TÜBİTAK
ULUSAL METROLOJİ ENSTİTÜSÜ

Certification Report

Elements in Spring Water
UME CRM 1201

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ABBREVIATIONS

ANOVA	analysis of variance
α	significance level
CRM	certified reference material
ICP-SFMS	inductively coupled plasma sector field mass spectrometry
ISO	International Organization for Standardization
$MS_{between}$	mean square between-bottle from ANOVA
MS_{within}	mean square within-bottle from ANOVA
n	number of replicates per bottle
PTFE	polytetrafluoroethylene
QC	quality control
RSD	relative standard deviation
s	standard deviation
s_{bb}	between-bottle standard deviation
SI	International System of Units
ST	single Grubbs' test
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_{rect}	standard uncertainty related to possible between-bottle heterogeneity modelled as rectangular distribution
u_{char}	standard uncertainty related to characterisation
u_{lts}	standard uncertainty related to long term stability
$\bar{y}$	average of all results of the homogeneity study

The subscript "rel" is added when a variable is expressed in relative terms (e.g. as percent)

ABSTRACT

Various maximum values was assigned in Water Intended for Human Consumption which was published in Official Journal dated 17 February 2005[1] and standardized as TS266/2005[2] taking Drinking water related 98/83/EC directive[3], Standard Methods for the Examination of Water and Waste Water, 1985, Guidelines for Drinking Water Quality Who World Health Organization Geneva 1993[4] into consideration. These criteria include poisonous metals as well as nutritional minerals. In order to control and improve measurement quality, the properties and native character of the spring water originated from and processed in Turkey made the production of a certified reference material inevitable. In this project, elemental analysis of spring water reference material in compliance with ISO/IEC 17025:2005 and ISO Guide 34:2009 has been performed. This reference material is intended to be a common reference point for method development and validation for analysis of a series of 21 elements in spring water.

INTRODUCTION

Spring water is one of the vital sources of life. It is the main supply of drinking water therefore it is inevitable to provide it to the citizens in a safe way.

The legislative framework for its effective protection is established by Water Intended for Human Consumption which was published in Official Journal dated 17 February 2005[1] and standardized as TS266/2005[2].

The matrix certified reference materials available in the market are starting points in the validation of analytical methods, ensuring accuracy and traceability of the measurement results.

UMECRM1201, the production of which was carried out by TÜBİTAK UME and described in this report, is intended to be used as a quality assurance and quality control tool especially by the laboratories involved in the mandatory monitoring prescribed by relevant environment legislations.

The parameters aimed to be certified in UMECRM1201 are the followings: Mass fractions of Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Sb, Sn, Sr, Pb, and Zn. The values are stated as mass concentrations in micrograms or milligrams per kilogram (µg/kg or mg/kg). The target concentration levels for all elements were decided to reflect laboratories' needs and unavailability of other certified reference materials at certain levels in the market.

PARTICIPANTS

Study	Laboratory
Sampling and processing	TÜBİTAK UME, Ulusal Metroloji Enstitüsü, Gebze, Kocaeli, TR (accreditation to ISO Guide 34 is ongoing)
Homogeneity study	TÜBİTAK UME, Ulusal Metroloji Enstitüsü, Gebze, Kocaeli, TR (accreditation to ISO Guide 34 is ongoing)
Stability studies	TÜBİTAK UME, Ulusal Metroloji Enstitüsü, Gebze, Kocaeli, TR (accreditation to ISO Guide 34 is ongoing)
Project management and data evaluation	TÜBİTAK UME, Ulusal Metroloji Enstitüsü, Gebze, Kocaeli, TR (accreditation to ISO Guide 34 is ongoing)
Characterisation study **(in alphabetical order)**	➢ AEM Çevre Laboratuar Analiz A.Ş. Bağlarbaşı Mah. Feyzullah Cad. No:111 Maltepe / İstanbul, TR (accredited to TS EN ISO/IEC 17025 for measurements of metals in groundwater, drinking water TÜRKAK Accreditation No. AB-0183-T). ➢ ALS Environmental, Na Harfě 336/9, 190 00, Praha 9, Czech Republic, CZ (accredited to ISO/IEC 17025 for chemical anaysis of water, CAI Accreditation No. 1163). ➢ ALS Scandinavia AB, Aurorum 10, SE-977 75 Luleå, Sweden, SE (accredited to ISO/IEC 17025 for measurements of metals in freshwater, SWEDAC Accreditation No. 10-3822-51.2030).

Study	Laboratory
Characterisation study (cont.)	➢ AST Çevre Ölçüm ve Laboratuvar Hizmetleri, Yeniyol Sok. Etap İş Merkezi B Blok D:7-8 K:2 Acıbadem/Kadıköy/İstanbul TR (accredited to TS EN ISO/IEC 17025 for measurements of metals in water, surface water, waste water, TÜRKAK Accreditation No. AB-0551-T). ➢ Çevre Endüstriyel Analiz Laboratuvar Hizmetleri Tic. A.Ş., Merkez Mah. Tatlıpınar Sok. Mart Plaza No:13 K:1-2 Kağıthane/ İstanbul TR (accredited to TS EN ISO/IEC 17025 for measurements of metals in water, waste water, eluate, TÜRKAK Accreditation No. AB-0363-T). ➢ TÜBİTAK BUTAL, Gaziakdemir Mah. Merinos Cad. No:11 Osmangazi 16190 Bursa TR (accredited to TS EN ISO/IEC 17025 for measurements of metals in water and waste water, TÜRKAK Accreditation No. AB-0494-T). ➢ TÜBİTAK UME, Ulusal Metroloji Enstitüsü, Gebze, Kocaeli, TR (accreditation to ISO Guide 34 is ongoing) ➢ UBA Wien, Spittelauer Lände 5 1090 Vienna/Austria AT (accredited to EN ISO/IEC 17025 for examination of water for chemical substance, BMWA Accreditation No. BMWA-92.714/0518-I/12/2007). ➢ VASYD, Bulltofta vattenverk, Vattenlaboratoriet, Rännemästaregatan 3 Malmö, SE-21223 SE (accredited to ISO/IEC 17025 for chemical analysis of freshwater, SWEDAC No. 10-3084-51.2011).

MATERIAL PROCESSING

The source of the sample chosen as the candidate reference material was a spring water bottled at premises located in Derince, Kocaeli, Turkey. The place was selected as a well known spring water source with respect to water composition and drinking quality as well as ease of sampling since it is close to TÜBİTAK UME.

The sampling was carried out by TÜBİTAK UME team with the logistical support and under the supervision of representatives of the bottling company.

Eight pre-cleaned polyethylene drums with a volume of 25 L was filled from a plastic tap directly coming from the source after being filtered. Immediately after the drums were filled, its content were acidified with 65% nitric acid (Merck EMSURE® ISO 1.00456.2500 Lot No:K42525956 128) in order to bring acid concentration to 2% (w/v). Then all the drums were transferred to TÜBİTAK UME laboratories and were stored at 4 °C in the dark for a month until further processing.

From the 25 L containers, the bulk water was pumped via an in-line filter (AcroPack™ 1000, Supor® Membrane 0.8/0.2 µm PN 12992, Pall Corp, Port Washington, NY, US, offering also bacterial retention) to another 114 L pre-cleaned drum. The drum, the PTFE/PVC tubes and air acid pump (PVDF) used for homogenisation were washed with an in-house prepared solution ~20% (v/v) of concentrated HNO_3 (Merck EMSURE ISO) and subsequently extensively rinsed with de-ionised water (Milli-Q, 18.2 $M\Omega \cdot cm^{-1}$) prior to usage.

The tubes and filter were also "conditioned" with the groundwater for few minutes, before starting the collection into the second drum intended to be used for spiking and homogenisation of the bulk water.

The Nalgene® HDPE bottles of 125 mL were checked for blank levels regarding the 21 elements to be certified. The bottles were left in contact with an in-house prepared solution of ~15 % (v/v) concentrated HNO_3 (Merck EMSURE® ISO) for 72 h. The leaching solutions were analysed by HR-ICP-MS (Thermo Finnigan, Element 2, Bremen Germany). The results showed that the levels of trace elements in the leaching solutions are not significant to lead any contamination to CRM at target levels. The bottles were rinsed several times with ultrapure water (Milli-Q, 18.2 $M\Omega \cdot cm^{-1}$), dried overnight in a laminar flow cabinet at room temperature and kept in double bag in the cabinets until filling with the material.

A preliminary characterisation of the water, regarding the parameters to be certified, was performed to find out whether spiking was necessary to obtain the target levels of the analytes (see Table 1).

Following these preliminary analyses, spiking with High Purity® and NIST single element calibration standards (solutions in HNO_3) was performed to increase the concentrations of some elements as shown in Table 1.

Table 1. Natural and target concentration levels of spring water

Element	Natural Levels (µg/kg)	Target Concentration (µg/kg)
Al	8.4	100
As	0.2	7
B	3.5	500
Ba	327	DS*
Ca	3262	DS*
Cd	0.05	4
Co	0.1	10
Cr	0.09	35
Cu	9	80
Fe	1.9	40
K	398	DS*
Mg	905	DS*
Mn	3.1	15
Na	3301	DS*
Ni	1.1	18
P	6.1	100
Pb	0.4	15
Sb	0.008	5
Sn	0.02	1.5
Sr	20	DS*
Zn	13	80

*NL: Natural Levels

The others were not spiked and kept at natural levels. These target levels were decided on the basis of the regulations and Turkish Standards. The spiking was performed after the 0.8/0.2 µm filtration and was followed by an homogenisation step with the PVDF air/acid pump for about 8 hours.

Quantities of at least 100 mL of water were subsequently filled into 125 mL HDPE bottles (Nalgene®). Subsequently, temporary labelling of the 967 units took place.

The water in the closed bottles of candidate certified reference material UMECRM1201 was sterilised by γ-irradiation with a ^{60}Co source at a minimum dose of 25 kGy. The irradiation caused the expected change in colour of the medium transparent HDPE bottles to pale yellow. After this step, the bottles were stored at 4 °C in the dark.

HOMOGENEITY

With the aim of checking the homogeneity of the material regarding the parameters to be certified, 10 units (another 10 are kept for safety) were selected using stratified sampling scheme, taking care that the complete batch was covered. The number of units is based on the produced batch size (approximately corresponding to the cubic root of the total number of units). The batch is divided into the same number of groups and one unit is randomly picked from each group. 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 permit distinction between possible trends in the analytical sequence and in the filling order. Quality control (QC) samples and blank samples were analysed within the sequence. All measurements were performed by HR-ICP-MS (Element 2, Thermo Finnigan, Bremen, Germany).

Total of 30 concentration values for each parameter obtained by the analysis of samples were evaluated by one-way analysis of variance (ANOVA). The unimodal distribution of data is an important prerequisite in order to apply the ANOVA statistical evaluation; therefore the distributions of sample averages as well as individual results were checked both for normality using normal probability plots and for unimodality using histograms. For all elements, the individual results and bottle averages showed an approximately normal and unimodal distribution, with the exception of the individual values for B, Ba, P, Mn and Fe for which bimodal distributions were observed. This minor deviation from unimodality does not significantly affect the estimation of the between-unit standard deviation.

Data were checked and statistically evaluated for the presence of any trend and/or outlier. No trends were observed either in filling or in analytical sequence. One outlying result was found for each of zinc (Grubbs' single test at α = 0.05), potassium (Grubbs' single test at α = 0.05), iron (Grubbs' single test at α = 0.05) and for cobalt (Grubbs' single test at α = 0.05). Since no technical reasons were identified for the outlying results, all data were retained for statistical analysis.

For B only, two outlying sample average was found, (unit numbers 77 and 259, Grubbs' single test at α = 0.05), see Annex 1) caused by a single outlying value which might be resulted from a problem during measurements.

In the case of presence of trends and of outlier averages, however, the evaluation by ANOVA might not be the most appropriate one and therefore an alternative approach for the estimation of the heterogeneity was followed (see Equation 4 below).

The ANOVA allowed the calculation of the within- (s_{wb}) and between-unit homogeneity (s_{bb}), estimated as standard deviations, according to the following equations:

$$s_{wb} = \sqrt{MS_{within}} \tag{1}$$

MS_{within} : Mean squares within-bottle

s_{wb} is equivalent to the s of the method, provided that subsamples are representative for the whole bottle.

$$s_{bb} = \sqrt{\frac{MS_{between} - MS_{within}}{n}} \tag{2}$$

$MS_{between}$: Mean squares between-bottle

n : Number of replicates per bottle

When $MS_{between}$ is smaller than MS_{within}, s_{bb} can not be calculated. Instead, u^*_{bb}, the heterogeneity that can be hidden by the method repeatability, is calculated, according to the following expression[5]:

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

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

For B, for which an outlying bottle mean was detected (see above), an alternative estimate of heterogeneity was calculated. Between-bottle heterogeneity was modelled as rectangular distribution limited by the outlying average. The standard uncertainty using this outlier (u_{rect}) was then estimated as;

$$u_{rect} = \frac{\left| \text{largest outlier - } \overline{y} \right|}{\sqrt{3}} \tag{4}$$

where $\overline{y}$ is the average of all results.

For the parameters for which ANOVA was applied, the larger value of s_{bb} or u^*_{bb} is taken as uncertainty contribution for homogeneity, u_{bb}.

u_{rect} will be taken as u_{bb} for B (Table 2).

Table 2. Results of the homogeneity study

Analyte	Mean Value	$s_{wb,rel}$ [%]	$s_{bb,rel}$ [%]	$u^*_{bb,rel}$ [%]	$u_{rect,rel}$ [%]	$u_{bb,rel}$ [%]
Al	103.2 µg/kg	2.13	$MS_{\text{between}} < MS_{\text{within}}$	0.69	-	0.69
As	6.5 µg/kg	1.12	0.50	0.36	-	0.50
B	0.48 mg/kg	0.83	-	-	0.88	0.88
Ba	0.32 mg/kg	0.98	0.67	0.32	-	0.67
Ca	3.9 mg/kg	1.63	0.89	0.53	-	0.89
Cd	4.0 µg/kg	1.87	$MS_{\text{between}} < MS_{\text{within}}$	0.61	-	0.61
Co	9.2 µg/kg	2.40	$MS_{\text{between}} < MS_{\text{within}}$	0.78	-	0.78
Cr	32.9 µg/kg	2.21	$MS_{\text{between}} < MS_{\text{within}}$	0.72	-	0.72
Cu	83.5 µg/kg	1.71	0.62	0.56	-	0.62
Fe	43.8 µg/kg	1.83	$MS_{\text{between}} < MS_{\text{within}}$	0.59	-	0.59
K	0.43 mg/kg	1.31	$MS_{\text{between}} < MS_{\text{within}}$	0.42	-	0.42
Mg	0.86 mg/kg	1.17	1.11	0.38	-	1.11
Mn	14.5 µg/kg	2.56	$MS_{\text{between}} < MS_{\text{within}}$	0.83	-	0.83
Na	3.1 mg/kg	0.81	0.15	0.26	-	0.26
Ni	16.0 µg/kg	2.27	$MS_{\text{between}} < MS_{\text{within}}$	0.74	-	0.74
P	93.4 µg/kg	2.33	$MS_{\text{between}} < MS_{\text{within}}$	0.76	-	0.76
Pb	14.7 µg/kg	2.25	$MS_{\text{between}} < MS_{\text{within}}$	0.73	-	0.73
Sb	4.7 µg/kg	1.12	$MS_{\text{between}} < MS_{\text{within}}$	0.36	-	0.36
Sn	1.5 µg/kg	1.24	$MS_{\text{between}} < MS_{\text{within}}$	0.40	-	0.40
Sr	20.7 µg/kg	2.32	$MS_{\text{between}} < MS_{\text{within}}$	0.75	-	0.75
Zn	100.3 µg/kg	3.06	$MS_{\text{between}} < MS_{\text{within}}$	0.99	-	0.99

The occurrence of $MS_{between} < MS_{within}$ (for 13 analytes) demonstrates that material heterogeneity is smaller than that can be detected by the analytical methodology used. Even with retention of outliers, the between-unit variation for all parameters is generally low (maximum 1.11%). Target maximum uncertainty for homogeneity written at the beginning of project (2%) was achieved.

The plotted data used for the evaluation of homogeneity can be found in Annex 1.

STABILITY

Stability studies are performed to simulate transportation conditions (short term stability) and storage conditions (long term stability).

14 bottles were kept for short term stability tests and 8 bottles were kept for long term stability tests where these bottles were selected in a random stratified manner.

For short term stability study, two different test temperatures was selected as +18 °C and +60 °C, with time periods of 1, 2 and 4 weeks. For each test period, 2 bottles were placed at +18 °C (total number of bottles is 6) and 2 bottles were placed at +60 °C (total number of bottles is 6). For the reference point, 2 extra reference temperature bottles were put aside at 4 °C. Right after each period of test time, the 2 bottles were transferred to reference temperature +4 °C. At the end of duration, the analysis of all samples kept at different temperatures for different period of time was performed isochronously.

For long term stability, 8 bottles were kept at room temperature (21 ± 4) °C for 0, 16, 31 and 35 weeks where 35 weeks time was the ultimate time period whilst this report is being written. Right after the storage time at room temperature, they were put at +4 °C stability cabinets. Again all the measurements were performed isochronously.

Short Term Stability Results:

The results obtained from isochronous measurements were first grouped according to the time period and then evaluated for each time point. These evaluations were carried out for both temperatures, separately.

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

Some outliers for Ca, Cd, Na and Zn were identified in the statistical evaluation (Grubbs' test) of the data; nevertheless, as there was no technical reason to exclude them from evaluation, they remained in the data set. The data points were plotted against storage time at the test temperature and the regression line was calculated. In all cases the slope of the regression line was not found to be significantly different from zero. The data evaluation results for the short-term stability at +18 °C and +60 °C are summarised in Table 3.

Table 3. Results of short term stability tests

Analyte	Slope significantly different from zero at test temperature 18 °C at a level of 95% and 99% confidence	Outliers*	Slope significantly different from zero at test temperature 60 °C at a level of 95% and 99% confidence	Outliers*
Al	no	-	no	-
As	no	-	no	-
B	no	-	no	-
Ba	no	-	no	-
Ca	no	One (SGT, 95%)	no	-
Cd	no	-	no	One (SGT, 95%)
Co	no	-	no	-
Cr	no	-	no	-
Cu	no	-	no	-
Fe	no	-	no	-
K	no	-	no	-
Mg	no	-	no	-
Mn	no	-	no	-
Na	no	One (SGT, 95%)	no	-
Ni	no	-	no	-
P	no	-	no	-
Pb	no	-	no	-
Sb	no	-	no	-
Sn	no	-	no	-
Sr	no	-	no	-
Zn	no	-	no	One (SGT, 95% & 99%)

*SGT: Single Grubbs' Test

The material is stable at 18 °C and 60 °C for up to 4 weeks. Thus, the samples can be safely dispatched under conditions where the temperatures do not exceed 60 °C for up to 4 weeks, i.e. at ambient temperature.

Long Term Stability Results:

Shelf life of the CRM has been determined through long term stability measurements. For the measurements, two bottles for each of the weeks of 0, 16, 31 and 35 has been stored at 21 °C and transferred to reference temperature after each period of time to be measured isochronously afterwards. Two bottles, designated as reference bottles, of the week 0 was stored at 4 °C.

The data for each time point has been calculated by 3 replicate measurements for each of two bottles. Thus, the average of 6 measurements for each time point is given in Annex 3. The error bars on each time point is calculated as the standard deviation of 6 measurement results.

The outlier data for elements of As, Cd, K, Na, Pb, Sb and Zn was detected by Grubbs' test. However, except one Zn measurements, no data were rejected since there is no clear indication of reason observed. For the week of 31, one of the replicates for Zn of the bottle 197 was obviously suffered from contamination as it was clearly standing out from the other two replicates of the same bottle. Thus, this measurement result was removed from the data set.

The graphs were plotted against time and the regression line calculated. The long term stability uncertainty, u_{lts}, of the material is then calculated for the required shelf life^6 as:

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

where

RSD : the relative standard deviation of all results of the stability study

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

The uncertainty contribution u_{lts} was established for 60 months (t) at 21 °C. This uncertainty was one of the three parameters of the overall uncertainty budget of the certified values. The results are given in Table 4. The graphs for long term stability are given in Annex 3.

Table 4. Results of the long-term stability tests of 60 months

Analyte	Slope significantly different from zero at 21 °C*	u_{lts} [%] for shelf-life of 60 months at 21 °C
Al	No	0.7
As	No	2.3
B	No	0.7
Ba	No	0.5
Ca	No	0.7
Cd	No	0.7
Co	No	0.7
Cr	No	0.7
Cu	No	0.6
Fe	No	0.7
K	No	1.6
Mg	No	0.6
Mn	No	0.6
Na	No	0.9
Ni	No	0.8
P	No	0.8
Pb	No	0.7
Sb	No	1.0
Sn	No	2.5
Sr	No	0.5
Zn	No	0.7

*Data are evaluated at confidence level of 95 %

Based on the results obtained, the storage temperature for the material was set to 21 °C. In addition, to ensure stability beyond the initial shelf life, it will be re-evaluated in certain periods, based on the results of regular post-certification monitoring.

CHARACTERISATION

According to ISO Guide 34, the characterization and the value assignment can be carried out in different ways. In this project, the characterisation of the material was carried out by an interlaboratory comparison exercise. The selection criteria for the selection of participating laboratories were their expertise in the analysis of water samples, accreditation for the same or similar samples and successful participation in proficiency testing schemes in the relevant field and/or previous characterisation exercises, presence of laboratory quality management system. Both international and national laboratories were contacted for this study. All laboratories have accreditation according to ISO/IEC 17025 for water analysis at the time of contact. The detailed information about the laboratories and their relevant accreditation information is given in participants section. The laboratories were asked and to use validated methods. The laboratories have confirmed the concentration level of the elements to be analysed and the methods they have chosen.

Each laboratory were sent two bottles of samples which was selected from the whole set of samples to represent the whole set. The samples were selected randomly from the set of samples by the random stratified sampling software TRaNS that was developed by TÜBİTAK UME Information Technologies Unit assigned for the characterization study. The laboratories were asked to treat each bottle as two separate samples. Each laboratory was asked to report 3 independent measurement results which were obtained on at least two different days. Therefore, each laboratory reported 6 independent measurement results for two sample bottle, together their associated measurement uncertainty values and the approach used for the estimation of measurement uncertainty. In the reports the details of the reference materials used in the calibration were also requested from the laboratories in order to assure the traceability of reported results.

The laboratories were also asked to perform an analysis of a QC sample in order to assess their results. The QC sample having the similar matrix and concentration level with the samples was prepared and characterised in TÜBİTAK UME laboratories. In addition to the samples, laboratories were asked to report 2 independent results for the QC sample which was analysed using the same method.

Another precaution for preventing biased measurement result is the selection of laboratories applying different methodologies but at least two laboratories applying the same methodology. Some of the laboratories were provided measurement results using more than one methodology. If the laboratory provided results using more than one method, both results were taken into account during the assignment of certified value. A list of laboratories with their lab codes and their corresponding methodology used in the assignment is summarized in Table 5.

The uncertainty arising from the characterization study, u_{char} was also taken into account for the calculation of uncertainty on the property value. The characterization uncertainty, u_{char}, which is equal to the standard deviation of the mean of the individual laboratories, is calculated according to the following equation:

$$u_{char}=\frac{SD}{\sqrt{n}}$$

where,

u_{char} : the uncertainty arising from characterisation
SD : the standard deviation of the mean of the results from participant laboratories
n : the number of laboratories participated to the interlaboratory study

Table 5: Techniques used by laboratories

	LAB 1	LAB 2	LAB 3	LAB 4	LAB 5	LAB 6	LAB 7	LAB 8	LAB 9	LAB 10	LAB 11	LAB 12	LAB 13	LAB 14	LAB 15	LAB 16
Al	ICP-MS	AES	ICP-OES	ICP-MS	ICP-OES	-	ICP-MS	ICP-OES	-	-	-	-	ICP-MS	ICP-MS	ICP-OES	ICP-MS
As	ICP-MS	-	-	ICP-MS	-	ICP-MS	ICP-MS	-	GFAAS	-	GFAAS	-	-	ICP-MS	-	ICP-MS
B	ICP-MS	AES	ICP-OES	-	ICP-OES	-	-	ICP-OES	-	ICP-OES	-	-	ICP-MS	-	ICP-OES	ICP-MS
Ba	ICP-MS	AES	ICP-OES	ICP-MS	ICP-OES	-	ICP-MS	ICP-OES	-	ICP-OES	GFAAS	-	ICP-MS	-	-	ICP-MS
Ca	ICP-MS	-	ICP-OES	-	ICP-OES	-	ICP-MS	ICP-OES	-	ICP-OES	-	-	ICP-MS	-	ICP-OES	ICP-MS
Cd	ICP-MS	-	ICP-OES	ICP-MS	-	ICP-MS	ICP-MS	-	GFAAS	ICP-OES	-	-	ICP-MS	ICP-MS	-	ICP-MS
Co	ICP-MS	AES	ICP-OES	ICP-MS	-	-	ICP-MS	-	-	ICP-OES	-	-	ICP-MS	ICP-MS	-	ICP-MS
Cr	ICP-MS	-	ICP-OES	ICP-MS	-	ICP-MS	ICP-MS	ICP-OES	-	ICP-OES	GFAAS	-	ICP-MS	ICP-MS	-	ICP-MS
Cu	ICP-MS	AES	ICP-OES	ICP-MS	ICP-OES	-	ICP-MS	ICP-OES	GFAAS	ICP-OES	-	-	ICP-MS	ICP-MS	ICP-OES	ICP-MS
Fe	ICP-MS	AES	ICP-OES	-	-	-	ICP-MS	ICP-OES	-	-	-	-	ICP-MS	ICP-MS	ICP-OES	ICP-MS
K	ICP-MS	AES	ICP-OES	-	ICP-OES	-	ICP-MS	ICP-OES	-	ICP-OES	-	-	ICP-MS	-	ICP-OES	ICP-MS
Mg	ICP-MS	AES	ICP-OES	ICP-MS	ICP-OES	-	ICP-MS	ICP-OES	-	ICP-OES	-	FAAS	ICP-MS	-	ICP-OES	ICP-MS
Mn	ICP-MS	-	ICP-OES	ICP-MS	-	ICP-MS	ICP-MS	-	-	ICP-OES	-	-	ICP-MS	ICP-MS	-	ICP-MS
Na	ICP-MS	AES	ICP-OES	-	ICP-OES	-	ICP-MS	ICP-OES	-	ICP-OES	-	FAAS	ICP-MS	-	ICP-OES	ICP-MS
Ni	ICP-MS	AES	ICP-OES	ICP-MS	-	ICP-MS	ICP-MS	-	GFAAS	ICP-OES	-	-	ICP-MS	ICP-MS	ICP-OES	ICP-MS
P	ICP-MS	AES	ICP-OES	-	-	-	-	ICP-OES	-	ICP-OES	-	-	ICP-MS	-	-	ICP-MS
Pb	ICP-MS	-	ICP-OES	ICP-MS	-	ICP-MS	ICP-MS	-	GFAAS	-	-	-	ICP-MS	ICP-MS	-	ICP-MS
Sb	ICP-MS	-	-	ICP-MS	-	ICP-MS	ICP-MS	-	-	-	-	-	ICP-MS	ICP-MS	-	ICP-MS
Sn	ICP-MS	-	-	ICP-MS	-	-	ICP-MS	-	-	-	-	-	-	ICP-MS	-	ICP-MS
Sr	ICP-MS	AES	ICP-OES	ICP-MS	-	-	ICP-MS	-	-	ICP-OES	-	-	ICP-MS	-	ICP-OES	ICP-MS
Zn	ICP-MS	AES	ICP-OES	ICP-MS	ICP-OES	-	ICP-MS	ICP-OES	-	-	-	FAAS	ICP-MS	ICP-MS	ICP-OES	ICP-MS

ICP-MS : Inductively Coupled Plasma Mass Spectrometry

AES : Atomic Emission Spectrometry

ICP-OES : Inductively Coupled Plasma Optical Emission Spectrometry

GFAAS : Graphite Furnace Atomic Absorption Spectrometry

FAAS : Flame Atomic Absorption Spectrometry

PROPERTY VALUE AND UNCERTAINTY ASSIGNMENT

Datasets from laboratories were received and technically evaluated. QC sample results were used to check absence of significant bias for these datasets. The results for quality samples are assessed according to ERM Application Note 1[7]. Datasets were rejected if a laboratory reported a technical problem about a measurement. Data were also rejected if any two of the following criteria is not fulfilled:

- QC agreement according to ERM Application Note 17
- Grubbs' test (99%) outlier
- If relative standard deviation of 6 independent results from one lab is greater than the RSD of a result of 16 labs.

