

Deltares

Mr. Alexander van Duinen

Postbus 177

2600 MH Delft

The Netherlands

Our reference 20-DSS-0868

Your reference

Subject N₂ adsorption (BET) and MIP

Date 16 December 2020

Determination of the specific surface area and porosity of twelve intact clay samples, analysed with nitrogen gas adsorption and mercury intrusion porosimetry.

Dear Mr Van Duinen

We are pleased to report the results of the nitrogen adsorption and mercury intrusion investigations and on your twelve intact clay samples in order to determine the specific surface area and porosity of the samples. All investigations have been performed in the laboratory of Delft Solids Solutions.

A summary of the methodologies used and the results obtained is described below.

Sample description

The samples were received in a period between the October 14, 2020 and December 11, 2020 and all investigations have been performed in the period between this date and the date of reporting. A visual inspection of the samples shows that all samples consist of a clay-like structure with different moisture contents.

The samples were stored at ambient conditions and are coded:

- ***B003 lab 3***
- ***B003 lab 5***
- ***B003 lab 11***
- ***B203 lab 15***
- ***B203 lab 17***
- ***B203 lab 21***
- ***Remoulded CI4.11***
- ***B003/B203 mix CI4_3***
- ***Meng 203/003 CI4_5***
- ***B003/B203 CI4_8***
- ***B003/B203 CI4_1***
- ***B003/B203 CI4_9***

Background

Mercury intrusion porosimetry

Mercury intrusion porosimetry (MIP) measurements are performed on a variety of samples to determine the pore volume, porosity, and the pore size distribution. This technique is based on the principle that mercury is a non-wetting liquid and requires a force to penetrate voids, which is described in ISO 15901-1:2016.¹

In a typical analysis, pressures from ~ 0.001 MPa to several 100's MPa are applied and application of the Washburn equation converts the pressure to pore diameter (d_{pore}) according to the following relationship:²

$$d_{pore} = \frac{-4\gamma \cos \theta}{p} \quad [1]$$

A value of 140° is used for the contact angle (θ), as this has proven to be a realistic value for most oxidic materials,² while the surface tension of mercury (γ) amounts to 480 dyne/cm. Measurement of the volume displacement by the solid sample, especially after determination of the *inter*-particle volume and/or *intra*-particle volume, also enables to assess its apparent density.³ The latter value would approach the skeletal (or true) density if all porosity has adequately been assessed and would result in lower values if not all (*intra*-) particle porosity has been taken into account.

Nitrogen adsorption

In N₂ physical gas adsorption, the sample cell holding the outgassed sample is evacuated and cooled to liquid nitrogen temperature (77 K). Portions of nitrogen are dosed into the sample cell and will be partly adsorbed on the surface, eventually getting into equilibrium with the gas phase. In this way adsorption and desorption points are recorded at different pressures and the ad- and desorption isotherm can be constructed, in accordance with ISO 9277:2010.⁴ Adsorbed nitrogen will first form a quasi-monolayer on the sample surface while further increase in pressure results in the formation of multilayers. In the region where monolayer and multilayers are formed, the specific surface area (S_{BET}) is determined according to the BET (Brunauer, Emmet and Teller) theory.⁵ This model is applicable to non-porous and meso- and macroporous materials and adsorption points in the relative pressure range between 0.05 and 0.25 are typically used.⁶ However, for microporous materials, such as zeolites and activated carbon, the relative pressure range < 0.1 is recommended.²

Equipment and methodology

Pre-treatment

Prior to the actual nitrogen adsorption and mercury intrusion investigations, the samples have been freeze-dried. The freeze-drying procedure is as follows: the samples were placed in a sample cell and the sample cell was placed in liquid nitrogen at ambient pressure for at least 5 minutes until the liquid nitrogen stopped boiling indicating that the cell and sample were adjusted to the liquid nitrogen temperature. Then a vacuum was applied till a stable vacuum was reached. When the stable vacuum was reached the sample cell was transferred to a circulating bath of -5°C for at least 48 hours and until a near vacuum was reached (<<0.01 mbar). The sample cell is then removed from the liquid bath and placed at ambient temperature for 24 hours to remove the last of the moisture present in the sample, the latter was confirmed by a stable and final vacuum reached. The dry samples were then analysed for nitrogen adsorption and mercury porosimetry.

