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Certified Reference Material

BAM-PM-102
Material: α-Alumina

with specific surface area (BET) of

$5.41\ m^2 g^{-1} \pm 0.04\ m^2 g^{-1}$

Mean of means [1]	**5.41 $m^2 g^{-1}$**
Uncertainty	
Standard deviation of the mean of means	**0.04 $m^2 g^{-1}$**
95% confidence interval	**0.09 $m^2 g^{-1}$**
Standard deviation of means	**0.24 $m^2 g^{-1}$**

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	Nitrogen
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 of small surface areas.
The parameters mentioned are material-specific quantities to characterize non-porous and macroporous solids by means of the gas adsorption method (Isotherm Type II).

[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.**

2015-10

CERTIFICATE

2. Measurement and evaluation

2.1 Pre-treatment of the sample

Heating the specimen for one hour at 523 K at 0.1 Pascal
Keeping this temperature for 3 hours at a specified vacuum, cooling slowly

2.2 Measurement

The quantity of nitrogen 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 nitrogen: $a_{nitrogen}$ = 0.162 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:

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

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 physikalische Kenngrößen; Porenstruktur, Berlin
Bundesanstalt für Materialforschung und -prüfung (BAM), Laboratorium Sekundäreigenschaften von Referenzmaterialien, Berlin
CONDEA Chemie GmbH, Anorganische Spezialchemikalien, Brunsbüttel
Degussa AG, ZFE - OT, Hanau
FISONS Instruments S.p.A., Milano, Italy
Forschungsinstitut für Leder- und Kunstledertechnologie gGmbH, Freiberg/Sa.
Forschungs- und Materialprüfungsanstalt Baden-Württemberg, Otto-Graf-Institut, Stuttgart
Freiberger NE-Metall GmbH, Material- und Umwelttechnik, Freiberg/Sa.
Friedrich-Schiller-Universität Jena, Institut für Physikalische Chemie, Jena
GSF-Forschungszentrum für Umwelt und Gesundheit, GmbH, Oberschleißheim
Hochschule für Architektur und Bauwesen, Forschungsbereich Baustoffe, Weimar
HÜLS AG, Zentrale Analytik, Marl
Institut für Angewandte Forschung, Reutlingen
Institut für Festkörper und Werkstoffforschung Dresden e.V., Dresden
Institut für Polymerforschung e. V., Dresden
Merck KGaA, Darmstadt
Leuna-Katalysatoren GmbH, Leuna
Micromeritics GmbH, Neuss
Philips GmbH, Aachen
Quantachrome, Eurasburg
Schaefer Kalk, Diez/Lahn
TU Bergakademie Freiberg, Institut Keramische Werkstoffe, Freiberg /Sa.

Universität Erlangen-Nürnberg, Lehrstuhl für Technische Chemie, Erlangen
Universität Gesamthochschule Essen, Fachbereich Bauphysik und Materialwirtschaft, Essen
Universität Kassel, Fachgruppe Thermodynamik, Kassel
Universität Leipzig, Institut für Physikalische und Theoretische Chemie, Leipzig
Universität des Saarlandes, Saarbrücken
Wissenschaftlich-technische Gesellschaft für Verfahrenstechnik, FIA e.V., Freiberg/Sa.

Table 1

Evaluation of the interlaboratory study for determining the specific surface area of α-alumina using the BET method.
Participating laboratories: 30
Parameter to be certified: *BET specific surface area*
Method: Gas adsorption at 77 K, adsorptive nitrogen

Laboratory	**Number of measurements**	**Laboratory mean of S_{BET} $m^2 g^{-1}$**	**Standard deviation $m^2 g^{-1}$**
L01-01	9	5.96	0.04
L03-02	8	5.21	0.08
L05-03	9	5.49	0.02
L08-04	8	5.63	0.43
L09-37	8	5.39	0.06
A11-06	3	5.46	0.09
L13-34	7	5.10	0.64
L15-07	8	5.91	0.12
L16-08	9	5.31	0.10
L21-40	9	5.52	0.12
L23-36	8	5.33	0.02
L25-12	8	5.40	0.02
L26-35	3	5.35	0.09
L30-13	9	5.32	0.08
L32-15	8	5.36	0.03
L34-17	7	5.40	0.06
L35-18	9	5.37	0.04
L38-20	8	5.51	0.13
L39-21	9	5.40	0.02
L41-22	9	5.45	0.02
L45-24	7	5.40	0.08
L46-25	9	5.52	0.03
L49-26	9	5.07	0.15
L52-28	9	4.82	0.12
L54-30	9	5.46	0.04
L55-31	9	5.84	0.24
L56-32	9	5.00	0.17
L57-33	9	5.53	0.07
S57-33	9	5.35	0.70
L61-41	6	5.52	0.03

3. Further information regarding the sample

3.1 Origin

The sample is a product of the Ceralox-Corp. Tucson, Arizona, USA.