RSD of all elements is less than 10% in general except Sb which is 14% as there could not be found any technical reason to reject datasets and they were kept as it is. The result for As from Lab 10 is rejected due to technical reason claimed by the laboratory. Summary of the results can be found in Table 6. Graphs for characterisation data are shown in Annex 4.

The certified values are given in Table 7 from the characterisation study as explained above. All the certified values reported are calculated as the mean of the laboratory means of all the accepted data sets.

The uncertainty of the certified values contains contributions of the characterisation u_{char}, the homogeneity u_{bb} and the long-term stability u_{lts}.

The different contributions to the CRM uncertainty are combined using the following equation:

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

The expanded uncertainty of the certified value U_{CRM} is calculated with a coverage factor of k = 2, representing a confidence level of approximately 95 %.

The certified values and uncertainties are summarised in Table 7 and uncertainty contribution percentages are given in Table 8.

Table 6. Summary of technical evaluation; rejection reasons

Lab Code	Tech.	Al	As	B	Ba	Ca	Cd	Co	Cr	Cu	Fe
1	ICP-MS	-	-	-	-	-	-	-	-	-	-
2	ICP-OES	-	-	-	-	-	-	-	-	-	-
3	ICP-OES	-	-	-	-	-	-	-	-	-	-
4	ICP-MS	-	-	-	-	-	-	-	-	-	-
5	ICP-OES	-	-	-	-	-	-	-	-	-	RSD, QC
6	ICP-MS	-	-	-	-	-	-	-	-	-	-
7	ICP-MS	-	-	-	-	-	-	-	-	-	-
8	ICP-OES	-	-	-	-	-	-	-	-	-	-
9	GFAAS	-	-	-	-	-	-	-	-	-	-
10	ICP-OES	QC, RSD	G (99%), QC, RSD, TR	-	-	-	-	-	-	-	RSD, QC
11	GFAAS	G (99%), QC	-	-	-	-	QC, RSD	G (99%), QC, RSD	-	G (99%), QC	-
12	FAAS	-	-	-	-	G (99%), QC	-	-	-	-	-
13	ICP-MS	-	RSD, QC	-	-	-	-	-	-	-	-
14	ICP-MS	-	-	-	-	-	-	-	-	-	-
15	ICP-OES	-	-	-	-	-	-	-	-	-	-
16	ICP-MS	-	-	-	-	-	-	-	-	-	-

Lab Code	Tech.	K	Mg	Mn	Na	Ni	P	Pb	Sb	Sn	Sr	Zn
1	ICP-MS	-	-	-	-	-	-	-	-	-	-	-
2	ICP-OES	-	-	-	-	-	-	-	-	-	-	-
3	ICP-OES	-	-	-	-	-	-	-	-	-	-	-
4	ICP-MS	-	-	-	-	-	-	-	-	-	-	-
5	ICP-OES	-	-	-	-	-	-	-	-	-	-	-
6	ICP-MS	-	-	-	-	-	-	-	-	-	-	-
7	ICP-MS	-	-	-	-	-	-	-	-	-	-	-
8	ICP-OES	-	-	-	-	-	-	-	-	-	-	-
9	GFAAS	-	-	-	-	-	-	-	-	-	-	-
10	ICP-OES	-	-	-	-	-	-	G (99%), QC, RSD	QC, RSD	G (99%), QC, RSD	-	QC, RSD
11	GFAAS	-	-	G (99%), QC	-	G (99%), QC	-	QC, RSD	-	-	-	-
12	FAAS	-	-	-	-	-	-	-	-	-	-	-
13	ICP-MS	-	-	-	-	-	-	-	-	-	-	-
14	ICP-MS	-	-	-	-	-	-	-	-	-	-	-
15	ICP-OES	-	-	-	-	-	-	-	-	-	-	-
16	ICP-MS	-	-	-	-	-	-	-	-	-	-	-

G : Grubbs' test where 99% correspond to $\alpha = 0.01$
QC : Quality control check
RSD : Relative standard deviation where rsd of lab's result is greater than rsd of 16 lab results
TR : Technical reason (see explanation above)

Table 7. Summary of certified values and their uncertainties

Element	**Certified Value Mass fraction**	U_{CRM} $k = 2$	$u_{Char,rel}$	$u_{bb,rel}$	$u_{LTS,rel}$	n_{Char}	$U_{CRM,rel}$ $k = 2$
Al	0.102 mg/kg	0.005 mg/kg	2.3 %	0.7 %	0.7 %	11	4.9 %
As	6.50 µg/kg	0.38 µg/kg	1.8 %	0.5 %	2.3 %	10	5.8 %
B	0.476 mg/kg	0.023 mg/kg	2.1 %	0.9 %	0.8 %	9	4.7 %
Ba	0.313 mg/kg	0.014 mg/kg	2.0 %	0.7 %	0.5 %	11	4.4 %
Ca	3.91 mg/kg	0.14 mg/kg	1.3 %	0.9 %	0.7 %	10	3.5 %
Cd	3.95 µg/kg	0.15 µg/kg	1.7 %	0.6 %	0.7 %	10	3.9 %
Co	9.60 µg/kg	0.30 µg/kg	1.1 %	0.8 %	0.7 %	9	3.1 %
Cr	34.6 µg/kg	1.2 µg/kg	1.4 %	0.7 %	0.7 %	12	3.4 %
Cu	83.1 µg/kg	2.6 µg/kg	1.3 %	0.6 %	0.6 %	13	3.1 %
Fe	45.6 µg/kg	2.7 µg/kg	2.8 %	0.6 %	0.7 %	9	5.9 %
K	0.410 mg/kg	0.028 mg/kg	3.1 %	0.4 %	1.6 %	10	6.9 %
Mg	0.867 mg/kg	0.033 mg/kg	1.5 %	1.1 %	0.6 %	12	3.8 %
Mn	14.5 µg/kg	0.5 µg/kg	1.4 %	0.8 %	0.6 %	10	3.5 %
Na	3.13 mg/kg	0.11 mg/kg	1.5 %	0.3 %	0.9 %	11	3.6 %
Ni	16.8 µg/kg	0.7 µg/kg	1.8 %	0.7 %	0.8 %	12	4.2 %
P	96.4 µg/kg	5.7 µg/kg	2.8 %	0.8 %	0.8 %	7	5.9 %
Pb	14.7 µg/kg	0.4 µg/kg	1.1 %	0.7 %	0.7 %	9	3.0 %
Sb	5.37 µg/kg	0.59 µg/kg	5.4 %	0.4 %	1.0 %	8	10.9 %
Sn	1.50 µg/kg	0.08 µg/kg	0.9 %	1.0 %	2.5 %	6	5.6 %
Sr	21.9 µg/kg	1.1 µg/kg	2.3 %	1.0 %	0.5 %	9	5.1 %
Zn	0.104 mg/kg	0.005 mg/kg	2.2 %	1.0 %	0.7 %	12	5.0 %

Table 8. Percent contribution of each uncertainty parameter to U_{CRM}.

Element	u_{bb}	u_{LTS}	u_{Char}
Al	7.8 %	7.1 %	85.1 %
As	3.0 %	60.2 %	36.8 %
B	13.8 %	10.0 %	76.2 %
Ba	9.1 %	5.9 %	85.0 %
Ca	25.6 %	17.7 %	56.7 %
Cd	10.0 %	12.8 %	77.2 %
Co	25.6 %	21.8 %	52.5 %
Cr	18.2 %	14.9 %	66.9 %
Cu	15.7 %	12.6 %	71.7 %
Fe	4.0 %	5.4 %	90.6 %
K	1.5 %	20.1 %	78.5 %
Mg	33.2 %	8.6 %	58.1 %
Mn	22.2 %	11.6 %	66.3 %
Na	2.1 %	24.8 %	73.1 %
Ni	12.4 %	14.5 %	73.1 %
P	6.5 %	6.4 %	87.1 %
Pb	24.1 %	19.7 %	56.2 %
Sb	0.4 %	3.0 %	96.5 %
Sn	12.7 %	76.0 %	11.4 %
Sr	15.6 %	4.5 %	79.9 %
Zn	15.8 %	7.3 %	76.9 %

TRACEABILITY

The metrological traceability of the certified reference material was ensured by using the SI traceable calibration standards by all the laboratories participating to the interlaboratory comparison. The laboratories were asked to provide detailed information about the calibration standards used in the measurements. The laboratories participating to the study were reported that they used SI traceable calibration standards. In the measurements carried out at TÜBİTAK UME laboratories, mono-elemental calibration standards purchased from NIST were used for all the elements measured. In order to check the accuracy of the measurements, matrix CRM, NIST SRM 1643e “Trace Elements in Water”, NRC Canada SLRS-5 “River Water Reference Material for Trace Metals” and ERM-CA022a-2 “Soft Drinking Water UK – Metals”. For only Sn and P, which were not certified in any of those CRMs, spiking experiments were carried out.

INSTRUCTIONS FOR USE

Storage conditions

The material should be stored at (18 ± 4) °C and in a clean environment. The bottle should be shaken before opening the cap in order to prevent the effect of condensation on the upper surfaces of the bottle. In order to prevent contamination, it is recommended that the bottle should be opened in a clean environment and pipette should not be inserted into the bottle.

Minimum sample intake

During the measurements performed for homogenization, characterization and long term and short term stabilities, the lowest volume used was 250 µL for major elements (B, Ba, Ca, K, Mg and Na) and no significant problem of heterogeneity have been observed. Therefore, this can be considered as the minimum sample volume to be used in the analysis for the other elements.

Safety precautions

The material contains 2% (w/v) nitric acid and toxic metals spiked into solution. Therefore, the usual laboratory safety measures apply as in the case of similar solutions.

ACKNOWLEDGMENTS

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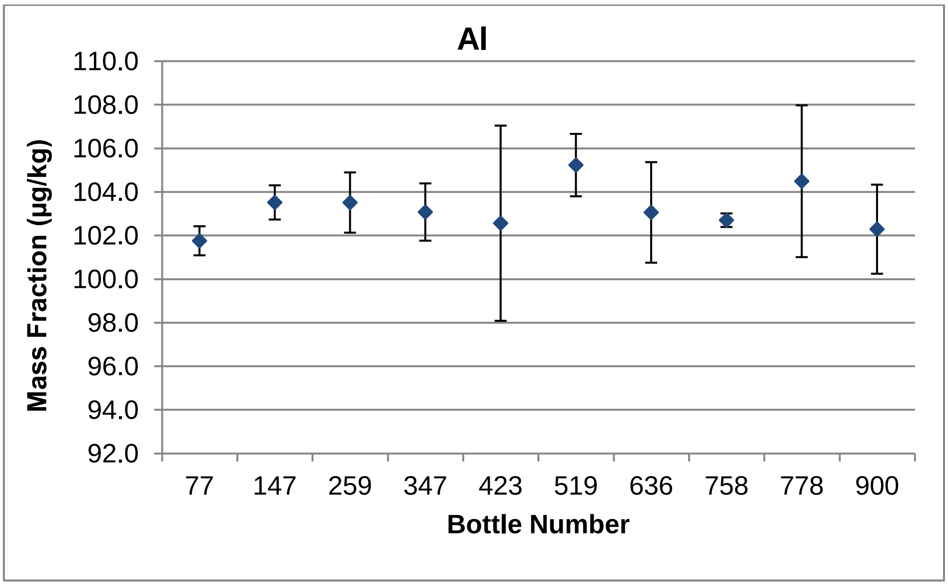
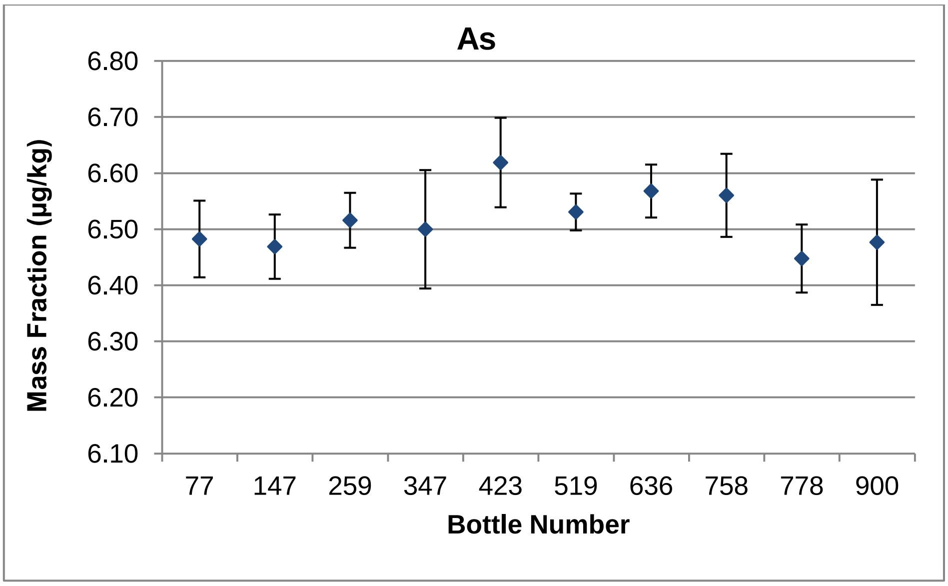
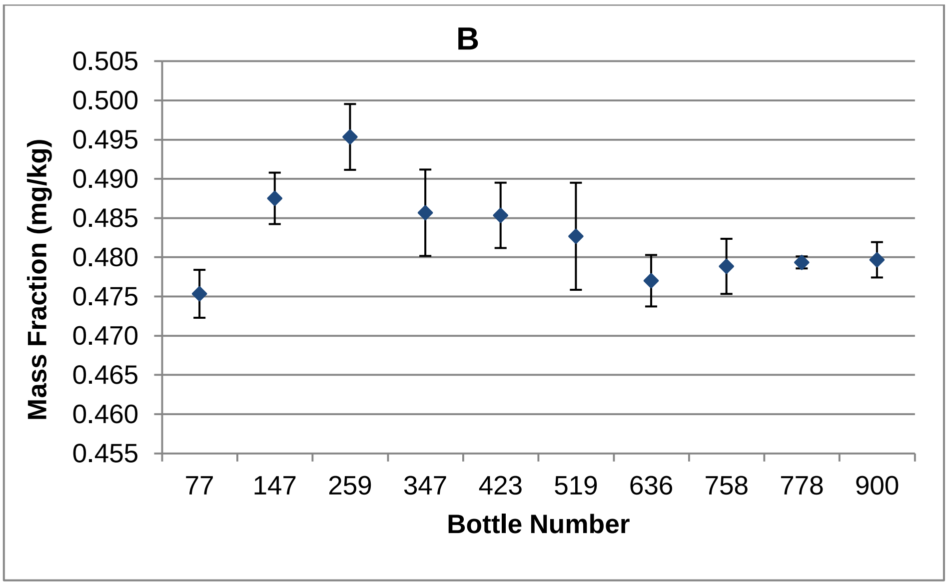
REVISION HISTORY

Date	Remarks
30.07.2013	First issue.

Annex 1 Graphs for Homogeneity Studies



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Mass Fraction (mg/kg)
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0.495
0.490
0.485
0.480
0.475
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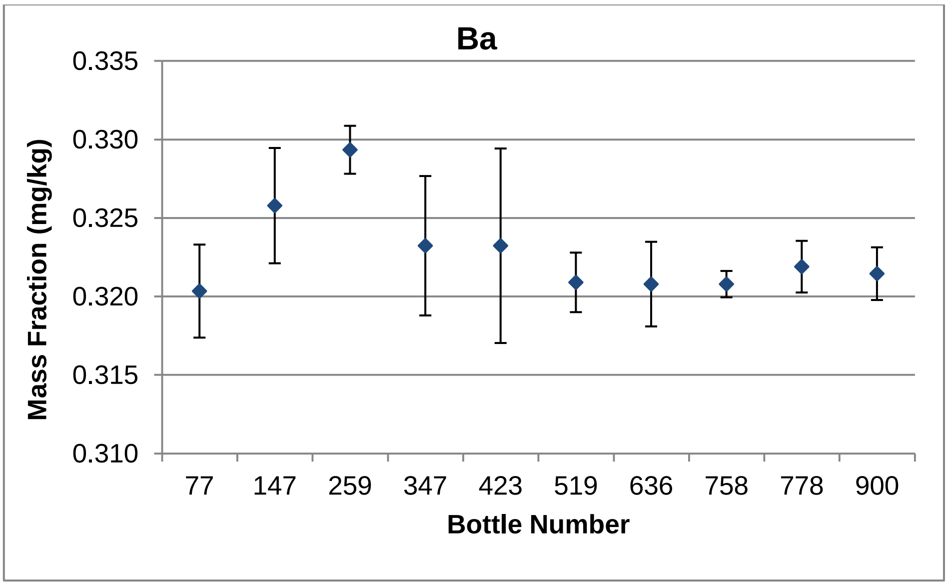
0.460
0.455
77
147
259
347
423
519
636
758
778
900
Bottle Number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0.315
0.310
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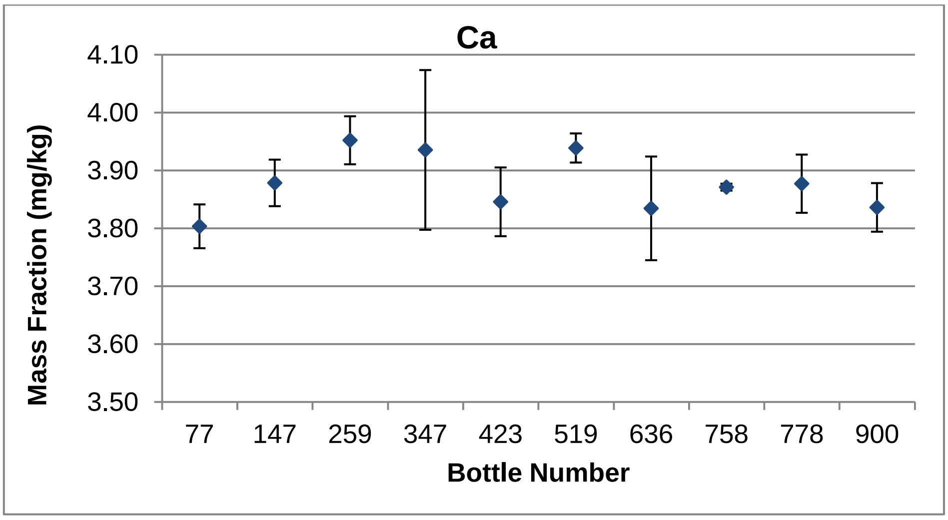
147
259
347
423
519
636
758
778
900
Bottle Number


Ca
Mass Fraction (mg/kg)
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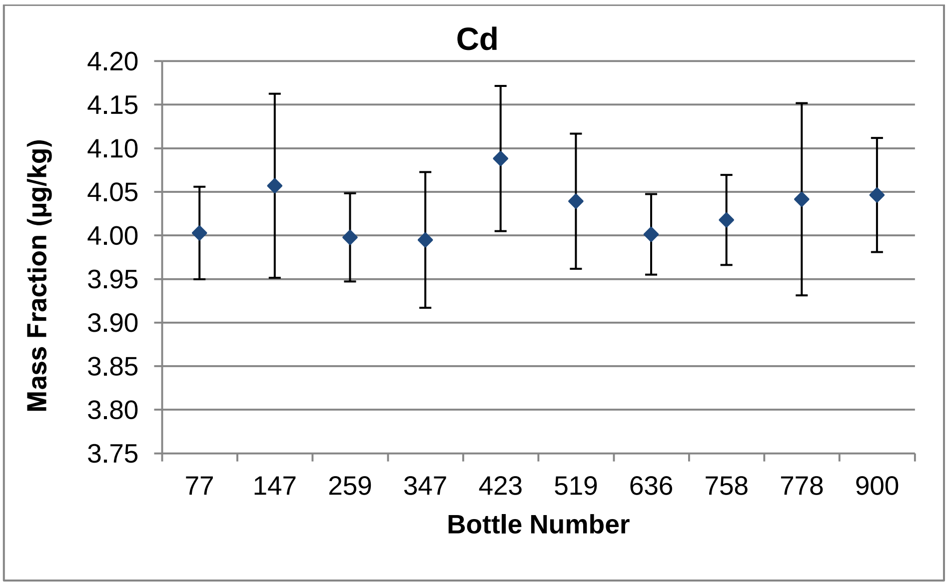
4.00
3.90
3.80
3.70
3.60
3.50
77
147
259
347
423
519
636
758
778
900
Bottle Number


Cd
Mass Fraction (µg/kg)
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4.10
4.05
4.00
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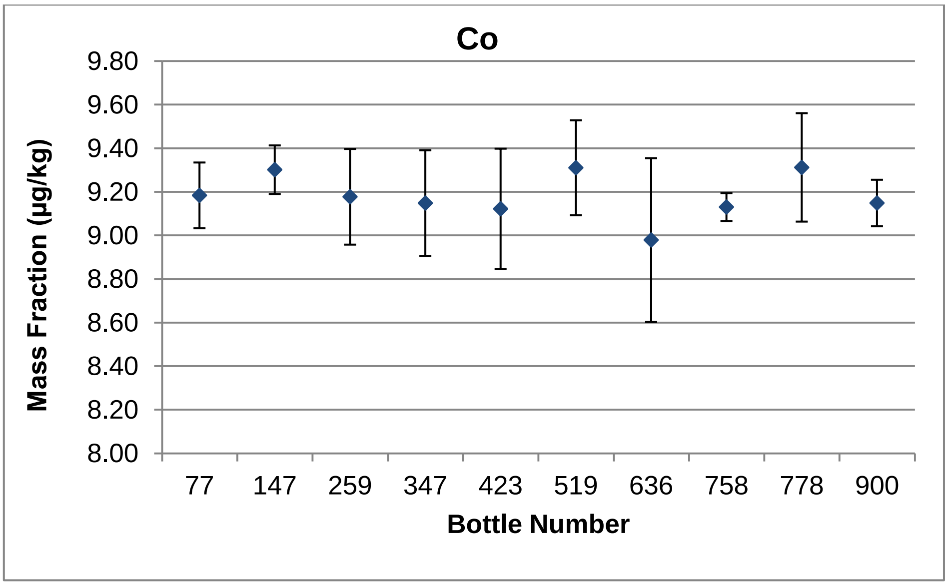
3.85
3.80
3.75
77
147
259
347
423
519
636
758
778
900
Bottle Number


Co
Mass Fraction (µg/kg)
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9.60
9.40
9.20
9.00
8.80
8.60
8.40
8.20
8.00
77
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423
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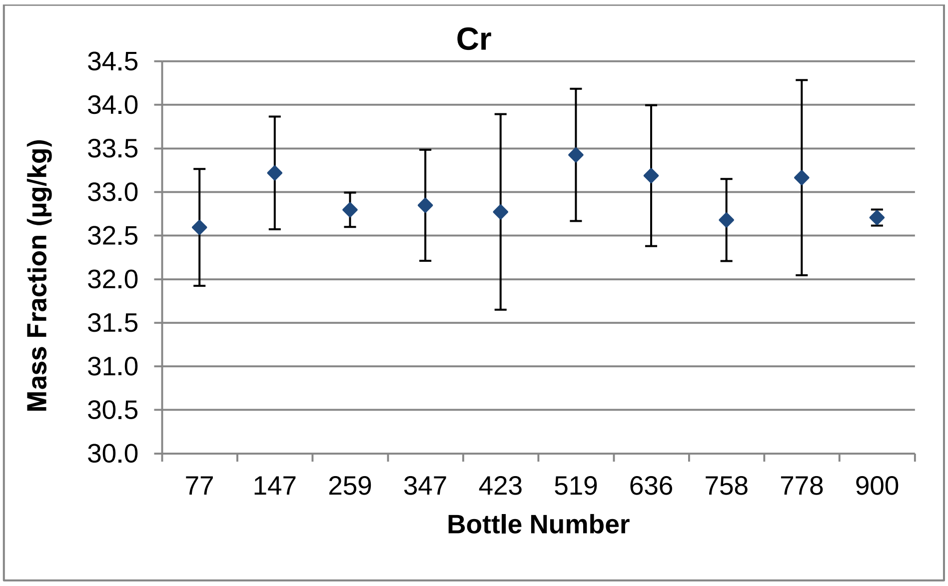
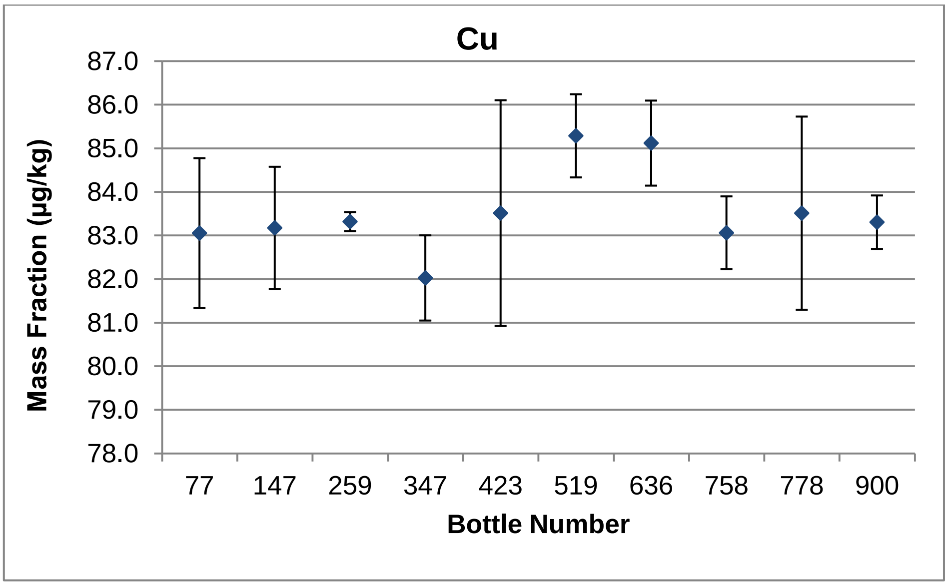
636
758
778
900
Bottle Number


Cr
Mass Fraction (µg/kg)
34.5
34.0
33.5
33.0
32.5
32.0
31.5
31.0
30.5
30.0
77
147
259
347
423
519
636
758
778
900
Bottle Number


