**D.I. Mendeleyev Institute for Metrology, ROSSTANDART,
RUSSIA (VNIIM)**

Report of the key comparison CCQM-K172

Measurement of Specific Adsorption A [mol/kg] of Ar on zeolite at liquid argon temperature (to enable a traceable determination of the Specific Surface Area by following ISO 9277)

FINAL REPORT

Pilot laboratory
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Laboratory for metrological assurance of nanoindustrie, analysis of spectral methods and reference materials (251)

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1 ABSTRACT

The CCQM-K172 key comparison on the determination of specific adsorption of Ar on microporous zeolite at liquid argon temperature has been organized by the Surface Analysis Working Group at CCQM to enable a traceable determination of the Specific Surface Area (BET) of microporous substances as a derived secondary measurand following procedures and parameters agreed and standardized in ISO 9277. Because of its importance in the chemical and catalysis industry a study of the comparability of the measurement of Specific Surface Area was strongly requested by stakeholders of the participating NMIs/DIs.

Ural Scientific Research Institute for Metrology - Affiliated branch of the D.I. Mendeleyev Institute for Metrology (VNIIM) acted as the coordinating laboratory. Five NMIs/DIs participated in this key comparison. All participants used the gas adsorption method. In general, very good agreement of the results has been observed.

2 INTRODUCTION

Specific argon adsorption and, as a secondary, derived measurand, the BET specific surface area[1] of microporous solids are highly relevant parameters because they are often used for the specification of microporous particulate materials and substances (ceramic, cement, sorbents, catalysts, etc.) used in advanced technologies. Another two important value for zeolite are specific pore volume and most frequency pore diameter.

The aim of the key comparison CCQM-K172 is to support National Measurement Institutes (NMIs) and Designated Institutes (DIs) demonstrating the validity of the procedure they employ for the measurement of specific argon adsorption at liquid argon temperature to enable a determination of the BET specific surface area of microporous materials. The space of measurement covered by the specific gas adsorption measurement comprises microporous (D<~2 nm) materials which are characterized by high values of BET specific surface area (300-1500 m^2/g). In an earlier key comparison (K-136) the specific gas adsorption on mesoporous (~2 nm<D<~50 nm) alumina, key comparison (K-153) the specific gas adsorption on non-porous materials (<1 m^2/g) were addressed already. This new key comparison was organized for microporous materials (D<~2 nm) to demonstrate CMC's for gas adsorption method.

The validity of the used procedure is of high importance because it is used to underpin the capabilities and measurement services of BET specific surface area measurements delivered by participating NMIs and DIs to their stakeholders.

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[1] BET specific surface area following ISO 9277, A_{BET}

3 LIST OF PARTICIPANTS

5 NMIs/DIs received the test sample and 5 of them returned results (BAM, NIM, INMRTERO, TUBITAK-UME, VNIIM). Table 1 contains the full names of all participating NMIs/DIs and contact persons.

Table 1 List of participants

Institute	**Abbrev.**	**Country**	**Contact persons**
Federal Institute for Materials Research and Testing	**BAM**	Germany	Carsten Prinz
National Institute of Metrology, P.R. China	**NIM**	China	Hai Wang
National Institute of Metrology, Quality and Technology	**INMETRO**	Brazil	Sandra M. Landi, Bianca P.S. Santos, Jailton C. Damasceno, Oleksii Kuznetsov
TUBITAK – National Metrology Institute	**TUBITAK-UME**	Turkey	Mine BİLSEL, Ali Enis SADAK
D.I. Mendeleyev Institute for Metrology (UNIIM - Affiliated branch of the D.I. Mendeleyev Institute for Metrology	**VNIIM**	Russia	Egor Sobina

4 SAMPLE

The source of the shared and distributed sample is a 1000 g batch of commercial zeolite which was homogenized using a «drunk barrel» type mixer C 2.0 Turbular. After homogenization of the sample its inhomogeneity and instability were studied. Results of the homogeneity test for the shared sample are presented in table 2.

Table 2 Results of homogeneity testing (2 replicates for each bottle)

Bottle №	**Specific surface area, m^2/g**	
1	792.5	790.2
2	796.5	792.0
3	784.0	785.9
4	795.5	790.2
5	792.1	797.6
6	779.3	797.2
7	779.3	796.6
8	805.8	778.2

In order to estimate the inhomogeneity contribution u_h, a one-way Analysis of Variances (ANOVA) was carried out using experimental data shown in table 2. The standard uncertainty due to (in)homogeneity, u_h, for the zeolite powder were calculated according to ISO Guide 35 using Equations (1) and (2) (see Table 3 and 4).

$$u_h = \sqrt{\frac{MS_{among} - MS_{within}}{n}} \tag{1}$$

$$u_h = \sqrt{\frac{MS_{within}}{n}} \sqrt[4]{\frac{2}{N(\mathrm{n}-1)}}, \tag{2}$$

where *N*– is the number of bottles, *n* is the number of replicates.

Table 3 ANOVA analysis

bottle	***number***	***sum***	***average***	***Dispersion***
1	2	1582.70	791.35	2.54
2	2	1588.53	794.27	9.94
3	2	1569.84	784.92	1.75
4	2	1585.65	792.83	14.03
5	2	1589.64	794.82	15.19
6	2	1576.50	788.25	160.38
7	2	1575.92	787.96	148.91
8	2	1583.94	791.97	380.87

Table 4 ANOVA analysis

source	***SS***	***df***	***MS***	***F***
Among	166.193	7	23.7419	0.258
Within	733.620	8	91.702	
Sum	899.814	15		
standard uncertainties due to inhomogeneity, u_h		-		Equation (1)
standard uncertainties due to inhomogeneity, $\boldsymbol{u_h}$		**4.79**	**m^2/g**	Equation (2)

Results of the stability test for the shared sample is presented in Table 5 and Figure 1.

Table 5 Results of measurements of specific surface area

№	Date	Specific surface area, m^2/g
1	14.12.2018	800.10
2	15.12.2019	791.00
3	14.12.2020	792.48
4	15.12.2020	796.50
5	16.12.2020	783.99
6	17.12.2020	795.47
7	16.12.2020	792.06
8	16.12.2020	779.29
9	13.01.2021	779.33
10	14.01.2021	805.77
11	14.01.2021	790.23
12	15.01.2021	792.04
13	20.01.2021	785.85
14	20.01.2021	790.18
15	03.02.2021	797.58
16	03.02.2021	797.20
17	03.02.2021	796.59
18	03.02.2021	778.17
mean of stability test, Xs		790.796
standard deviation of the data, S		7.745
Xs+2S		806.286
Xs-2S		775.305
slope, *b*		-0.010
standard uncertainty of slope, u_{slope}		0.009
standard uncertainty due to long-term (in)stability, u_s		1.1
time measurements in key comparison, $t_{\max}$, days		120

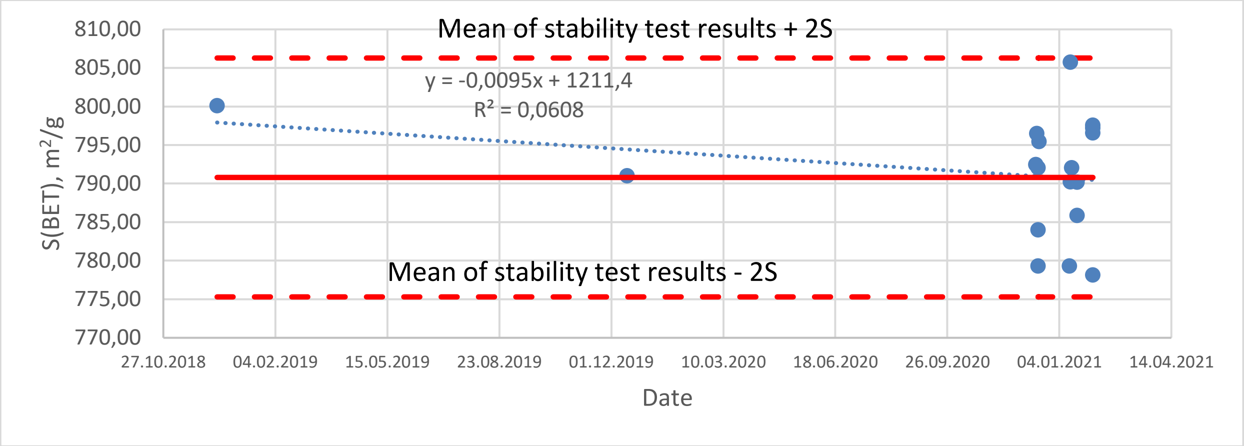

Fig.1 - Stability test for the microporous zeolite.

(blue dots: experimental data, bold line: mean of stability test Xs, dotted line:(Xs±2S)

Data in Table 5 was accounted using linear regression method. The standard uncertainty due to instability was calculated using formula:

$$u_{slope} = bt_{\max}, \qquad (3)$$

where b is the slope, u_{slope} is the standard uncertainty of the slope and $t_{\max}$ is the time of measurement, given by date and expressed as days.

The standard uncertainty due to long-term (in)stability for specific surface area is estimated to be 1.1 m^2/g. The standard uncertainty due to inhomogeneity for specific surface area is estimated to be 4.8 m^2/g. The relative standard uncertainty due to long-term (in)stability for the derived BET specific surface area is estimated to be 0.14 %. The relative standard uncertainty due to inhomogeneity for the derived BET specific surface area is estimated to be 0.6 %. Target uncertainty for BET specific surface area is (1.5-3.0) %. According to this result, the material is enough homogeneous and stable for the key comparison.

After the investigation of homogeneity and stability, the homogenized material was evenly distributed among glass bottles closed by metallic caps. Each bottle contains about 4 g of the material. Five bottles were randomly selected from the set of 12 bottles and sent off to participants.

The samples were shipped to the participant by DHL on 07th October. All samples arrived at their destination without damage within twenty days. The dispatch dates and receipt dates are given in Table 6.

Table 6 Sample sent dates and report dates

Institute	Sample No.	Sample dispatch date	Date report sent
BAM	#03	02 November 2020	29 March 2021
TUBITAK-UME	#02	10 November 2020	17 March 2021
NIM	#04	28 October 2020	26 February 2021
INMETRO	#01	07 December 2020	27 July 2021
VNIIM	#05	07 October 2020	05 March 2021

5 INSTRUCTIONS TO PARTICIPANTS

Each participant should use the gas adsorption method for the measurement of the specific adsorption argon, specific surface area, specific pore volume and pore diameter of zeolite as defined in ISO 15901-3 [1] and ISO 9277 [2].

Some details about measurement procedure of gas adsorption method are shown below

Please perform at least 5 replicate measurements on separate aliquots of zeolite. The recommend minimum sample amount is about 0.3 gram for each run.

Sample pretreatment

Heat the sample of zeolite to 90 °C, then the sample is vacuumed at a rate of 0.67 kPa/sec to a residual pressure of 10 Pa and kept at this pressure for 30 minutes. Then heat slowly the sample at a rate of not more than 10 °C/min to 350 °C. Maintain the temperature at 350 °C for at least 6 hour.

Measurement of the complete Isotherm (adsorption branch) at 87 K and specific adsorption of argon at P/Po=1,0·10^{-5}; P/Po=1,0·10^{-4}; P/Po=1,0·10^{-3}; P/Po=1,0·10^{-2}; P/Po=1,0·10^{-1}.

First isotherm data point should be taken at P/Po=1,0·10^{-5}, last adsorption isotherm data point should be taken at P/Po=1,0·10^{-1}. Intermediate points (from 8 to 10), are selected uniformly within each order of magnitude of relative pressure. The free volumes of the tube with the sample, "warm" and "cold", should be measured after the measurements of specific adsorption of argon, and then registered in the files in which the measurements are recorded for the adjustment.

Specific surface area S, m^2/g

For the determination of S, n_m must be measured at least for five pressure points in the P/Po range from 0.001 to 0.03. Specific surface area must be calculated according to equation

$$S = n_m N_a a_m \quad (1)$$

where N_a is Avogadro constant, mol^{-1}; a_m is area occupied by one argon molecule 0.142·10^{-18} m^2; n_m is specific monolayer capacity of adsorbate, mol·g^{-1}.

Specific monolayer capacity of adsorbate must be calculated according to BET equation (ISO 9277):

$$\frac{P/P_o}{A\left(1-P/P_o\right)} = \frac{1}{n_m C} + \frac{C-1}{n_m C}\frac{P}{P_o} \quad (2)$$

where n_m is specific adsorption of argon, mol·g^{-1}; C is BET constant; P is pressure of the adsorptive in equilibrium with the adsorbate, Pa.

