Certified Electrolytic Conductivity Solutions
UME CRM 1404-1
UME CRM 1404-2

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ABBREVIATIONS

ANOVA	Analysis of variance
ISO	International Organization for Standardization
µS	Micro Siemens
KCl	Potassium chloride
k	Coverage factor
$MS_{between}$	Mean square between units from ANOVA
MS_{within}	Mean square within unit from ANOVA
NIST	National Institute of Standards and Technology (USA)
PTB	The Physikalisch-Technische Bundesanstalt (Germany)
RSD	Relative standard deviation
s	Standard deviation
s_{bb}	Standard deviation between bottles
$s_{bb,rel}$	Relative standard deviation between bottles
SGT	Single Grubbs Test
SI	International System of Units
CRM	Certified Reference Material
s_{wb}	Standard deviation within-bottle
$s_{wb,rel}$	Relative standard deviation within-bottle
$\bar{t}$	Mean of whole time points
t_{α}	Critical t value (Two-tailed)
t_i	Time point for each parallel
TRaNS	Random Stratified Sample Selection
u_{bb}	Standard uncertainty related to between bottle homogeneity
u^*_{bb}	Standard uncertainty of heterogeneity that can be hidden by method repeatability
$u_{char.rel}$	Relative standard uncertainty related to characterization
u_{CRM}	Standard uncertainty of the certified value
$u_{CRM.rel}$	Relative standard uncertainty of the certified value
U_{CRM}	Expanded uncertainty of the certified value
$U_{CRM.rel}$	Relative expanded uncertainty of the certified value
u_{lts}	Standard uncertainty related to long term stability
$u_{lts.rel}$	Relative standard uncertainty related to long term stability
u_{sts}	Standard uncertainty related to short term stability
$u_{sts.rel}$	Relative standard uncertainty related to short term stability
$\nu_{MSwithin}$	Degrees of freedom related to MS_{within}

SUMMARY

Conductivity is a measure of the ability of a solid, liquid or gaseous substance to conduct an electricity current. In solutions, conductivity is provided by positively or negatively charged ions, and this type of conductivity is called electrolytic conductivity. Electrolytic conductivity measurements and controls are of great importance both in research studies applied in fields such as chemistry, medicine, food and environment in industrial processes and in determining the compliance of a product with legal requirements. In all these measurements, devices that measure conductivity are used. Certified reference conductivity solutions (CRMs) are used for calibrations of these devices.

INTRODUCTION

Electrolytic conductivity (EC) is a measure of ability to conduct electrical current. In liquids, the magnitude of the conductivity depends on the nature of the ions in the solution (charge, size, mobility, etc.) and the nature of the solvent (viscosity, dielectric constant, etc.). Conductivity measurements are not substance-specific, as all ions in solution contribute to conductivity. Therefore, electrolytic conductivity measurements do not give any qualitative information.

The conductivity is determined by measuring the resistance in a conductivity cell. The resistance changes in proportion to the ratio of the effective distance between the electrodes to the effective cross-sectional area.

$$\boldsymbol{R} = \boldsymbol{\rho}\frac{\boldsymbol{l}}{\boldsymbol{A}} \tag{1}$$

The resistivity, ρ, is a constant for the solution used. Conductivity is also expressed as the inverse of resistivity.

$$K = \frac{1}{\rho} = \frac{1}{\mathrm{R}}\frac{l}{A} \tag{2}$$

In the calibration of electrolytic conductivity meters, a cell constant is determined. The notation of the cell constant is K_{cell} and the cell constant is formulated as below:

$$K_{cell} = \frac{l}{A} \tag{3}$$

$$K = \frac{K_{cell}}{R} \tag{4}$$

The dependence of conductivity on temperature is given as:

$$K = \frac{\frac{K_{cell}}{R}}{1+0{,}0195(T-T_{ref})} \tag{5}$$

T : Measured Temperature,

T_{ref} : Reference temperature value (20 °C, 25 °C etc.)

According to the above equations, the conductivity of the sample solution is determined by measuring the resistance of the relevant solution in a cell with a known cell constant.

In primary level electrolytic conductivity measurements, the Jones cell filled with the solution whose conductivity is to be measured is connected to an LCR meter that oscillates AC current and it is immersed in a water bath that measures temperature with high precision (temperature stability ≤ 0.004 °C) set at 25.000 °C. The measurement of the temperature in the bath is carried out by using a PT-100 SRT probe immersed in the bath. With and without the central tube in the conductivity cell, resistance measurements are made in the range of 1-8 kHz, and the difference of these is replaced in equation (4), where the cell constant is also known, and the conductivity value is calculated. In the calculation of the cell constant, the center tube thickness is used instead of the effective distance between the electrodes, and the area of the middle part of the central tube is used instead of the effective cross-sectional area. In addition, in cases where the temperature measured by the SRT probe deviates from 25 °C, temperature correction is also applied with the help of equation (5).

