Elemental Calibration Solutions Certification Report UME CRM 2200 Series (As, Cd, Co, Zn)

Dr. Murat TUNÇ
Dr. Süleyman Z. CAN
Gökhan AKTAŞ
Dr. F. Gonca COŞKUN
Tülin ERDOĞAN
Assoc. Prof. Oktay CANKUR
Özkan GÜLERYÜZ

Date
02.12.2025

Assoc. Prof. Mustafa ÇETİNTAŞ
Director

TABLE OF CONTENTS

TABLE OF CONTENTS 2
ABBREVIATIONS 3
ABSTRACT 4
INTRODUCTION 5
PARTICIPANTS 6
MATERIAL PROCESSING 6
Material Definitions and Sources 6
Material Preparation 6
Gravimetric Weighing 7
Homogenization and Bottling 7
HOMOGENEITY 8
STABILITY 10
Short-Term Stability Study Results 10
Long-Term Stability Study Results 11
CHARACTERIZATION 12
PROPERTY VALUE AND UNCERTAINTY ASSIGNMENT 13
INFORMATIVE VALUES 15
TRACEABILITY 15
INSTRUCTIONS FOR USE 15
REFERENCES 16
REVISION HISTORY 17
ANNEXES 18
Annex 1. Graphs for Homogeneity Studies 18
Annex 2. Graphs for Short Term Stability Studies 20
Annex 3. Graphs for Long Term Stability Studies 22

ABBREVIATIONS

α	Significance level
AAS	Atomic Absorptipn Spectrometry
CRM	Certified reference material
GUM	Guide to the Expression of Uncertainty in Measurement
HDPE	High density polyethylene
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
HP-ICP-OES	High Performance Inductively Coupled Plasma Optical Emission Spectrometry
ISO	International Organization for Standardization
LTS	Long term stability
$MS_{between}$	Mean square between-bottle from ANOVA
MS_{within}	Mean square within-bottle from ANOVA
N	Number of replicates per unit
PS	Primary standard
RSD	Relative standard deviation
s	Standard deviation
s_{bb}	Between-bottle standard deviation
SGT	Single Grubbs' test
SI	International System of Units
STS	Short term stability
s_{wb}	Within-bottle standard deviation
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 characterization
$u_{char,rel}$	Relative standard uncertainty related to characterization
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
$v_{MSwithin}$	Degrees of freedom for MS_{within}

ABSTRACT

This report covers the production of Elemental Calibration Solution - Certified Reference Materials (CRMs) prepared using Primary Standards (PS) of pure elements or elemental salts, and the certification of CRM mass fractions. The reference material production processes consist of gravimetric CRM preparation, and the tests for homogeneity, short-term stability, long-term stability, and characterization stages. The certification of the materials was carried out in accordance with the requirements of ISO 17034:2016 standard [1] and ISO 33405:2024 guideline [2]. The chemical measurements performed during the certification process met the requirements of TS EN ISO/IEC 17025:2017 [3]. Uncertainties of the certified values were calculated in accordance with the JCGM 100:2008 Measurement Uncertainty Guide (GUM) [4].

The planning of all stages of this reference material production project, the coordination of the activities performed, the execution of the experiments, and the evaluation of all obtained data were carried out by TÜBİTAK UME experts using the institutional infrastructure.

Element calibration solutions are intended to be used as calibration standards for the determination of elements.

INTRODUCTION

One of the fundamental requirements for obtaining reliable measurements in chemical measurements is the implementation of calibration using accurate and traceable sources. Elemental calibration solutions are one of the fundamental components used to ensure the accuracy of inorganic chemical measurements. These solutions are produced as certified reference materials (CRM) and must be traceable to the International System of Units (SI) [5-7]. This report comprehensively covers the preparation, certification, value assignment processes, and information, as well as the conditions of use, of these solutions for elemental analysis.

Elemental calibration solutions are liquid reference materials in solution form, prepared with known concentrations of elements in elemental or salt form of known purity. These materials are used for instrument calibration to ensure traceability of measurement results to the International System of Units (SI). These solutions must be prepared and made available to users by manufacturers whose competence is accredited in accordance with the requirements of the ISO 17034 standard [1]. Materials are expected to have an assigned value along with its uncertainty, a clear traceability statement, production and recommended consumption dates, and clear and concise information about conditions of use.

Many laboratories operating in public institutions and private sectors in our country and around the world conduct elemental analyses. Laboratories operating in a variety of fields, including environmental pollutant monitoring, food safety, mining and geology, material development studies, and clinical analyses, require these materials for accurate and traceable analyses. When analysis results often need to be interpreted according to a specific value for scientific or legal reasons, the uncertainty of the measurement plays a crucial role in the application of the decision rule. Obtaining low uncertainty and high accuracy requires that the SRMs produced for elemental calibration used in these measurements have very low uncertainties.

This study aims to produce SI traceable calibration standards to meet the calibration standard needs of laboratories conducting elemental analysis in our country, and to ensure metrological traceability of measurements made in our country to the SI unit system through TÜBİTAK UME. Calibration standards with nominal concentrations of 1000 mg/kg for arsenic, cadmium, cobalt, and zinc were produced using UME CRM 2203, UME CRM 2211, UME CRM 2213, and UME CRM 2270, respectively, and the mass fractions for each material were certified. The assigned mass fractions were determined using the results of gravimetric solution preparation and High-Performance Inductively Coupled Plasma Optical Emission Spectrometry (HP-ICP-OES) [8, 9] analysis, with high-purity metals and salts, whose purity was determined by TÜBİTAK UME. The calibration Primary Standards (PS) used in material preparation and HP-ICP-OES measurements were stored in an inert environment (in a glove box) and dried before use.

The certification process was carried out in accordance with the requirements established by the ISO 17034:2016 standard [1] and the ISO 33405:2024 [2] guideline. Measurements during the certification process were made in accordance with the requirements of the TS EN ISO/IEC 17025:2017 standard [3]. Uncertainties of the certified values were calculated in accordance with the JCGM 100:2008 Measurement Uncertainty Guide (GUM) [4].

