Certified Reference Material

BAM
Bundesanstalt für
Materialforschung
und -prüfung

12200 Berlin, Germany
T: +49 30 8104-0
F: +49 30 8104-7 2222

BAM-PM-101
Silicon dioxide (quartz)

with specific surface area (BET) of

0.177 ± 0.004 $m^2 g^{-1}$

Mean of means[1)]	**0.177**	**$m^2 g^{-1}$**
Uncertainty		
Standard deviation of the mean of means	**0.004**	**$m^2 g^{-1}$**
95% confidence interval	**0.008**	**$m^2 g^{-1}$**
Standard deviation of means	**0.014**	**$m^2 g^{-1}$**

according to interlaboratory study carried out in accordance with the "Guidelines for the Production and Certification of BCR Reference Materials" (1)

Method	Gas adsorption at 77 K
Adsorptive	Krypton
Evaluation	BET method according to DIN ISO 9277 (2)

1. Scope

The reference material is intended for the calibration and checking of instruments, especially for determining very small surface areas.
The parameters mentioned are material-specific quantities to characterize non-porous and macroporous solids by means of the gas adsorption method.

[1)] The results were rounded off according to DIN 1333. Outliers determined by the Grubbs test (95% significance level) were not included in the calculation of the mean value.

CERTIFICATE

2. Measurement and evaluation

2.1 Pre-treatment of the sample

Heating the specimen for one hour at 623 K at 0.1 Pascal
Keeping this temperature for 3 hours at a specified vacuum, cooling slowly

2.2 Measurement

The quantity of krypton adsorbed was measured by the static volumetric method.
BET range: p/p_0 from 0.05 to 0.3

2.3 Assumptions

- BET theory (3)
- molecular cross-sectional area of krypton: $a_{krypton} = 0.21\ nm^2$ (4)

2.4 Evaluation

The specific surface area in $m^2\ g^{-1}$ was determined in accordance with DIN 66131 using the following equation:

$$S_{BET} = n_m \cdot a_{krypton} \cdot N_A$$

The monolayer capacity n_m was calculated by linear regression analysis from the slope and the intercept on the y-axis, $n_m = 1/(a+b)$, a = slope, b = intercept (BET-equation).
N_A is the Avogadro's constant.

Participants in the interlaboratory study:

BASF Aktiengesellschaft, Ammoniaklaboratorium, Ludwigshafen
Bundesanstalt für Materialforschung und -prüfung (BAM), Laboratorium Biowerkstoffe, Berlin
Bundesanstalt für Materialforschung und -prüfung (BAM), Laboratorium Sekundäreigenschaften von Referenzmaterialien, Berlin
Degussa AG, Hanau
FISONS Instruments S.p.A., Milano, Italy
Fraunhofer-Institut für Keramische Technologien und Sinterwerkstoffe, Dresden
Friedrich-Schiller-Universität Jena, Institut für Physikalische Chemie, Jena
GSF-Forschungszentrum für Umwelt und Gesundheit GmbH, Institut für Hydrologie, Oberschleißheim
Institut für Technologie und Umweltschutz e.V., Berlin
Leuna-Katalysatoren GmbH, Forschung/Texturlabor, Leuna
Micromeritics GmbH, Neuss
Universität des Saarlandes, Lehrstuhl für Werkstofftechnologie, Saarbrücken
Universität Erlangen-Nürnberg, Lehrstuhl für Technische Chemie, Erlangen
Universität Leipzig, Institut für Technische Chemie, Leipzig

Table 1

Evaluation of the interlaboratory study for determining the specific surface area of silica using the BET method.
Parameter to be certified: *BET specific surface area in* $m^2\,g^{-1}$
Participating laboratories: 14
Method: gas adsorption at 77 K, adsorptive krypton

Laboratory	Number of measurements	Laboratory mean of S_{BET} $m^2\,g^{-1}$	Standard deviation $m^2\,g^{-1}$
L01-01	9	0.173	0.003
L03-02	9	0.184	0.006
L11-06	3	0.149	0.008
L22-11	9	0.174	0.006
L25-12	9	0.166	0.004
L26-35	2	0.161	0.005
L31-14	9	0.172	0.005
L37-19	6	0.169	0.003
L41-22	9	0.176	0.004
S52-28	7	0.188	0.055
L54-30	9	0.208	0.004
L56-32	8	0.189	0.005
L57-33	9	0.181	0.005
L60-40	9	0.183	0.004

3. Further information regarding the reference material

3.1 Origin

The material was prepared from ground pegmatite granite which was mechanically prepared and chemically purified.

