BET Specific Surface Area of Porous SiO_2
UME CRM 1503

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ABBREVIATIONS

BET	Brunauer-Emmett-Teller
T_{STD}	Gas temperature in the system volume
P_{STD}	Atmospheric pressure
P/P_0	Relative pressure
σ_{N2},	Cross section of N_2 molecule
N_A	Avagadro's constant
n_a	Number of atoms per unit area
A_{BET}	BET specific surface area
ISO	International Standardization Organization
$MS_{between}$	Mean Square Between Units ANOVA
MS_{within}	Mean Square Within Units ANOVA
n	Number of repetitions within the unit
RSD	Relative standard deviation
s	Standard deviation
s_{bb}	Standard deviation between units
SI	International System of Units
SGT	Single Grubbs' Test
u_{bb}	Standard uncertainty related to a possible between-unit inhomogeneity
u^*_{bb}	Standard uncertainty related to a maximum between-unit inhomogeneity that could be hidden by method repeatability
u_{char}	Standard uncertainty of the material characterisation
$u_{char,rel}$	Relative standard uncertainty due to characterization
UDK	Long term stability
u_{lts}	Standard uncertainty due to long-term stability
$u_{lts,rel}$	Relative standard uncertainty due to long-term stability
u_{rect}	Standard uncertainty of inter-unit heterogeneity modeled by a rectangular distribution
$u_{rect,rel}$	Relative standard uncertainty of inter-unit heterogeneity modeled with a rectangular distribution
u_{sts}	Standard uncertainty due to short-term stability
$u_{sts,rel}$	Relative standard uncertainty due to short term stability
$v_{MSwithin}$	MS_{within} degrees of freedom

ABSTRACT

The use of Certified Reference Material (CRM) as one of the means of providing traceability contributes to the increase of measurement quality. Solid materials that are of great importance in daily life, science and industrial uses, such as polymers, ceramics, mineral and mineral products, sintered materials, building materials, catalysts, ion exchange resins, activated carbon, zeolite pharmaceutical raw materials, metallurgical powders and abrasives. The BET device is used to determine the pore size and distribution at high and low pressures by physical adsorption method in powder or solid samples containing micro, meso or macro-sized pores.

This report includes the details of production of BET specific surface area of the porous silicon dioxide (SiO_2) material according to ISO 17034: 2016, including the production process, certification of the UME CRM 1503 CRM and the other details of the work done within the process. This process consists of sample preparation, homogeneity test, short and long term stability tests, characterization and value assignment stages. In this report, the findings from the mentioned stages, statistical evaluations are presented as well as results and measurement uncertainties associated with these results which were determined in accordance with ISO Guide 35:2017. The certified value and uncertainty were determined by fulfilling the requirements of the relevant guides and calculated according to the measurement uncertainty guideline (GUM).

INTRODUCTION

Regarding the specific area of study, it is important to determine the resistance of the material against external forces such as surface properties, particle size, temperature, pressure and the ambient atmosphere after the chemical synthesis of the desired material. While different methods and devices are used to determine the physical properties of these materials, SEM (scanning electron microscope), AFM (atomic force microscope), solid NMR (nuclear magnetic resonance), TGA (Thermogravimetric analysis), XRD (X-ray diffraction distribution) and BET (Surface area measuring device) are the most used devices. Together with the appropriate device to be used for the determination of the properties of the material, the measurement accuracy, precision and repeatability of the device are of great importance in the evaluation of the results to be obtained. For the reliability of the results, the device should be checked periodically with appropriate CRM and RMs to assure the quality and suitability of the analysis results.

This report includes the production of the BET specific surface area of the porous silicon dioxide (SiO_2) material according to ISO 17034:2016 [1], including the production process, certification of the UME CRM 1503 CRM and the details of the work done in this process. This process consists of sample preparation, homogeneity test, short and long term stability tests, characterization and value assignment stages. In this report, the findings from UME CRM 1503 production stages, statistical evaluations in accordance with ISO Guide 35:2017 [2] are presented. Uncertainties were determined by fulfilling the requirements of the relevant guides and calculated according to the measurement uncertainty guideline (GUM) [3].

With the BET device, samples from ceramics, adsorbents, activated carbon, catalysts, paint and coating products, implants, geological samples, electronics and cosmetics industries can be analyzed. Using the BET method, the size of the surface area is determined with physical adsorption isotherm data. This determination includes two steps. In the first step, it is necessary to construct the BET point and derive the monolayer capacity (nm) from it. In the second step, the detailed surface area is calculated and the average area (A) information for each molecule in the completed monolayer (nm) is determined. Gas adsorption has become one of the most used methods to determine the surface area and pore size distributions of powder and porous materials [7]. "Nitrogen adsorption" is accepted as a method for mesopore size analysis. The total volume of pores in one gram of solid is called the specific pore volume, and the total surface of the walls possessed by these pores is called the specific surface area. As the pores become smaller, the number of walls will increase, and the specific surface area will also increase. That is, the size of the specific surface area depends on the size of the pores rather than the size of the specific pore volume. The size distribution of the pores is called the pore size distribution of the adsorber. The adsorption power of a solid varies depending on the nature of this solid as well as its specific surface area, specific pore volume and pore size distribution. Most of the methods used to measure the surface areas of porous solids and powders rely on the adsorption measurement. Adsorption properties such as specific pore volume, specific surface area and pore size distribution are determined by evaluating the adsorption isotherms of nitrogen at 77 K.