Cu
Mass Fraction (µg/kg)
87.0
86.0
85.0
84.0
83.0
82.0
81.0
80.0
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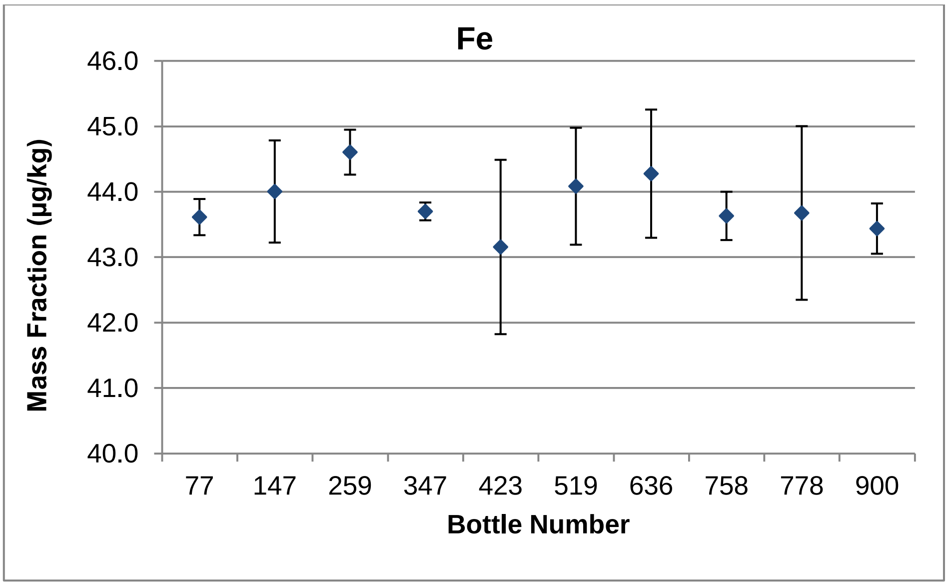
78.0
77
147
259
347
423
519
636
758
778
900
Bottle Number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Mass Fraction (µg/kg)
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45.0
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147
259
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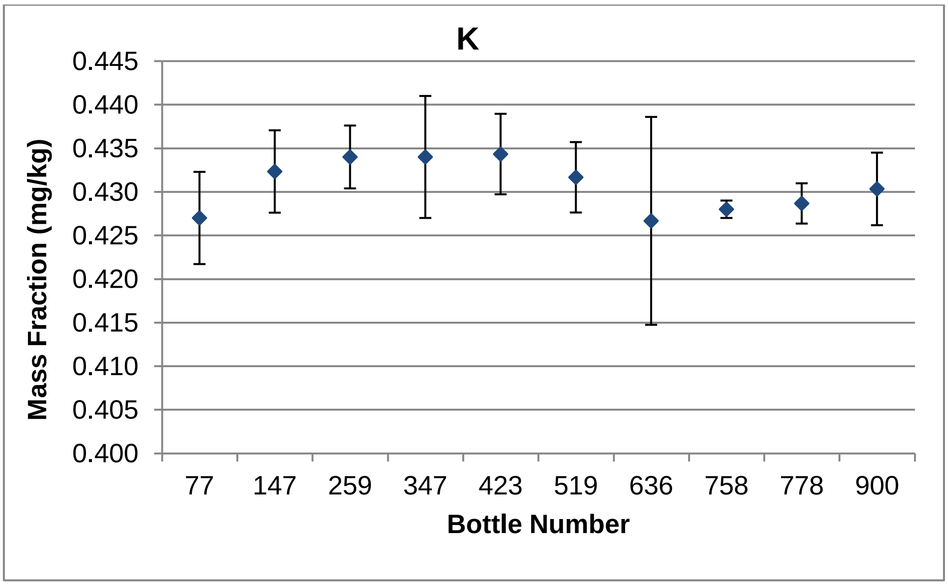
519
636
758
778
900
Bottle Number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Mass Fraction (mg/kg)
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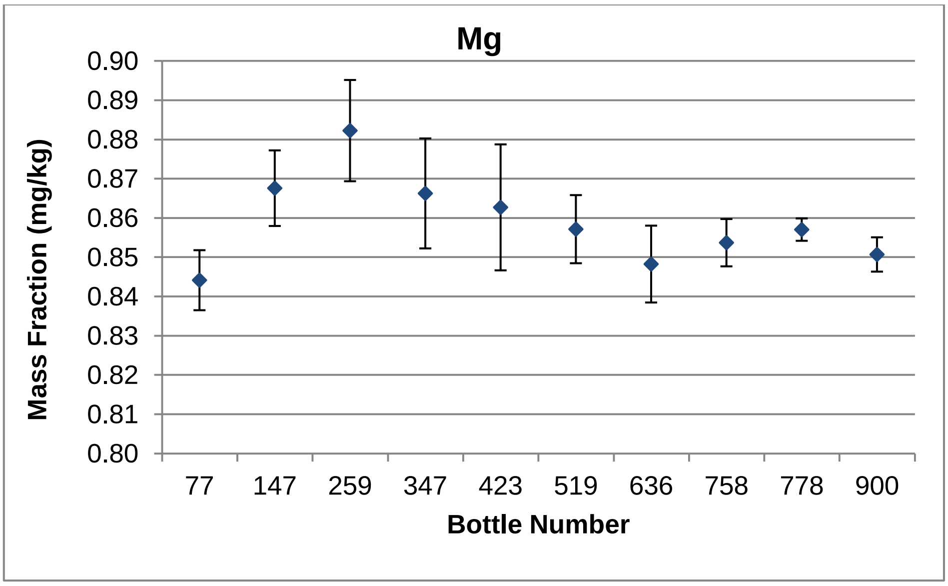
0.440
0.435
0.430
0.425
0.420
0.415
0.410
0.405
0.400
77
147
259
347
423
519
636
758
778
900
Bottle Number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Mass Fraction (mg/kg)
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0.88
0.87
0.86
0.85
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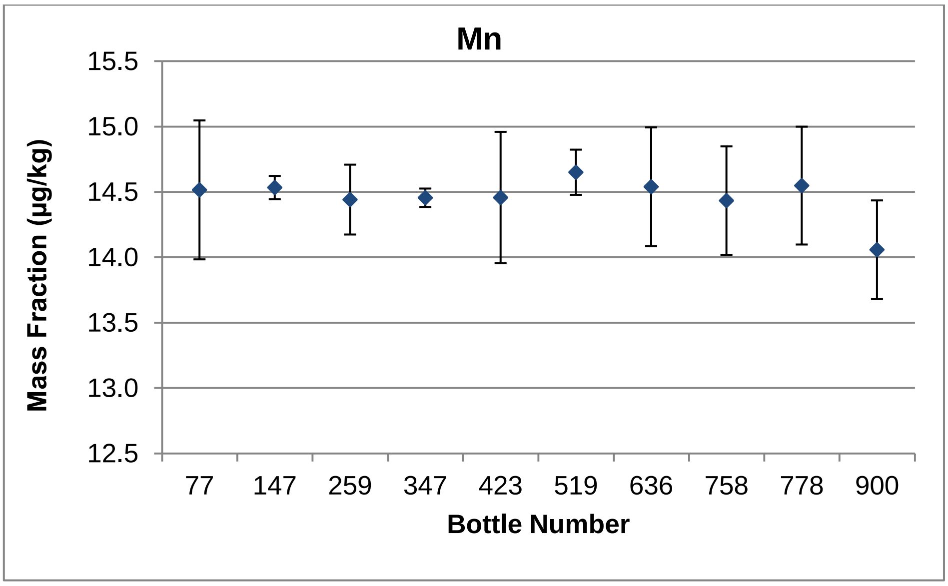
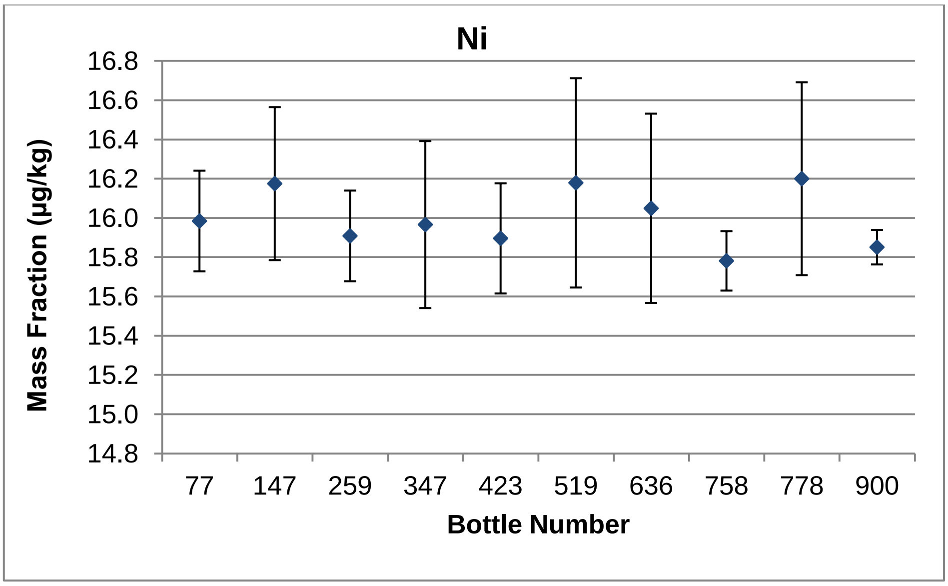
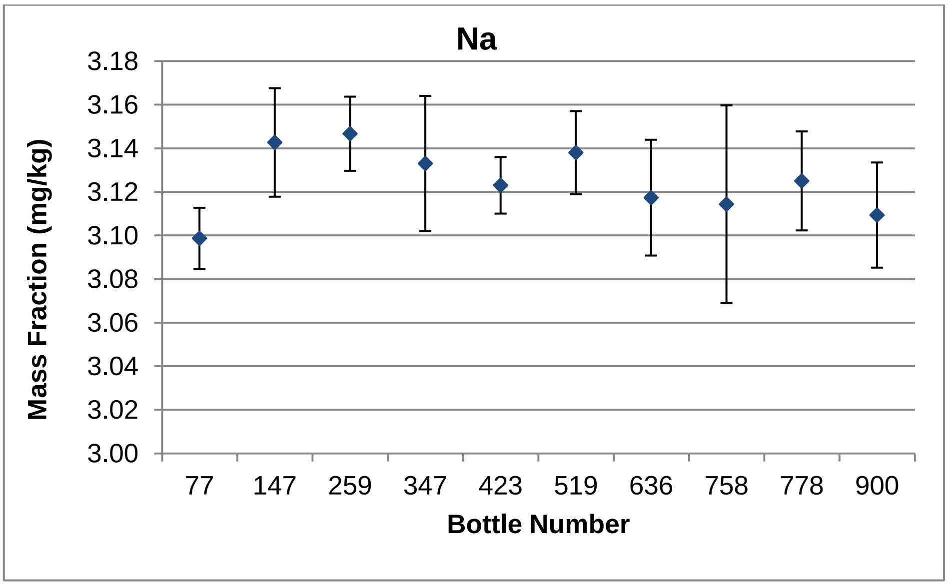
0.83
0.82
0.81
0.80
77
147
259
347
423
519
636
758
778
900
Bottle Number


Mn
Mass Fraction (µg/kg)
15.5
15.0
14.5
14.0
13.5
13.0
12.5
77
147
259
347
423
519
636
758
778
900
Bottle Number


Ni
Mass Fraction (µg/kg)
16.8
16.6
16.4
16.2
16.0
15.8
15.6
15.4
15.2
15.0
14.8
77
147
259
347
423
519
636
758
778
900
Bottle Number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Mass Fraction (mg/kg)
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3.12
3.10
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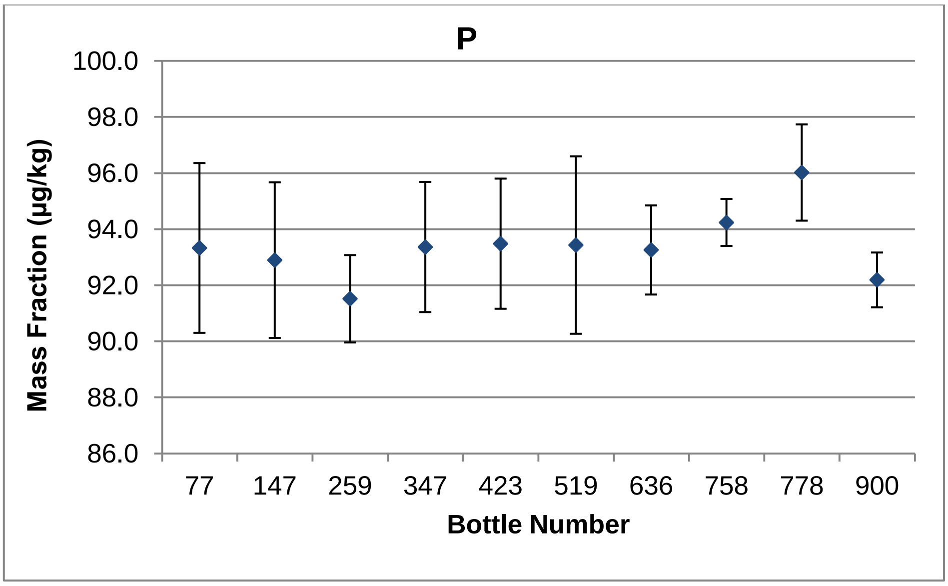
3.06
3.04
3.02
3.00
77
147
259
347
423
519
636
758
778
900
Bottle Number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92.0
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77
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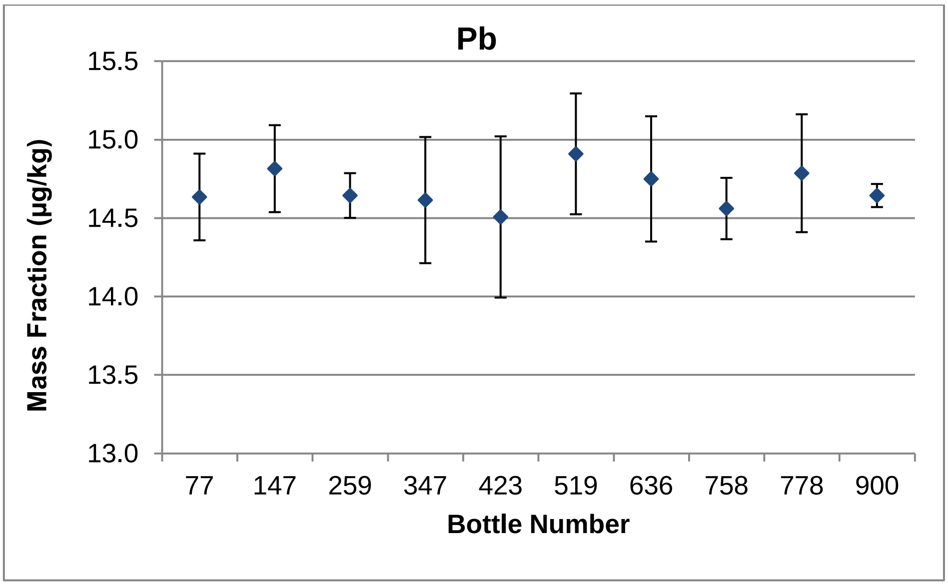
636
758
778
900
Bottle Number


Pb
Mass Fraction (µg/kg)
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13.5
13.0
77
147
259
347
423
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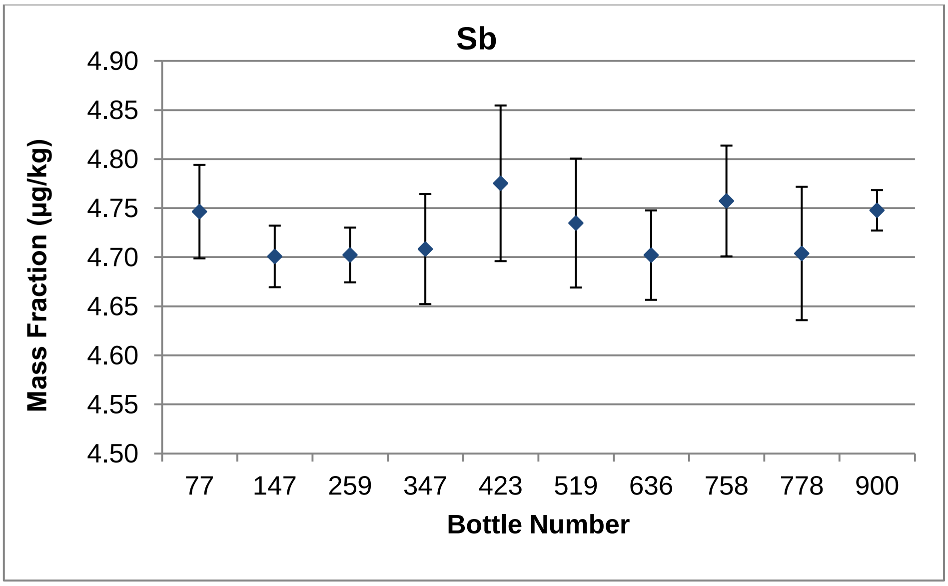
636
758
778
900
Bottle Number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Mass Fraction (µg/kg)
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4.80
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4.65
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4.55
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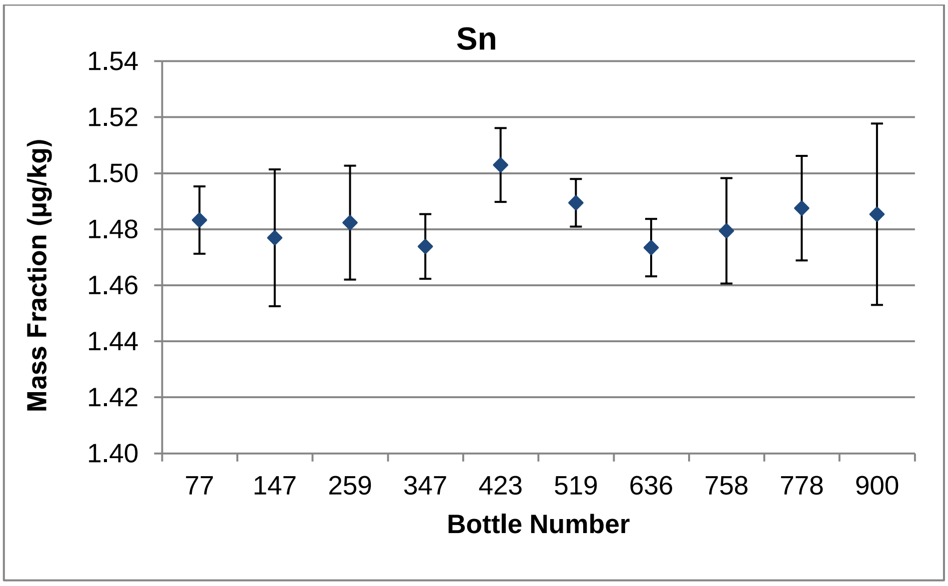
77
147
259
347
423
519
636
758
778
900
Bottle Number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Mass Fraction (µg/kg)
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1.50
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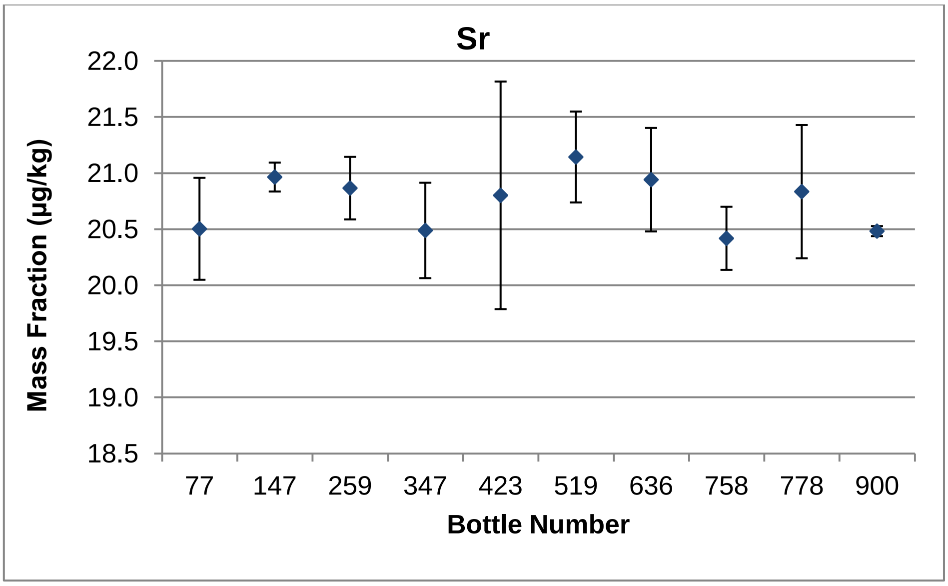
147
259
347
423
519
636
758
778
900
Bottle Number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20.0
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77
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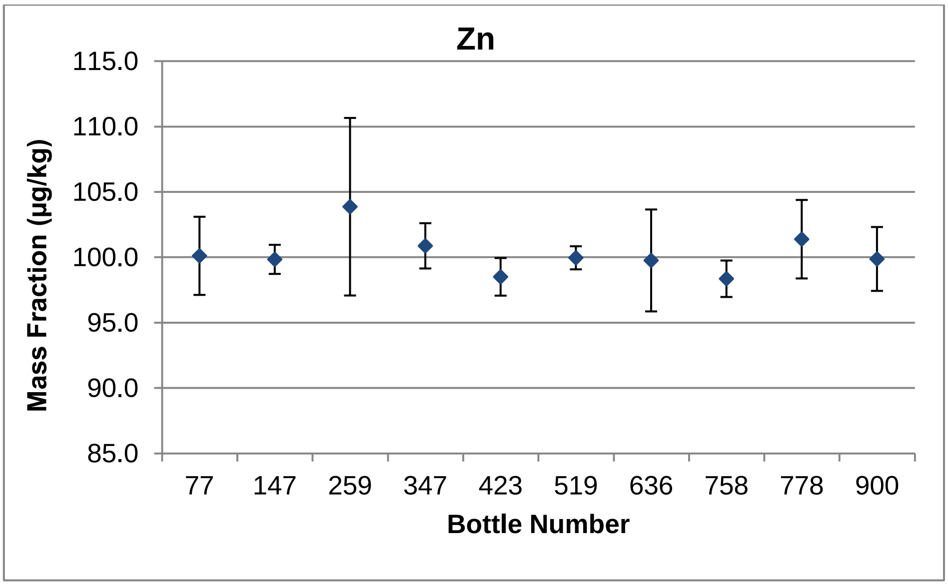
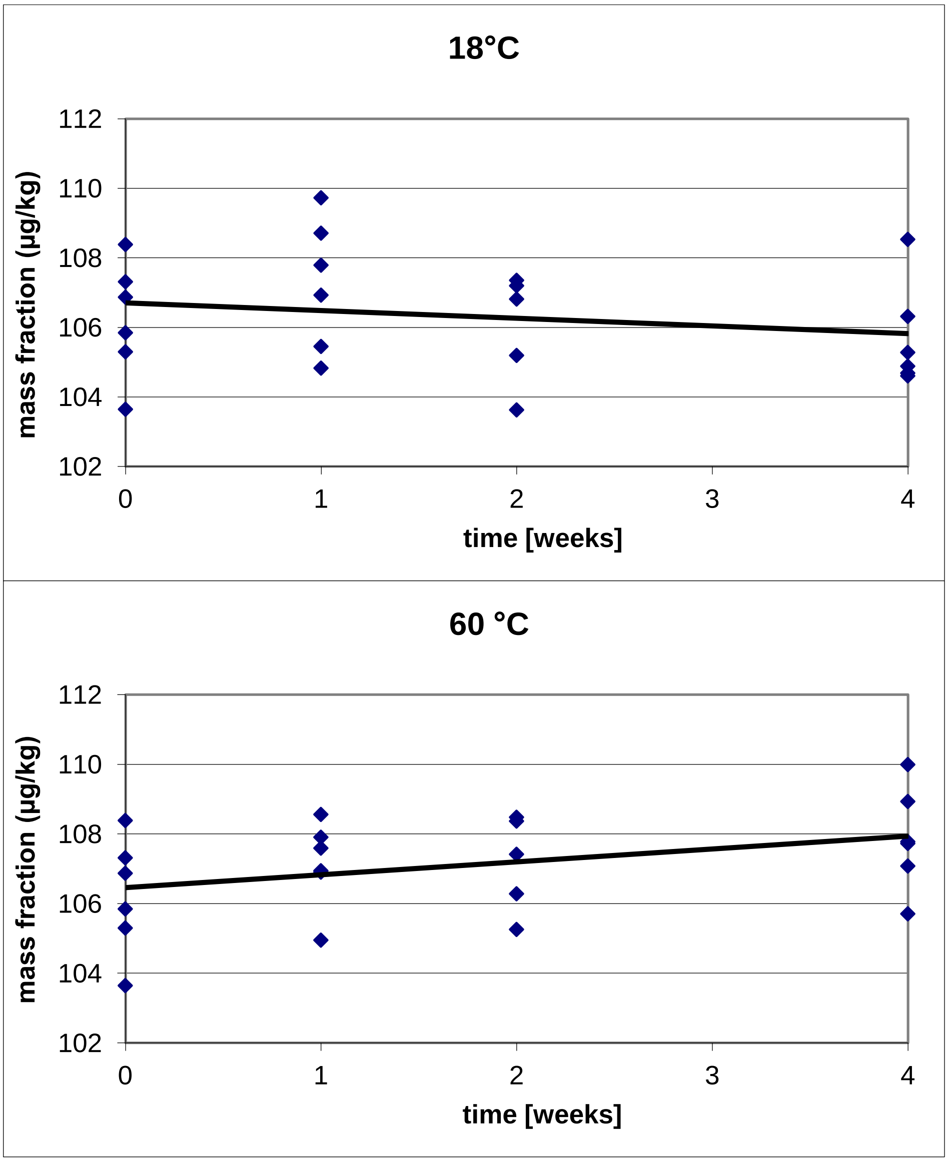
636
758
778
900
Bottle Number

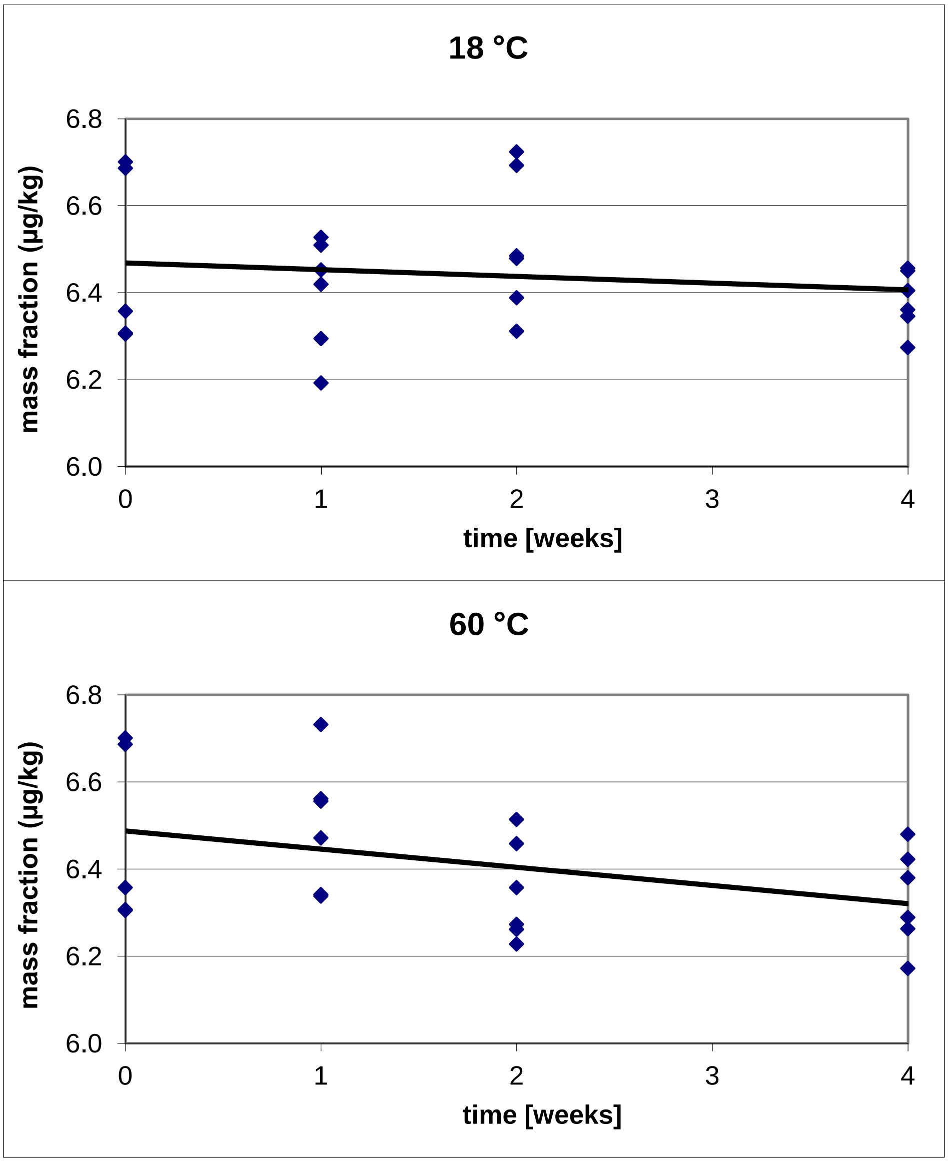

Zn
Mass Fraction (µg/kg)
115.0
110.0
105.0
100.0
95.0
90.0
85.0
77
147
259
347
423
519
636
758
778
900
Bottle Number