The certified reference materials UME CRM 2203, UME CRM 2211, UME CRM 2213, and UME CRM 2270, produced by TÜBİTAK UME, are intended to be used as calibration standards for the determination of the elements As, Cd, Co, and Zn.

PARTICIPANTS

Information on the organizations involved in the material processing, homogeneity, stability, and characterization studies for the production of certified reference materials, as well as other project activities, is presented in Table 1.

Table 1. Organizations Participating in Production and Certification Processes

Activity	Laboratory/Organization
Material Processing	TÜBİTAK Ulusal Metroloji Enstitüsü (UME) Gebze - Kocaeli, Türkiye
Homogeneity Study	
Stability Studies	
Characterization Study	
Project Management and Data Evaluation	

MATERIAL PROCESSING

Material Definitions and Sources

The high-purity materials (PS) used in the production of certified reference materials and their purity values are given in Table 2.

Table 2. Primary Standards and Purity Values Used in Material Production

CRM	PS	Material	Assigned Purity (%)
UME CRM 2203 (As)	UME PS 2203	As metal	99.9877 ± 0.0035
UME CRM 2211 (Cd)	UME PS 2211	Cd metal	99.9953 ± 0.0012
UME CRM 2213 (Co)	UME PS 2213	Co metal	98.104 ± 0.097
UME CRM 2270 (Zn)	UME PS 2270	Zn metal	99.9908 ± 0.0054

Material Preparation

The primary standards (PS) used in the production of each SRM were gravimetrically weighed according to their target mass fraction. For each material, the amount of acid consumed during the acid solubilization process, based on the known reaction rate, and the target acid concentration in the final solution were calculated. The total amount of acid was used to dissolve the weighed metal. Information on the acid solvent content and the target acid concentration in the final solution are provided in Table 3.

Table 3. Acid Used in the Dissolution Process and Target Concentrations

CRM	PS Dissolution Composition	Target Final Concentration
UME CRM 2203 (As)	60-65 % (w/w) HNO_3	2 % (w/w) HNO_3
UME CRM 2211 (Cd)	60-65 % (w/w) HNO_3	2 % (w/w) HNO_3
UME CRM 2213 (Co)	60-65 % (w/w) HNO_3	2 % (w/w) HNO_3
UME CRM 2270 (Zn)	60-65 % (w/w) HNO_3	2 % (w/w) HNO_3

Gravimetric Weighing

The nominal mass fraction value for certified reference materials was set at 1000 mg/kg. The amount of PS required to achieve the target mass fraction for each material was determined and weighed using substitution weighing. This method utilizes a substitution weighing procedure in which a standard and an unknown weight are compared to determine the average difference between the two weights. This eliminates the balance's calibration bias, as the balance acts as a comparator. When substitution weighing is performed, traceability to the International System of Units (SI) is achieved directly through the mass standards, thus reducing the uncertainty of the measurement result. Because the mass difference between the mass standards and the sample is quite small, the linearity component in the balance uncertainty is negligible.

Weighing was performed using a Sartorius MSA524S balance using an OIML Class E2 mass set. Balance and mass set calibrations were performed by the TÜBİTAK UME Mass Laboratory. The 60 L HDPE drum in which the reference material would be prepared was cleaned, checked for contamination, and dried in a laminar flow cabinet. The empty weighing of the cleaned drum (including its lid) was performed using substitution weighing by the Mass Laboratory. The empty weighed drum was filled with 40 L of ultrapure water (18.2 MΩ·cm) using an end filter (0.22 µm) and a UV lamp water purification system in an ISO Class 7 clean room. The beaker was weighed weighed using substitution weighing and the solution formed by acid dissolution was transferred to the drum. The beaker was rinsed at least 10 times with ultrapure water, and this water was then transferred to the drum. The drum was filled up to approximately 60 kg with ultrapure water, the lid was closed, and it was taken to the TÜBİTAK UME Mass Laboratory. The target weight was adjusted with ultrapure water and it was homogenized for at least 17 hours in the weighing laboratory before weighing, allowing the SRM to reach ambient temperature before weighing. The homogenized material was weighed by substitution weighing the following day.

Homogenization and Bottling

The reference material was bottled in an ISO Class 7 clean laboratory. Approximately 600 units of 125 mL HDPE bottles, previously cleaned, checked for contamination, dried, and labelled using an automatic labelling system (Farmatek, Turkey), were manually filled with (100 ± 5) mL solution. Each bottle was placed in aluminium sachets, each with a second label affixed to the same serial number.

The sachets were then heated and sealed. Approximately 600 bottles (hereafter referred to as "units") were placed in the sachets and transferred to the storage area under the specified storage conditions.

HOMOGENEITY

Homogeneity tests were conducted by selecting 10 units from a batch numbered in the order of filling, using the principle of stratified random sampling, for each material. Random sample selection was performed using "TRaNS" software developed by TÜBİTAK UME. This ensured that the selected samples represented the total sample size. Homogeneity tests were conducted by preparing three subsamples from each of the 10 units. Measurements for the tests were made using the HP-ICP-OES method validated with the Spectro Arcos ICP-OES system. To independently identify potential trends that might arise during filling and analysis, measurements were made in random order.

Statistical evaluation of the mass fraction values obtained for each parameter as a result of the analyses was performed using single-factor analysis of variance (ANOVA). Data distributions were examined prior to statistical evaluation using ANOVA. For this purpose, the results obtained within and between units were checked for single-peaked distribution using histograms. In addition, the Shapiro-Wilk test was applied to the obtained data, which was generally found to be normally distributed. These statistical tests were performed using templates created and validated in Microsoft Excel® by the TÜBİTAK UME Chemistry Group. The results are presented in Table 4.

As a result of the evaluations, it was determined that the distribution of 10 units (between units) derived from the unit means for all materials can be considered a normal distribution. In addition, a double-peaked distribution was observed in the normal distribution for UME CRM 2270 (Zn).