3.2 Chemical analysis

The silica content of the material (SiO_2) is >99.99%.

3.3 Thermal analysis

When the silica material is heated its mass losses are extremely low, i. e. ca. 0.1%, occurring mainly in the temperature range of up to 673 K (see Figure 1). They are essentially attributable to the desorption of adsorbed water. The reversible DTA effect with a peak temperature of 850 K has a characteristic shape with a shifted base line and a somewhat asymmetric peak, as is characteristic for modification change of quartz (low and high modification).

3.4 Phase analysis by X-ray powder diffraction

The material consists of crystalline quartz. No other crystalline SiO_2 modifications or phases can be identified. The detection limit under the test conditions is better than 0.5% by mass.

3.5 Particle size distribution

The particle range of the material is quite narrow, i. e. between 100 and 600 µm, with an average particle size of circ. 260 µm; it was determined by laser diffraction analysis (see Figure 2).

3.6 Density

The density is 2.65 g/cm^3, determined by applying helium at 293 K.

3.7 Morphology

The particles have sharp and irregular surfaces (see Figure 3).

3.8 Recommendations

When the reference material will be used for calibrating measurement of instruments, it should be taken into account that the dead volume was measured by using helium.

3.9 Durability

Durability of the reference material is guaranteed for three years from date of shipment provided the material is stored and handled appropriately.

4. References

(1) Guidelines for the production and certification of BCR reference materials, European Commission, Standards, Measurement & Testing Program, 1994

(2) DIN ISO 9277: Determination of the specific surface area of solids by gas adsorption – BET method (ISO 9277:2010), January 2014; Beuth Verlag GmbH, Berlin

(3) S. Brunauer, P.H. Emmett u. E. Teller, J. Amer. Chem. Soc. 60, 309 (1938)

(4) K.S.W. Sing, D.H. Everett, R.A.W. Haul, L. Moscou, R. A. Pierotti, J. Rouquerol, T. Siemieniewska, Pure & Appl. Chem. 57 (1985) 603 (IUPAC Recommendations 1984)