Specific pore volume (informative characteristic)

Computed by the equation Dubinin-Radushkevich in the range of P/Po from 0.005 to 0.10:

$$\lg V = \lg V_{micro} - D\left(\lg\frac{p_o}{p}\right)^2, \quad (2)$$

where V - specific volume adsorbed, cm^3/g;

V_{micro} - the sorption capacity of argon under normal conditions under filled micropores, calculated by regression analysis of data using equation (2), cm^3/g.

The density of argon liquid is equal to 1.40 g/cm^3 (87.29 K). The density of argon under normal conditions is equal to1,7840 mg/cm^3. The calculations used the ratio $\frac{\rho_g}{\rho_L} = 1,28\cdot 10^{-3}$. Calculate the specific volume of pores according to the formula:

$$V = \frac{V_{micro}\rho_g(STP)}{\rho_L} \quad (3)$$

where V_{micro} - the sorption capacity of argon under normal conditions under filled micropores, calculated by regression analysis of data using equation (2), cm^3/g.

Most frequent pore diameter D, nm (informative characteristic)

It is calculated as a mode of pore distribution over diameters with a modal interval equal to 0.01 nm (as a rule, it is calculated automatically using the software of gas adsorption analyzers). The pore diameter is calculated by the Horvath-Kawazoe and Saito-Foley method:

$$\ln\left(\frac{P}{P_o}\right)=\frac{3}{4}\frac{\pi N_A}{RT}\frac{\left(N_s K_{As}+N_a K_{Aa}\right)}{d_o^4}f_{SF}\left(\alpha,\beta,l,d_o\right) \quad (4)$$

The following parameters of the adsorbent and adsorbate given in tables 7, 8 are used to perform calculations by the Horvath -Kawazoe and Saito-Foley method.

Table 7 — Parameters for zeolite adsorbent

Physical quantity	Unit	Symbol	Zeolite
Polarizability	10^{-24} cm^3	$\alpha_{(s*)}$	2,50
Magnetic susceptibility	10^{-29} cm^3	χ_s	1,30
Surface density (atoms per square metre of pore wall)	10^{19} m^{-2}	N_s	1,31
Diameter	nm	Ds	0,28

Table 8 — Parameters of adsorbate - argon

Physical quantity	Unit	Symbol	Argon
Polarizability	10^{-24} cm^3	$\alpha_{(s*)}$	1,63
Magnetic susceptibility	10^{-29} cm^3	χ_s	3,25
Surface density (atoms per square metre of pore wall)	10^{18} m^{-2}	N_a	8,85
Diameter	nm	ds	0,34

Participants were requested to provide the results for argon specific adsorption, specific surface area, specific pore volume and most frequent pore diameter for microporous zeolite test sample. The results must have been reported with a full uncertainty statement (including a combined standard uncertainty and an expanded uncertainty with a coverage factor applied). In addition, the report had to include technical details on the measurement procedure, traceability links (as calibrations) and uncertainty contributions. Each report had to include tabular reports and graphs for the isotherm (dependence of specific adsorption from relative pressure) and for the BET calculation.

6 METHODS OF MEASUREMENT

Details on measurements as derived from the reports of participants are given in Table 9 and Table 10.

Table 9 Details of sample pretreatment

Institute	Approx. sample mass, g	Sample pretreatment	Corrected for buoyancy
BAM	~ 0.3	Heat the sample zeolite to 90 °C then the sample is vacuumed at a rate of 0.67 kPa/sec to a residual pressure of 10 Pa and vacuumed for 30 minutes. Then slom heating at a rate of not more than 10 °C/min to 350 °C. The hold temperature at 350 °C for at 12 hours.	no
TUBITAK-UME	~ 0.2-0.3	The samples were heated in a vacuum of (0.67) kPa/sec with rate 10°C/min to 90°C and kept at 90°C for 30 minutes. Then slow heating with rate10°C/min to 350°C and hold the temperature at 350 °C for 6 hours. Afterwards, the samples were cooled slowly back to ambient temperature	no
NIM	~ 0.3	. The sample amount was about 0.3g for each measurement. Before each measurement, the sample was heated for degassing in vacuum at 90°C (the ramp rate of 5°C /min) for 1hourand then 350°C (the ramp rate of 5°C /min) for more than 6hours.Afterwards, the sample cooledslowly to ambient temperature. The mass loss of specimens was about 10% after degassing in vacuum.	no
INMETRO	~ 0.03-0.06	The sample was heated in a vacuum to 90 °C and kept at 90 °C for 0.5 hours.. Then, it was slowly heated at a rate of not more than 10 °C/min to 350 °C and hold at this temperature (350 °C) overnight. Afterwards, the sample was cooled slowly back to the ambient temperature.	no
VNIIM	~ 0.2-0.3	Heat the sample zeolite to 90 °C then the sample is vacuumed at a rate of 0.67 kPa/sec to a residual pressure of 10 Pa and vacuumed for 30 minutes. Then slom heating at a rate of not more than 10 °C/min to 350 °C. The hold temperature at 350 °C for 6 hours.	yes

Table 10 Details of gas adsorption procedures used

Institute	Adsorbate	Type of instrument and producer	Traceability
BAM	Ar	ASAP 2010 Micromeritics, USA	CRM BCR-704
TUBITAK-UME	Ar	Micromeritics 3FlexMicromeritics, USA	Calibration of instrument: XP205 Mettler Toledo from 0.01 mg to 220 g range. Uncertainty was determined with U (L) = [4.875*0.000001 x L] equation. High precision pressure sensor Baratron 690A with the measurement range from 0 to 133 300 Pa, relative expanded uncertainty (k=2) 0.05 %, manufactured by "MKS Instruments", Germany. High precision resistance thermometer measurement range from 10 to 60 ° C, expanded uncertainty (k=2) 0.002 ºC..
NIM	Ar	Autosorb-1-MP Quantachrome Instruments, USA	The analytical balance (readability up to 0.1mg) to weigh samples were calibrated using E_2 grade standard weights. The temperature and pressure transducers were also calibrated and their indications can be traceable to corresponding national measurement standards. The volume of adsorbed gas can be traceable to national measurement standard of solid density. Additionally, using NIM CRMs for inert gas physical adsorption, the measurement instrument was checked and the analytical method was also validated.
INMETRO	Ar	AUTOSORB-1, Quantachrome Instruments	All the mass measurements were performed in an AB 265-S/FACT (Mettler Toledo) balance with 0.01 mg resolution and standard uncertainty of 0.02 mg. Traceability to the International System of Units is assured by the certificate of calibration (DIMCI-0408/2021). Prior to the experiments, the equipment successfully passed a verification procedure. This procedure consisted on determining the BET specific area for the certified reference material BCR®-173 (titanium dioxide), provided by the Institute of Reference Materials and Measurement (IMRM).
VNIIM	Ar	ASAP 2020MP Micromeritics, USA	- high precision resistance thermometer PTSV-1-1 with a measurement range of 10 to 60 ° C, expanded uncertainty (k=2) 0.002 ºC, manufactured by the Federal state unitary enterprise "VNIIFTRI", Moscow, Russia, and the twin channel precision temperature measuring device MIT 2.05 manufactured by the limited liability company "IzTekh", Zelenograd, Russia; - mass comparator CCE 2004 with a measurement range of 0.0001 to 2500g, standard deviation 0.0002 g, manufactured by "Sartorius Weighing Technology GmbH", Germany; - 2 kg scale weight (accuracy class E1), manufactured by CJSC "Sartogosm"; - high precision pressure sensor Baratron 690A with a measurement range of 0 to 133 300 Pa, relative expanded uncertainty (k=2) 0.05 %, manufactured by "MKS Instruments", Germany

7 RESULTS AND DISCUSSION

7.1 Uncertainty

Participants used different approaches for calculation of the uncertainty by the gas adsorption method and have taken into account different sources of uncertainty in the budget of uncertainty. Details on sources of uncertainty addressed are given in Table 11.

Table 11 Details about sources of uncertainty

Institute	Tabular reports for the isotherm	Accounted sources of uncertainty
BAM	+	**Type A** - repeatability measurement of the sample (type A), **Type B** - uncertainty of certified value of the CRM BCR-704.
TUBITAK-UME	+	**Type A** - repeatability measurement of the sample, - uncertainty of fitting. **Type B** - uncertainties of measurement mass of the sample, temperature, pressure, volumes.
NIM	-	**Type A** - repeatability measurement of the sample, **Type B** - uncertainties of measurement mass, temperature, pressure and volumes, - uncertainty of fitting.
INMETRO	+	**Type A** - repeatability measurement of the sample. - uncertainty of fitting. **Type B** - uncertainties of measurement mass, temperature, pressure and volumes.
VNIIM	+	**Type A** - repeatability measurement of the sample, - uncertainty fitting. **Type B** - mass of sample, temperature, pressure, volumes. - uncertainty for specific adsorption was calculated by Monte-Carlo method.

7.2 Formulas

A consistency check was performed according to the CCQM guidance note [4] using the algorithm shown below

$$\bar{x}_u = \sum_{i=1}^{m} \frac{x_i / u(x_i)^2}{\sum_{i=1}^{m} 1/u(x_i)^2}, \tag{5}$$

$$\chi^2_{obs} = \sum_{i=1}^{m} \left(\frac{x_i - \bar{x}_u}{u(x_i)} \right)^2, \tag{6}$$

where x_i is the result of the value of *i* NMI, $u(x_\mathrm{i})$ is the standard uncertainty of x_i, m is number of participants of the key comparison.

After calculations using formulas (5), (6) χ^2_{obs} with m-1 and with $\chi^2_{0.05,\mathrm{m}-1}$ the 95 percentile of χ^2 with m-1 of freedom ($\chi^2_{0.05,\mathrm{m}-1}$ - has been taken from Microsoft Excel) were compared.

If $\chi^2_{obs} < m-1$ it is normally safe to proceed with the assumption that the results are mutually consistent and that the uncertainties account fully for the observed dispersion of values.

If $m-1 < \chi^2_{obs} < \chi^2_{0.05,\mathrm{m}-1}$ the data does not provide strong evidence that the reported uncertainties are inappropriate, but it remains a risk that additional factors are contributing to the dispersion. Referring to the prior working group decision on presumptive consistency we proceed accordingly.

If $\chi^2_{obs} > \chi^2_{0.05,\mathrm{m}-1}$ the data should be considered mutually inconsistent.

If the data should be considered mutually inconsistent the detecting outliers had done before calculation of reference value.

Detecting outliers

The formulas for the calculation of the decision criteria (equation 7) for the detection of outliers are shown below [5]

$$K = \frac{x_i - med(x)}{med\left|x_i - med(x)\right|} > |\pm 3|, \tag{7}$$

Calculation of reference value

Candidates of the key comparison reference value (KCRV) were estimated following the CCQM guidance note [4] using different approaches. Results and uncertainties were taken from the participants' reports as were stated. Formulas for calculation are shown below.

Arithmetic mean

$$\bar{x} = \frac{1}{m} \sum_{i=1}^{m} x_i, \tag{8}$$

$$u^2(\bar{x}) = \frac{\sum_{i=1}^{m} (x_i - \bar{x})^2}{m(m-1)}, \tag{9}$$

where x_i - is the result of the value of *i-th* NMI, $u(\bar{x})$ - is the standard uncertainty of $\bar{x}$.

Uncertainty-weighted mean

$$\bar{x}_u = \sum_{i=1}^{m} w_i x_i \,, \tag{10}$$

$$w_i = \frac{1/u^2\left(x_i\right)}{\sum_{i=1}^{m} 1/u^2\left(x_i\right)} \,, \tag{11}$$

$$\frac{1}{u^2\left(\bar{x}_u\right)} = \sum_{i=1}^{m} 1/u^2\left(x_i\right), \tag{12}$$

$$u_{corr}^2\left(\bar{x}_u\right) = \frac{\chi_{obs}^2}{m-1} u^2\left(\bar{x}_u\right) = \frac{\sum_{i=1}^{m}\left(\frac{x_i - \bar{x}_u}{u\left(x_i\right)}\right)^2}{m-1} u^2\left(\bar{x}_u\right), \tag{13}$$

where $u\left(x_i\right)$ - is the standard uncertainty of x_i.