The measurement results were statistically evaluated for outliers and any trends due to the analytical measurement and/or filling order. No outliers were observed for any of the materials.

When the measurement results were examined for any trends due to the measurement order and filling order, a trend due to filling was observed in the analysis of UME CRM 2203 (As) material, at a 95 % confidence level. The data evaluation included the uncertainty contribution of this trend in the total homogeneity uncertainty. For UME CRM 2211 (Cd), a trend related to the analysis order is observed. This trend was corrected using a template and normalization based on the data mean, and the corrected data was taken into account in the calculations.

No outliers were detected when one-sided and two-sided Grubb's tests were applied.

Table 4. Statistical Evaluation of Homogeneity Test Results

Material	Any Trend?		Any Outlier?		Distribution
	Analytical Sequence	Filling Sequence	All Data	Unit Averages	Normal / Unimodal
UME CRM 2203 (As)	No	Yes	No	No	Yes / Yes
UME CRM 2211 (Cd)	Yes	No	No	No	Yes / Yes
UME CRM 2213 (Co)	No	No	No	No	Yes / Yes
UME CRM 2270 (Zn)	No	No	No	No	Yes / No

To calculate the within-unit (s_{wb}) and between-unit (s_{bb}) standard deviation using ANOVA, Equation (1) and Equation (2) are applied, respectively [10]:

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

MS_{within} : Mean squares of within-unit,

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

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

$MS_{between}$: Mean squares between-unit,

N : Number of replicates per unit.

In cases where the method repeatability is not good enough to determine the homogeneity of the material or due to random fluctuations during the measurement, the $MS_{between}$ may be less than MS_{within}. Since s_{bb} cannot be calculated in these cases, the highest heterogeneity uncertainty, u^*_{bb}, is calculated using Equation (3).

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

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

The results obtained from the homogeneity study are reported in Table 5. In the calculations performed by applying ANOVA, the larger of s_{bb} and u^*_{bb} values was taken as the homogeneity uncertainty component u_{bb}.

Table 5. Results of the Homogeneity Study

Material	$s_{bb,rel}$ (%)	$u^*_{bb,rel}$ (%)	$u_{bb,rel}$ (%)
UME CRM 2203 (As)	0.01	0.01	0.02**
UME CRM 2211 (Cd)	0.029	0.03	0.03
UME CRM 2213 (Co)	$MS_{between} < MS_{within}$	0.05	0.05
UME CRM 2270 (Zn)	0.08	0.05	0.08

** Homogeneity uncertainty component $u_{bb,rel}$ (%) was calculated using u_{rec} , which includes the uncertainty of the filling trend.

The heterogeneity-based uncertainty values obtained for all parameters to be certified in the candidate CRM were found to be below the targeted maximum uncertainty value of 0.2 %. The graphs of the data obtained in homogeneity tests are presented in Annex 1.

STABILITY

Stability studies were conducted in a laboratory environment using environmental conditions (short-term stability, KDK) and storage conditions (long-term stability, UDK) that might occur during the shipment of the certified reference material to the user. The 14 units selected for the short-term stability test and the 14 units selected for the long-term stability test were determined using the principle of random stratified sample selection using TRaNS software. Stability measurements of the elements to be certified were conducted using the HP-ICP-OES method with the Spectro Arcos ICP-OES system.

For the short-term stability studies, the test temperatures were +21 °C and +45 °C, and the durations were 1, 2, and 4 weeks. For each time period to be tested at each temperature, two units were placed in the test chamber/oven at that temperature. In the stability test, two units were set aside for the reference point, and these units were placed directly at the reference temperature of +4°C. At the end of each test period, the relevant units from both temperature environments were transferred to the reference temperature. At the completion of the four-week test period, all units transferred to the reference temperature were analysed simultaneously (isochronously) with the reference units.

The long-term stability test was conducted using the conventional method for a single temperature at +4 °C. All selected test samples were placed at the reference temperature (+4 °C). The initial value was determined at the beginning of the study by three parallel analyses of three reference units. Then, two units were taken from the UDK samples at the reference temperature every 60 days and analysed in three parallels from each unit.

For both stability tests, measurements were analysed using an analytical measurement sequence created in a random order of test duration and filling order to distinguish between potential trends due to filling or test duration and trends due to analytical order. Statistical calculations of the obtained data were performed using templates created and validated in Microsoft Excel® by experts at the TÜBİTAK UME Chemistry Group.

Short-Term Stability Study Results

The simultaneously measured results in the short-term stability study were first grouped according to the same time points and evaluated for each time point. These evaluations were performed separately for both temperatures.

The measured values obtained for each time period were examined for outliers at 95 % and 99 % confidence levels using Grubb's test to determine their compatibility with other values in that temperature group. The examination revealed an outlier only in the +45 °C test of UME CRM 2270 (Zn). This outlier was detected in a replicate measurement of a unit (unit 401) from the second month test point, and no discrepancies were detected in the other two replicates of the same unit. Consequently, it was concluded that this outlier was due to contamination. However, since the inclusion of this data in the calculation contributed insignificantly to the total uncertainty, calculations were performed without removing it from the data set.

To evaluate short-term stability data, the calculated values for each time point were plotted against time, and the relationship between variables was examined to determine any significant changes in concentration values against time (regression analysis). Linear graphs were plotted for each anion, and a *t*-test (two-tailed regression test) was used to test whether these slopes were significantly different

from zero at the 95 % confidence level (α = 0.05). Short-term stability test results are presented in Table 6 and graphs in Annex 2.

Uncertainty calculations regarding short-term stability were calculated using Equation (4), taking into account the uncertainty of this slope and the longest exposure time [8].

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

where,

RSD : Relative standard deviation of the points on the regression line,
t_i : Time point for each replicate,
$\bar{t}$: Mean of all time points,
t : 2 weeks of maximum time suggested for transfer.

