

Benzoic Acid  
Certified Reference Material  
UME CRM 1504

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### ABBREVIATIONS

ANOVA	Analysis of variance
BA	Benzoic acid
J/g	Joule/gram
STS	Short term stability
ISO	International Organization for Standardization
$MS_{Between}$	Mean square between-bottle from ANOVA
$MS_{within}$	Mean square within-bottle from ANOVA
$n$	number of replicates per bottle
PT	Potentiometric Titration
qNMR	Quantitative Nuclear Magnetic Resonance
RSD	Relative standard deviation
$s$	Standard deviation
$S_{bb}$	Standard deviation between bottles
SI	International System of Units
CRM	Certified Reference Material
$U_{bb}$	Standard uncertainty related to possible between-bottle heterogeneity
$U^*_{bb}$	Standard uncertainty of heterogeneity that can be hidden by method repeatability
$U_{char}$	Standard uncertainty related to characterisation
$U_{char,rel}$	Relative standard uncertainty related to characterisation
LTS	Long term stability
$U_{lts}$	Standard uncertainty related to long term stability
$U_{lts,rel}$	Relative standard uncertainty related to long term stability
$U_{rect}$	Standard uncertainty of between bottles heterogeneity modelled by a rectangular distribution
$U_{rect,rel}$	Relative standard uncertainty of between bottles heterogeneity modelled by a rectangular distribution
$U_{sts}$	Standard uncertainty related to short term stability
$U_{sts,rel}$	Relative standard uncertainty related to short term stability
$V_{MS_{within}}$	Degrees of freedom related to $MS_{within}$

## ABSTRACT

Calorimeters are used to calculate the energy content of substances. To ensure the accuracy of calorific value measurements performed by calorimeters, benzoic acid (BA) with known calorific value is used as a reference material. The exact determination of the actual calorific value of materials also depends on the purity of these materials.

Calorimeter is a system used to measure the amount of energy released by burning fuels in a temperature controlled environment. The principle of the system is the measurement of the increase in temperature occurring in the homogeneously mixed liquid as a consequence of the combustion reaction.

Calorimeters are calibrated at certain time intervals with reference materials of known calorific value. This ensures that the measurements made in calorimeters are reliable and repeatable.

It is important to measure the energy content of substances accurately. In this regard, in sectors such as, energy, food, textile, medicine, etc., the energies of substances are measured.

Many accredited organizations are operating in the field of calorific value measurement. Meeting the needs of these organizations for BA certified reference material, ensuring measurement uniformity and traceability have been the motivation for the production of this reference material.

The production of the reference material basically consists of material processing, homogeneity, short-term and long-term stability, characterisation, value assignment and post-certification monitoring steps.

## INTRODUCTION

### Calorific Value Measurements

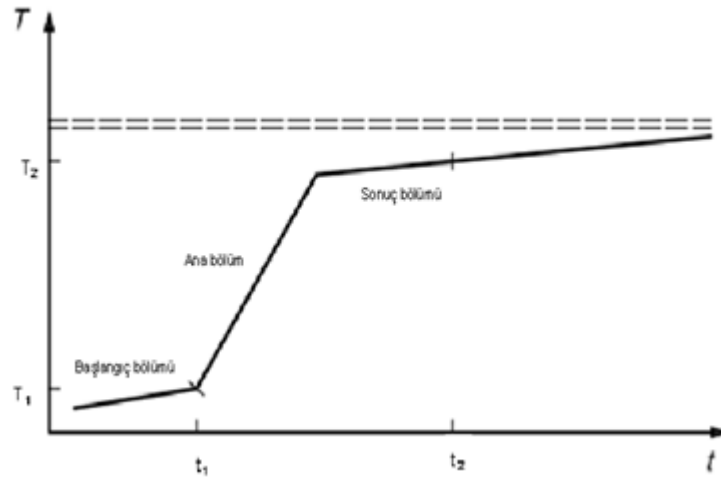
"Calorimeters" are used for the determination of the heat of chemical reactions experimentally. The calorimeter consists of a thermally insulated chamber filled with pure water and placed in an environment where there is no heat exchange with the external environment [1, 2]. The experiment is carried out in a combustion chamber (reactor) inside this chamber. The combustion chamber is enriched with oxygen to ensure complete combustion of the materials inside. The heat generated by this combustion causes a change in the initial temperature of the water and this temperature change is used to calculate the calorific values of the substances. The first law of thermodynamics is used in combustion [3-6]. According to this law, the heat generated in combustion is absorbed by the water in the calorimeter. Thus, the heat received by the water is equal to the heat released by the combustion of the substance. Calorific values are calculated by utilizing this principle.

An ideal calorimeter should be thermally isolated from the environment [7-10]. The observed temperature values should only be the values of the heat exchange occurring in the reaction. In practice, it may not be possible to completely isolate the calorimeter from the environment. A calorimeter is made by placing containers in a temperature controlled environment with some space between them. The calorimeter is designed as an environment with thermal insulation on all sides [11-16].

There are three external parameters that cover all energy sources;

- Water stirrer,
- Self-heating of the temperature measuring device,
- Energy flows through the jacket of the calorimeter as a result of temperature differences.

Figure 1 shows the temperature - time curve of a typical experiment (combustion or calibration). Data monitoring starts at a predefined temperature. Due to the effects mentioned above, the temperature of the calorimeter is allowed to rise until time  $t_1$ . At time  $t_1$ , the main section is started either by switching on the heater or by combustion. Combustion continues in the main section with a sudden increase in temperature. It is waited until the end of combustion and the temperature value resulting from the change in the temperature of the system reaches equilibrium.