BET instruments are used in many research laboratories in universities and in many factories. A new certified reference material production project has been carried out under the name of UME CRM 1503, considering the production of reference and certified reference materials, which are common needs of users, to be able to control their analysis accurately.

Availability of appropriate certified reference materials is a problem for both validation of applied methods and traceability of measurement results and accuracy. Within the scope of the project, the BET specific surface area of the porous powder silicon dioxide material was certified. In this report, the production and certification processes of the UME CRM 1503 SRM are presented, as well as information about the data of the studies, used techniques and statistical analysis are given in detail.

PARTICIPANTS

All production and certification stages of UME CRM 1503 have been performed at TÜBİTAK UME except the characterization study. Participant information and their contribution are presented in Table 1.

Table 1. Participating organizations and definition of the work

Activity	Laboratory / Organization
Project management and data evaluation Processing Homogeneity study Stability studies	TÜBİTAK UME, Ulusal Metroloji Enstitüsü, Gebze - Kocaeli, TÜRKİYE
Characterization study	TÜBİTAK UME, Ulusal Metroloji Enstitüsü, Gebze - Kocaeli, TÜRKİYE Ural Research Institute for Metrology (UNIIM), Krasnoarmeyskaya Ulitsa, 4, Yekaterinburg, Sverdlovsk Oblast, 620000, RUSSIA

MATERIAL PROCESSING

The porous silicon dioxide solid powder (Merck, 1.07730.5000, Germany) was supplied as raw material. The product was homogenized by mixing in a 3-D mixer (WAB, T10-B, Switzerland). All equipment contacting with the product were cleaned against the risk of contamination. A total of 3 kg of silicon dioxide was placed in the tank, paying attention to leave enough space (at least 30% empty volume) to allow it to mix easily. The powder material was attached to the 3-D mixer with a 5 liter capacity tank lock system. Stirring was carried out in a 3-D mixer for not less than four hours. The material was filled into amber colored glass bottles in 5 g using a precision filling device (MCPI, FD-SPA-4A, France). After filling, plastic screw caps immediately sealed, labeled in order of bottles filling (Farmatek, Türkiye) certification and monitoring units after certification and reserves were separated total 500 units was stored at +4 °C.

HOMOGENEITY

In accordance with the ISO Guide 35 [2], 10 units were randomly chosen by random stratified sampling method to represent the whole batch in order to assess the homogeneity in the production of porous SiO_2 CRM.

Determination of homogeneity has been reported with the BET instrument measurement results. The quality control of the measurements was carried out using the BAM-P108 reference material.

In the BET measurements for homogeneity determination, analyzes were carried out under repeatability conditions, with the same operator on the same device, in succession. The analyzes could not be completed on the same day because of the fact that the analysis time was 18 hours, four repeated measurements were made from each unit, and the total number of units was 10.

The statistical analysis defined in ISO Guide 35 can only be applied to data with a normal distribution. All results (all replicate measurement data) obtained while creating the chart were used. The data are presented in Annex 1. Using the data, histogram diagrams and normal probability distribution curves, it was visually checked whether all data followed a single-peaked (normal) distribution, and no trends were found due to filling and measurement sequence during analysis. In addition, the data show a unimodal distribution (Annex 1, Figure A1).

In order to determine whether there is an outlier in the data group, the results were checked with the Grubbs test between the bottles and within the bottle, and it was observed that there was no contradictory data. In the analyzes, it was checked whether there was a trend (drift) caused by the device. Repeat measurements with a sample were analyzed using the *t*-test to distinguish whether the deviation in the measurement result was due to a bias of the device or the inhomogeneity of the sample. Based on these results, it was determined that there was no trend due to analytical and filling sequence (Table 2).

Table 2. Statistical evaluation of homogeneity data for UME CRM 1503

Parameter	Any trend?		Any Outlier?		Distribution
	Analytical Order	Filling Sequence	All Data	Averages of Units	All Data
BET	No	No	No	No	Normal/Unimodal

The uncertainty estimation for the data belonging to the homogeneity study was made using the ANOVA method. Results are presented in Table 3.

Equations 1 and 2 are applied in calculating the standard deviation between the bottle (s_{wb}) and between bottles (s_{bb}) using ANOVA:

$$s_{wb} = \sqrt{MS_{within}} \quad (1)$$

MS_{within} : mean of squares within-unit,
s_{wb} : equivalent to the standard deviation of the method as long as the subsamples represent the whole unit.

$$s_{bb} = \sqrt{\frac{MS_{between} - MS_{within}}{n}} \quad (2)$$

$MS_{between}$: mean of squares between-units,
n : number of repetitions per unit.

When $MS_{between}$ is smaller than MS_{within}, s_{bb} cannot be calculated. Instead, the heterogeneity that can be hidden by the method repeatability, u^*_{bb} is calculated according to the equation 3 [4]:

$$u^*_{bb} = \frac{s_{wb}}{\sqrt{n}} \sqrt[4]{\frac{2}{\nu_{MSwithin}}} \quad (3)$$

$\nu_{MSwithin}$: Degrees of freedom of MS_{within}

Table 3. Results of the homogeneity study

Parameter	$s_{wb,rel}$, %	$s_{bb,rel}$, %	$u^*_{bb,rel}$, %	$u_{bb,rel}$, %
BET	0.51	0.14	0.13	0.14

The uncertainty value obtained as a result of the between bottles homogeneity assessment was found to be lower than the target homogeneity uncertainty value (0.5%) (Table 3).