Table 6. Results of Short Term Stability Tests and Uncertainty Values for 2 Weeks

Parameter	Number of outliers in 95 % confidence level		Is there a significant trend in 95 %confidence interval?		+21 °C 2 weeks $u_{sts,rel}$ (%)	+45 °C 2 weeks $u_{sts,rel}$ (%)
	+21 °C	+45 °C	+21 °C	+45 °C		
UME CRM 2203 (As)	-	-	No	No	0.01	0.01
UME CRM 2211 (Cd)	-	-	No	No	0.03	0.03
UME CRM 2213 (Co)	-	-	Hayır	No	0.02	0.01
UME CRM 2270 (Zn)	-	1	No	No	0.04	0.10

The evaluation revealed that the parameters to be certified in the certified reference material were stable for two weeks at both +21 °C and +45 °C. This study concluded that the samples could be delivered to the end user without any cooling, provided the temperature did not exceed +45 °C and the storage period did not exceed two weeks. The uncertainties listed in the certificate are calculated based on a maximum transfer temperature of +45 °C and a transfer period of two weeks.

Long-Term Stability Study Results

The shelf life of the produced SRMs is determined based on the results of long-term stability studies. As mentioned above, two units were used for each time point, and three independent parallel samples were prepared from each unit for long-term stability test measurements. The test period in this study was designed to cover a 12-month period, totalling seven time points. Graphs of the results of three replicate measurements at each time point are provided in Annex 3. Error lines at each time point were calculated as the standard deviation of three results obtained for each of the three units.

The obtained data were examined for outliers at the 95 % and 99 % confidence levels using one- and two-sided Grubb's tests. According to this analysis, no outliers were detected for any material at the 95 % and 99 % confidence levels.

The values obtained in the study were examined by plotting a fit line (regression line) on a graph of concentration versus time. At the tested temperature (4 ± 3) °C, a *t*-test was performed at a 95 %

confidence level for the plotted slope lines, and it was determined that the slope for all parameters was not significantly different from zero. Long-term stability is one of the four parameters contributing to the total uncertainty budget. The uncertainty value resulting from the long-term stability of the certified reference material was calculated using Equation (5) [11].

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

where,

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 +21 °C (18 months).

The results calculated in this manner are presented in Table 7, and the graphs are presented in Annex 3. A shelf life of 18 months was determined to account for the contribution of uncertainty arising from long-term stability to the total uncertainty. To ensure stability beyond the specified shelf life, re-evaluations will be conducted periodically based on post-certification monitoring (SSI) results.

Tablo 7. Long-Term Stability Test Results and Uncertainty Values for 18 Months

Material	Number of outliers in 95 % confidence level	Is the slope different from zero at 95 % confidence level?	+21 °C, 18 month $u_{lts,rel}$ (%)
UME CRM 2203 (As)	-	No	0.05
UME CRM 2211 (Cd)	-	No	0.07
UME CRM 2213 (Co)	-	No	0.07
UME CRM 2270 (Zn)	-	No	0.09

CHARACTERIZATION

Characterization measurements are one of the most important stages in assigning values to materials. The ISO 17034:2016 standard describes different methods for characterization. One option is to conduct a characterization study using a reference method in a single laboratory. Another option is based on a weighted or unweighted average of the results of multiple methods. Characterization was performed using the average of the gravimetric solution preparation and HP-ICP-OES analysis results for all analytes during this production process.

In gravimetric solution preparation, both the weighing of the purified materials and the empty drum and final solution weighings were performed by the TÜBİTAK UME Mass Laboratory. The HP-ICP-OES

measurement for the characterization study was taken as the arithmetic average of the homogeneity measurements. These measurements were performed using validated measurement methods that adhere to gravimetric measurement principles. NIST 3100 series standard solutions were used to verify the method, and are listed in Table 8.

Table 8. Standards Used for Method Verification

Material	Name	Code	Traceability
UME CRM 2203 (As)	As Standard Solution	NIST SRM 3103a	SI
UME CRM 2211 (Cd)	Cd Standard Solution	NIST SRM 3108	SI
UME CRM 2213 (Co)	Co Standard Solution	NIST SRM 3113	SI
UME CRM 2270 (Zn)	Zn Standard Solution	NIST SRM 3168a	SI

Uncertainty calculations were performed in accordance with the "Guide to the Expression of Uncertainty in Measurements (GUM)" [13] and the "EURACHEM/CITAC Guide Quantifying Uncertainty in Analytical Measurement" documents for gravimetric solution preparation and HP-ICP-OES. Characterization uncertainties were combined using equations (6) – (8) specified by M. S. Lenson et al. (2000) [12].

$$\boldsymbol{u(B) = \frac{|X_{m1} - X_{m2}|}{2\sqrt{3}}} \quad (6)$$

$$\boldsymbol{u(X) = \sqrt{\left(\frac{1}{2}\right)^2 u^2(m_1) + \left(\frac{1}{2}\right)^2 u^2(m_2)}} \quad (7)$$

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

where,

$u(B)$: Standard uncertainty due to the difference in the results of the two methods,
$u(X)$: Standard uncertainty obtained by combining the uncertainty of the two methods,
u_{char} : Characterization standard uncertainty.

PROPERTY VALUE AND UNCERTAINTY ASSIGNMENT

The assignment of certified property values and their associated uncertainties was carried out by considering the contributions of uncertainties calculated from the data obtained from the homogeneity and stability tests, in addition to the data obtained from the characterization study and the accompanying uncertainty values for each parameter.

The property value to be stated in the certificate was calculated by taking the arithmetic average of the value obtained from the gravimetric solution preparation and the HP-ICP-OES measurement data from the characterization study (Equation 9).

$$C_{CRM} = (C_{m1} + C_{m2})/2 \quad (9)$$

Here, C_{CRM} represents the certified value as a mass fraction.

