Ural Scientific Research Institute for Metrology,
ROSSTANDART, RUSSIA

Report of the key CCQM-K153

Measurement of Specific Adsorption A [mol/kg] of N_2 and Kr on nonporous SiO_2 at LN temperature (to enable a traceable determination of the Specific Surface Area (BET) by following ISO 9277)

FINAL REPORT

Pilot laboratory
Ural Scientific Research Institute for Metrology, ROSSTANDART, Ekaterinburg (UNIIM)
Laboratory for metrological assurance of nanoindustrie, analysis of spectral methods and reference materials (251)

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1 ABSTRACT

The CCQM-K153 key comparison on the determination of specific adsorption of N_2 or Kr on nonporous silicon dioxide at liquid nitrogen temperature has been organized by the Surface Analysis Working Group at CCQM to enable a traceable determination of the Specific Surface Area (BET) of non-porous particulate substances as a derived secondary measurand following procedures and parameters agreed and standardized in ISO 9277. Because of its importance in the chemical and construction 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 (UNIIM) 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 nitrogen adsorption, specific krypton adsorption and, as a secondary, derived measurand, the BET specific surface area[1] of non-porous solids are highly relevant parameters because they are often used for the specification of particulate non-porous materials and substances (ceramic, cement, sorbents, catalysts, etc.) used in advanced technologies.

There are CMCs for BET specific surface area measurement for nonporous substances claimed by BAM 15 years ago. A key comparison testing the comparability of such measurements has never been carried out yet.

The aim of the key comparison CCQM-K153 is to support National Measurement Institutes (NMIs) and Designated Institutes (DIs) demonstrating the validity of the procedure they employ for the measurement of specific nitrogen and krypton adsorption at liquid nitrogen temperature to enable a determination of the BET specific surface area of non-porous particulate materials. The space of measurement covered by the specific gas adsorption measurement comprises non-porous and macroporous (D>50 nm) materials which are characterized by low values of BET specific surface area (< ~ 1 m^2/g). In an earlier key comparison (K-136) the specific gas adsorption on mesoporous (2<D<50 nm) alumina was addressed already. Only one new a key comparison needs to organize in future for microporous materials (D<2 nm) to demonstrating CMC's for gas adsorption method.

The validity of used procedure is 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.

[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, NMIJ, NIM, TUBITAK-UME, UNIIM). 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	Franziska Emmerling
National Institute of Metrology, P.R. China	**NIM**	China	Hai Wang
National Metrology Institute of Japan	**NMIJ**	Japan	Akira Kurokawa, Kohei Mizuno
TUBITAK – National Metrology Institute	**TUBITAK-UME**	Turkey	Ali Enis SADAK and Erman KARAKUS
Ural Scientific Research Institute for Metrology	**UNIIM**	Russia	Egor Sobina

4 SAMPLE

The source of the shared and distributed sample is a 1000 g batch of commercial sand (white quartz) of silicon dioxide (modal diameter of particles ~30 μm) 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 is presented in table 2.

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

Bottle №	**Specific adsorption of N_2, A(P/Po=0.05), mol/kg**	
1	0.00835	0.00801
2	0.00837	0.00785
3	0.00791	0.00820
4	0.00836	0.00748
5	0.00835	0.00734
6	0.00884	0.00801
7	0.00835	0.00785
8	0.00837	0.00820
9	0.00791	0.00748
10	0.00836	0.00734
11	0.00835	0.00837
12	0.00884	0.00791

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 1. The standard uncertainty due to (in)homogeneity, u_h, for the SiO_2 powder were calculated according to ISO Guide 35 using Equations (1) and (2) (see Table 3 and 4).

$$u_h = \sqrt{\frac{MS_{among} - MS_{within}}{n}} \quad (1)$$

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

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

Table 3 ANOVA analysis

bottle	***number***	***sum***	***average***	***dispersion***
1	2	0.016362	0.008181027	5.948E-08
2	2	0.016222	0.008110985	1.326E-07
3	2	0.016108	0.008054093	4.258E-08
4	2	0.015849	0.007924676	3.872E-07
5	2	0.015688	0.007843911	5.173E-07
6	2	0.016846	0.008423205	3.438E-07
7	2	0.016207	0.008103468	1.250E-07
8	2	0.016569	0.008284258	1.420E-08
9	2	0.015393	0.00769644	8.967E-08
10	2	0.01570	0.007849997	5.298E-07
11	2	0.016721	0.008360502	1.285E-10
12	2	0.016746	0.008373013	4.321E-07

Table 4 ANOVA analysis

source	***SS***	***df***	***MS***	***F***
Among	1.22E-06	11	1.11145E-07	0.4987954
Within	2.67E-06	12	2.22826E-07	
Sum	3.90E-06	23		
standard uncertainties due to inhomogeneity, u_h		-		Equation (1)
standard uncertainties due to inhomogeneity, $\boldsymbol{u_h}$		**0,00021**	**mol/kg**	Equation (2)

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

Table 5 Results of measurement of specific adsorption of N_2, A(P/Po=0,05)

№	Date	Specific adsorption of N_2, A(P/Po=0,05), mol/kg
1	30.12.2016	0.00835
2	29.12.2016	0.00837
3	15.09.2016	0.00791
4	15.09.2016	0.00836
5	14.09.2016	0.00835
6	13.09.2016	0.00884
7	12.09.2016	0.00801
8	12.09.2016	0.00785
9	05.09.2016	0.00820
10	07.09.2016	0.00748
11	07.09.2016	0.00734
mean of stability test, Xs		0,00810
standard deviation of the data of key comparison participants, S		0.00020
Xs+2S		0.00850
Xs-2S		0.00770
slope, b		$3.3 \cdot 10^{-6}$
standard uncertainty of slope, u_{slope}		$3.1 \cdot 10^{-6}$
standard uncertainty due to long-term (in)stability, u_s		0.00027
time measurements in key comparison, t_{max}, days		90

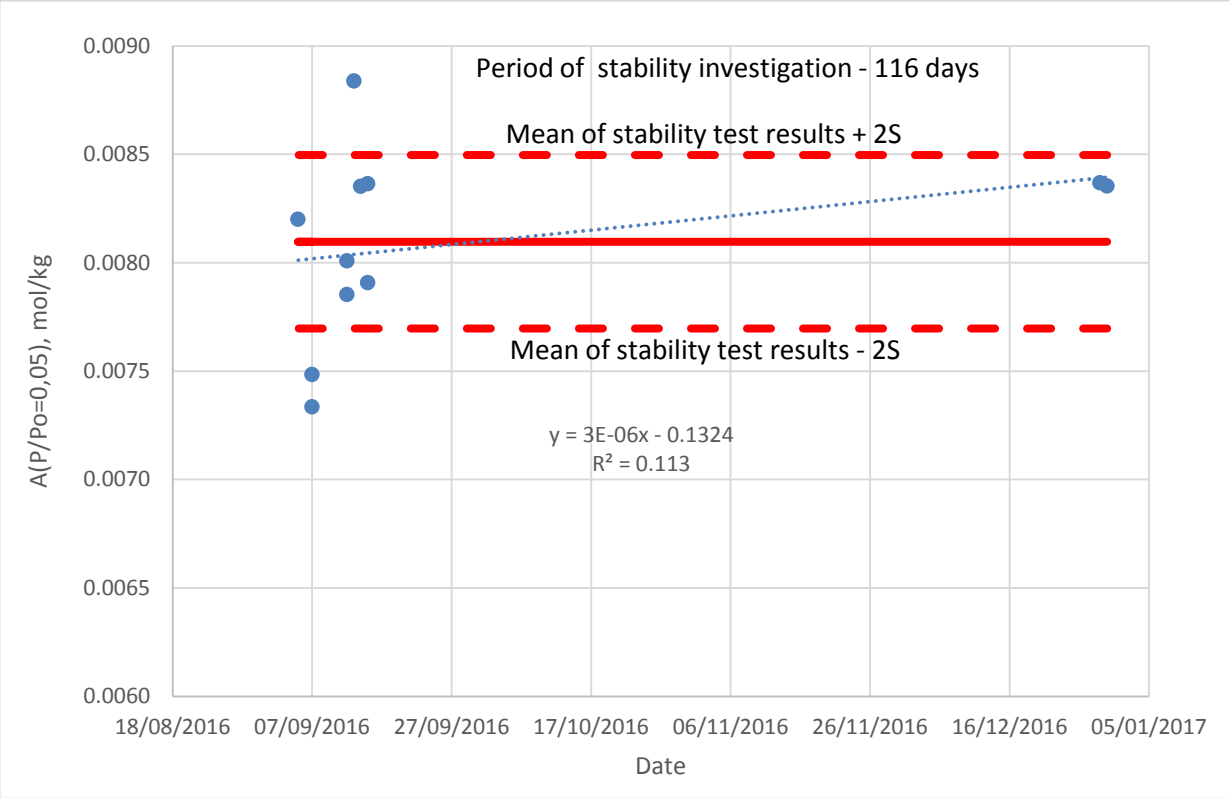

Fig.1 - Stability test for the nonporous silicon dioxide powder shared sample.