Mercury intrusion porosimetry

The intrusion and extrusion curves were recorded on a Micromeritics Autopore 9505 analyzer from a pressure range of 0.002 – 220 MPa, all in accordance with ISO 15901-1:2016.¹ The mass loss obtained upon pre-treatment has been recorded and the dry sample mass has been used in the various calculations.

Nitrogen adsorption

The adsorption analysis with N₂ as adsorptive was recorded at 77 K on a Micromeritics Tristar 3000. A relative pressure range from $p/p_0 = 0.01$ up to $p/p_0 = 0.30$ has been applied. The dry sample mass obtained after the freeze-drying pre-treatment has been used in the various calculations according to ISO 9277:2010.⁴

Results & Discussion

Mercury intrusion porosimetry

For the mercury intrusion porosimetry a single chunk of clay with dimensions of approx. 15 x 15 x 11 mm is used. The mercury intrusion-extrusion curves of the twelve clay samples are depicted in Figures 1 and 2. Since the samples consist of a single chunk, re-organization of (loose) powder particles followed by filling of *inter*-particle porosity is not applicable. The intrusion observed should therefore be fully attributed to the filling of *intra*-particle voids.

All samples display a single intrusion step over a wide pressure range, from a pressure of ~ 0.02 MPa – up to the maximum pressure of 220 MPa, indicating that a wide pore size range is present in the samples. At a pressure of 220 MPa the intrusion still increases and a plateau is not reached. The observation that a plateau is not reached at the maximum pressure is an indication that porosity < 6 nm, the lower limit of the mercury intrusion technique, is present in the samples. The presence of smaller pores can be determined via e.g. nitrogen adsorption. It can furthermore be seen in the Figures that the total intruded volume of sample ***B203 lab 21*** is the highest and that all other samples have rather similar intruded volumes. Quantitative information on the total pore volume, the thereof derived porosity and related parameters of the samples is summarized in Table 1.

Table 1. Textural properties of the twelve clay samples measured by mercury intrusion porosimetry.

Sample	V_{total} cm³ g⁻¹	Porosity %	ρ_{apparent} g cm⁻³	Total Pore Area m² g⁻¹
<i>B003 lab 3</i>	0.21	35	2.55	6.9
<i>B003 lab 5</i>	0.25	39	2.54	7.8
<i>B003 lab 11</i>	0.24	38	2.54	5.3
<i>B203 lab 15</i>	0.23	37	2.57	3.2
<i>B203 lab 17</i>	0.27	41	2.56	6.6
<i>B203 lab 21</i>	0.54	56	2.40	8.6
<i>Remoulded CI4.11</i>	0.20	34	2.54	5.1
<i>B003/B203 mix CI4_3</i>	0.23	36	2.49	5.0
<i>Meng 203/003 CI4_5</i>	0.21	35	2.56	5.3
<i>B003/B203 CI4_8</i>	0.18	32	2.54	4.9
<i>B003/B203 CI4_1</i>	0.22	36	2.54	5.2
<i>B003/B203 CI4_9</i>	0.26	40	2.54	4.8

The total intruded volume of the twelve clay samples ranges from $0.18 - 0.54 \text{ cm}^3 \text{ g}^{-1}$ and the total intruded volume of sample **B203 lab 21** is the indeed the highest at $0.54 \text{ cm}^3 \text{ g}^{-1}$, while the intruded volume of sample **B003/B203 mix CI4_8** is the lowest around $0.18 \text{ cm}^3 \text{ g}^{-1}$. Since most of the intruded volumes vary only slightly, the porosities of eleven samples are also quite similar compared to each other and range from just 32 – 41%, while sample **B203 lab 21** has a porosity of 56%.

Interestingly, the apparent density of the samples does not variate severely, as the apparent density of the samples ranges from $2.40 - 2.57 \text{ g cm}^{-3}$. This results in a maximum relative difference of approx. 5%, which is acceptable for the mercury intrusion technique, when it is considered that the samples consist of the same material.

The pore size distributions derived from the intrusion curves are displayed in Figures 3 and 4 and it can be observed that the twelve distributions indeed show somewhat similar pore size ranges and sample **B203 lab 21** has a much larger contribution of pores compared to the other samples. All samples show a predominant contribution of pores between approx. $0.02 \mu\text{m}$ to $10 \mu\text{m}$. All samples also still show a small contribution at $0.006 \mu\text{m}$ indicating that smaller pores are be present in the sample.