**Figure 1.** The temperature change with time before, during and after combustion of fuel

## Purity Measurements

### Determination of Benzoic Acid Purity by Potentiometric Titration

Potentiometric titration is a technique in which the potential measurement is used as an indicator and the amount of the analyte of interest is determined by the jump in potential. In potentiometric titration, purity can be determined for many analytes whose potential changes with the addition of titrant. Benzoic acid is one of these analytes. The method is based on the addition of ethanol to some amount of benzoic acid dissolved in water followed by titration with adjusted sodium hydroxide. As a result of the titration, the purity of benzoic acid is determined by equation (1).

$$\text{Benzoic acid purity (\%)} = \frac{(EP1 - BL1) \times TF \times C1 \times K1}{m} \quad (1)$$

*EP1* : Amount of titrant consumed in titration (mL)

*BL1* : Blind level (0.00 mL)

*TF* : Titrant factor

*C1* : Concentration conversion coefficient (12.212 mg/mL)

(1 mg benzoic acid is equivalent to 1 mol/L 1 mL NaOH)

*K1* : Unit conversion coefficient (0.1)

*m* : Amount of sample (g)

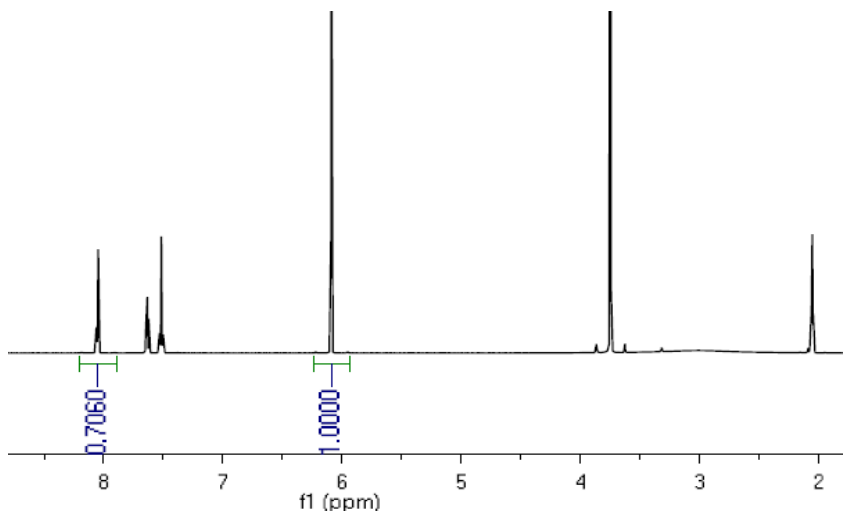
### Determination of Benzoic Acid Purity by Nuclear Magnetic Resonance Spectroscopy

Nuclear magnetic resonance (NMR) spectroscopy was first described in 1946 [17-18] and was used as one of the main analytical techniques for the elucidation of chemical structures, purity and impurity analyses. NMR technique is an important spectroscopy method used especially in the analysis of small organic molecules and large polymer structures [19].

<sup>1</sup>H-NMR spectroscopy is well suited for quantitative analyses due to the high sensitivity of the proton nucleus, relatively low settling time and almost 100% natural abundance of the proton nucleus. The intensity of the NMR signal and peak intensity are directly dependent on the proton numbers. Since the areas of the peaks are used in quantitative analyses, the intensity of the selected peaks is also important. The low uncertainty of the qNMR technique is the reason why it is preferred for precise and highly accurate measurements. Quantification by qNMR can be performed in two different ways [19]. The first one is the relative calculation technique, which is based on the mole ratios of two substances. The second technique is the addition of an external standard and is calculated by measuring the peak area of the sample to be analysed and the peak area of the appropriate standard. If the standard used is an SI traceable certified standard material, SI traceability is ensured. Benzoic acid and dimethylsulfone certified reference materials produced for qNMR analyses can be given as examples of chemicals containing these properties [20]. Since accurate and traceable measurements can be made with very low uncertainties, qNMR is an ideal technique for the certification of organic molecules [21].

qNMR has been widely used by metrology institutes and reference material manufacturers around the world for the production of certified reference materials and purity determination due to the developments in probe and magnet technology in recent years [22].

In qNMR method, material purity is ensured by comparing molecular structures with equivalent signals for a reference material and a sample subject to analysis. In these analyses, UME CRM 1301 - Chloramphenicol reference material was used to ensure the traceability chain. Trimethoxybenzene reference, whose purity was determined using chloramphenicol, was preferred in the analyses to determine BA purity. Since the peak groups of trimethoxybenzene do not overlap with BA and dissolve very well in DMSO-d<sub>6</sub> solvent with benzoic acid, it is considered as a very suitable reference material (Figure 2).



**Figure 2.** <sup>1</sup>H NMR spectrum of benzoic acid and trimethoxybenzene in DMSO-d<sub>6</sub> solvent

The mathematical equation (2) for qNMR purity calculation is given below. As can be seen from the equation, it is very important to weigh the substances, prepare NMR samples and select the integral areas correctly when processing the data. For this reason, it is necessary to use calibrated balances in the appropriate weighing range.

$$P_x = \frac{I_x}{I_{Std}} \frac{N_{Std}}{N_x} \frac{M_x}{M_{Std}} \frac{W_{Std}}{W_x} P_{Std} \quad (2)$$

- $P_x$  : Purity of analyte (X) (%)
- $I_x$  : Integrated area of the selected proton of the analyte
- $I_{Std}$  : Integrated area of the selected proton of the standard
- $N_x$  : Proton number of analyte
- $N_{Std}$  : Proton number of the standard
- $M_x$  : Molecular mass of analyte (g/mol)
- $M_{Std}$  : Molecular mass of the standard (g/mol)
- $W_x$  : Gravimetric weight of analyte (g)
- $W_{Std}$  : Gravimetric weight of standard (g)
- $P_{Std}$  : Purity of the standard (Std) (%)

This report covers the details of the production process of the UME CRM 1504 BA material in accordance with ISO 17034:2016 [23], certification of BA and the studies carried out during this process. This process consists of sample preparation, homogeneity, short and long term stability, characterisation tests and value assignment.