(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 statistical evaluation of the homogeneity and stability testing results for different P/Po values in the isotherms are shown in table 6.

Table 6 – Estimation of standard uncertainties due to inhomogeneity and long-term instability

Relative pressure, P/Po	Standard uncertainties due to inhomogeneity, u_h, mol/kg	Standard uncertainty due to long-term instability, u_s, mol/kg	Adsorbate
0.05	0.00021	0.00028	N_2
0.10	0.00018	0.00021	N_2
0.20	0.00021	0.00026	N_2
0.05	0.00022	0.00031	Kr
0.10	0.00034	0.00029	Kr
0.20	0.00015	0.00029	Kr
Average	0.00022	0.00025	

The standard uncertainty due to long-term (in)stability for specific adsorption of krypton and nitrogen is estimated to be 0.00025 mol/kg. The standard uncertainty due to inhomogeneity for specific adsorption of krypton and nitrogen is estimated to be 0.00022 mol/kg. The relative standard uncertainty due to long-term (in)stability for the derived BET specific surface area is estimated to be 1.0 %. The relative standard uncertainty due to inhomogeneity for the derived BET specific surface area is estimated to be 1.5 %. Standard uncertainties due to long-term (in)stability and inhomogeneity are given above and shall be included in uncertainty budget.

After investigation of homogeneity and stability, the homogenized material was shared in 25 glass bottles closed by metallic caps. Each contains about 25 g of the material. Five bottles were randomly selected from the set of 40 bottles and submitted to participants.

The samples were distributed to the participant by DHL on 07th November. All samples arrived at their destination without damage within twenty days. The dispatch dates and receipt dates are given in Table 7.

Table 7 Sample sent dates and report dates

Institute	Sample No.	Sample dispatch date	Date report sent
BAM	#03	07 November 2017	30 March 2018
TUBITAK-UME	#01	07 November 2017	30 March 2018
NIM	#02	07 November 2017	27 February 2018
NMIJ	#07	07 November 2017	06 March 2018
UNIIM	#09	07 November 2017	05 March 2018

5 INSTRUCTIONS TO PARTICIPANTS

The technical protocol was sent to each participant by e-mail. The technical protocol (appendix A) contained background information, timing of the comparison and information on the participating institutes. Information about sample preparation and recommended measurement conditions were also given.

Each participant used the gas adsorption method for the measurement of the specific adsorption nitrogen and/or krypton on a nonporous alumina sample to enable, in a next step, a traceable determination of the parameter Specific Surface Area (BET) following ISO 15901-2 [1] and ISO 9277 [2].

Some details about measurement procedure of the gas adsorption method were recommended**:**

- At least 5 replicate measurements on separate aliquots of SiO_2 were recommended. The minimum sample amount is about 5 g for each run.
- During sample pretreatment heat the sample for degassing in a vacuum (1-5) Pa with a rate of 5-10 ^{o}C/min to 150 ^{o}C, hold temperature at 150 ^{o}C for at least 0.5 hour. Afterwards, allow the sample to cool slowly back to ambient temperature.
- Measure the complete Isotherm (adsorption branch) at 77.3 K and specific adsorption of nitrogen/krypton at at P/Po=0.05 P/Po=0.20.
- First isotherm data point should be taken at P/Po=0.01, last adsorption isotherm data point should be taken at P/Po=0.30. In between data should be taken at least for P/Po=0.05 and 0.20 (non-ideal correction factor, equal to $0.464 \cdot 10^{-6}$ Pa^{-1} for nitrogen at 77.35 K, non-ideal correction factor, equal to $0.225 \cdot 10^{-6}$ Pa^{-1} for krypton at 77.35 K).
- Determine the BET specific surface area *S* using at least 10 isotherm data points at the adsorption branch of the isotherm within relative pressure range $0.05 \leq P/Po \leq 0.23$ (cross-selection area for the N_2 molecule in the monolayer: a_{N2} = 0.162 nm^2, cross selection area for the Kr molecule in the monolayer: a_{Kr} = 0.210 nm^2).

Participants were requested to provide the results for specific adsorption nitrogen and/or krypton and BET specific surface area for the nonporous SiO_2 test sample. The results must have been reported accompanied by 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 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 8 and Table 9.

Table 8 Details of sample pretreatment

Institute	Approx. sample mass, g	Sample pretreatment	Corrected for buoyancy
BAM	~ 5.0	Sample was heated for degassing in vacuum to 150℃, held at the temperature for 1,5 hours. Afterwards, the sample cooled slowly to ambient temperature.	no
TUBITAK-UME	~ 5.0	The samples were heated in a vacuum of 1.3 Pa with rate 10 °C/min to 150°C and kept at 150°C for 5 hours. Afterwards, the samples were cooled slowly back to ambient temperature. Weight loss by during the degassing process was 0.3% in average.	no
NIM	~ 5.0	Sample was heated for degassing in vacuum with the ramp rate of 10℃/min to 150℃ and then held for 2 hours to meet the outgas pressure rise less than 0.0067 Pa/min. Afterwards, the sample cooled slowly to ambient temperature.	no
NMIJ	~ 5.0	The sample was heated in a vacuum of (3–5) Pa with rate 12 °C/min to 150 °C and kept at 150 °C for 0.5 hours. Afterwards, it was cooled slowly back to the ambient temperature. Weight loss during the degassing process was 0.03 % in average.	no
UNIIM	~ 5.0	The sample was heated for degassing in a vacuum 1 Pa with rate 10 ^{o}C/min to 150 ^{o}C, the hold temperature at 150 ^{o}C for 1 hour. Afterwards, allow the sample to cool slowly back to ambient temperature. Weight loss during the degassing process was 0.08 % in average	yes

Table 9 Details of gas adsorption procedures used

Institute	Adsorbate	Type of instrument and producer	Traceability
BAM	N_2, Kr	ASAP 2020 Micromeritics, USA	CRM BAM P-101, CRM BAM P-102
TUBITAK-UME	Kr	Micromeritics 3FlexMicromeritics, USA	Calibration of instrument: XP205 Mettler Toledo from 0.01 mg to 220 g range. Uncertainty of mass was determined with U (L) = [0.000009 g + 2.8 x10^{-6} 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 ranges from 10 to 60 ° C, expanded uncertainty (k=2) 0.002 ºC.
NIM	N_2, Kr	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 data is traceable to national measurement standards. The volume of adsorbed Kr and N_2 gas is traceable to a 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.
NMIJ	N_2	BELSORP-mini II Microtrac	Balance, platinum resistance thermometer, pressure transducers, and dosing volume used to measure the specific adsorption were calibrated traceable to the International System of Units (SI). Specific surface area was determined by the multipoint BET method based on the traceable measurement of specific adsorption.
UNIIM	N_2, Kr	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 10.

Table 10 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), - repeatability measurement of the CRM BAM P-101, - repeatability measurement of the CRM BAM P-102, - deviation between certified value of the CRM BAM P-101 and arithmetic mean of measurement results of the CRM BAM P-101, deviation between certified value of the CRM BAM P-102 and arithmetic mean of measurement results of the CRM BAM P-102. **Type B** - uncertainty of certified value of the CRM BAM P-101, - uncertainty of certified value of the CRM BAM P-102, - uncertainty due to inhomogeneity of the sample, - uncertainty due to instability of the sample.
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, - uncertainty of fitting. **Type B** - uncertainties of measurement mass, temperature, pressure and volumes, - uncertainty due to inhomogeneity of the sample, - uncertainty due to instability of the sample.
NMIJ	+	**Type A** - repeatability measurement of the sample. - uncertainty of fitting. **Type B** - uncertainties of measurement mass, temperature, pressure and volumes, - uncertainty due to inhomogeneity of the sample, - uncertainty due to instability of the sample.
UNIIM	+	**Type A** - repeatability measurement of the sample, - uncertainty fitting, - uncertainty due to inhomogeneity of the sample, - uncertainty due to instability of the sample. **Type B** - mass of sample, temperature, pressure, volumes, molar volume of ideal gas. *- uncertainty for specific surface area 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

$$\bar{x}_u = \sum_{i=1}^{m} \frac{x_i / u(x_i)^2}{\sum_{i=1}^{m} 1/u(x_i)^2}, \quad (4)$$

$$\chi^2_{obs} = \sum_{i=1}^{m} \left(\frac{x_i - \bar{x}_u}{u(x_i)} \right)^2, \quad (5)$$

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

After calculations using formulas (4), (5) 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.

