## Federal Institute for Materials Research and Testing

# CERTIFIED REFERENCE MATERIAL
# FOR THE GAS ADSORPTION

### *BAM-PM-104*
### *Material: Alumina Type 150*

***with specific surface area (BET) of***

***79.8 $\pm$ 0.4 $m^2 g^{-1}$***

| | |
|---|---|
| **Mean of means [1)]** | **79.8 $m^2 g^{-1}$** |
| **Uncertainty** | |
| **Standard deviation of the mean of means** | **0.4 $m^2 g^{-1}$** |
| **95%-confidence interval** | **0.8 $m^2 g^{-1}$** |
| **Standard deviation of means** | **2.0 $m^2 g^{-1}$** |

***with specific pore volume***
***(adsorption, Gurvich) of***

***0.210 $\pm$ 0.002 $cm^3 g^{-1}$***

| | |
|---|---|
| **Mean of means[1)]** | **0.210 $cm^3 g^{-1}$** |
| **Uncertainty** | |
| **Standard deviation of the mean of means** | **0.002 $cm^3 g^{-1}$** |
| **95%-confidence interval** | **0.004 $cm^3 g^{-1}$** |
| **Standard deviation of means** | **0.009 $cm^3 g^{-1}$** |

Certificate

[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.

***with hydraulic pore radius of***

***5.31 ± 0.05 nm***

| | |
|---|---|
| **Mean of means [2)]** | **5.31 nm** |
| **Uncertainty** | |
| **Standard deviation of the mean of means** | **0.05 nm** |
| **95%-confidence interval** | **0.11 nm** |
| **Standard deviation of means** | **0.24 nm** |

***with most frequent pore radius of***

***3.23 ± 0.05 nm***

| | |
|---|---|
| **Mean of means [2)]** | **3.23 nm** |
| **Uncertainty** | |
| **Standard deviation of the mean of means** | **0.05 nm** |
| **95%-confidence interval** | **0.10 nm** |
| **Standard deviation of means** | **0.23 nm** |

according to the 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 66131 (2)<br>Pore volume, mean pore radius and most frequent pore radius according to DIN 66134 (3) |

## *1. Scope*

The reference material is intended for the calibration and checking of instruments, especially for determining the surface area, the specific pore volume, the mean pore radius, and the most frequent pore radius.
The parameters mentioned are material-specific quantities to characterize mesoporous solids by means of the gas adsorption method.
(Isotherm Type IV according to the IUPAC classification(4)).

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[2)] 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.

## 2. Measurement and evaluation

### 2.1 Pretreatment of the sample

Heating the specimen for one hour at 523 K at 0.1 Pascal
Keeping this temperature for 5 hours at a specified vacuum, cooling slowly

### 2.2 Measurement

The quantity of nitrogen adsorbed and desorbed was measured using 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 nm² (4)
- capillary condensation theory (5)

### 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.

The specific pore volume after Gurvich was determined from adsorption branch of the isotherm at $p/p_0 = 0.99$ according to DIN 66134.

The hydraulic pore radius was determined using the relation $2V/S_{BET}$ according to DIN 66134 with V being the pore volume calculated from the desorption branch of the isotherm by means of the model of Barrett, Joyner und Halenda using the Kelvin and Halsey equations.

The most frequent pore radius according to DIN 66134 was determined from the maximum of the pore size distribution dV/dr calculated from the desorption branch of the isotherm by means of the model of Barrett, Joyner und Halenda using the Kelvin and Halsey equations.