Median

$$med\left(x\right) = \begin{Bmatrix} \frac{1}{2}\left(x'_{m/2} + x'_{m/2+1}\right), & m \ even \\ x'_{(m+1)/2}, & m \ \ odd \end{Bmatrix}, \tag{14}$$

$$u^2\left(med\left(x\right)\right) = \frac{\pi}{2m}\hat{\sigma}^2 \,, \tag{15}$$

$$\hat{\sigma} = 1.483 med\left(\left|d_i\right|\right), \tag{16}$$

where $d_i = x_i - med\left(x\right)$.

7.3 KCRV for specific adsorption of Ar at P/Po=0.0001

The reported values of the specific adsorption of Ar at P/Po=0.0001 and the uncertainties of all results are summarized in Table 12. Estimations of KCRV have been obtained by different approaches (arithmetic mean, uncertainty weighted mean, median) and are presented in Table 12. The same results are displayed graphically in Figures 2 and 3.

The arithmetic mean was used for assessment of the KCRV because:

- $\chi^2_{obs} > \chi^2_{0.05,N-1}$, in this case the data is inconsistent,
- there are no extreme values according to criteria (7),
- the uncertainties do not vary significantly.

Table 12 – Reported values of specific adsorption of argon at P/Po=0.0001 and uncertainties

№	**NMI/DIS**	**Specific adsorption of Ar, mol/kg**	**Combined standard uncertainty, uc, mol/kg**	**Expanded uncertainty, U(k=2), mol/kg**	**di, mol/kg**	**U(di), mol/kg**	**Verdict**	**K**
1	TUBITAK-UME	1.320	0.045	0.090	-0.13	0.13	-	-1.8
2	INMETRO	1.390	0.047	0.120 (k=2.57)	-0.06	0.13	+	-0.9
3	VNIIM	1.460	0.020	0.040	0.01	0.10	+	0.0
4	BAM	1.540	0.020	0.040	0.09	0.10	+	1.0
5	NIM	1.560	0.060	0.120	0.11	0.15	+	1.3
Uncertainty weighted mean		**1.480**	**0.034**					
Median		1.460	0.066					
Mean		1.454	0.045	**KCRV (N=5)**				
Consistency test				**Conclusion**				
X^2_{obs}		$X^2_{tab, 0.05;N-1}$	N	$X^2_{obs} > X^2_{tab, 0.05;N-1}$				
28.13		9.49	5	inconsistent				

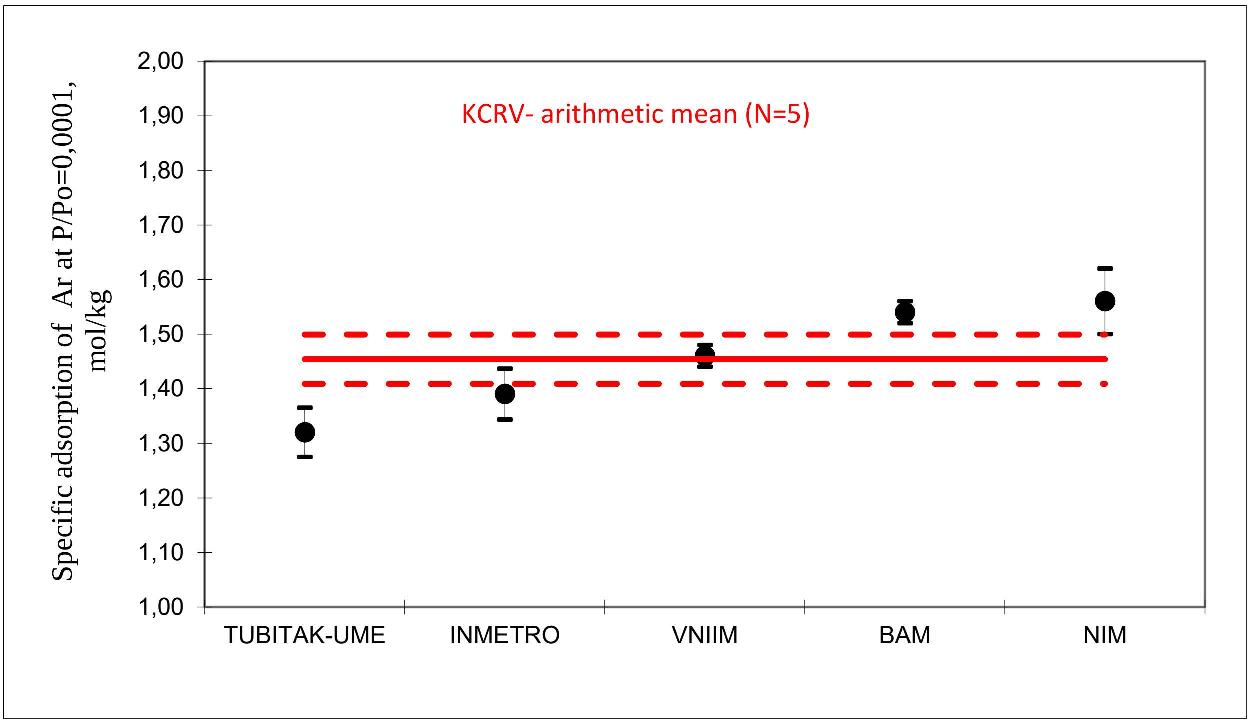

Figure 2 KCRV for specific adsorption of Ar on zeolite. Error bars show standard uncertainty. The dashed lines represent the values of KCRV+/- standard uncertainty.

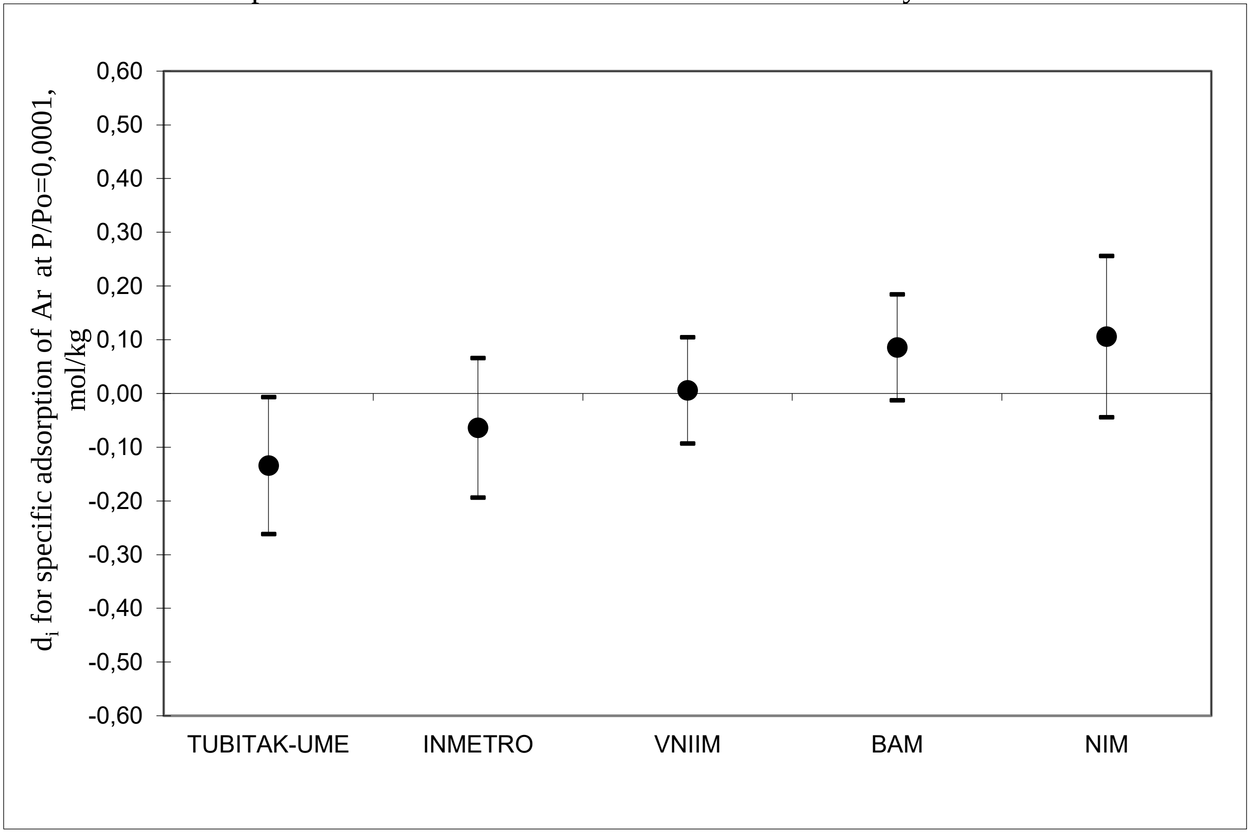

Figure 3 Degrees of equivalence d_i and expanded uncertainty $U(d_i)$ (k=2) for specific adsorption of Ar on zeolite

7.4 KCRV for specific adsorption of Ar at P/Po=0.001

The reported values of the specific adsorption of Ar at P/Po=0.001 and the uncertainties of all results are summarized in Table 13. Estimations of KCRV have been obtained by different approaches (arithmetic mean, uncertainty weighted mean, median) and are presented in Table 13. The same results are displayed graphically in Figures 4 and 5.

The arithmetic mean of outlier-rejected data was used for assessment of the KCRV because:

- $\chi^2_{obs} > \chi^2_{0.05,N-1}$, in this case the data is inconsistent,
- there is one extreme value according to criteria (7), so the results from INMETRO (K=-4.8) was excluded before calculation of KCRV,
- the uncertainties do not vary significantly.

Table 13 – Reported values of specific adsorption of Ar at P/Po=0.001 and uncertainties

№	**NMI/DIS**	**Specific adsorption of Ar at P/Po=0.001, mol/kg**	**Combined standard uncertainty, u_c, mol/kg**	**Expanded uncertainty, U(k=2), mol/kg**	**di, mol/kg**	**U(di), mol/kg**	**Verdict**	**K**
1	**INMETRO**	6.710	0.121	0.280 (k=2.31)	-0.54	0.26	-	-4.8
2	BAM	7.140	0.035	0.070	-0.11	0.12	+	-0.5
3	VNIIM	7.190	0.035	0.070	-0.06	0.12	+	0
4	NIM	7.290	0.050	0.100	0.04	0.14	+	1
5	TUBITAK-UME	7.370	0.080	0.160	0.12	0.19	+	1.8
Uncertainty weighted mean		7.197	0.037					
Median		7.240	0.070					
Mean		**7.248**	**0.051**		**KCRV (N=4)**			
Consistency test					**Conclusion**			
X^2_{obs}		$X^2_{tab,\ 0.05;N-1}$		N	$X^2_{obs} > X^2_{tab,\ 0.05;N-1}$			
24.24		9.49		5	inconsistent			

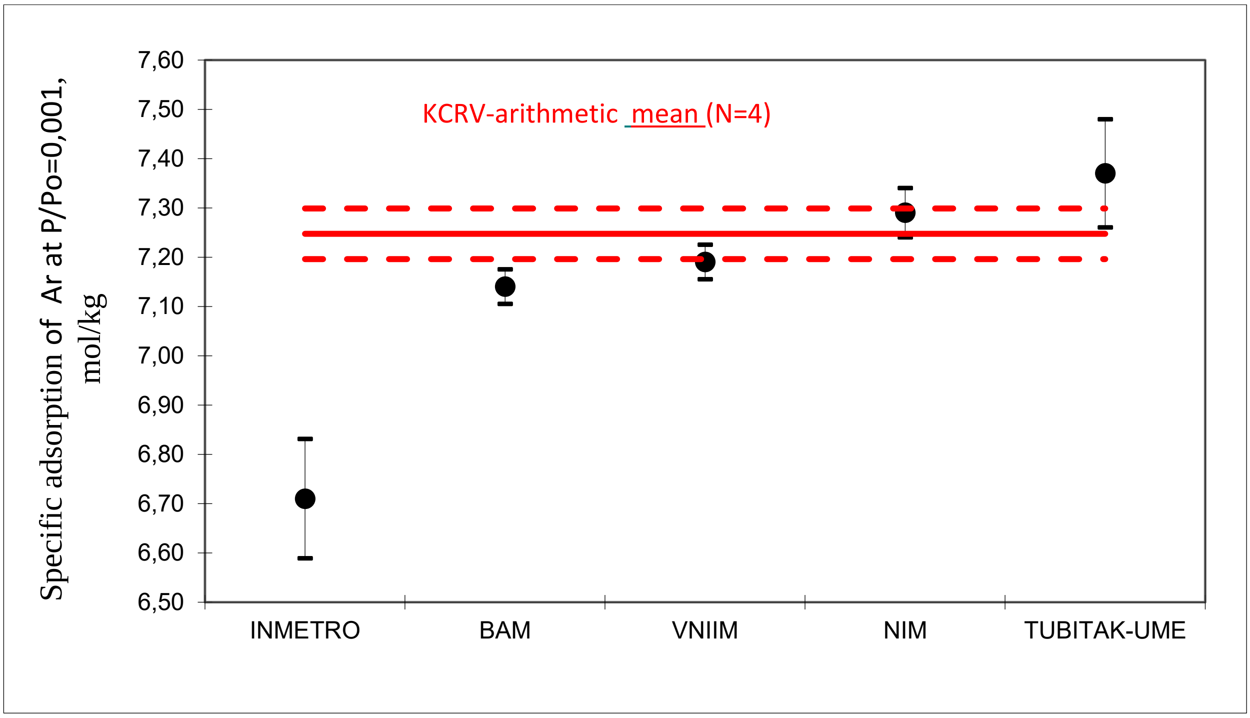

Figure 4 KCRV for specific adsorption of Ar on zeolite. Error bars show standard uncertainty. The dashed lines represent the values of KCRV+/- standard uncertainty.