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 they were. Formulas for calculation are shown below.

Arithmetic mean

$$\bar{x} = \frac{1}{m} \sum_{i=1}^{m} x_i, \quad (6)$$

$$u^2(\bar{x}) = \frac{\sum_{i=1}^{m} (x_i - \bar{x})^2}{m(m-1)}, \quad (7)$$

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

Uncertainty-weighted mean

$$\bar{x}_u = \sum_{i=1}^{m} w_i x_i, \quad (8)$$

$$w_i = \frac{1/u^2(x_i)}{\sum_{i=1}^{m} 1/u^2(x_i)}, \quad (9)$$

$$\frac{1}{u^2(\bar{x}_u)} = \sum_{i=1}^{m} 1/u^2(x_i), \quad (10)$$

$$u_{corr}^2\left(\bar{x}_u\right)=\frac{\chi_{obs}^2}{m-1}u^2\left(\bar{x}_u\right)=\frac{\sum_{i=1}^{m}\left(\frac{x_i-\bar{x}_u}{u\left(x_i\right)}\right)^2}{m-1}u^2\left(\bar{x}_u\right), \quad (11)$$

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

Median

$$med\left(x\right)=\begin{Bmatrix}\frac{1}{2}\left(x'_{m/2}+x'_{m/2+1}\right), & even\ \ m\ \ even\\ x'_{(m+1)/2}, & m\ \ odd\end{Bmatrix}, \quad (12)$$

$$u^2\left(med\left(x\right)\right)=\frac{\pi}{2m}\hat{\sigma}^2, \quad (13)$$

$$\hat{\sigma}=1.483med\left(\left|d_i\right|\right), \quad (14)$$

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

7.3 KCRV for specific adsorption of Kr at P/Po=0.05

The reported values of the specific adsorption of Kr at P/Po=0.05 and the uncertainties of all results are summarized in Table 11. Estimations of KCRV have been obtained by different approaches (arithmetic mean, uncertainty weighted mean, median) and are presented in Table 10. The same results are displayed graphically in Figures 2 and 3.

The uncertainty-weighted mean was used for assessment of the KCRV because:

- $\chi_{obs}^2<\chi_{0.05,\mathrm{m}-1}^2$, in this case the data is mutually consistent,
- there are no extreme values,
- the uncertainties do not vary significantly.

Table 11 – Reported values of specific adsorption of krypton at P/Po=0.050 and uncertainties

№	NMI/DIS	Specific adsorption of Kr at P/Po=0.990, mol/kg	Combined standard uncertainty, u_c, mol/kg	Expanded uncertainty, U(k=2), mol/kg	di, mol/kg	U(di), mol/kg	Verdict
1	UNIIM	0.00480	0.00047	0.00094	-0.00011	0.00077	+
2	TUBITAK-UME	0.00488	0.00034	0.00067	-0.00003	0.00039	+
3	BAM	0.00489	0.00039	0.00077	-0.00002	0.00055	+
4	NIM	0.00505	0.00040	0.00080	0.00014	0.00059	+
Median		0.00489	0.00004	0.00008			
Mean		0.00491	0.00005	0.00010			
Uncertainty weighted mean		**0.00491**	0.00005	0.00010	**KCRV**		
Consistency test					**Conclusion**		
χ_{obs}^2		$\chi_{0.05,\mathrm{m}-1}^2$		*m*	$\chi_{obs}^2<\chi_{0.05,\mathrm{m}-1}^2$		
0.19		7.81		4	**consistent**		

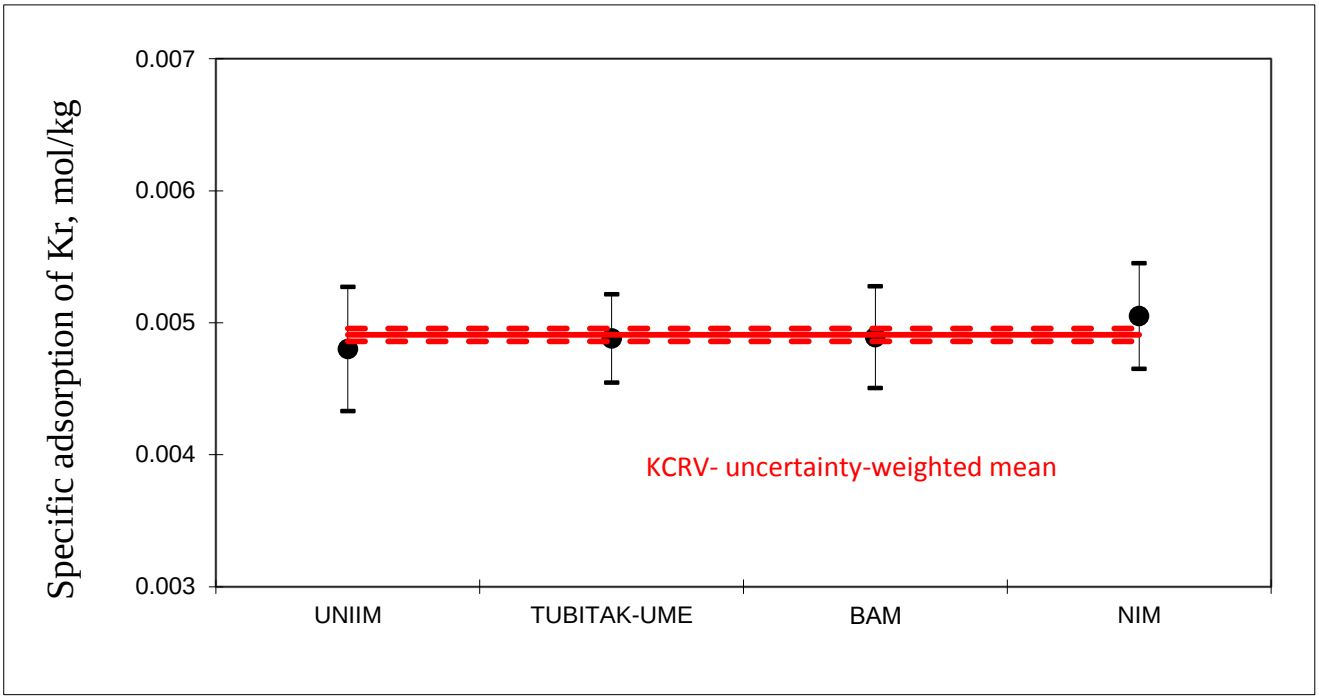

Figure 2 KCRV for specific adsorption of Kr on nonporous silica. Error bars show standard uncertainty. The solid and horizontal line is the KCRV, the dashed lines show upper and lower limits of the corresponding standard uncertainty, respectively.