In the report, production and analysis processes of UME CRM 1504, the data for homogeneity, stability and characterisation studies, statistical evaluations, results and associated measurement uncertainties were determined according to ISO Guide 35:2017 [24] and certificate values and uncertainties were calculated by fulfilling the requirements of the relevant guide.

## PARTICIPANTS

All stages of the production of UME CRM 1504 (except for the conversion of the material into tablet form) were carried out at TÜBİTAK UME as shown in Table 1.

**Table 1.** Participating institute and definition of the work

Activity	Laboratory / Organization
Material Processing	TÜBİTAK National Metrology Institute (UME), Gebze-Kocaeli, Türkiye TÜBİTAK Marmara Research Center (MAM), Gebze-Kocaeli, Türkiye
Homogeneity Study	
Stability Studies	
Characterisation Study	TÜBİTAK National Metrology Institute (UME), Gebze-Kocaeli, Türkiye
Project Management and Data Evaluation	

## MATERIAL PROCESSING

In the first stage of the material processing, the BA obtained with a particle size larger than 1 mm was sieved with the help of a 1 mm mesh sieve. The sieved BA (< 1 mm) was dried at 30 °C in an oven with HEPA filter for 24 hours. BA was homogenised in a 3D mixer (HKTM Megamix, Türkiye) for 4 hours and transferred into vacuum plastic containers of 1 kg each. The BA in powder form was pressed in a tablet machine (Kaan Kalıp, Türkiye) in the amount of approximately 1 gram each. The tablets were then bottled in 10 or 50 pieces (approximately 10 g or 50 g) per bottle. The bottles were labelled according to their filling order in a labelling machine (Farmatek, Türkiye). After separating the units selected for certification tests, all other units were stored in a temperature-controlled environment.

## HOMOGENEITY

For the homogeneity study, 10 bottles were selected and allocated according to the stratified random sample selection principle. Thus, the selected samples were guaranteed to represent the total number of bottles. Homogeneity study was performed by calorimeter for calorific value, and potentiometric titration method for purity and then measurement results were reported. The traceability of the calorific value and purity measurements was ensured with NIST 39j reference material. Alpha AR 208 reference material was used in quality control analyses. Measurements for homogeneity determination were performed in random order to eliminate possible trends that may arise from the filling and analysis sequence under repeatability conditions.



Analyses of the samples were analysed by one-way analysis of variance (ANOVA). The unimodal distribution of the data is an important prerequisite for statistical evaluation by ANOVA. Therefore, the distribution of each measurement result as well as the sample means was checked for normality using normal distribution plots and for unimodality using histograms. For all parameters, a normal and unimodal distribution was observed for individual results and averages.

The data were statistically analysed to check for the presence of any trends and/or outliers. No trend due to the order of filling and measuring order was observed. No outliers were detected (single Grubbs test,  $\alpha = 0.05$ ).

With the ANOVA method, the standard deviation values of homogeneity within ( $s_{wb}$ ) and between bottles ( $s_{bb}$ ) were calculated using the equations (equation (3) and equation (4)) below:

$$s_{wb} = \sqrt{MS_{within}} \quad (3)$$

$MS_{within}$  : mean square within-bottle from ANOVA

$s_{wb}$  : equivalent to the s of the method, provided that subsamples are representative for the whole unit

$$s_{bb} = \sqrt{\frac{MS_{between} - MS_{within}}{n}} \quad (4)$$

$MS_{between}$  : mean square between-bottle from ANOVA

$n$  : number of replicates per bottle

When  $MS_{between}$  is smaller than  $MS_{within}$ ,  $s_{bb}$  cannot be calculated. Instead,  $u^*_{bb}$  is calculated by equation (5) for heterogeneity, which can be hidden by method repeatability [25]:

$$u^*_{bb} = \frac{s_{wb}}{n} \sqrt[4]{\frac{2}{v_{MS_{within}}}} \quad (5)$$

$v_{MS_{within}}$  : Degrees of freedom related to  $MS_{within}$ .

The results of the homogeneity study for benzoic acid are presented in Table 2. The graphs related to the homogeneity test for the gross calorific value and purity parameters are given in Annex 1.

**Table 2.** Results of the homogeneity study

Parameter	$s_{wb,rel}$ (%)	$s_{bb,rel}$ (%)	$u^*_{bb,rel}$ (%)	$u_{bb,rel}$ (%)
<b>Gross Calorific Value</b>	0.07	$MS_{between} < MS_{within}$	0.02	0.02
<b>Purity (By potentiometric titration)</b>	0.15	0.06	0.05	0.06

## STABILITY

Stability test studies were carried out by creating similar conditions in the laboratory to the environmental conditions (short-term stability) and storage conditions (long-term stability) that may occur during the delivery of the certified reference material to the user.

### Short Term Stability Study Results

For short-term stability studies, 26 units (13 main, 13 spare) were determined by stratified random sample selection method. Temperatures to be tested for short-term stability studies were determined as -20 °C and 50 °C and time periods as 1, 2 and 4 weeks. For each temperature and time point, 2 main and 2 spare units were placed at the test temperature and 1 main and 1 spare unit for the reference point were placed at 18 °C, which was selected as the reference temperature. At the end of the test period, all units from both temperatures were transferred to the reference temperature. At the end of the 4-week period, all units transferred to the reference temperature were analysed under repeatability conditions together with the units to be used as reference.

The results obtained were analysed for outliers at 95% and 99% confidence levels by applying "Grubbs Test". It was observed that there were no outliers. In the evaluation of short-term stability data, the values calculated for each time point were plotted against time. In order to determine whether there is any significant change in the values against time, the relationship between the variables was analysed (*regression analysis*). As a result of the statistical evaluation applied at 95% confidence interval for the plotted slope lines, it was determined that the slope was not significantly different from zero (

Table 3). Graphs related to the short-term stability test are given in Annex 2.

