TÜBİTAK
ULUSAL METROLOJİ ENSTİTÜSÜ

Certification Report

ELEMENTS in WASTE WATER
UME CRM 1204

Report Prepared by

Betül ARI
Assoc. Prof. Dr. Oktay CANKUR
Dr. F. Gonca COŞKUN
Dr. Süleyman CAN
Murat TUNÇ

Date **Dr. Mustafa ÇETİNTAŞ**

12/08/2016 **Director**

TABLE OF CONTENT

ABBREVIATIONS

ANOVA	Analysis of variance
CRM	Certified Reference Material
ERM	European reference material
GF-AAS	Graphite Furnace Atomic Absorption Spectrometry
GUM	Guide to the expression of uncertainty in measurement
HR	High Resolution
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
IDMS	Isotope Dilution Mass Spectrometry
IRMM	Institute of Reference Measurements and Materials
ISO	International Organization for Standardization
LTS	Long Term Stability
NIST	National Institute of Standards and Technology
PTFE	Polytetrafluoroethylene
PVDF	Polyvinylidene fluoride
SGT	Single Grubbs Test
SI	International System of Units
STS	Short Term Stability

SYMBOLS

k	Coverage Factor
$MS_{between}$	Mean square between-bottle from ANOVA
MS_{within}	Mean square within-bottle from ANOVA
n	number of replicates per bottle
RSD	Relative standard deviation
s	Standard deviation
s_{bb}	Between-bottle standard deviation (ANOVA)
$s_{bb,rel}$	Relative between-bottle standard deviation
s_{wb}	Within-bottle standard deviation (ANOVA)
$s_{wb,rel}$	Relative within-bottle standard deviation
u_{bb}	Standard uncertainty related to possible between-bottle heterogeneity
$u_{bb.rel}$	Relative standard uncertainty related to possible between-bottle heterogeneity
u^*_{bb}	Standard uncertainty of heterogeneity that can be hidden by method repeatability
$u^*_{bb,rel}$	Relative 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
U_{CRM}	Expanded uncertainty related to certified value
$U_{CRM,rel}$	Relative expanded uncertainty related to 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
$v_{MSwithin}$	Degrees of freedom related to MS_{within}

ABSTRACT

This report describes production and certification of UME CRM 1204 which includes total concentration of Al, As, B, Cd, Co, Cr, Cu, Fe, Hg, Mo, Mn, Ni, P, Pb, Sb, Tl, V ve Zn in waste water. This material has been produced in accordance with ISO Guide 34:2009 [1]. The raw material was collected via a waste water treatment plant located in Dilovası organized industrial zone. The water was acidified and filtered before filling into 100 mL HDPE bottles. All units were sterilised by 25 kGy γ-radiation via ^{60}Co source.

Homogeneity and stability studied have been assessed in accordance with ISO Guide 35:2009 [2] and the certified values were defined by using more than one independent reference methods applied by one laboratory or using primary measurement method (ID-ICP-MS) applied by one laboratory. Certified values have been calculated by fulfilling all requirements in related guides mentioned above and Guide to the Expression of Uncertainty in Measurement (GUM) [3].

TÜBİTAK UME organised and coordinated all the steps of this project including evaluation of data.

UME CRM 1204 is intended to be a reference point for method development and validation and also quality control measurements, and can be also used for quality control charts.

INTRODUCTION

To keep wastewater discharges under control in line with water pollution control regulations, which are implemented by countries in order to protect ground and surface waters, and to prevent water pollution in compliance with sustainable development goals, has a great importance. European Commission Urban Waste Water Treatment Directive (91/71/EEC) and amended directive for priority substances (2013/39/EU) set limits for wastewater discharges. In Turkey, with the Water Pollution Control Regulation, which was published in the Official Gazette number 25687, dated 31.12.2004, discharge criterias were set for the various industrial wastewater to prevent pollution of ground and surface water of the country, and to ensure sustainable water protection.

The chemical properties certified in CRMs are agreed on, justified using scientific methods, and published in accordance with certain criteria. Besides pure reference materials used in calibration, certified matrix reference materials are essential in method validation where especially matrix differences need an additional care in chemical mesurements. It is quite important to select and use a suitable CRM by users as well.

The production and certification of UME CRM 1204 in accordance with ISO Guide 34 and ISO Guide 35 was performed using TÜBİTAK UME infrastructure. Target concentration level of each analytes was decided to meet laboratory’s needs, and based on the absence of similar certified reference materials in the market. This CRM was produced to be used by laboratories who have to monitor parameters defined by legislations and by research laboratories for method development, validation and quality control.

PARTICIPANTS

Sampling, processing the raw material (except sterilisation), homogeneity, stability and characterisation measurements were performed by specialists in TÜBİTAK UME using existing infrastructure. The list showing the participants involved and their contributions to the project is presented in Table 1.

Table 1. The participants and their roles

Participants	Work Package
TÜBİTAK UME TÜBİTAK Gebze Yerleşkesi, Barış Mahallesi Dr. Zeki Acar Cad. No.1, 41470, Gebze, Kocaeli, Türkiye	Project management, Material processing and Certification
GAMMA PAK Sterilizasyon Sanayi ve Ticaret A.Ş. Organize Sanayi Bölgesi Gazi Osman Paşa Mahallesi 2. Cad. No. 6, 59500, Çerkezköy, Tekirdağ, Türkiye	Material Processing (Sterilisation)

MATERIAL PROCESSING

The source of the raw material of candidate reference material was wastewater treatment plant located in Dilovası/Kocaeli/Turkey. Due to its location, the plant also collects and treats industrial waste water in addition to domestic waste water. It was mentioned that approximately 45 % of collected wastewater was industrial waste. Sampling of this water from collecting pool was done by researchers of TÜBİTAK UME and a technician of the plant.

Wastewater exposed to chemical and biological treatment was directly taken to pre-cleaned 3 units of 25 L polypropylene (PP) drums using submersible pump. Water in drums were acidified with 65 % nitric acid (Merck EMSURE®) and stored at +4 °C in dark conditions until further processing. After a while, whole water was taken into pre-cleaned 114 L HDPE drum, and left for completion of precipitations of any colloidal particles in the matrix. After visible completion of precipitation, water was filtered through rough filter and again left for one month at +4 °C in dark conditions to make sure that no more precipitation occurs. Following this step, water was filtered through 5 µm (PN 12121, Filling Machine Capsules, Pall Corporation), 3 µm (PN 12116, Plated capsules with Versapor, Pall Corporation) 0.8/0.45 µm (PN 12992, AcroPack™ 1000, Supor® Membrane, Pall Corporation) filters, respectively. And, the whole batch was left at +4 °C for 10 days in dark conditions. Subsequently, all target analytes in the raw material were measured, and spiking of analytes except Fe was performed in the target concentrations. The batch was homogenized using a second 114 L HDPE drum. The drum, the PTFE/PVC tubes and air acid pump (PVDF) used for homogenization were washed with an in-house prepared solution ~20% (v/v) of HNO_3 (Merck EMSURE ISO), and subsequently extensively rinsed with de-ionized water (Milli-Q, 18.2 $M\Omega \cdot cm^{-1}$) beforehand.

In order to minimize existing particulates from co-precipitations in the bottles, spiked and homogenized water was stored at 4 °C in dark conditions for two days. Following this process, whole batch was filtered from one drum to another via 0.8/0.2 µm (Pall Corp, Supor® Membrane, AcroPack™ 1000, PN 12992) which also used for removing bacterial retention.

The Nalgene® (Thermo Scientific) HDPE low particulate bottles (<30 particulates/mL >0.3 µm) of 125 mL were used for bottling of waste water. Cleanness of bottles regarding 20 target elements were checked in 59 bottles which were chosen randomly one from each package. The bottles were filled fully with 2 % (v/v) ultrapure HNO_3, and left for two days. The measurements of these leaching solutions were performed by HR-ICP-MS (Thermo Finnigan, Element 2, Bremen, Germany). The results showed that levels of trace elements in the leaching solutions are not significant to lead any contamination to CRM at target levels. Therefore, cleaning of all bottles were performed by filling with ultrapure water (ELGA PureLab, 18.2 $M\Omega \cdot cm^{-1}$) in ISO Class 6 clean laboratory, and leaving for three days. All cleaned bottles were dried in ISO Class 4 laminar flow cabins at ISO Class 6 clean laboratory.

Target levels were decided based on the regulations and Turkish Standards, and the natural levels of processed wastewater were measured firstly to determine how much spike should be added to reach the target levels. The natural levels in the original wastewater and the target concentration levels are given in Table 2. As it is seen, the natural levels of analytes except of Al, Fe and Mn was below the target concentration.

In order to get target concentration levels of analytes, mono elemental calibration solutions of High Purity® ve NIST SRM 3100 series had been used in spiking. Spiking of waste water was done after the filtration of water through 0.8/0.45 µm, but before through 0.8/0.2 µm. Homogenization had been performed by using air acid pump (PVDF) for 6 hours.

Table 2. Natural and target concentration levels of waste water

Analyte	Natural Levels, µg/L	Target Levels, µg/L
Al	370	NL*
As	< LOD	60
B	380	1500
Cd	4	100
Co	7	410
Cr	33	225
Cu	< LOD	325
Fe	2020	NL*
Hg	< LOD	45
Mn	380	NL*
Mo	< LOD	85
Ni	24	175
P	480	815
Pb	6	150
Sb	7	125
Tl	< LOD	150
V	6	185
Zn	210	450

*NL: Natural level

Approximately 100 mL (~± 5) of material was filled into 554 units of 125 mL HDPE bottles (Nalgene®), and labelled in order of filling sequence.

The water in the closed bottles of candidate certified reference material was sterilised by γ-irradiation with a ^{60}Co source at a minimum dose of 25 kGy. The irradiation caused the expected change in color of the medium transparent HDPE bottles to pale yellow. After this step, the bottles were stored at temperature controlled (+4 °C) dark room.

HOMOGENITY

The study of between unit homogeneity is done to prove that the certified values are valid for each unit produced within the uncertainties stated at a certain confidence level. In accordance with ISO Guide 34, checking the homogeneity of the whole material for the parameters to be certified should not be done less than for 10 units. In this project, the number of units to be measured in homogeneity study was determined by cubic root of the total number of units in the batch. In order to represent whole batch, randomly stratified sampling scheme was applied to select 10 units and 10 spare units (Master Unit No: 3, 81,125, 193, 234, 295, 338, 414, 462 and 516). This was done by dividing whole batch into equal fragments, and a representative unit was randomly selected from each one so that the whole batch was covered. The samples were analysed in triplicate for all elements. The measurements were performed under repeatability conditions, i.e. during one analytical run and using validated methods, and according to a random sequence to allow distinction between possible trends in the analytical sequence and in the filling order if any. Samples of certified reference material and blank were also measured within the same sequence. All measurements were performed by HR-ICP-MS (Element 2, Thermo Finnigan, Bremen, Germany).

The data for all parameters were evaluated statistically by regression analysis for presence of any trend in analytical and filling sequence. It was observed that there were significant trend in filling sequence order for Cr and Mn and in analytical sequence order for Al, B, Ni, Sb and Tl at 95% confidence levels. As the analytical sequence and the unit numbers were not correlated, correction for these trends can improve the sensitivity of the subsequent statistical analysis to determine more accurate uncertainty related to homogeneity. Therefore, trends in the analytical sequence determined at 95% confidence level were corrected using the Equation (1).

$$C_{Corrected} = C_{Measured} - b \cdot i \qquad (1)$$

where;

b : slope of the linear regression,
i : position of the result in the analytical squence.

All dataset was investigated for consistency using Grubbs outlier tests on a confidence level of 95 %. It was identified that there are some outlying individual results for Al, B, Co, Cu, Fe, Mn, Ni ve Tl (Table 3). One replicate of unit 193 for Cu and Ni, one replicates for each of units 81 and 193 for Al and one replicate of unit 3 for Tl, Co, Fe, Mn and B were observed as outlier. The Grubbs outlier test was also performed for average values of units, and it was found that unit 3 was outlier for B. The same data resulted also in observing filling sequence order of Mn. Since there was no technical reason for these outlier data, all were retained in homogeneity assessment.

Table 3. Result of Statistical Evaluation of Homogeneity Data Set

Element	Trends		Outlier		Distribution
	Analytical Sequence	**Filling Sequence**	**Individual Results**	**Mean value of Unit**	**Individual results**
Al	Yes	-	2	-	Normal/Unimodal
As	-	-	-	-	Normal/Unimodal
B	Yes	-	1	1	Normal/Unimodal
Cd	-	-	-	-	Normal/Unimodal
Co	-	-	1	-	Normal/Unimodal
Cr	-	Yes	-	-	Normal/Unimodal
Cu	-	-	1	-	Normal/Unimodal
Fe	-	-	1	-	Normal/Unimodal
Hg	-	-	-	-	Normal/Unimodal
Mn	-	Yes	1	-	Normal/Unimodal
Mo	-	-	-	-	Normal/Unimodal
Ni	Yes	-	1	-	Normal/Unimodal
P	-	-	-	-	Normal/Unimodal
Pb	-	-	-	-	Normal/Unimodal*
Sb	Yes	-	-	-	Normal/Unimodal
Tl	Yes	-	1	-	Normal/Unimodal
V	-	-	-	-	Normal/Unimodal
Zn	-	-	-	-	Normal/Unimodal

* Data set of short term stability was evaluated.

Analysis of Variance (ANOVA) is a statistical tool used to estimate uncertainty contribution from homogeneity of the materials. All data were examined for normal data distribution using Shapiro-Wilk test and histograms before applying one way ANOVA test. The results of evaluation was done by excluding the outliers and normal distribution was observed for all analytes except Pb. It was observed that Pb is showing minor deviation from the unimodality and it was re-evaluated using the short term data set of +18 ºC. Even the samples were exposed more struggle conditions, this evaluation resulted in unimodal distribution in each test (Annex 2). Means of units were also tested by Shapiro-Wilk and Histogram to show the normal distribution of data.

Uncertainties of homogeneity between units were evaluated with one way ANOVA. The following equation (2) is used for repeatability of method (s_{wb}), and equation (3) is used for the calculation of standard deviation between units (s_{bb}).

$$\mathrm{s}_{\mathrm{wb}} = \sqrt{MS_{within}} \quad (2)$$

Here, MS_{within} is the mean of square of variance within the unit, and s_{wb} equals to “s” of the method as long as sub samples represent the whole unit.

$$\mathrm{s}_{\mathrm{bb}} = \sqrt{\frac{MS_{between} - MS_{within}}{n}} \quad (3)$$

In this equation, $MS_{between}$ is mean of square of variance between units, and n stands for the number of replicates per unit.

$MS_{between}$ is found to be smaller than MS_{within} in conditions for which the heterogeneity of the material is smaller than heterogeneity that can be determined by the applied analytical method or measurement fluctuations that may have occurred randomly. In these cases, since s_{bb} cannot be calculated, u^*_{bb} is calculated as heterogeneity contributing to uncertainty including method repeatability using equation (4).

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

Here, $\nu_{MSwithin}$ is the degree of freedom for MS_{within}.

Since filling sequence trend was observed for Cr and Mn as mentioned above, an alternative estimation of uncertainty related to heterogeneity was applied [7].

$$u_{rect} = \frac{|the\ highest\ value - the\ lowest\ value|}{2\sqrt{3}} \quad (5)$$

An alternative estimate of heterogeneity was calculated for B, which has an outlying bottle mean (see above). Although it was detected that this outlying result was resulting from one outlying data of three individual results where the other two individual results were in consistency with the rest of dataset obtained from all other units, this data was retained in the evaluation of homogeneity. Between-bottle heterogeneity for B was modelled as rectangular distribution. The standard uncertainty using this outlier (u_{rect}) was then estimated using the following equation (6).

$$u_{rect} = \frac{|Aykırı\ değer - Ortalama\ değer|}{\sqrt{3}} \qquad (6)$$

In this equation, $\bar{y}$ is the average of all results.

The results of evaluation of the between-unit variation are given in the Table 4 and the highest value between s_{bb}, u^*_{bb} and u_{rec} was assigned as u_{bb}, uncertainty of homogeneity [7].

Table 4. Results of Homogeneity Study

Element	Average Value, µg/kg	$s_{wb,rel}$ %	$s_{bb,rel}$ %	$u^*_{bb,rel}$ %	$u_{rec,rel}$ %	$u_{bb,rel}$ %
Al	330.8	1.81	0.32	0.59	-	0.59
As	66.5	1.39	0.68	0.45	-	0.68
B	1356	1.74	$MS_{between}<MS_{within}$	0.57	2.22	2.22
Cd	102.9	1.23	0.30	0.40	-	0.40
Co	428	1.47	$MS_{between}<MS_{within}$	0.48	-	0.48
Cr	232.4	1.54	$MS_{between}<MS_{within}$	0.50	0.46	0.50
Cu	327	1.25	$MS_{between}<MS_{within}$	0.41	-	0.41
Fe	1970	1.6	$MS_{between}<MS_{within}$	0.52	-	0.52
Hg	50.0	1.22	0.91	0.4	-	0.91
Mn	368	1.75	$MS_{between}<MS_{within}$	0.57	0.72	0.72
Mo	94.9	1.63	0.38	0.53	-	0.53
Ni	173.6	1.84	$MS_{between}<MS_{within}$	0.60	-	0.60
P	685	3.1	2.02	1.01	-	2.02
Pb	72.1	7.89	$MS_{between}<MS_{within}$	2.71	-	2.71
Sb	139.6	1.56	0.67	0.51	-	0.67
Tl	161.2	1.31	$MS_{between}<MS_{within}$	0.43	-	0.43
V	197.8	0.95	0.17	0.31	-	0.31
Zn	413.7	1.07	0.58	0.35	-	0.58

The occurrence of $MS_{between} < MS_{within}$ for nine elements demonstrates that material heterogeneity is smaller than that can be detected by the analytical methodology used. It is established that even if the outlier data was kept in the evaluation homogeneity, the uncertainty contribution from homogeneity of material is small (<1 %). Except for B, P and Pb, the uncertainty contribution from between unit homogeneity did not exceed 2 % which was the target uncertainty value related to homogeneity. All the dataset used in evaluating the homogeneity of the material and graphs related to between unit homogeneity is given in Annex 1 and Annex 2, respectively.