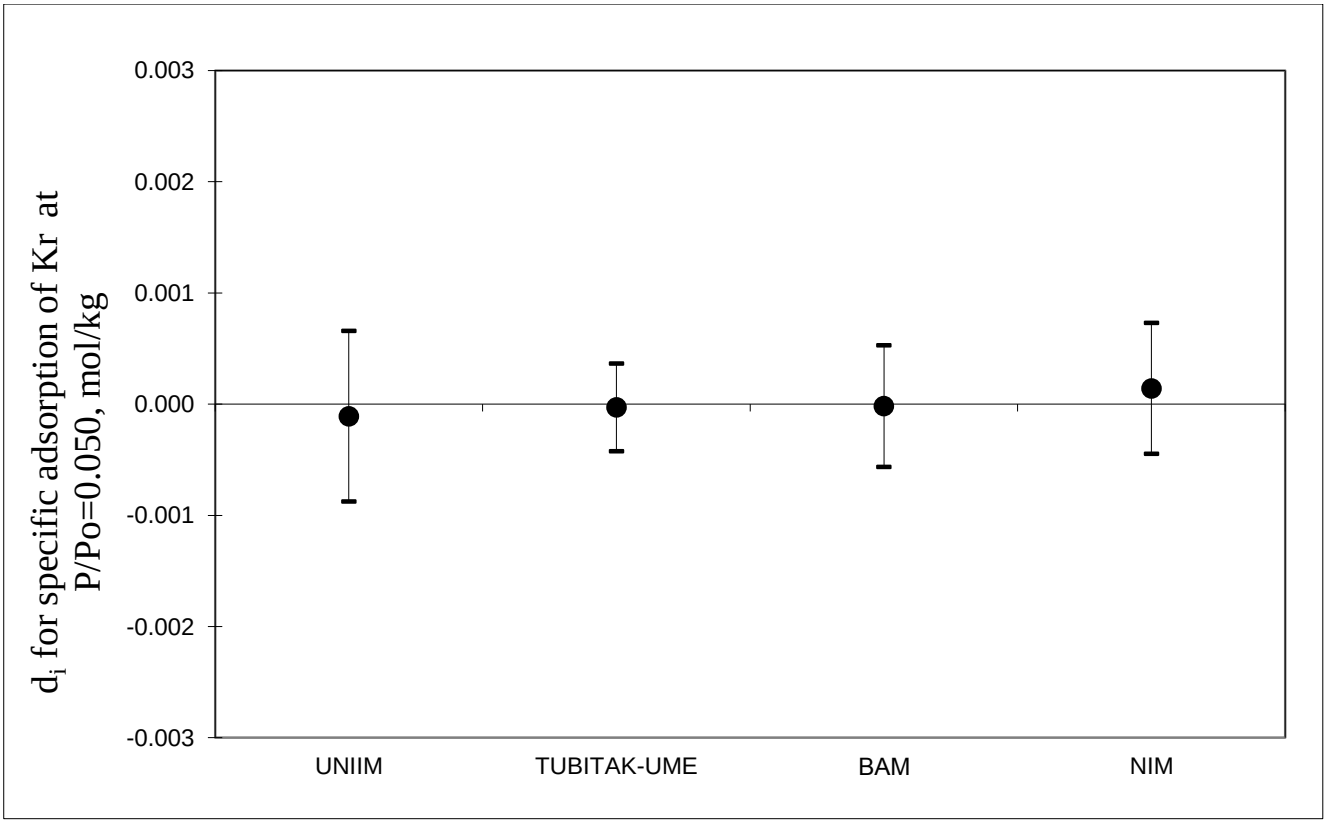

Figure 3 Degrees of equivalence d_i and expanded uncertainty $U(d_i)$ (k=2) for specific adsorption of Kr on nonporous silica

7.4 KCRV for specific adsorption of Kr at P/Po=0.200

The reported values of the specific adsorption of Kr at P/Po=0.200 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 4 and 5.

The uncertainty-weighted mean was used for assessment of the KCRV because:

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

Table 12 – Reported values of specific adsorption of krypton at P/Po=0.200 and uncertainties

№	NMI/DIS	Specific adsorption of Kr at P/Po=0.200, mol/kg	Combined standard uncertainty, u_c, mol/kg	Expanded uncertainty, U(k=2), mol/kg	di, mol/kg	U(di), mol/kg	Verdict
1	TUBITAK-UME	0.00740	0.00034	0.00067	-0.00015	0.00038	+
2	BAM	0.00759	0.00039	0.00078	0.00004	0.00055	+
3	NIM	0.00767	0.00040	0.00080	0.00012	0.00058	+
4	UNIIM	0.00770	0.00060	0.00120	0.00015	0.00107	+
Median		0.00763	0.000033	0.00007			
Mean		0.00759	0.000067	0.00013			
Uncertainty weighted mean		**0.00755**	**0.000074**	**0.00015**	**KCRV**		
Consistency test					**Conclusion**		
χ^2_{obs}		$\chi^2_{0.05,m-1}$		m	$\chi^2_{obs} < \chi^2_{0.05,m-1}$		
0.36		7.81		4	**consistent**		

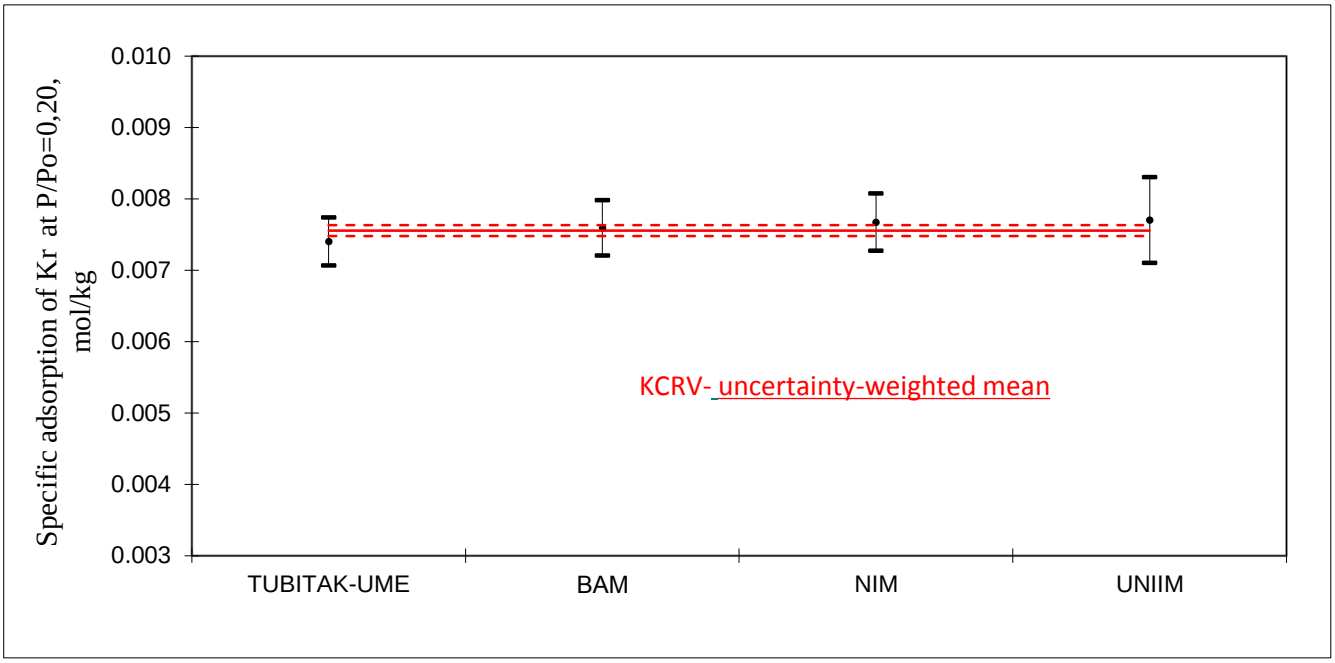

Figure 4 KCRV for specific adsorption of Kr on nonporous silica. Error bars show standard uncertainty. The solid and horizontal line is the KCRV, the dashed lines show upper and lower limits of the corresponding standard uncertainty, respectively.