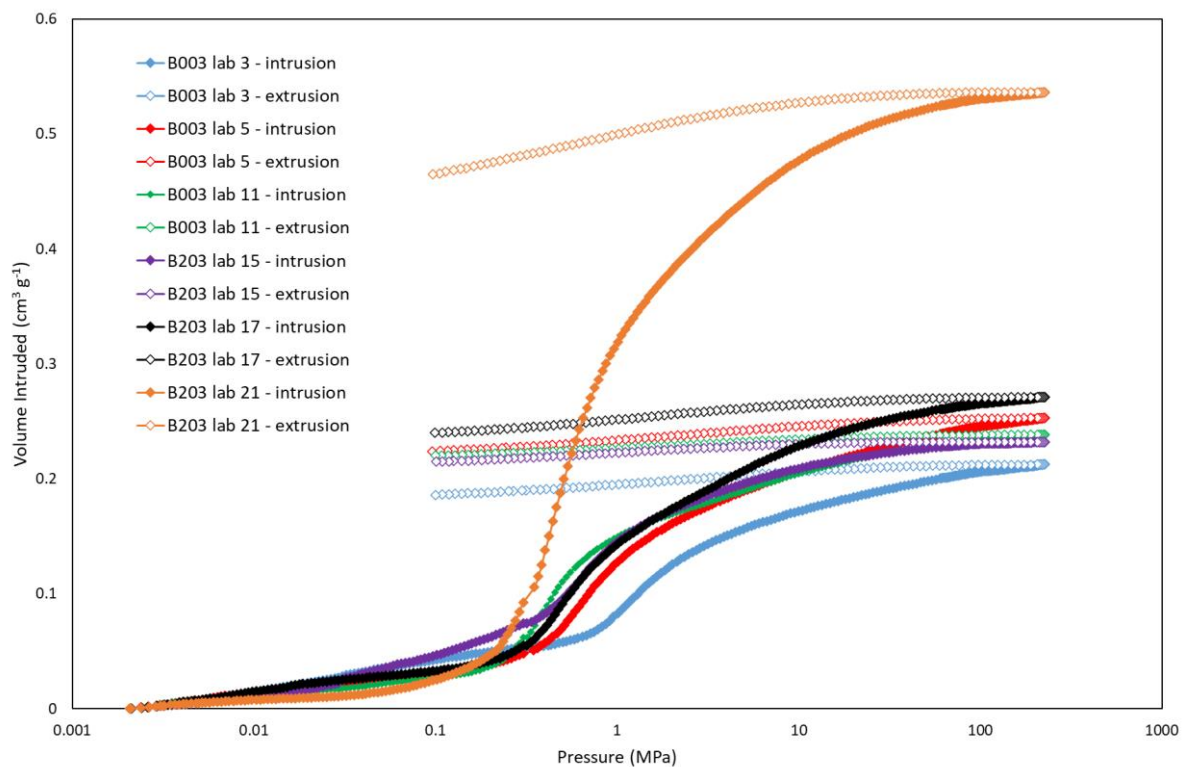


Figure 1. Mercury intrusion and extrusion curves of six of the twelve clay samples. Closed symbols denote intrusion, open symbols denote extrusion.