STABILITY

Stability test studies were carried out by creating similar conditions in the laboratory environment for transfer conditions (short-term stability) and storage conditions (long-term stability) that may occur when sending the certified reference material to the user and storage by the user.

Short-term stability

For short-term stability studies, 14 units (7 main, 7 spare) were determined by random stratified sample selection. The temperatures to be tested for short term stability study are 18 °C and 60 °C; durations: 1, 2 and 4 weeks. For each of the temperature and time point, 2 units are placed at the test temperature, and 2 units for the reference point are placed at 4 °C, which is selected as the reference temperature. At the end of the test period, units were transferred from test cabinets to the reference temperature. When the 4-week period was completed, all units transferred to the reference temperature were analyzed under repeatability conditions with the units to be used as reference.

The numbers, test temperatures and test periods of the units used in the short term stability study are given in Table 4. Evaluations were carried out separately for each temperature.

Table 4. Simultaneous monitoring (isochronous setup) data of the short-term stability study

Unit Number	Temperature, °C	Time, Week
240	4	0
7	18	1
198	18	2
219	18	4
379	60	1
402	60	2
442	60	4

Results obtained were examined in terms of outliers at 95% and 99% confidence level by applying the "Grubbs' Test" (Table 5). As a result of the evaluation, it was seen that the certified reference material produced was stable at 18 °C for 4 weeks and there was no outlier. However, a significant decrease was observed in the BET value when the material was exposed to a temperature of 60 °C. When the regression curves were examined in terms of statistical significance, it was observed that the slope of the regression curve belonging to 60 °C was different from zero.

Table 5. Results of Short Term Stability Grubbs' Test

Test Temperature	Is the slope of the graph significantly different from zero at the 95% and 99% confidence level?
18 °C	No
60 °C	Yes

Regarding short-term stability, uncertainty is calculated using equation 4 considering the uncertainty of this slope and the longest time to be exposed [4].

$$u_{sts,rel} = \frac{RSD}{\sqrt{\sum (t_i - \bar{t})^2}} \times t \qquad (4)$$

here:

RSD : Relative standard deviation of points on the regression line,

T_i : Time point for each replicate,

$\bar{t}$: Mean of all time points,

t : Maximum time suggested for transfer: 4 weeks.

Uncertainty values obtained in short term stability study is given in Table 6. While the relative uncertainty value at 18 °C is quite low, it has been observed that the value at 60 °C is quite high. The graphs for short term stability are presented in Annex 2.

Table 6. UME CRM 1503 short-term stability uncertainty values

Short Term Stability Test Temperature	$u_{sts,rel}$ **, %** (4 weeks)
18 °C	0.29
60 °C	8.16

The material is found to be stable at 18°C. Thus, the samples can be safely dispatched under conditions where the temperatures do not exceed 18 °C for up to 4 weeks, i.e. at ambient temperature without applying any cooling elements.

Long-term stability

The usage time of the produced CRM has been determined according to the results of long-term stability studies. In the measurements, two units that were kept at 18 ° C for each time point for 1, 3, 6 and 12 months were used and 3 independent samples were prepared from each unit and long-term stability analyzes were carried out. At the end of the specified test period, the samples taken from the test temperature were transferred to +4 °C and at the end of 12 months, the analyzes were carried out simultaneously. 2 units determined as reference have been stored at +4 °C for 12 months.

Three replicate results were obtained from each selected unit for each time point. Among the data obtained, the one-way Grubbs test was applied to examine whether there was an outlier at 95% and 99% confidence intervals. No outliers were detected for the analysis made accordingly. The average of 3 measurement results obtained for each time point is given in Annex 3. The error lines at each time point were calculated as the standard deviation of the 3 results obtained. The values found were analyzed by drawing the concordance line (regression line) in the graph of concentration versus time. The uncertainty value of the certified reference material due to long-term stability is calculated using equation 5 [4].

$$u_{lts,rel} = \frac{RSD}{\sqrt{\sum (t_i - \bar{t})^2}} \times t \qquad (5)$$

Here,

RSD : Relative standard deviation of points on the regression line,
t_i : Time point for each replicate,
$\bar{t}$: Mean of all time points,
t : Recommended usage time at 18 °C (12 months)

The uncertainty contribution, u_{lts} was calculated for 12 months (t) at 18 °C. This parameter is one of the four parameters that contribute to the total uncertainty of certified value. The results is given in Table 7. The graphs for long term stability are given in Annex 3.

Table7. CRM 1503 Long Term Stability Test Results

Parameter	$u_{lts,rel}$ (%, 12 months) **+18°C**	Number of Outliers at 95% Confidence Interval*	Number of Outliers at 99% Confidence Interval*	Is there a significant trend at 95% confidence interval?	Is there a significant trend at 99% confidence interval?
BET	0.40	-	-	No	No

*SGT: Single Grubbs Test

CHARACTERIZATION

Characterization study, which can be carried out in different ways according to the TS EN ISO 17034 standard, was carried out in this study by bilateral comparison study between TÜBİTAK UME and UNIIM Surface Area Laboratory (Russia), another reference material producer. The quality control of the measurements were carried out using 6-SiO_2 CRM KD-1 produced by UNIIM Surface Area Laboratory. In the measurements performed by TÜBİTAK UME, two units of the candidate CRM were measured. Experiments were performed by analyzing two UME CRM 1503 units samples and one UNIIM 6-SiO2 CRM KD-1 CRM sample for each day for six days. Analyzes were carried out by changing the order so that the parallel studies of the units, which were analyzed for separate days at the device ports, were transferred to different ports.