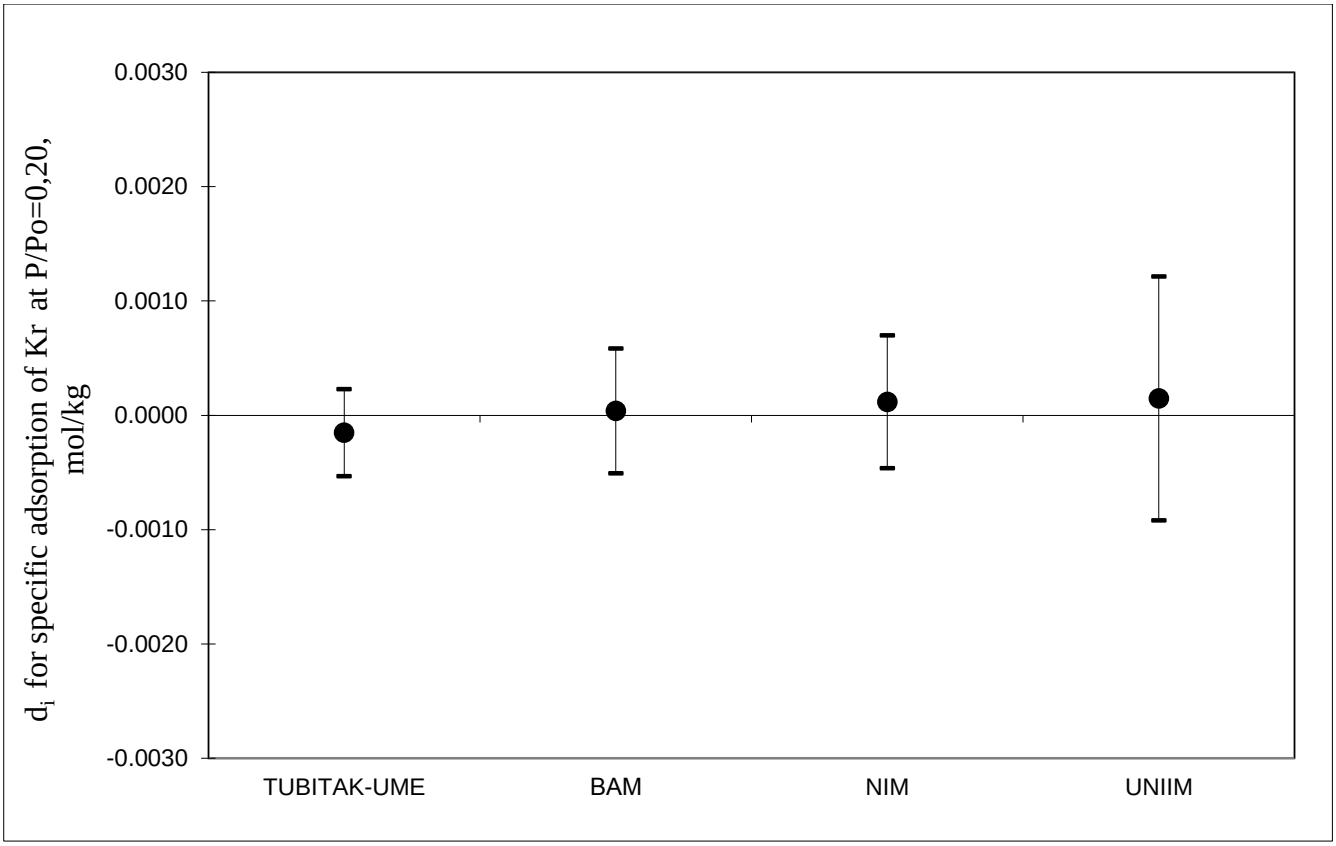

Figure 5 Degrees of equivalence d_i and expanded uncertainty $U（d_i）$ (k=2) for specific adsorption of Kr on nonporous silica

7.5 KCRV for specific adsorption of N_2 at P/Po=0.050

The reported values of the specific adsorption of nitrogen at P/Po=0.050 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 12. The same results are displayed graphically in Figures 6 and 7.

The uncertainty-weighted mean was used for assessment of the KCRV because:

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

Table 13 – Reported values of specific adsorption of nitrogen at P/Po=0.050 and uncertainties

№	NMI/DIS	Specific adsorption of nitrogen at P/Po=0.050, mol/kg	Combined standard uncertainty, u_c, mol/kg	Expanded uncertainty, U(k=2), mol/kg	di, mol/kg	U(di), mol/kg	Verdict
1	BAM	0.00783	0.00038	0.00077	-0.00025	0.00059	+
2	NIM	0.00803	0.00044	0.00088	-0.00005	0.00073	+
3	UNIIM	0.00810	0.00035	0.00070	0.00002	0.00050	+
4	NMIJ	0.00830	0.00035	0.00070	0.00022	0.00050	+
	median	0.00807	0.00012	0.00025			
	mean	0.00807	0.00010	0.00019			
	weighted mean	**0.00808**	**0,00010**	**0,00020**	**KCRV**		
Consistency test					**Conclusion**		
χ^2_{obs}		$\chi^2_{0.05,m-1}$		m	$\chi^2_{obs} < \chi^2_{0.05,m-1}$		
0.83		7.81		4	**consistent**		

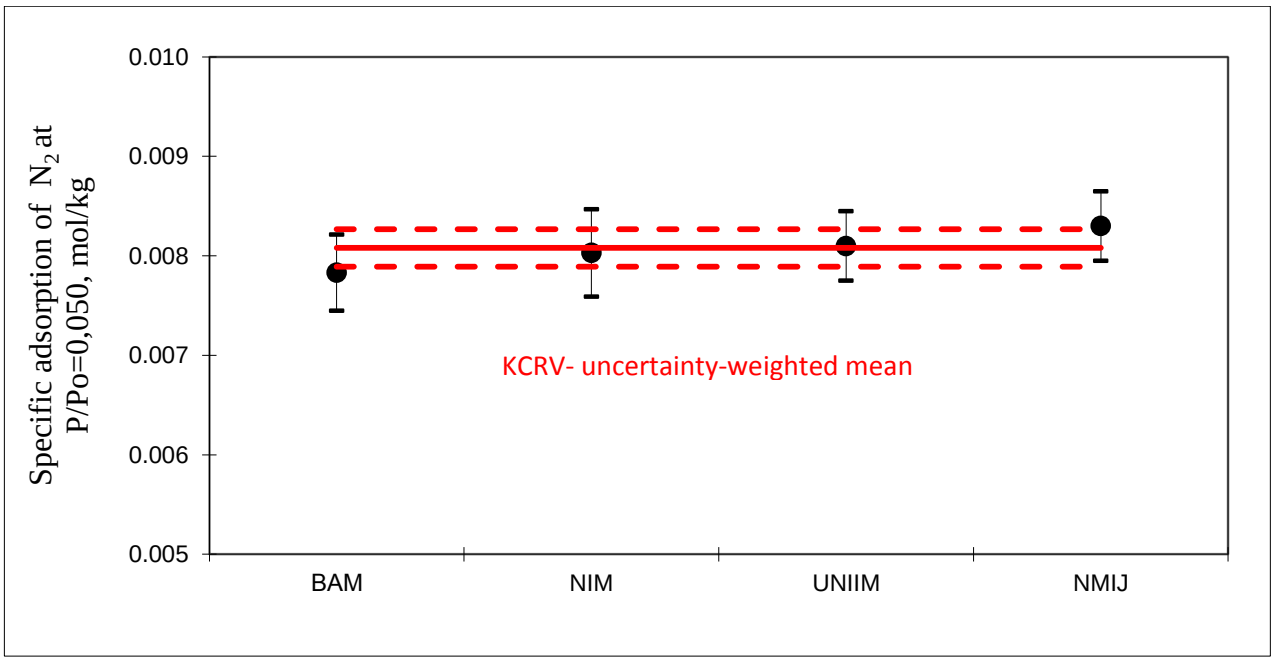

Figure 6 KCRV for specific adsorption of N_2 on nonporous silica. Error bars show standard uncertainty. The solid and horizontal line is the KCRV, the dashed lines show upper and lower limits of the corresponding standard uncertainty, respectively.

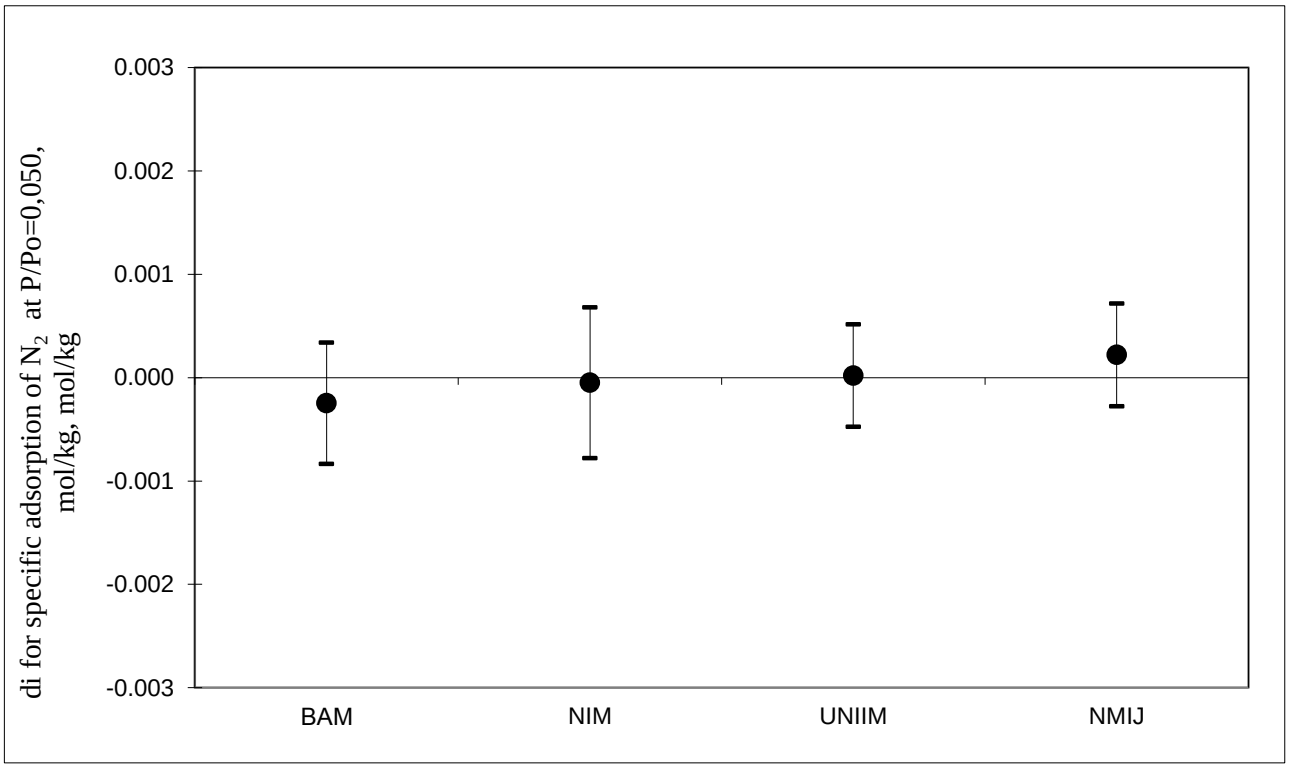

Figure 7 Degrees of equivalence d_i and expanded uncertainty $U（d_i）$ (k=2) for specific adsorption of N_2 on nonporous silica

7.6 KCRV for specific adsorption of N_2 at P/Po=0.200

The reported values of the specific adsorption of nitrogen at P/Po=0.200 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. The same results are displayed graphically in Figures 8 and 9.