**Table 3.** Short-term stability Grubbs Test results

Parameter		Calorific Value	Purity
Is the slope of the graph significantly different from zero at 95% and 99% confidence level?	-20 °C	No	No
	50 °C	No	No

Uncertainty calculations for short-term stability are made using equation (6) [26].

$$u_{sts,rel} = \frac{RSD}{\sqrt{\sum(t_i - \bar{t})^2}} \times t \quad (6)$$

*RSD* : the relative standard deviation of the points on the regression line,

$t_i$  : being the time point for each replicate,

$\bar{t}$  : being the average of all time points,

$t$  : being the proposed shelf life at -20 °C and 50 °C: 4 weeks

The uncertainty values obtained in the short-term stability studies for calorific value and purity are given in Table 4.

**Table 4.** Short-term stability uncertainty values of UME CRM 1504 calorific value and purity measurement data

Short-term Stability Uncertainty Values	$u_{sts,rel}$ (%)	
	-20 °C	50 °C
Gross Calorific Value, 4 weeks	0.03	0.04
Purity, 4 weeks (by potentiometric titration)	0.09	0.09

According to these results, it was concluded that the certified reference material produced is suitable for transport without additional cooling elements, provided that the temperature does not exceed 50 °C for up to 4 weeks.

### Long Term Stability Study Results

Shelf life of the CRM was determined according to the long term stability measurements. Two units (2 main and 2 spare) stored at 18 °C for each time point for 1, 3, 6 and 12 months were used in the measurements and long-term stability analyses were performed. For each time point, 2 replicate results were obtained from each selected bottle. While no trend was found at 99% confidence interval, a trend was determined at 95% confidence interval.

Within the obtained data, the one-way and two-way Grubbs test was applied and it was examined whether there were any outliers at 95% and 99% confidence intervals. Accordingly, no outlier was detected for the analyses performed.

The values found were analysed against time by drawing a line of fit (regression line). The uncertainty value arising from the long-term stability of the certified reference material was calculated using equation (7) [26]. The graphs related to the long-term stability test are given in Annex 3.

$$u_{lts,rel} = \frac{RSD}{\sqrt{\sum(t_i - \bar{t})^2}} \times t \quad (7)$$

$RSD$  : the relative standard deviation of the points on the regression line,

$t_i$  : being the time point for each replicate,

$\bar{t}$  : being the average of all time points,

$t$  : being the proposed shelf life at 18 °C: 12 months

For the contribution of the uncertainty arising from long-term stability to the total uncertainty, the period of use was determined as 12 months and the storage temperature as 18 °C. This uncertainty was one of the four parameters of the overall uncertainty budget of the certified values. The long-term stability uncertainty value results of UME CRM 1504 for calorific value and purity measurement data are given in Table 5.

**Table 5.** Long-term stability uncertainty values of UME CRM 1504 calorific value and purity measurement data

Long-term Stability Uncertainty Values	$u_{lts,rel}$ (%)
Gross Calorific Value, 12 months	0.03
Purity, 12 months (by potentiometric titration)	0.04

## CHARACTERIZATION

According to the ISO 17034 standard and the ISO Guide 35, the characterization and the assignment of values can be carried out in a number of different ways [23, 24]. In this study, the approach of using a reference measurement method in a single laboratory was chosen. The traceability of the measurements was ensured with NIST 39j BA reference material, and quality control analyses were performed with the Alpha AR 208 reference material. Measurements were performed on 6 units of the candidate CRM. The experiments were performed within 2 days. 6 different samples were analyzed together with one CRM sample for each day. Uncertainty calculations for calorific value and purity were performed in accordance with the "Guide to the Expression of Uncertainty in Measurements (GUM)" and the "EURACHEM/CITAC Guide Quantifying Uncertainty in Analytical Measurement" and the results are presented in Annex 4. The uncertainties of the potentiometric titration and qNMR purity measurements were combined using equations (8) - (10) given by M. S. Lenson et al [27].

$$U(B) = \frac{|X_{PT} - X_{qNMR}|}{2\sqrt{3}} \quad (8)$$

$$u(X) = \sqrt{\left(\frac{1}{2}\right)^2 u^2(PT) + \left(\frac{1}{2}\right)^2 u^2(qNMR)} \quad (9)$$

$$u_{char} = \sqrt{u^2(X) + u^2(B)} \quad (10)$$

$u(B)$  : Standard uncertainty resulting from the difference in the results of two methods,

$u(X)$  : Standard uncertainty obtained by combining the uncertainties of the two methods,

$u_{char}$  : Standard uncertainty of the characterization study

The value assignment for the purity of the material was carried out by averaging the results of the two methods. All data related to the characterization study are given in Annex 4.

## PROPERTY VALUE AND UNCERTAINTY ASSIGNMENT

Uncertainty in the certificate includes the uncertainty resulting from the characterization study ( $u_{char}$ ), the uncertainty due to homogeneity ( $u_{bb}$ ), the uncertainty due to short-term stability ( $u_{sts}$ ) and the uncertainty due to long-term stability ( $u_{lts}$ ).

The different contributions to the CRM uncertainty are combined using equation (11) given below.

$$U_{CRM} = k \times \sqrt{u_{char}^2 + u_{bb}^2 + u_{sts}^2 + u_{lts}^2} \quad (11)$$

The expanded uncertainty value on the certificate value is calculated based on the coverage factor,  $k=2$ , which represents approximately 95% confidence interval. The certified values and the uncertainties are given in Table 6, and the percentage contribution of each parameter to the uncertainty of the certified value is given in Table 7.

The results of the characterization and the uncertainty values obtained from two methods (potentiometric titration and NMR spectroscopy) were used in the assignment of the purity value.