A conductivity meter and a conductivity probe were used for working level electrolytic conductivity measurements. First of all, the calibration of the probe with the cell constant suitable for the solution to be measured is performed at the appropriate temperature with the appropriate certified conductivity solution. The cell constant obtained should be within the tolerance limits specified by the manufacturer, otherwise the probe must be replaced. After this stage, sample measurement can be started. All these measurements are generally applied at 25 °C [1-2].

A primary level electrolytic conductivity measurement system was established at TÜBİTAK UME, which is required for the characterization and certification measurements of the candidate CRM solutions.

PARTICIPANTS

All stages of production for UME CRM 1404-1 and UME CRM 1404-2 are performed at TÜBİTAK UME.

Job Discription	Laboratory / Organisation
Project Management and Data Evaluation	TÜBİTAK National Metrology Institute (UME) TÜBİTAK Gebze Yerleşkesi, Barış Mahallesi Dr. Zeki Acar Cad. No.1, 41470, Gebze, Kocaeli, Türkiye
Material Processing	
Homogeneity Study	
Stability Studies	
Characterisation Study	

MATERIAL PROCESSING

Potassium chloride was used in the preparation of certified reference solutions at the determined electrolytic conductivity values, and ultrapure water was used as the solvent. In the preparation of the solutions, the document "Standard Reference Materials: Primary Standards and Standard Reference Materials for Electrolytic Conductivity" (NIST Special Publication 260-142, 2004) was used [3].

As per this document, 300 units (in 500 mL bottles) of homogenized solution were prepared by adding 0.01 m KCl for low level and 0.1 m KCl for high level into approximately 160 kg ultrapure water using the IKA Ultra Turrax device as a result of mixing for 8 hours at 300 rpm. The prepared solutions were labeled according to the order of filling and stored at +4 °C.

HOMOGENEITY

After the solutions were prepared, the control of whether the intended electrolytic conductivity values were achieved was made with a conductivity meter. Some of the 300 bottles (approximately 100) were reserved for characterization, short-term stability (STS), long-term stability (LTS), and homogeneity testing. For the homogeneity test studies, 20 bottles, 10 original and 10 spare, were reserved for each electrolytic conductivity level. The selection of these samples was made randomly with the software TRaNS (stratified random sample selection, developed by TÜBİTAK UME) to represent the whole produced batch.

Analyses of the samples were evaluated by one-way analysis of variance (ANOVA). The data were statistically evaluated to check for the presence of any trends and/or outliers. No trend related to filling and measuring order was observed.

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

$$s_{wb} = \sqrt{MS_{within}} \tag{6}$$

$$s_{bb} = \sqrt{\frac{MS_{between} - MS_{within}}{n}} \tag{7}$$

s_{wb} : Standard deviation within-bottle,
MS_{within} : Mean Square within unit,
s_{bb} : Standard deviation between units,
$MS_{between}$: Mean Square between units,
n : Number of measurements for each unit.

When $MS_{between}$ is smaller than MS_{within}, s_{bb} cannot be calculated. In this case u^*_{bb} standard uncertainty of the maximum heterogeneity which may be hidden by method repeatability is calculated by the formula given below:

$$u^*_{bb} = \frac{s_{wb}}{\sqrt{n}} \sqrt[4]{\frac{2}{\nu_{MSwithin}}} \tag{8}$$

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

The analyzes were evaluated statistically and the uncertainty values arising from homogeneity are stated in Table 1.

Table 1. The homogeneity study test results

CRM	$u_{bb,rel}$ (%)
UME CRM 1404-1	0.064
UME CRM 1404-2	0.032

STABILITY

Stability studies were carried out by simulating environmental conditions in the laboratory for transportation of certified reference material to user (short term stability) and for storage conditions (long term stability). Stability test measurements were realized by a conductivity meter employing a electrolytic conductivity electrode together with a thermostat to select and stabilize the temperature value. Calibration and intermediate controls of the system were carried out with standard electrolytic conductivity solutions traceable to certified reference materials produced by NIST and PTB.

Units to be tested for short term stability and long term stability were selected by stratified random sample selection method using TRaNS software.