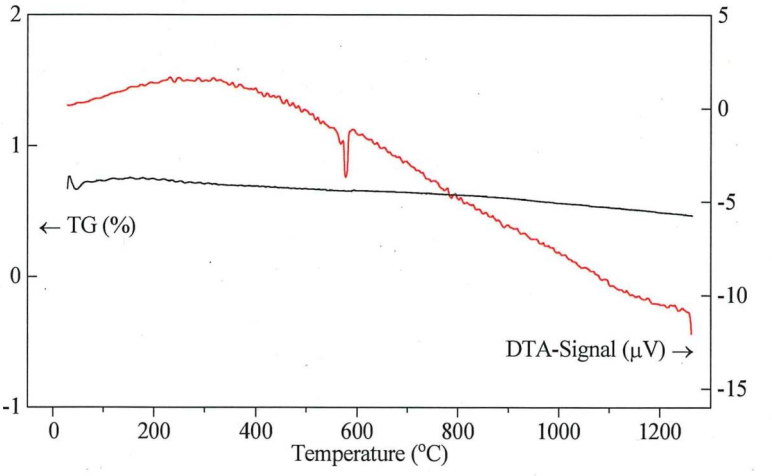


Figure 1: TG and DTA curves of silica

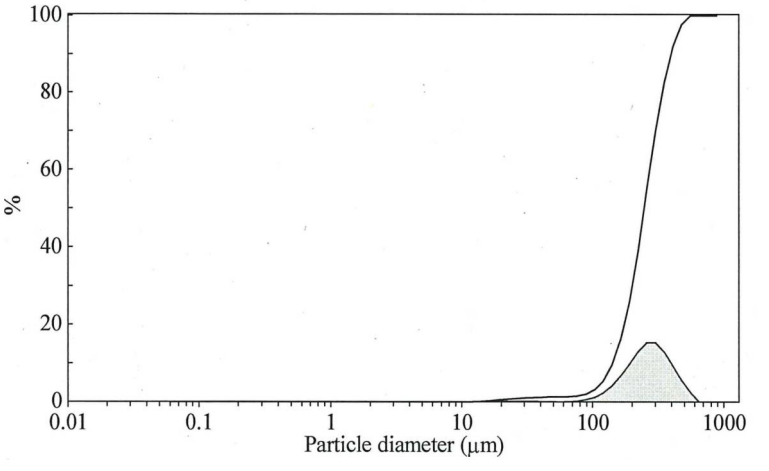


Figure 2: Particle size distribution of silica

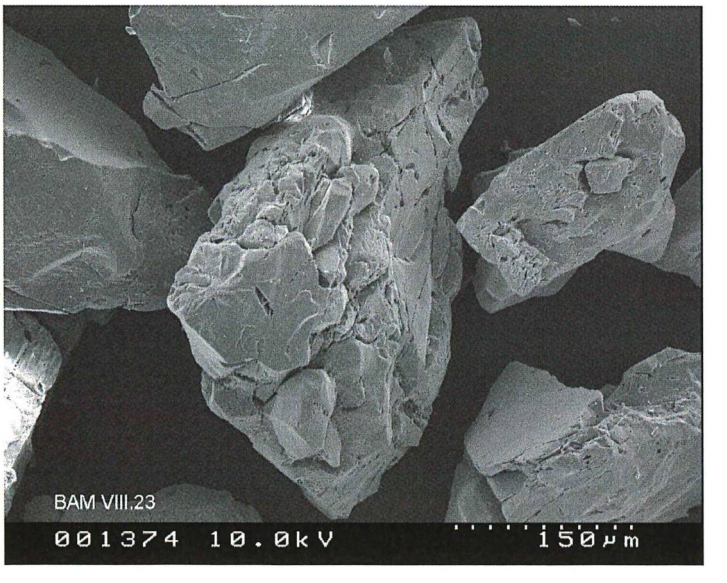


Figure 3: Scanning electron micrograph of silica

Date of certification: 1996-08-30

Date of shipment: .....

BAM
for certified true copy

Dr. Silke Richter
Committee for Certification

Dr. Franziska Emmerling
Project Coordinator
Head of Division 6.3
Structure Analysis

This reference material is offered by:

Bundesanstalt für Materialforschung und -prüfung (BAM),
Richard-Willstätter-Straße 11, D-12489 Berlin, Germany

Phone: +49 30 8104 2061
Fax: +49 30 8104 72061

E-Mail: sales.crm@bam.de
Internet: www.webshop.bam.de

Appendix

Statistical evaluation

The statistical evaluation of the quantities determined from the isotherms can be carried out according to DIN/ISO 5725 [11] or according to BCR Guidelines. Evaluation according to DIN/ISO 5725 presupposes, however, that the number of measured values is nearly the same for all laboratories, and that the variances are homogeneous.

According to the BCR Guidelines, "pooling of all individual data" (i. e. all sets of data produced by the various laboratories may be considered as samples from a single population of data and therefore they can be treated as one single set of data) is recommended only if the means and variances do not differ significantly. In the present case the means and variances of the laboratories are heterogeneous due to the use of different measurement apparatus, such that pooling was not allowed.

In the case of "no pooling", the BCR Guidelines uses a very simplified model for the calculation of the certified value. This means that laboratory mean values xi are modeled and not the individual values. The laboratory means are modeled as the sum of the "true" value μ of the property to be certified, and the deviation (bias) $\Delta\mu i$ of laboratory i, where the $\Delta\mu i$ are considered to be statistically independent and have expectation zero.

$$x_i = \mu + \Delta\mu_i \qquad i = 1, .., n \text{ (n - number of laboratories)} \qquad (1)$$

Let $k_i \geq 2$ is the number of repeated measurements of laboratory i. The sample mean of laboratory i is used as an estimate for the laboratory mean (Eq. 2)