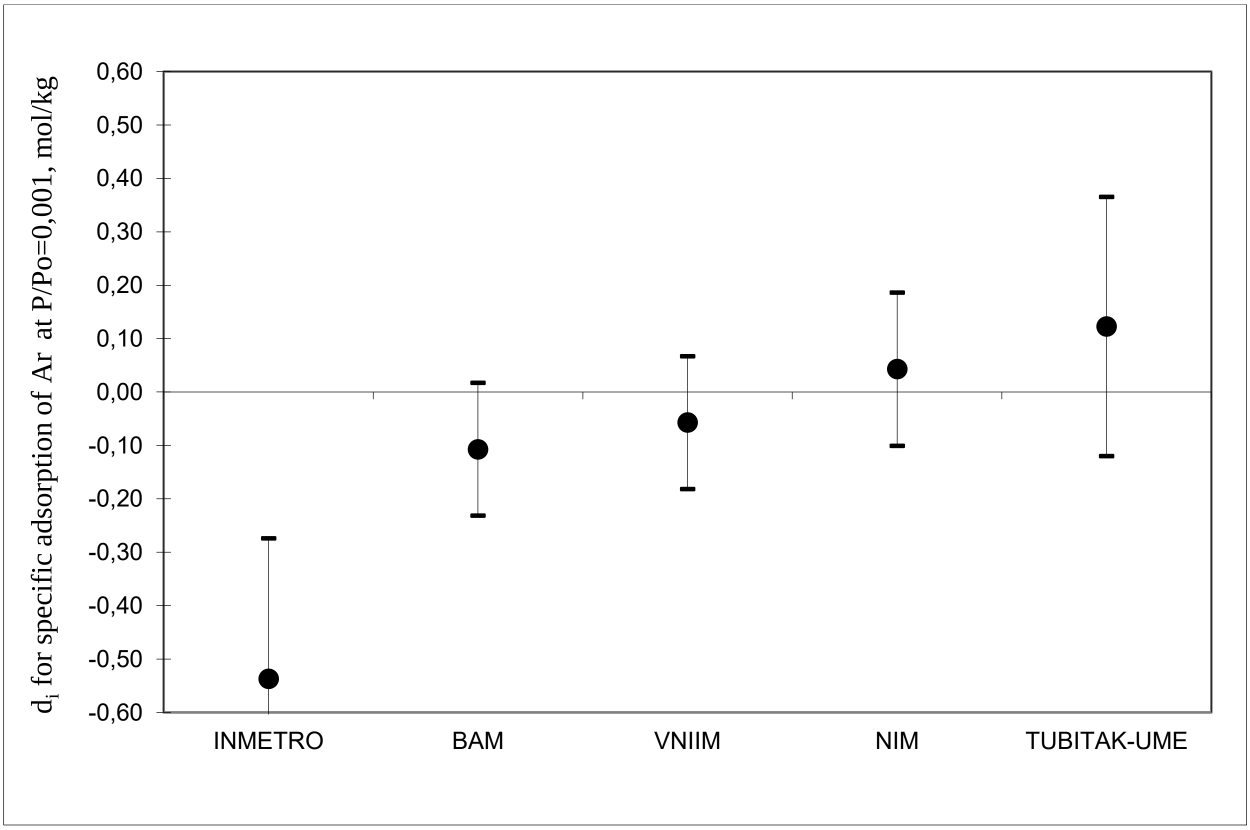

Figure 5 Degrees of equivalence d_i and expanded uncertainty U（d_i）(k=2) for specific adsorption of Ar on zeolite

7.5 KCRV for specific adsorption of Ar at P/Po=0.01

The reported values of the specific adsorption of Ar at P/Po=0.01 and the uncertainties of all results are summarized in Table 14. Estimations of KCRV have been obtained by different approaches (arithmetic mean, uncertainty weighted mean, median) and are presented in Table 14. The same results are displayed graphically in Figures 6 and 7.

The arithmetic mean of outlier-rejected data was used for assessment of the KCRV because:

- $\chi^2_{obs} > \chi^2_{0.05,N-1}$, in this case the data is inconsistent,
- there is one extreme value according to criteria (7), so the results from INMETRO (K=-6.9) was excluded before calculation of KCRV,
- the uncertainties do not vary significantly.

Table 14 – Reported values of specific adsorption of Ar at P/Po=0.01 and uncertainties

№	**NMI/DIS**	**Specific adsorption of Ar at P/Po=0.01, mol/kg**	**Combined standard uncertainty, u_c, mol/kg**	**Expanded uncertainty, U(k=2), mol/kg**	**di, mol/kg**	**U(di), mol/kg**	**Verdict**	**K**
1	INMETRO	8.410	0.150	0.340 (k=2.26)	-0.64	0.31	-	-6.9
2	BAM	8.940	0.050	0.100	-0.11	0.13	+	-1.0
3	VNIIM	9.030	0.045	0.090	-0.02	0.13	+	0.0
4	TUBITAK-UME	9.070	0.120	0.240	0.02	0.26	+	0.4
5	NIM	9.150	0.075	0.150	0.10	0.17	+	1.3
Uncertainty weighted mean		9.018	0.042					
Median		9.050	0.056					
Mean		**9.048**	**0.044**		**KCRV (N=4)**			
Consistency test					**Conclusion**			
X^2_{obs}		$X^2_{tab, 0.05;N-1}$		N	$X^2_{obs} > X^2_{tab, 0.05;N-1}$			
21.35		9.49		5	inconsistent			

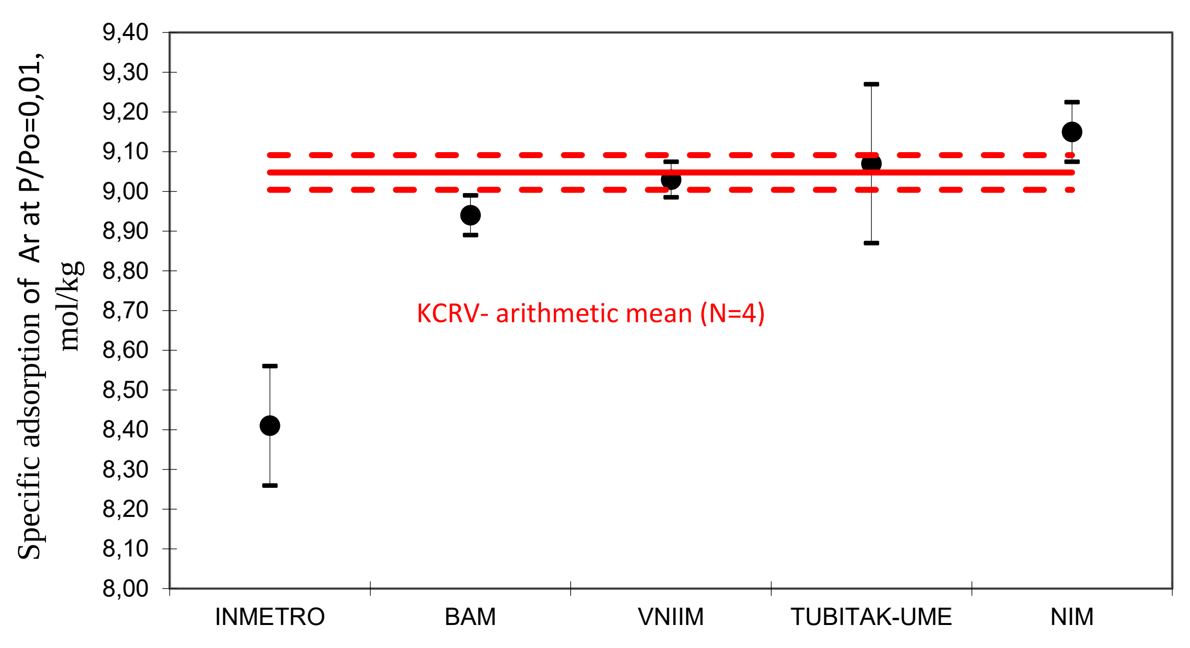

Figure 6 KCRV for specific adsorption of Ar on zeolite. Error bars show standard uncertainty. The dashed lines represent the values of KCRV+/- standard uncertainty.

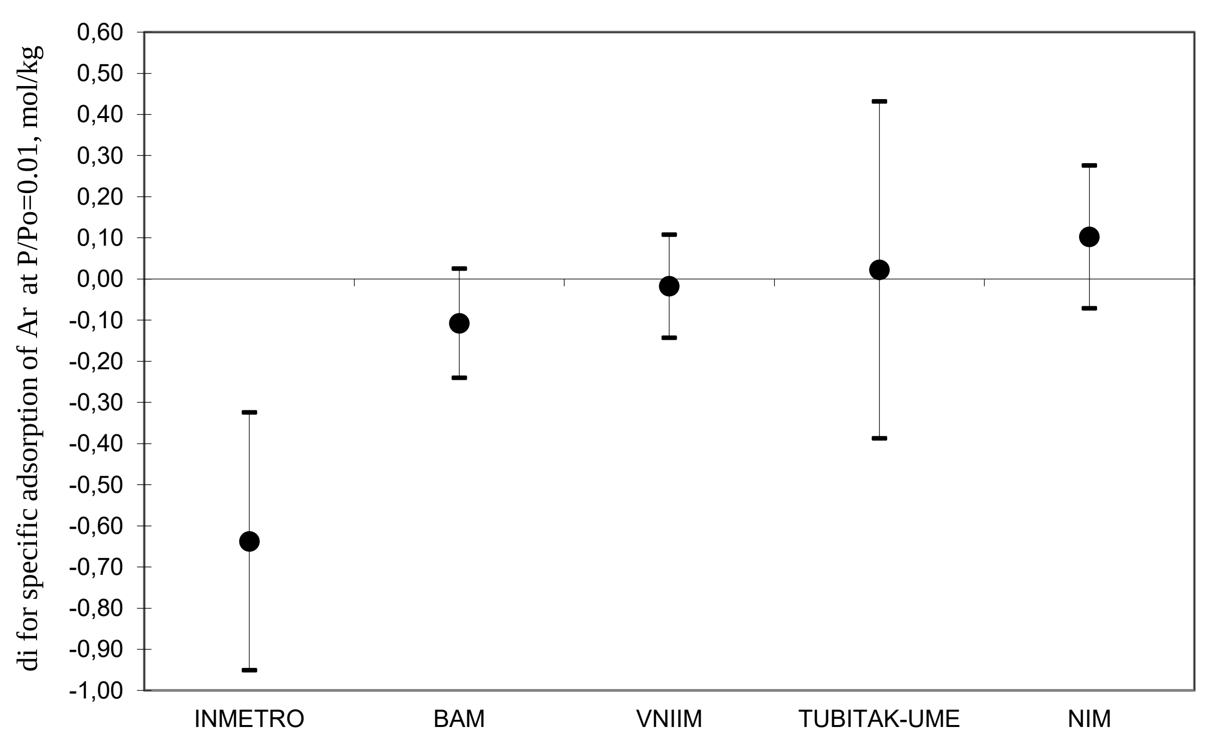

Figure 7 Degrees of equivalence d_i and expanded uncertainty U（d_i）(k=2) for specific adsorption of Ar on zeolite

7.6 KCRV for specific adsorption of Ar at P/Po=0.1

The reported values of the specific adsorption of Ar at P/Po=0.1 and the uncertainties of all results are summarized in Table 15. Estimations of KCRV have been obtained by different approaches (arithmetic mean, uncertainty weighted mean, median) and are presented in Table 15. The same results are displayed graphically in Figures 8 and 9.