Temperatures for the short term stability were specified as 18 °C and 50 °C. For each time interval to be tested at both temperatures, 4 units for UME CRM 1404-1 and UME CRM 1404-2, 2 units of main and 2 units of spare, were placed in test cabinets. For the reference point in the short-term stability test, 4 units of samples, 2 units of main and 2 units of spare, were allocated and these units were placed directly at +4 °C, which is the reference temperature. At the end of each test period, 4 units from 2 test temperatures were transferred to the reference temperature. When the four-week test period was completed, all the units transferred to the reference temperature were analyzed at the same time as the main units to be used as the reference. Since there is no leakage, cap loosening and cracking in the main units, spare units were not used in short-term stability measurements.

For long-term stability studies, both main and spare test samples were kept at 18 °C for 3, 6 and 9 months, similar to short-term stability studies in terms of application. At the end of each period, the samples were transferred to +4 °C and the measurements of these units were carried out at the end of 9 months.

In addition, the usage stability of the produced electrolytic conductivity solutions was evaluated using 2 units each stored under laboratory conditions. Measurements were carried out at the end of each month using the same samples to see the effect of use for a total of 6 months. The deviation values obtained were found to be compatible with the certificate values of the certified reference materials produced. The results obtained were not used in uncertainty assessments.

Short Term Stability Study Results

Evaluations for 18 °C and 50 °C were realized separately.

The results were screened for single outliers by applying the Grubbs' test at confidence levels of 95% and 99%. The measured concentration values were plotted against time and the regression lines were calculated to check for significant trends indicating possible changes in the concentrations of the analytes by time. The calculated slope values were tested for significance using a *t*-test with $t_{\alpha.df}$ being the critical t-value (two-tailed) for a significance level α = 0.05 (95% confidence level). The graphs are presented in Annex 2.

The uncertainty for the short term stability is calculated from the uncertainty of the slope of the regression line and chosen transfer time using equation (9).

$$u_{sts,rel} = \frac{RSD}{\sqrt{\sum(t_i - \bar{t})^2}} \times t \tag{9}$$

RSD : Relative standard deviation of the points on the regression line
t_i : Time point for each replicate
$\bar{t}$: Average of all time points
t : Transfer time proposed: 4 weeks

The data points were plotted against storage time at the test temperature and the regression line was calculated. In all cases the slope of the regression line was not found to be significantly different from zero. The data evaluation results for the short-term stability at +18 °C and +50 °C are summarised in Table 2.

Table 2. The short term stability test results

Parameter		UME CRM 1404-1	UME CRM 1404-2
Slope significantly different from zero at test temperature 18 °C at a level of 95% and 99% confidence	**18 °C**	No	No
	50 °C	No	No
Outlier*		-	-

* SGT: Single Grubbs Test

As a result of evaluation, it was observed that the produced certified reference materials were stable for 4 week at 18 °C and 50 °C.

Thus, it was concluded that the samples can be delivered to the end user without any cooling application, in conditions where the temperature is between 18 °C and 50 °C and the duration does not exceed 4 weeks.

Uncertainty values obtained in short-term stability studies are given in Table 3.

Table 3. Uncertainty values of the short term stability

Uncertainty values of the short term stability		UME CRM 1404-1	UME CRM 1404-2
$u_{sts,rel}$ (%)	**18 °C**	0.029	0.009
	50 °C	0.034	0.013

Long Term Stability Study Results

Shelf life of the CRM has been determined according to the long term stability measurements. For these measurements, 3, 6 and 9 months samples for UME CRM 1404-1 and UME CRM 1404-2 were kept at 18 °C (2 main, 2 spare, and reference, total 16 units). At the end of every three months, the determined samples were taken and transferred to the reference temperature, 4 °C, the electrolytic conductivity value was determined for all units at the end of the 9 month period.

The uncertainties related to the long-term stability of the produced materials were calculated using equation (10). The shelf life of the UME CRM 1404-1 and UME CRM 1404-2 certified reference material was predicted to be 12 months after the sale, and the long-term stability uncertainty was calculated accordingly.

$$u_{lts,rel} = \frac{RSD}{\sqrt{\sum \left(t_i - \bar{t}\right)^2}} \times t \qquad (10)$$

RSD : Relative standard deviation of the points on the regression line
t_i : Time point for each replicate
$\bar{t}$: Average of all time points
t : Shelf life proposed: 12 months

The values found were plotted against time and the agreement between them was determined. Uncertainty values arising from long-term stability of the produced materials are given in Table 4.