It was observed that the data obtained in the characterization studies showed a normal distribution and the uncertainties of the measurements were determined in accordance with the "Guide to the Expression of Uncertainty in Measurements (GUM)" and "EURACHEM/CITAC Guide Quantifying Uncertainty in Analytical Measurement" documents, and by using equations (6) – (8) reported in the literature by M. S. Levenson et al. [5].

$$u(B) = \frac{|X_{METHOD_UME} - X_{METHOD_UNIIM}|}{2\sqrt{3}} \quad (6)$$

$$u(X) = \sqrt{\left(\frac{1}{2}\right)^2 u^2(Method_UME) + \left(\frac{1}{2}\right)^2 u^2(Method_UNIIM)} \quad (7)$$

$$u_{char} = \sqrt{u^2(X) + u^2(B)} \quad (8)$$

where,

$u(B)$: the standard uncertainty based on the difference of results of two methods,
$u(X)$: the standard uncertainty obtained by combining uncertainties of two methods,
u_{char} : the standard uncertainty of characterisation by two methods.

The value assignment of the material is made by taking the average of the results of the two methods. All measurement results of the characterization study are given in Annex 4.

Additional Measurements

Candidate certified reference material was also analyzed by competent laboratories within the scope of interlaboratory comparison study. In this study, in accordance with the ISO 17034 standard, accredited laboratories or laboratories using reference methods were selected. The results of this study are presented in Annex 5, Figure A7. It was observed that the results obtained in this study were consistent with the results of the characterization study obtained by TÜBİTAK UME and UNIIM.

PROPERTY VALUE AND UNCERTAINTY ASSIGNMENT

Assigned value is the average of the characterization measurement results by two laboratories.

Characterization uncertainty (u_{char}), uncertainty due to homogeneity (u_{bb}), uncertainty due to short-term (u_{sts}) and long-term stability (u_{lts}) were combined using equation 9. The uncertainty value is calculated by using the coverage factor k = 2, which corresponds to approximately 95% confidence level.

$$\mathrm{U_{CRM}} = k\sqrt{\mathrm{u_{char}^2} + \mathrm{u_{bb}^2} + \mathrm{u_{lts}^2} + \mathrm{u_{sts}^2}} \quad (9)$$

Certified value and uncertainty is given in Table 8, and the contribution of each parameter to the total uncertainty of the certified value is given in Table 9.

Table 8. Certificate Values and Uncertainty Components

Parameter	Certified Value ($m^2\ g^{-1}$)	U_{CRM} ($m^2\ g^{-1}$), (k = 2)	$U_{CRM,rel}$ (%, k = 2)	$u_{char,rel}$ (%)	$u_{bb,rel}$ (%)	$u_{lts,rel}$ (%)	$u_{sts,rel}$ (%)
BET	377.9	5.6	1.48	0.53	0.14	0.40	0.29

Table 9. Contribution of Each Parameter to the u_{CRM} Value

Parameter	$u_{char,\ rel}$ (%)	$u_{bb,\ rel}$ (%)	$u_{lts,\ rel}$ (%)	$u_{sts,\ rel}$ (%)
BET	51.8	3.5	29.1	15.6

COMMUTABILITY

Commutability is the mathematical relation of equality between the results produced by different measurement methods that can be used in the measurement of the reference material and the routine samples it represents [9]. The measurements performed in this study depend on the method, and the results obtained with different measurement methods for the parameters measured are not in question.

The SiO_2 used in the production of the reference material was obtained from Merck company (Germany). Therefore, it can be said that it represents other SiO_2 samples with similar properties and range of BET surface area.

TRACEABILITY

The surface analysis measurement result parameter of the certified reference material (after degassing at 350 °C for at least 6 hours) is a parameter that can be measured depending on the method and can be obtained by fully applying the procedures specified in ISO 9277: 2010 method [6]. Certified value assigned for CRM depends on the method and therefore is operationally defined. The metrological traceability of the certified values were ensured by using SI traceable tools (calibrators, reference materials) for the calibration and verification of the instruments and equipments used by TÜBİTAK UME (Türkiye) and UNIIM (Russia) laboratories for the characterization study.

INSTRUCTIONS FOR USE

Before opening and taking a sample, the bottle should be shaken to re-homogenize the content. Minimum sample intake is 200 mg. After use, the bottle should be immediately and tightly recapped.

Degassing of the sample (200-500 mg) has to be carried out under vacuum. Starting at room temperature, the sample is heated up to 350 °C (623 K) in vacuum with rate of 5-10 °C/min followed by degassing the sample at 350 °C for at least 6 hours. The final pressure should be 1-5 Pa. The measurement should be carried out at a temperature of -198.85 °C (77.3 K) using N_2 as probe gas. The first isotherm data point should be taken at P/P_o = 0.01 and the last isopterm data point should be taken at P/P_o = 0.35.