The arithmetic mean of outlier-rejected data was used for assessment of the KCRV because:

- $\chi^2_{obs} > \chi^2_{0.05,N-1}$, in this case the data is inconsistent,
- there is one extreme value according to criteria (7), so the results from INMETRO (K=-5.0) was excluded before calculation of KCRV,
- the uncertainties do not vary significantly.

Table 15 – Reported values of specific adsorption of Ar at P/Po=0.1 and uncertainties

№	**NMI/DIS**	**Specific adsorption of Ar at P/Po=0.1, mol/kg**	**Combined standard uncertainty, u_c, mol/kg**	**Expanded uncertainty, U(k=2), mol/kg**	**di, mol/kg**	**U(di), mol/kg**	**Verdict**	**K**
1	INMETRO	9.300	0.278	0.600 (k=2.16)	-0.57	0.57	-	-5.0
2	BAM	9.740	0.055	0.110	-0.13	0.16	+	-1.0
3	TUBITAK-UME	9.850	0.155	0.310	-0.02	0.33	+	0.0
4	VNIIM	9.860	0.055	0.110	-0.01	0.16	+	0.1
5	NIM	10.020	0.075	0.150	0.15	0.19	+	1.5
Uncertainty weighted mean		9.847	0.060					
Median		9.855	0.050					
Mean		**9.868**	**0.058**		**KCRV (N=4)**			
Consistency test					**Conclusion**			
X^2_{obs}		$X^2_{tab,\ 0.05;N-1}$		N	$X^2_{obs} > X^2_{tab,\ 0.05;N-1}$			
12.98		9.49		5	inconsistent			

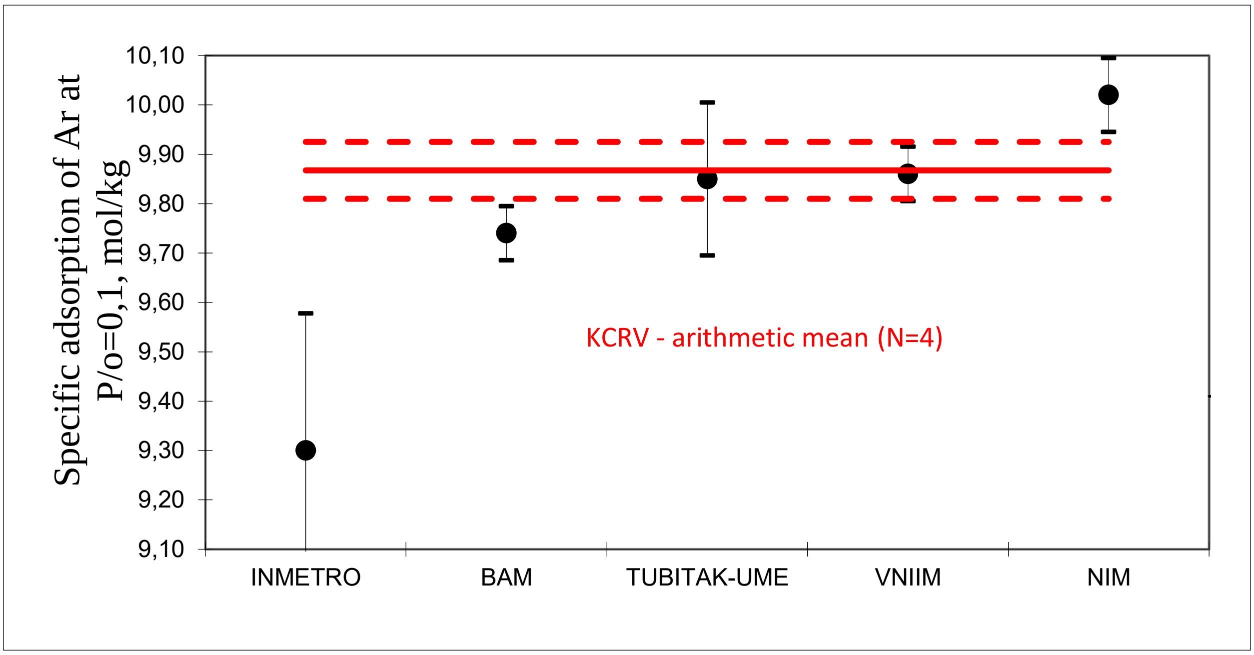

Figure 8 KCRV for specific adsorption of Ar on zeolite. Error bars show standard uncertainty. The dashed lines represent the values of KCRV+/- standard uncertainty.

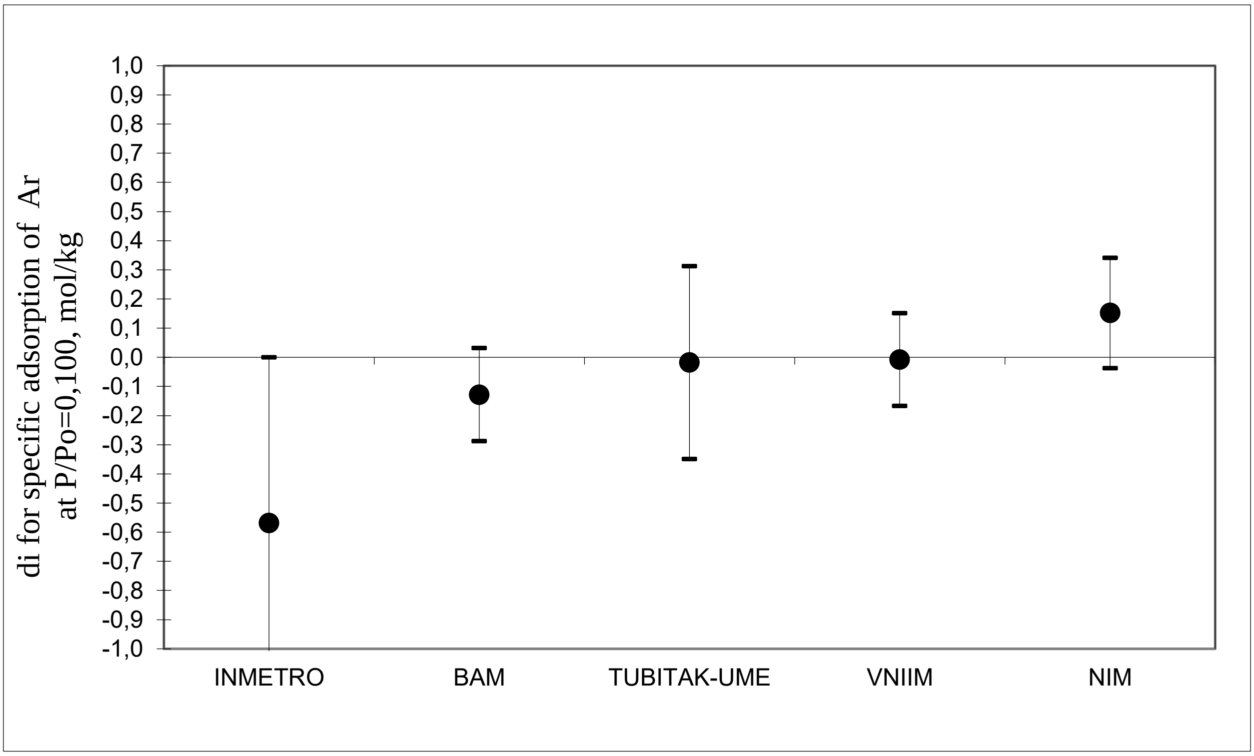

Figure 9 Degrees of equivalence d_i and expanded uncertainty U（d_i）(k=2) for specific adsorption of Ar on zeolite

7.7 Reference value for BET specific surface area as derived from measurement of specific adsorption of Ar

The reported values of BET specific surface area and the uncertainties of all results are summarized in Table 16. Estimations of reference values (RV) obtained by different approaches (arithmetic mean, uncertainty weighted mean, median) are presented in Table 16. The same results are displayed graphically in Figures 10 and 11.

The arithmetic mean of outlier-rejected data was used for assessment of the RV because:

- $\chi^2_{obs} > \chi^2_{0.05,N-1}$, in this case the data is inconsistent,
- there is one extreme value according to criteria (7), so the results from INMETRO (K=-9.8) was excluded before calculation of KCRV,
- the uncertainties vary significantly.

Table 16 – Reported values of BET specific surface area and uncertainties

№	**NMI/DIS**	BET specific surface area, m^2/g	Combined standard uncertainty, u_c, m^2/g	Expanded uncertainty, U(k=2), m^2/g	di, m^2/g	U(di), m^2/g	Verdict	**K**
1	INMETRO	744.0	18.2	39.0 (k=2.14)	-49.7	37.3	-	-9.8
2	BAM	786.0	4.5	9.0	-7.7	12.1	+	-1.0
3	VNIIM	790.8	4.7	9.3	-2.9	12.3	+	0.0
4	TUBITAK-UME	792.9	15.0	30.0	-0.8	31.1	+	0.4
5	NIM	805.0	6.0	12.0	11.3	14.5	+	3.0
Uncertainty weighted mean		792.1	4.1					
Median		791.9	3.2					
Mean		793.7	4.0		**KCRV (N=4)**			
Consistency test					**Conclusion**			
X^2_{obs}		$X^2_{tab, 0.05;N-1}$		N	$X^2_{obs} > X^2_{tab, 0.05;N-1}$			
13.35		9.49		5	inconsistent			

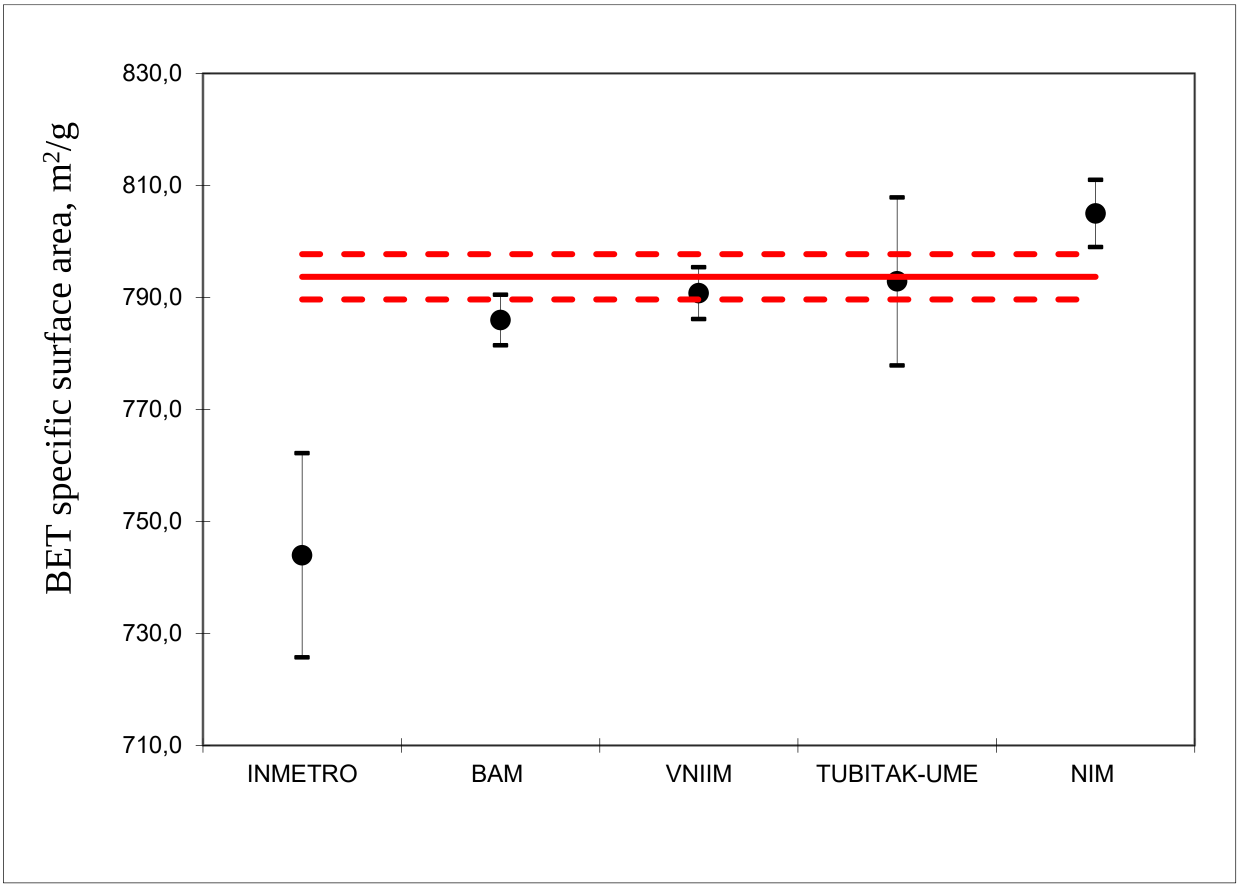

Figure 10 BET specific surface area derived from measurement of Ar specific adsorption data. The dashed lines represent the values of KCRV+/- standard uncertainty.