In calculating the uncertainty value of the property value, the contributions of characterization, homogeneity, short-term, and long-term stability uncertainties were combined as given in Equation (10).

$$u_{CRM} = \sqrt{u_{char}^2 + u_{bb}^2 + u_{sts}^2 + u_{lts}^2} \quad (10)$$

Here, u_{CRM} represents the combined standard uncertainty of the property value. This value is converted to the expanded uncertainty of the certification value by multiplying it by the coverage factor *k*, as shown in Equation (11).

$$U_{CRM} = k \cdot u_{CRM} \quad (11)$$

The uncertainty values given with the certification values are expanded uncertainties obtained from combined uncertainties by multiplying them by the coverage factor *k* = 2, corresponding to a 95 % confidence level. The certification values and their associated uncertainties for each parameter are given in Table 9. For customer convenience, the mass concentration values obtained by multiplying the certification values obtained as mass fractions by the density value given as the Informational Value are also given in the same table. The contribution of the uncertainty components to the total uncertainty is given in Table 10.

Table 9. Certified Values and Uncertainties

Malerial	Certified Value (Mass Fraction)		Derived Value (Mass Concentration)	
	C_{CRM} (mg/kg)	U_{CRM} (mg/kg) (*k* = 2)	C_{CRM} (mg/L)	U_{CRM} (mg/L) (*k* = 2)
UME CRM 2203 (As)	997.3	1.4	1009.3	1.4
UME CRM 2211 (Cd)	999.7	2.2	1010.7	2.2
UME CRM 2213 (Co)	998.6	2.1	1011.1	2.2
UME CRM 2270 (Zn)	998.4	3.6	1010.3	3.6

Table 10. Contribution of Uncertainty Components to Total Uncertainty

SRM	u_{char} (%)	u_{bb} (%)	u_{lts} (%)	u_{sts} (%)
UME CRM 2203 (As)	39.7	7.3	49.7	3.2
UME CRM 2211 (Cd)	36.6	7.5	48.9	7.0
UME CRM 2213 (Co)	35.1	20.2	43.4	1.3
UME CRM 2270 (Zn)	22.0	22.0	25.9	30.1

INFORMATIVE VALUES

Density measurements of the materials were made at the TÜBİTAK UME Volume, Density, and Viscosity Laboratory using 3 parallel readings from 3 different units. These data are provided in Table 11 for informational purposes.

Table 11. Density Value Given for Informational Purposes (20 °C)

Material	Value (kg/m^3)	U (kg/m^3) (k = 2)
UME CRM 2203 (As)	1012.028	0.044
UME CRM 2211 (Cd)	1010.966	0.044
UME CRM 2213 (Co)	1012.475	0.044
UME CRM 2270 (Zn)	1011.855	0.044

TRACEABILITY

In this study, validated methods were used in all certification experiments, including homogeneity and stability tests. Samples were prepared gravimetrically for the preparation and measurements of the reference material. Weighing was done using balances traceable to national measurement standards, and the balances used were checked using appropriate mass set weights. The balances and mass set weights used are traceable to national measurement standards that implement units defined in the International System of Units (SI). In the preparation of the certified reference material and in the characterization, homogeneity, and stability studies, Primary Standards (PS), whose purity was determined and certified by TÜBİTAK UME through the determination of impurities, were used to ensure SI traceability. The Primary Standards used for traceability in the certification studies are listed in Table 2.

INSTRUCTIONS FOR USE

Intended Use

These materials are intended to be used as calibration standards in the determination of the relevant elements. These materials can be used for calibration in Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES), Inductively Coupled Plasma Mass Spectrometry (ICP-MS), Atomic Absorption Spectrometry (AAS), Microwave Plasma Atomic Emission Spectrometry (MP-AES), and other elemental analysis techniques.

Storage Conditions

All materials should be stored at (21 ± 3) °C before and after use. TÜBİTAK UME cannot be held responsible for any changes that may occur in the material due to non-compliance with the storage conditions and instructions for use specified for the materials.

Transfer Conditions

The materials can be transported without additional cooling measures, provided that the temperature does not exceed +45 °C and the transport duration does not exceed 2 weeks.

Safety Warnings

The materials are manufactured for laboratory use only. General laboratory precautions should be applied during storage and use of the material. It is recommended that the material be handled and disposed of according to existing safety regulations. The Safety Data Sheet (SDS) should be carefully read before using the material.

Material Handling

The bottle should be shaken before opening, and all precautions should be taken to prevent contamination and evaporation of the material during opening and use.

Minimum Sample Intake

The minimum sample intake should be determined by the end user based on their measurement capability, taking into account its impact on the uncertainty of the working solution to be prepared.

REFERENCES

[1] ISO 17034:2016, General requirements for the competence of reference material producers
[2] ISO 33405:2024, Reference materials — Approaches for characterization and assessment of homogeneity and stability
[3] TS EN ISO/IEC 17025:2017 General requirements for the competence of testing and calibration laboratories
[4] JCGM 100:2008 Evaluation of measurement data - Guide to the expression of uncertainty in measurement
[5] VIM (2012) – International Vocabulary of Metrology – Basic and General Concepts and Associated Terms
[6] Eurachem/CITAC Guide (2012), Traceability in Chemical Measurement: A Guide to Achieving Comparable Results in Chemical Measurement
[7] NIST (National Institute of Standards and Technology) – Certified Reference Materials and Measurement Traceability
[8] M.L. Salit, G.C. Turk, A.P. Lindstrom, T.A. Butler, C.M. Beck, B. Norman, Single element solution comparisons with a high-performance inductively coupled plasma optical emission spectrometric method. Anal Chem. 73(20) 2001 4821 - 4829
[9] M. Tunc, C. Paredes, F.G. Coskun, J. Serna, M. Caner. "Comparison of Different Characterization Approaches for Monoelemental Calibration Solutions at Two National Metrology Institutes", Anal Bioanal Chem, 417:12 (2025) : 2603-2616
[10] T. P. J. Linsinger, J. Pauwels, A. M. H. Van der Veen, H. Schimmel, A. Lamberty, Homogeneity and stability of reference materials, Accred. Qual. Assur. 6 (2001) 20 - 25
[11] T. P. J. Linsinger, J. Pauwels, A. Lamberty, H. Schimmel, A. M. H. van der Veen, L. Siekmann, Estimating the uncertainty of stability for matrix CRMs, Fresenius J. Anal. Chem. 370 (2001) 183-188
[12] M. S. Levenson, D. L. Banks, K. R. Eberhardt, L. M. Gill, W. F. Guthrie, H. K. Liu, M. G. Vangel, J. H. Yen, and N. F. Zhang, "An Approach to Combining Results From Multiple Methods Motivated by the ISO GUM", Journal of Research of the National Institute of Standards and Technology, Volume 105, Number 4, July–August 2000 Method in page 577: Between-Method Uncertainty

REVISION HISTORY

Date	Remarks
02.12.2025	First issue.