Table 4. Results of the long-term stability tests of 12 months

Parameter	UME CRM 1404-1	UME CRM 1404-2
Is the slope of the graph plotted with the concentration values calculated against time at 18 °C significantly different from zero?*	No	No
$u_{lts,rel}$ (%) (for a shelf life of 12 months at 18 °C)	0.046	0.035

* The data were evaluated at the 95% confidence level.

According to the results obtained, the storage temperature for the materials were set to 18 °C. In addition, to ensure stability beyond the initial shelf life, it will be re-evaluated in certain periods based on the results of regular post-certification monitoring.

CHARACTERIZATION

According to ISO 17034:2016, the characterization and the value assignment can be carried out in different ways. In this study, a single laboratory and primary method approach among these approaches was selected. The characterization of materials was carried out using primary level electrolytic conductivity measurement system.

The uncertainty arising from the characterization study, u_{char}, was also taken into account for the calculation of the uncertainty of the certified value. The characterization uncertainty values, u_{char}, were calculated from the data obtained from the measurement results of 6 units for each material at 25 °C on 2 different days for each CRM using a primary level electrolytic conductivity measurement system.

PROPERTY VALUE AND ASSIGNMENT OF UNCERTAINTY

Uncertainty values in the certificate include characterization uncertainty (u_{char}), homogeneity uncertainty (u_{bb}), short term stability uncertainty (u_{sts}) and long term stability uncertainty (u_{lts}).
These different parameters were combined using equation 11 to obtain the uncertainty of CRM:

$$U_{CRM} = k \cdot \sqrt{u_{char}^2 + u_{bb}^2 + us_{sts}^2 + u_{lts}^2} \tag{11}$$

The expanded uncertainty of the certified value U_{CRM} is calculated with a coverage factor of *k=2* representing a confidence level of approximately 95%. The certified values and uncertainties are summarised at Table 5 and the uncertainty contribution percentages are given at Table 6.

Table 5. Certified values and their uncertainties

CRM	*EC* (μS·cm^{-1})	U_{CRM} (*k=2*) (μS·cm^{-1})	$U_{CRM,rel}$ (*k=2*) (%)	$u_{bb,rel}$ (%)	$u_{sts,rel}$ (%)	$u_{lts,rel}$ (%)	$u_{char,rel}$ (%)
UME CRM 1404-1	1409.5	2.7	0.19	0.064	0.034	0.046	0.040
UME CRM 1404-2	12804	13	0.10	0.032	0.013	0.035	0.014

Table 6. The percentage contribution of each parameter which constitutes to U_{CRM}

CRM	$u_{bb,rel}$ (%)	$u_{sts,rel}$ (%)	$u_{lts,rel}$ (%)	$u_{char,rel}$ (%)
UME CRM 1404-1	45.8	12.8	23.5	17.9
UME CRM 1404-2	39.6	6.3	46.5	7.6

COMMUTABILITY

Commutability is the mathematical relationship of the equation between the reference material and the results produced by the different measurement methods that can be used to measure the routine samples it represents. The compatibility of the certified reference material is important in terms of its fitness for use and the application of different measurement methods.

The certified reference electrolytic conductivity solutions produced in this project are compatible with the matrices of the materials/samples that the users generally measure.

TRACEABILITY

The metrological traceability of the assigned values of the produced certified reference materials is ensured by using the primary level electrolytic conductivity measurement system. The verification measurements of the primary level electrolytic conductivity measurement system were carried out by using DFM (Danish National Metrology Institute) certified electrolytic conductivity solutions [(1.0002 ± 0.0011) $S{\cdot}m^{-1}$ (25 °C) and (99.99 ± 0.15) $mS{\cdot}m^{-1}$ (25 °C)].

All of the solutions used in characterization studies realised by using this method were prepared gravimetrically. All of the weighings were made using analytic balance which are traceable to national measurement standards, and the control of the balances was carried out with appropriate mass set weights. The balance and the mass set weights used are traceable to national measurement standards realised units defined in the International System of Units (SI). Temperature measurements were carried out with the PT-100 probe (with an uncertainty of 0.03 °C) calibrated by TÜBİTAK UME and continuously monitored. The measurement uncertainty calculations of the characterization measurements were calculated using the data obtained as a result of the measurements performed by using the primary level electrolytic conductivity measurement system.