Multipoint BET Evaluation

The monolayer capacity per unit mass of adsorbed nitrogen $n_{a,m}$ needs to be calculated from the isotherm data in accordance with the international standard ISO 9277 [2] as follows. Plot the BET function $y_{BET} = (p/p_0) / [n_a (1- p/p_0)]$ against relative pressure p/p_0, where n_a is the amount of adsorbate per unit mass at the equilibrium pressure p and p_0 is the saturated vapor pressure of the adsorptive at the temperature of adsorption. 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 $0.05 \leq P/P_o \leq 0.3$ (cross sectional area for the N_2 molecule in the monolayer: a_{N2} = 0.162 nm^2). From the gradient k_{BET} and the intercept on the y-axis, i_{BET}, calculate the monolayer capacity per unit mass of the adsorbent using $n_{a,m} = 1/(k_{BET} + i_{BET})$.

The BET specific surface area, A_{BET}, is then given by

$$A_{BET} = n_{a,m} \cdot N_A \sigma_{N_2},$$

Where, N_A is the Avogadro constant and σ_{N_2}, the cross sectional area for the N_2 molecule in the monolayer.

If your instrument records the adsorption isotherm in the form of the adsorbed specific gas volume V_a, at standard temperature and pressure (STP) as a function of relative pressure, V_a must be converted into n_a, using

$$n_a = \frac{P_{STD}}{R \times T_{STD}} \times V_a$$

with P_{STD} =101325 Pa, T_{STD} = 273.15 K, R = 8.314 Pa m^3 K^{-1} (molar gas constant).

Storage conditions

The material should be stored at (21 ± 3) °C in a dry place.

This material can be safely dispatched under conditions where the temperatures do not exceed 18 °C for up to 4 weeks.

TÜBİTAK UME cannot be held responsible for changes that might happen to the material at customer's premises due to noncompliance with the instructions for use, and the storage conditions given in the certificate.

Safety Information

Normal laboratory precautions are applied. It is highly recommended to use and dispose the material in accordance with the existing safety rules. While working with the material, it should be worked in gloves, dust mask and well ventilated environment. Please read the Material Safety Data Sheet (SDS) before use.

Intended Use

Porous SiO_2 certified reference material is aimed to be used for the method validation, verification and quality control of specific surface area measurements with the gas adsorption method as described in ISO-9277 [5] for the BET surface area.

Evaluation of the Measurement Results

The user can use the CRM RE: result evaluation application online at https://rm.ume.tubitak.gov.tr/en/crm_re/ or the ERM Application Note 1 [8] document to compare the results of the measurements made with the UME CRM 1503 reference material with the certified values.

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REVISION HISTORY

Date	Remarks
11.10.2021	First publication

ANNEXES

Annex 1. Homogeneity Data

Table A1. Homogeneity test results

		ANALYSIS ORDER				BET (m^2 g^{-1})			
No	**Unit number**	**Repeat 1**	**Repeat 2**	**Repeat 3**	**Repeat 4**	**Repeat 1**	**Repeat 2**	**Repeat 3**	**Repeat 4**
1	39	21	20	19	30	384.222	386.694	382.578	380.120
2	83	18	17	16	33	385.345	387.777	381.812	380.068
3	145	15	14	22	35	384.607	383.613	380.456	380.974
4	166	37	38	39	40	385.032	384.471	384.888	386.986
5	243	11	10	9	36	383.355	385.520	381.037	385.437
6	308	8	7	24	34	382.300	385.037	382.083	381.954
7	340	6	5	29	31	383.325	381.905	382.785	380.601
8	411	4	3	25	27	382.228	383.700	381.892	382.341
9	420	1	2	26	28	382.985	380.149	380.630	381.745
10	214	13	12	23	32	383.911	383.878	381.968	380.506