Annex 2 Graphs for Short Term Stability Studies

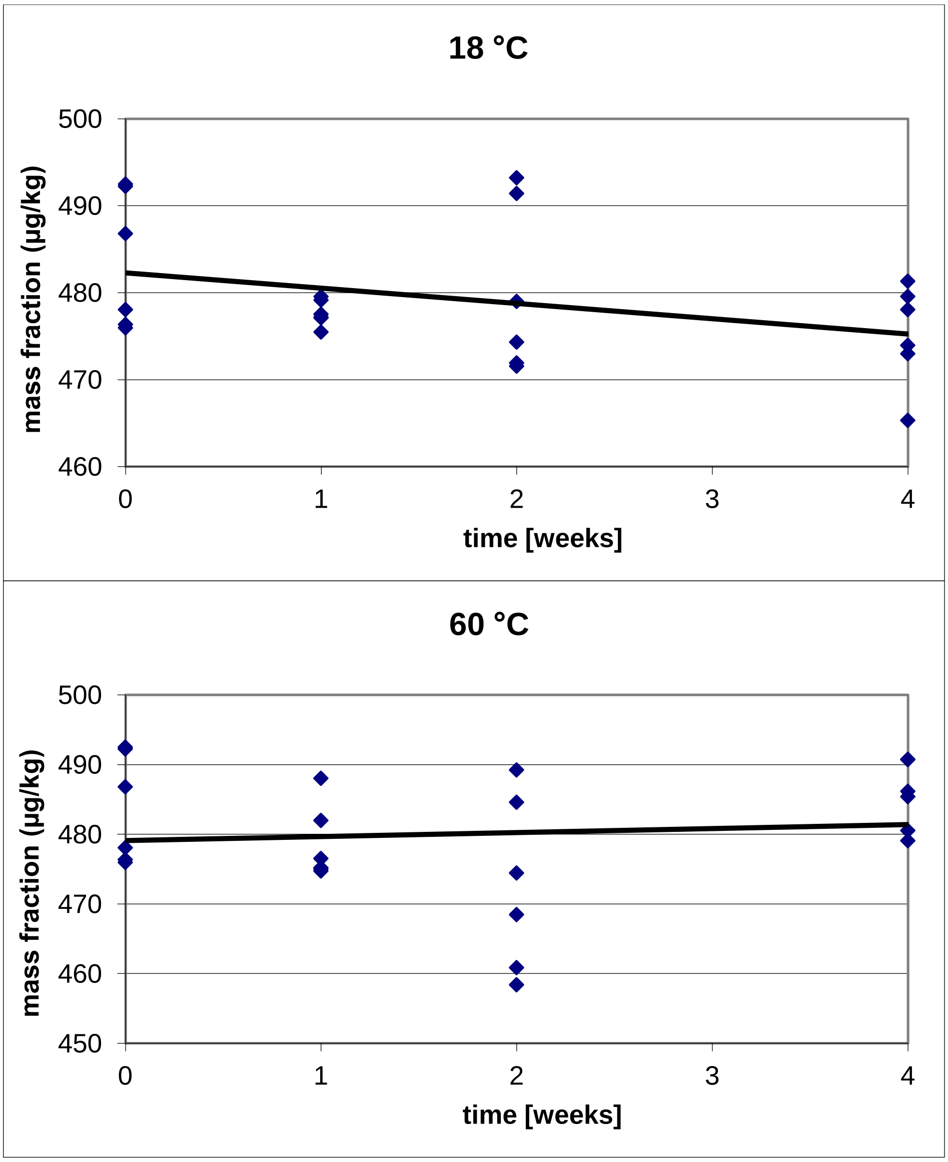
Short term stability graphs, Al



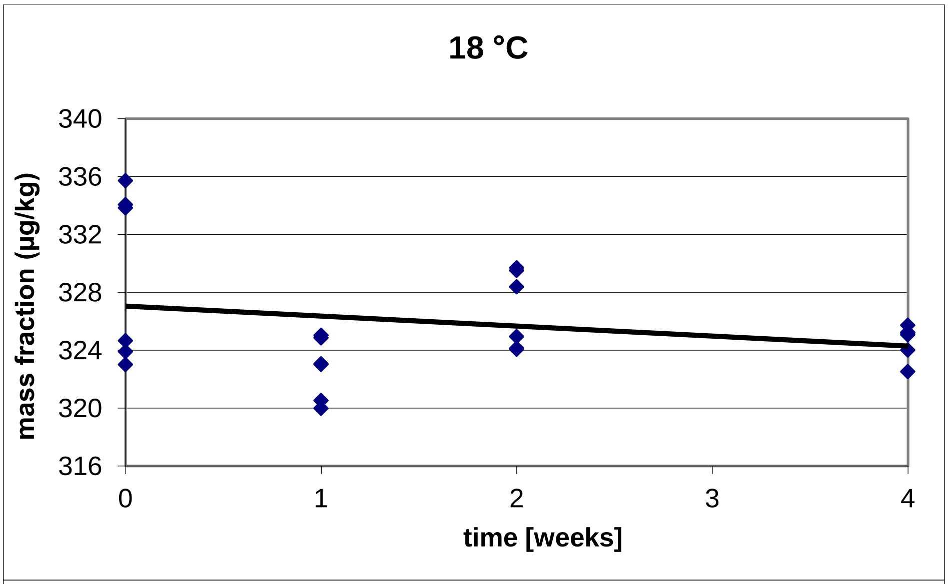
Short term stability graphs, As

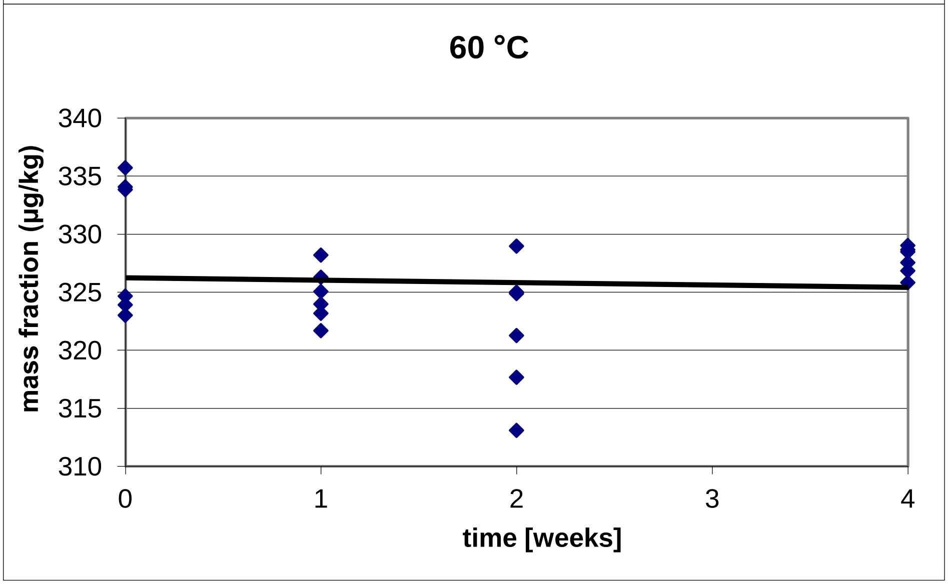


Short term stability graphs, B

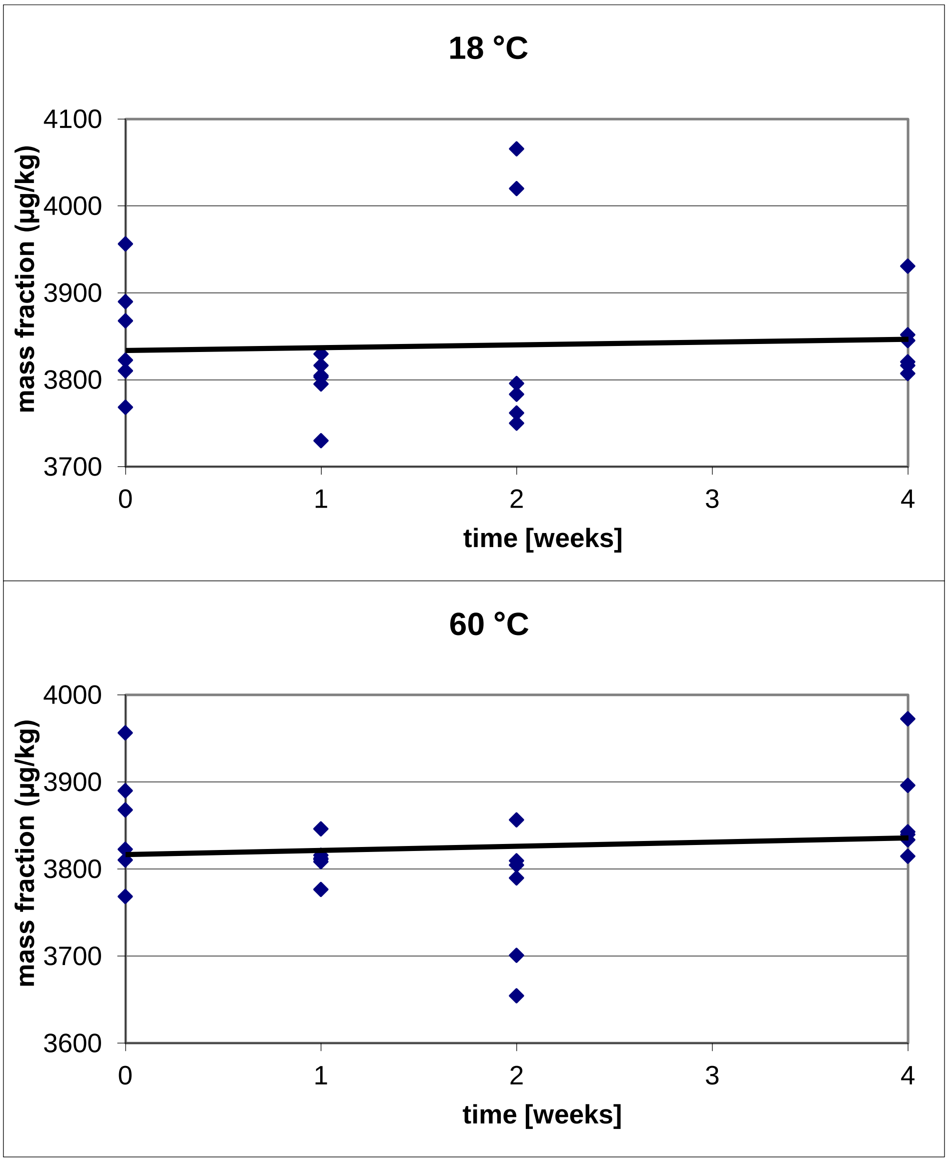


Short term stability graphs, Ba

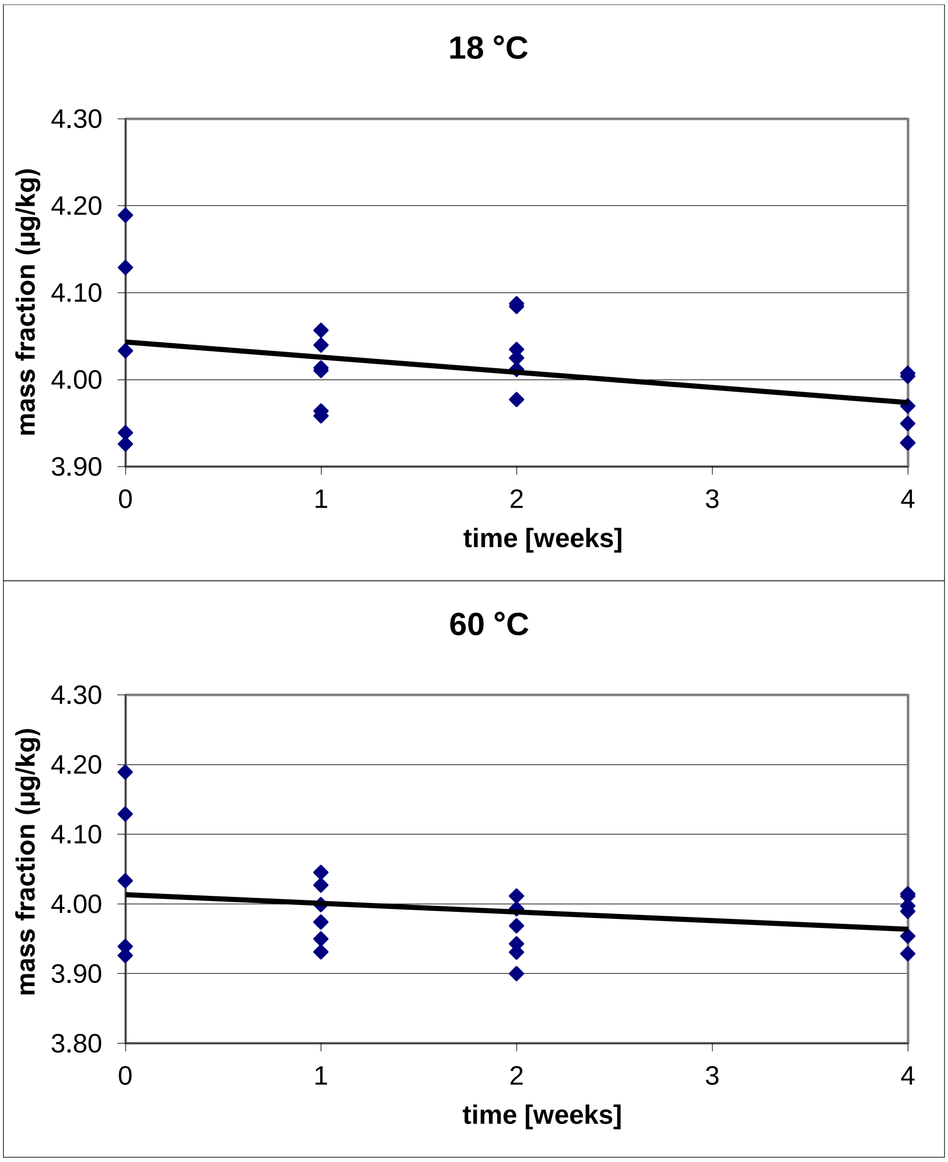




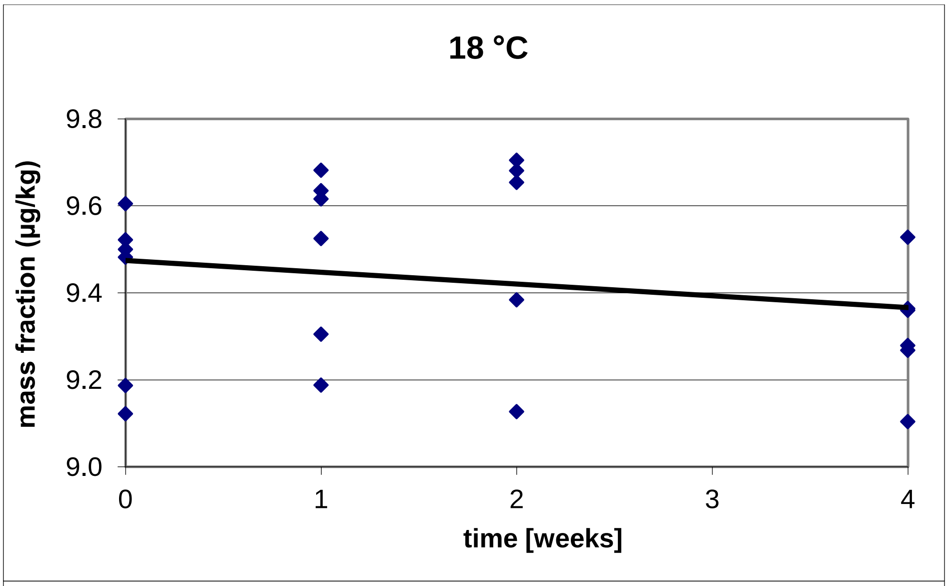
Short term stability graphs, Ca

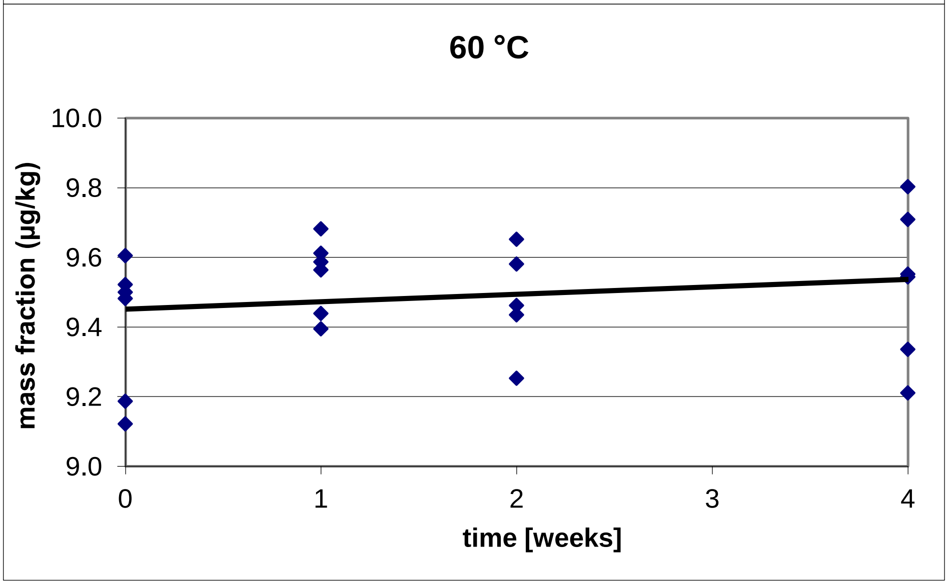


Short term stability graphs, Cd

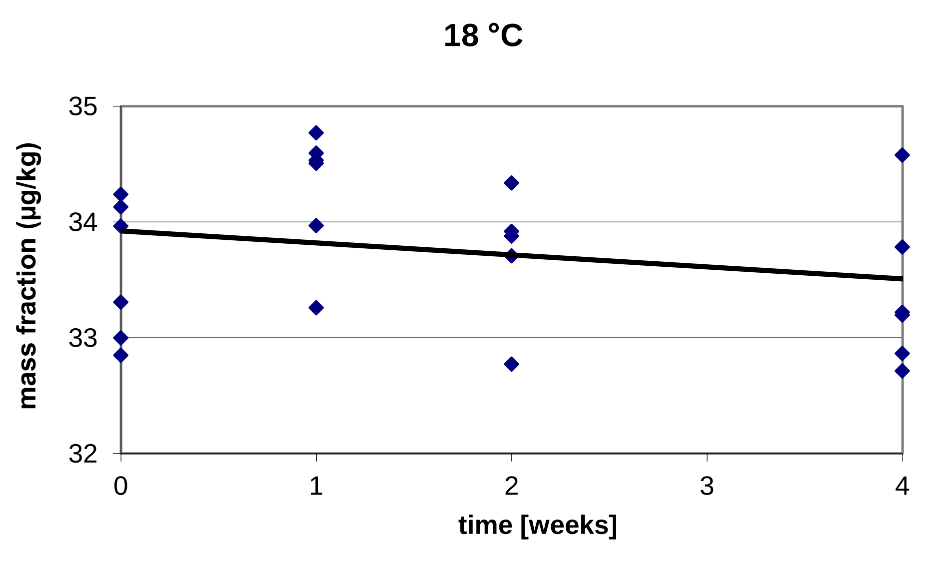


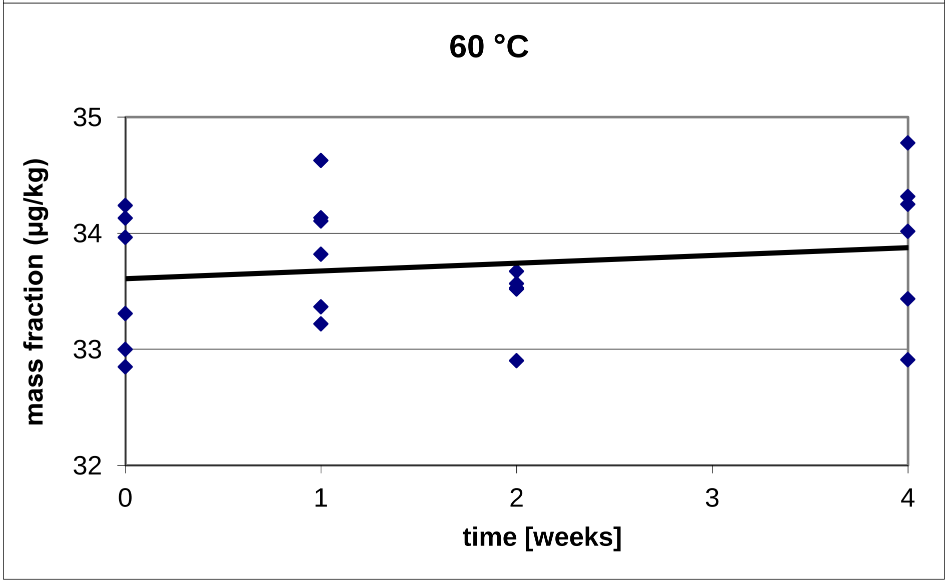
Short term stability graphs, Co



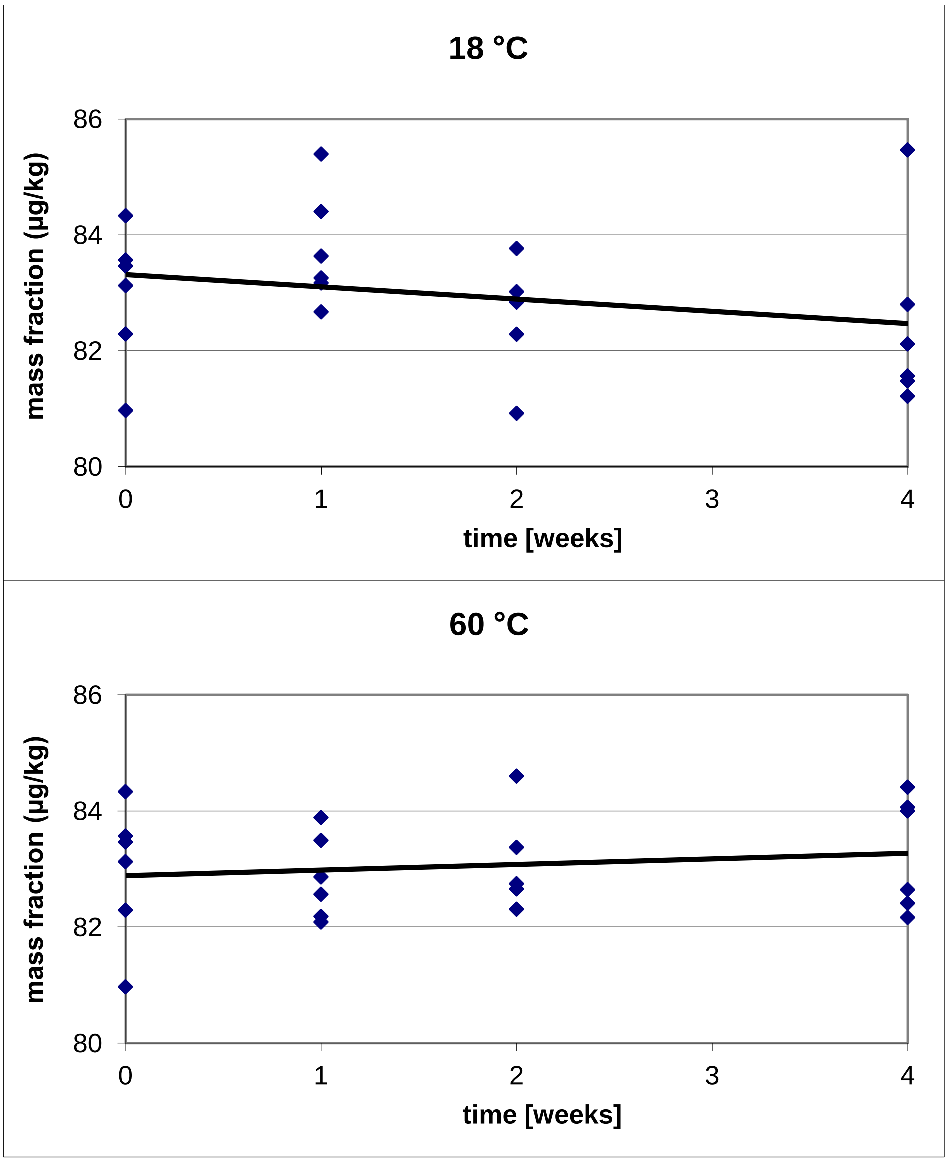


Short term stability graphs, Cr

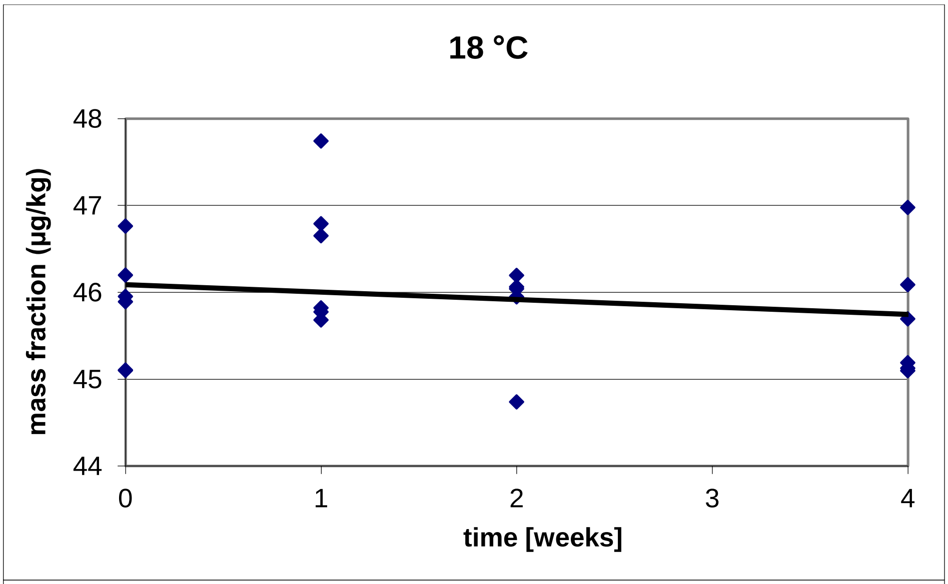


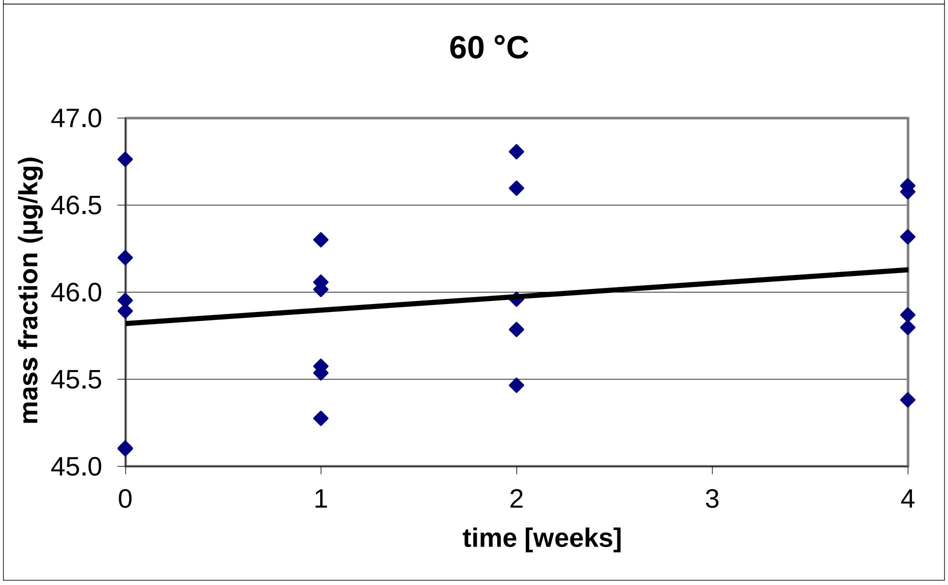


Short term stability graphs, Cu

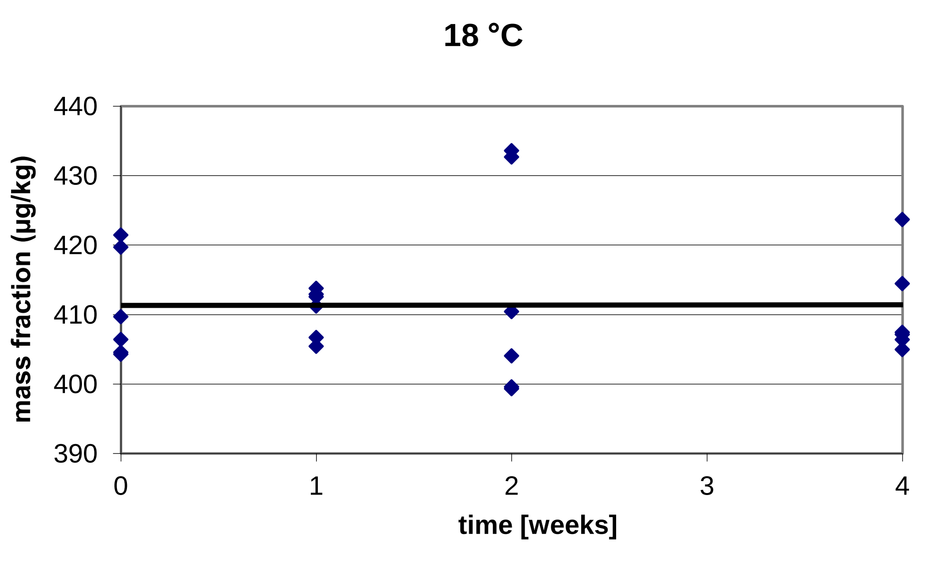


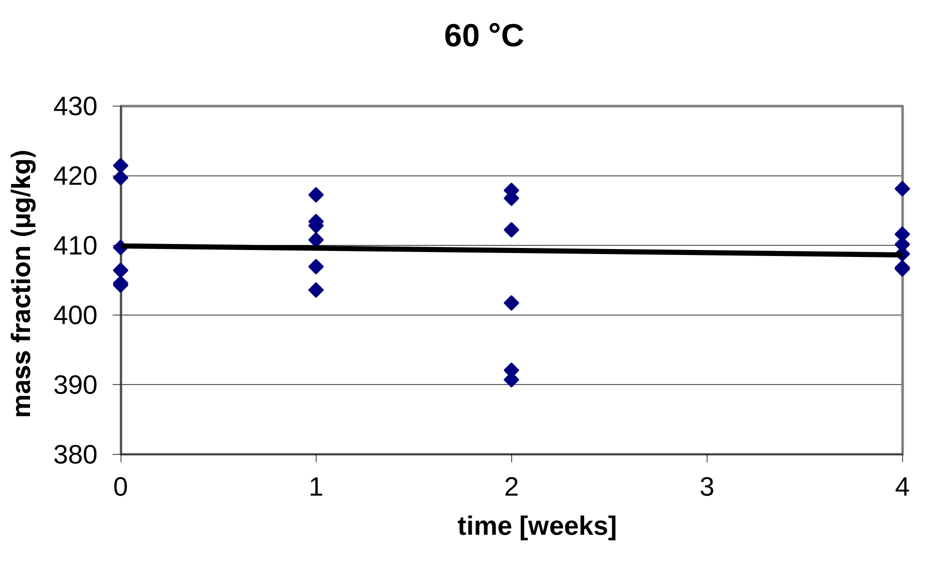
Short term stability graphs, Fe



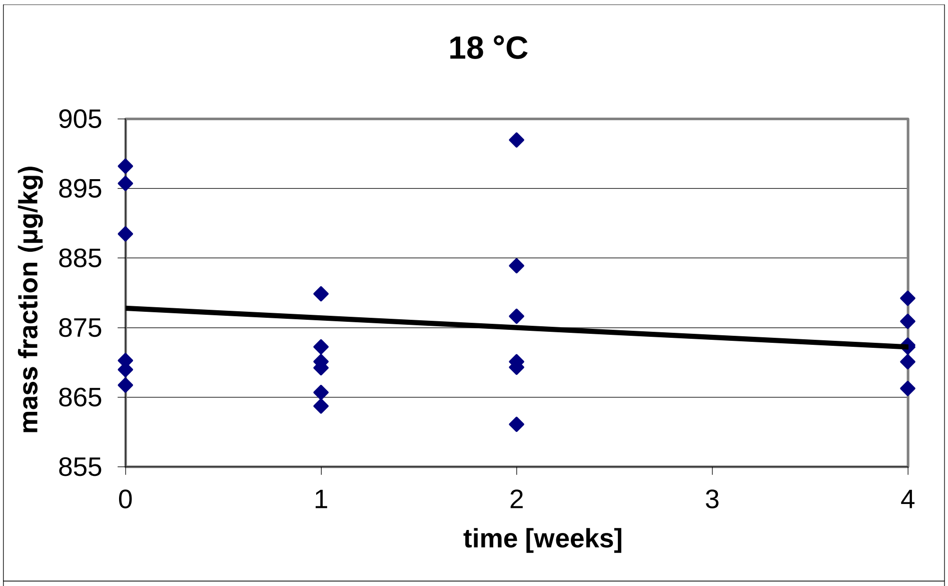