3.2 Chemical analysis

The α-alumina content of the sample (Al_2O_3) is >99.76% +/- 0.03.

3.3 Thermal analysis

When α-alumina is heated its mass losses are extremely low, 0.03%. DTA-effects can be not identified. The failure of DTA-effects and the low mass losses confirm the presence of α-alumina (see Figure 1).

3.4 Phase analysis by X-ray powder diffraction

The material consists of corundum. No other alumina forms 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 between 40 and 500 µm with an average particle size of circ. 150 µm; it was determined by laser diffraction analysis (see Figure 2).

3.6 Density

The density is 3.97 g/cm³, 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 Programme, 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)

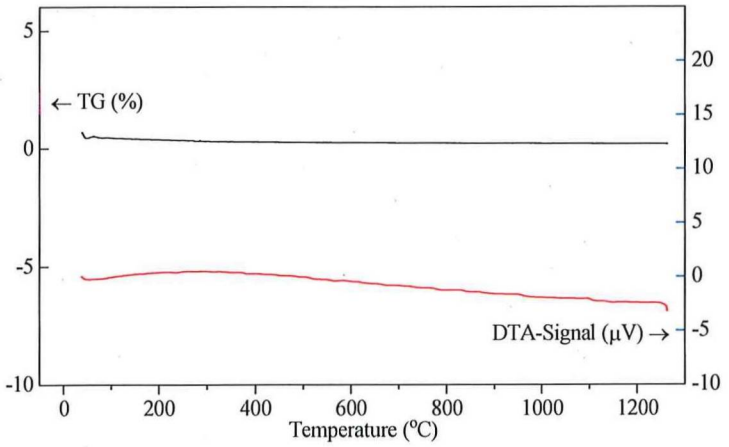

Figure 1: TG and DTA curves of α-alumina

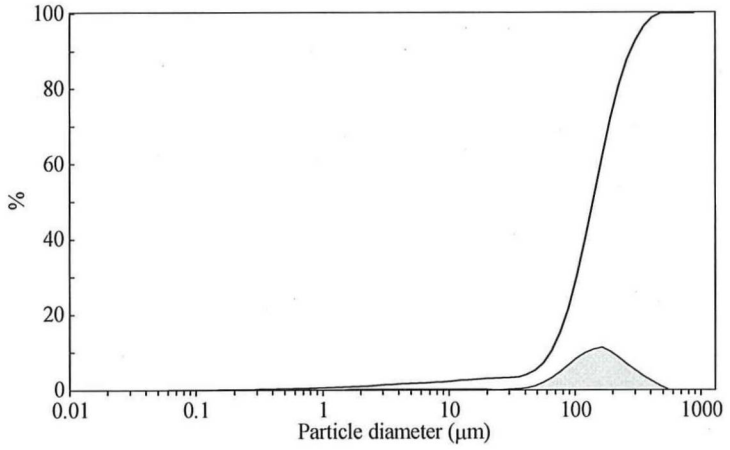

Figure 2: Particle size distribution of α-alumina

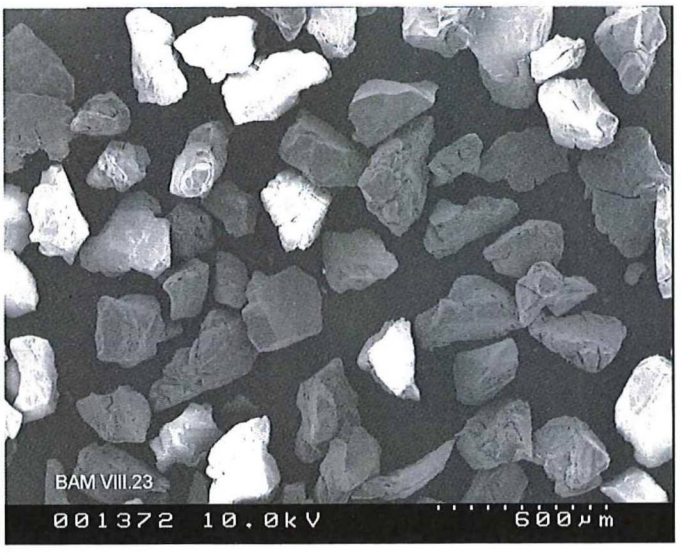

Figure 3: Scanning electron micrograph of α-alumina

Date of certification: 1996-08-30

Date of shipment: .....