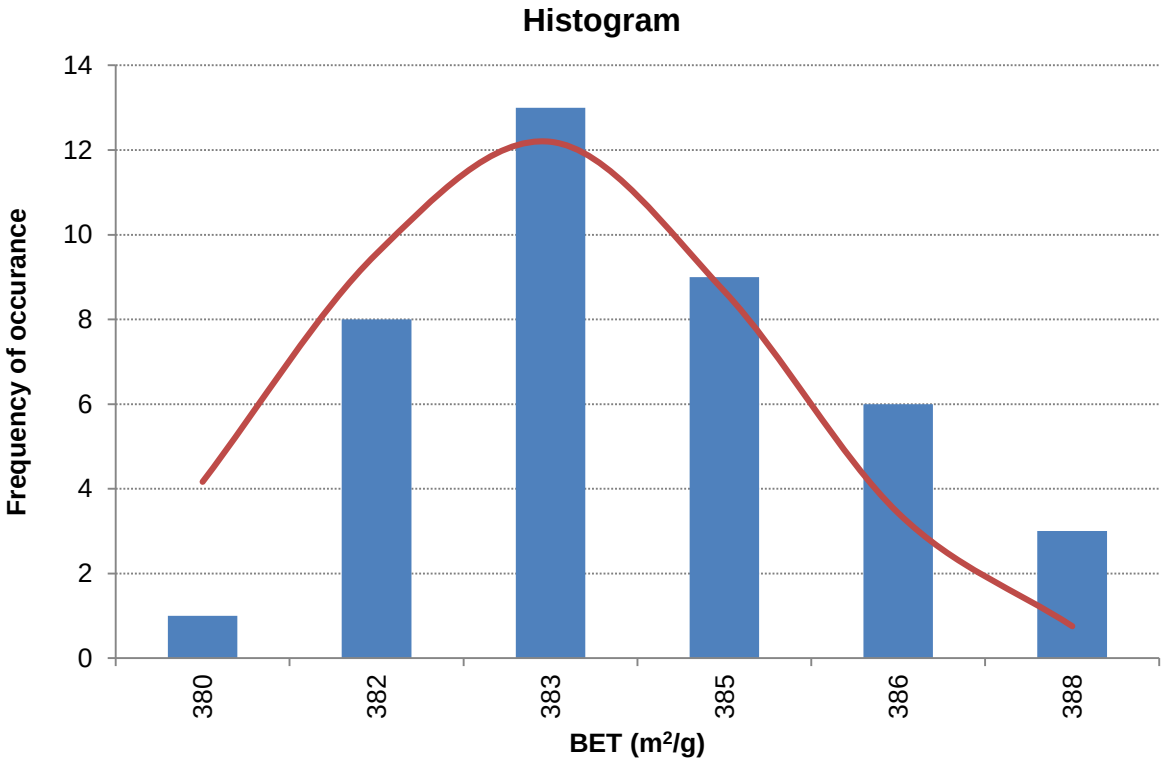


Figure A1. Histogram graph for homogeneity data

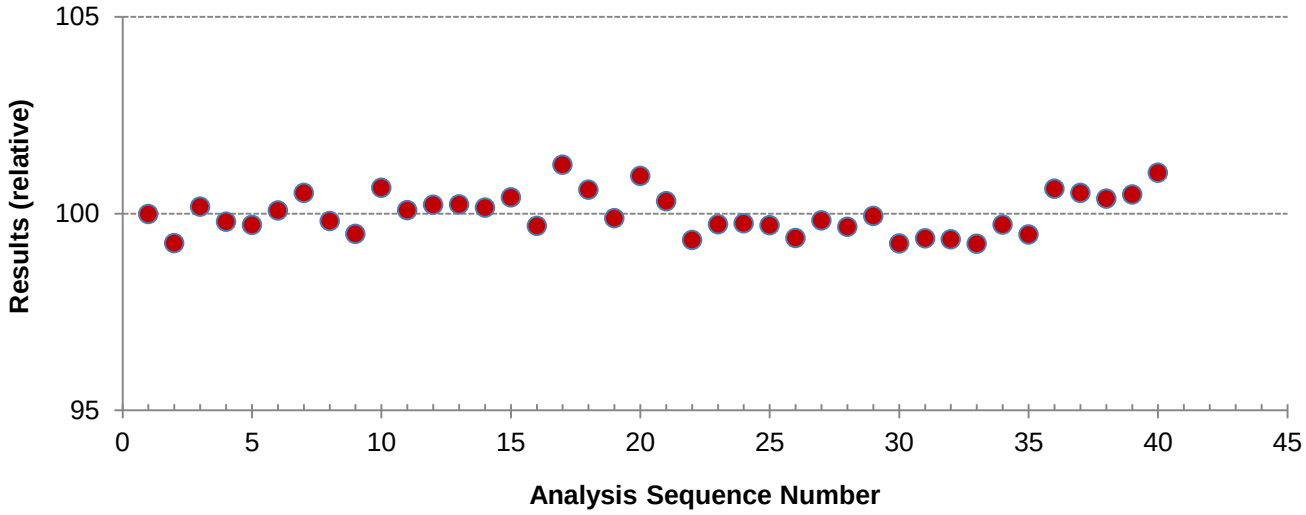


Figure A2. Scatter plot of homogeneity data with analysis sequence order

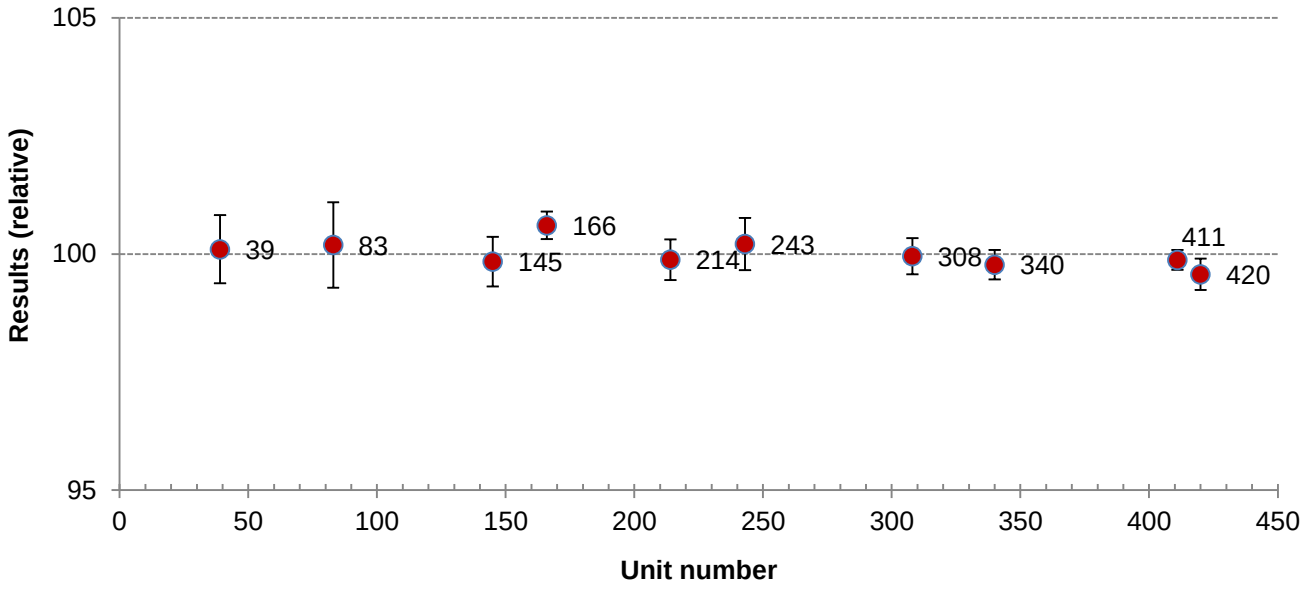


Figure A3. Scatter plot with the mean of unit repetitions of the homogeneity data