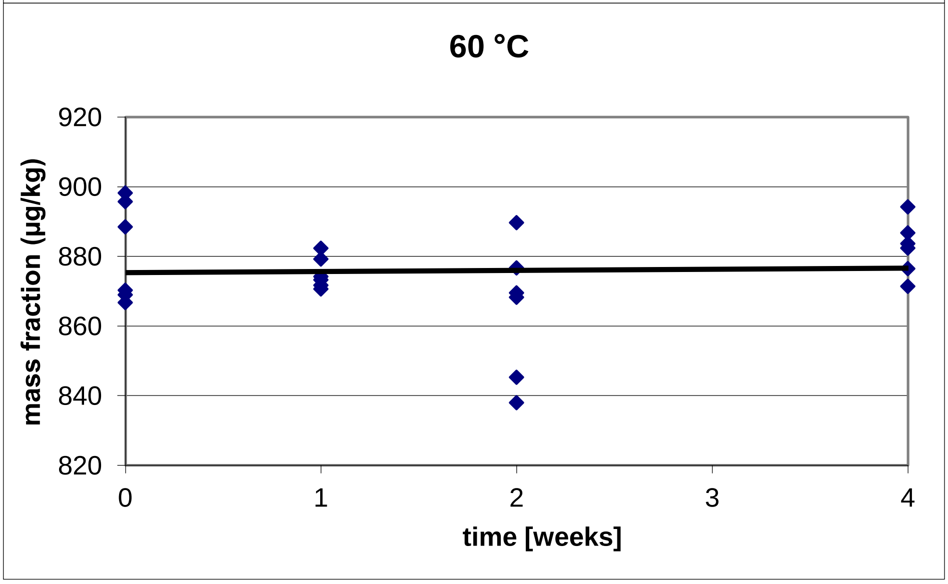
Short term stability graphs, K



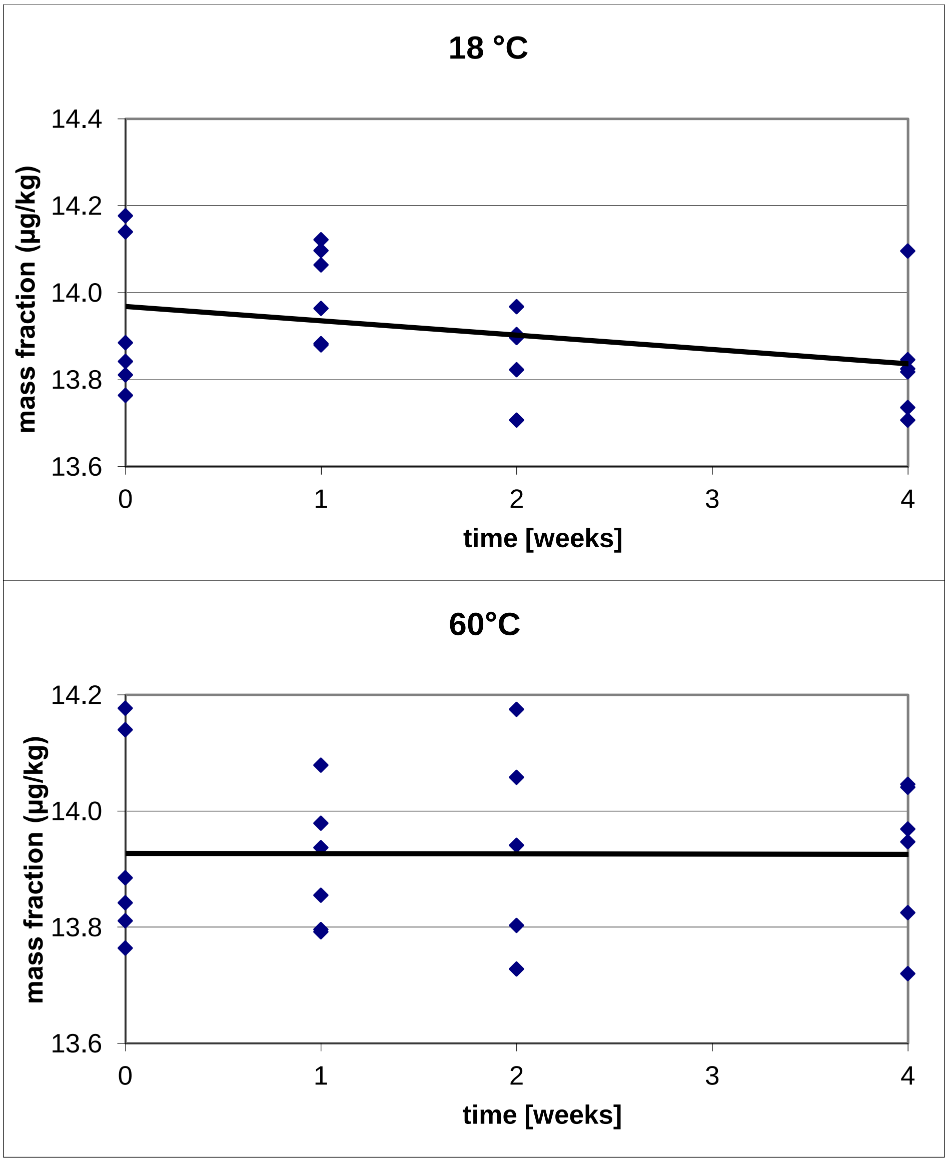


Short term stability graphs, Mg

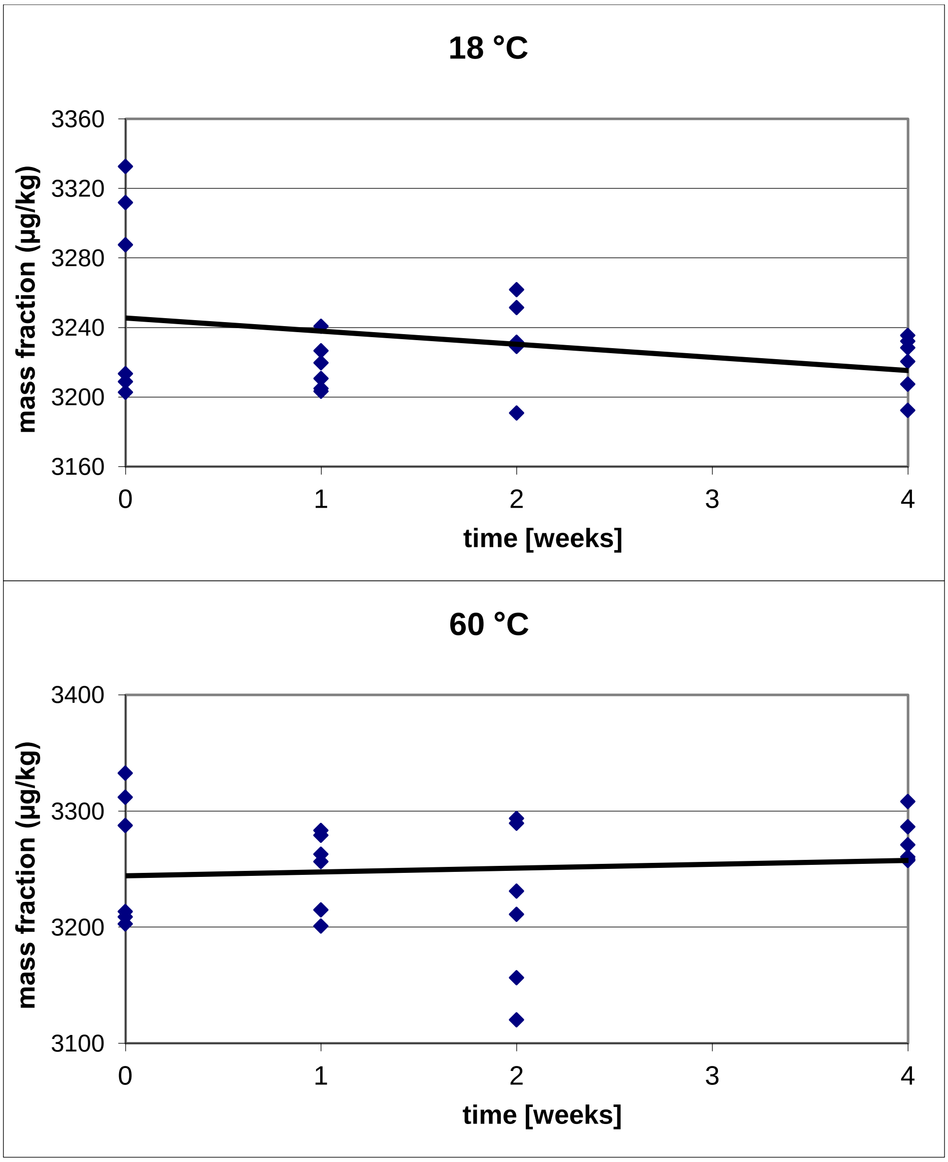




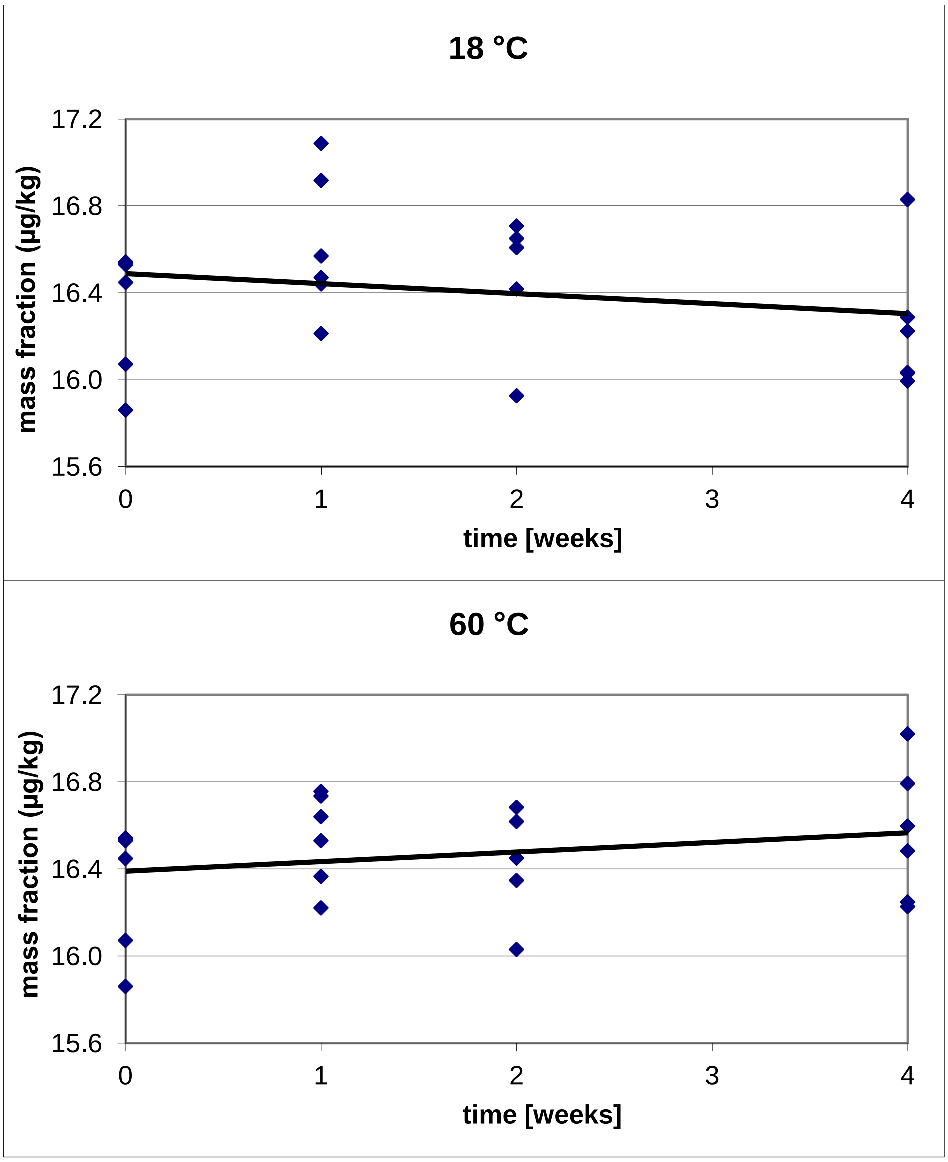
Short term stability graphs, Mn



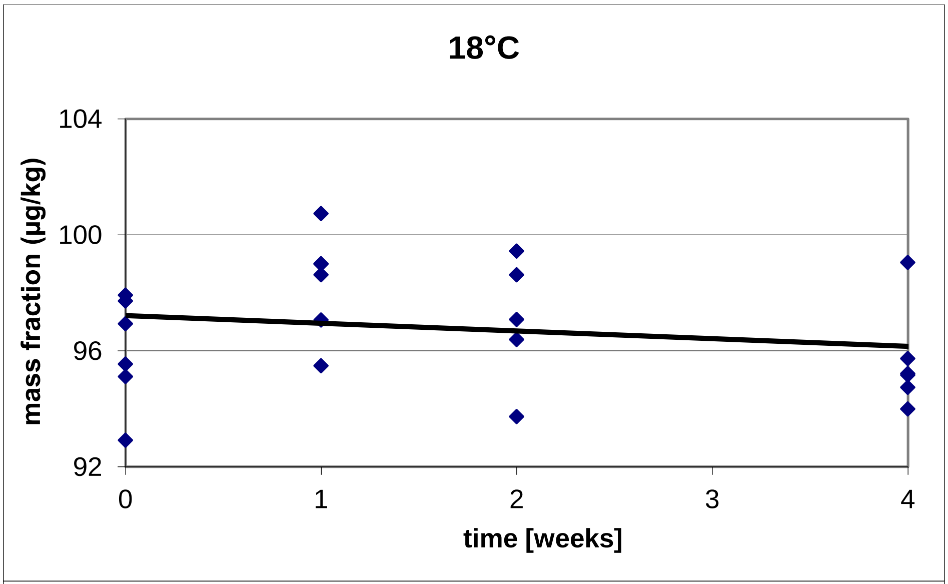
Short term stability graphs, Na

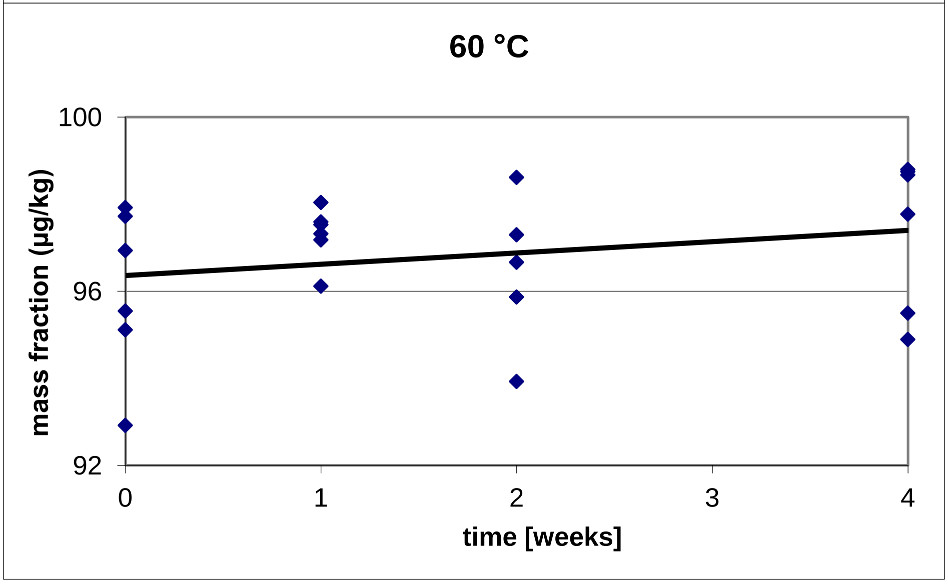


Short term stability graphs, Ni

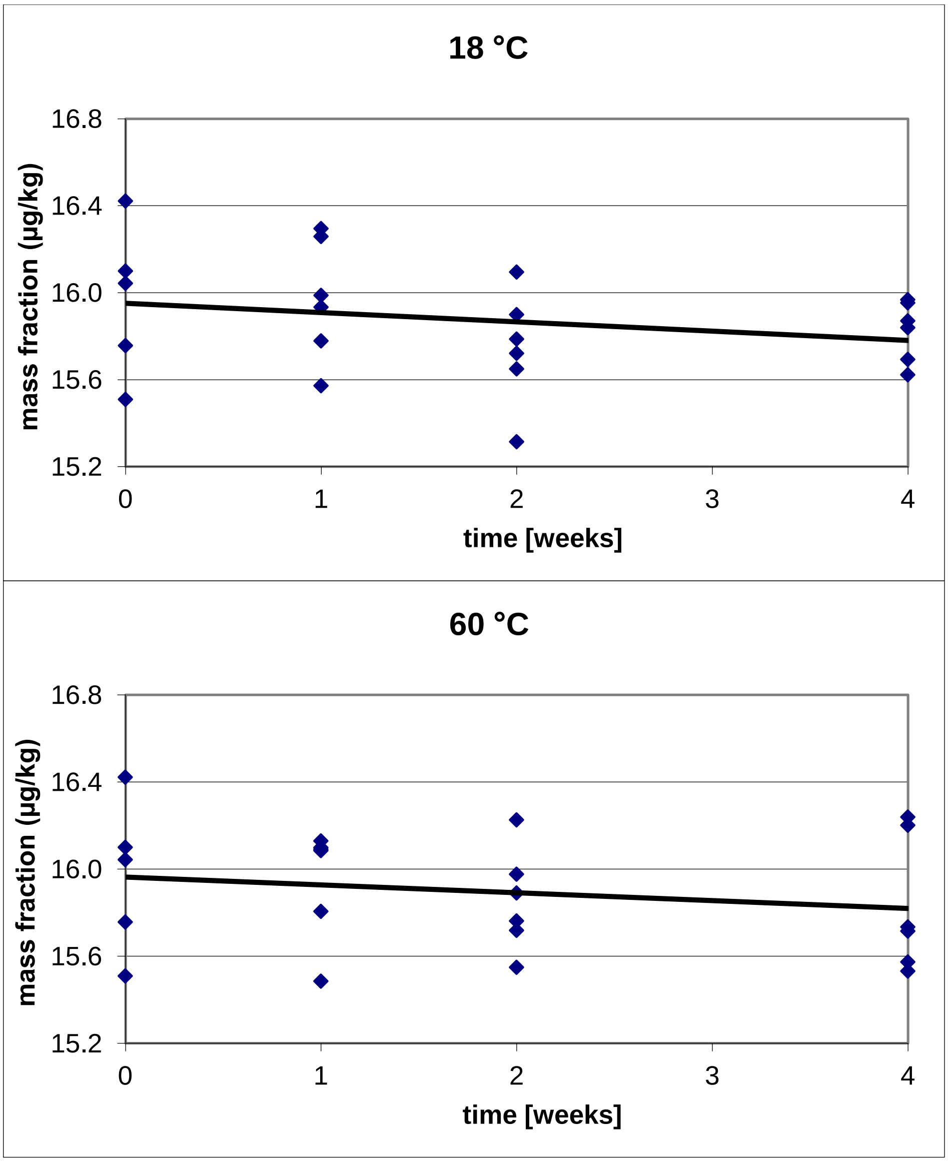


Short term stability graphs, P

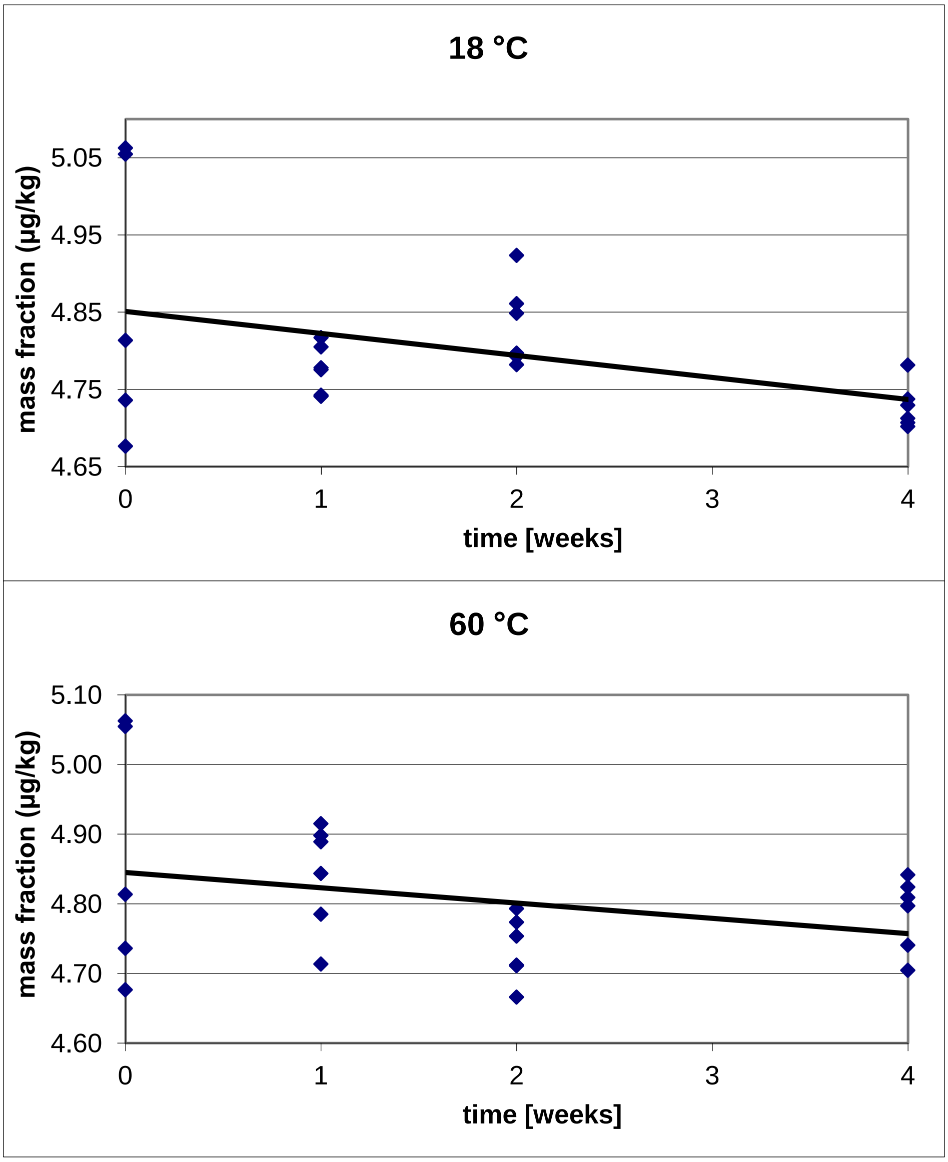




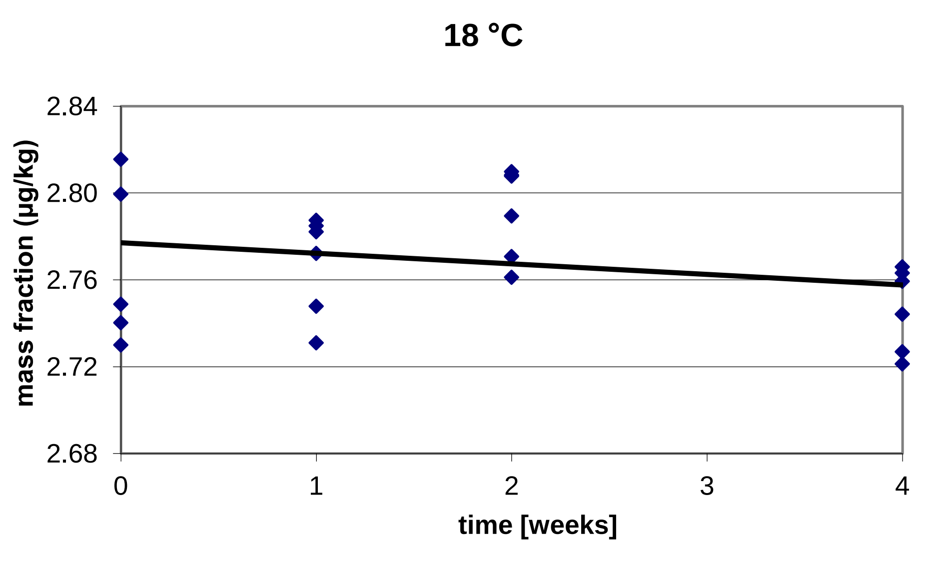
Short term stability graphs, Pb

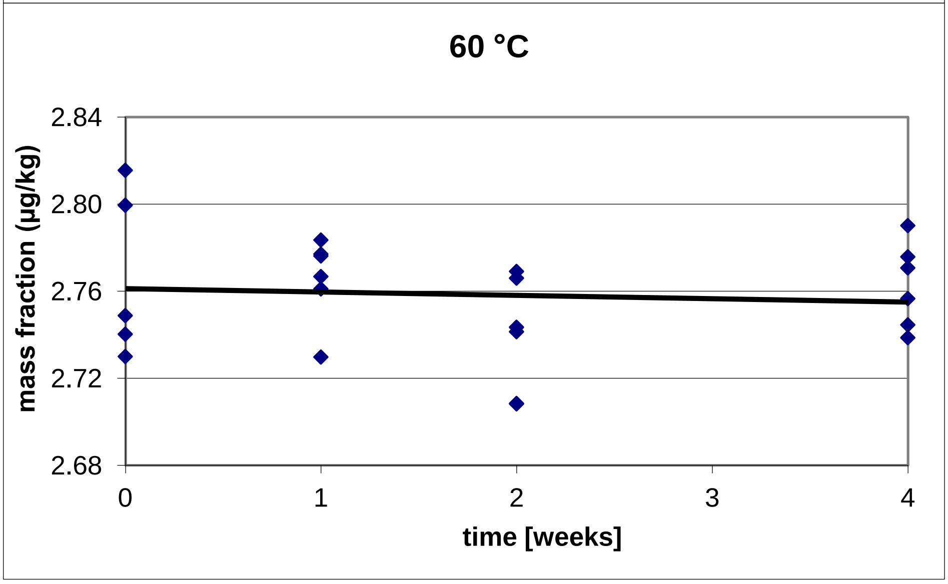


Short term stability graphs, Sb

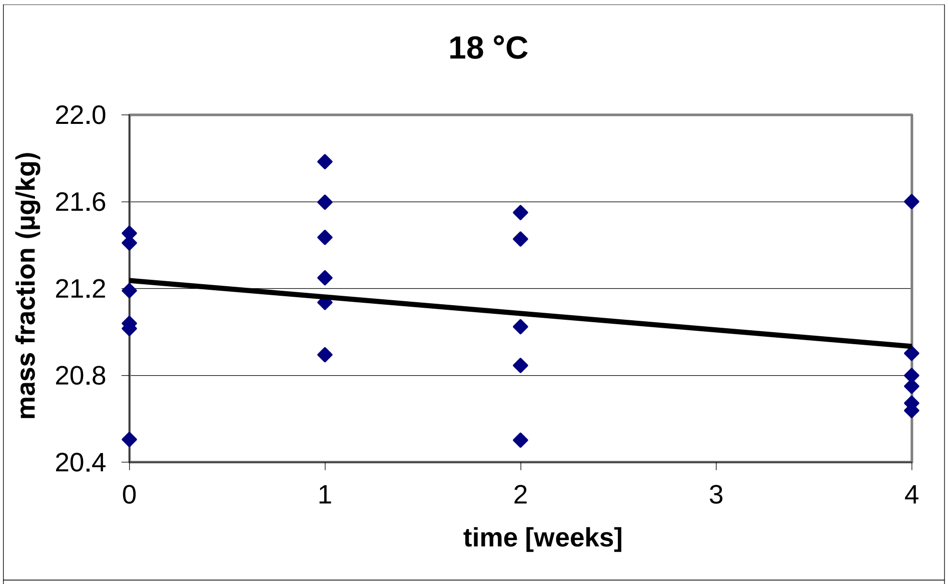


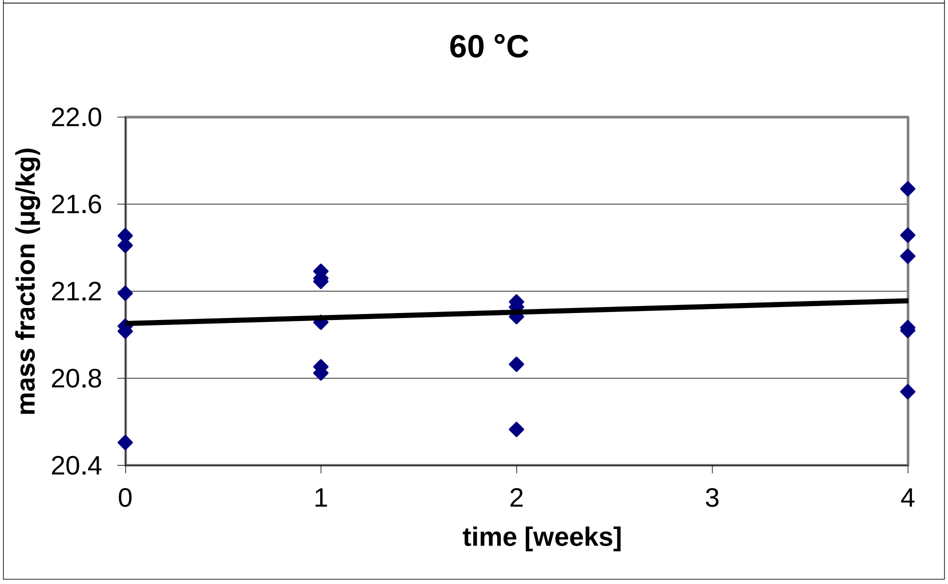
Short term stability graphs, Sn



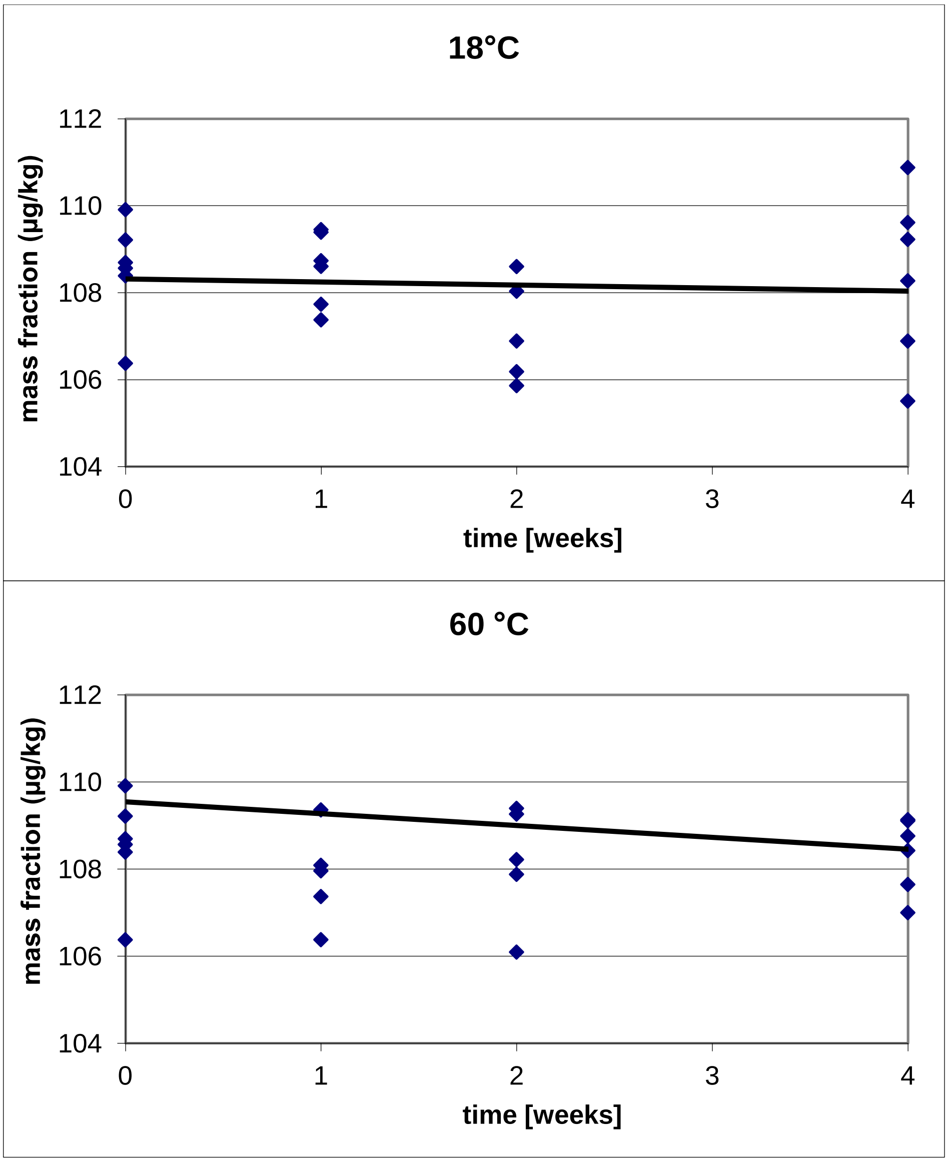


Short term stability graphs, Sr

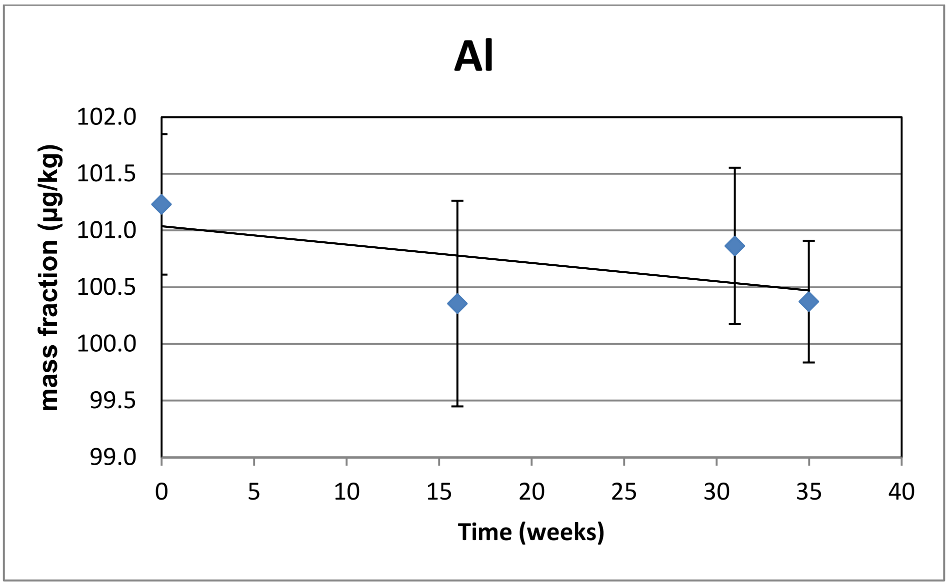


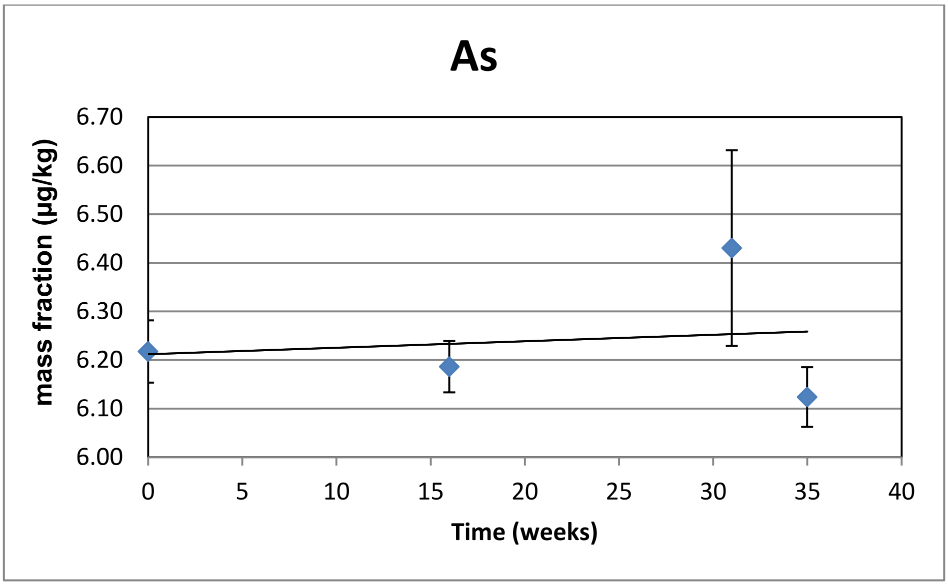