$$x_i = 1/k_i \, \Sigma_j x_{ij} \qquad i = 1, .., n \qquad (2)$$

with a laboratory standard deviation s_i given by

$$s_i^2 = 1/(k_i-1) \, \Sigma_j (x_{ij}-x_i)^2 \; j = 1, ..., k_i \qquad (3)$$

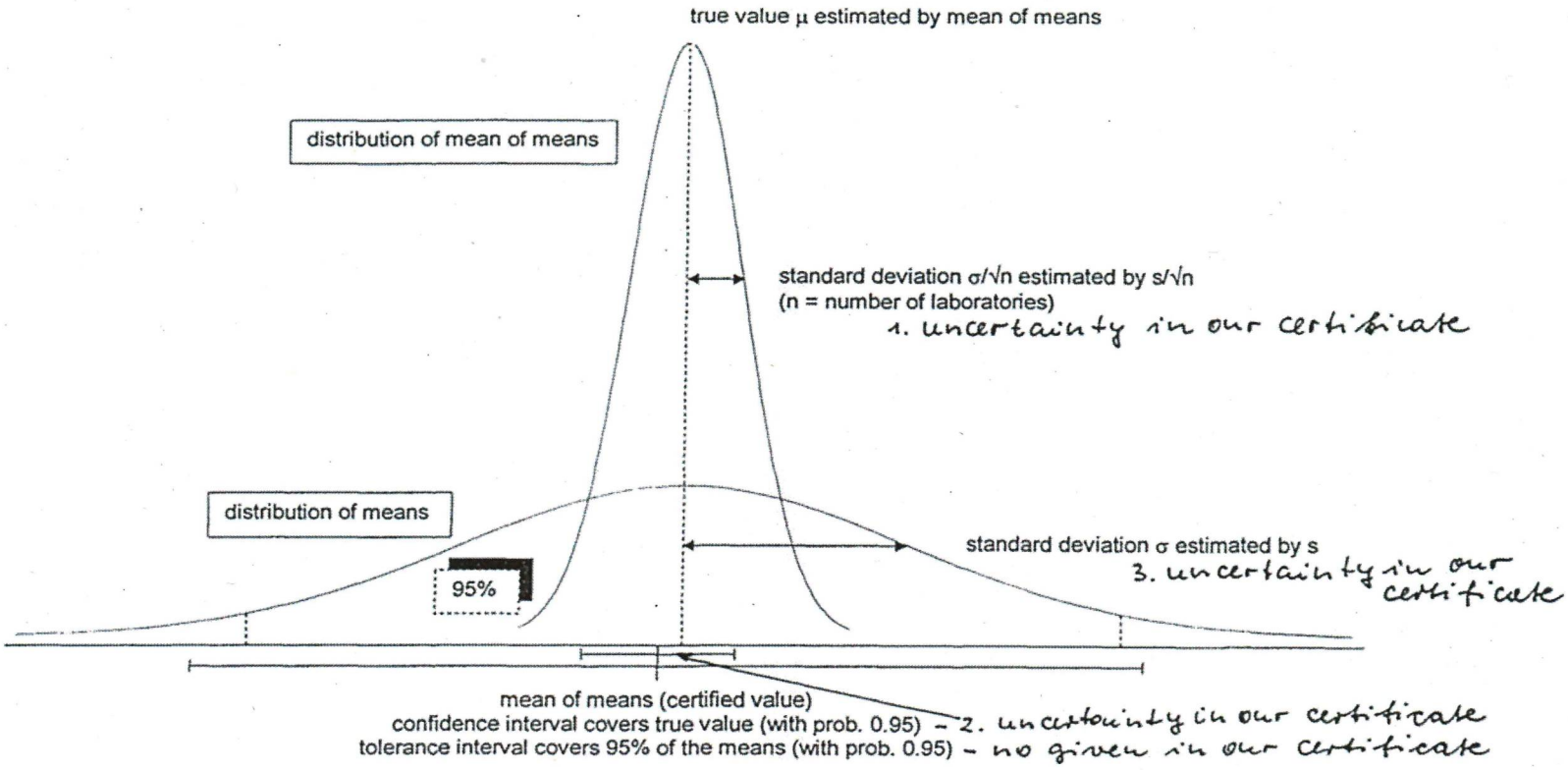
The "mean of means"

$$x = 1/n \, \Sigma_i \, x_i \qquad i = 1, .., n \qquad (4)$$

provides a reasonable estimate for μ and is used as the certified value.
The standard deviation s of laboratory means is

$$s^2 = 1/(n-1) \, \Sigma_i (x_i-x)^2 \qquad i = 1, .., n \qquad (5)$$

Therefore, the procedure used was: 1) Test for and eliminate outliers in the mean values of the laboratories using Dixon's method (1%, two-sided, iterative); 2) Because of the mentioned heterogeneity, the laboratory dispersions were not subjected to an outlier test; 3) Test for normal distribution of the mean values of the laboratories using the Lilliefors version of the Kolmogorov-Smirnov test; 4) Determine the certified value; and 5) Determine the uncertainty of the certified value as a 95% confidence interval.



General statistical scheme of the certified value and its uncertainties in connection with the true value

B. Röhl-Kuhn, BAM, Berlin