ANNEXES

Annex 1. Graphs for Homogeneity Studies

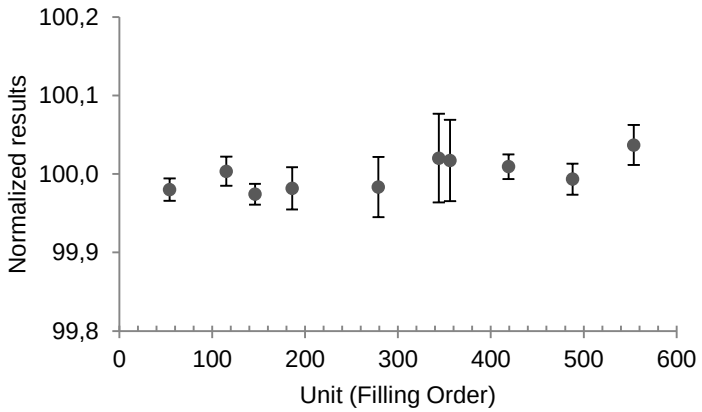

Figure A1.1. Homogeneity Plot for UME CRM 2203 (As)

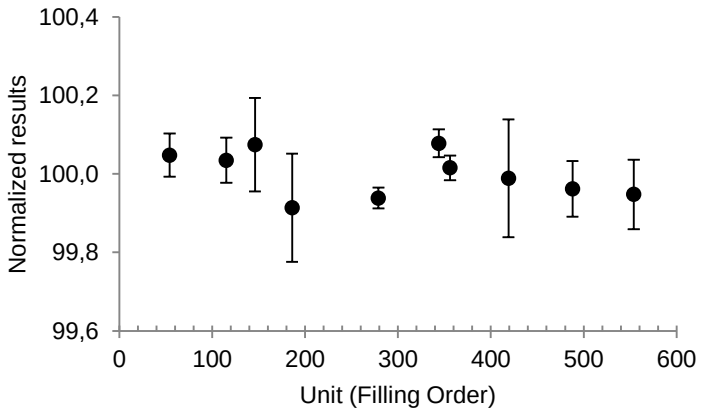

Figure A1.2. Homogeneity Plot for UME CRM 2211 (Cd)

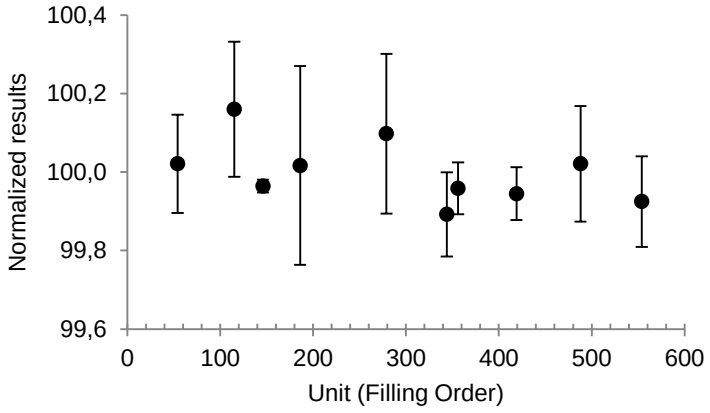

Figure A1.3. Homogeneity Plot for UME CRM 2213 (Co)

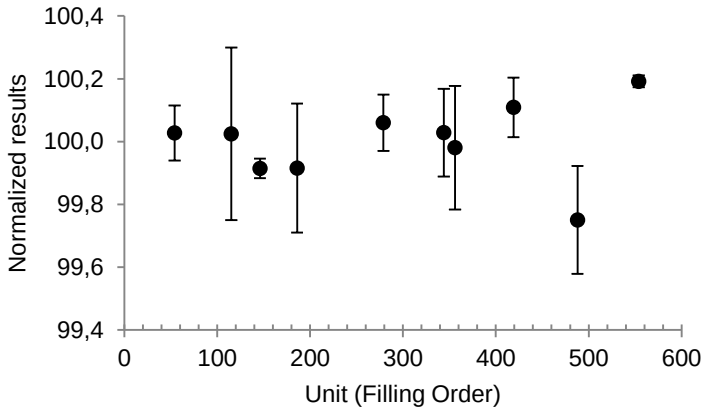

Figure A1.4. Homogeneity Plot for UME CRM 2270 (Zn)