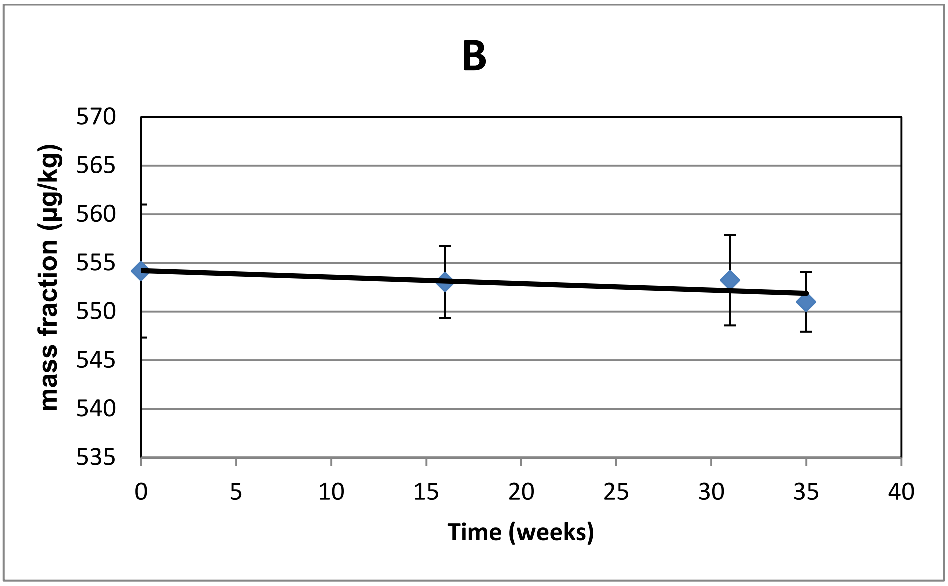
Short term stability graphs, Zn

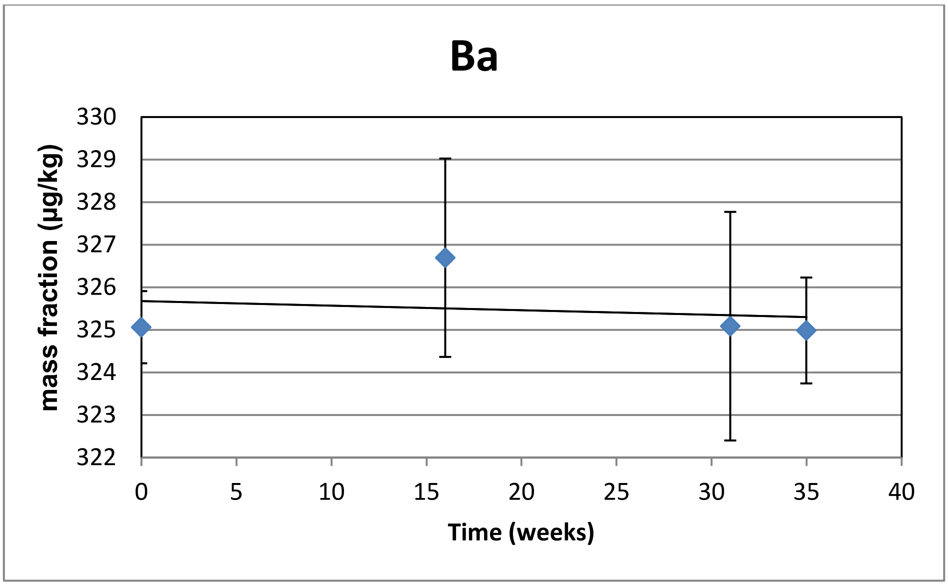


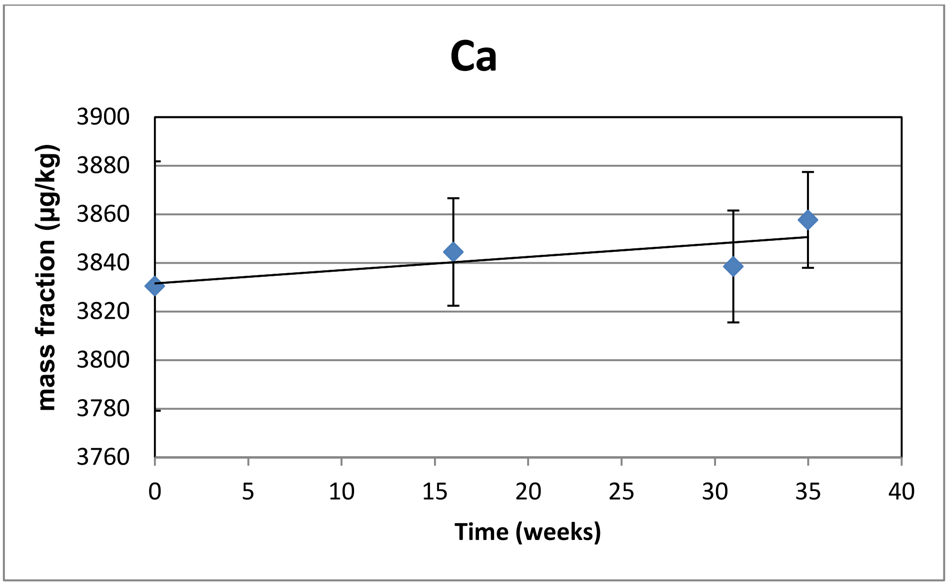
Annex 3 Graphs for Long Term Stability Studies

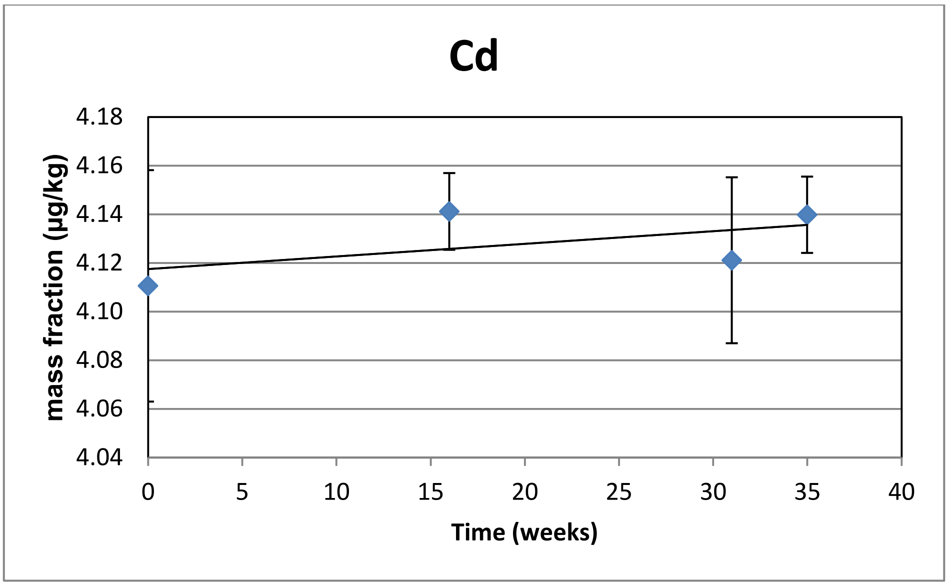


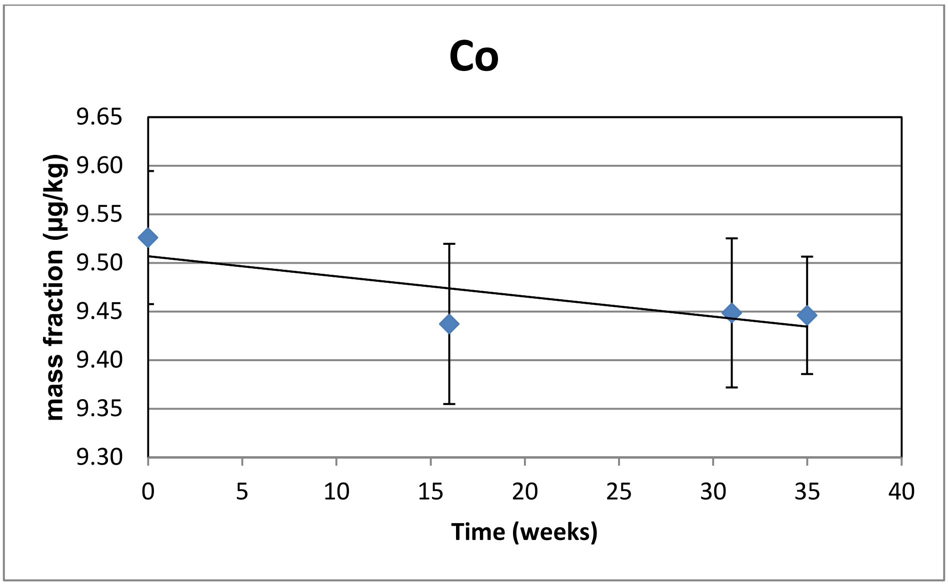


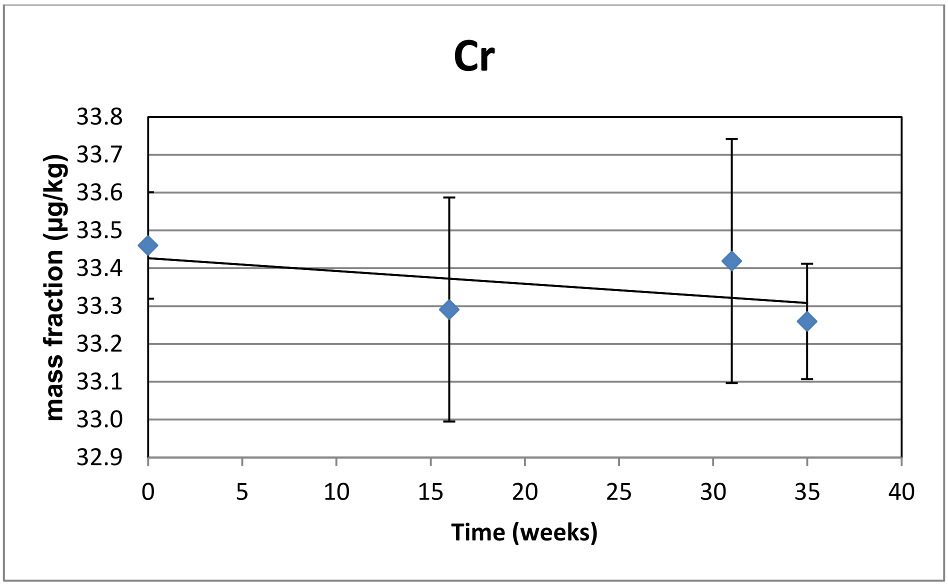

B
mass fraction (µg/kg)
570
565
560
555
550
545
540
535
0
5
10
15
20
25
30
35
40
Time (weeks)

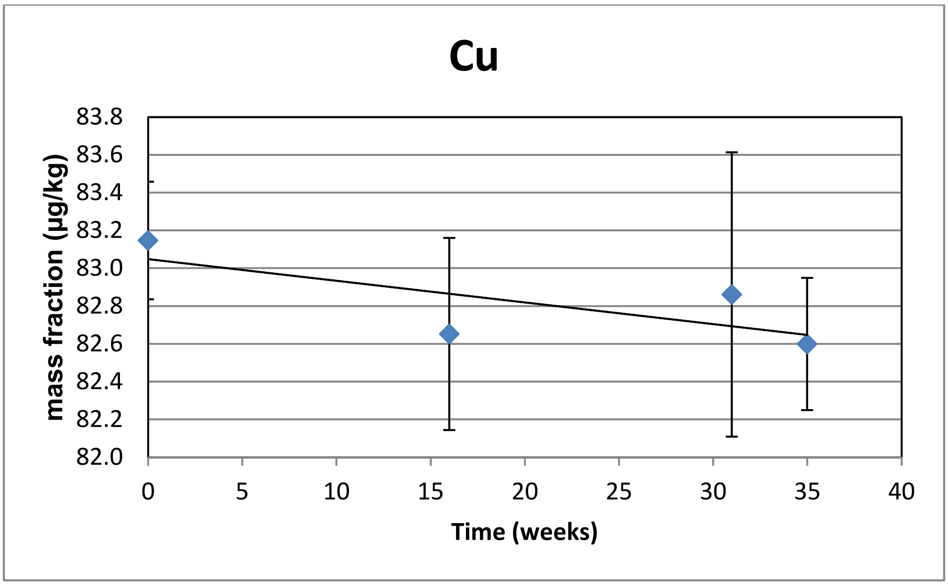

Ba
mass fraction (µg/kg)
330
329
328
327
326
325
324
323
322
0
5
10
15
20
25
30
35
40
Time (weeks)

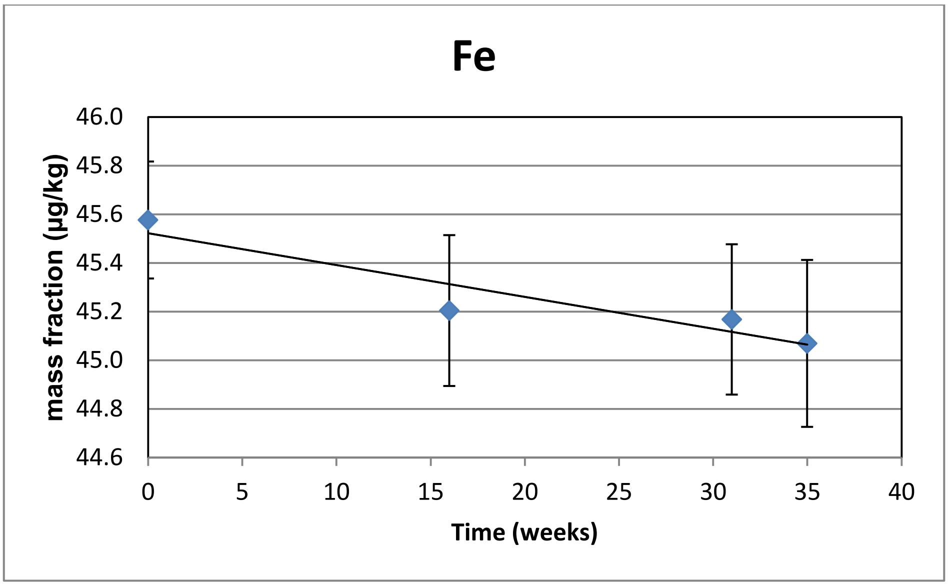

Ca
mass fraction (µg/kg)
3900
3880
3860
3840
3820
3800
3780
3760
0
5
10
15
20
25
30
35
40
Time (weeks)

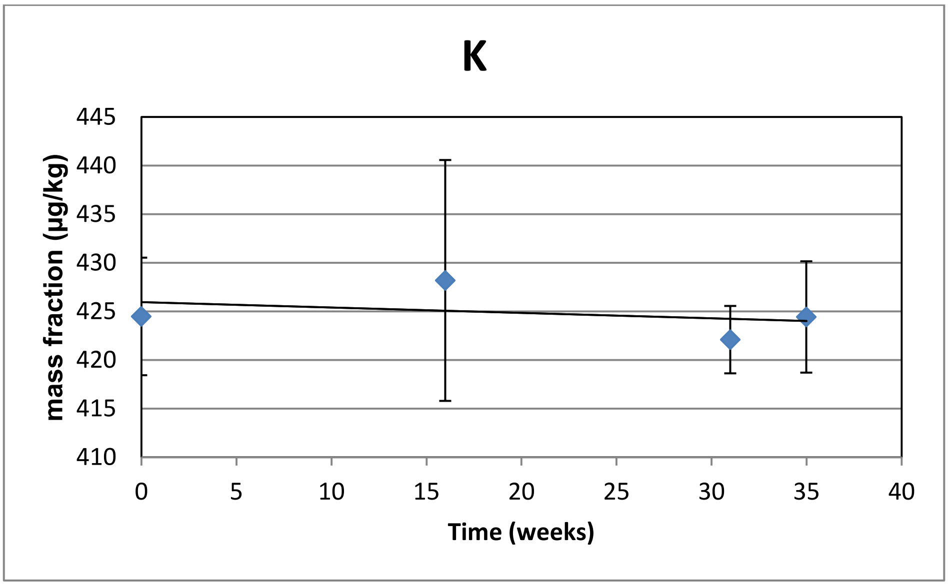

Cd
mass fraction (µg/kg)
4.18
4.16
4.14
4.12
4.10
4.08
4.06
4.04
0
5
10
15
20
25
30
35
40
Time (weeks)

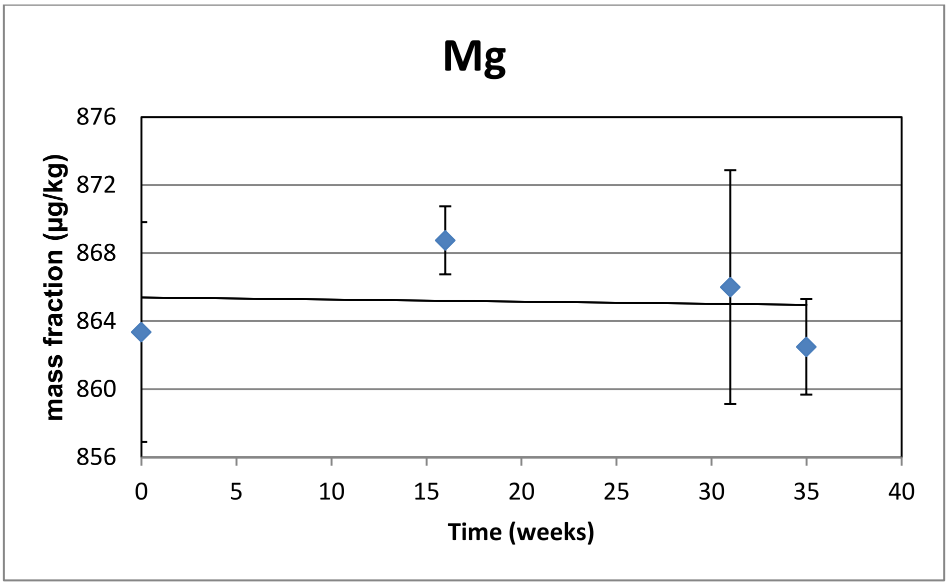

Co
mass fraction (µg/kg)
9.65
9.60
9.55
9.50
9.45
9.40
9.35
9.30
0
5
10
15
20
25
30
35
40
Time (weeks)