INSTRUCTIONS FOR USE

Minimum Sample Intake

All precautions should be taken to prevent contamination and evaporation of the material during opening and subsequent use of the bottle. The bottle should be shaken before opening the cap to avoid a bias due to condensed water at the bottleneck. The minimum amount of material to be used in the measurements should be arranged such that the diaphragm of the electrode to be calibrated is completely immersed into the solution. Although this amount may vary depending on the electrode type, it is approximately 25 mL. Calibration should be made at a temperature of 25 °C, and measurements of the electrolytic conductivity value of the sample solutions should be the same as the temperature at which the calibration was performed. Electrode or any other substance must not be immersed into the bottle for measurement. The measurement should be carried out by transferring the amount to be used from the bottle to a clean container. The material transferred to the container must not be returned to the bottle. The cap of the bottle should not be left open. This material can be safely dispatched under conditions where the temperature does not exceed 50 °C for up to 4 weeks. Material should not be used longer than 3 months after opening of the bottle.

Users can evaluate the results of the measurements carried out with the reference materials UME CRM 1404-1 and UME CRM 1404-2 with the certified values using the website https://rm.ume.tubitak.gov.tr/srm_sd/ or the ERM Application Note 1 document [4-5].

Storage Conditions

The material should be stored at (21 ± 3) °C temperature range.

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 described in the certificate.

Safety Information

Usual laboratory precautions apply. 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.

REFERENCES

[1] Sørensen, J. N. Establishment of a Primary Standard for Electrolytic Conductivity and New Reference Solutions, Ph. D. Thesis, Technical University of Denmark and Danish Institute of Fundamental Metrology, 2000.

[2] Pratt, K. W., Koch, W. F., Wu, Y. C. and Berezansky, P. A. IUPAC Technical Report: Molality-Based Primary Standards of Electrolytic Conductivity, PureAppl. Chem., 73, 1783-1793, 2001.

[3] Shreiner, R. H. and Pratt, K. W. Standard Reference Materials: Primary Standards and Standard Reference Materials for Electrolytic Condutivity, NIST Special Publication 260-142, 2004.

[4] ERM Application Note 1: Comparison of a Measurement Result with Certified Value, January 2010.

[5] https://rm.ume.tubitak.gov.tr/crm_re/, Certified Reference Material Result Evaluation.