Annex 2. Short-Term Stability Charts

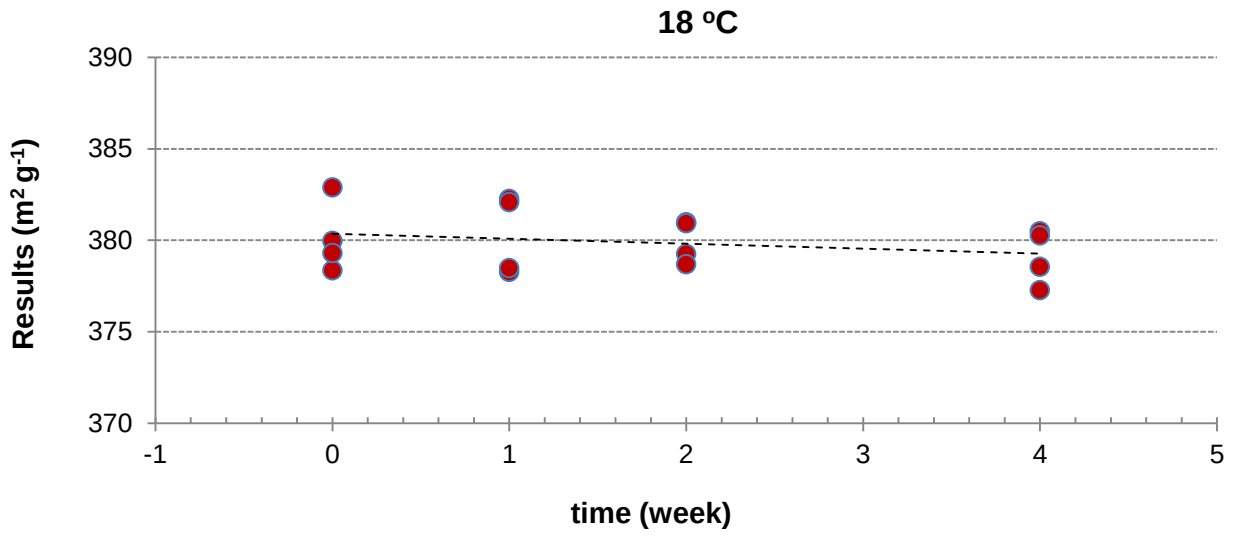


Figure A4. Short-term stability graph for 18 ºC

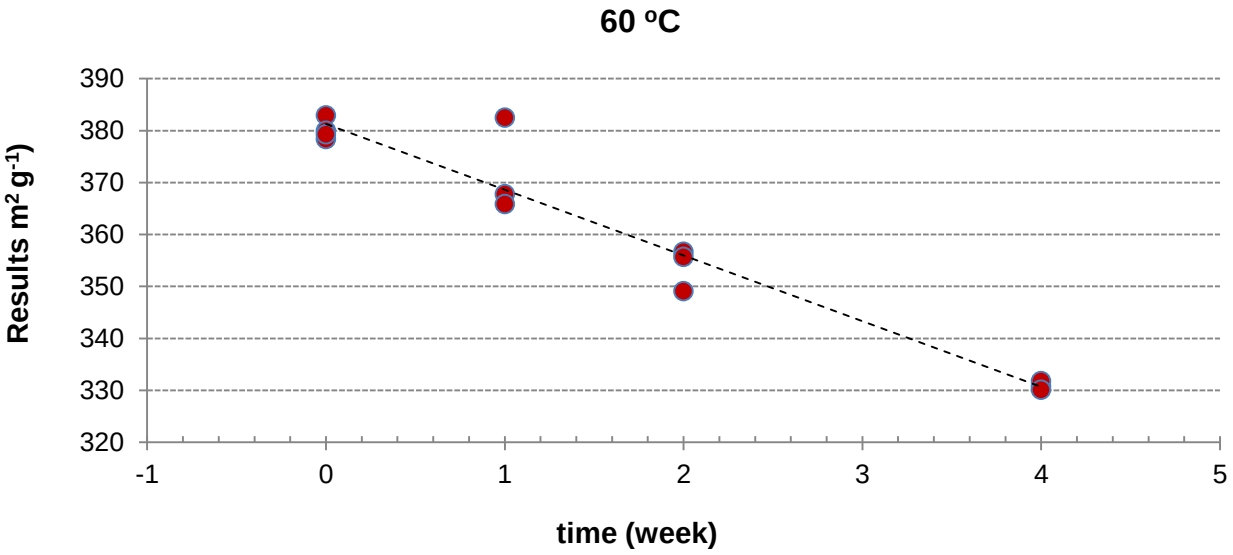


Figure A5. Short-term stability graph for 60 °C

Annex 3. Long Term Stability Chart

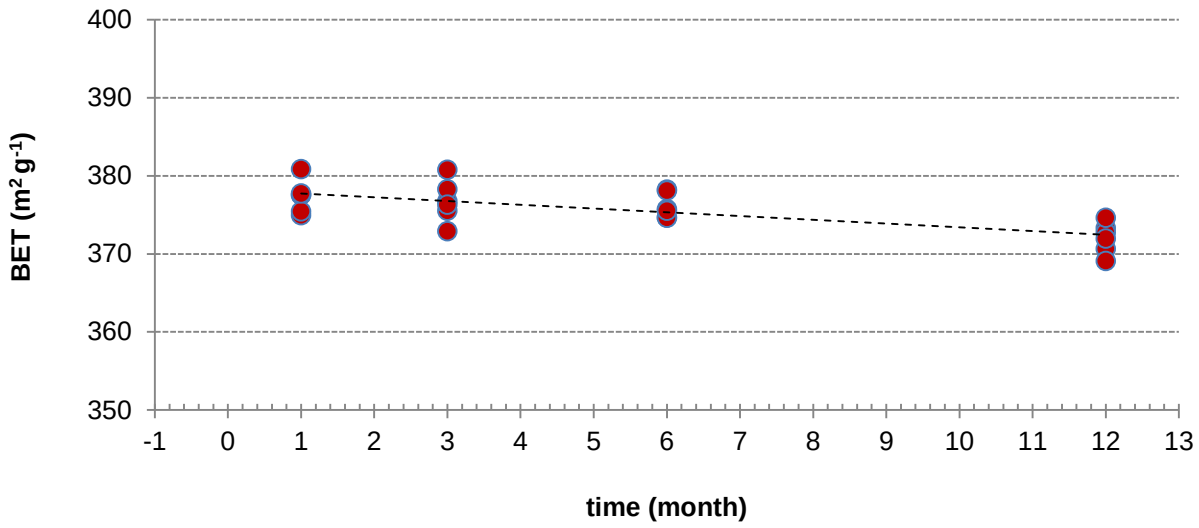


Figure A6. Long-term stability graph for 18 °C

Annex 4. Characterization Data

Table A2. Results of the characterization study

UNIIM		TÜBİTAK UME	
№	**BET ($m^2\ g^{-1}$)**	**№**	**BET ($m^2\ g^{-1}$)**