## 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), Sekundäreigenschaften von Referenzmaterialien, Berlin

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Degussa AG, ZFE - OT, Hanau
FISONS Instruments S.p.A., Milano, Italy
Freiberger NE-Metall GmbH, Material- und Umwelttechnik, Freiberg/Sa.
Friedrich-Schiller-Universität, Institut für Physikalische Chemie, Jena
Fraunhofer-Institut für Keramische Technologien und Sinterwerkstoffe, Dresden
Forschungs- und Materialprüfungsanstalt Baden-Württemberg, Otto-Graf-Institut, Stuttgart
Grace Davison, R & D, Silica/Adsorbents, Worms
HÜLS AG, Zentrale Analytik, Marl
Institut für Festkörper- und Werkstofforschung Dresden e.V., Dresden
Institut für Angewandte Forschung, Reutlingen
Karl-Winnacker-Institut der Dechema e.V., Frankfurt/M.
KGaA Merck, Darmstadt
Leuna-Katalysatoren GmbH, Leuna
Micromeritics GmbH, Neuss
Quantachrome, Eurasburg
Schaefer Kalk, Diez/Lahn
Süd-Chemie AG, Forschung und Entwicklung/Analytik, Moosburg
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 Leipzig, Institut für Physikalische und Theoretische Chemie, Leipzig
Universität Leipzig, Institut für Technische Chemie, Leipzig
Universität des Saarlandes, Saarbrücken
Wissenschaftlich-technische Gesellschaft für Verfahrenstechnik, FIA e.V., Freiberg

**Table 1**

Evaluation of the interlaboratory study for determining the specific surface area of alumina type 150 using the BET method.
Participating laboratories: 26
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 $m^2 g^{-1}$** |
|---|---|---|---|
| A01-01 | 5 | 82.7 | 1.9 |
| A11-06 | 3 | 80.0 | 0.5 |
| D01-01 | 4 | 80.1 | 0.4 |
| L08-04 | 9 | 81.0 | 1.5 |
| L09-37 | 9 | 77.3 | 1.2 |
| L16-08 | 9 | 80.4 | 0.5 |
| L18-10 | 9 | 86.3 | 5.5 |

**Table 1 (cont.)**

| Laboratory | Number of measurements | Laboratory mean of $S_{BET}$ $m^2 g^{-1}$ | Standard deviation $m^2 g^{-1}$ |
|---|---|---|---|
| L23-36 | 9 | 77.2 | 0.5 |
| L25-12 | 9 | 79.6 | 0.5 |
| L26-35 | 3 | 78.7 | 0.7 |
| L31-14 | 8 | 79.3 | 0.1 |
| L32-15 | 8 | 77.8 | 0.3 |
| L34-17 | 8 | 78.3 | 0.6 |
| L35-18 | 7 | 80.4 | 0.8 |
| L37-19 | 9 | 79.2 | 1.7 |
| L38-20 | 7 | 79.9 | 0.6 |
| L39-21 | 9 | 77.4 | 0.8 |
| L41-22 | 9 | 78.6 | 0.4 |
| L49-26 | 9 | 78.8 | 0.4 |
| L54-30 | 9 | 79.9 | 0.6 |
| L55-31 | 9 | 79.4 | 0.9 |
| L56-32 | 9 | 80.9 | 0.3 |
| L57-33 | 9 | 79.5 | 0.4 |
| L58-38 | 9 | 77.7 | 0.5 |
| L61-41 | 6 | 80.6 | 0.2 |
| S57-33 | 9 | 83.3 | 2.1 |

**Table 2**

Evaluation of the interlaboratory study for determining the specific pore volume of alumina type 150.
Participating laboratories: 22
Parameter to be certified: *Gurvich specific pore volume (adsorption at $p/p_0 = 0.99$)*
Method: Gas adsorption at 77 K, adsorptive nitrogen

| Laboratory | Number of measurements | Laboratory mean of specific pore volume $cm^3\ g^{-1}$ | Standard deviation $cm^3\ g^{-1}$ |
|---|---|---|---|
| A01-01 | 5 | 0.211 | 0.005 |
| A11-06 | 3 | 0.211 | 0.002 |
| D01-01 | 4 | 0.212 | 0.002 |
| L08-04 | 8 | 0.208 | 0.002 |
| L09-37 | 9 | 0.200 | 0.007 |
| L13-34 | 7 | 0.188 | 0.002 |
| L16-08 | 9 | 0.211 | 0.004 |
| L18-10 | 9 | 0.213 | 0.012 |
| L23-36 | 9 | 0.208 | 0.003 |
| L25-12 | 9 | 0.205 | 0.012 |
| L26-35 | 1 | 0.218 | 0.000 |
| L32-15 | 9 | 0.209 | 0.003 |
| L35-18 | 7 | 0.213 | 0.004 |
| L37-19 | 5 | 0.211 | 0.004 |
| L38-20 | 7 | 0.210 | 0.002 |
| L41-22 | 4 | 0.208 | 0.006 |
| L54-30 | 9 | 0.220 | 0.004 |
| L55-31 | 9 | 0.193 | 0.002 |
| L56-32 | 9 | 0.226 | 0.004 |
| L57-33 | 7 | 0.210 | 0.002 |
| L61-41 | 6 | 0.224 | 0.002 |
| S57-33 | 9 | 0.217 | 0.005 |