REVISION HISTORY

Date	Remarks
20.10.2020	First publication

ANNEX 1. Graphs for Homogeneity Studies

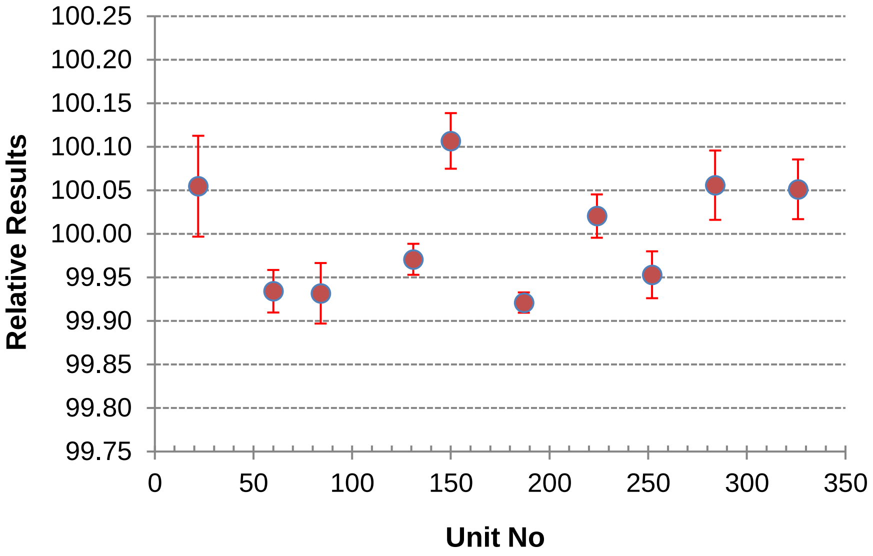

Figure 1. Homogeneity Graph for UME CRM 1404-1

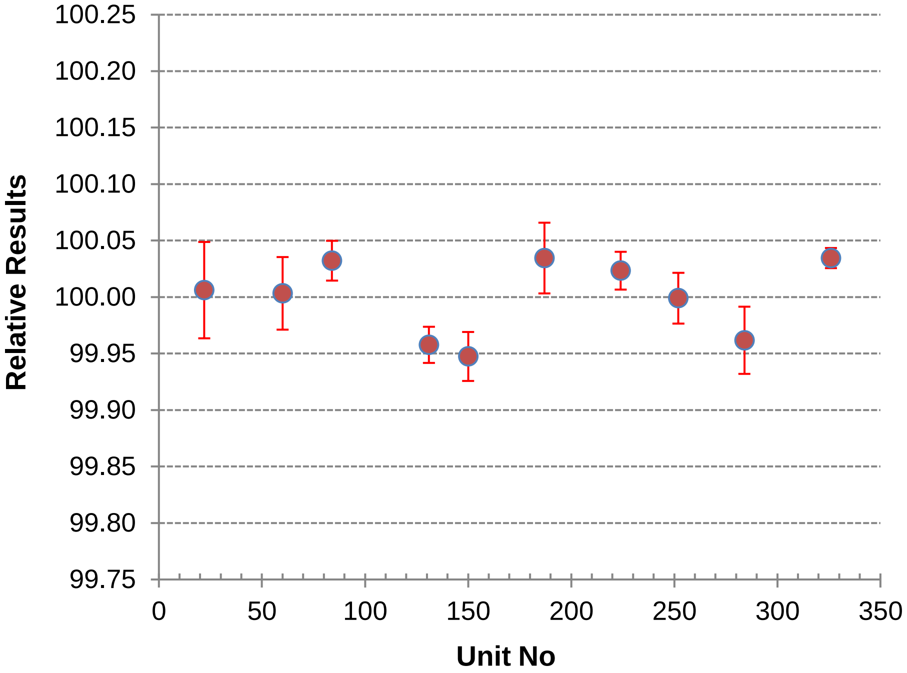

Figure 2. Homogeneity Graph for UME CRM 1404-2

ANNEX 2. Graphs for Short Terms Stability Studies

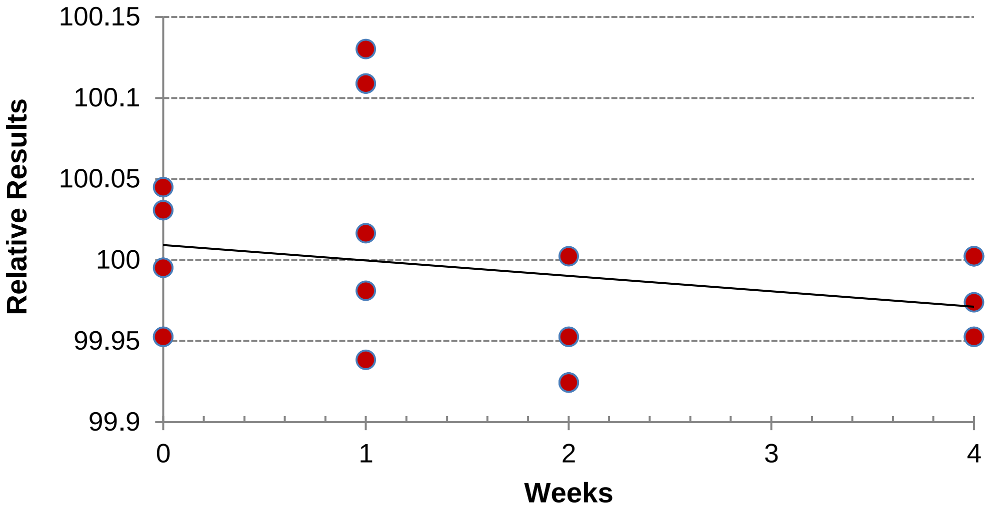

Figure 3. Short Term Stability Plot for UME CRM 1404-1 at 18 °C

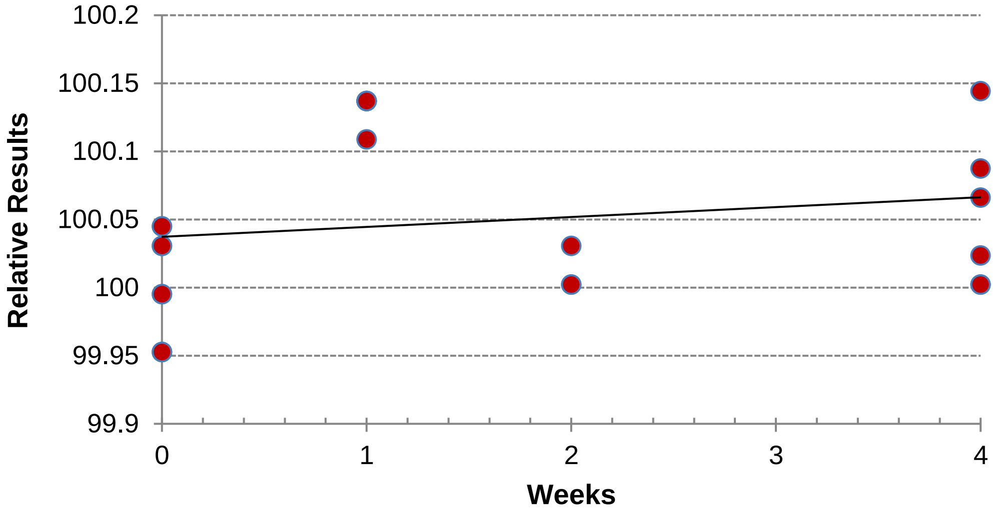

Figure 4. Short Term Stability Plot for UME CRM 1404-1 at 50 °C

