}	325	11	m^2/g

7. Metrological traceability

The certified value of specific surface area based on the BET method described in ISO 9277 and is traceable to the base units of the SI via calibrated measurements of the quantities pressure, volume and mass.

8. Information on the proper use of the CRM

8.1 Recommended use

Prior to the measurement, outgassing of the sample is necessary. Outgassing has to be carried out in a vacuum with a final pressure < 10 Pa. Heat the sample for degassing in a vacuum with a rate of about 5 K/min to 453.15 K, then hold temperature at 453.15 K for at least three hours. During sample pre-treatment, a mass loss of 10% is to be expected. Afterwards, allow the sample to cool slowly back to ambient temperature.
The adsorption branch of the N_2 isotherm must be measured at 77.3 K. Perform the analysis following the instrument manufacturer's instructions. The recommended minimum sample intake is 0.5 g.
The sample preparation station should have a separate vacuum circuit in addition to the analysis station or the preparation should be carried out at a separate heating station. For instruments with a combined vacuum system, measurements and sample preparation should not be performed together, as condensation in glass vessels can occur during sample preparation.

8.2 Transport, storage and handling

CRM BAM-P116 can be shipped at ambient temperature. Upon receipt the material should be stored at a temperature below 303 K in its original tightly closed bottle. When handling the sample, the bottle shall be left unclosed as briefly as possible. Care should be taken to avoid moisture pick-up once the bottle is opened. BAM cannot be held responsible for changes that happen during storage of the material at the customer's premises, especially of opened bottles. The material should be used as it is from the bottle. However, before taking a sub-sample re-homogenisation by manual shaking of the closed bottle is strongly recommended.

8.3 Shelf life

The initial stability study after storage of selected units at different temperatures did not reveal any statistically significant deterioration of the certified properties. However, starting with dispatch of the material from BAM the validity of the certificate expires after 24 months. Post-certification monitoring measurements will be conducted in appropriate periods to keep this information up to date.

8.4 Safety information

The usual laboratory safety precautions have to be applied. No hazardous effects are to be expected when the material is used under conditions commonly adopted for the analysis of samples. It is strongly recommended to handle and dispose the reference material in accordance with the guidelines for hazardous materials legally in force at the site of end use and disposal.

8.5 Legal notice

Neither BAM, its contractors nor any person acting on their behalf:

(a) make any warranty or representation, express or implied, that the use of any information,

material, apparatus, method or process disclosed in this document does not infringe any privately-owned intellectual property rights; or

(b) assume any liability with respect to, or for damages resulting from, the use of any information, material, apparatus, method or process disclosed in this document.

9. Information on and purchase of the RM

Certified reference material CRM BAM-P116 is supplied by

Bundesanstalt für Materialforschung und -prüfung (BAM)
Fachbereich 1.6: Anorganische Referenzmaterialien
Richard-Willstätter-Str. 11, D-12489 Berlin, Germany
Phone +49 (0)30 - 8104 2061
Fax: +49 (0)30 – 8104 72061
E-Mail: sales.crm@bam.de

Each bottle of CRM BAM-P116 will be distributed together with a detailed certificate containing the certified values and their uncertainties, the mean values and standard deviations of all accepted data sets and information on the analytical methods used and the names of the participating laboratories.
Information on certified reference materials can be obtained from BAM,
https://www.bam.de.
www.webshop.bam.de

10. References

[1] ISO 9277
Determination of the specific surface area of solids by gas adsorption – BET method.
International Organization for Standardization, Geneva (2010)

[2] ISO Guide 35
Reference materials - Guidance for characterization and assessment of homogeneity and stability.
International Organization for Standardization, Geneva (2017)

[3] ISO/IEC Guide 98-3: Uncertainty of Measurement – Part3: Guide to the expression of uncertainty in measurement (GUM: 1995).
International Organization for Standardization, Geneva (2008)

[4] Brunauer, S., Emmet, P. H., Teller, E.
Adsorption of Gases in Multimolecular Layers.
J. Amer. Chem. Soc., 60 (1938) 309 – 319

[5] ISO/IEC 17025: General requirements for the competence of testing and calibration laboratories,
International Organization for Standardization, Geneva (2017)

[6] Guidelines for the Development and Production of BAM Reference Materials
Bundesanstalt für Materialforschung und –prüfung (BAM), Berlin 2016

[7] ISO 17034, General requirements for the competence of reference material producers,
International Organization for Standardization, Geneva (2016)