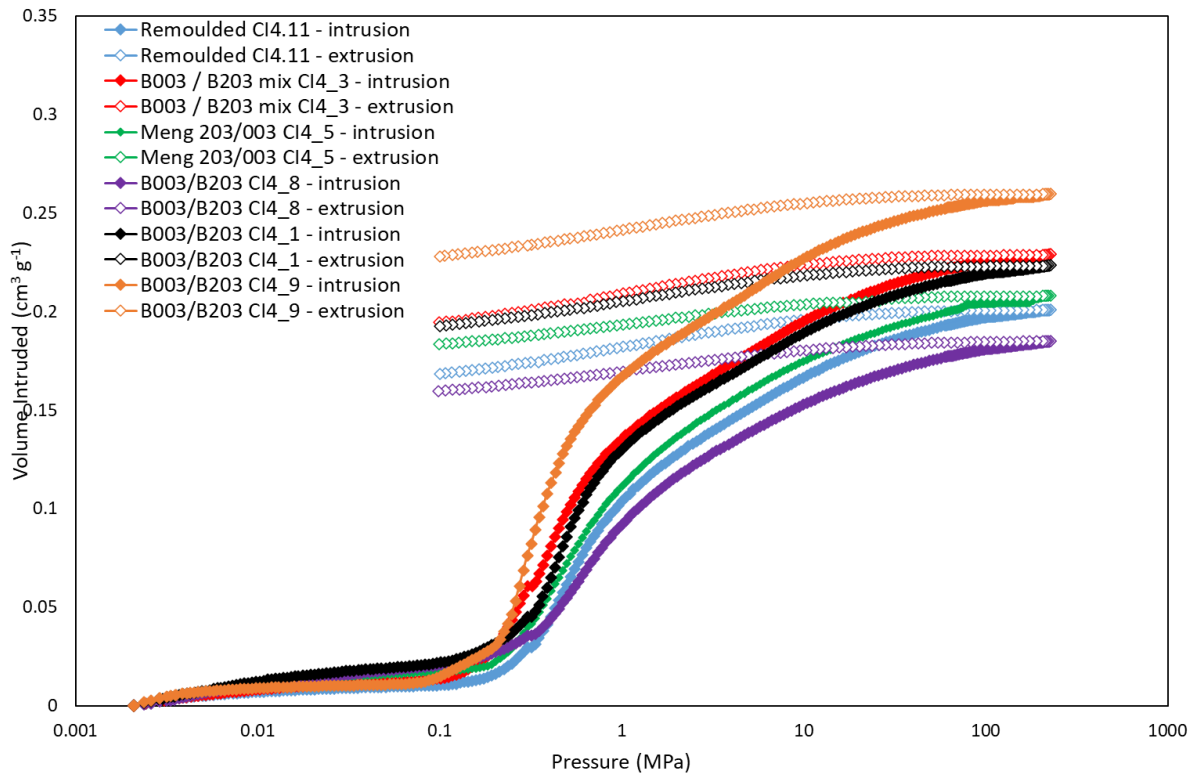


Figure 2. Mercury intrusion and extrusion curves of six of the twelve clay samples. Closed symbols denote intrusion, open symbols denote extrusion.

