

Elements in Soil UME EnvCRM 03

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ABBREVIATIONS

AAS	atomic emission spectrometry
ANOVA	analysis of variance
ASV	anodic stripping voltammetry
α	significance level
BAM	Bundesanstalt für materialforschung und -prüfung (BAM), Germany
CRM	certified reference material
CV-AAS	cold vapour AAS
DMDM	Directorate of measures and precious metals, Serbia
HDPE	high density polyethylene
ICP-MS	inductively coupled plasma mass spectrometry
ICP-OES	inductively coupled optical emission spectrometry
ID ICP-MS	isotope dilution ICP-MS
ID TIMS	isotope dilution thermal ionization mass spectrometry
IJS	Jožef Stefan Institute, Slovenia
IS	internal standard
ISO	International Organization for Standardization
k_0 -INAA	k_0 instrumental neutron activation analysis
MP-AES	microwave plasma atomic emission spectroscopy
$MS_{between}$	mean square between-bottle from ANOVA
MS_{within}	mean square within-bottle from ANOVA
n	number of replicates per unit
NTUA	National Technical University of Athens, Greece
QC	quality control
RSD	relative standard deviation
s	standard deviation
s_{bb}	between-bottle standard deviation
SGT	single Grubbs' test
SI	International System of Units
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
UME	TÜBİTAK National Metrology Institute of Turkey, Turkey
u_{char}	standard uncertainty related to characterisation
u_{Its}	standard uncertainty related to long term stability
UW	University of Warsaw, Poland

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

ABSTRACT

The need for quality assessment of anthropogenic impact on environmental pollution is increasing due to discharge from various industries, the use of chemicals in agriculture and the consumption of fossil fuels. Diminishing resources such as soil used for the cultivation of agricultural products, plant and animal habitats are under severe pollution pressure and are at constant risk. The elemental composition of soil is a good indicator for determining soil quality for agriculture, detecting soil contamination, monitoring contamination events and atmospheric deposition. Within the scope of the joint research project in the framework of European Metrology Programme for Innovation and Research (EMPIR) “Matrix Reference Materials for Environmental Analysis”, it was aimed to develop capacity to produce certified reference materials (CRMs) for environmental analysis by transferring know-how between the partners and combining their skills to focus on environmental CRM production. The project is co-funded by the EU Horizon 2020 research and innovation programme and the EMPIR Participating States. As one of the outputs of this project, the production of a soil reference material in compliance with requirements of ISO Guide 34:2009 and ISO 17034:2016 has been performed. This reference material is intended to be a reference point for method development and validation for analysis of elements in soil. Selected target parameters (As, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Sb, V and Zn) were chosen due to toxicological or nutritional relevance.

INTRODUCTION

Reliable analysis of chemical indicators in soil samples for the purpose of environmental pollution assessment and monitoring poses one of the greatest analytical challenges, due to the complexity of sample matrix. Elements (As, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Sb, V and Zn) in soil represent target parameters for the candidate certified reference material (CRM). Laboratories performing sampling and tests in this field need matrix CRMs enabling appropriate quality control. National metrology institutes and designated institutes with proven metrological capabilities for the production and certification of such materials are necessary for the provision of quality data. The EMPIR joint research project ENVCRM [1] is aiming to develop capacity to produce CRMs for environmental analysis by transferring the theoretical and practical know-how between the partners and combining their skills to focus on environmental CRM production according to ISO Guide 34:2009 [2] and ISO 17034:2016 [3].

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

UME ENVCRM 03, the production of which was carried out by a project consortium described in this report, is intended to be used as a quality assurance and quality control tool especially by the laboratories involved in the monitoring prescribed by relevant environment legislations.

The parameters aimed to be certified in UME ENVCRM 03 are the following: mass fractions of As, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Sb, V and Zn. The values are stated as mass fractions in milligrams per kilogram (mg/kg). The target concentration levels for all elements were decided to reflect laboratories' needs.

PARTICIPANTS

The laboratories /organisations involved in production of the CRM and their contribution is summarized in Table 1.