**Table 6.** Certified values and their uncertainties

Parameter	Certified Value	$U_{CRM}$ ( $k=2$ )	$u_{bb,rel}$ (%)	$u_{sts,rel}$ (%)	$u_{lts,rel}$ (%)	$u_{char,rel}$ (%)	$U_{CRM,rel}$ (%)
<b>Gross Calorific Value (J/g)</b>	26473	32	0.02	0.04	0.03	0.01	0.12
<b>Purity (g/100g)</b>	99.96	0.27	0.06	0.09	0.04	0.07	0.264

**Table 7.** Percentage contribution of each parameter to the  $U_{CRM}$  value

Parameter	$u_{bb,rel}$ (%)	$u_{sts,rel}$ (%)	$u_{lts,rel}$ (%)	$u_{char,rel}$ (%)
<b>Gross Calorific Value</b>	20.1	39.9	29.2	10.8
<b>Purity</b>	23.9	35.5	14.9	25.7

## TRACEABILITY

Metrological traceability of the certified values of the produced certified reference material is ensured by using primary level measurement systems. All samples used in the characterization studies were prepared gravimetrically. Weighings were made using balances traceable to national measurement standards, and the control of the balances used was carried out with appropriate mass set weights. The balances and mass set weights used are traceable to national measurement standards implementing units defined in the International System of Units (SI). The thermometers used during the measurements were calibrated according to the international temperature scale ITS-90 and traceability was ensured. Measurement uncertainty calculations for characterization measurements were performed using the data obtained as a result of measurements made with the primary level measurement method. Performed measurements are traceable to NIST SRM 39j BA reference material.

## INSTRUCTIONS FOR USE

### Intended Use

This material is intended for use in the calibration of calorimeters used in gross calorific value measurements, calibration of BA determinations and method validation and quality control activities in these fields.

### Storage Conditions

The material should be stored at  $(18 \pm 5)$  °C in a dark place. When opening and using the bottle, all precautions should be taken to prevent the material from contamination and moisture and the bottle cap should not be left open for a long time.

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

### Safety Warnings

The material should not come into contact with skin and eyes. After the calorific value measurement is carried out, the gases formed in the bomb must not be inhaled. It is strongly recommended that the material must be handled and disposed according to the safety guidelines where applicable. Please refer to the Safety Datasheet before any use of the material.

### Minimum Sample Intake

Each tablet in the bottle is produced in a unit mass (approximately 1 gram) which does not damage the calorimeter's combustion chamber. The user can use the appropriate amount of material in the combustion chamber according to the calorimetric standard used. The minimum sample intake used for the determination of benzoic acid purity by potentiometric titration is 120 mg, and the minimum sample intake used for the determination of purity by qNMR is 10 mg.

### Use of the Certified Value

For assessing the method performance, the measured values of the CRMs are compared with the certified values [28]. The procedure can be summarized briefly as follows:

- The absolute difference between the mean value and the certified value is found ( $\Delta_m$ )
- The measurement uncertainty ( $u_{meas}$ ) and the standard uncertainty in the certified value ( $u_{CRM}$ ) are combined using equation (12),

$$u_{\Delta} = \sqrt{u_{meas}^2 + u_{CRM}^2} \quad (12)$$

The expanded uncertainty is calculated by multiplying the composite uncertainty by the coverage factor ( $k = 2$ ) equation (13), corresponding to a confidence level of 95%.

$$U_{\Delta} = 2 \times u_{\Delta} \quad (13)$$

If  $\Delta_m \leq U_{\Delta}$  then it is assumed that there is no significant difference between the measurement result and the certified value at 95% confidence level.

An online result evaluation application, where measurement results can be evaluated and quality control charts can be created by users, is available at the following address;

[https://rm.ume.tubitak.gov.tr/srm\\_sd](https://rm.ume.tubitak.gov.tr/srm_sd)

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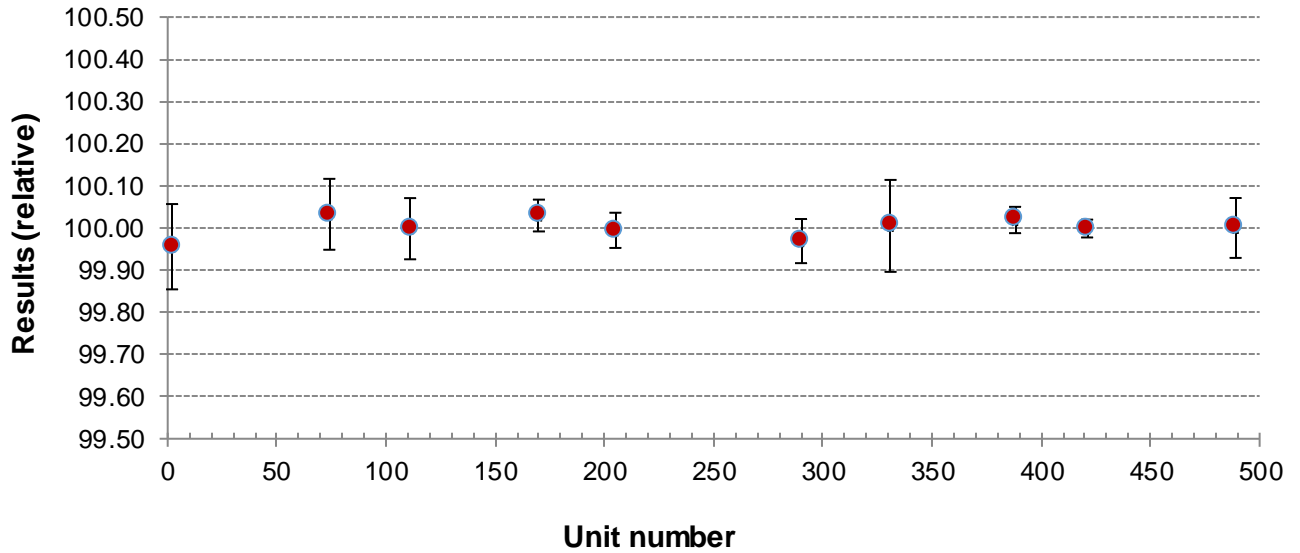
## REVISION HISTORY

Date	Remarks
24.09.2021	First publication.
27.12.2022	The expression of "50 tablets" has been added to the description of the material.
16.02.2024	Characterization uncertainty value for gross calorific value and its contribution to the $U_{CRM}$ value have been updated. Expressions about traceability and quality control have been added to the characterization section. The statement regarding the traceability of measurements has been updated in traceability section. The link for reference [28] has been updated.