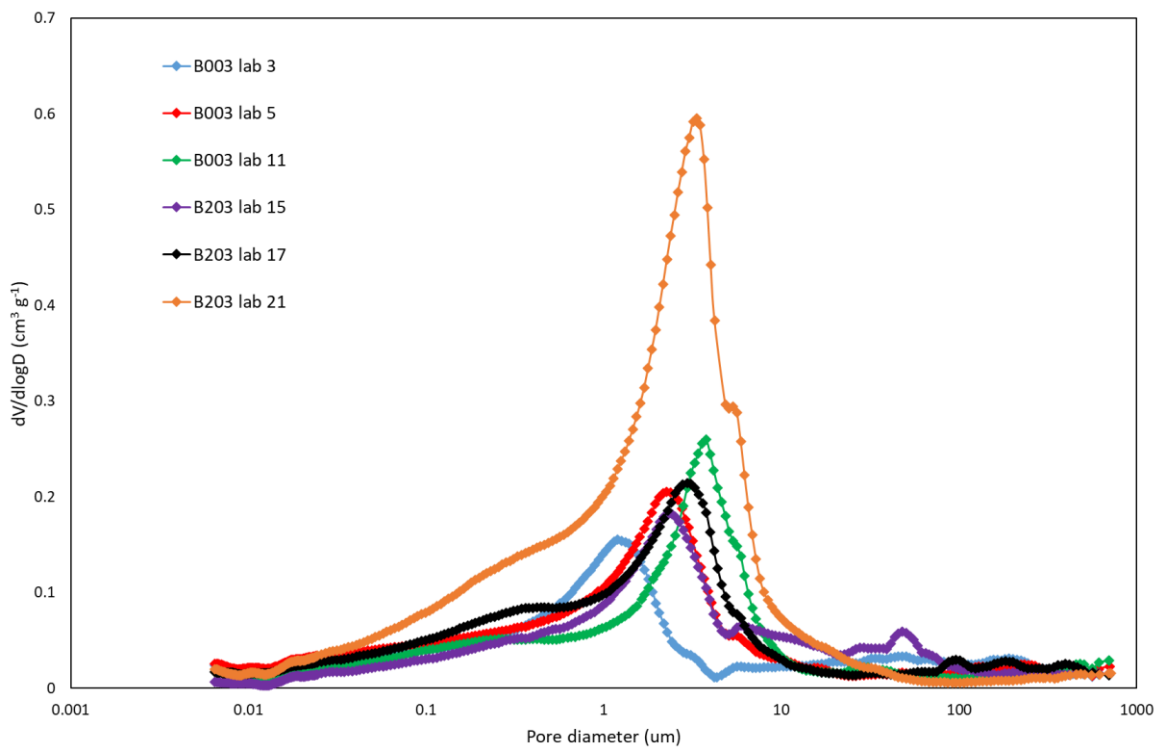


Figure 3. Differential pore size distributions of six of the twelve clay samples derived from the intrusion curves in Figure 1.

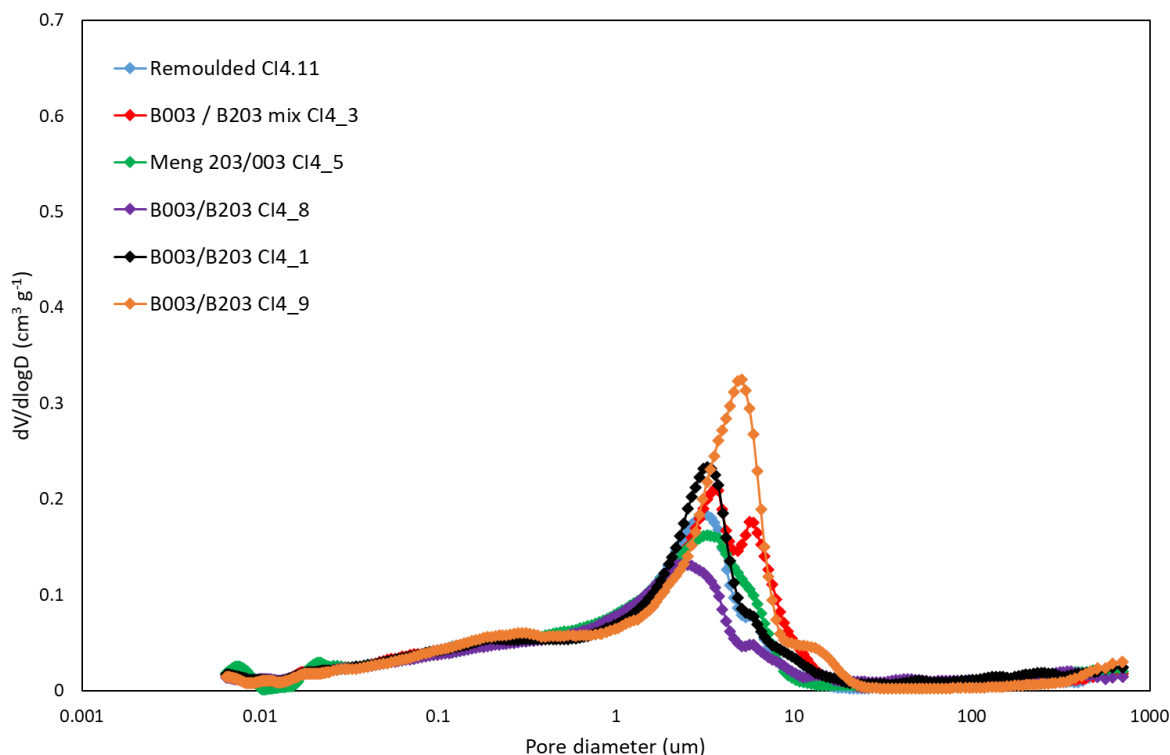


Figure 4. Differential pore size distributions of six of the twelve clay samples derived from the intrusion curves in Figure 2.

Nitrogen adsorption

From the clay small chunks were extracted and as much sample as possible was fitted in the sample cell in order to obtain the most representative sample, resulting in approx. 1.9 – 5.8 grams of sample being used during the investigations. The textural properties derived from the adsorption isotherms are listed in Table 2.

Table 2. Textural properties of the twelve clay samples derived from the N₂ adsorption isotherms.