STABILITY

Stability studies were carried out with the simulation of conditions in the laboratory, considering environmental conditions that may occur during shipment to the user and storage conditions.

Stability studies were carried out using an isochronous design [2[2]. Total of 14 units for short term stability, and 8 unit for long term stability was picked using randomly stratified sampling scheme.

For short term stability study, samples were stored at +18 °C ve +60 °C for periods of 1, 2 and 4 weeks. For each of time point at two temperatures, two units were placed related test cabinets meaning that six units for each test temperature were used. The reference temperature was set to +4 °C and two units for reference point was stored at reference temperature conditions for 4 weeks. After samples were stored for a certain period at different temperature conditions, two unit per each were transferred to reference temperature where further degradation is assumed to be negligible. After completion of four-week period, all the transferred units and the two units stored at reference temperature for four weeks were analysed simultaneously. For long term stability study, six units were stored at room temperature (22 ± 3) °C for 0, 13 and 27 weeks. After each time period was over, two units were transferred to reference temperature, and at the end of overall time period, all units were analysed simultaneously as described in short term stability study.

Short Term Stability Study

The results obtained from isochronous measurements were first grouped according to the time period, and evaluated for each time point separately. These evaluations were carried out for both temperatures, separately. As mentioned above, two units for each time point and three replicates from each unit were measured in short term stability analysis. In the short term stability study, Unit 22 and Unit 365 were defined as reference point as Unit 59, Unit 134, Unit 161, Unit 204, Unit 443 and Unit 531 were analysed for +18 °C and Unit 100, Unit 232, Unit 264, Unit 279, Unit 322 and Unit 501 were analysed for +60 °C. Since measurement of mercury was performed separately, Unit 146 and Unit 425 were used as reference point in those measurements.

The results were screened for single outliers by applying the Grubbs' test at confidence levels of 95 % and 99 %. In the evaluation of dataset of +18 °C, one outlier for Mo, 2 outliers for P and 4 outliers for B were determined. Since no technical reason for outliers of B, Mo and P was found, all of them retained in the evaluation of short term stability study. However, it was identified that there was a systematic error in the sample preparation step of Unit No 501 for Al, and it resulted in determination of it as half of the mean mass fraction. Therefore, this data was omitted in the evaluation of STS.

In the evaluation of short term stability dataset, 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 (*regression analysis*). The calculated slopes of the regression line were tested using two-tailed *t*-test using $t_{\alpha,df}$ as the critical *t* value at α = 0.05 (95 % confidence level). The plots are given in Annex 3.

Calculation of uncertainty contribution related to short term stability study was performed by using the following equation (7). The longest time period that samples can be exposed during transportation conditions was taken into account in the calculation. The results obtained were given in Table 5.

$$u_{sts,rel} = \frac{RSD}{\sqrt{\Sigma(t_i - \bar{t})^2}} \times t \qquad (7)$$

Where;

RSD : the relative standard deviation of the all values obtained in the stability study,
t_i : the time point for each replicate,
$\bar{t}$: the mean of the all time points,
t : the maximum time suggested for the transfer (4 week).

Table 5. Results of Short Term Stability Study

Element	*18* °C $u_{sts,rel}$ *(%)*	*60* °C $u_{sts,rel}$ *(%)*	Number of individual outlying result at %95 confidence level		Significance of the trend on a %95 confidence level	
			18 °C	*60* °C	*18* °C	*60* °C
Al	0.53	0.58	-	2	No	**No**
As	1.08	1.01	-	-	No	**No**
B	0.78	0.87	4	2	No	**No**
Cd	0.14	0.61	-	-	No	**No**
Co	0.37	0.32	-	-	No	**No**
Cr	0.33	0.34	-	-	No	**No**
Cu	0.57	0.40	-	-	No	**No**
Fe	0.47	0.53	-	-	No	**No**
Hg	1.15	1.19	-	-	No	**No**
Mn	0.37	0.37			No	**No**
Mo	0.96	0.77	1	-	No	**No**
Ni	0.55	0.28	-	-	No	**No**
P	1.77	1.30	1	-	No	**No**
Pb	3.47	4.15	-	-	No	**No**
Sb	0.91	0.49	-	-	No	**No**
Tl	0.49	0.67	-	**-**	No	**No**
V	0.23	0.34	-	**-**	No	**No**
Zn	0.72	0.53	-	**-**	No	**No**

The result of measurements showed that the certified reference material is stable at +18 °C and +60 °C for 4 weeks. According to this study, UME CRM 1204 can be safely dispatched under conditions where the temperature do not exceed 60 °C for up to 4 weeks.

Long Term Stability Study

Shelf life of the CRM has been determined through long term stability measurements (LTS). Two units for each time point and three replicates from each unit were measured in long term stability analysis. This study has been designed for 27 weeks. Unit 85 and Unit 168 were designated as reference point bottles, and stored at 4 °C during the whole period. Unit 220, Unit 297, Unit 367 and Unit 468 were transferred to reference temperature at 13^{th} and 27^{th} week, respectively.

All the data obtained for LTS was screened for outlier using single Grubbs test at 95 % and 99 % confidence levels. Two outlying individual results were found for B, whereas one outlying individual results was found for each of Fe and Mo. Except the one outlier of B, all outlying data kept in the evaluation of LTS since there was no clear indication of technical reason observed. One of the outliers of B was not taken into account in the evaluation since it was concluded that the outlying value was the result of contamination as it was higher than the mass fraction values obtained in homogeneity, stability (STS and LTS) and characterization studies.

The graphs were plotted against time and the regression line calculated. The slopes of regression line was evaluated to determine if any significant trend by time exists using *t*-test at 95 % confidence level. For all elements except Hg, the slopes of the regression lines were not significant at room temperature, (22 ± 4) °C. However, a significant trend was observed for Hg, even at 99 % confidence level in the same conditions. Therefore, it was concluded that mercury is not stable at room temperature. For mercury, the evaluation of LTS was done with data obtained for samples kept at +4 °C in homogenity, short term and long term stability studies. As a conclusion, no significant trend was observed in the data, which were measured independently within different days at 95 % confidence level, and 1.6 % uncertainty related to LTS was determined for Hg. All other parameters were also investigated in a similar way for the stability at +4 °C, and no significant trend was observed except for Co and Sb. However, the uncertainty of LTS calculated by using classical design includes the intermediate precision of the method and results in overestimation of uncertainty related to stability of material. Therefore, the storage condition of CRM was assigned as +4 °C in order to ensure the stability of Hg while the data obtained from room temperature conditions were used in evaluation of LTS for other parameters. The stability of Co and Sb at +4 °C will be evaluated further in the post-certification monitoring. Uncertainty contribution of long term stability, u_{lts}, is calculated using equation (8).

$$u_{lts,rel} = \frac{RSD}{\sqrt{\Sigma(t_i - \bar{t})^2}} \times t \qquad (8)$$

Where,

RSD : the relative standard deviation of the all values obtained in the stability study,
t_i : the time point for each replicate,
$\bar{t}$: mean of the all time points,
t : suggested shelf life (4 °C, for 12 months).

The shelf life of UME CRM 1204 certified reference material was defined as 12 months after sales date provided that it is stored at 4 °C. The uncertainty contribution of LTS calculated based on this period is given in Table 6. Additionally, post-certification monitoring is going to be done in certain periods.

The uncertainty of long term stability study for lead exceeded than the target uncertainty. The graphs of LTS were given in Annex 4.

Table 6. The Results of Long Term Stability Study

Element	$u_{lts,rel}$ (%)	Significance of the trend on a 95 % confidence level	Number of individual outlying result at 95 % confidence level	Number of individual outlying result at 99 % confidence level
Al	1.22	No	-	**-**
As	1.55	No	-	**-**
B	2.31	No	2	**1**
Cd	1.42	No	-	**-**
Co	1.03	No	-	**-**
Cr	1.31	No	-	**-**
Cu	1.24	No	-	**-**
Fe	1.47	No	1	**1**
Hg*	1.60	No	-	**-**
Mn	1.09	No	-	**-**
Mo	1.33	No	1	**1**
Ni	1.04	No	-	**-**
P	1.07	No	-	**-**
Pb	5.51	No	-	**-**
Sb	1.33	No	-	**-**
Tl	1.23	No	-	**-**
V	0.80	No	-	**-**
Zn	1.42	No	-	**-**

*Data were evaluated using classical experimental design at +4 °C.

CHARACTERIZATION

Based on ISO Guide 34, characterization can be done with four different approaches [1]. In this project, characterization was done by applying two of these defined approaches: i) *using primary measurement method* and ii) *two or more independent reference methods applied by one laboratory.* The characterization of Cd, Cr, Cu, Hg and Fe were performed by ID-ICP-MS, a potential primary measurement technique, and the results of validated HR-ICP-MS method (matrix matched external calibration) was used for verification. The characterization of Al, As, Co, Mn, Ni, Sb, Pb, V and Zn was performed by using two independent reference methods. While HR-ICP-MS and Grafite Furnace Atomic Absorption Spectrometry (GF-AAS) were used for Al, As, Co, Mn, Ni, Sb and V, ID-ICP-MS and HR-ICP-MS (matrix matched external calibration) were applied for Pb and Zn (Table 7).

In the characterization study, three units for each method was measured. The measurement design for HR-ICP-MS and GF-AAS was consisting of measurement of three replicates per unit at two different days with independent calibration graphs and independent sample preparation. Therefore, six independent results were obtained for each of those techniques. The characterization study done by ID-ICP-MS consisted of nine independent results (three independent replicates per unit). For Cd, Cu, Hg, Fe and Pb, as the sample preparation was done in three days, the measurement of those samples were done in two days. The measurement of independent samples of Cr and Zn were performed in a single day. For verification of ID-ICP-MS results, the results of HR-ICP-MS method obtained from three replicates per each unit were used.

Table 7. Techniques Used in Characterization Study

Element	Technique		
	HR-ICP-MS	GF-AAS	ID-ICP-MS
Al	+	+	
As	+	+	
B	+		+
Cd			+
Co	+	+	
Cr			+
Cu			+
Fe			+
Hg			+
Mn	+	+	
Mo	+		
Ni	+	+	
P	+		
Pb	+		+
Sb	+	+	
Tl	+		
V	+	+	
Zn	+		+

The results of characterization was checked whether all individual data follow a unimodal distribution, and the measurement uncertainties were estimated based on bottom up approach using GUM Workbench software. The uncertainty of study (u_{char}) for the elements characterization by using primary measurement method was assigned as the measurement uncertainty of the method. On the other hand, the uncertainties for the elements characterized by using more than one method was obtained by combining the uncertainties of methods and according to the Guide to the Expression of Uncertainty in Measurements (GUM) as described in ISO Guide 35. The consistency of the results with their uncertainties that produced by more than one method for each element was investigated based on the approach of ERM Application Note [18]. All the results of different methods were in agreement except for Pb and Zn. The average of ID-ICP-MS and HR-ICP-MS results for Pb and Zn was assigned as informative and certified value, respectively. The inconsistency in these results were covered by applying B type of rectangular distribution in the uncertainty budget of each. The data related to characterization was given in Annex 5.

PROPERTY VALUE AND UNCERTAINTY ASSIGNMENT

For each element, assignment of property values and uncertainty values were performed considering the characterization strategy followed measurement results and associated uncertainties, and the uncertainty contributions from homogeneity and stability measurements.

The certified value of the elements (Cd, Cr, Cu, Hg and Fe) characterized by primary measurement method ID-ICP-MS was the average of 9 independent results and the uncertainty of the measurement estimated by bottom up approach defined as u_{char}.

The value assignment of the elements (B, Al, As, Co, Mn, Ni, Pb, Sb, V and Zn), of which characterization studies were performed using the *application of two or more reference methods by a single laboratory* approach, were carried out by unweighted mean of the results obtained by each method. The uncertainty value, u_{char}, were determined by merging the uncertainty values obtained for each method.

The uncertainty component of the certified value is composed of the uncertainty contributions from the characterization study (u_{char}), the homogeneity study (u_{bb}), the short-term stability study (u_{sts}) and the long-term stability study (u_{lts}). The uncertainty of the CRM were determined by combining the components affecting value of the assigned uncertainty are calculated using the following equation:

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

The circumstances for inclusion of uncertainty related to short term stability was investigated by comparing two conditions in STS. Since the long term stability study covers the 18 °C conditions for a longer time period, uncertainty of STS was included in merging the uncertainty when $u_{sts,rel}$ (60 °C) > $u_{sts,rel}$ (18 °C). According to this evaluation, u_{sts} was not included in calculation of uncertainty assignment of certified value except for Al, Cd, Cr, Fe, Hg, Pb, Tl and V.

The uncertainty of the certified value was expanded by a coverage factor of $k = 2$ for a confidence level 95 %. Certified values and associated uncertainties are given in Table 8, and the contribution of each parameter to U_{CRM} is given in Table 9.

Table 8. Certified value and uncertainty components

Element	Certified Value (µg/kg)	U_{CRM}, (µg/kg, k=2)	$U_{CRM,rel}$ (%, k=2)	$u_{char,rel}$ (%)	$u_{bb,rel}$ (%)	$u_{sts,rel}$ (%)	$u_{lts,rel}$ (%)
As	63.2	2.8	4.4	1.34	0.68	-	1.55
B	1388	120	8.6	2.88	2.22	-	2.31
Cd	104.5	4.0	3.8	0.99	0.40	0.61	1.42
Co	419	12	2.7	0.75	0.48	-	1.03
Cr	243	8	3.1	0.62	0.50	0.34	1.31
Cu	334	9	2.7	0.33	0.41	-	1.24
Fe	1943	67	3.4	0.51	0.52	0.53	1.47
Hg	49.9	2.6	5.1	1.32	0.91	1.19	1.60
Mn	372	13	3.5	1.16	0.72	-	1.09
Ni	173	5	2.9	0.83	0.60	-	1.04
V	197	6	2.8	1.04	0.31	0.34	0.80
Zn	403	18	4.4	1.55	0.58	-	1.42

Table 9. Relative contribution of each parameters to U_{CRM}

Element	$u_{bb,rel}$ (%)	$u_{sts,rel}$ (%)	$u_{lts,rel}$ (%)	$u_{char,rel}$ (%)
As	9.8	-	51.6	38.6
B	26.5	-	28.7	44.8
Cd	4.5	10.4	57.1	28.0
Co	12.4	-	56.8	30.8
Cr	10.2	4.6	69.8	15.4
Cu	9.1	-	84.9	6.0
Fe	9.1	9.5	72.5	8.9
Hg	12.6	21.6	39.0	26.8
Mn	16.9	-	38.8	44.3
Ni	16.8	-	51.1	32.1
V	4.9	5.8	33.3	56.0
Zn	7.13	-	42.44	50.43

INFORMATIVE VALUES

Although the homogeneity and stability studies were performed for informative values, due to the different technical reasons appeared in characterization study, the values given in Table 10 were informative. These informative values might be certified during the studies of post certification if the technical reasons can be removed successfully.

Table 10. Values and uncertainties of informative values

Element	Value, µg/kg	U (*k*=2)
Al	349	14
Mo	95	4
P	698	34
Pb	81	15
Sb	132	6
Tl	157	7

The measurements of density and pH of UME CRM 1204 were performed three replicates of three units by expert laboratories of TÜBİTAK UME. These values are given as information and listed in Table 11.

Table 11. Values of density and pH given as informative values

Parameter	Value
Density (20 °C)	1.0006 g/cm^3
pH (20 °C)	1.8

TRACEABILITY

In this study, all measurements including the homogeneity and stability studies were performed by validated methods. All sample preparations for the measurements were performed gravimetrically using calibrated mass balances and weights, which are traceable to SI via TÜBİTAK UME. Metrological traceability of measurements were also ensured by using the calibration standards of NIST SRM 3100 series traceable to SI. Isotopically enriched certified reference materials (ERM and NIST) traceable to SI were used in ID-ICP-MS measurements in the characterization of Cd, Cr, Cu, Hg, Fe and Zn. The source of traceability of standards used in the measurements were given in Table 12. The certified or IUPAC values of isotopic ratios were used in ID-ICP-MS measurements.

Table 12. The Standard used for traceability of the measurement results

No	Name of Standard	Standard No	Traceability
1	Al Standard Solution	SRM 3101a	NIST
2	As Standard Solution	SRM 3103a	NIST
3	B Standard Solution	SRM 3107	NIST
4	Cd Standard Solution	SRM 3108	NIST
5	Co Standard Solution	SRM 3113	NIST
6	Cr Standard Solution	SRM 3112a	NIST
7	Cu Standard Solution	SRM 3114	NIST
8	Fe Standard Solution	SRM 3126a	NIST
9	Hg Standard Solution	SRM 3133	NIST
10	Mn Standard Solution	SRM 3132	NIST
11	Mo Standard Solution	SRM 3134	NIST
12	P Standard Solution	SRM 3139a	NIST
13	Pb Standard Solution	SRM 3128	NIST
14	Sb Standard Solution	SRM 3102a	NIST
15	Tl Standard Solution	SRM 3158	NIST
16	V Standard Solution	SRM 3165	NIST
17	Zn Standard Solution	SRM 3168a	NIST
18	Cd Isotopic Reference Material	IRMM 621	IRMM
19	Cr Isotopic Reference Material	IRMM 624	IRMM
20	Cr Isotopic Reference Material	IRMM 625	IRMM
21	Cu Isotopic Reference Material	IRMM 632	IRMM
22	Fe Isotopic Reference Material	IRMM 620	IRMM
23	Hg Isotopic Reference Material	ERM-AE640	IRMM
24	Hg Isotopic Reference Material	ERM-AE639	IRMM
24	Pb Isotopic Reference Material	SRM 981	NIST
26	Pb Isotopic Reference Material	SRM 982	NIST
27	Pb Isotopic Reference Material	SRM 991	NIST
28	Zn Isotopic Reference Material	IRMM 654	IRMM

INSTRUCTION FOR USE

Storage Conditions

The material must be stored at (4 ± 2) °C under dark conditions.