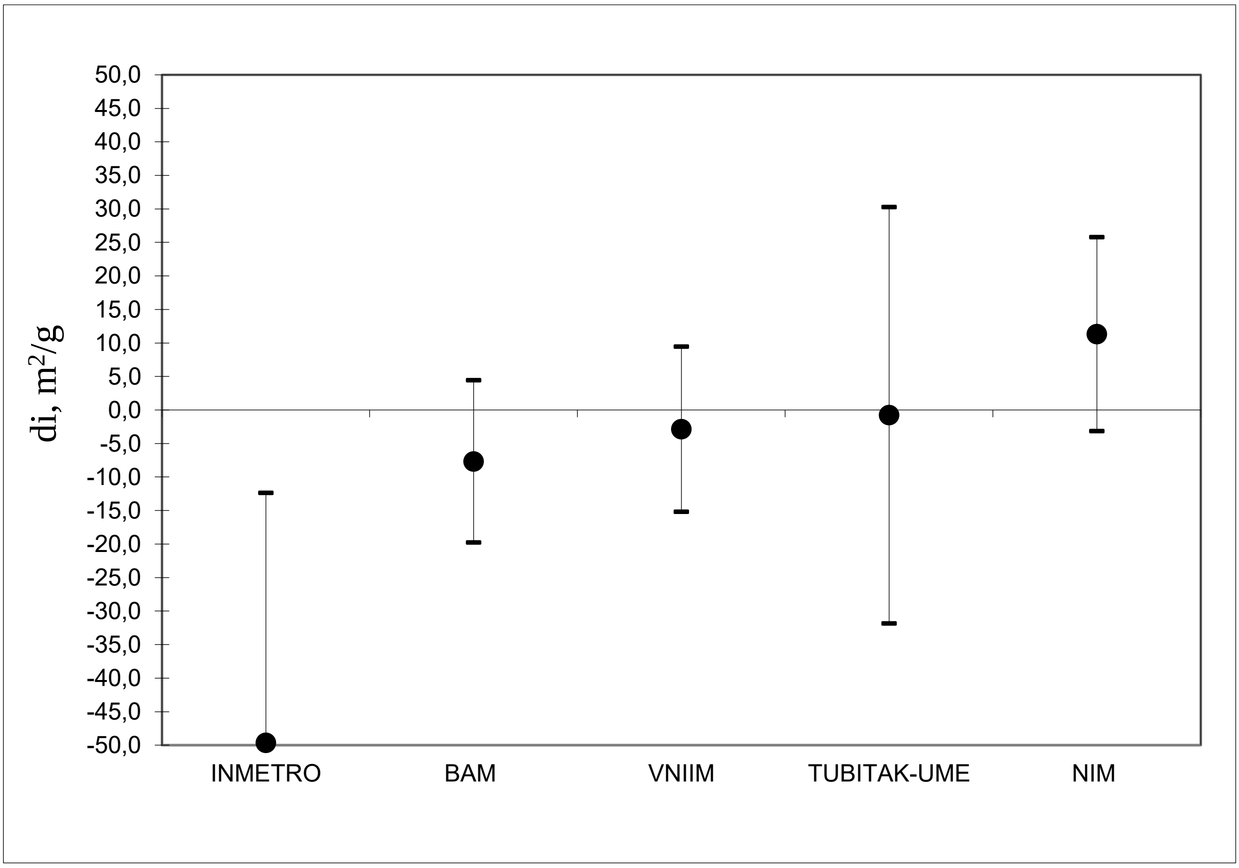

Figure 11 Degrees of equivalence d_i and expanded uncertainty U（d_i）(k=2)

7.8 Reference value for most frequent pore diameter as derived from measurement of specific adsorption of Ar

The reported values of most frequent pore diameter and the uncertainties of all results are summarized in Table 17. Estimations of reference values (RV) obtained by different approaches (arithmetic mean, uncertainty weighted mean, median) are presented in Table 16. The same results are displayed graphically in Figures 12 and 13.

The arithmetic mean of outlier-rejected data was used for assessment of the RV because:

- $\chi^2_{obs} > \chi^2_{0.05,N-1}$, in this case the data is inconsistent,
- there are no extreme values,
- the uncertainties do not vary significantly.

Table 17 – Reported values of most frequent pore diameter and uncertainties

№	NMI/DIS	Most frequent pore dimeter, nm	Combined standard uncertainty, uc, nm	Expanded uncertainty, U(k=2) , nm	di, nm	U(di) , nm	Verdict	K
1	BAM	0.643	0.0015	0.0030	-0.011	0.011	-	-1.2
2	VNIIM	0.645	0.0060	0.0120	-0.009	0.016	+	-1.0
3	TUBITAK-UME	0.655	0.0050	0.0100	0.001	0.014	+	0.0
4	NIM	0.656	0.0070	0.0140	0.002	0.017	+	0.1
5	INMETRO	0.670	0.0100	0.0200	0.016	0.022	+	1.5
Uncertainty weighted mean		0.645	0.003					
Median		0.655	0.008					
Mean		**0.654**	**0.005**		**RV (N=5)**			
Consistency test					**Conclusion**			
X^2_{obs}		$X^2_{tab, 0.05;N-1}$		N	$X^2_{obs} > X^2_{tab, 0.05;N-1}$			
14.50		9.49		5	inconsistent			

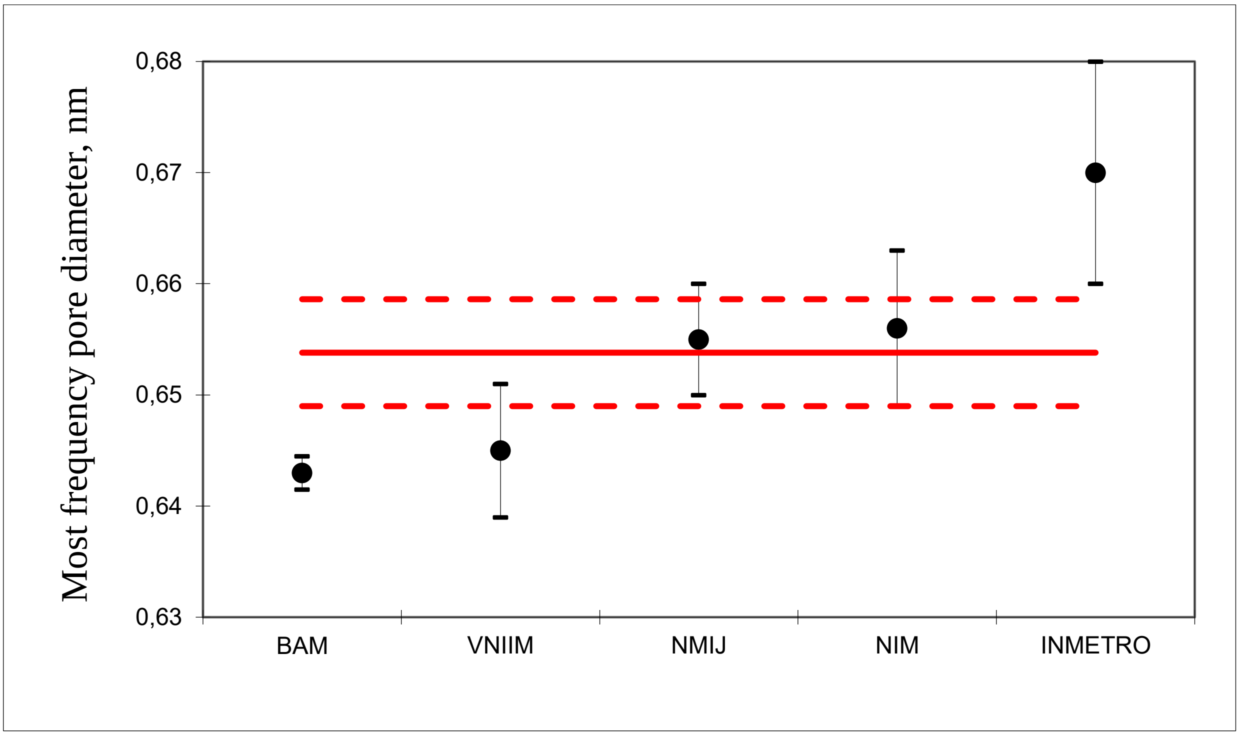

Figure 12 Most frequent pore diameter derived from measurement of Ar specific adsorption data. Error bars show standard uncertainty. The dashed lines represent the values of RV+/- standard uncertainty.

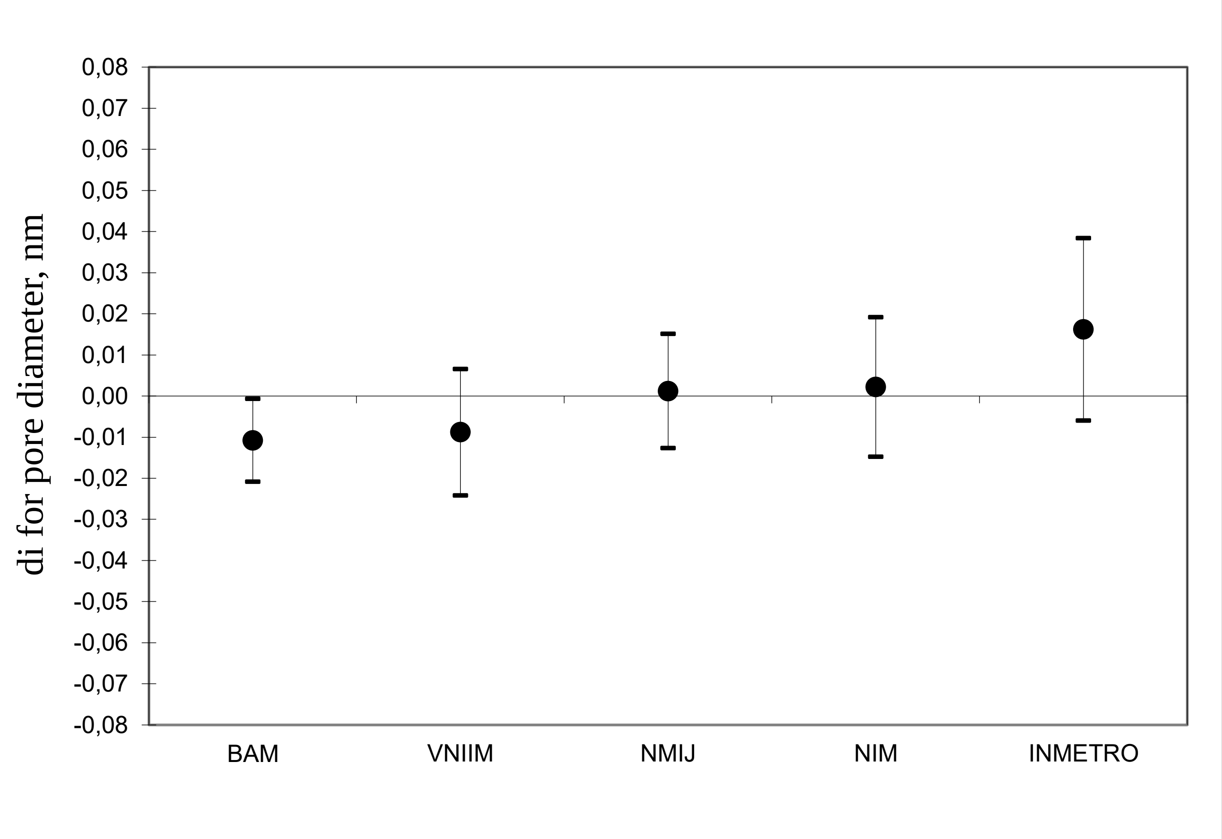

Figure 13 Degrees of equivalence d_i and expanded uncertainty U（d_i）(k=2)

7.9 Reference value for specific pore volume as derived from measurement of specific adsorption of Ar

The reported values of specific pore volume and the uncertainties of all results are summarized in Table 18. Estimations of reference values (RV) obtained by different approaches (arithmetic mean, uncertainty weighted mean, median) are presented in Table 18. The same results are displayed graphically in Figures 14 and 15.