Annex 2. Graphs for Short Term Stability Studies

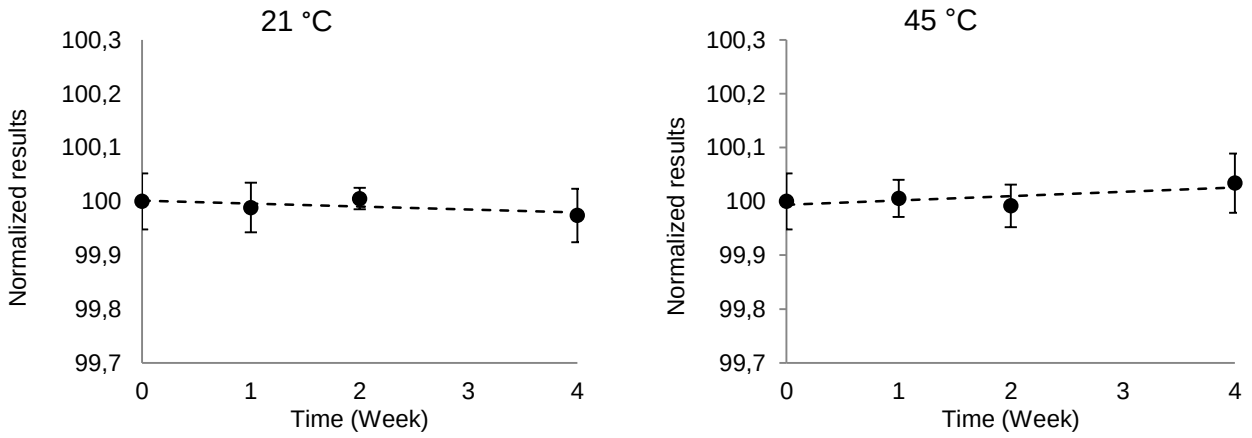

Figure A2.1. STS Plots for UME CRM 2203 (As) at +21 °C and +45 °C

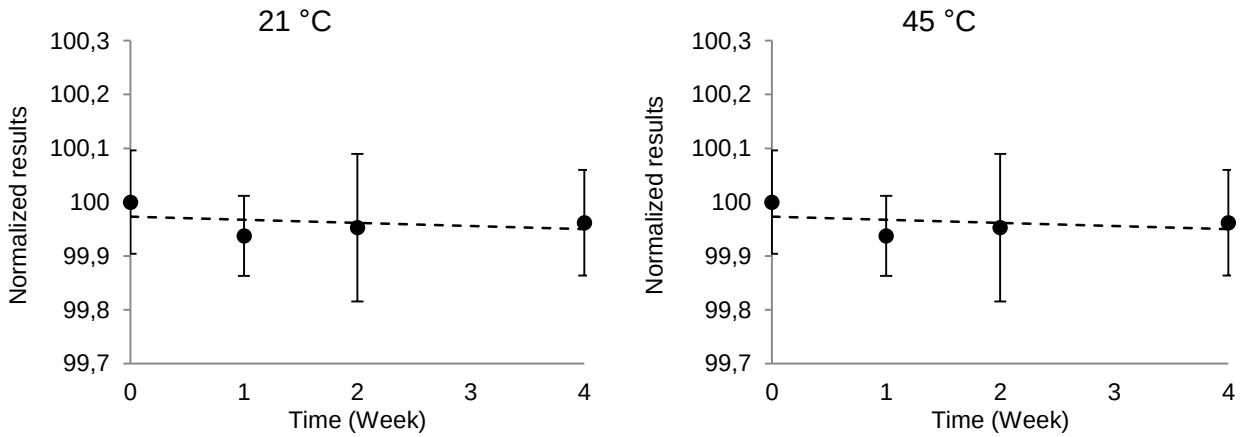

Figure A2.2. STS Plots for UME CRM 2211 (Cd) at +21 °C and +45 °C

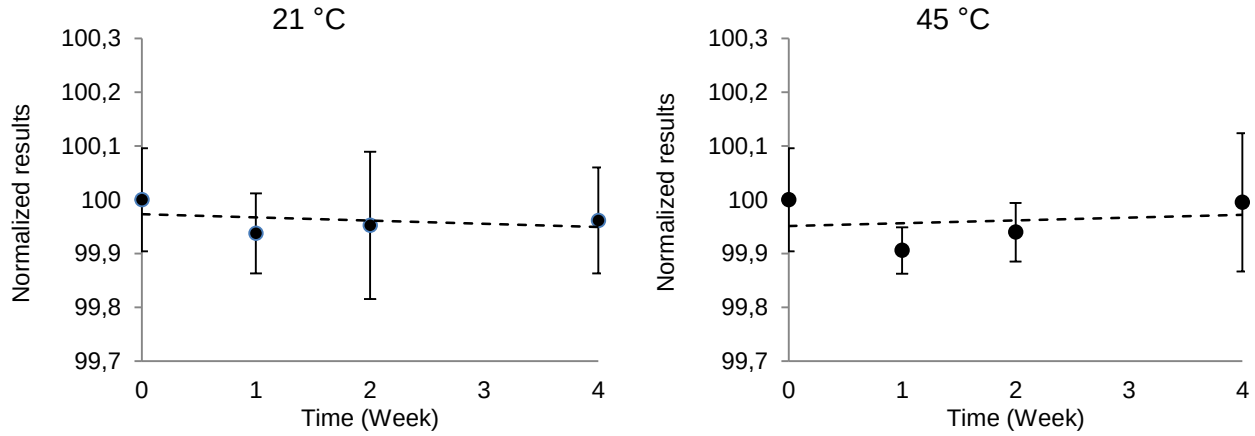

Figure A2.3. STS Plots for UME CRM 2213 (Co) at +21 °C and +45 °C

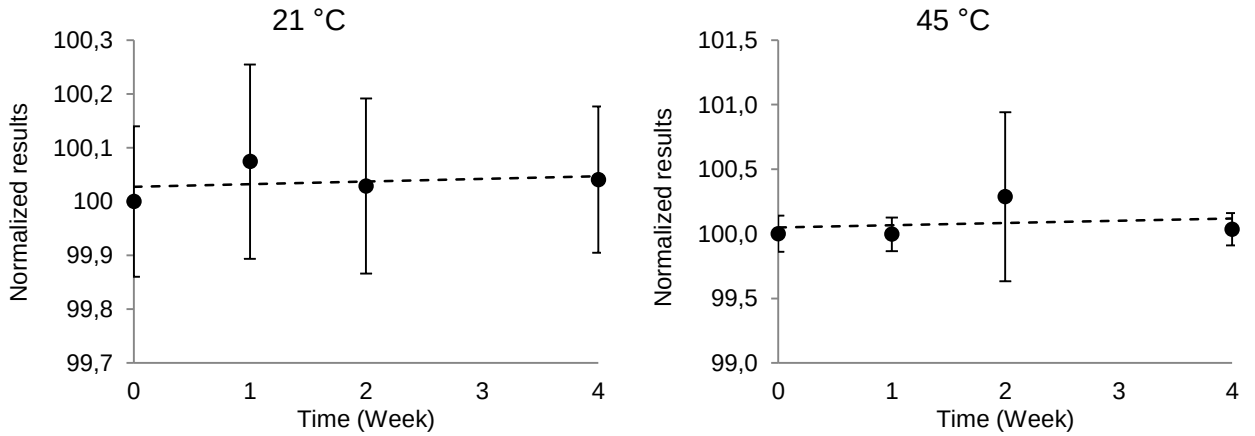

Figure A2.4. STS Plots for UME CRM 2270 (Zn) at +21 °C and +45 °C