TÜBİTAK UME cannot be held responsible for changes that may happen during storage of the material at customer's premises, especially of opened samples.

Minimum sample intake

The bottle must be shaken for a minute before opening for assurance of homogeneity.

All precautions must be taken in order to prevent contamination and evaporation. Minimum sample intake is 0.5 mL for Al, As, Cu, Hg, Ni, P, Pb, Sb and Zn, and 0.1 mL for B, Cd, Co, Cr, Fe, Mn, Mo, Tl and V. It is proven that samples are homogenous within these amounts.

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] ISO Guide 34:2009. General requirements for the competence of reference materials producers
[2] ISO Guide 35:2006, Reference materials – General and statistical principles for certification
[3] Evaluation of uncertainty in measurement - Guide to the expression of uncertainty in measurement, JCGM 100:2008
[4] European Commission 91/271/EEC “Urban Waste Water” Directive
[5] European Parliament and of the Council 2013/39/EU “Priority Substances” Directive
[6] Water Pollution Control Regulation, Official Gazette of the Republic of Turkey No. 25687, dated December 31, 2004
[7] 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.
[8] ERM Application Note 1: Comparison of a measurement result with certified value, January 2010.

REVISION HISTORY

Date	Remark
12.08.2016	First Publication.

Annex 1. Data for Homogeneity Study

Table E 1. Homogeneity data for Al and As

Unit No	**Al** (µg/kg)			**As**(µg/kg)		
	Replicate 1	Replicate 2	Replicate 3	Replicate 1	Replicate 2	Replicate 3
3	325.8	329.9	332.2	67.3	66.3	66.8
516	335.8	332.0	331.4	65.7	67.0	67.8
81	329.2	349.7	330.3	67.5	66.7	66.3
462	329.5	320.7	321.0	66.5	65.7	64.8
125	329.9	330.9	326.2	65.2	66.4	66.4
414	325.2	330.8	330.8	67.8	66.8	67.2
193	330.1	347.5	327.7	66.3	64.8	64.8
338	327.3	332.6	335.1	67.8	68.3	67.3
234	327.9	330.5	336.6	67.0	65.6	67.9
295	332.1	324.4	330.5	67.2	67.3	64.2

Table E 2. Homogeneity data for B and Cd

Unit No	**B** (µg/kg)			**Cd**(µg/kg)		
	Replicate 1	Replicate 2	Replicate 3	Replicate 1	Replicate 2	Replicate 3
3	1549	1347	1337	105.5	103.7	103.2
516	1407	1351	1343	104.7	101.2	100.6
81	1338	1367	1380	102.8	101.6	103.4
462	1373	1357	1356	102.2	101.4	102.1
125	1385	1373	1326	102.3	102.0	103.4
414	1376	1372	1325	101.0	103.0	102.8
193	1341	1371	1332	103.7	103.5	105.5
338	1327	1361	1376	105.3	101.5	101.8
234	1364	1383	1355	104.3	103.8	102.2
295	1342	1354	1313	102.5	103.2	102.9

Table E 3. Homogeneity data for Co and Cr

Unit No	**Co** (µg/kg)			**Cr** (µg/kg)		
	Replicate 1	Replicate 2	Replicate 3	Replicate 1	Replicate 2	Replicate 3
3	447	427	429	237.4	229.3	232.7
516	428	436	425	233.6	236.7	230.6
81	415	428	431	227.0	236.6	237.1
462	415	427	428	227.2	231.9	233.7
125	425	420	432	230.3	231.8	238.7
414	432	427	432	235.8	234.6	232.5
193	424	428	426	229.7	231.4	234.4
338	425	426	429	226.8	233.3	234.8
234	429	426	429	233.2	229.4	230.2
295	424	436	424	234.0	228.0	229.8

Table E 4. Homogeneity data for Cu and Fe

Unit No	**Cu** (µg/kg)			**Fe** (µg/kg)		
	Replicate 1	Replicate 2	Replicate 3	Replicate 1	Replicate 2	Replicate 3
3	325	320	328	2068	1972	1973
516	330	326	326	1982	1997	1936
81	326	334	329	1940	1958	1988
462	334	328	322	1920	1954	1975
125	325	323	323	1930	1950	2031
414	325	327	327	2015	1957	1969
193	325	349	326	1954	1961	1969
338	330	326	334	1979	1961	1952
234	318	334	328	1984	1952	1965
295	331	324	329	1982	1957	1976

Table E 5. Homogeneity data for Hg and Mn

Unit No	**Hg** (µg/kg)			**Mn** (µg/kg)		
	Replicate 1	Replicate 2	Replicate 3	Replicate 1	Replicate 2	Replicate 3
3	50.5	49.3	50.3	388	362	366
516	50.3	50.7	49.8	376	373	361
81	50.6	50.5	49.8	359	368	375
462	50.7	50.4	51.0	366	370	371
125	49.9	50.2	49.3	364	368	369
414	49.2	49.2	50.1	379	371	364
193	49.3	50.4	48.5	369	365	368
338	49.6	49.8	50.3	363	365	370
234	50.6	52.0	50.3	367	363	369
295	50.0	48.6	49.0	365	360	363

Table E 6. Homogeneity data for Mo and Ni

Unit No	**Mo** (µg/kg)			**Ni** (µg/kg)		
	Replicate 1	Replicate 2	Replicate 3	Replicate 1	Replicate 2	Replicate 3
3	97.9	93.1	95.9	173.9	170.7	174.2
516	93.1	95.9	95.1	175.5	171.3	172.9
81	94.6	96.0	97.2	171.8	177.1	175.4
462	96.4	94.5	94.9	176.5	174.1	171.3
125	94.5	96.0	95.0	171.4	171.3	170.9
414	95.2	93.0	93.6	174.4	173.0	173.2
193	97.3	94.6	94.2	171.8	185.5	173.3
338	93.5	92.0	96.2	174.4	170.2	175.9
234	96.9	95.6	95.1	169.6	176.5	172.6
295	93.8	94.3	91.0	174.8	171.6	172.8

Table E 7. Homogeneity data for P, Sb and Tl

Unit No	**P** (µg/kg)			**Sb** (µg/kg)			**Tl** (µg/kg)		
	Replicate 1	Replicate 2	Replicate 3	Replicate 1	Replicate 2	Replicate 3	Replicate 1	Replicate 2	Replicate 3
3	641	680	710	135.5	132.4	136.8	167.6	158.4	159.6
516	655	677	670	134.2	131.9	135.8	161.5	160.8	159.1
81	709	740	719	133.8	130.0	131.8	160.4	162.1	162.7
462	680	681	645	137.2	132.7	134.7	162.0	159.3	158.9
125	702	719	678	134.5	131.9	131.7	165.6	162.9	161.5
414	678	655	676	134.9	130.8	133.5	162.6	159.2	159.6
193	675	736	687	132.8	129.2	127.7	164.3	162.7	160.1
338	670	656	689	135.6	133.8	129.6	161.3	161.2	160.9
234	685	696	660	132.4	131.3	134.0	160.4	162.1	159.6
295	687	656	668	132.8	131.6	131.4	159.8	159.1	159.8

Table E 8. Homogeneity data for V and Zn

Unit No	**V** (µg/kg)			**Zn** (µg/kg)		
	Replicate 1	Replicate 2	Replicate 3	Replicate 1	Replicate 2	Replicate 3
3	200.7	197.1	199.7	408.0	408.4	411.3
516	199.3	199.4	197.3	415.5	426.8	414.0
81	196.3	200.8	200.8	413.9	419.8	410.9
462	196.1	197.2	197.6	419.1	419.5	412.5
125	196.1	192.8	199.0	411.6	415.3	407.7
414	200.3	198.2	196.3	410.6	412.3	417.7
193	197.2	198.6	199.1	408.0	423.0	416.0
338	193.6	197.1	198.7	415.2	412.8	421.8
234	197.8	198.0	197.3	410.5	413.6	410.6
295	198.4	197.0	196.0	410.3	407.7	405.6

Table E 9. Homogeneity data for Pb

Unit No	**Pb** (µg/kg)		
	Replicate 1	Replicate 2	Replicate 3
22	78.6	69.5	79.6
59	71.5	73.4	69.1
134	62.3	73.5	70.0
161	78.7	64.2	76.4
204	75.3	66.8	71.8
365	74.7	67.0	81.4
443	72.4	81.4	66.9
531	66.5	67.7	71.0