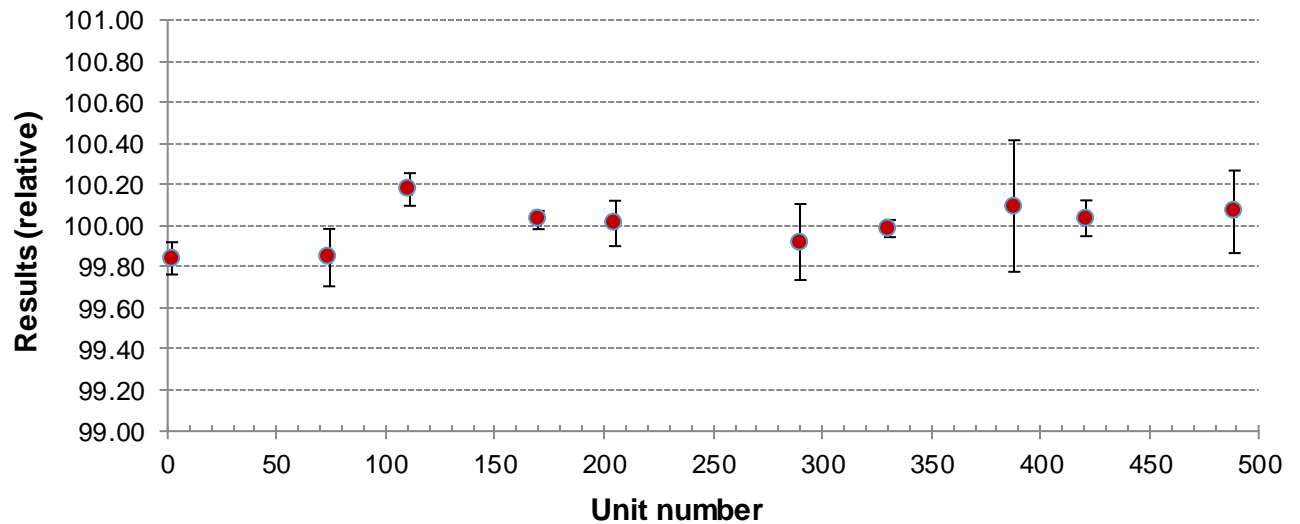


## ANNEXES

### Annex 1. Graphs for Homogeneity Studies

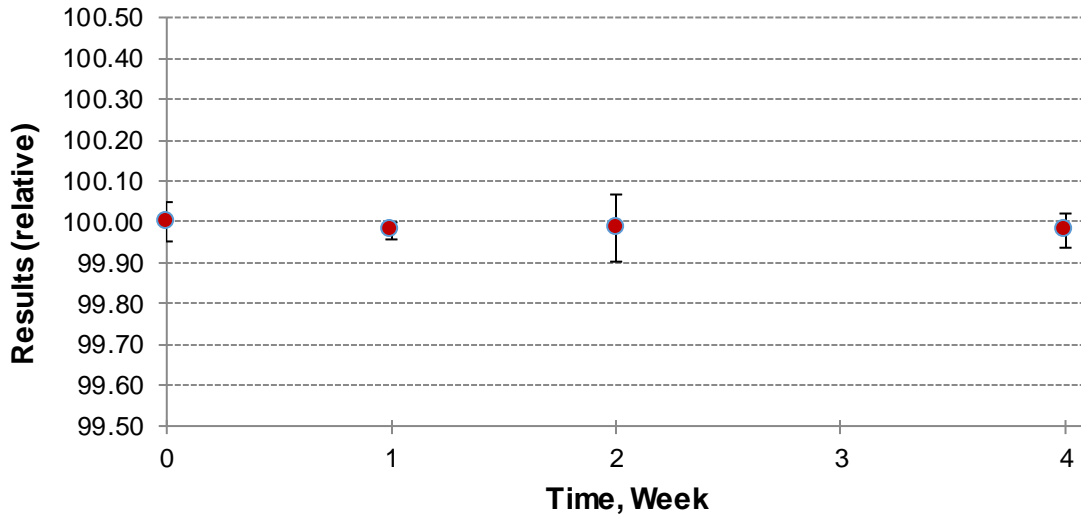


**Figure A1.** UME CRM 1504, Homogeneity plot, Gross calorific value

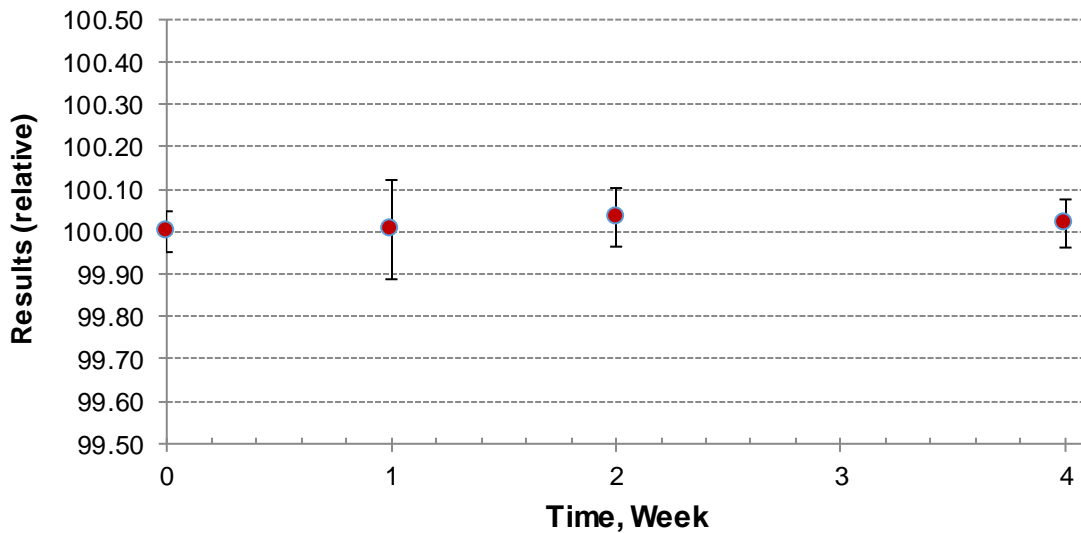