The uncertainty-weighted mean was used for assessment of the KCRV because:

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

Table 14 – Reported values of specific adsorption of nitrogen at P/Po=0.200 and uncertainties

№	NMI/DIS	Specific adsorption of nitrogen at P/Po=0.200, mol/kg	Combined standard uncertainty, u_c, mol/kg	Expanded uncertainty, U(k=2), mol/kg	di, mol/kg	U(di), mol/kg	Verdict
1	UNIIM	0.01040	0.00040	0.00080	-0.00027	0.00059	+
2	BAM	0.01070	0.00042	0.00085	0.00003	0.00065	+
3	NIM	0.01077	0.00048	0.00096	0.00010	0.00079	+
4	NMIJ	0.01080	0.00035	0.00070	0.00013	0.00044	+
	median	0.01074	0.00005	0.00009			
	mean	0.01067	0.00010	0.00020			
	weighted mean	**0.01067**	**0.00009**	**0.00019**	**KCRV**		
Consistency test					**Conclusion**		
χ^2_{obs}		$\chi^2_{0.05,m-1}$		m	$\chi^2_{obs} < \chi^2_{0.05,m-1}$		
0.64		7.81		4	**consistent**		

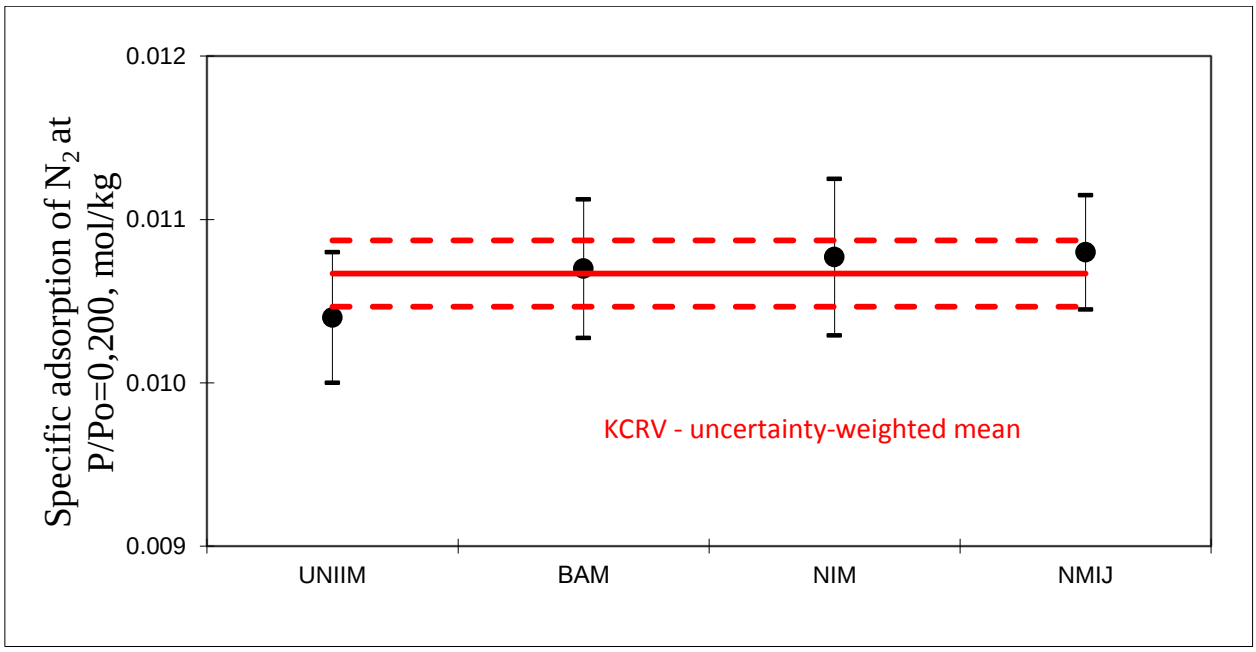

Figure 8 KCRV for specific adsorption of N_2 on nonporous silica. Error bars show standard uncertainty. The solid and horizontal line is the KCRV, the dashed lines show upper and lower limits of the corresponding standard uncertainty, respectively.

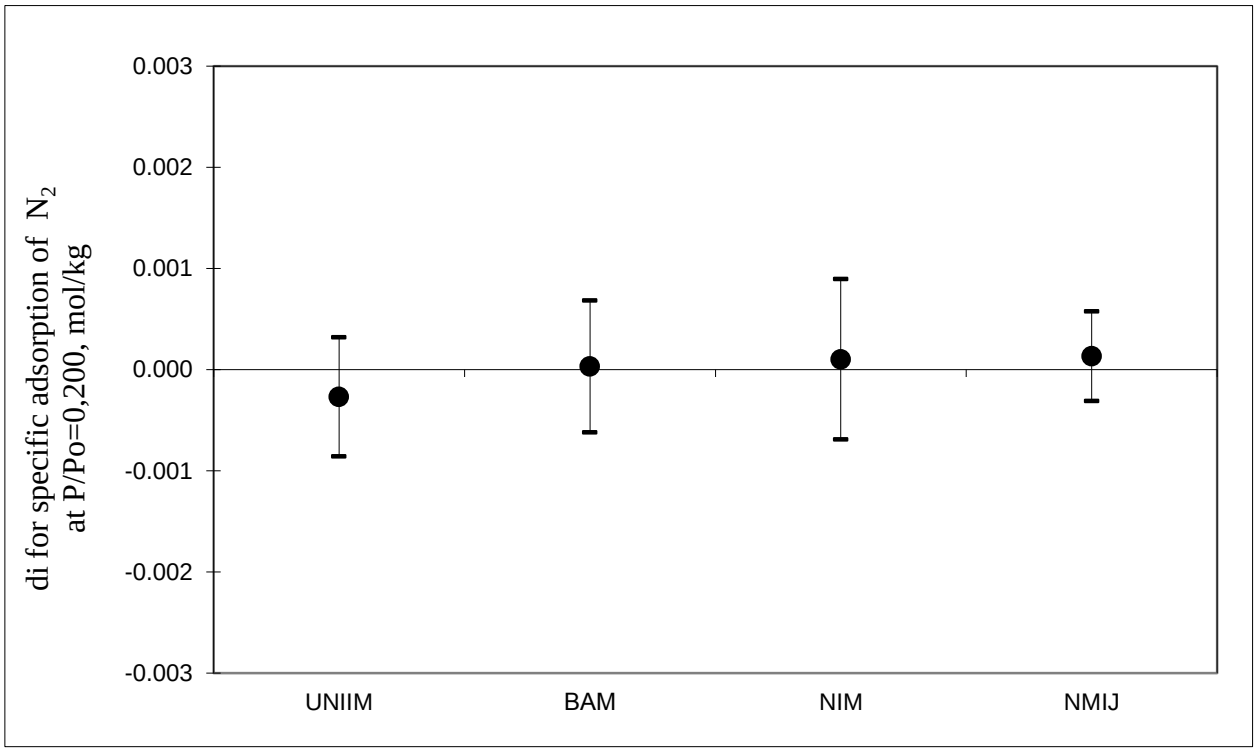

Figure 9 Degrees of equivalence d_i and expanded uncertainty $U（d_i）$ (k=2) for specific adsorption of N_2 on nonporous silica

7.7 Reference value for BET specific surface area as derived from measurement of specific adsorption of N_2 and Kr

The reported values of BET specific surface area and the uncertainties of all results are summarized in Table 15. Estimations of reference values (RV) have been obtained by different approaches (arithmetic mean, uncertainty weighted mean, median) are presented in Table 15. The same results are displayed graphically in Figures 10 and 11.

The uncertainty-weighted mean was used for assessment of the RV because:

- $\chi^2_{obs} < \chi^2_{0.05,m-1}$, in this case the data is mutually consistent,
- there are no extreme values,
- the uncertainties are varying significantly.

All results of participants are agreed, but comparing the results of BET specific surface area using N_2 and Kr as adsorbates the following issues have to be mentioned:

- the uncertainties for the results of BET specific surface area are smaller when krypton used as adsorbate in comparison with the nitrogen case. The reason here is that in the measurements using krypton a much higher value of saturation pressure was used.