The arithmetic mean of outlier-rejected data was used for assessment of the RV because:

- $\chi^2_{obs} > \chi^2_{0.05,N-1}$, in this case the data is inconsistent,
- there is one extreme value according to criteria (7), so the results from INMETRO (K=-9.8) was excluded before calculation of KCRV,
- the uncertainties do not vary significantly.

Table 18 – Reported values of specific pore volume and uncertainties

№	NMI/DIS	Specific pore volume, cm^3/g	Combined standard uncertainty, uc, cm^3/g	Expanded uncertainty, U(k=2), cm^3/g	di, cm^3/g	U(di), cm^3/g	Verdict	K
1	INMETRO	0.273	0.007	0.014 (k=2.14)	-0.018	0.013	-	-9.8
2	BAM	0.288	0.002	0.004	-0.003	0.005	+	-1.0
3	TUBITAK-UME	0.290	0.002	0.005	-0.001	0.005	+	0.0
4	VNIIM	0.291	0.001	0.003	0.000	0.004	+	0.5
5	NIM	0.294	0.002	0.004	0.004	0.005	+	2.8
Uncertainty weighted mean		0.2905	0.0012					
Median		0.2901	0.0012					
Mean		**0.2907**	**0.0014**		**RV (N=4)**			
Consistency test					**Conclusion**			
X^2_{obs}		$X^2_{tab, 0.05;N-1}$		N	$X^2_{obs} > X^2_{tab, 0.05;N-1}$			
11.87		9.49		5	inconsistent			

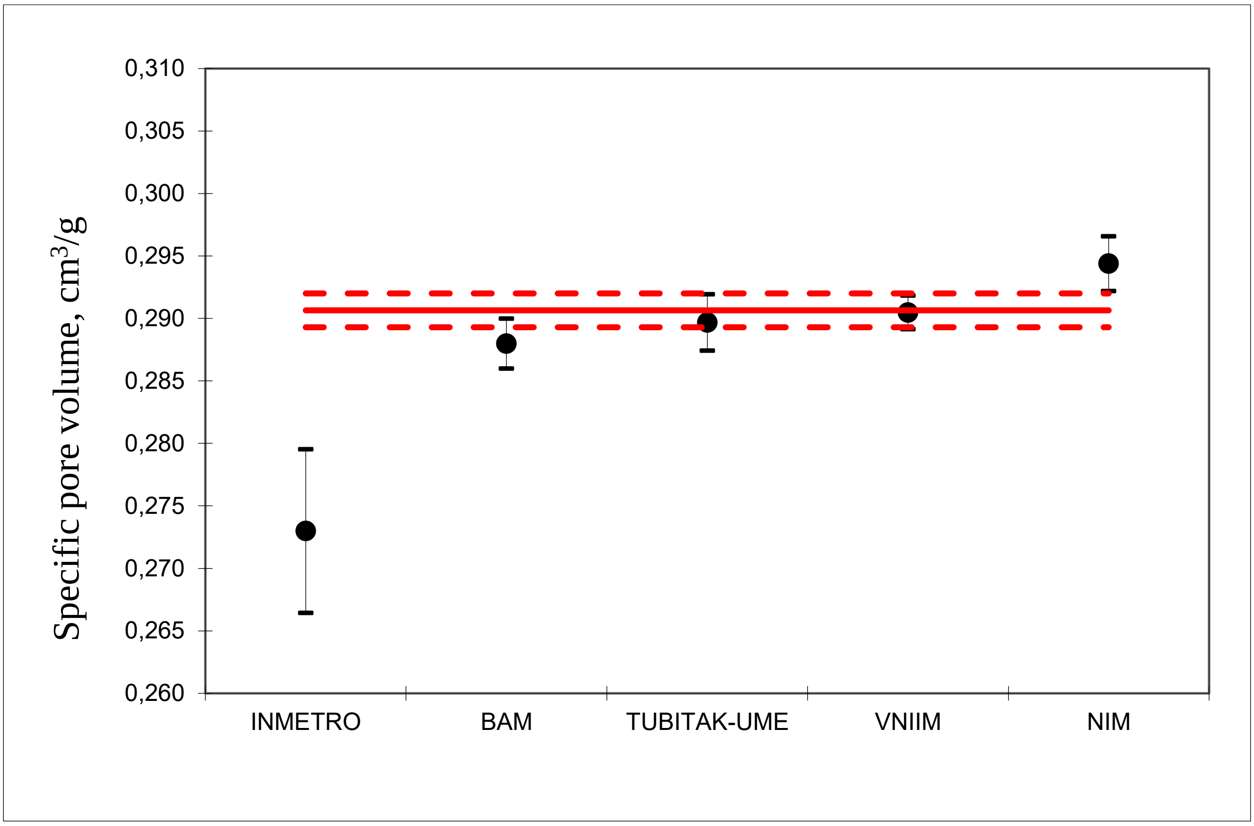

Figure 14 Specific pore volume derived from measurement of Ar specific adsorption data. Error bars show standard uncertainty. The dashed lines represent the values of RV+/- standard uncertainty.

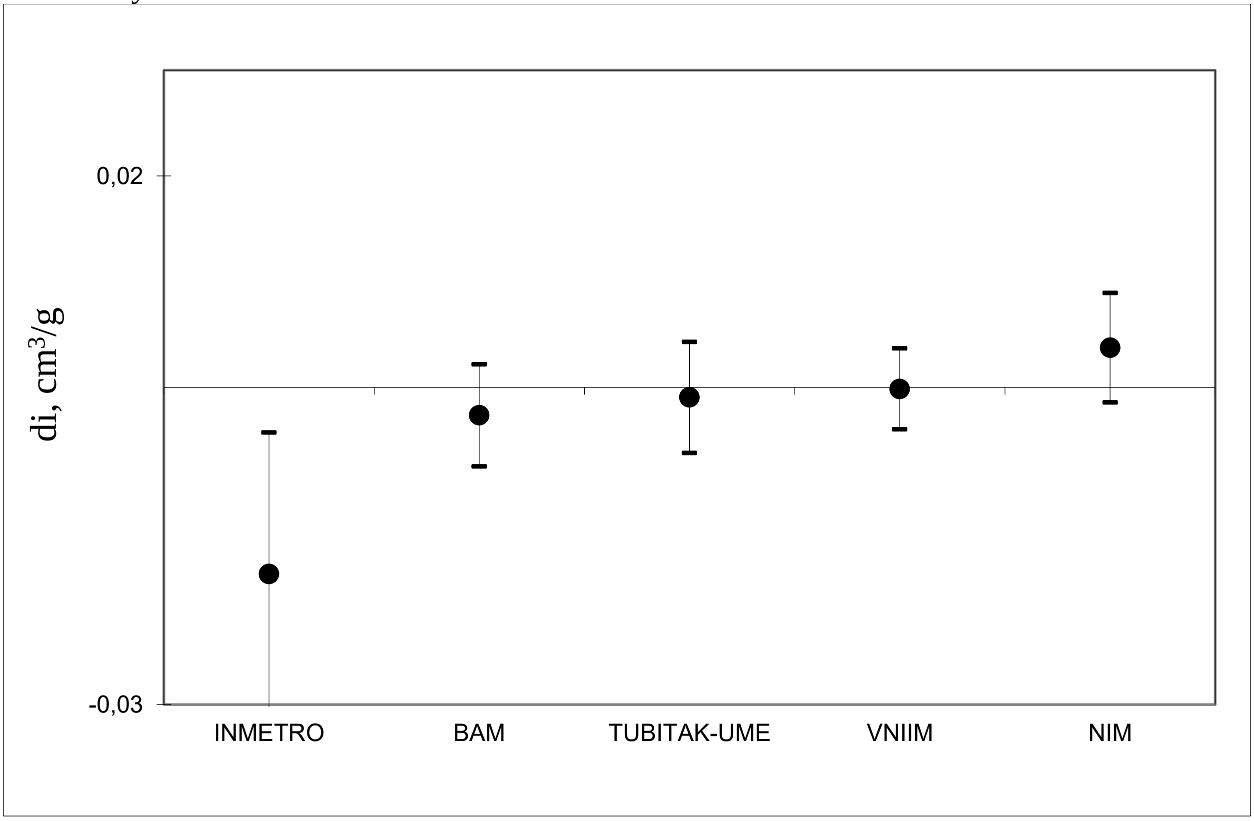

Figure 15 Degrees of equivalence d_i and expanded uncertainty U（d_i）(k=2)

7.10 Discussion

The key comparison CCQM K-172 has demonstrated very good agreement between the five participating NMIs/DIs concerning the primary measurands of the KC, the specific argon adsorption at microporous zeolite at liquid argon temperature. It’s suggested results from Inmetro could be affected by sample degassing procedure. The duration of the degassing was more than 12 hours. Although the temperature of degassing was relatively low 350 °C, the long dwell time might be enough to initiate microstructural (or even structural) changes in the sample. Such changes would result in a reduction of specific surface area.

Derived from specific adsorption data the BET specific surface area of microporous zeolite was determined as a secondary measurand following ISO 9277. Most frequency pore diameter and specific pore volume were determined as a secondary measurand following ISO 15901.

8 EQUIVALENCE STATEMENTS

The equivalence statements have been calculated according to the BIPM guideline. The degree of equivalence (and its uncertainty) between NMI/DI results and the KCRV has been calculated according to the following equations:

$$d_i = x_i - x_{ref}\,, \tag{17}$$

$$U\left(d_i\right) = 2\sqrt{\left(u\left(x_i\right)^2 + u\left(x_{ref}\right)^2 - 2\operatorname{cov}\left(x_i, x_{ref}\right)\right)}\,, \tag{18}$$

where d_i is the degree of equivalence between the NMI result x_i and the KCRV x_{ref}, and $U(d_i)$ is the expanded uncertainty $(k = 2)$ of the d_i calculated using the standard uncertainty $u(x_i)$ of the NMI result x_i, the standard uncertainty $u(x_{ref})$ of the KCRV x_{ref} and $\operatorname{cov}\left(x_i, x_{ref}\right)$.

The arithmetic mean was chosen as KCRV in this key comparison CCQM-K172. In this case $U(d_i)$ has been calculated using the following equation:

$$U\left(d_i\right) = 2\sqrt{u\left(x_i\right)^2 + u^2\left(\overline{x}_{ref}\right)}\,. \tag{19}$$

The equivalence statements for CCQM-K172 are given in Table 12-15 and Figures 3, 5, 7, 9.

9 CONCLUSIONS

Good agreement between the participating laboratories for a measurement of specific argon adsorption at liquid argon temperature were obtained. Data were used to determine a second, derived measurand, the BET specific surface area of microporous substances. The arithmetic mean of all results is used for the KCRV. The suitability of the gas adsorption method for determination of BET specific surface area of microporous solid substances in advanced technology has been demonstrated.

10 HOW FAR THE LIGHT SHINES STATEMENT

Successful participation in the key comparisons CCQM-K172 can support CMCs for the measurement of the specific adsorption of argon in the 1-20 mol/kg range and BET specific surface area, for numbers in the 300-1500 m^2/g for microporous zeolite as well as other similar microporous substances. Reference value for specific pore volume and pore diameter estimated only for information

11 ACKNOWLEDGEMENTS

VNIIM thanks for the help and cooperation of colleagues from the participant institutes for all their efforts.