Table 1. Institutes/organisations involved in activities

Activity	Laboratory / Organization
Project management and data evaluation	TÜBİTAK UME, Ulusal Metroloji Enstitüsü, Gebze - Kocaeli, TURKEY
Preliminary measurements	TÜBİTAK UME, Ulusal Metroloji Enstitüsü, Gebze - Kocaeli, TURKEY UW-University of Warsaw, Warsaw, POLAND
Sampling and processing	TÜBİTAK UME, Ulusal Metroloji Enstitüsü, Gebze - Kocaeli, TURKEY
Sterilization	GAMMA PAK Sterilizasyon Sanayi ve Ticaret A.Ş., Çerkezköy - Tekirdağ, TURKEY

Activity	Laboratory / Organization
Homogeneity study	TÜBİTAK UME, Ulusal Metroloji Enstitüsü, Gebze - Kocaeli, TURKEY IJS, Jožef Stefan Institute, Ljubljana, SLOVENIA
Stability studies	TÜBİTAK UME, Ulusal Metroloji Enstitüsü, Gebze - Kocaeli, TURKEY IJS, Jožef Stefan Institute, Ljubljana, SLOVENIA
Characterization study (in alphabetical order)	BAM, Bundesanstalt für Materialforschung und prüfung, Berlin, GERMANY DMDM, Directorate of Measures and Precious Metals, Belgrade, SERBIA IMBIH, Institute of Metrology of Bosnia and Herzegovina, Sarajevo, BOSNIA and HERZEGOVINA IJS, Jožef Stefan Institute, Ljubljana, SLOVENIA NTUA, National Technical University of Athens, Athens, GREECE TÜBİTAK UME, Ulusal Metroloji Enstitüsü, Gebze - Kocaeli, TURKEY UW, University of Warsaw, Warsaw, POLAND

MATERIAL PROCESSING

The soil used as raw material was collected from a previously investigated area [4], which is approximately 2 km far from the coal burning Çayırhan Power Plant, Ankara, Turkey to ensure levels of elements similar to the determined target levels. Collection site covered an area of approximately 1 m². Prior to collection, approximately the upper 10 cm was scraped to clean surface vegetation. Collected soil samples transported (in 30 L HDPE containers) to TÜBİTAK UME for further processing. About 60 kg of soil was obtained. Upon arrival at the TÜBİTAK UME, 60 kg of soil was placed in aluminum trays and dried at 35 °C for a week in an oven (BINDER ED 720, Germany) equipped with HEPA filtered fresh air supply. Large visible impurities (roots, stones, etc.) were removed manually.

For preliminary measurements, approximately 2 kg of dried soil were milled with a Planetary Ball Mill (FRITSCH Pulverisette 5, Germany) equipped with agate bowl and balls. Milled material was then sieved (Retsch AS200 Control, Germany) and material smaller than 90 micrometer size was collected and homogenized with a 3-D Mixer (WAB-Willy A. Bachofen AG Maschinenfabrik, Turbula T-10 B, Switzerland). Homogenized material was then riffle mixed with a sample divider equipped with a vibrating feeder (FRITSCH Laborette 24 and Laborette 27, Germany). Riffle mixed material was then filled into amber glass bottles. 0.5 g subsamples were digested, diluted and analyzed by HR-ICP MS (THERMO Element 2, Germany). Results of these preliminary measurements are summarized in Table 2.

Table 2. Preliminary analysis results of soil subsample

Element	Mass Fraction (mg/kg)	Target Range (mg/kg)	Maximum Target Uncertainty (%)
As	44 ± 5	40-80	20
Cd	0.11 ± 0.02	0.5-1.5	7
Co	6.3 ± 0.5	20-60	20
Cr	61 ± 7	50-110	20
Cu	10 ± 1	40-80	20
Hg	0.078 ± 0.022	0.2-1.5	20
Ni	29 ± 2	40-80	20
Pb	6.4 ± 0.1	40-80	11
Sb	0.43 ± 0.02	1.0-3.0	20
V	85 ± 5	30-100	20
Zn	36 ± 4	100-200	20

* Values written in the table with sign ± represents standard deviation.

Results showed that the candidate raw material is below the targeted amount of most elements (Cd, Co, Cu, Hg, Ni, Pb, Sb, Zn). Cadmium and lead were found to be significantly lower compared with the previously reported values [4]. Arsenic, vanadium and chromium were found to be within the target range. It was decided to blend this soil with a contaminated soil to reach target elemental content in the final product. Arsenic, chromium, iron, manganese and vanadium levels were decided to be accepted as they are present in the candidate soil.