**Figure A2.** UME CRM 1504, Homogeneity plot, Purity

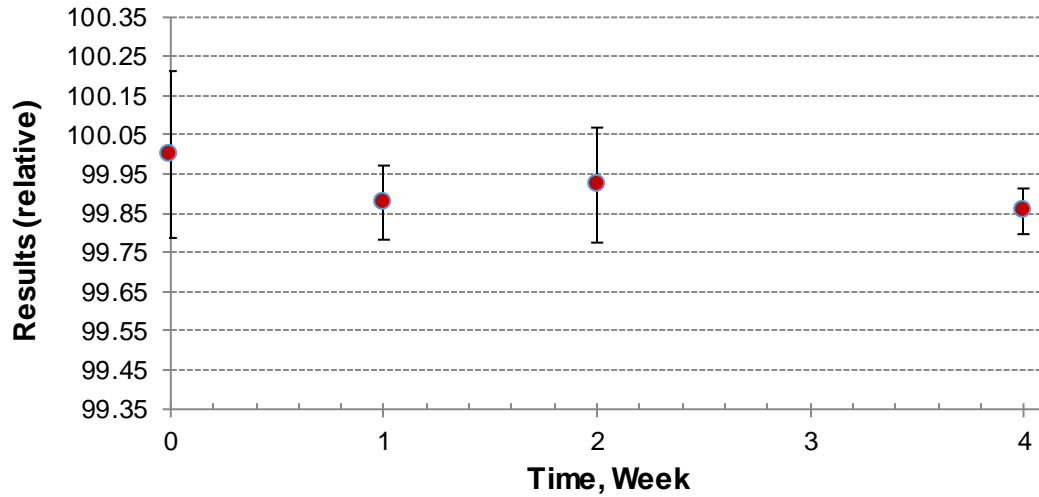
## Annex 2. Graphs for Short Term Stability Studies



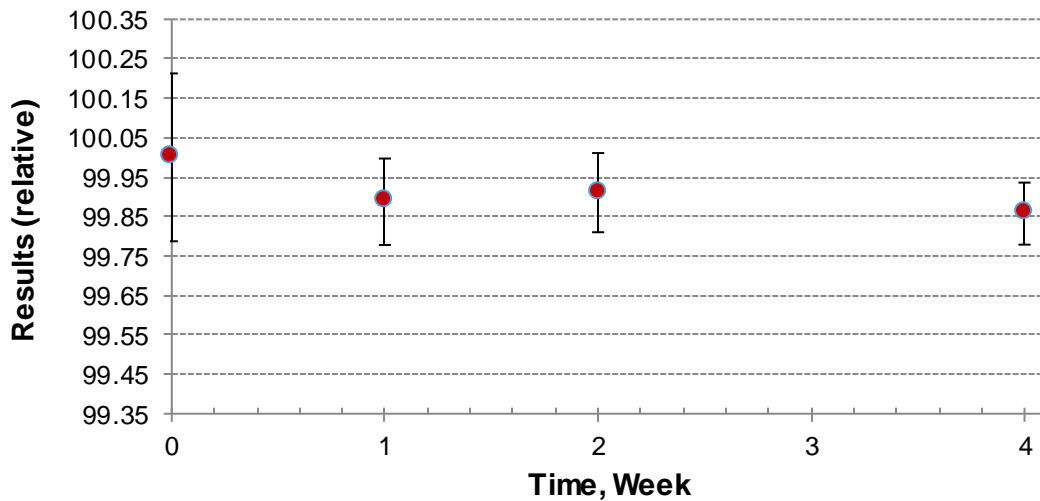
**Figure A3.** UME CRM 1504, Short term stability plot, Gross calorific value, -20 °C