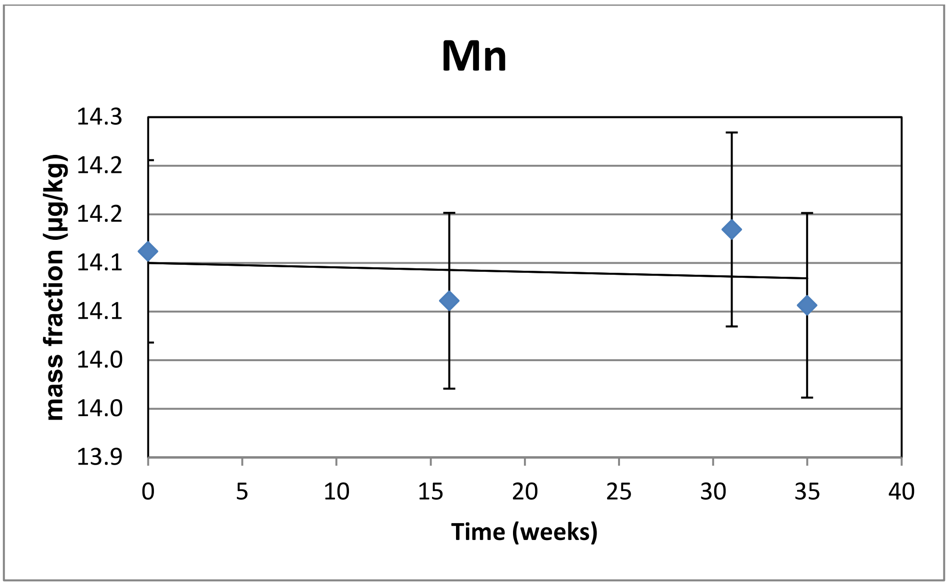

Cr
mass fraction (µg/kg)
33.8
33.7
33.6
33.5
33.4
33.3
33.2
33.1
33.0
32.9
0
5
10
15
20
25
30
35
40
Time (weeks)

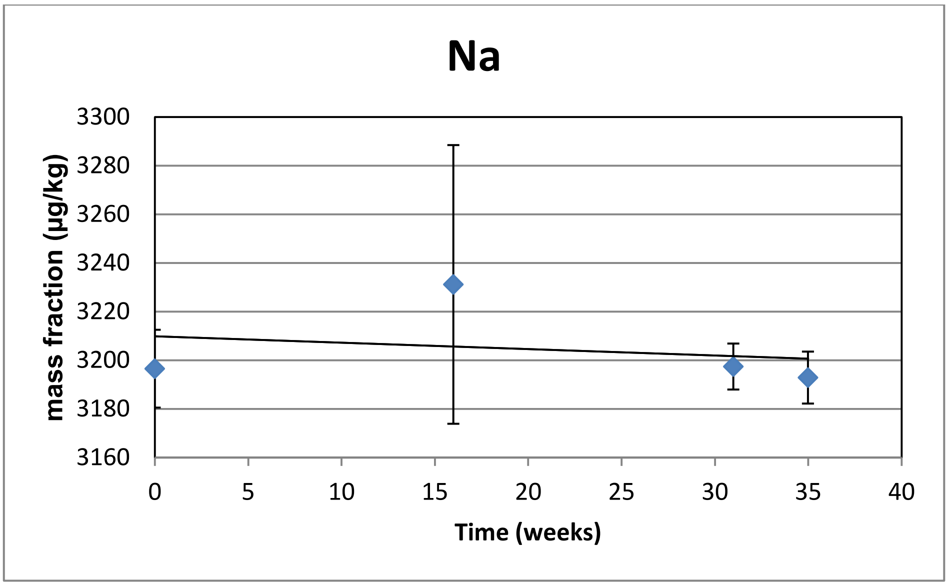

Cu
mass fraction (µg/kg)
83.8
83.6
83.4
83.2
83.0
82.8
82.6
82.4
82.2
82.0
0
5
10
15
20
25
30
35
40
Time (weeks)

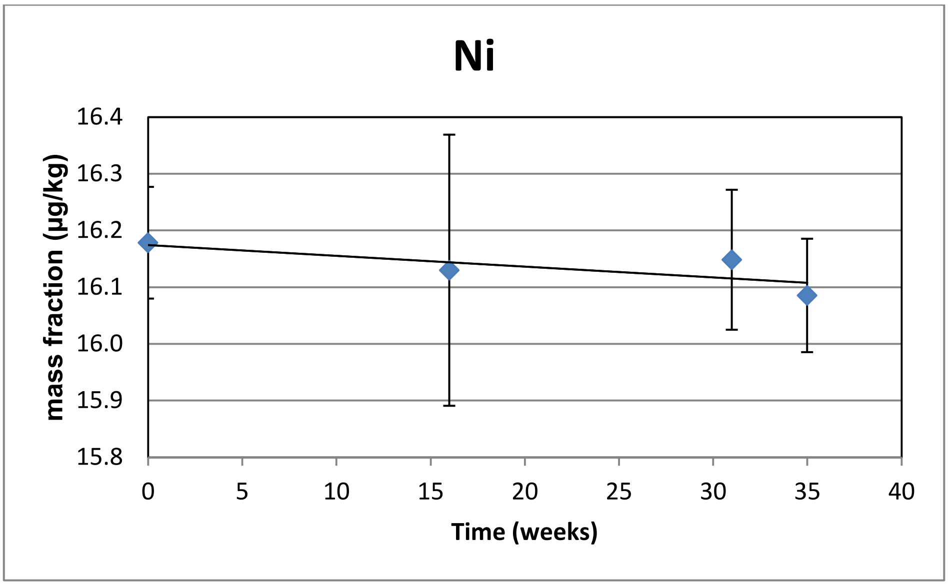

Fe
mass fraction (µg/kg)
46.0
45.8
45.6
45.4
45.2
45.0
44.8
44.6
0
5
10
15
20
25
30
35
40
Time (weeks)

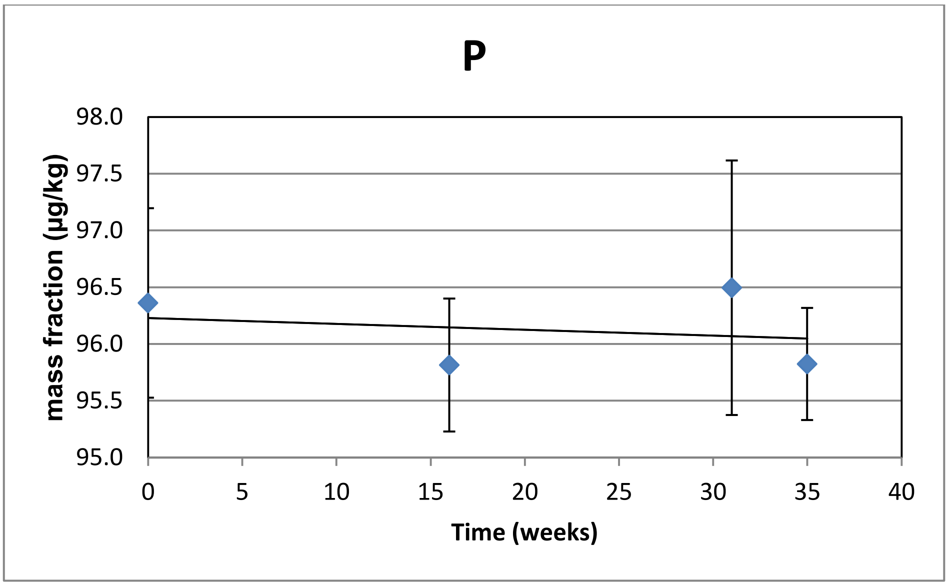

K
mass fraction (µg/kg)
445
440
435
430
425
420
415
410
0
5
10
15
20
25
30
35
40
Time (weeks)

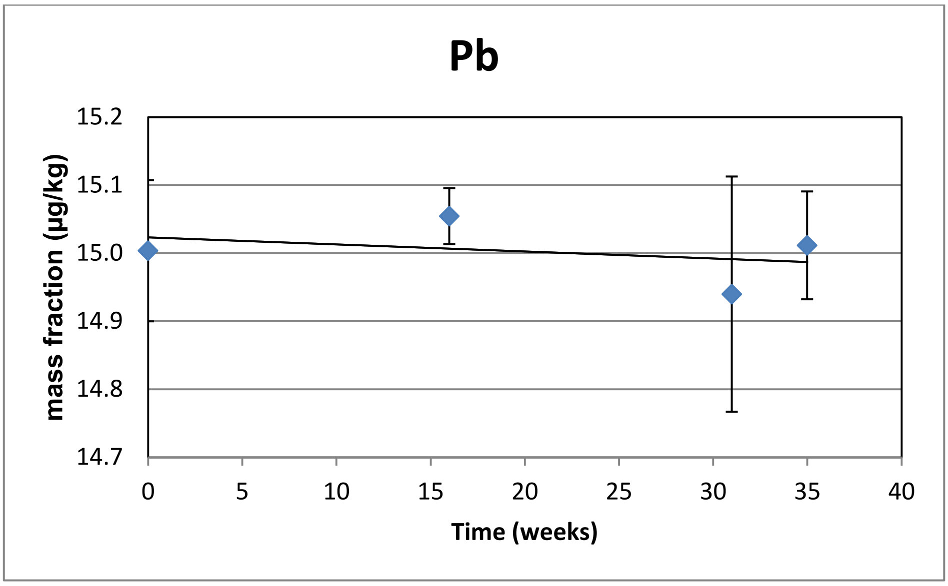

Mg
mass fraction (µg/kg)
876
872
868
864
860
856
0
5
10
15
20
25
30
35
40
Time (weeks)

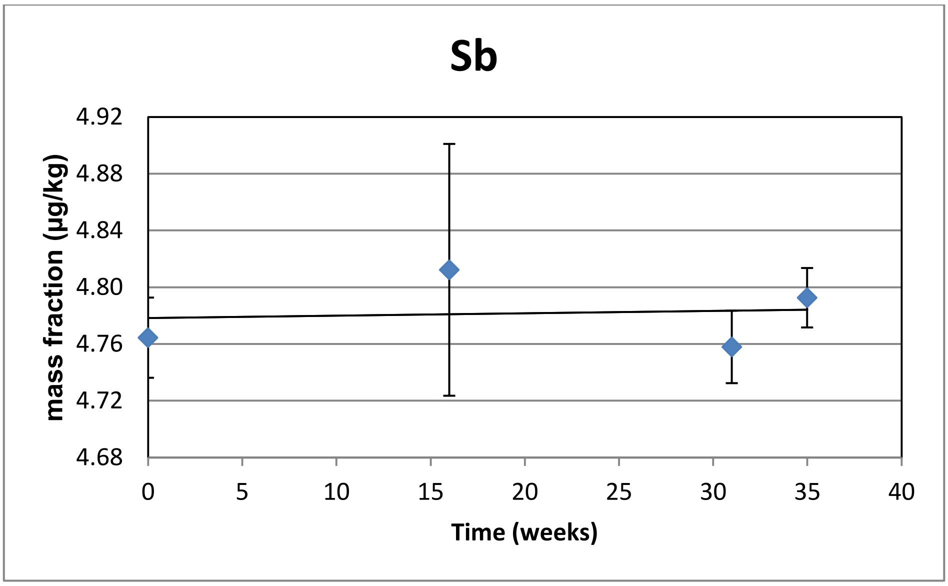

Mn
mass fraction (µg/kg)
14.3
14.2
14.2
14.1
14.1
14.0
14.0
13.9
0
5
10
15
20
25
30
35
40
Time (weeks)

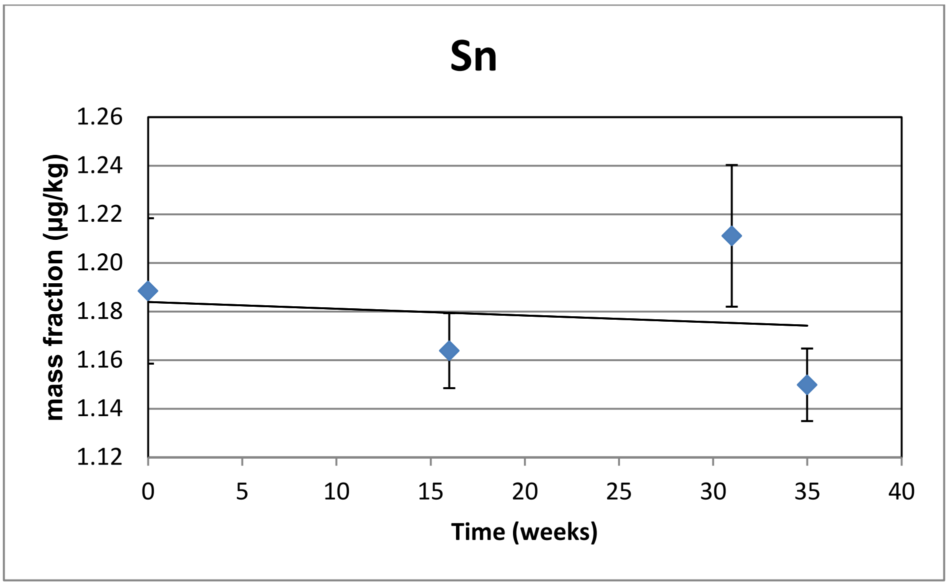

Na
mass fraction (µg/kg)
3300
3280
3260
3240
3220
3200
3180
3160
0
5
10
15
20
25
30
35
40
Time (weeks)

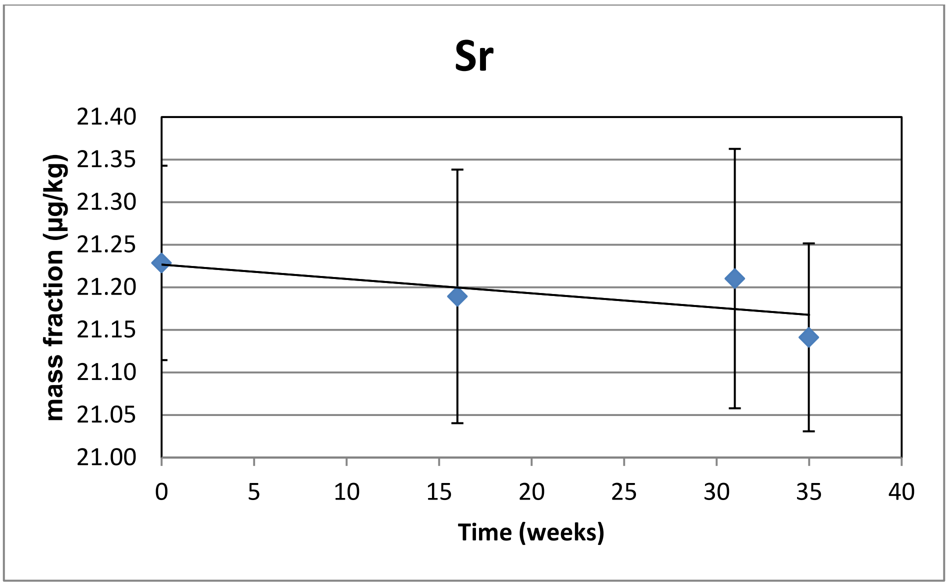

Ni
mass fraction (µg/kg)
16.4
16.3
16.2
16.1
16.0
15.9
15.8
0
5
10
15
20
25
30
35
40
Time (weeks)

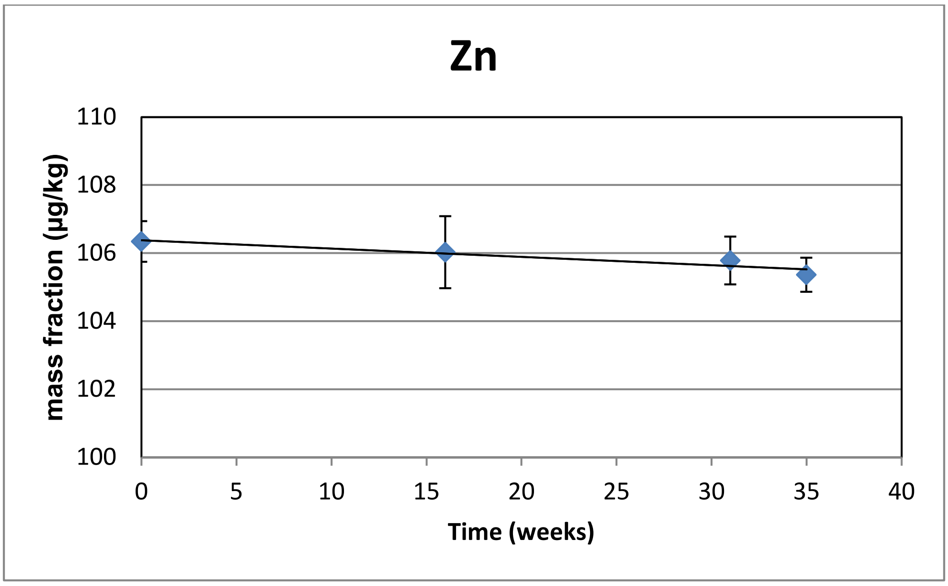

P
mass fraction (µg/kg)
98.0
97.5
97.0
96.5
96.0
95.5
95.0
0
5
10
15
20
25
30
35
40
Time (weeks)


Pb
15.2
15.1
15.0
14.9
14.8
14.7
mass fraction (µg/kg)
0
5
10
15
20
25
30
35
40
Time (weeks)

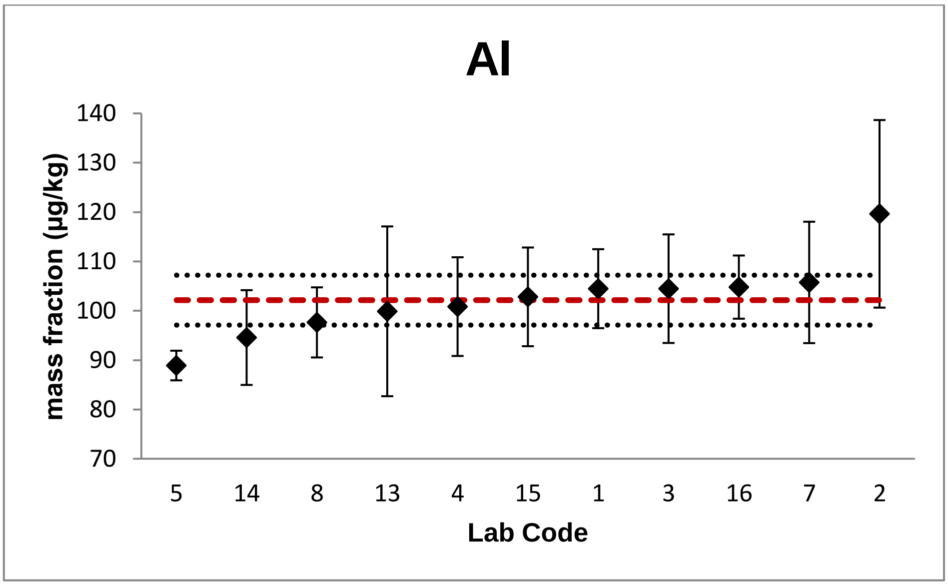

Sb
4.92
4.88
4.84
4.80
4.76
4.72
4.68
mass fraction (µg/kg)
0
5
10
15
20
25
30
35
40
Time (weeks)

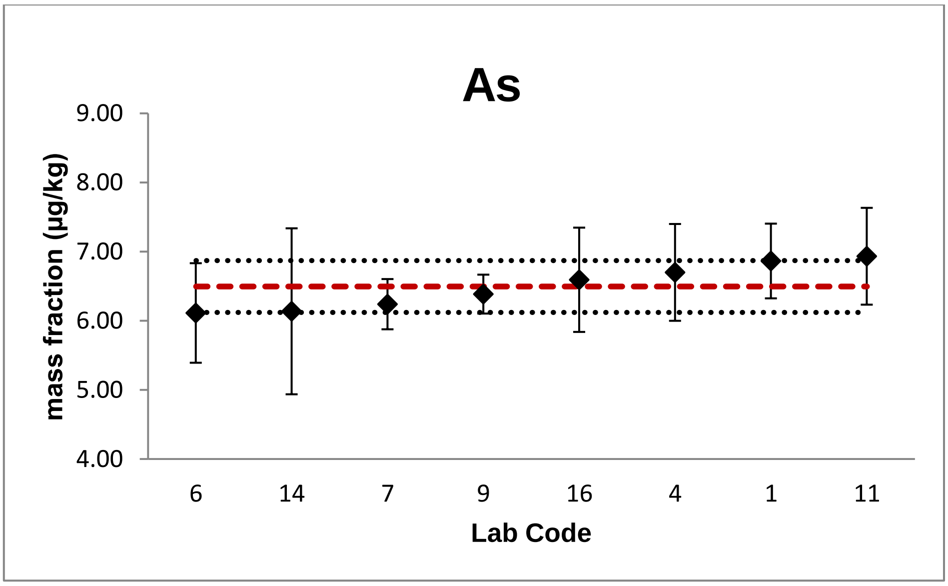

Sn
mass fraction (µg/kg)
1.26
1.24
1.22
1.20
1.18
1.16
1.14
1.12
0
5
10
15
20
25
30
35
40
Time (weeks)

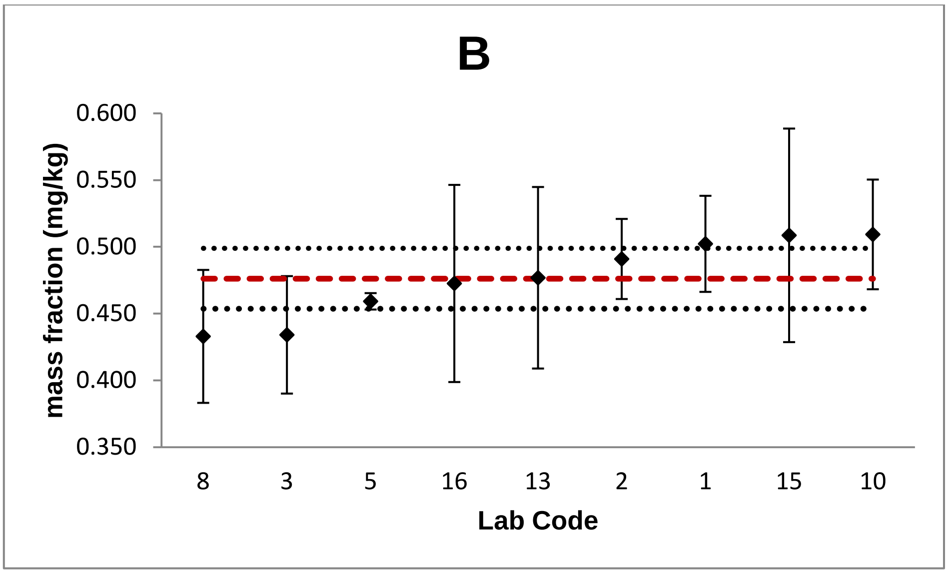

Sr
mass fraction (µg/kg)
21.40
21.35
21.30
21.25
21.20
21.15
21.10
21.05
21.00
0
5
10
15
20
25
30
35
40
Time (weeks)

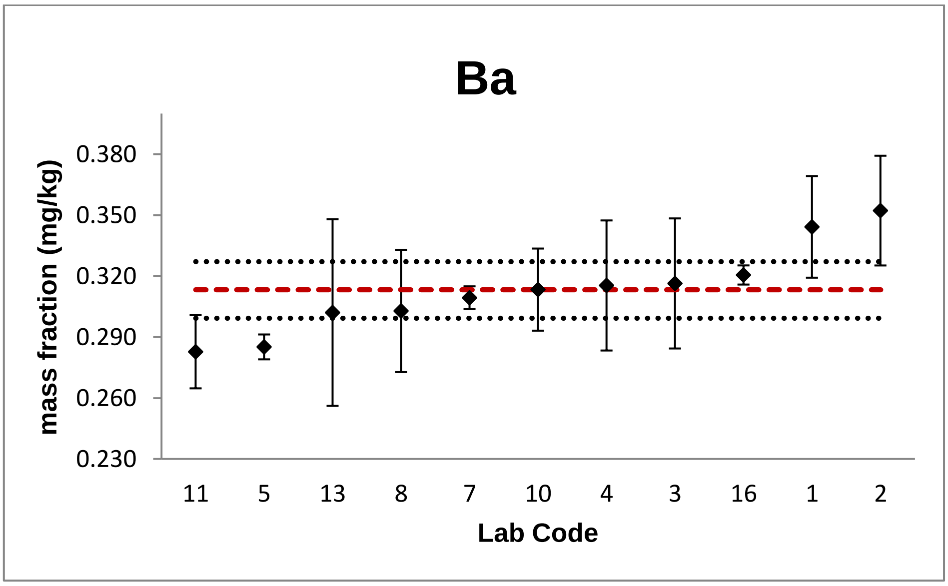

Zn
110
108
106
104
102
100
mass fraction (µg/kg)
0
5
10
15
20
25
30
35
40
Time (weeks)

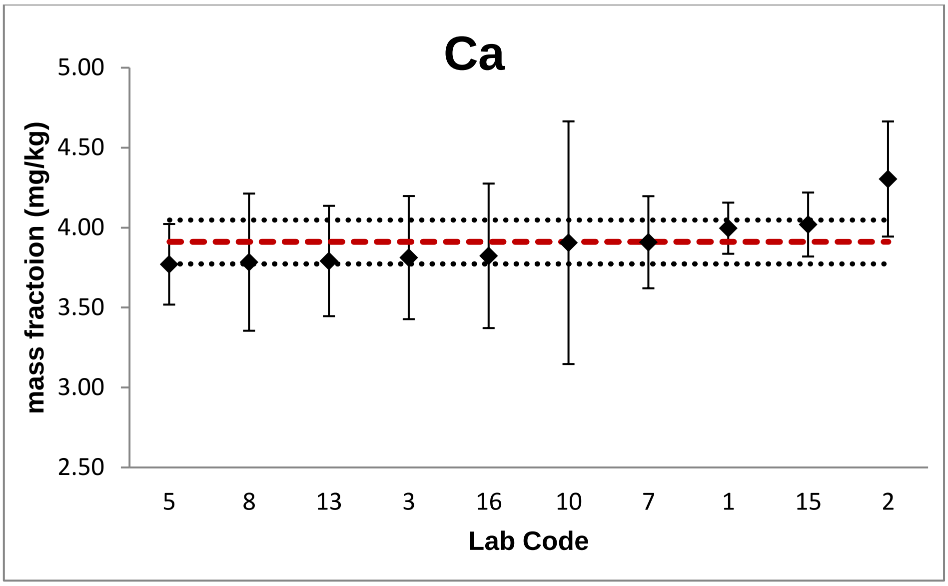
Annex 4 Graphs for Characterisation Study