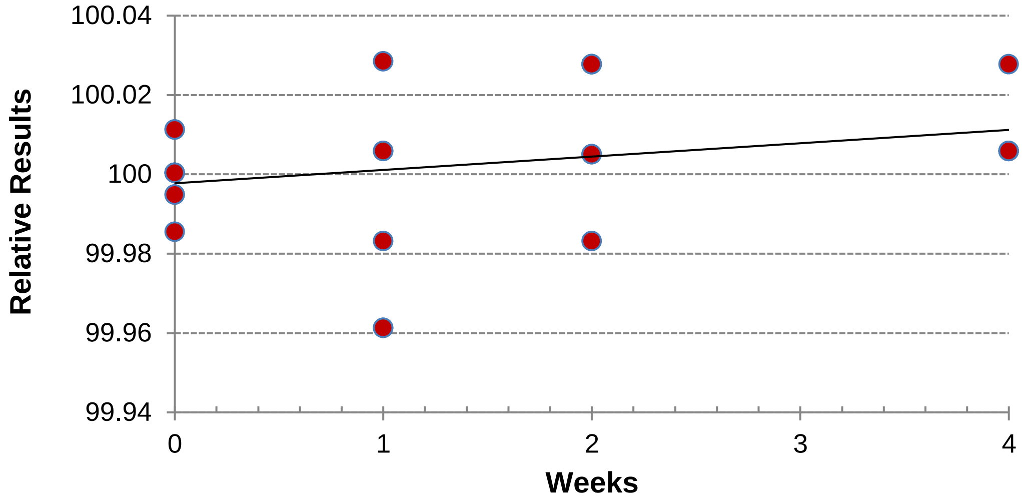

Figure 5. Short Term Stability Plot for UME CRM 1404-2 at 18 °C

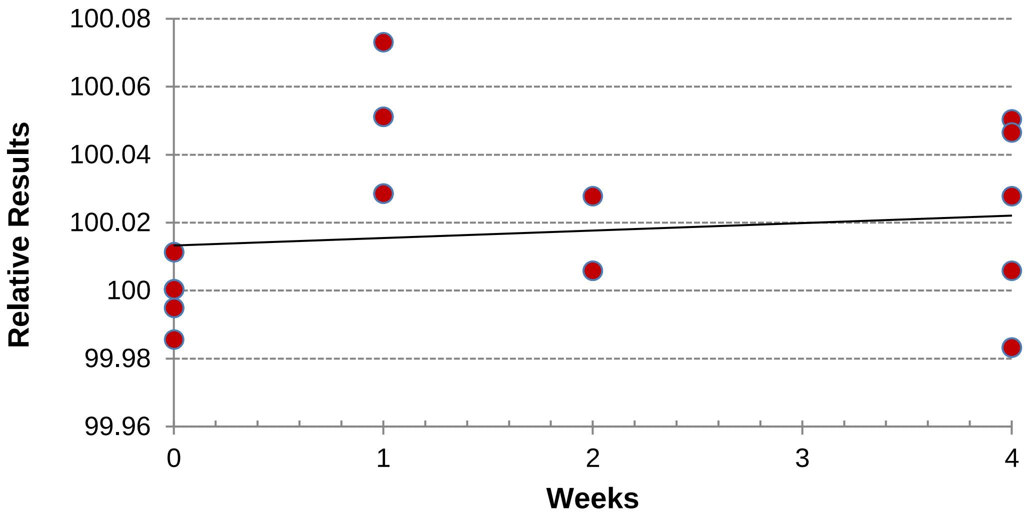

Figure 6. Short Term Stability Plot for UME CRM 1404-2 for at 50 °C

ANNEX 3. Graphs for Long Terms Stability Studies

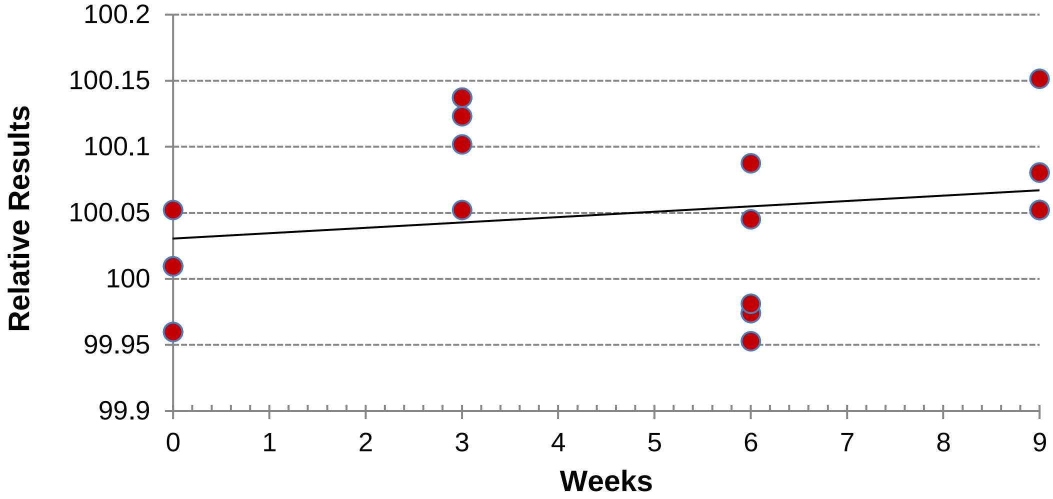

Figure 7. Long Term Stability Plot for UME CRM 1404-1

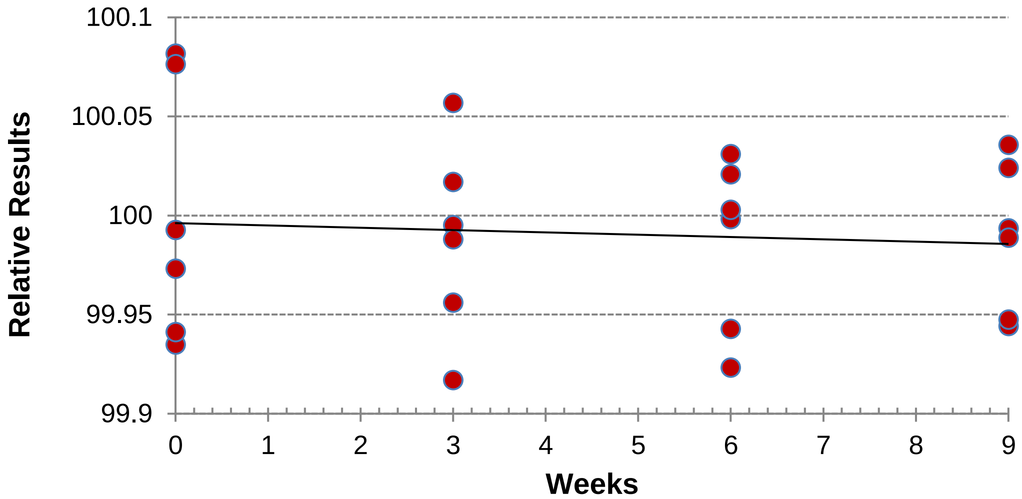

Figure 8. Long Term Stability Plot for UME CRM 1404-2

ANNEX 4. Data for Characterization Studies

Table 7. Measurement Results of the Characterization Study for UME CRM 1404-1

Unit No	EC ($\mu S \cdot cm^{-1}$)	SD ($\mu S \cdot cm^{-1}$)
32	1409.0	0.4
97	1409.0	0.4
162	1409.0	0.7
202	1412.0	0.4
264	1410.0	0.4
328	1408.0	0.5
Mean	**1409.5**	
SD	**1.4**	

Table 8. Measurement Results of the Characterization Study for UME CRM 1404-2

Unit No	EC ($\mu S \cdot cm^{-1}$)	SD ($\mu S \cdot cm^{-1}$)
32	12805.9	8.1
97	12795.5	8.6
162	12804.4	2.0
202	12806.4	2.1
264	12806.6	1.9
328	12802.1	2.0
Mean	**12803.5**	
SD	**4.3**	