[8] ISO Guide 31, Reference materials - Contents of certificates, labels and accompanying documentation,
International Organization for Standardization, Geneva (2015)

[9] PDF-2
powder diffraction file (pdf) database
International Centre for Diffraction Data (ICDD), Pennsylvania, U.S.A. (2015)

[10] Van der Veen, A. H. M. and Nater, D. A. G.
Sample preparation from bulk samples: an overview.
Fuel Processing Technology, 36 (1993) 1 - 7

[11] Bonas, G., Zervou, M., Papaeoannou, T. and Lees, M.
"SoftCRM": A new Software for the Certification of Reference Materials.
Accreditation and Quality Assurance, 8 (2003) 101 - 107

[12] DIN 1333
Zahlenangaben
DIN, Berlin 1992

11. Annexes

Annex 1: Homogeneity study (measurement results)

Annex 2: Measurement results of ILC-participants

Annex 1: Calculation of uncertainty contribution of potential inhomogeneity

	TiO_2 - HOMBIKAT-6								
	Value:	A_BET							
	$0{,}08 \leq p/p_0 \leq 0{,}25$								
	Homogeneity:	10 samples x 3 replicates							
		Replicates							
	Bottle-No.	1	2	3					
		m^2/g	m^2/g	m^2/g					
	A1(04)	337.2947	333.2455	334.7688					
	B4(01)	338.6953	332.4716	334.4214					
	C7(06)	329.7679	333.3437	331.7291					
	D4(01)	333.9599	332.5378	323.0227					
	D7(05)	332.4456	332.0870	333.3264					
	E5(01)	317.1313	333.1363	329.3459					
	F1(06)	332.6906	332.0462	330.4263					
	G3(08)	333.8005	332.6249	334.2173					
	G6(04)	334.3538	332.8885	330.1888					
	H8(05)	334.0929	324.4428	333.1360					
	ANOVA								
	Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*		
	Between Groups	178.7918	9	19.86576	1.257144975	0.31787074	2.392814		
	Within Groups	316.0457	20	15.80228					
	Total	494.8375	29						
	s_bb	1.163827			mean_total	331.921317			
	s_bb_min	1.290623			s_method	3.97520852		s_method = s_{within}	
	u_bb	1.290623			s_method_r	0.01197636			
	u_bb_r	0.003888							
	s_bb_r	0.003506							

Annex 2: Measurement results of ILC-participants

Inter-laboratory comparison for the certification of BAM-P116								
Data set no.	Specific surface area A_{BET} [m²/g]						Mean value	Standard deviation
	Replicate							
	1	**2**	**3**	**4**	**5**			
C01	322.5140	329.5560	320.5410	324.9890	320.0910		323.5382	3.8805
C02	338.0210	338.3620	333.1480	335.9500	332.0780		335.5118	2.8280
C04	326.8520	334.0940	340.3360	331.0800	323.1350		331.0994	6.6286
C06	329.9562	330.2114	328.2733	328.6618	330.2702		329.4746	0.9370
C07	316.010	311.472	254.304	255.334	258.716		279.167	31.644
C08	292.4009	285.1950	286.4682	289.7285	288.8133		288.5212	2.8228
C09	334.4500	330.4200	331.7100	332.4300	332.6400		332.3300	1.4691
C10	299.7800	297.6830	318.1920	316.5200	299.0490		306.2448	10.1881
C11	330.2600	326.8900	325.2600	316.4700	329.4500		325.6660	5.5148
C13	302.9200	304.3400	303.9700	302.5300	305.9600		303.9440	1.3481
C14	241.1421	206.0741	217.4207	235.4347	276.2620		235.2667	26.8601
C15	313.1325	315.9206	311.8340	313.1501	312.6589		313.3392	1.5387
C16	320.2770	317.9920	319.5690	318.1310	316.8870		318.5712	1.3483
C17	326.2540	329.6270	330.2920	330.0950	326.8480		328.6232	1.9185
C18	327.8857	327.0333	331.7807	328.4194	329.8240		328.9886	1.8613
C19	323.8903	323.1036	322.5873	338.8382	303.4621		322.3763	12.5659
C26	332.9728	331.5298	330.3388	332.7648	332.9742		332.1161	1.1612
C27	331.9807	332.0072	330.6770	332.5457	331.1388		331.6699	0.7492
C28	332.7061	328.7097	328.9392	330.9708	330.5739		330.3799	1.6327