Annex 2. The Graphs of Homogeneity Study

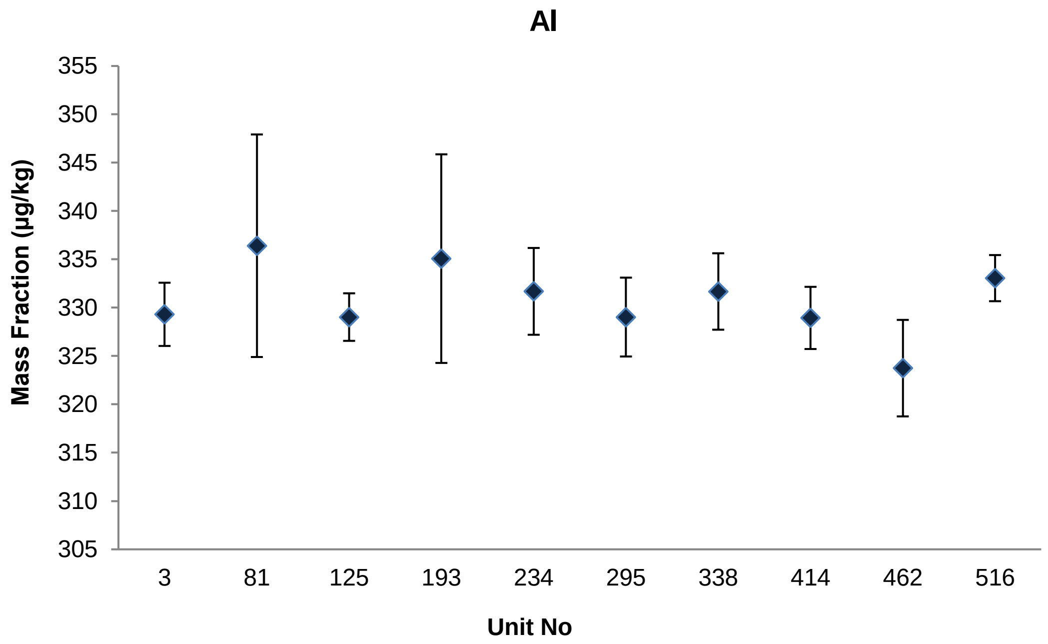


Figure 1. UME CRM 1204 Al, Homogeneity graph

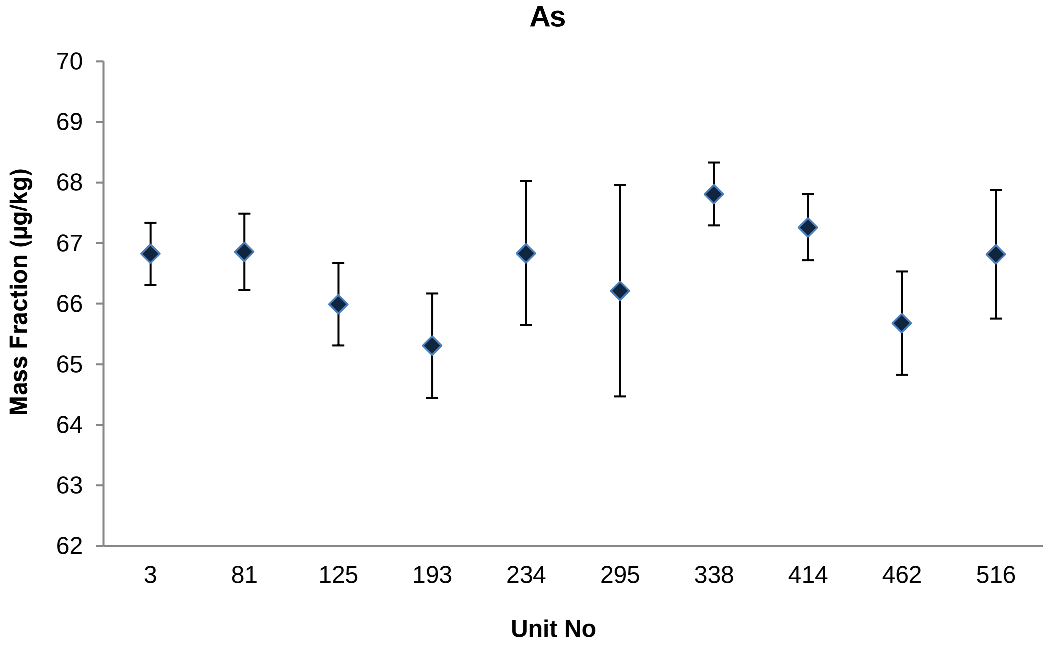


Figure 2. UME CRM 1204 As, Homogeneity graph

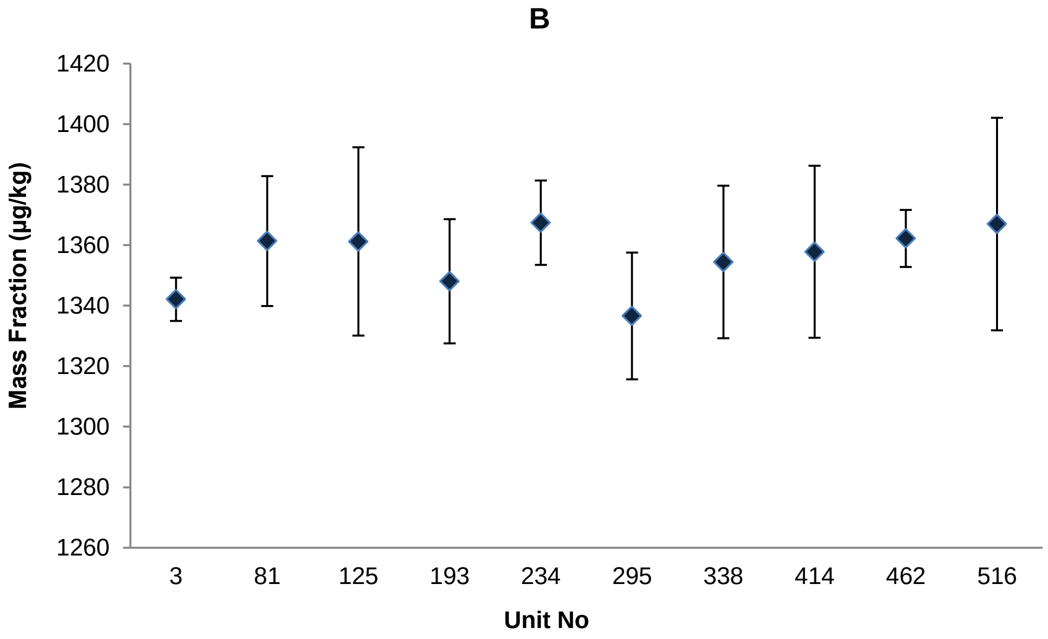


Figure 3. UME CRM 1204 B, Homogeneity graph

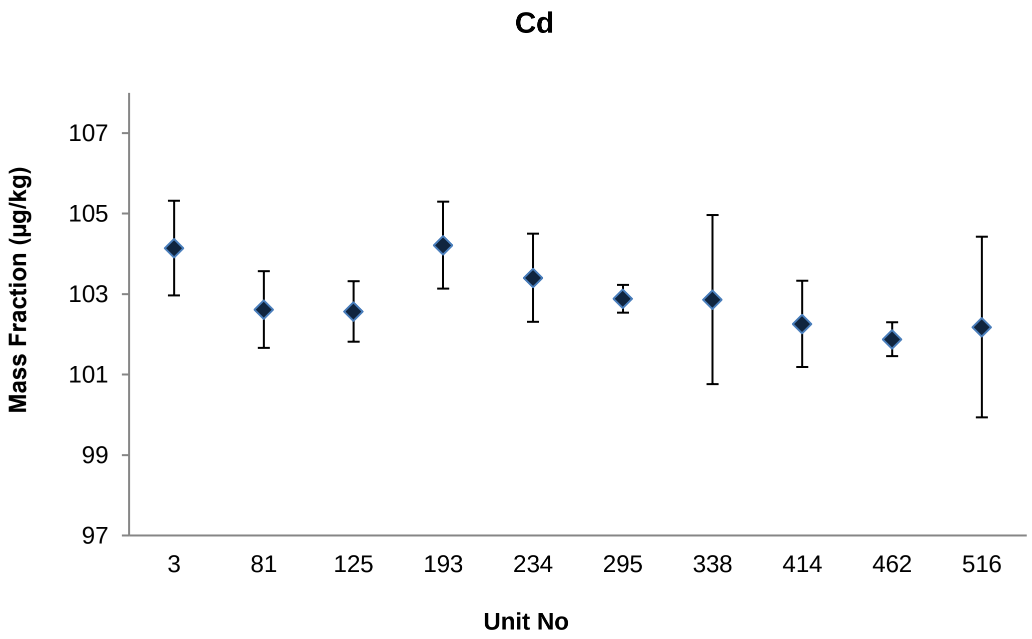


Figure 4. UME CRM 1204 Cd, Homogeneity graph

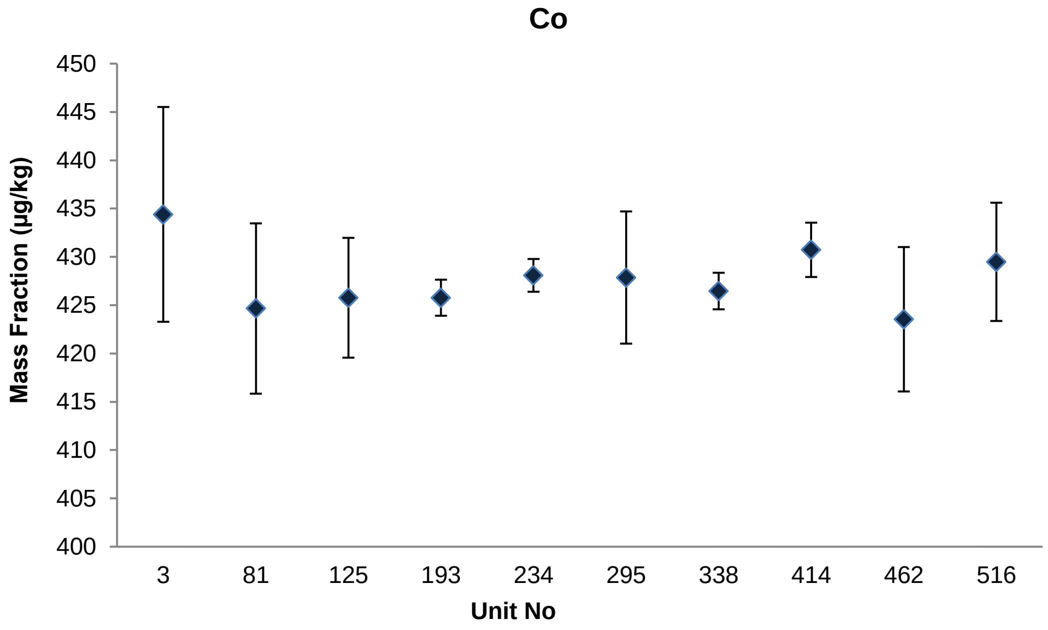


Figure 5. UME CRM 1204 Co, Homogeneity graph

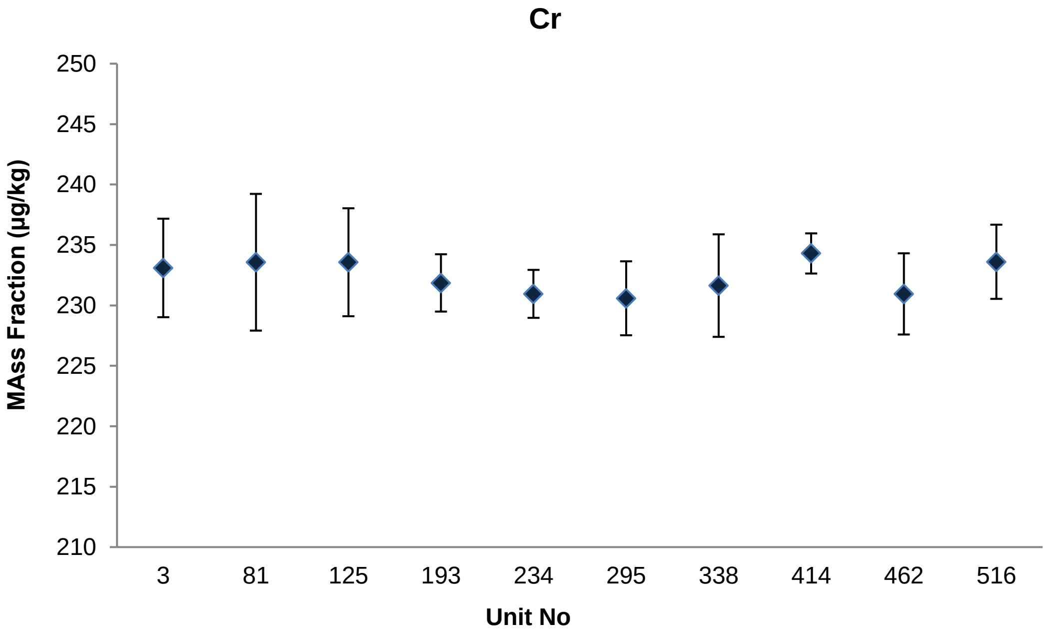


Figure 6. UME CRM 1204 Cr, Homogeneity graph

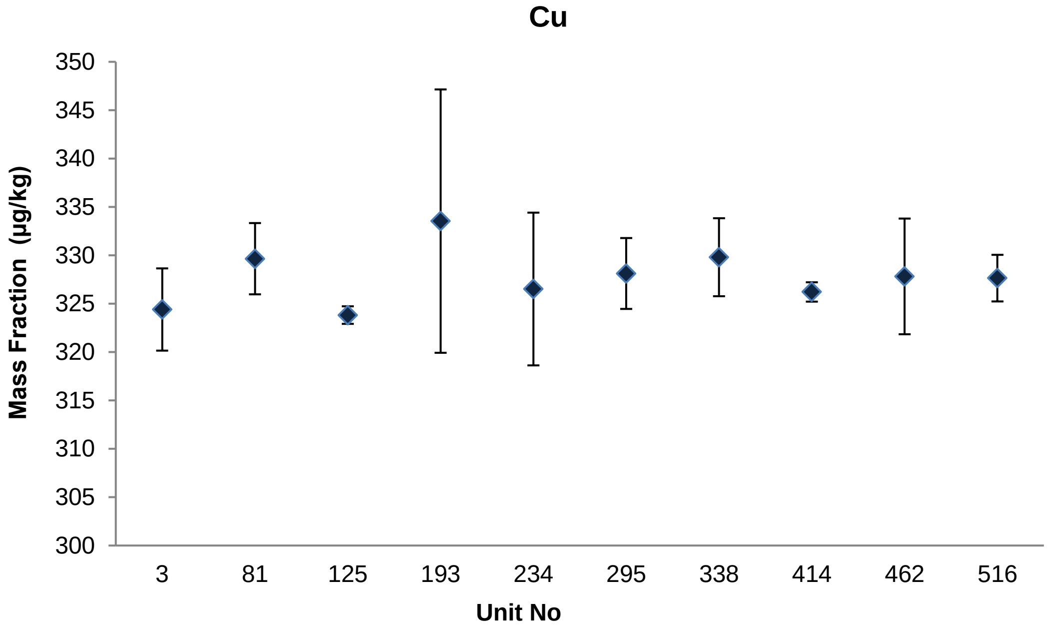


Figure 7. UME CRM 1204 Cu, Homogeneity graph

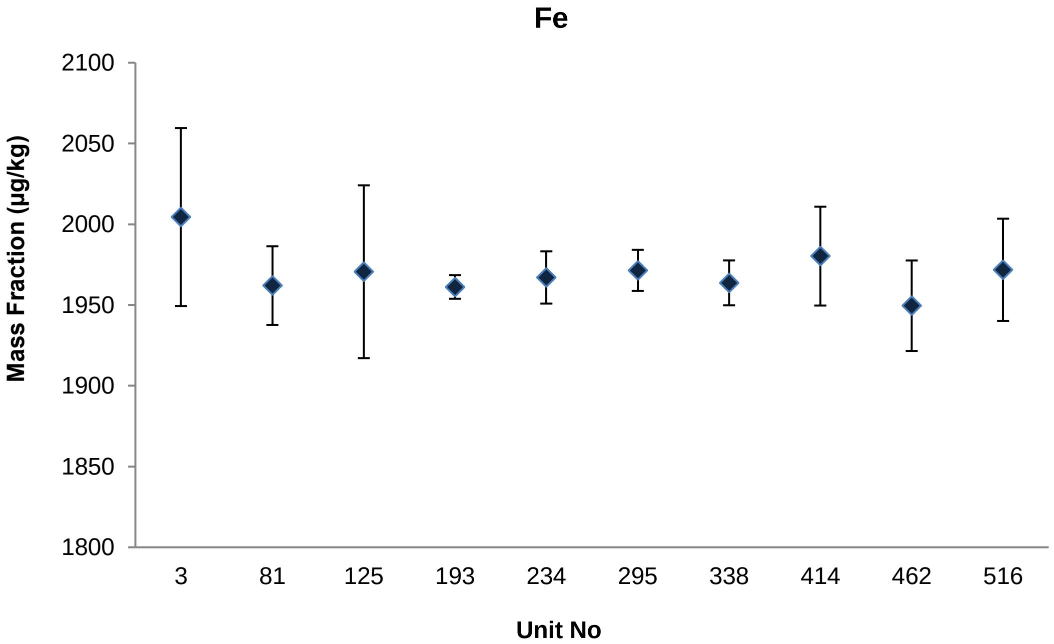


Figure 8. UME CRM 1204 Fe, Homogeneity graph

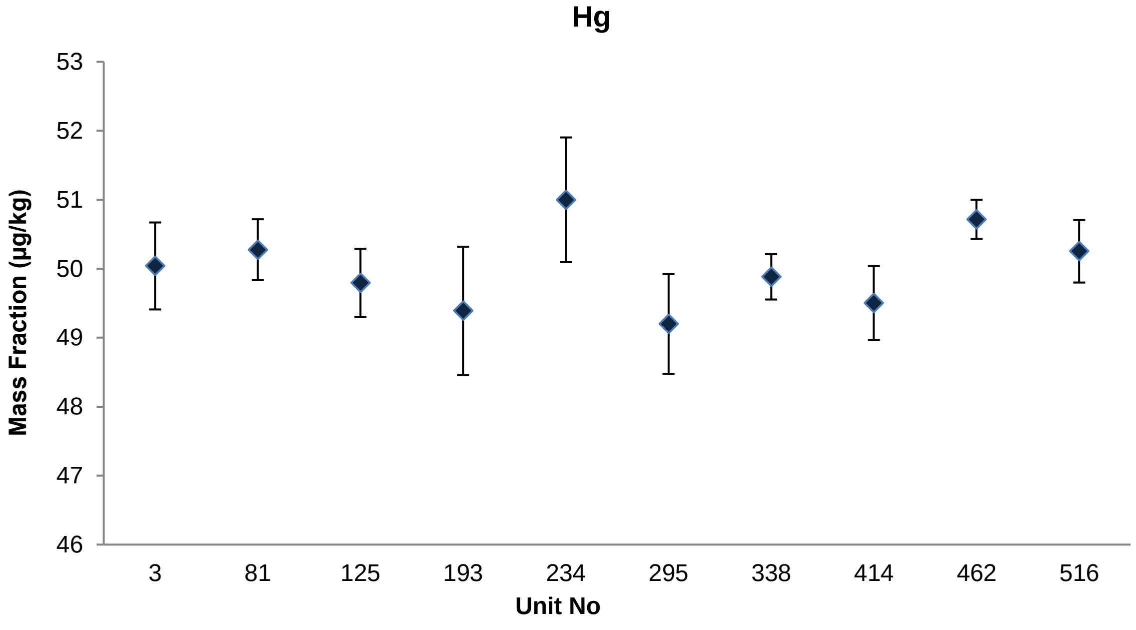


Figure 9. UME CRM 1204 Hg, Homogeneity graph

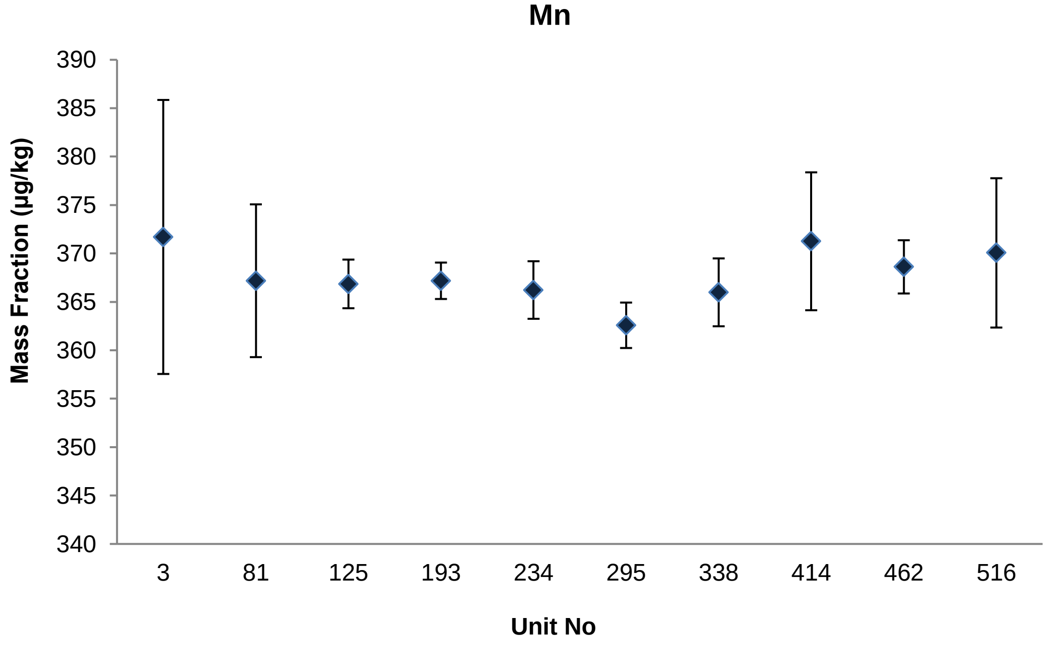


Figure 10. UME CRM 1204 Mn, Homogeneity graph

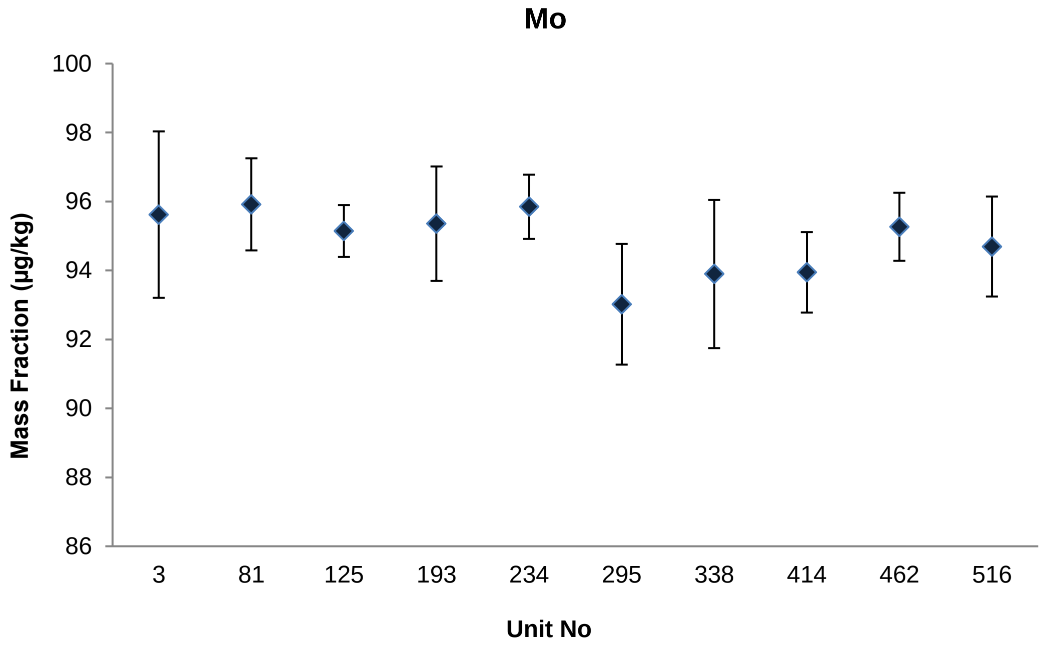