1	379.20	**1**	378.84
2	376.20	**2**	380.17
3	378.60	**3**	382.45
4	377.80	**4**	380.81
5	375.80	**5**	380.33
6	372.50	**6**	379.65
Average	**376.68**	**7**	377.87
s	**2.44**	**8**	376.86
u (k=1)	**0.98**	**9**	378.84
		10	376.78
		11	379,77
		12	377,73
		Average	**379.18**
		s	**1.69**
		u (k=1)	**3.61**

Annex 5. Interlaboratory Comparison Study

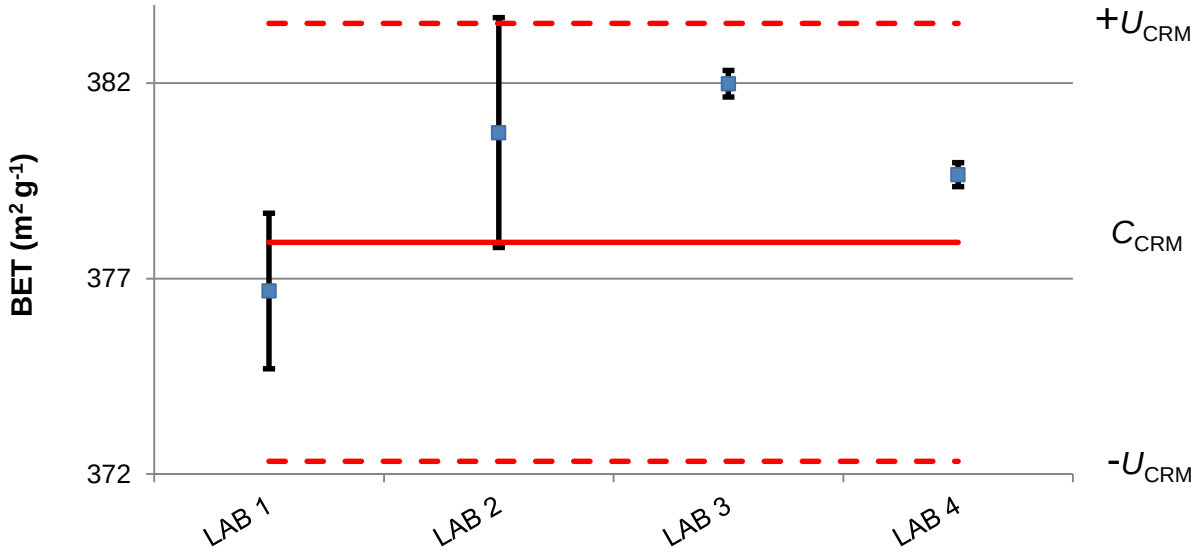


Figure A7. Interlaboratory comparison study plot (error bars represent the expanded uncertainties reported by the laboratories)