Annex 3. Graphs for Long Term Stability Studies

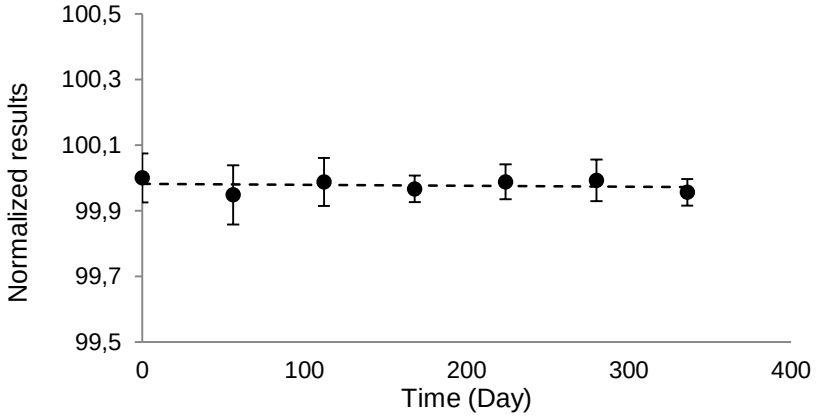

Figure A3.1. LTS Plot for UME CRM 2203 (As) at +21 °C

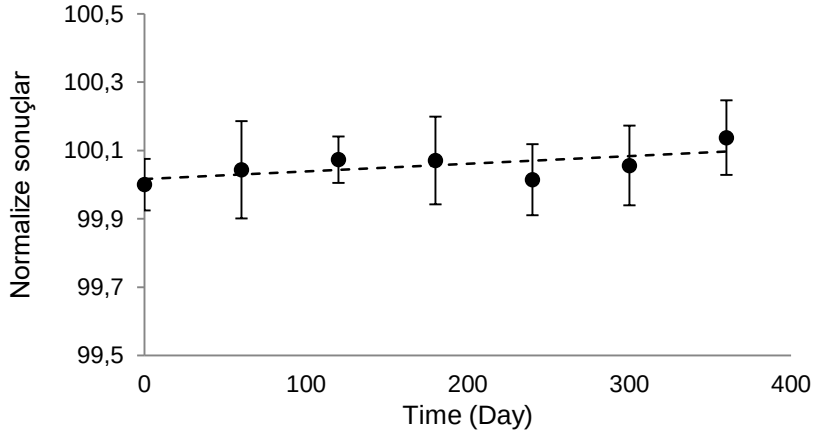

Figure A3.2. LTS Plot for UME CRM 2211 (Cd) at +21 °C

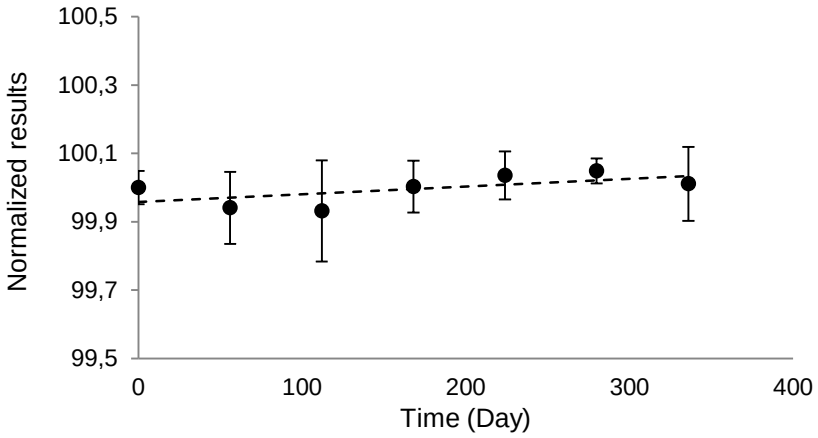

Figure A3.3. LTS Plot for UME CRM 2213 (Co) at +21 °C

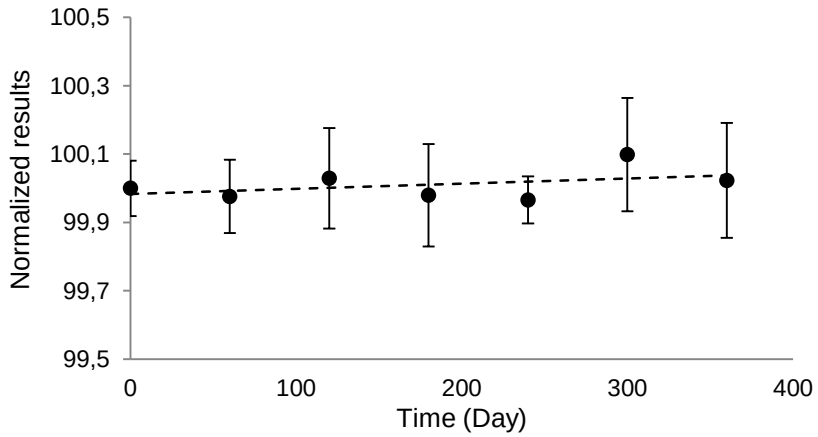

Figure A3.4. LTS Plot for UME CRM 2270 (Zn) at +21 °C