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for certified true copy

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Structure Analysis

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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

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

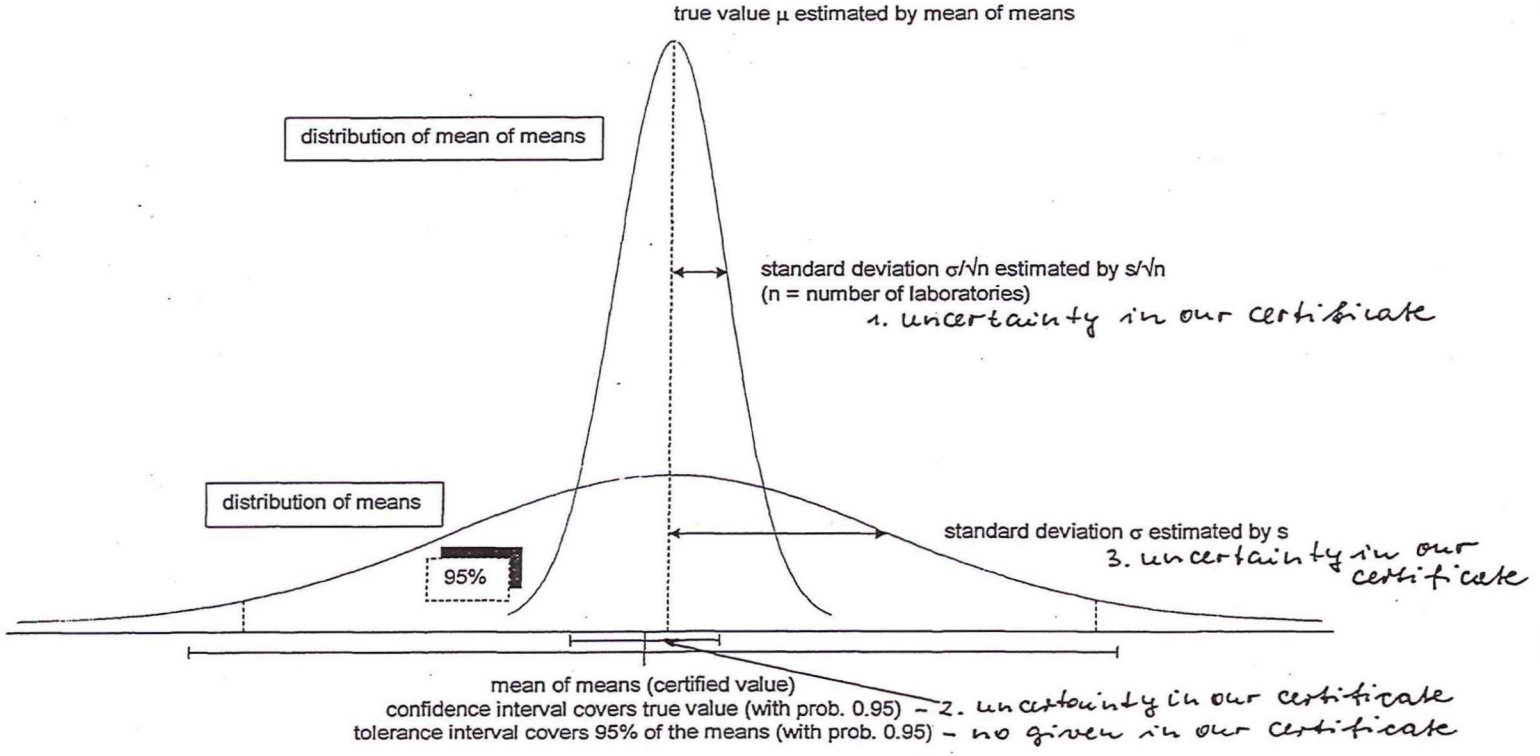
The "mean of means"

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

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

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