Figure 11. UME CRM 1204 Mo, Homogeneity graph

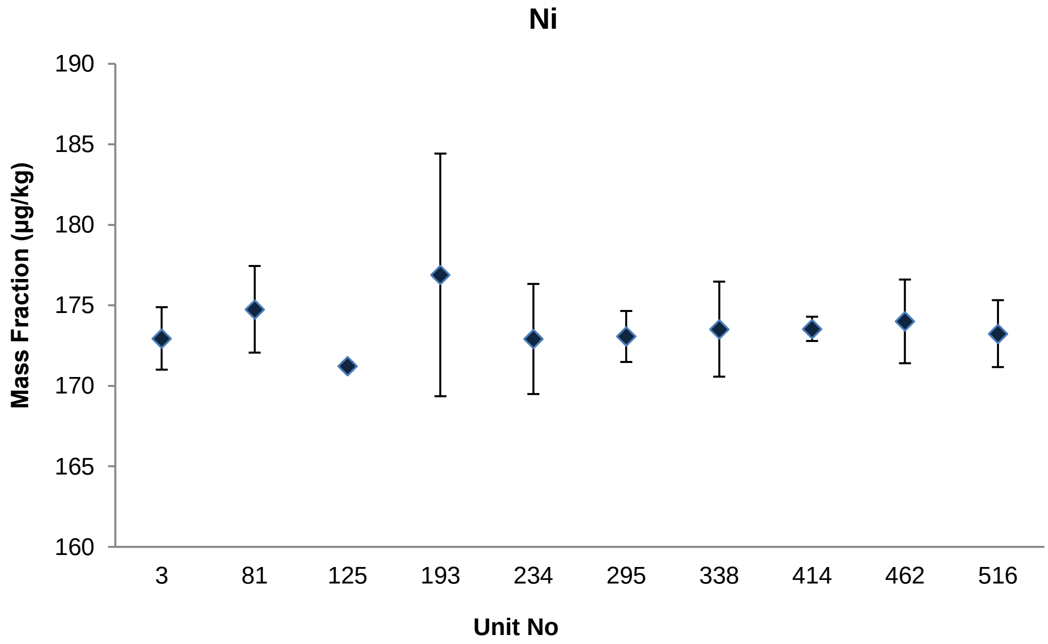


Figure 12. UME CRM 1204 Ni, Homogeneity graph

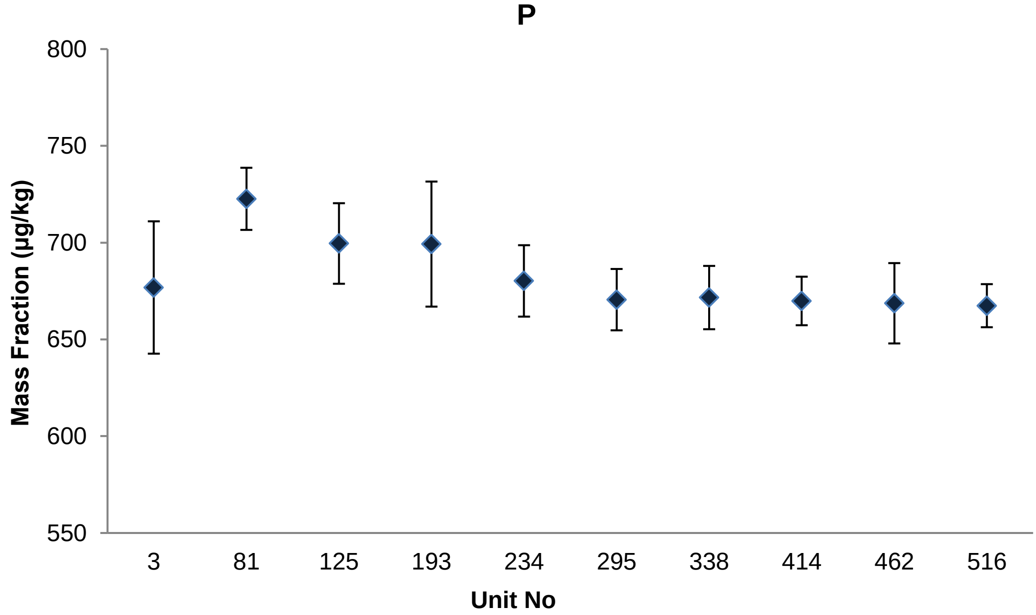


Figure 13. UME CRM 1204 P, Homogeneity graph

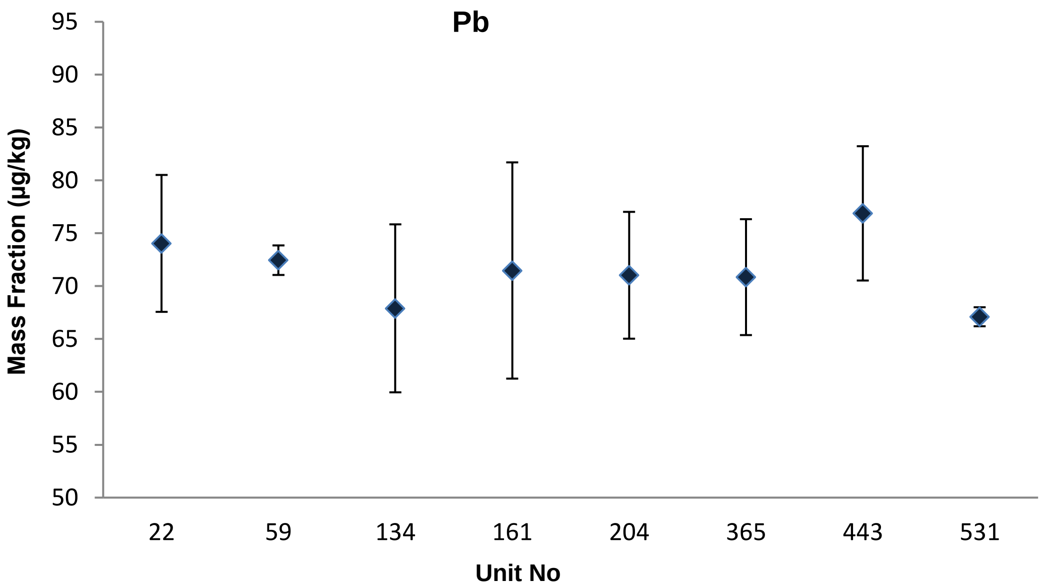


Figure 14. UME CRM 1204 Pb, Homogeneity graph

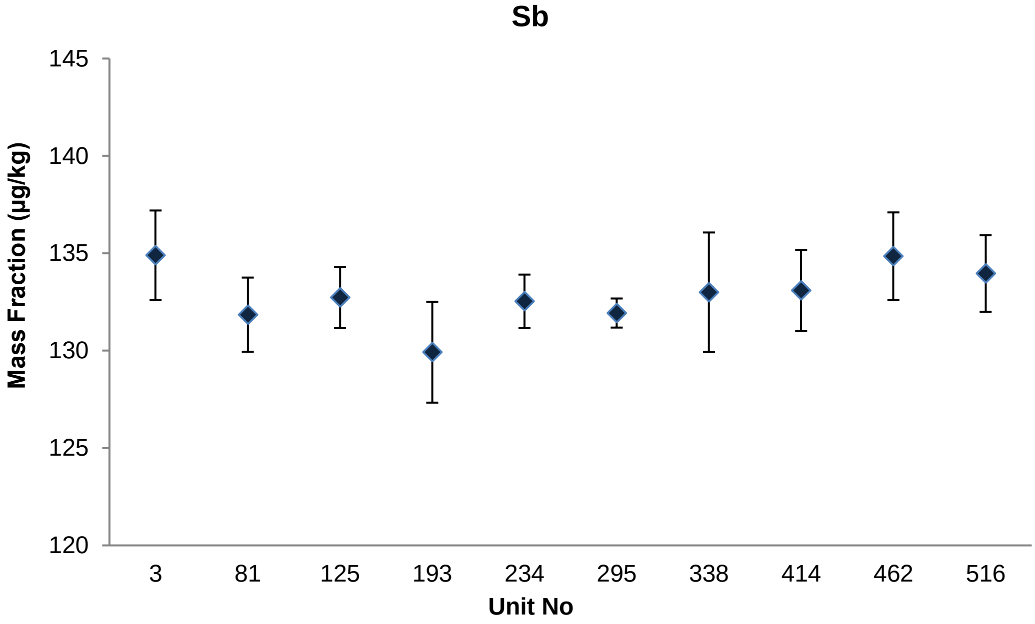


Figure 15. UME CRM 1204 Sb, Homogeneity graph

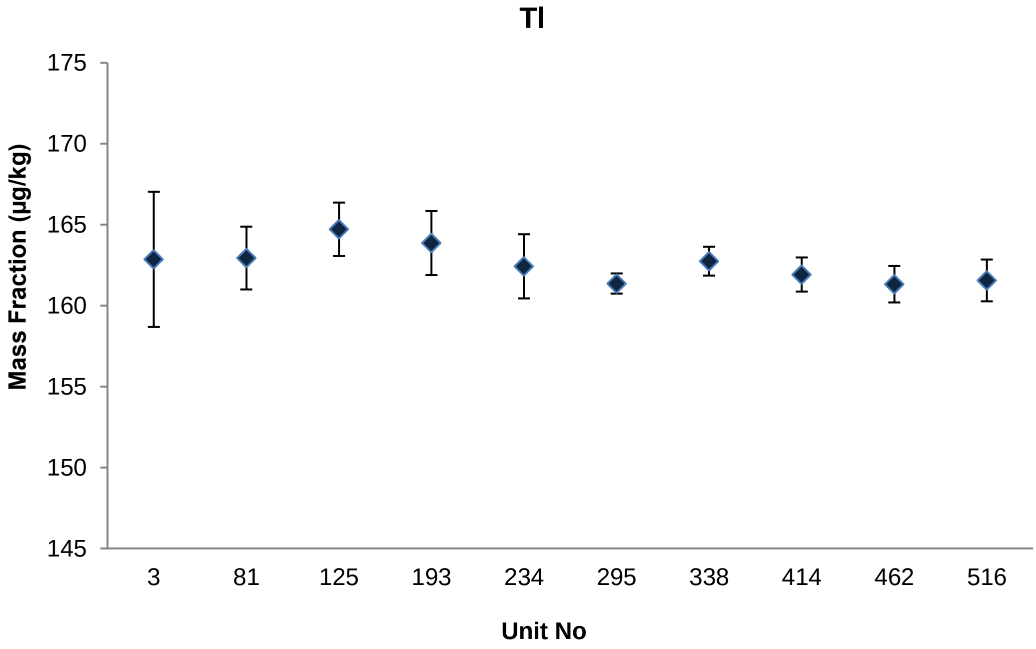


Figure 16. UME CRM 1204 Tl, Homogeneity graph

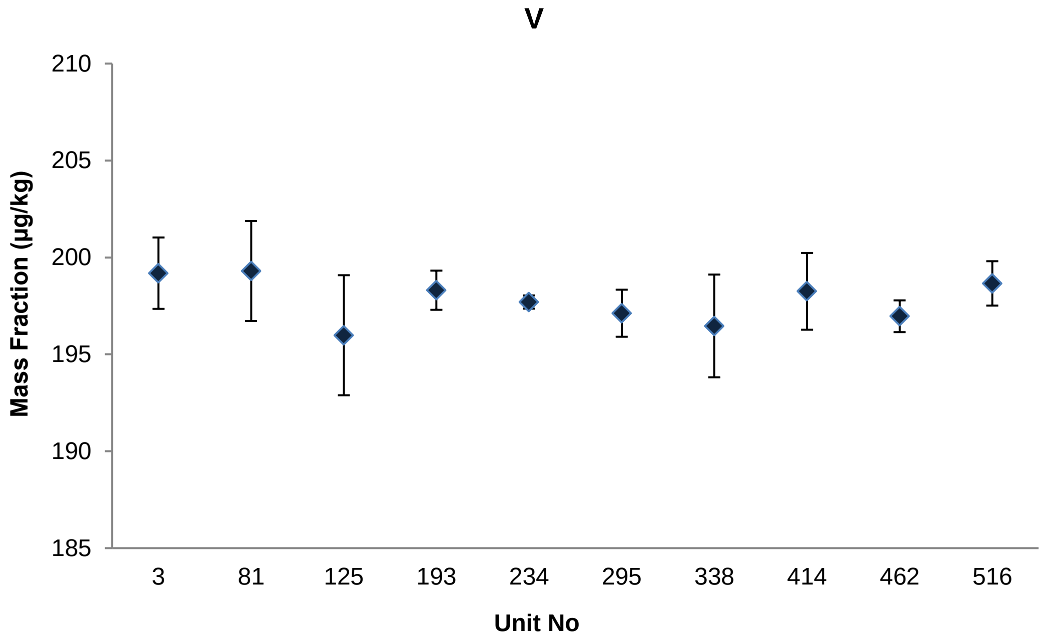


Figure 17. UME CRM 1204 V, Homogeneity graph

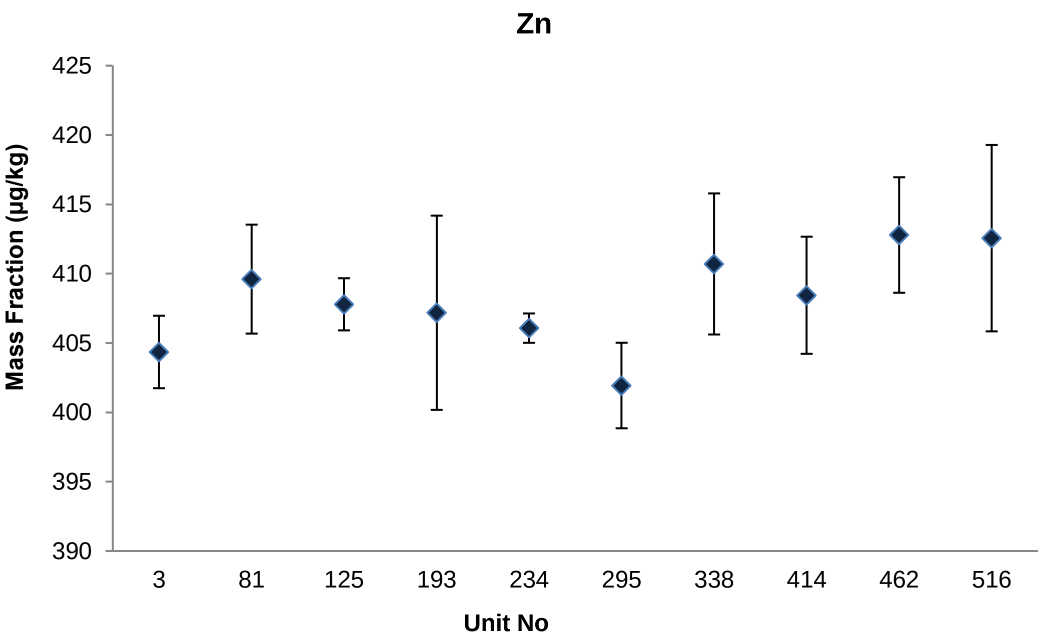


Figure 18. UME CRM 1204 Zn, Homogeneity graph

Annex 3. Graphs of Short Term Stability Study

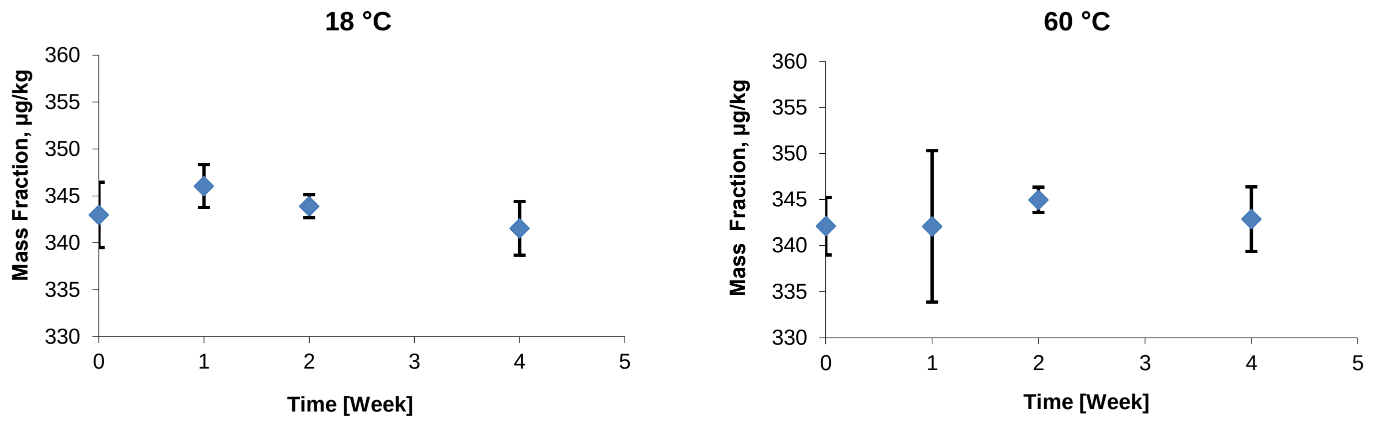


Figure 19. Graphs of short term stability, Al

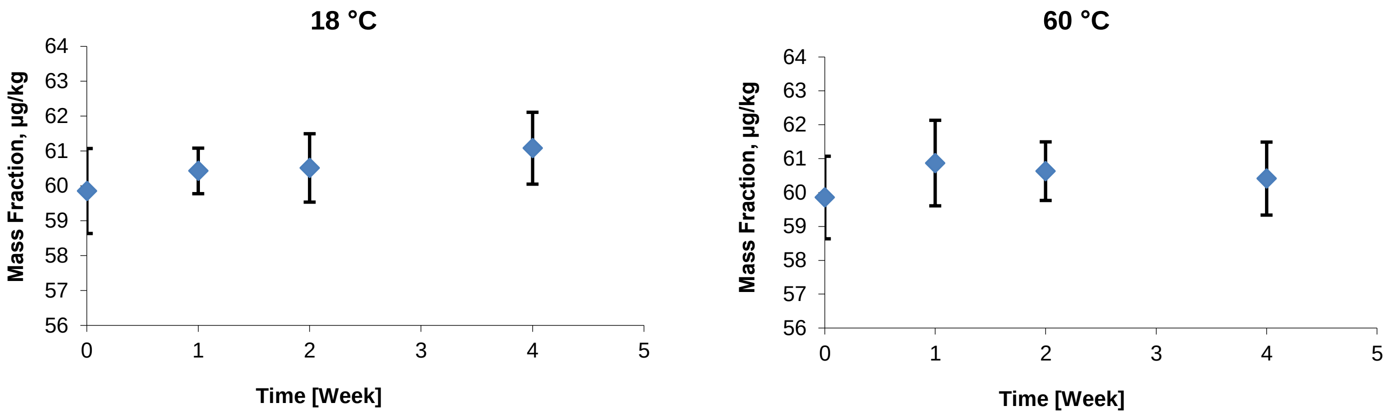


Figure 20. Graphs of short term stability, As

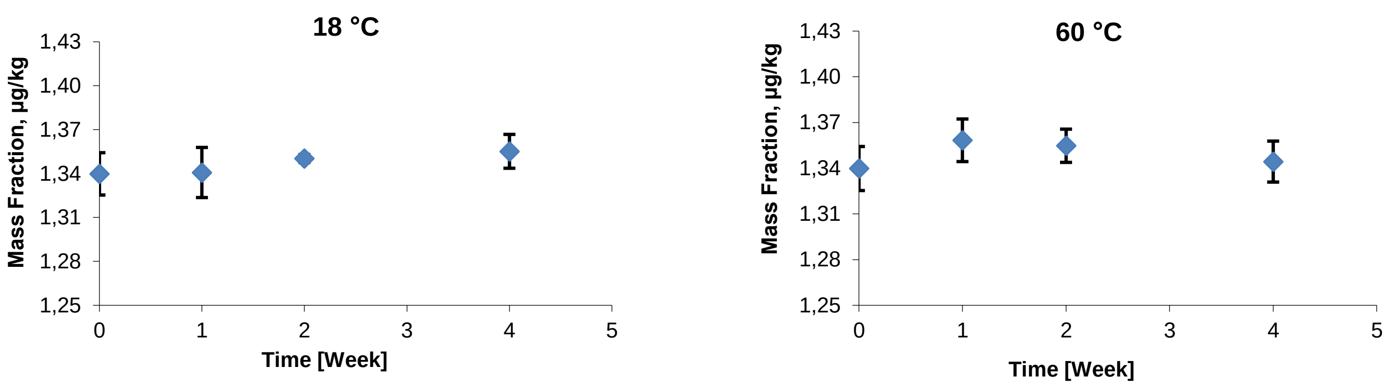
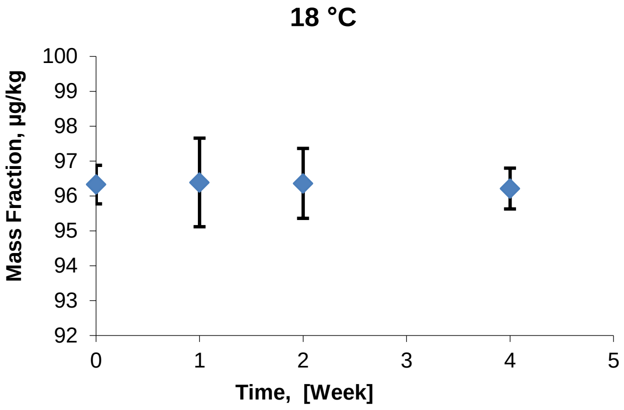