Table 15 – Reported values of BET specific surface area and uncertainties

№	Adsorbat	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
1	Kr	UNIIM (Kr)	0.808	0.027	0.054	-0.023	0.051	+
2	Kr	TUBITAK-UME (Kr)	0.815	0.022	0.045	-0.017	0.041	+
3	Kr	BAM (Kr)	0.834	0.010	0.019	0.003	0.006	+
4	Kr	NIM (Kr)	0.838	0.025	0.050	0.007	0.047	+
5	N2	UNIIM (N2)	0.819	0.024	0.048	-0.012	0.044	+
6	N2	NIM (N2)	0.857	0.036	0.072	0.026	0.070	+
7	N2	NMIJ (N2)	0.860	0.055	0.110	0.029	0.109	+
8	N2	BAM (N2)	0.869	0.055	0.110	0.038	0.108	+
		median	0.836	0.014	0.028			
		mean	0.837	0.008	0.016			
		weighted mean	**0.831**	**0.005**	**0.009**	**RV**		

Consistency test			**Conclusion**
χ^2_{obs}	$\chi^2_{0.05,m-1}$	m	$\chi^2_{obs} < \chi^2_{0.05,m-1}$
2.97	**14.07**	**7**	**consistent**

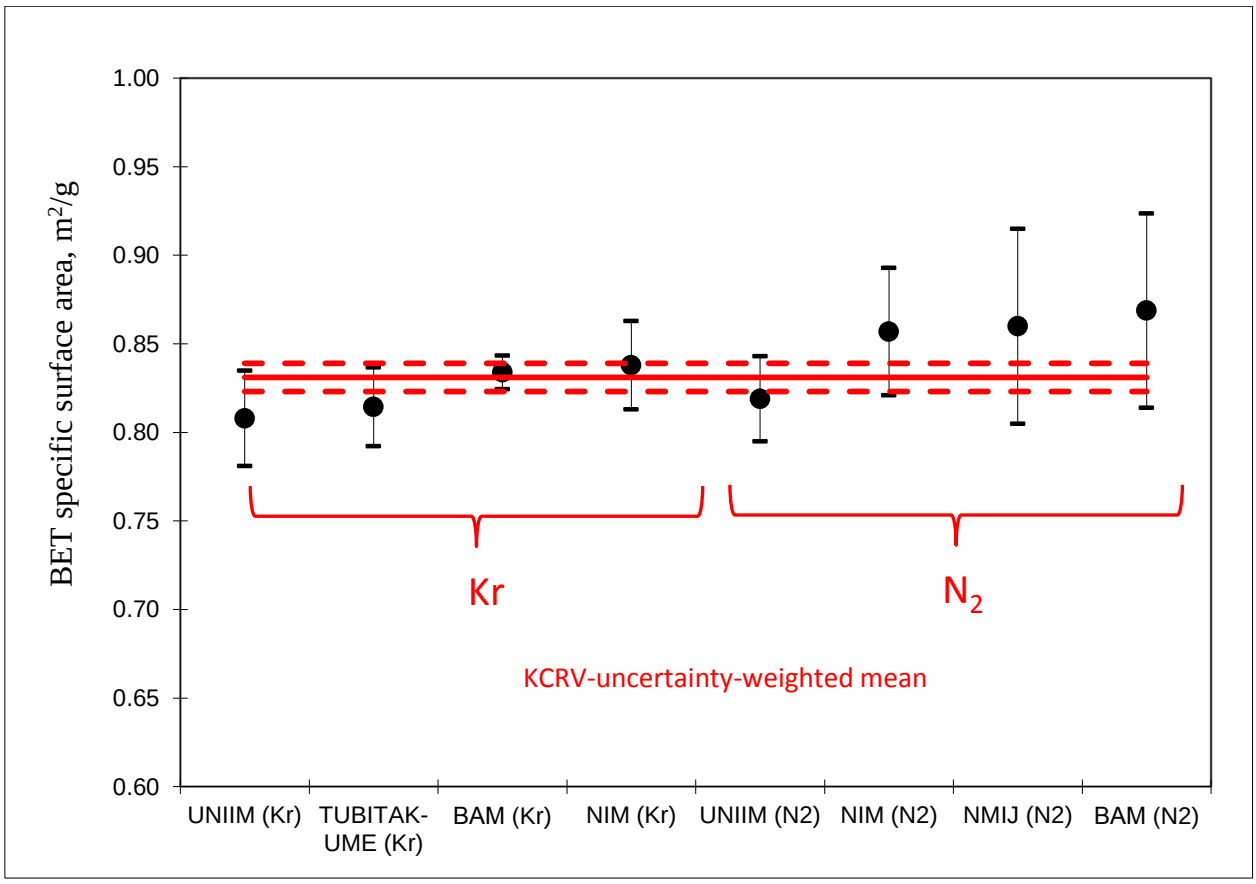

Figure 10 BET specific surface area derived from measurement of Kr and N_2 specific adsorption data. Error bars show standard uncertainty. The solid and horizontal line is the RV, the dashed lines show upper and lower limits of the corresponding standard uncertainty, respectively.

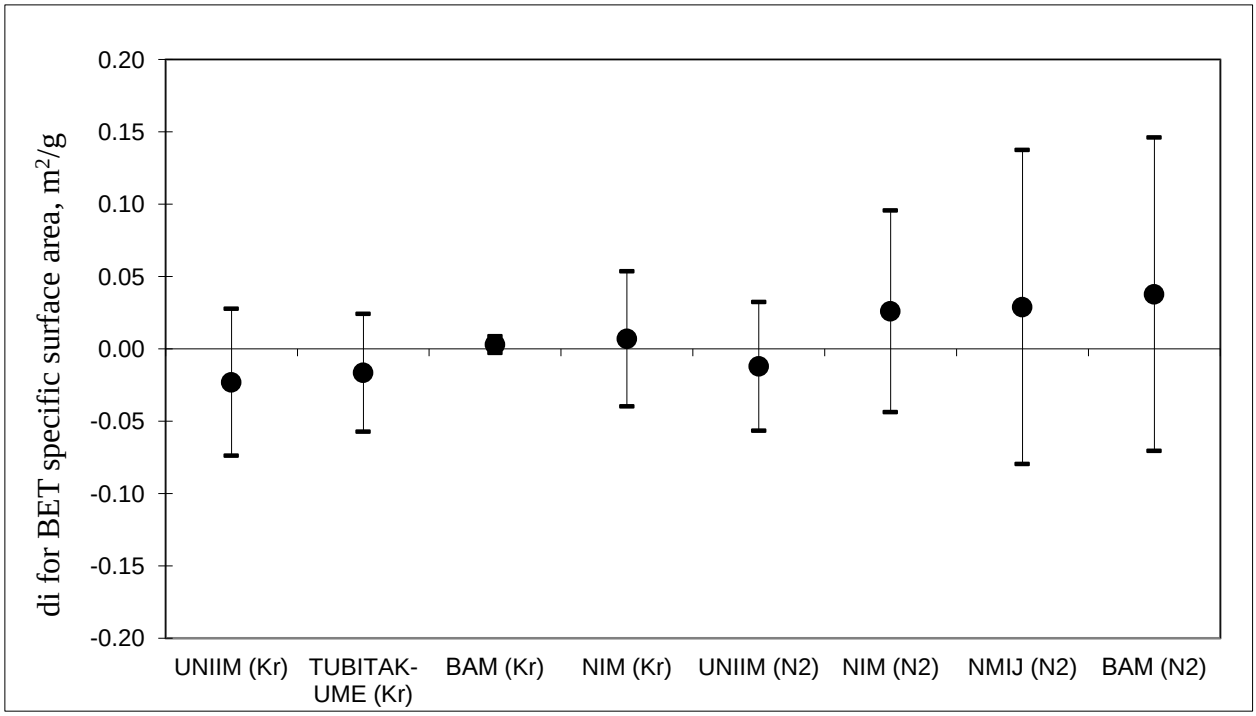

Figure 11 Degrees of equivalence d_i and expanded uncertainty $U(d_i)$ (k=2)

7.8 Discussion

The key comparison CCQM K-153 has demonstrated very good agreement between the five participating NMIs/DIs concerning the primary measurands of the KC, the specific nitrogen and krypton adsorption at non-porous silica at liquid nitrogen temperature.

Derived from specific adsorption data the BET specific surface area of non-porous silica was determined as a secondary measurand following ISO 9277. It turned out that all the results for the BET specific surface submitted by participants agreed within their uncertainties. Comparing the results of BET specific surface area using N_2 and Kr as adsorbates we observed that the uncertainties for the results of BET specific surface area are quite smaller when krypton is used as adsorbate.