Sample	Mass loss m/m%	S _{BET} m ² g ⁻¹	TAE ⁴ m ² g ⁻¹
<i>B003 lab 3</i>	15.2 / 15.8	23.6	± 0.8
<i>B003 lab 5</i>	19.4 / 19.8	20.8	± 0.7
<i>B003 lab 11</i>	18.5 / 18.9	17.1	± 0.6
<i>B203 lab 15</i>	14.3 / 14.6	7.13	± 0.2
<i>B203 lab 17</i>	19.4 / 20.0	22.1	± 0.8
<i>B203 lab 21</i>	36.4*	19.9	± 0.7
<i>Remoulded CI4.11</i>	17.3 / 17.5	13.1	± 0.4
<i>B003/B203 mix CI4_3</i>	19.2 / 19.7	13.0	± 0.4
<i>Meng 203/003 CI4_5</i>	16.5 / 17.0	14.5	± 0.5
<i>B003/B203 CI4-8</i>	14.4 / 14.7	10.8	± 0.4
<i>B003/B203 CI4_9</i>	20.7 / 21.1	11.3	± 0.4
<i>B003/B203 CI4_1</i>	17.4 / 17.9	10.8	± 0.4

*Total mass loss.

Table 2 displays two mass losses per sample, the lower mass loss is the mass loss obtained after pre-treatment at -5°C . The second and slightly higher mass loss is the mass loss after the second pre-treatment step which was at 25°C until a final and stable vacuum was reached. The largest difference between the two mass loss values is $< 4\%$ relatively, indicating that most of the moisture was removed by freeze drying at -5°C . Overall the mass losses for the twelve clay samples are quite substantial as $14.6 - 36.4 \text{ m/m}\%$ is removed upon pre-treatment.

The BET specific surface areas of the twelve clay samples are quite different from each other, ranging from 7.1 to $23.6 \text{ m}^2 \text{ g}^{-1}$. The specific surface areas obtained via the N_2 adsorption investigations coupled to the sample masses used during the investigations are adequate to obtain accurate results. The good reversibility of the desorption isotherms compared to the adsorption isotherms are again an indication of the good accuracy of the measurements. The estimated relative Total Analytical Error⁴ (TAE) determined over a reference material for this instrument is 3.4% . Overall, it can be concluded that sample **B003 lab 3** has the highest surface area and sample **B203 lab 15** has the lowest specific surface area.

The total pore areas derived from mercury porosimetry that are given in Table 1 are all lower than the specific surface areas obtained with nitrogen adsorption, albeit not much lower. This indicates that there are pores $< 6 \text{ nm}$ present in the samples, which is in line with the observation that the intrusion curves in Figures 1 and 2 did not reach a plateau. In any case, when it comes to surface area assessment, the BET specific surface area results should be considered most accurate.

The reported results relate to the received materials measured with the described gas adsorption and mercury intrusion instruments and measurement methods. The results may be valid for the bulk provided that the samples have been obtained representatively. Nevertheless, there is always a chance of batch to batch variations and material inhomogeneity.

We trust to have given you a complete overview of the specific surface area and porosity of your products and we hope that the results in line with your expectations. Should there be any questions, please do not hesitate to contact us.

Sincerely yours
Delft Solids Solutions B.V.



Chris Esseboom



Patrick Verolme - Reviewer

References

- [1] ISO 15901-1:2016 – Evaluation of pore size distribution and porosity of solid materials by mercury porosimetry and gas adsorption – Part 1: Mercury porosimetry.
- [2] J.C. Groen, J. Pérez-Ramírez and L.A.A. Peffer, in: F. Rodriguez-Reinoso, B. McEnaney, J. Rouguerol, K.K. Unger (Eds.) “Incorporation of appropriate contact angles in textural characterization by mercury porosimetry”, *Characterization of Porous Solids VI, Studies in Surface Science and Catalysis*, Vol. 144, Elsevier, Amsterdam, 2002, pp. 91-98.
- [3] ASTM D 4404-18 – Standard Test Method for Determination of Pore Volume and Pore Volume Distribution of Soil and Rock by Mercury Intrusion Porosimetry.
- [4] ISO 9277:10 - Determination of the specific surface area of solids by gas adsorption – BET method.
- [5] J.C. Groen, L.A.A. Peffer, J. Pérez-Ramírez, *Microporous Mesoporous Mater.* **60** (2003) 1.
- [6] S.J. Gregg, K.S.W. Sing, “*Adsorption, Surface Area and Porosity*”, 2nd ed., Academic Press, London, 1982.
- [7] Westgard JO, Carey RN, Wold S. *Criteria for judging precision and accuracy in method development and evaluation.* Clin Chem 1974;20:825–33.