Figure 21. Graphs of short term stability, B



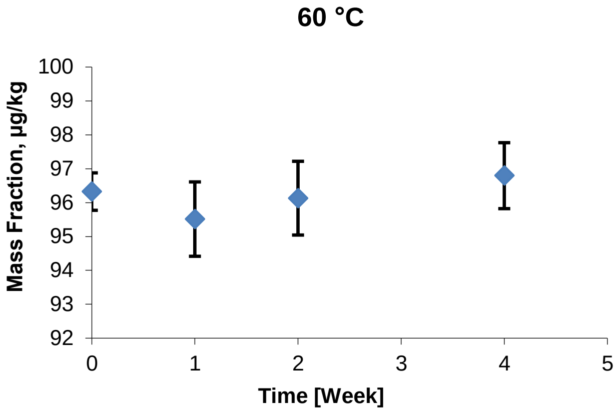
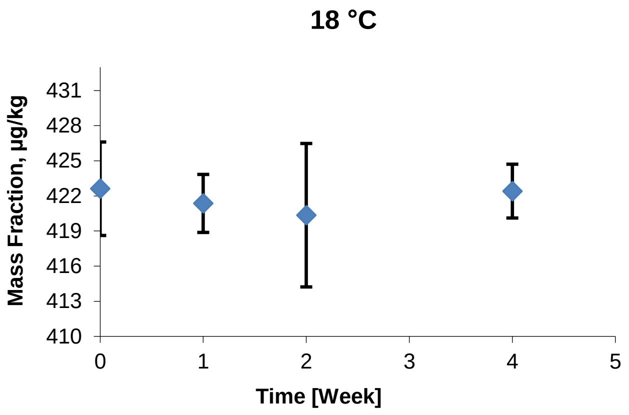


Figure 22. Graphs of short term stability, Cd



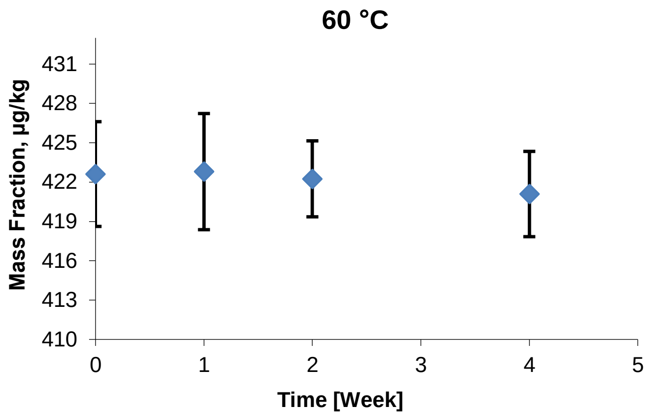
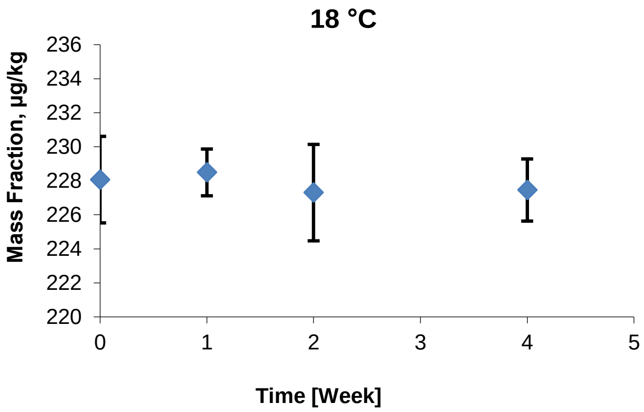