**Table 3**

Evaluation of the interlaboratory study for determining the hydraulic pore radius of alumina type 150
Participating laboratories: 22
Parameter to be certified: *Hydraulic pore radius* $(2V/S_{BET})$
Method: Gas adsorption at 77 K, adsorptive nitrogen

| **Laboratory** | **Number of measurements** | **Laboratory mean of hydraulic pore radius nm** | **Standard deviation nm** |
|---|---|---|---|
| A01-01 | 5 | 5.11 | 0.02 |
| A11-06 | 3 | 5.28 | 0.02 |
| D01-01 | 4 | 5.30 | 0.05 |
| L08-04 | 9 | 5.13 | 0.11 |
| L09-37 | 9 | 5.19 | 0.15 |
| L13-34 | 7 | 6.02 | 0.41 |
| L16-08 | 9 | 5.24 | 0.08 |
| L18-10 | 8 | 4.96 | 0.08 |
| L23-36 | 9 | 5.38 | 0.06 |
| L25-12 | 9 | 5.16 | 0.28 |
| L26-35 | 1 | 5.50 | 0.00 |
| L32-15 | 9 | 5.38 | 0.11 |
| L35-18 | 7 | 5.29 | 0.09 |
| L37-19 | 5 | 5.36 | 0.12 |
| L38-20 | 8 | 5.26 | 0.02 |
| L41-22 | 4 | 5.30 | 0.14 |
| L54-30 | 9 | 5.51 | 0.09 |
| L55-31 | 9 | 4.85 | 0.05 |
| L56-32 | 9 | 5.60 | 0.08 |
| L57-33 | 8 | 5.31 | 0.09 |
| L61-41 | 6 | 5.55 | 0.06 |
| S57-33 | 9 | 5.23 | 0.17 |

**Table 4**

Evaluation of the interlaboratory study for determining the most frequent pore radius of alumina type 150
Participating laboratories: 25
Parameter to be certified: *Most frequent pore radius (BJH model, desorption branch)*
Method: Gas adsorption at 77 K, adsorptive nitrogen

| **Laboratory** | **Number of measurements** | **Laboratory mean of most frequent pore radius**<br>**nm** | **Standard deviation**<br>**nm** |
|---|---|---|---|
| A01-01 | 5 | 3.45 | 0.005 |
| A11-06 | 3 | 3.47 | 0.011 |
| D01-01 | 3 | 3.44 | 0.001 |
| L03-02 | 8 | 2.80 | 0.224 |
| L09-37 | 8 | 3.25 | 0.010 |
| L13-34 | 6 | 2.87 | 0.119 |
| L16-08 | 8 | 3.00 | 0.068 |
| L18-10 | 9 | 2.84 | 0.122 |
| L23-36 | 9 | 3.50 | 0.007 |
| L25-12 | 8 | 3.07 | 0.114 |
| L31-14 | 9 | 3.10 | 0.136 |
| L32-15 | 9 | 3.47 | 0.007 |
| L35-18 | 7 | 3.30 | 0.154 |
| L37-19 | 9 | 3.49 | 0.025 |
| L38-20 | 8 | 3.41 | 0.006 |
| L39-21 | 9 | 3.38 | 0.248 |
| L41-22 | 9 | 3.48 | 0.008 |
| L49-26 | 9 | 3.35 | 0.008 |
| L54-30 | 8 | 3.03 | 0.087 |
| L55-31 | 9 | 3.05 | 0.039 |
| L56-32 | 9 | 3.07 | 0.074 |
| L57-33 | 8 | 3.47 | 0.010 |
| L58-38 | 9 | 3.30 | 0.002 |
| L61-41 | 6 | 3.08 | 0.021 |
| S57-33 | 9 | 3.02 | 0.232 |

## 3. Further information regarding the sample

### 3.1 Origin

The sample is a product of Merck KGaA, Darmstadt, Germany.