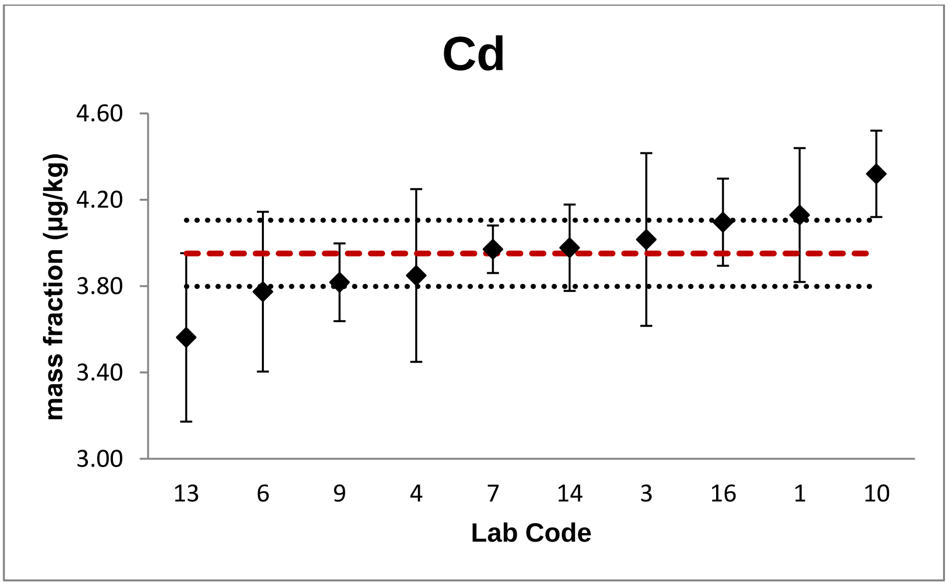


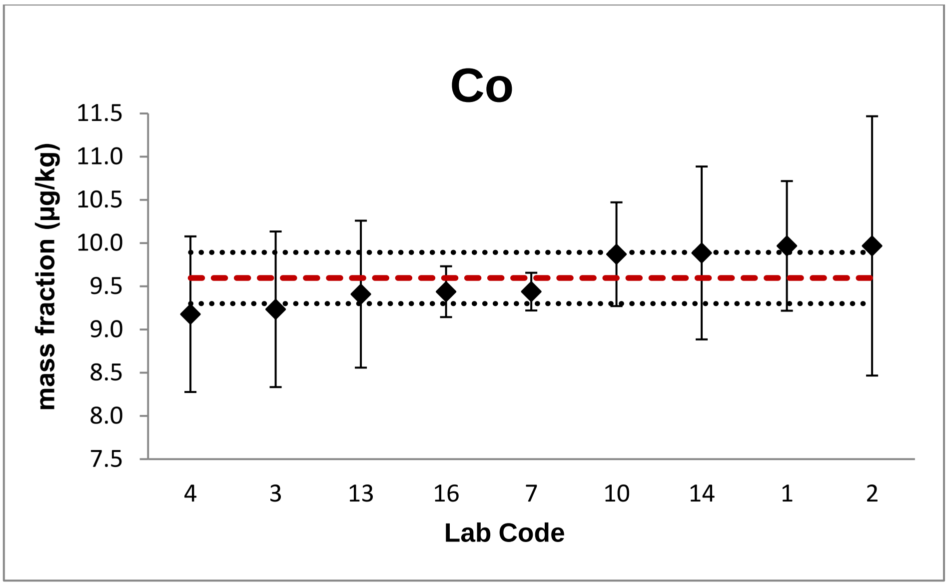


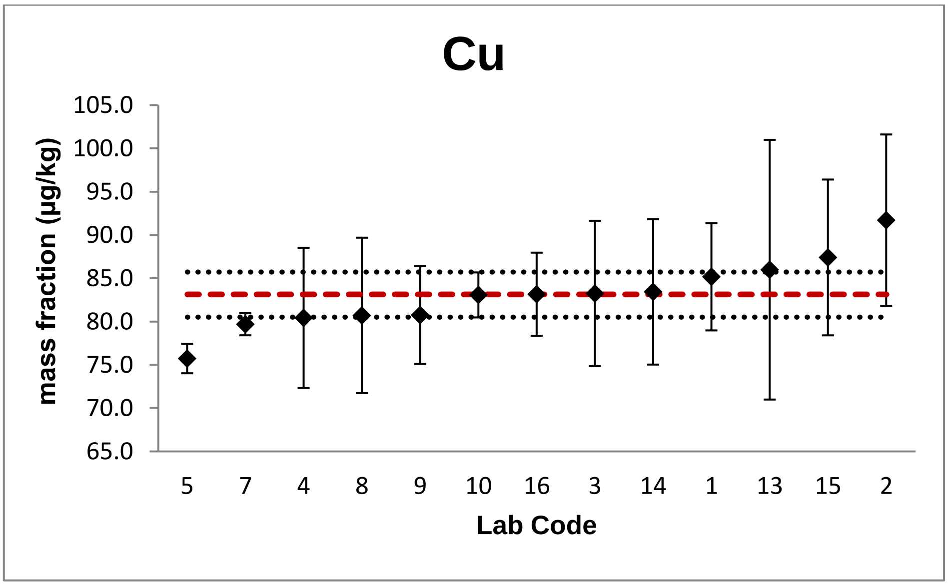

B
mass fraction (mg/kg)
0.600
0.550
0.500
0.450
0.400
0.350
8
3
5
16
13
2
1
15
10
Lab Code

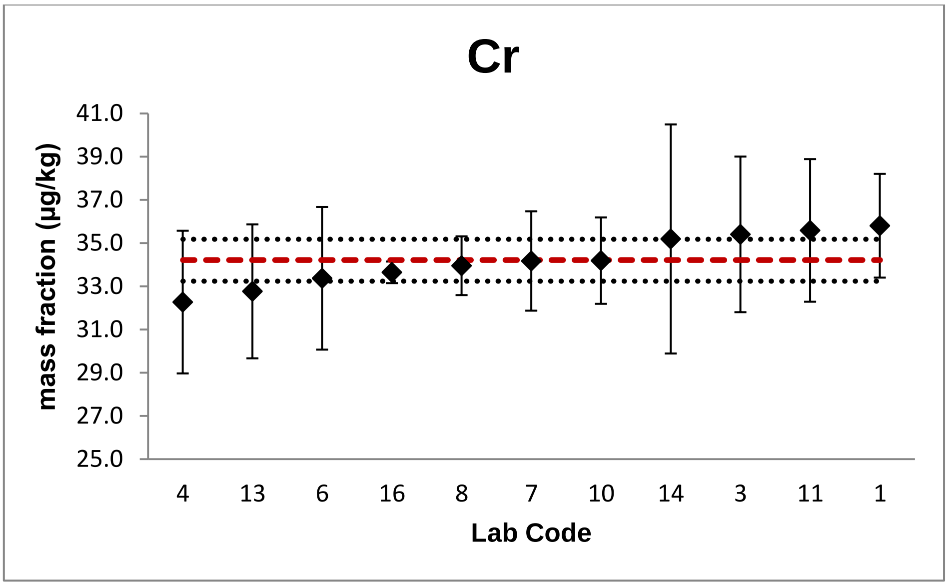

Ba
mass fraction (mg/kg)
0.380
0.350
0.320
0.290
0.260
0.230
11
5
13
8
7
10
4
3
16
1
2
Lab Code

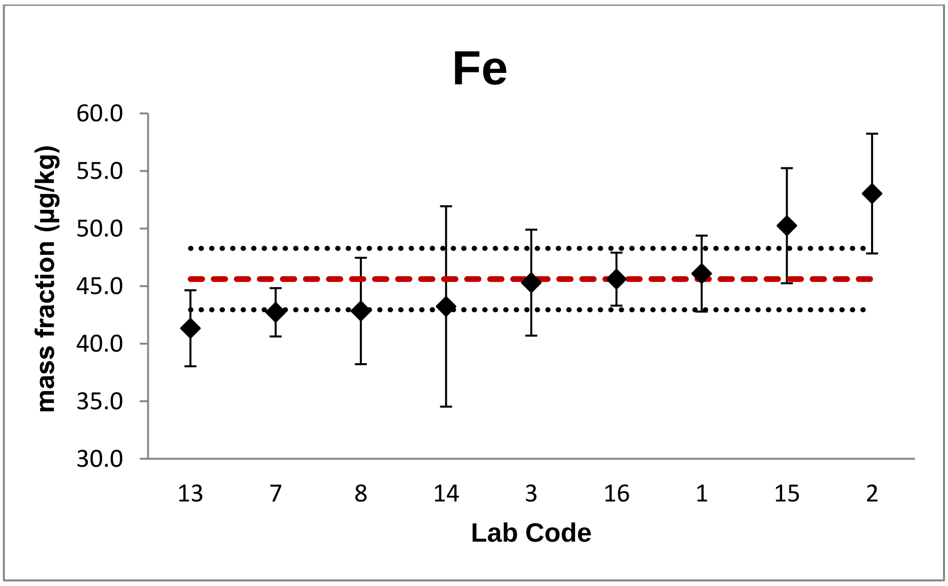

Ca
mass fractoion (mg/kg)
5.00
4.50
4.00
3.50
3.00
2.50
5
8
13
3
16
10
7
1
15
2
Lab Code

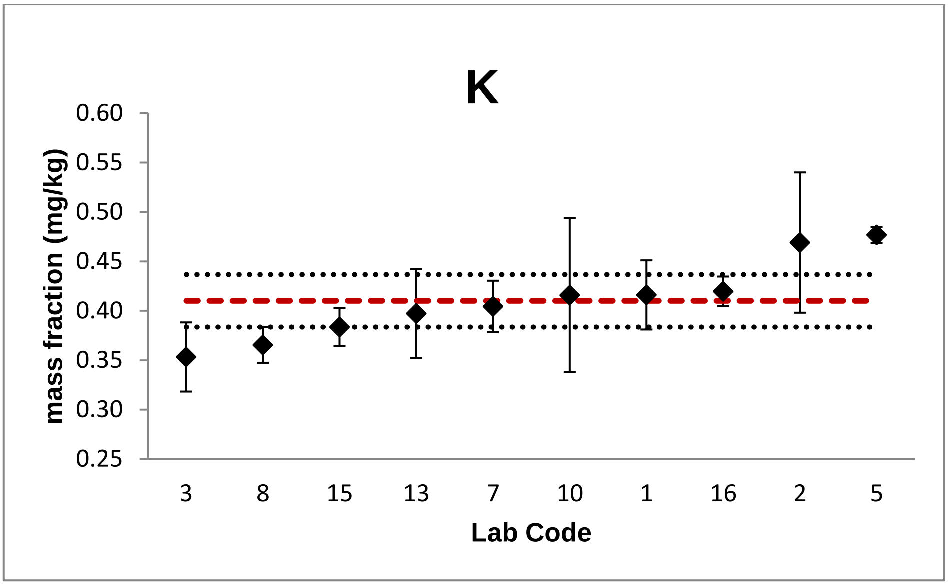

Cd
mass fraction (µg/kg)
4.60
4.20
3.80
3.40
3.00
13
6
9
4
7
14
3
16
1
10
Lab Code

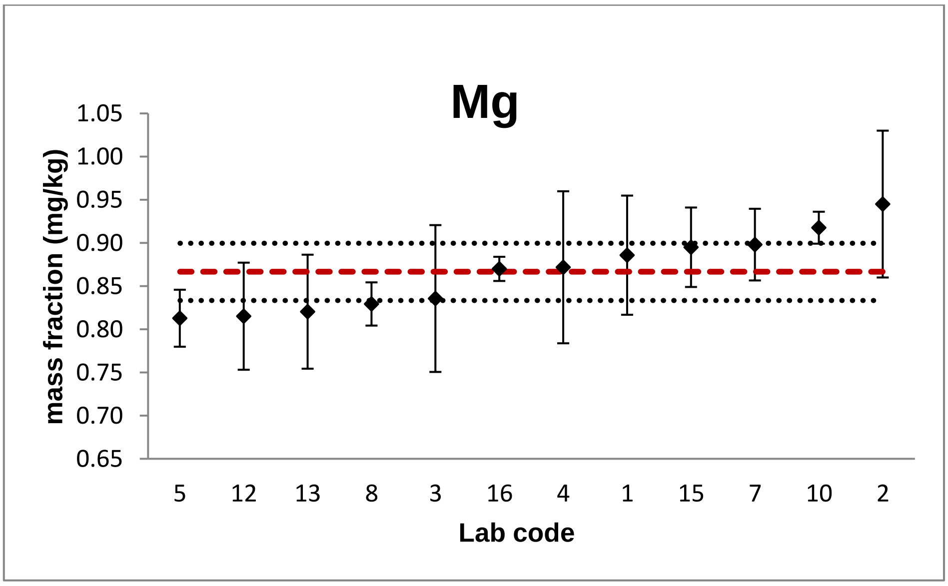

Co
mass fraction (µg/kg)
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
4
3
13
16
7
10
14
1
2
Lab Code

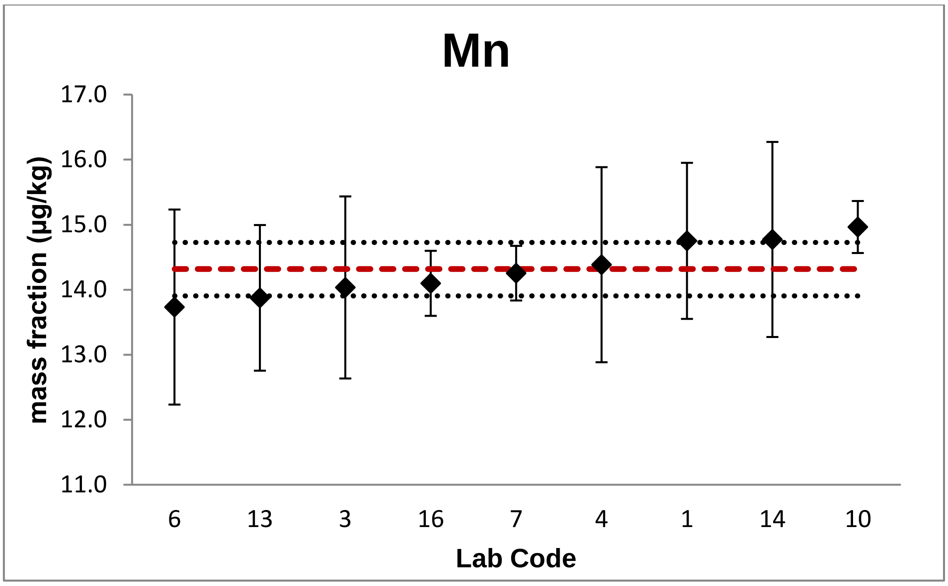

Cu
mass fraction (µg/kg)
105.0
100.0
95.0
90.0
85.0
80.0
75.0
70.0
65.0
5
7
4
8
9
10
16
3
14
1
13
15
2
Lab Code

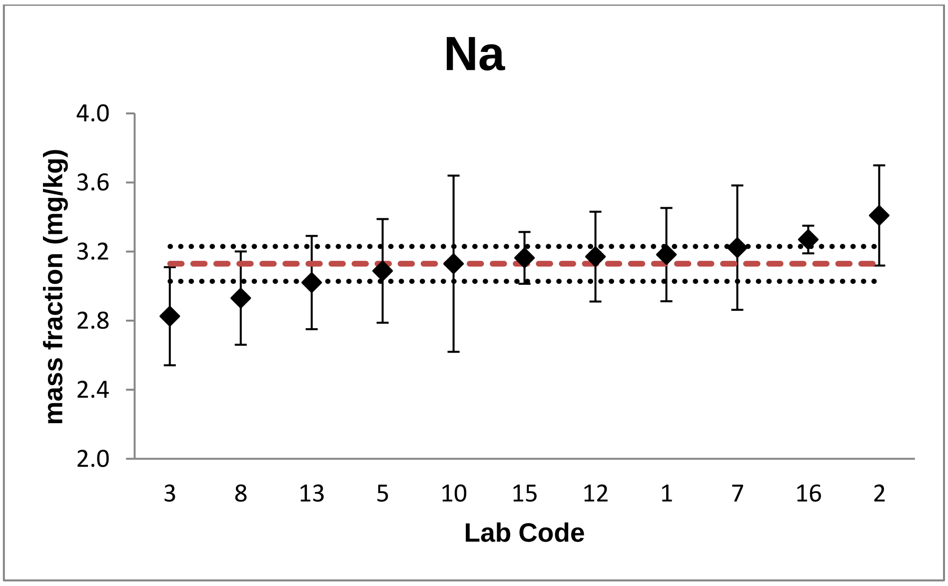

Cr
mass fraction (µg/kg)
41.0
39.0
37.0
35.0
33.0
31.0
29.0
27.0
25.0
4
13
6
16
8
7
10
14
3
11
1
Lab Code

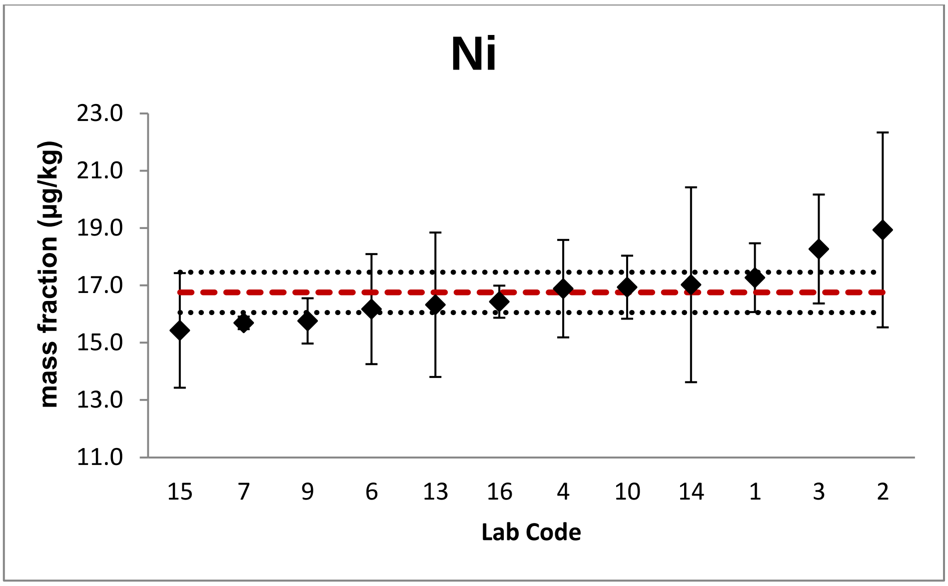

Fe
mass fraction (µg/kg)
60.0
55.0
50.0
45.0
40.0
35.0
30.0
13
7
8
14
3
16
1
15
2
Lab Code

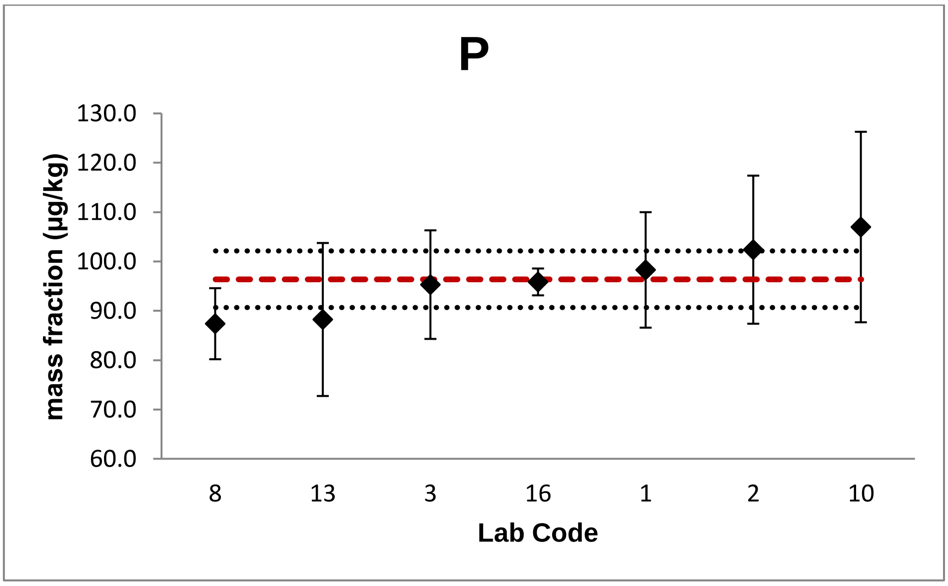

K
mass fraction (mg/kg)
0.60
0.55
0.50
0.45
0.40
0.35
0.30
0.25
3
8
15
13
7
10
1
16
2
5
Lab Code

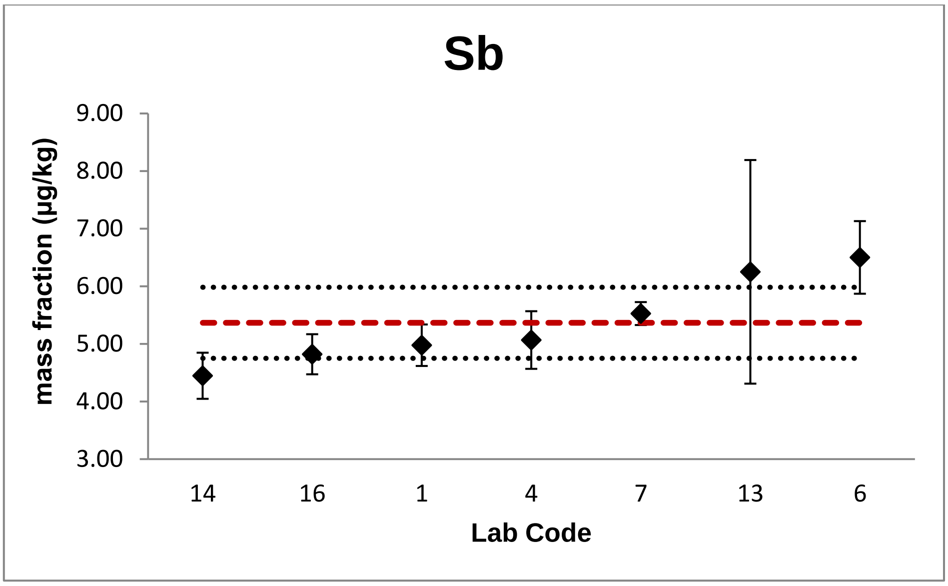

Mg
mass fraction (mg/kg)
1.05
1.00
0.95
0.90
0.85
0.80
0.75
0.70
0.65
5
12
13
8
3
16
4
1
15
7
10
2
Lab code

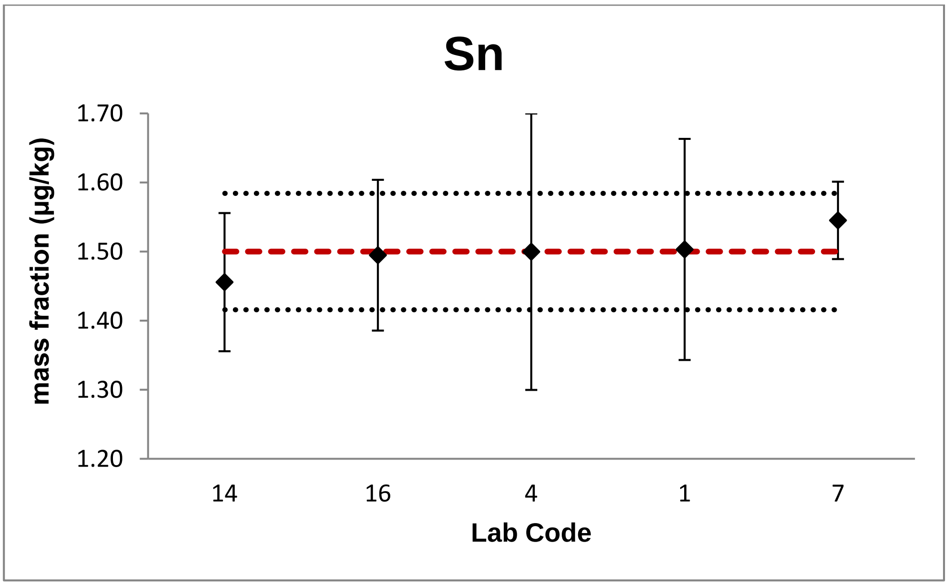

Mn
mass fraction (µg/kg)
17.0
16.0
15.0
14.0
13.0
12.0
11.0
6
13
3
16
7
4
1
14
10
Lab Code

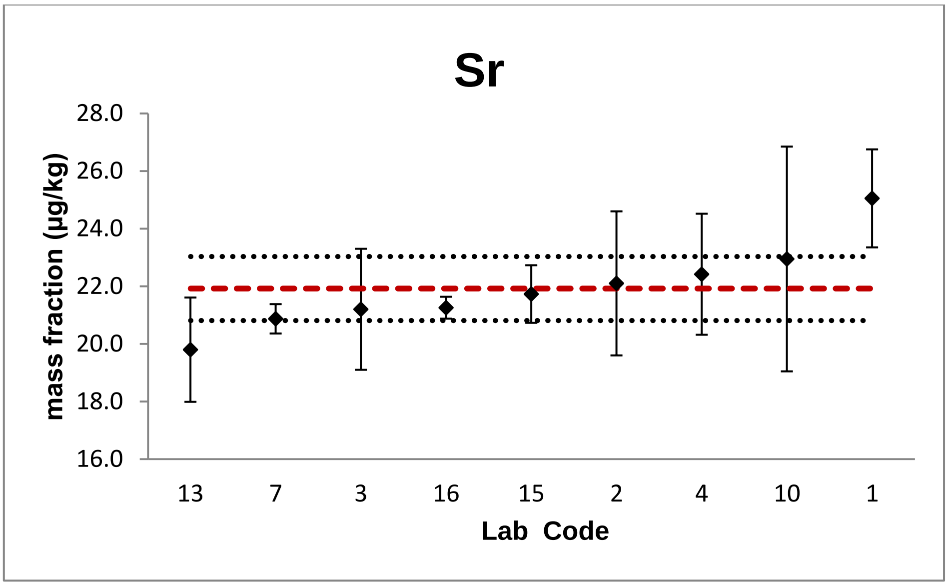

Na
mass fraction (mg/kg)
4.0
3.6
3.2
2.8
2.4
2.0
3
8
13
5
10
15
12
1
7
16
2
Lab Code

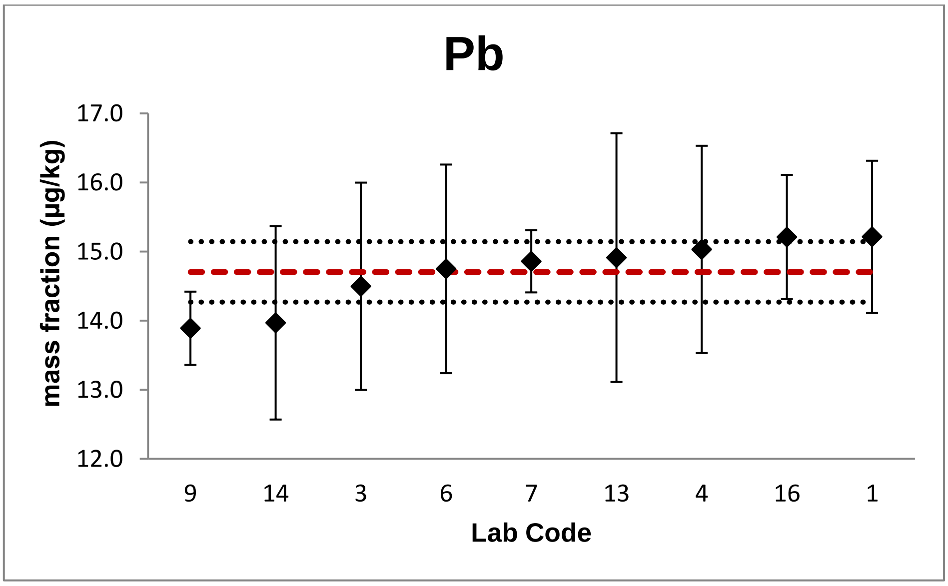

Ni
mass fraction (µg/kg)
23.0
21.0
19.0
17.0
15.0
13.0
11.0
15
7
9
6
13
16
4
10
14
1
3
2
Lab Code

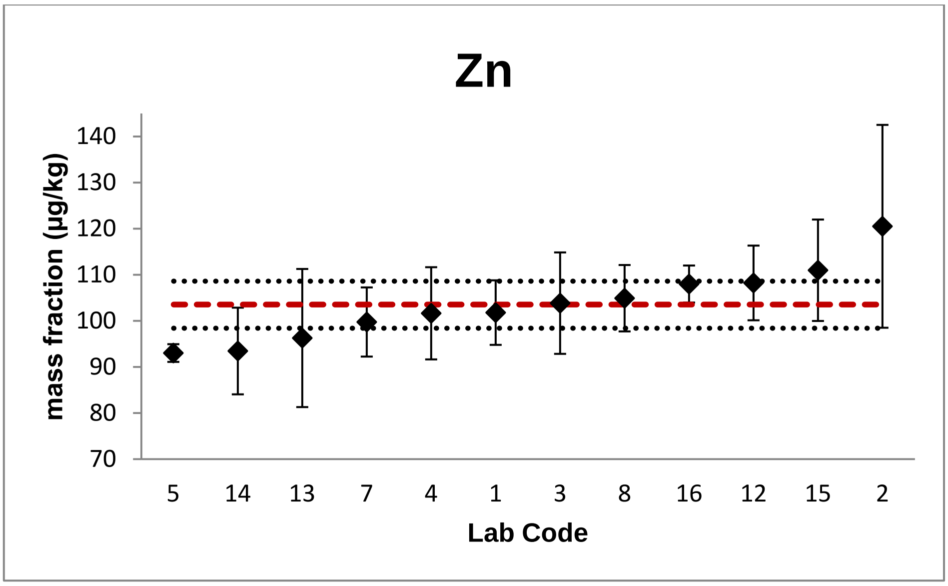

P
mass fraction (µg/kg)
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
8
13
3
16
1
2
10
Lab Code


Sb
mass fraction (µg/kg)
9.00
8.00
7.00
6.00
5.00
4.00
3.00
14
16
1
4
7
13
6
Lab Code


Sn
mass fraction (µg/kg)
1.70
1.60
1.50
1.40
1.30
1.20
14
16
4
1
7
Lab Code


Sr
mass fraction (µg/kg)
28.0
26.0
24.0
22.0
20.0
18.0
16.0
13
7
3
16
15
2
4
10
1
Lab Code


Pb
mass fraction (µg/kg)
17.0
16.0
15.0
14.0
13.0
12.0
9
14
3
6
7
13
4
16
1
Lab Code


Zn
mass fraction (µg/kg)
140
130
120
110
100
90
80
70
5
14
13
7
4
1
3
8
16
12
15
2
Lab Code