Figure 23. Graphs of short term stability, Co



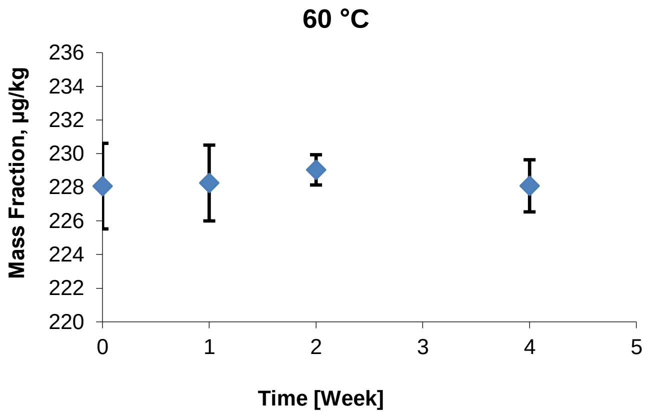


Figure 24. Graphs of short term stability, Cr

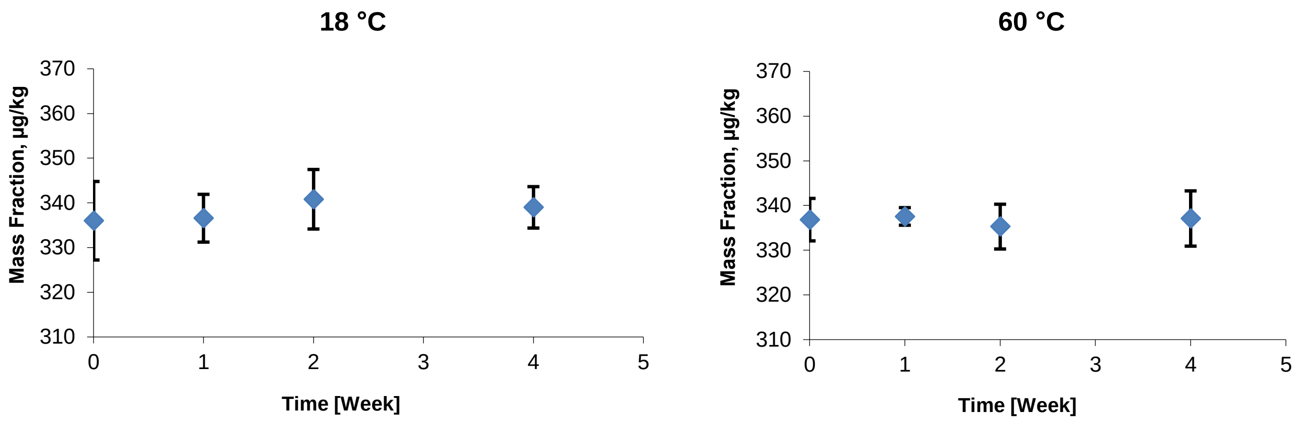


Figure 25. Graphs of short term stability, Cu

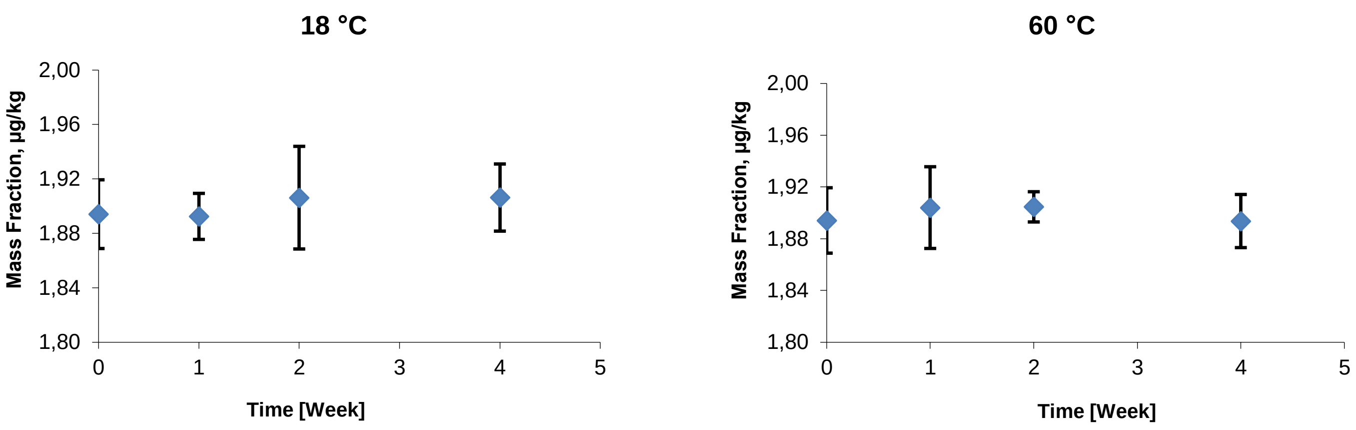


Figure 26. Graphs of short term stability, Fe

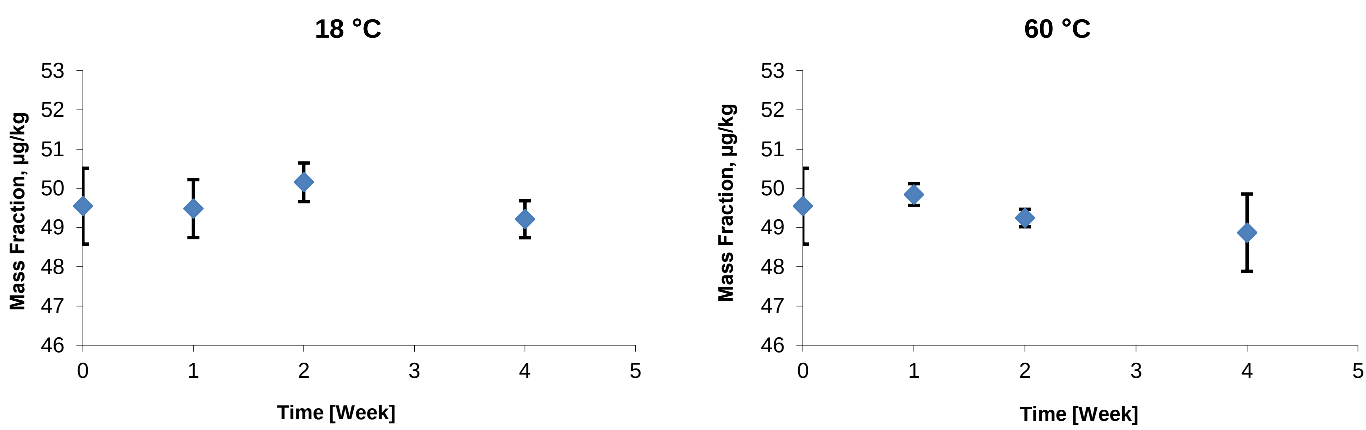


Figure 27. Graphs of short term stability, Hg

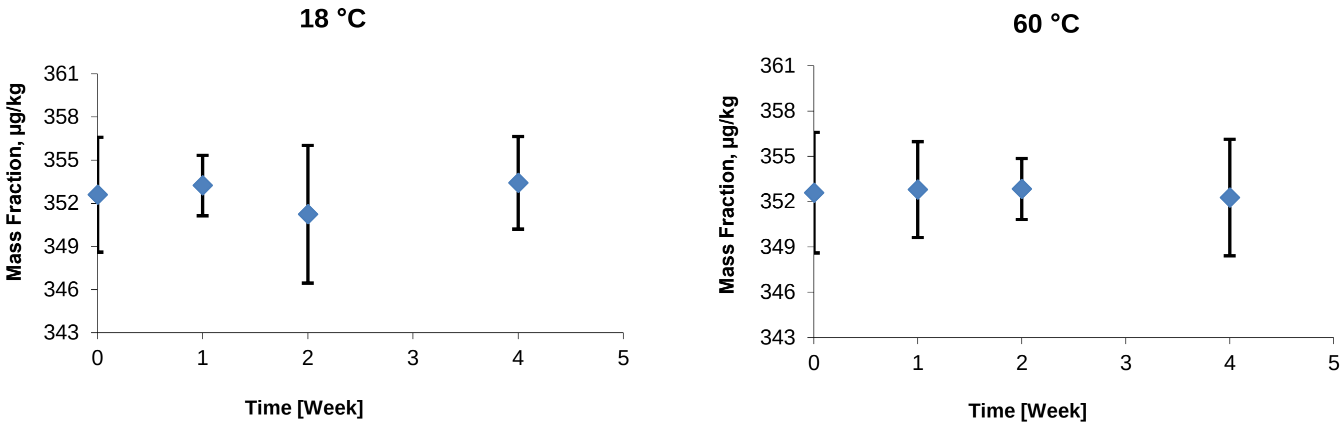


Figure 28. Graphs of short term stability, Mn

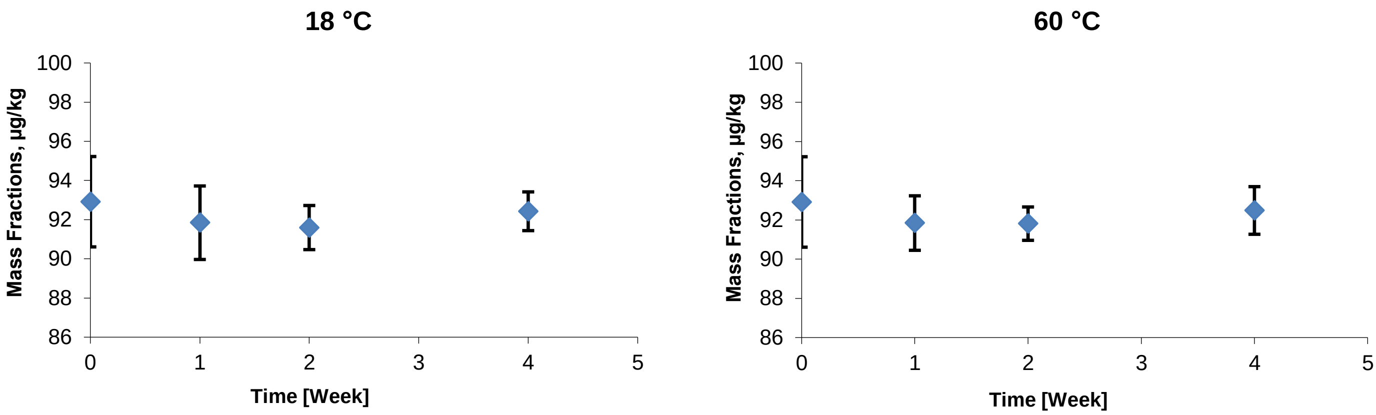


Figure 29. Graphs of short term stability, Mo

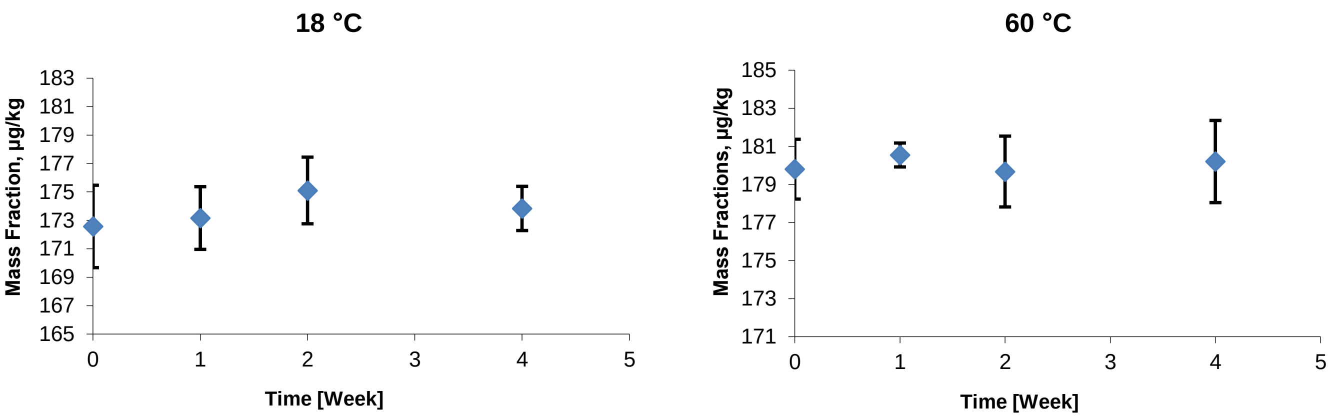


Figure 30. Graphs of short term stability, Ni

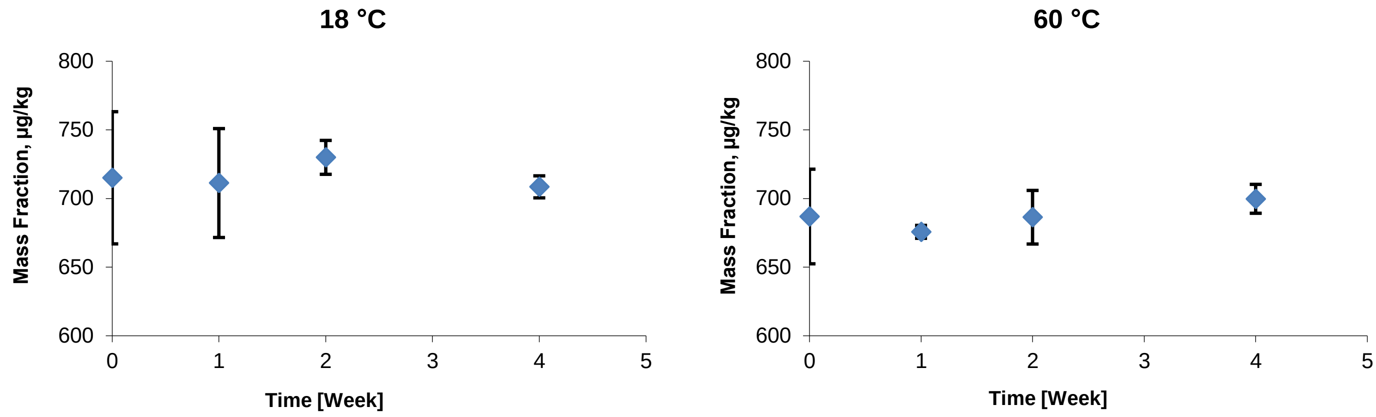


Figure 31. Graphs of short term stability, P

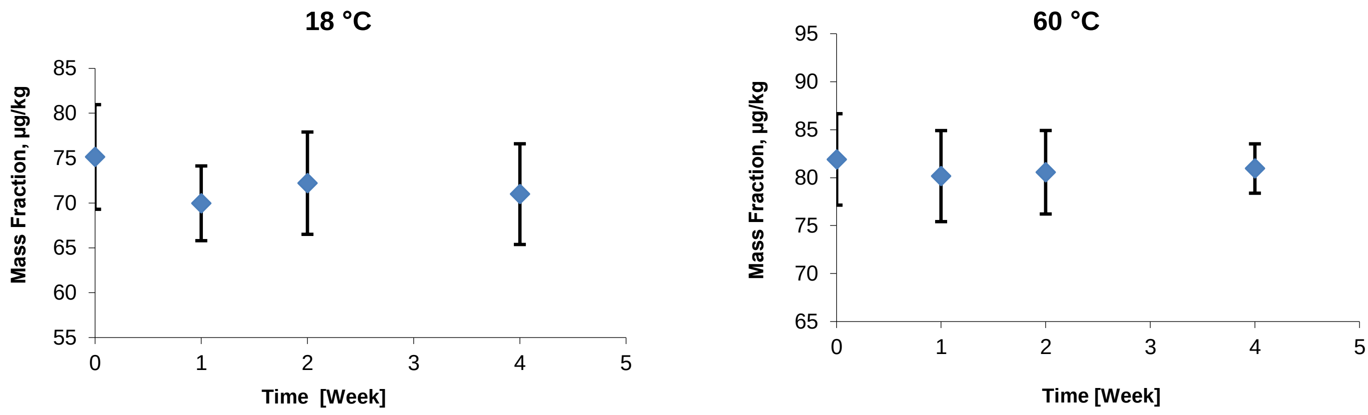


Figure 32. Graphs of short term stability, Pb

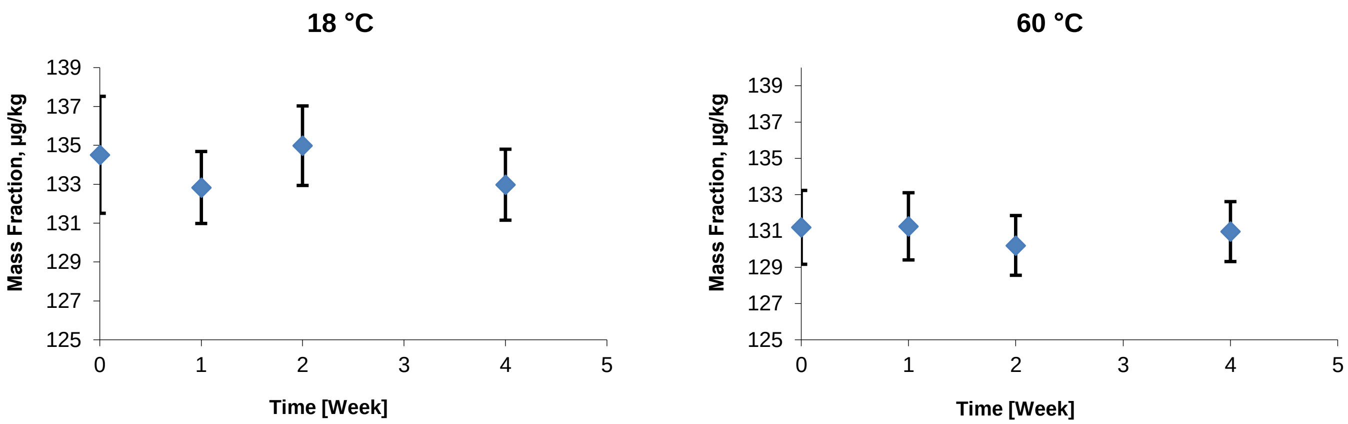


Figure 33. Graphs of short term stability, Sb

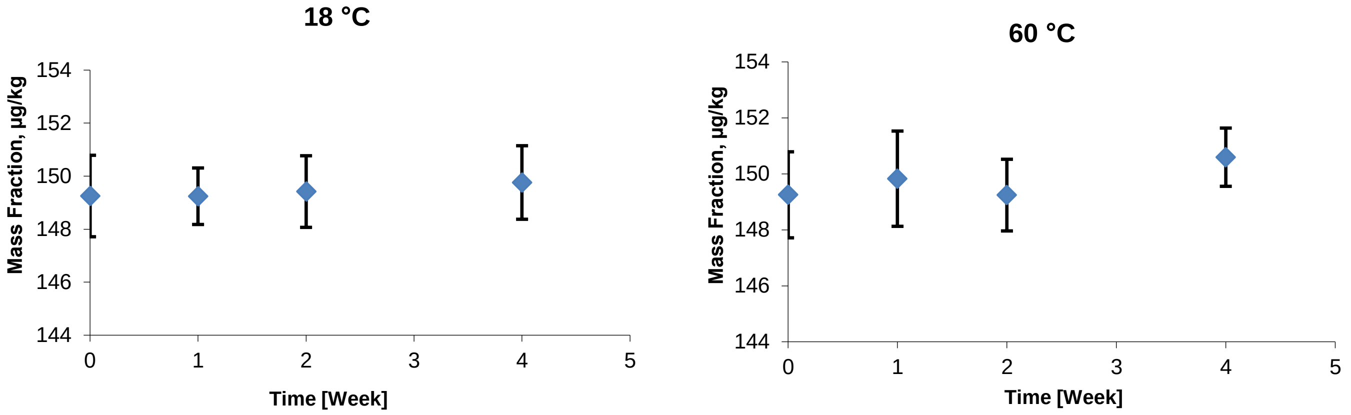


Figure 34. Graphs of short term stability, Tl

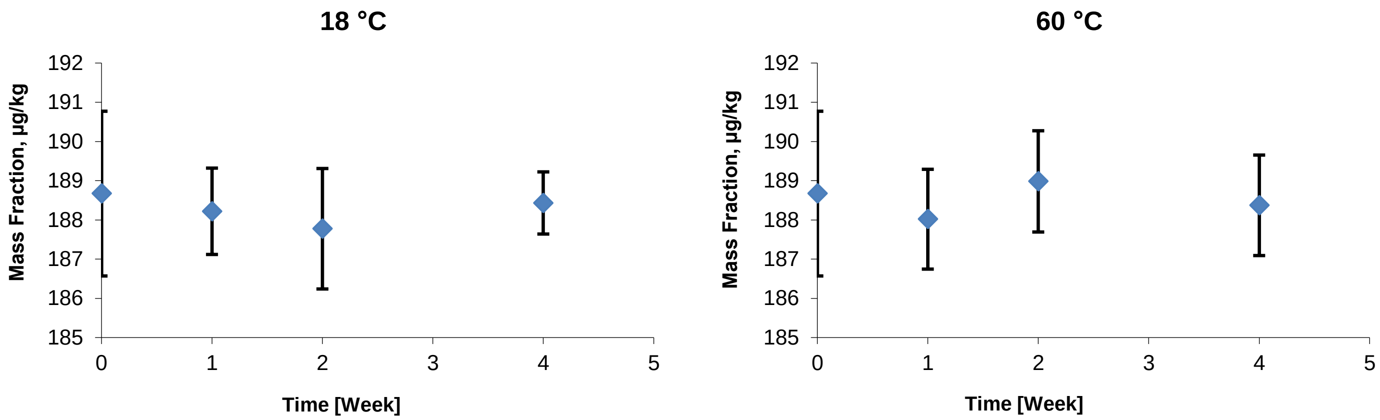


Figure 35. Graphs of short term stability, V

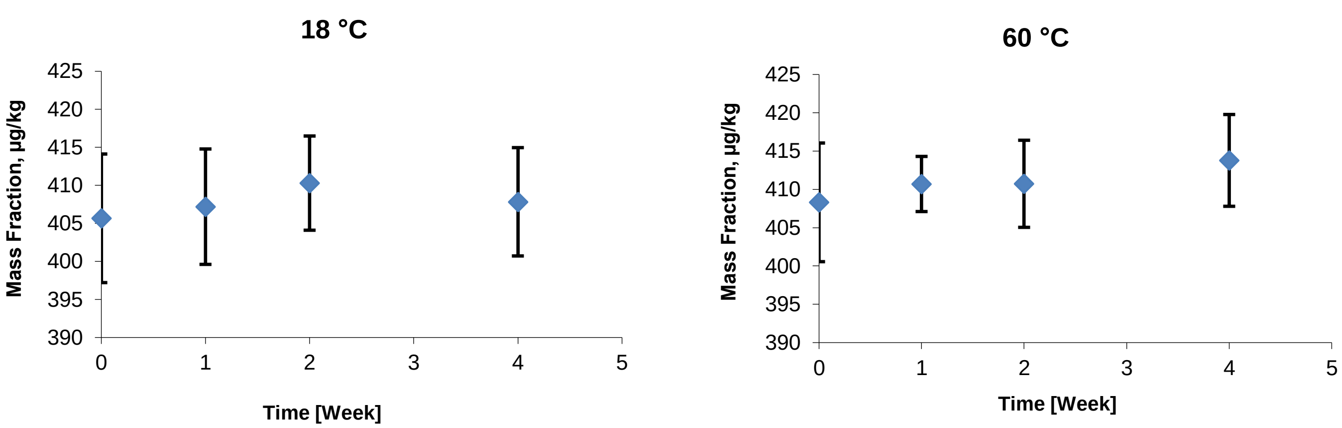


Figure 36. Graphs of short term stability, Zn

Annex 4. Graphs of Long Term Stability Study

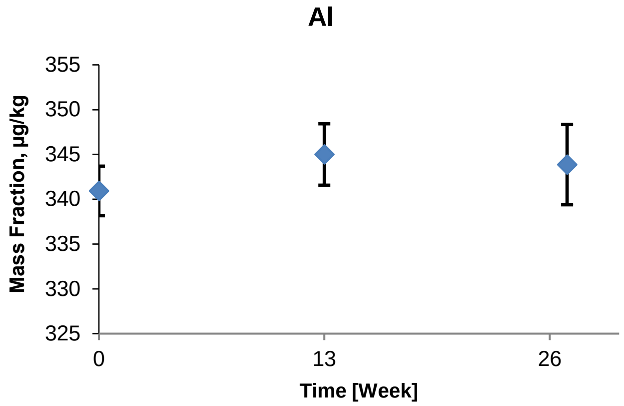


Figure 37. Graphs of long term stability, Al

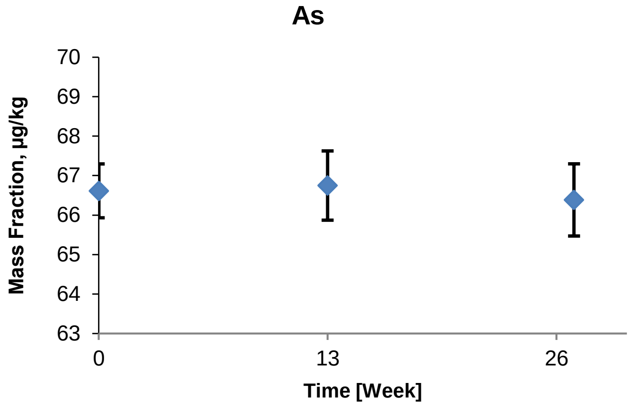


Figure 38. Graphs of long term stability, As

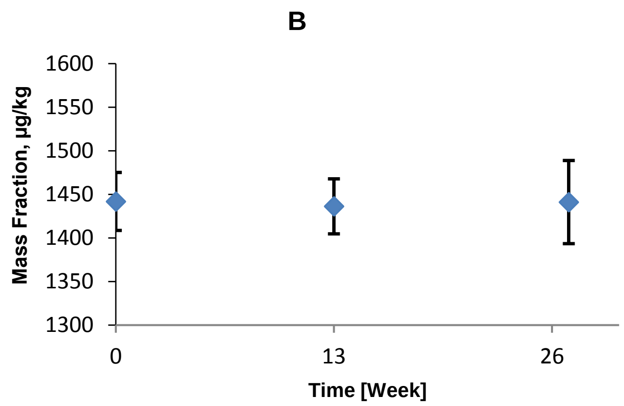


Figure 39. Graphs of long term stability, B

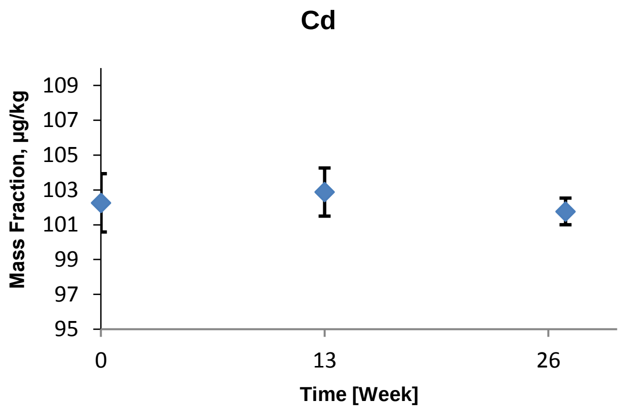


Figure 40. Graphs of long term stability, Cd

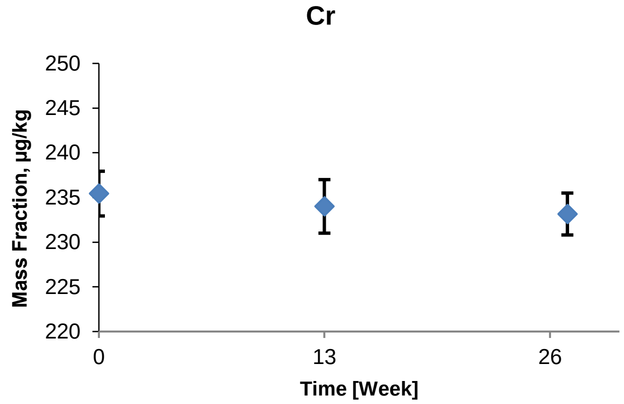


Figure 41. Graphs of long term stability, Cr

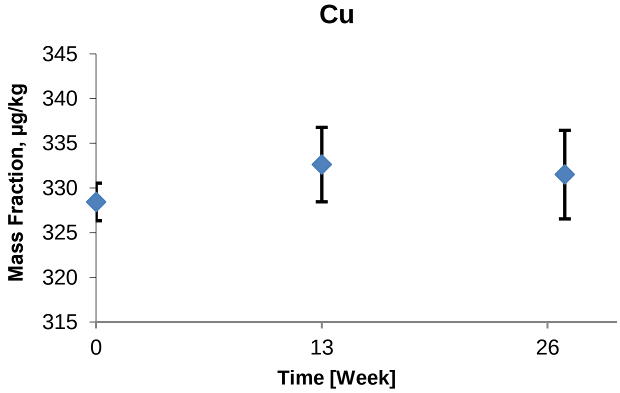


Figure 42. Graphs of long term stability,Cu

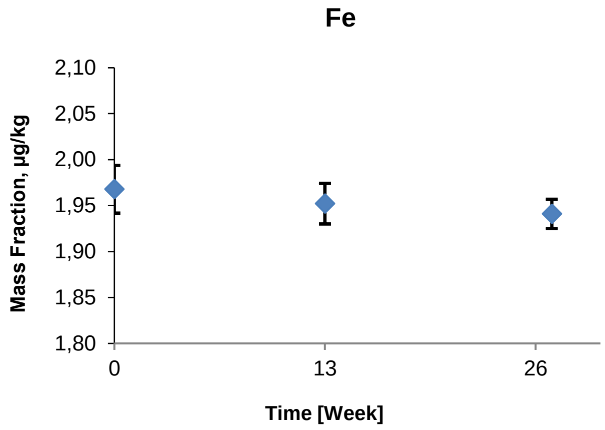


Figure 43. Graphs of long term stability, Fe

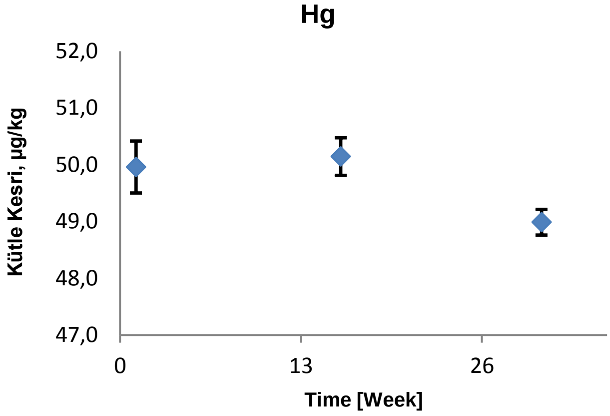


Figure 44. Graphs of long term stability, Hg

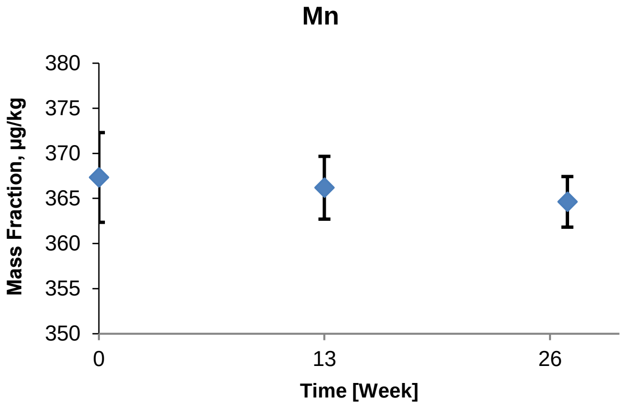


Figure 45. Graphs of long term stability, Mn

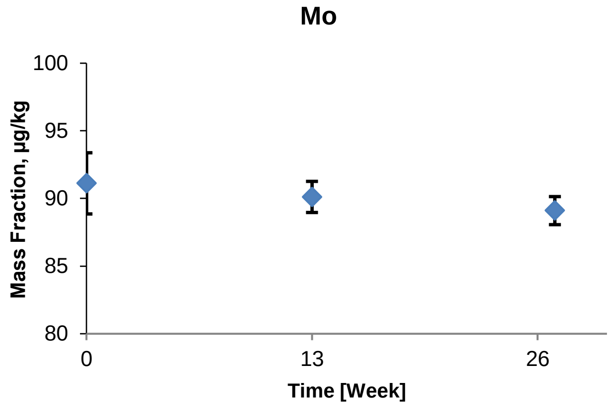


Figure 46. Graphs of long term stability, Mo

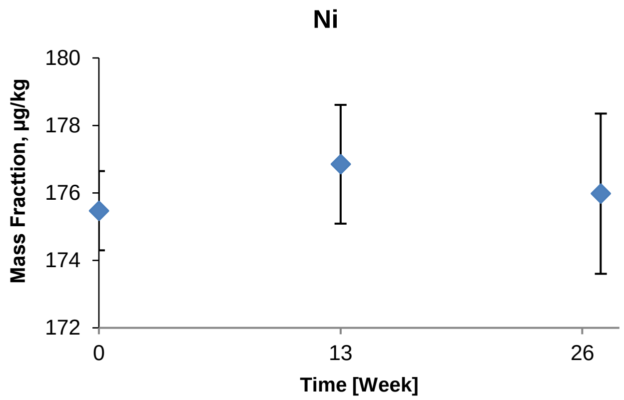


Figure 47. Graphs of long term stability, Ni

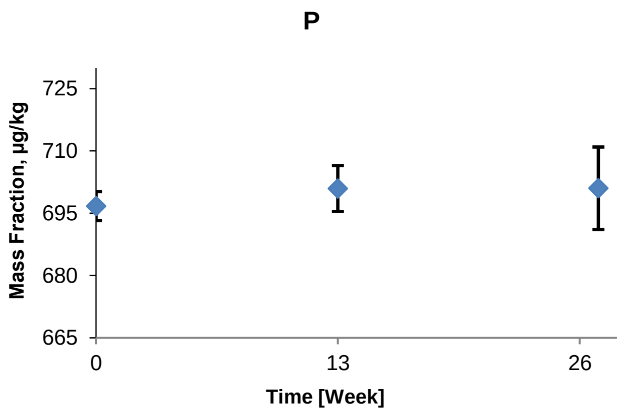


Figure 48. Graphs of long term stability, P

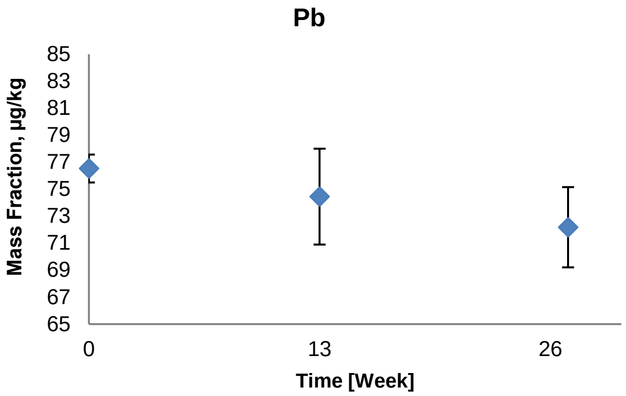


Figure 49. Graphs of long term stability, Pb

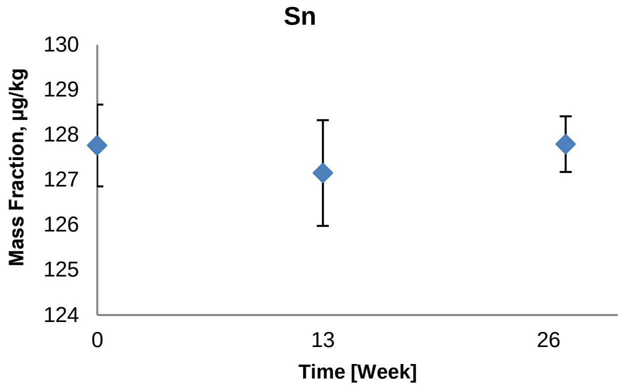


Figure 50. Graphs of long term stability, Sb

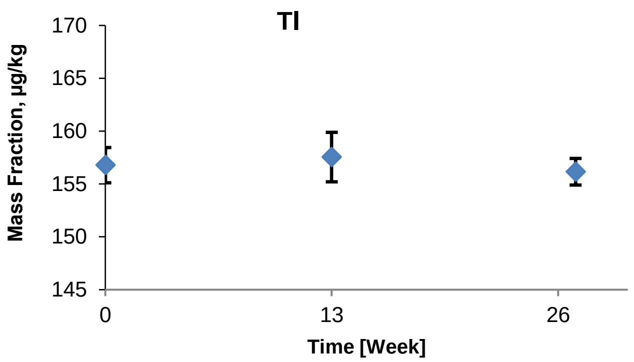


Figure 51. Graphs of long term stability, Tl

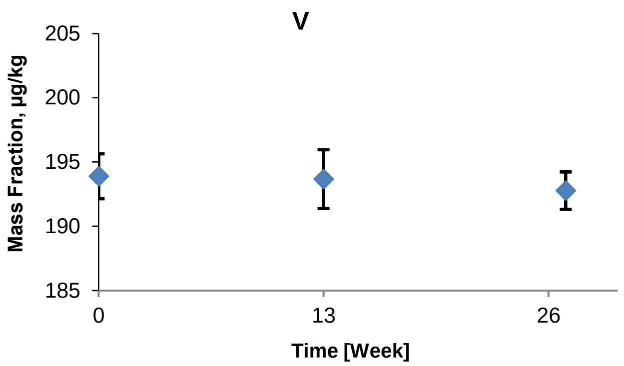


Figure 52. Graphs of long term stability, V

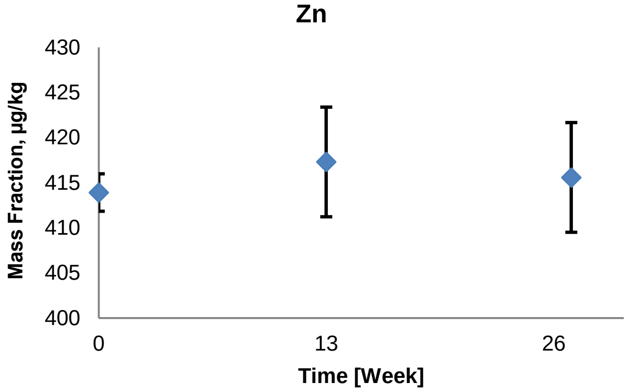


Figure 53. Graphs of long term stability, Zn

Annex 5. Data of Characterization

Table E 10. UME CRM 1204 Characterization Data, Al

Technique	Unit No/Independent Result	Mass Fraction, µg/kg
HR-ICP-MS	*54/1*	340.4
	54/2	343.6
	334/1	343.5
	334/2	347.2
	407/1	341.4
	407/2	344.2
	Average mass fraction	343.4
	Standard uncertainty (k=1)	2.8

Technique	Unit No/Independent Result	Mass Fraction, µg/kg
GF-AAS	*68/1*	366
	68/2	353
	278/1	353
	278/2	356
	407/1	340
	407/2	355
	Average mass fraction	354
	Standard uncertainty (k=1)	9

Table E 11. UME CRM 1204 Characterization Data, As

Technique	Unit No/Independent Result	Mass Fraction, µg/kg
HR-ICP-MS	*54/1*	64.7
	54/2	64.1
	334/1	64.7
	334/2	64.8
	407/1	64.0
	407/2	65.1
	Average mass fraction	64.6
	Standard uncertainty (k=1)	0.8

Technique	Unit No/Independent Result	Mass Fraction, µg/kg
GF-AAS	*68/1*	60.5
	68/2	60.5
	278/1	62.6
	278/2	61.0
	407/1	65.5
	407/2	60.6
	Average mass fraction	61.8
	Standard uncertainty (k=1)	1.5

Table E 12. UME CRM 1204 Characterization Data, B

Technique	Unit No/Independent Result	Mass Fraction, µg/kg
HR-ICP-MS	*54-1*	1394
	54-2	1373
	334-1	1342
	334-2	1342
	407-1	1338
	407-2	1334
	Average mass fraction	1354
	Standard uncertainty (k=1)	15

Technique	Unit No/Independent Result	Mass Fraction, µg/kg
ID-ICP-MS	*54/1*	1445
	54/2	1421
	54/3	1416
	334/1	1422
	334/2	1425
	334/3	1417
	521/1	1420
	521/2	1420
	521/3	1413
	Average mass fraction	1422
	Standard uncertainty (k=1)	5

Table E 13. UME CRM 1204 Characterization Data, Cd

Technique	Unit No/Independent Result	Mass Fraction, µg/kg
ID-ICP-MS	*54/1*	103.5
	54/2	104.4
	54/3	104.3
	239/1	104.3
	239/2	105.2
	239/3	105.3
	464/1	103.0
	464/2	105.5
	464/3	105.1
	Average mass fraction	104.5
	Standard uncertainty (k=1)	1.0

Table E 14. UME CRM 1204 Characterization Data, Co

Technique	Unit No/Independent Result	Mass Fraction, µg/kg
HR-ICP-MS	*54/1*	425
	54/2	424
	334/1	421
	334/2	421
	407/1	422
	407/2	417
	Average mass fraction	422
	Standard uncertainty (k=1)	4

Technique	Unit No/Independent Result	Mass Fraction, µg/kg
GF-AAS	*68/1*	410
	68/2	408
	278/1	414
	278/2	428
	407/1	415
	407/2	423