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:

$$d_i = x_i - x_{ref}\,, \tag{15}$$

$$U\left(d_i\right) = 2\sqrt{\left(u\left(x_i\right)^2 + u\left(x_{ref}\right)^2 - 2\,\mathrm{cov}\left(x_i, x_{ref}\right)\right)}\,, \tag{16}$$

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 $\mathrm{cov}\left(x_i, x_{ref}\right)$.

Weighted mean was chosen as KCRV in this key comparison CCQM-K153. In this case U (d_i) has been calculated using the following equation:

$$\begin{aligned} U\left(d_i\right) &= 2\sqrt{u\left(x_i\right)^2 + u_{corr}^2\left(\bar{x}_u\right) - 2w_i u\left(x_i\right)^2} = \\ &= 2\sqrt{u_{corr}^2\left(\bar{x}_u\right) + (1-2w_i)u\left(x_i\right)^2} \end{aligned}\,, \tag{17}$$

The equivalence statements for CCQM-K153 are given in Table 11-15 and Figures 3, 5, 7, 9 and 11.

9 CONCLUSIONS

Good agreement between the participating laboratories for a measurement of specific nitrogen krypton adsorption at liquid nitrogen temperature were obtained. Data were used to determine a second, derived measurand, the BET specific surface area of nonporous substances. The uncertainty-weighted mean of all results is used for the KCRV. The suitability of the gas adsorption method for determination of BET specific surface area of nonporous solid substances in advanced technology has been demonstrated. It seems that for a measurement of the BET specific surface area Krypton as the adsorbate delivers more precise results.

10 HOW FAR THE LIGHT SHINES STATEMENT

Successful participation in the key comparisons CCQM-K153 can support CMCs for the measurement of the specific adsorption of nitrogen/krypton in the 0.0001-0.1 mol/kg range and eventually (depends on the decision of CCQM on a coverage of the BET measurand in its portfolio in the future) also those for the secondary (derived) measurand, the BET specific surface area, for numbers less than 1 m^2/g for non-porous silicon dioxide as well as other similar non-porous substances.

Key comparison CCQM-K153 cannot used to underpin CMCs for microporous materials.

11 ACKNOWLEDGEMENTS

UNIIM gratefully acknowledges the help and collaboration from BAM, especially thanks are due to Dr. Wolfgang Unger from BAM. Many thanks to all of the colleagues from the participant institutes for all their efforts.

12 REFERENCES

1. ISO 15901-2:2006 Pore size distribution and porosity of solid materials by mercury porosimetry and gas adsorption – Part 2: Analysis of mesopores and macropores by gas adsorption International Organization for Standardization, Geneva (2006).
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Appendix A – Technical Protocol
CCQM-K153
Measurement of Specific Adsorption A [mol/kg] of N2 and Kr on nonporous SiO_2 at LN temperature
(to enable a traceable determination of the Specific Surface (BET) following ISO 9277)
Technical protocol

1. Introduction

BET specific surface area of nonporous solids is a highly relevant parameter because it is often used for specification of a vast majority of materials and substances (ceramic, cement, catalysts, etc) used in advanced technology. From the point of view of metrology BET specific surface area is a secondary measurand because it relies on a convention. It is calculated using primary data, the specific adsorption of an amount of gas, which is measured in terms of the relative pressure of this gas in a volume containing the sample.

To check the comparability of measurement protocols at NMIs and DIs addressing the BET specific surface of technologically relevant nonporous solids a Key comparison is launched by the Surface Analysis Working Group at CCQM/BIPM. The comparison is being carried out for the purpose to enable participating NMIs and DIs to claim CMCs as detailed in table 1.

Table 1 Layout of CMC claims to be underpinned by key comparison CCQM-K153

Meas. Serv. Category	Matrix	Measurand		Dissemination Range of Measurement Capability			Range of Expanded Uncertainties as Disseminated				Adsorbat
		Analyte or component	Quantity	From	To	Unit	From	To	Unit	Cov. factor	
Advanced Materials	Silicon dioxide	Silicon dioxide	Specific adsorption of krypton	0.001	0.05	mol/kg			mol/kg	2	**Kr**
Advanced Materials	Silicon dioxide	Silicon dioxide	Specific adsorption of nitrogen	0.001	0.05	mol/kg			mol/kg	2	**N_2**

2. Measurand and reporting

The primary measurand in CCQM-K 153 is the specific adsorption of krypton or nitrogen on nonporous SiO_2 at liquid nitrogen temperature. Derived from that data the secondary measurand is the BET specific surface area of SiO_2.

Each participant shall report the results for the values of the specific adsorption of krypton or (and) nitrogen BET specific surface area of SiO_2 according to table 3.

The standard uncertainty due to long-term (in)stability for specific adsorption of krypton and nitrogen is 0.00022 mol/kg. The standard uncertainty due to inhomogeneity for specific adsorption of krypton and nitrogen is 0.00025 mol/kg. Both standard uncertainties have been determined by the pilot lab.

The results shall 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. It is recommended to study the two documents in the attachment addressing uncertainties in BET specific surface area [5, 6].

Standard uncertainties due to long-term (in)stability and inhomogeneity are given above and shall be included in uncertainty budget). In addition, the report should include all technical details on the measurement procedure, traceability links (as calibrations) and uncertainty

contributions. Each report shall include tabular reports and graphs for the isotherm (dependence of specific adsorption from relative pressure) and for the BET calculation.

3. Guidance values and target uncertainty

Analyte/matrix: The test material used for the comparisons is nonporous SiO_2. The ranges of specific adsorption of krypton/nitrogen and BET specific surface area and the target uncertainty are shown in table 2.

Table 2

Quantity	Measurand	Range	Target relative expanded uncertainty
Specific adsorption of krypton at P/Po=0.05*	Primary	(0.001-0.05) mol/kg	(4-10) %
Specific adsorption of krypton at P/Po=0.20*	Primary		
Specific adsorption of nitrogen at P/Po=0.05*	Primary		
Specific adsorption of nitrogen at P/Po=0.20*	Primary		
BET specific surface area**	Secondary	(0.2-2.0) m^2/g	

** it is a primary information from an instrument. If relative pressure is not exactly equal to 0,05 or 0,20 please calculate specific adsorption using linear interpolation;*

****** *BET specific surface area can be considered as an optional measurand.* The relative standard uncertainty due to long-term (in)stability for BET specific surface area is 1.0 %. The relative standard uncertainty due to inhomogeneity for BET specific surface area is 1.5 %.

Table 3

№	P/Po	A, mol/kg	U(k=2), mol/kg
1			
…			
n			

4. KCRVs

- The processing of measurement results of specific adsorption of krypton/nitrogen and BET specific surface area submitted 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: 10, Date 2013-04-12, Released for reference)
- 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 shall use the gas adsorption method for the measurement of the BET specific surface area of SiO_2 as defined in ISO 15901-2 [3] and ISO 9277 [4]. Kr and N_2 can be used as adsorbates, but Kr is more appropriate. Details about measurement procedure of gas adsorption method are:

Replications

Please perform at least 5 replicate measurements on separate aliquots of SiO_2. The recommend minimum sample amount is about 5 grams for each run

Sample pretreatment

Heat the sample SiO_2 for degassing in a vacuum (1-5) Pa with rate (5-10) ^oC/min to 150 ^oC, the hold temperature at 150 ^oC for at least 0.5 hour. Afterwards, allow the sample to cool slowly back to ambient temperature.

Measurement of the complete Isotherm (adsorption branch) at 77.3 K and specific adsorption of nitrogen/krypton at at P/Po=0.05 P/Po=0.20.

First isotherm data point should be taken at P/Po=0.01, last adsorption isotherm data point should be taken at P/Po=0.30. In intermediate adsorption isotherm data point should be taken at least P/Po=0.05; 0.20 (non-ideal correction factor, equal to $0.464 \cdot 10^{-6}$ Pa^{-1} for nitrogen at 77.35 K, non-ideal correction factor, equal to $0.225 \cdot 10^{-6}$ Pa^{-1} for krypton at 77.35 K).

BET specific surface area

Determine the BET specific surface area *S* using at least 10 isotherm data points at the adsorption branch of the isotherm within relative pressure range $0.05 \leq P/Po \leq 0.23$ (cross selection area for the N_2 molecule in the monolayer: a_{N2} = 0.162 nm^2, cross selection area for the Kr molecule in the monolayer: a_{Kr} = 0.210 nm^2).

6. Time schedule

call for participants:	by end of September 2017
latest registration of participant:	by end of October 2017 (updated)
latest arrival of samples at participants:	by end of November 2017
latest report of results:	25 March 2018
report A:	by end of June 2018
report B:	by end of August 2018

7. Sample

A bottle will contain about 25 g of SiO_2.

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

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