12 REFERENCES

1. ISO 15901-3 Pore size distribution and porosity of solid materials by mercury porosimetry and gas adsorption — Part 3: Analysis of micropores by gas adsorption. International Organization for Standardization (2017).
2. ISO 9277 Determination of the specific surface area of solids by gas adsorption – BET method. International Organization for Standardization (2016).
3. Gregg, S. J., Sing, K. S. W., Adsorption, Surface Area and Porosity. Academic Press, London 1982.
4. CCQM Guidance note: Estimation of a consensus KCRV and associated Degrees of Equivalence. Version: 10.
5. Alexander Badalyan and Phillip Pendleton Analysis of Uncertainties in Manometric Gas-Adsorption Measurements. I: Propagation of Uncertainties in BET Analyses// Langmuir 2003, 19, 7919-7928.
6. Christophe Leysa, ChristopheLeyb, Olivier Kleina, PhilippeBernarda, LaurentLicataa Detecting outliers: Do not use standard deviation around the mean, use absolute deviation around the median// Journal of Experimental Social Psychology, Volume 49, Issue 4, July 2013, Pages 764-766.

Appendix A – Technical Protocol
CCQM-K172
Measurement of Specific Adsorption A [mol/kg] of Ar on zeolite at liquid argon temperature (to enable a traceable determination of the Specific Surface Area by following ISO 9277)

1. Introduction

Specific argon adsorption to enable a traceable determination of specific surface area, specific pore volume and pore diameter in microporous solids are highly relevant parameters because they are often used for the specification of the vast majority of porous materials and substances (sorbents, catalytic agents, cross-linkers, zeolites, etc) used in advanced technology. To check the comparability of measurement protocols at NMIs and DIs addressing the porosity properties of technologically relevant microporous solids a Key comparison is launched by the Surface Analysis Working Group at CCQM/BIPM.

There was intensive discussion about a method defined measurands. CCQM agreed to introduce the decision criteria proposed by the task group on method defined measurands. Final report of the TG can be found as CCQM19-43. For a specific surface area determined by using BET theory (BET SSA), only one criteria,"The method, as applied at the relevant NMI or DI, is considered as the highest metrological reference within a calibration hierarchy." was reported as question mark. BET SSA is "Specific amount of gas molecules/atoms monolayer-adsorbed on a material" x "cross-sectional area of single molecule/atom of the adsorbed gas". i.e. "amount of substances at the specific state" x constant. Although the metrological traceability of the BET SSA to SI should through physical measurands such as Weight, Pressure, Volume and Temperature, it is obvious that the BET SSA is the highest metrological reference of material/chemical basis.

The comparison is being carried out for the purpose to enable participating NMIs and DIs to claim CMCs as detailed in table A.1.

Table A.1 Layout of CMC claims to be underpinned by Key comparison CCQM-K172

Meas. Serv. Category	Matrix	Measurand		Dissemination Range of Measurement Capability			Range of Expanded Uncertainties as Disseminated			
		Analyte or component	Quantity	From	To	Unit	From	To	Unit	Cov. factor
Advanced Materials	zeolite	zeolite	Specific adsorption of argon	1	20	mol/kg			mol/kg	2
Advanced Materials	zeolite	zeolite	Specific surface area	300	1500	m^2/g			m^2/g	2

Only specific adsorption of gas and specific surface area potentially can be CMC claims. **Specific pore volume and pore diameter are informative characteristics and using as an optional information.**

2. Measurand and reporting

The primary measurand values for CCQM-K172 are specific adsorption of argon on zeolite at liquid argon temperature. Derived from that data the secondary measurand are specific surface area, specific pore volume and pore diameter of zeolite. **Only for specific adsorption of argon and specific surface area KCRV will be established. RV will be established for specific pore volume and pore diameter only for information.**

Each participant shall report the results for the values of specific adsorption argon, specific surface area, specific pore volume and pore diameter of zeolite. The results should be reported accompanied by a full uncertainty statement (including a combined standard uncertainty and an expanded uncertainty with a coverage factor applied).

For the estimation of the measurement uncertainty for specific adsorption of gases these issues have to be taken into account: mass of the analyzed sample, system volume, initial pressures, pressures after reaching equilibrium, gas temperatures, sample holder volume at cryogenic bath temperature, free space volume with sample holder immersed in cryogenic bath and uncertainty due to interpolation.

In addition the report should include technical details on the measurement procedure, traceability links (as calibrations) and uncertainty contributions. Each of report should include tabular reports and graphs for the isotherm (dependence specific adsorption from relative pressure) and for the specific surface area

3. Guidance values and target uncertainty

Analyte/matrix: The test material used for the comparisons is zeolite. A range of measurands and target uncertainty are shown in table A.2. A range of informative characteristic parameters and target uncertainty are shown in table A.3 Points of relative pressure of argon for specific adsorption of Ar is presented in table A.4.

Table A.2

Quantity	Measurand	Range	Target relative expanded uncertainty
Specific adsorption of argon at $1.0\cdot10^{-4}\leq P/Po\leq1.0\cdot10^{-1}$	Primary	(1-20) mol/kg	(1-10) %
Specific surface area	Secondary	(300-1500) m^2/g	

Table A.3

Quantity	Informative characteristic	Range	Target relative expanded uncertainty
Specific pore volume	Secondary	(0.05-1.0) cm^3/g	-
Most frequent pore diameter	Secondary	(0.4–2) nm	

Table A.4

№	P/Po*	A, mol/kg	U(k=2), mol/kg
1	$1.0\cdot10^{-4}$		
2	$1.0\cdot10^{-3}$		
3	$1.0\cdot10^{-2}$		
4	$1.0\cdot10^{-1}$		

*If relative pressure is not exactly equal to **$P/Po=1,0\cdot10^{-4}$; $P/Po=1,0\cdot10^{-3}$; $P/Po=1,0\cdot10^{-2}$; $P/Po=1,0\cdot10^{-1}$**, please calculate specific adsorption values using linear interpolation.*

4. KCRVs

- The processing of measurement results of specific adsorption nitrogen, specific surface area to the pilot lab will be carried out according to the following documents:CCQM Guidance note: Estimation of a consensus KCRV and associated Degrees of Equivalence (version: 6, Date 2010-03-01, Draft)
- Cox M.G. “The evaluation of key comparison data” [1]

- Jorg W.Muller. “Possible Advantages of a Robust Evaluation of Comparisons” [2].

5. Methods of measurement

Each participant should use the gas adsorption method for the measurement of the specific adsorption argon, specific surface area, specific pore volume and pore diameter of zeolite as defined in ISO 15901-3 [3] and ISO 9277 [4].

Some details about measurement procedure of gas adsorption method are shown bellow

Please perform at least 5 replicate measurements on separate aliquots of zeolite. The recommend minimum sample amount is about 0.3 gram for each run.

Sample pretreatment

Heat the sample zeolite to 90 °C then the sample is vacuumed at a rate of 0.67 kPa/sec to a residual pressure of 10 Pa and vacuumed for 30 minutes. Then slom heating at a rate of not more than 10 °C/min to 350 °C. The hold temperature at 350 °C for at least 6 hour.

Measurement of the complete Isotherm (adsorption branch) at 87 K and specific adsorption of argon at $P/Po=1,0\cdot10^{-5}$; $P/Po=1,0\cdot10^{-4}$; $P/Po=1,0\cdot10^{-3}$; $P/Po=1,0\cdot10^{-2}$; $P/Po=1,0\cdot10^{-1}$.

First isotherm data point should be taken at $P/Po=1,0\cdot10^{-5}$, last adsorption isotherm data point should be taken at $P/Po=1,0\cdot10^{-1}$. Intermediate points are selected uniformly at the rate of (8-10) points for each order. The free volumes of the tube with the sample "warm" and "cold" should be measured after the measurements of specific adsorption of argon and then entered into the files in which the measurements are made for adjustment.

Specific surface area S, m^2/g

For determination n_m must be measured at least five points in the P/Po Range from 0.001 to 0.03. Specific surface area must be calculated according to equation

$$S = n_m N_a a_m \tag{A.1}$$

where N_a is Avogadro constant, mol^{-1}; a_m is area occupied by one argon molecule $0.142\cdot10^{-18}$ m^2; n_m is specific monolayer capacity of adsorbate, mol$\cdot$g^{-1}.

Specific monolayer capacity of adsorbate must be calculated according to BET equation (ISO 9277):

$$\frac{P/P_o}{A(1-P/P_o)} = \frac{1}{n_m C} + \frac{C-1}{Cn_m}\frac{P}{P_o} \tag{A.2}$$

where A is specific adsorption of argon, mol$\cdot$g^{-1}; C is BET constant; P - pressure of the adsorptive in equilibrium with the adsorbate, Pa.

Specific pore volume (informative characteristic)

Computed by the equation Dubinin-Radushkevich in the range P/Po from 0.005 to 0.10:

$$\lg V = \lg V_{micro} - D\left(\lg\frac{p_o}{p}\right)^2, \tag{A.3}$$

where V - specific volume adsorbed, cm^3/g;

V_{micro} - the sorption capacity of argon under normal conditions under filled micropores, calculated by regression analysis on the equation Dubinin, cm^3/g.

The density of argon liquid =1.40 g/cm^3 (87.29 K). The density of argon under normal conditions =1,7840 mg/cm^3. The calculations used the ratio $\frac{\rho_g}{\rho_L} = 1,28 \cdot 10^{-3}$. Calculate the specific volume of pores according to the formula:

$$V = \frac{V_{micro} \rho_g (STP)}{\rho_L} \qquad \text{(A.4)}$$

where V_{micro} - the sorption capacity of argon under normal conditions under filled micropores, calculated by regression analysis on the equation Dubinin, cm^3/g.

Most frequency pore diameter D, nm (informative characteristic)

It is calculated as a mode of pore distribution over diameters with a modal interval equal to 0.01 nm (as a rule, it is calculated automatically using the software of gas adsorption analyzers). The pore diameter is calculated by the Horvath-Kawazoe and Saito-Foley method:

$$\ln\left(\frac{P}{P_o}\right) = \frac{3}{4} \frac{\pi N_A}{RT} \frac{\left(N_s K_{As} + N_a K_{Aa}\right)}{d_o^4} f_{SF}\left(\alpha, \beta, l, d_o\right) \qquad \text{(A.5)}$$

The following parameters of the adsorbent and adsorbate given in tables 5, 6 are used to perform calculations by the Horvath -Kawazoe and Saito-Foley method.

Table 5 — Parameters for zeolite adsorbent

Physical quantity	Unit	Symbol	Zeolite
Polarizability	10^{-24} cm^3	$\alpha_{(s^*)}$	2.50
Magnetic susceptibility	10^{-29} cm^3	χ_s	1.30
Surface density (atoms per square metre of pore wall)	10^{19} m^{-2}	N_s	1.31
Diameter	nm	ds	0.28

Table 6 — Parameters of adsorbate - argon

Physical quantity	Unit	Symbol	Argon
Polarizability	10^{-24} cm^3	$\alpha_{(s^*)}$	1.63
Magnetic susceptibility	10^{-29} cm^3	χ_s	3.25
Surface density (atoms per square metre of pore wall)	10^{18} m^{-2}	N_a	8.85
Diameter	nm	ds	0.34

6. Planned time schedule

call for participants:	by end of September 2020
latest registration of participant:	by end of October 2020 (updated)
latest arrival of samples at participants:	by end of December 2020
latest report of results:	by end of February 2021
report A:	by end of July 2021
report B:	by end of September 2021

7. Samples

A bottle is planned to contain about 4 g of zeolite.

8. Pilot laboratory

Laboratory for metrological assurance of nanoindustrie, analysis of spectral methods and reference materials (251)

NMI's name and abbreviation

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9. References

1. Cox M.G. The evaluation of key comparison data, Metrologia 39 (2002) 589-595.
2. Jorg W.Muller. Possible Advantages of a Robust Evaluation of Comparisons, Journal of Research of the National Institute of Standards and Technology Vol.105, No.4 (2000) 551-555.
3. ISO 15901-3 Pore size distribution and porosity of solid materials by mercury porosimetry and gas adsorption – Part 3: Analysis of micropores by gas adsorption. Geneva (2007).
4. ISO 9277 Determination of the specific surface area of solids by gas adsorption – BET method. International Organization for Standardization, Geneva (2010).
5. Gregg, S. J., Sing, K. S. W., Adsorption, Surface Area and Porosity. Academic Press, London 1982.
6. Sobina E. P. National Primary Standard Get 210-2014 for the Units of Specific Absorption of Gases, Specific Surface, Specific Volume, and Pore Size of Solid Substances and Materials // Measurement Techniques. January 2016, Volume 58, Issue 10, pp 1083-1089.
7. E. P. Sobina Development of a State Verification Scheme for Instruments Measuring the Specific Adsorption of Gases and Specific Surface Area, Specific Volume, and Size of Pores of Solid Substances and Materials. // Measurement Techniques. 60(4), August 2017.