	Average mass fraction	416
	Standard uncertainty (k=1)	5

Table E 15. UME CRM 1204 Characterization Data, Cr

Technique	Unit No/Independent Result	Mass Fraction, µg/kg
ID-ICP-MS	*54-1*	241.1
	54-2	242.9
	54-3	245.0
	239-1	240.9
	239-2	243.7
	239-3	244.2
	464-1	244.0
	464-2	244.4
	464-3	243.4
	Average mass fraction	243.3
	Standard uncertainty (k=1)	1.5

Table E 16. UME CRM 1204 Characterization Data, Cu

Technique	Unit No/Independent Result	Mass Fraction, µg/kg
ID-ICP-MS	*54-1*	331.4
	54-2	333.9
	54-3	333.7
	239-1	334.5
	239-2	332.5
	239-3	334.0
	464-1	333.6
	464-2	334.0
	464-3	334.8
	Average mass fraction	333.6
	Standard uncertainty (k=1)	1.1

Table E 17. UME CRM 1204 Characterization Data, Fe

Technique	Unit No/Independent Result	Mass Fraction, µg/kg
ID-ICP-MS	*54-1*	1962
	54-2	1938
	54-3	1932
	239-1	1960
	239-2	1933
	239-3	1937
	464-1	1957
	464-2	1949
	464-3	1921
	Average mass fraction	1943
	Standard uncertainty (k=1)	10

Table E 18. UME CRM 1204 Characterization Data, Hg

Technique	Unit No/Independent Result	Mass Fraction, µg/kg
Reverse ID-ICP-MS	*54-1*	47.6
	54-2	51.4
	54-3	50.7
	239-1	48.7
	239-2	51.1
	239-3	50.6
	464-1	47.3
	464-2	50.7
	464-3	50.5
	Average mass fraction	49.9
	Standard uncertainty (k=1)	0.7

Table E 19. UME CRM 1204 Characterization Data, Mn

Technique	**Unit No/Independent Result**	**Mass Fraction, µg/kg**
HR-ICP-MS	*54-1*	376
	54-2	375
	334-1	374
	334-2	374
	407-1	374
	407-2	371
	Average mass fraction	374
	Standard uncertainty (k=1)	3

Technique	**Unit No/Independent Result**	**Mass Fraction, µg/kg**
GF-AAS	*68-1*	369
	68-2	365
	278-1	370
	278-2	366
	407-1	383
	407-2	363
	Average mass fraction	369
	Standard uncertainty (k=1)	8

Table E 20. UME CRM 1204 Characterization Data, Mo

Technique	**Unit No/Independent Result**	**Mass Fraction, µg/kg**
HR-ICP-MS	*54-1*	98.0
	54-2	96.5
	334-1	95.0
	334-2	94.4
	407-1	94.6
	407-2	94.1
	Average mass fraction	95.5
	Standard uncertainty (k=1)	1.1

Table E 21. UME CRM 1204 Characterization Data. Ni

Technique	**Unit No/Independent Result**	**Mass Fraction, µg/kg**
HR-ICP-MS	*54-1*	173.5
	54-2	175.2
	334-1	174.5
	334-2	175.5
	407-1	173.9
	407-2	174.4
	Average mass fraction	174.5
	Standard uncertainty (k=1)	1.6

Technique	**Unit No/Independent Result**	**Mass Fraction, µg/kg**
GF-AAS	*68-1*	170.3
	68-2	177.9
	278-1	171.8
	278-2	170.0
	407-1	173.9
	407-2	164.8
	Average mass fraction	171.4
	Standard uncertainty (k=1)	2.4

Table E 22. UME CRM 1204 Characterization Data, P

Technique	**Unit No/Independent Result**	**Mass Fraction, µg/kg**
HR-ICP-MS	*54-1*	692
	54-2	697
	334-1	699
	334-2	702
	407-1	695
	407-2	701
	Average mass fraction	698
	Standard uncertainty (k=1)	6

Table E 23. UME CRM 1204 Characterization Data, Pb

Technique	**Unit No/Independent Result**	**Mass Fraction, µg/kg**
HR-ICP-MS	*54-1*	81.5
	54-2	94.1
	334-1	81.2
	334-2	88.7
	407-1	78.0
	407-2	80.9
	Average mass fraction	84.1
	Standard uncertainty (k=1)	1.0

Technique	**Unit No/Independent Result**	**Mass Fraction. µg/kg**
Ters ID-ICP-MS	*54-1*	76.6
	54-2	61.0
	54-3	87.4
	239-1	83.4
	239-2	83.2
	239-3	71.8
	464-1	79.0
	464-2	78.4
	464-3	76.0
	Average mass fraction	77.4
	Standard uncertainty (k=1)	0.5

Table E 24. UME CRM 1204 Characterization Data, Sb

Technique	**Unit No/Independent Result**	**Mass Fraction, µg/kg**
HR-ICP-MS	*54-1*	129.6
	54-2	130.0
	334-1	129.5
	334-2	130.0
	407-1	129.4
	407-2	130.3
	Average mass fraction	129.8
	Standard uncertainty (k=1)	0.8

Technique	**Unit No/Independent Result**	**Mass Fraction, µg/kg**
GF-AAS	*68-1*	134.2
	68-2	131.2
	278-1	139.5
	278-2	133.4
	407-1	137.4
	407-2	133.3
	Average Mass Fraction	134.8
	Standard uncertainty (k=1)	3.3

Table E 25. UME CRM 1204 Characterization Data, Tl

Technique	Unit No/Independent Result	Mass Fraction, µg/kg
HR-ICP-MS	*54-1*	155.4
	54-2	156.7
	334-1	157.7
	334-2	157.5
	407-1	156.9
	407-2	158.7
	Average mass fraction	157.2
	Standard uncertainty (k=1)	2.2

Table E 26. UME CRM 1204 Characterization Data, V

Technique	Unit No/Independent Result	Mass Fraction, µg/kg
HR-ICP-MS	*54-1*	198.6
	54-2	196.9
	334-1	197.0
	334-2	196.7
	407-1	198.2
	407-2	196.4
	Average mass fraction	197.3
	Standard uncertainty (k=1)	1.7

Technique	Unit No/Independent Result	Mass Fraction, µg/kg
GF-AAS	*68-1*	195
	68-2	201
	278-1	196
	278-2	194
	407-1	193
	407-2	195
	Average mass fraction	196
	Standard uncertainty (k=1)	3.7

Table E 27. UME CRM 1204 Characterization Data, Zn

Technique	Unit No/Independent Result	Mass Fraction, µg/kg
HR-ICP-MS	*54-1*	412.1
	54-2	403.7
	334-1	409.4
	334-2	406.6
	407-1	409.6
	407-2	410.1
	Average mass fraction	408.6
	Standard uncertainty (k=1)	2.7

Technique	Unit No/Independent Result	Mass Fraction, µg/kg
ID-ICP-MS	*54-1*	401.5
	54-2	404.0
	54-3	393.9
	239-1	394.7
	239-2	391.0
	239-3	407.1
	464-1	392.0
	464-2	398.8
	464-3	396.8
	Average mass fraction	397.7
	Standard uncertainty (k=1)	3.2