**Figure A4.** UME CRM 1504, Short term stability plot, Gross calorific value, 50 °C

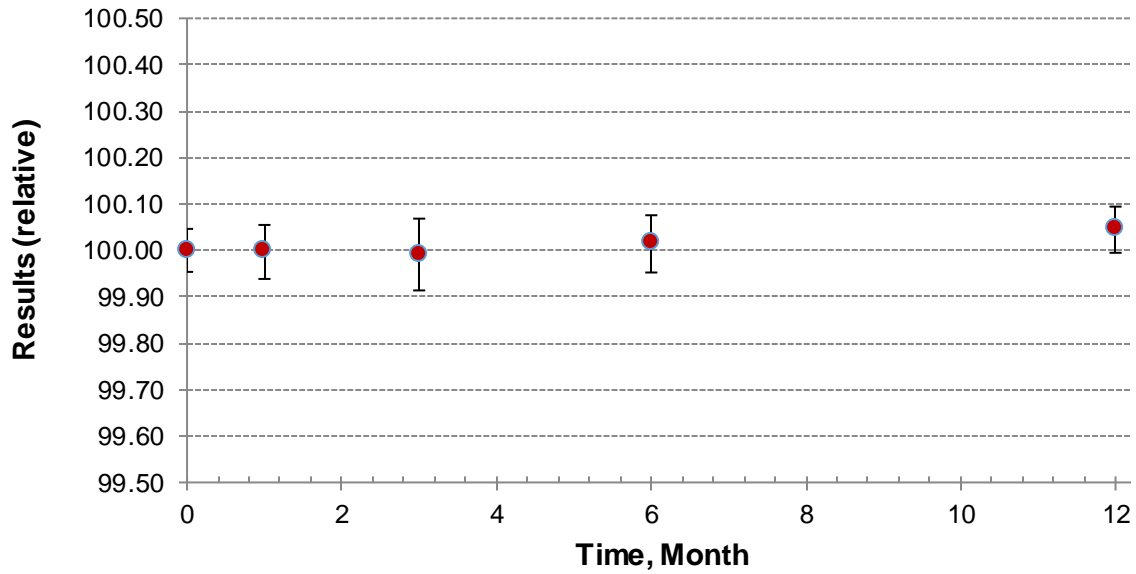


**Figure A5.** UME CRM 1504, Short term stability plot, Purity, -20 °C

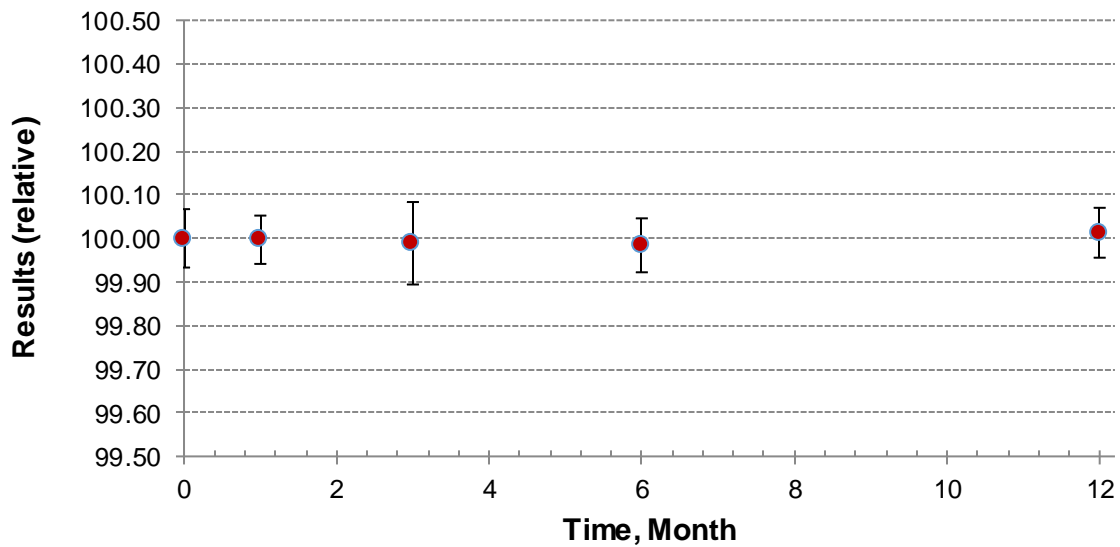


**Figure A6.** UME CRM 1504, Short term stability plot, Purity, 50 °C

### Annex 3. Graphs for Long Term Stability Studies



**Figure A7.** UME CRM 1504, Long term stability plot, Gross calorific value, 18 °C



**Figure A8.** UME CRM 1504, Long term stability plot, Purity, 18 °C

#### Annex 4. Characterization Data

**Table A1.** UME CRM 1504 Gross calorific value characterisation measurement results

Technique	Bottle No	Gross Calorific Value Measurement Results (J/g)	
Bomb Calorimeter	1-1	26471.8	
	1-2	26476.7	
	132-1	26472.2	
	132-2	26476.5	
	211-1	26467.1	
	211-2	26473.2	
	272-1	26468.6	
	272-2	26485.4	
	398-1	26463.9	
	398-2	26484.4	
	484-1	26463.8	
	484-2	26473.9	
	<b>Gross Calorific Value (Average)</b>		<b>26473.1</b>
	<b>Standard Uncertainty (<math>k = 1</math>)</b>		<b>3.2</b>

**Table A2.** UME CRM 1504 Purity characterisation measurement results

Technique	Bottle No	Purity Measurement Results (%)	
Potentiometric Titration	1-1	99.931	
	1-2	100.017	
	132-1	100.038	
	132-2	99.987	
	211-1	100.096	
	211-2	99.907	
	272-1	99.997	
	272-2	100.018	
	398-1	100.098	
	398-2	99.829	
	484-1	99.957	
	484-2	100.049	
	<b>Purity (Average)</b>		<b>99.994</b>
	<b>Standard Uncertainty (<math>k = 1</math>)</b>		<b>0.074</b>

**Table A3.** UME CRM 1504 Purity characterisation measurement results

Technique	Bottle No	Purity Measurement Results (%)
qNMR	4-1	99.879
	4-2	99.771
	4-3	99.806
	52-1	99.993
	52-2	99.957
	52-3	99.944
	97-1	99.965
	97-2	99.906
	97-3	100.004
	126-1	99.897
	126-2	99.820
	126-3	99.795
	258-1	99.969
	258-2	99.902
	258-3	99.942
	318-1	100.003
	318-2	99.932
	318-3	99.981
	325-1	100.016
	325-2	99.971
	325-3	100.069
	341-1	99.917
	341-2	99.871
	341-3	99.981
	354-1	99.845
	354-2	99.832
	354-3	99.858
	471-1	99.939
	471-2	99.840
	471-3	99.851
	<b>Purity (Average)</b>	<b>99.915</b>
	<b>Standard Uncertainty (k = 1)</b>	<b>0.097</b>