### 3.2 Isotherm and pore size distribution

See Figures 1 and 2.

### 3.3 Thermal analysis

When alumina type 150 is heated its mass losses are 3.1 % until a temperature of 1273 K. Below 573 K, adsorbed water was removed. At a temperature of 1398 K an exothermic effect begins which ends at 1533 K showing the crystallization of α-alumina (see Figure 3).

### 3.4 Phase analysis by X-ray powder diffraction

Alumina phase $\kappa$ with parts of $\alpha$.

### 3.5 Particle size distribution

The particle range of the material is between 30 and 120 µm. It was determined by laser diffraction analysis (see Figure 4).

### 3.6 Density

The density is 3.38 g $cm^{-3}$, determined by applying helium at 293 K.

### 3.7 Morphology

See Figure 5.

### 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 66131: Determination of specific surface area of solids by means of gas adsorption after Brunauer, Emmett and Teller (BET), July 1993; 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)

(5) L. H. Cohan, J. Am. Chem. Soc. **66**, 98 (1944)


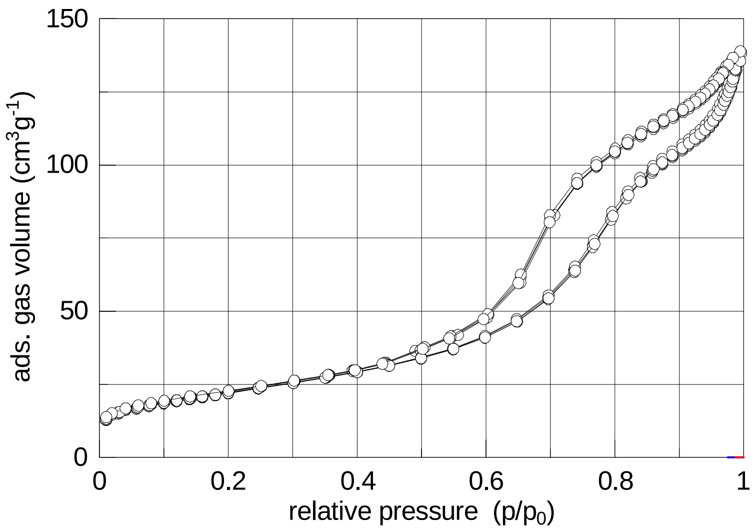


**Figure 1:** Adsorption isotherm for nitrogen at 77 K on alumina type 150 (overlay of 9 measurements)

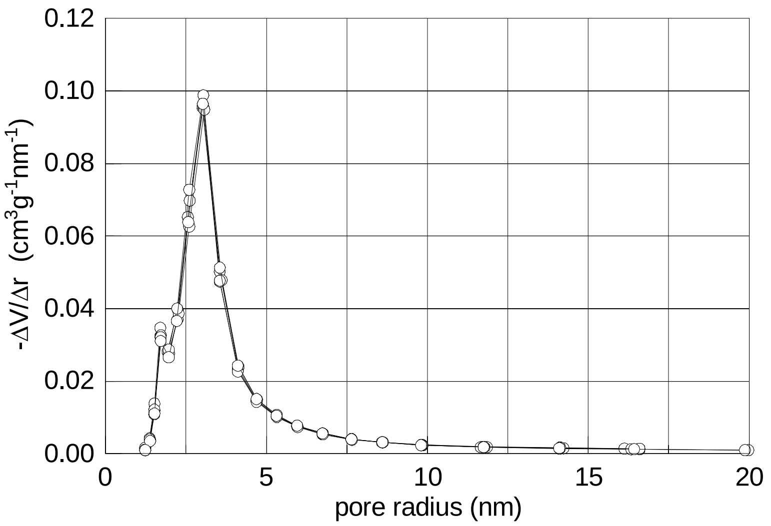


**Figure 2:** Pore size distribution of alumina type 150 (overlay of 9 measurements)

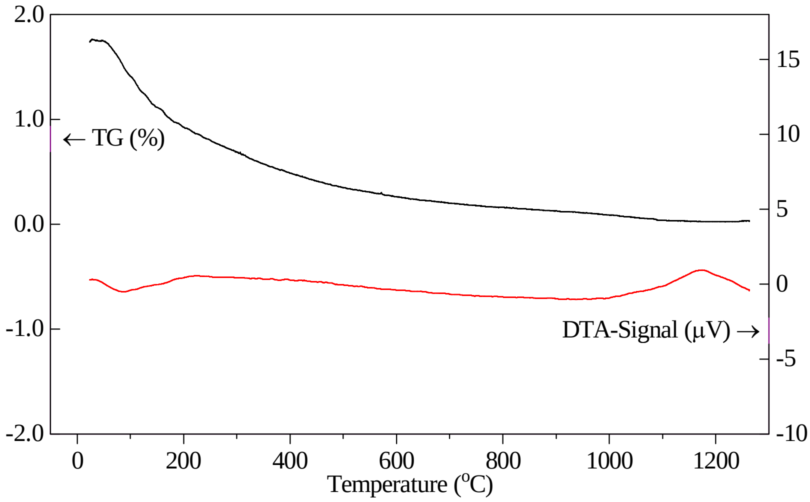


**Figure 3:** TG and DTA curves of alumina type 150

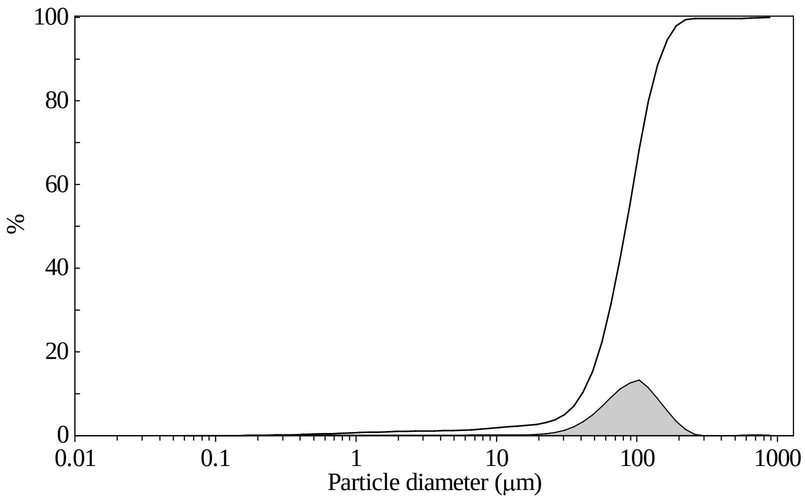


**Figure 4:** Particle size distribution of alumina type 150

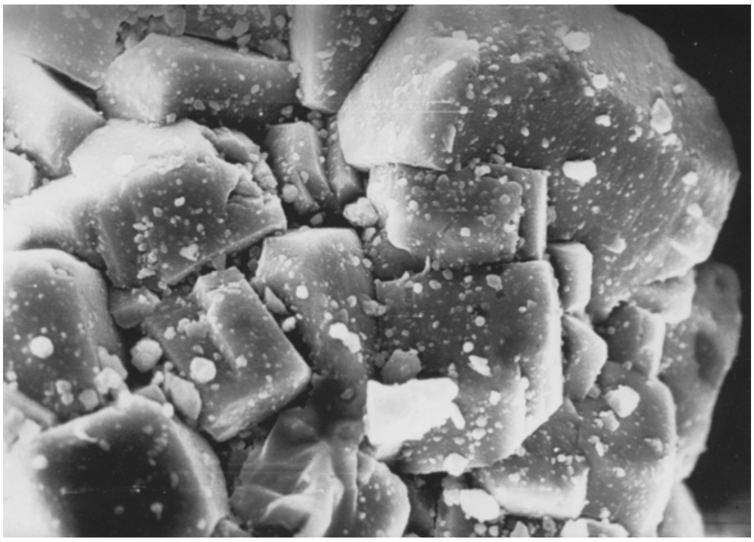

**Figure 5:** Scanning electron micrograph of alumina type 150

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Date of shipment: ..................

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