Dried soil material was first sieved through 1940 micrometer sieve (SWECO, LS24S54, Belgium). Material smaller than 1940 micrometer was further sieved through 100 micrometer sieve. Materials bigger than 1940 and 100 micrometer were successively milled with Planetary Ball Mill (FRITSCH Pulverisette 5, Germany) equipped with agate bowl and balls and further sieved to yield fine soil smaller than 100 micrometer particle size. The homogenization of 32 kg of soil with a three-dimensional mixing was performed in one run of 4 hours on 3-D mixer (HKTM, MegaMix, Turkey) in a 60 L HDPE container. Homogenized material was then riffle mixed with sample divider equipped with a vibrating feeder (FRITSCH Laborette 24 and Laborette 27, Germany). Riffle mixed material was then split into vacuumed HDPE containers and stored at room temperature.

Particle size distribution (MALVERN, Mastersizer 2000, United Kingdom) was measured with laser diffraction method. The particle size analysis was consistent with the sieving step as the > 95% of the top particles were below 100 µm (Annex 1). Micrographs are valuable complements to sieve analysis and particle size distribution measurements because they reveal different fractions due to shape differences and they provide an accurate estimate of the particle size based on direct comparison with a certified length scale for individual particles. Micrographs of the homogenized soil were obtained using a light

microscope (LEICA, DM-1000, Germany) (Annex 1). The water content was measured at $(102 \pm 3) ^\circ\text{C}$ on two sub-samples; overall average was found as 3.5 % (m/m).

In order to obtain a soil product close to the target levels of elements in the final product, it was decided to produce a contaminated soil which will be blended with the homogenized original soil ($<100 \mu\text{m}$). Contaminated soil was also planned to be prepared from the original soil. A mix solution for spiking is prepared from Cd, Hg, Sb standard solutions (SCP Science), Co (metal powder, Riedel-de Haen, 12930, dissolved in conc. HNO_3), Cu (high purity metal, COOMET-RU-645 intercomparison study material, dissolved in conc. HNO_3), Ni (Ni(II)-nitrate hexahydrate, ALDRICH, 24,407-4, dissolved in deionized water), Pb (Lead(II)-nitrate, Merck, 1.07398.1000, dissolved in deionized water), Zn (metal, NIST SRM 728, dissolved in conc. HNO_3) to be mixed with 100 g of original soil. A slurry of soil (100 g) and mix solution (173 g) is mixed, placed into an aluminum tray and dried in oven (BINDER ED 720, Germany) equipped with HEPA filtered fresh air supply at $45 ^\circ\text{C}$ (1 day), $35 ^\circ\text{C}$ (3 days). Total of 15 trays of material prepared as described above were dried. Ball milling, sieving (< 90 micrometer, RETSCH, AS200 Control, Germany) followed by 3-D homogenization (WAB-Willy A. Bachofen AG Maschinenfabrik, Turbula T-10 B, Switzerland) yielded the desired contaminated soil. Particle size analysis (Annex 1) of the contaminated soil showed that there is no significant difference with the original soil, which is a good indication for good mixing of these soils to each other. Stepwise blending was performed as follows: first 0.9 kg spiked soil was mixed with 0.9 kg original soil, then 2 kg more original soil was added and mixed. A 4 kg portion of the original soil was added and mixed again. Stepwise addition and mixing continued until reaching a total of 30.1 kg mixture of spiked soil and original soil. Final homogenization for total 12 hours (3 x 4 hours) on 3-D mixer (HKTm, MegaMix, Turkey) in a 60 L HDPE container followed by splitting the homogenized final product into HDPE containers. Filling and capping were done manually using a balance (Sartorius, MSA524S-100-DA, Germany) in a HEPA filtered laminar flow cabinet (AQUARIA, Bio Activa 180, Italy). Filled bottles were labelled following the filling order. 25 g material was filled per unit, and total 1179 units were filled within two days. The candidate CRM was sterilized by γ -irradiation with a ^{60}Co source at a minimum dose of 25 kGy. After this step, the bottles were stored at $4 ^\circ\text{C}$ in the dark. All stages of processing are summarized and presented as a flow diagram in Annex 2.

HOMOGENEITY

Homogeneity study between the units is performed to show that the assigned values are valid for all units within the stated uncertainty. Homogeneity study between the units is performed with a number of samples representing the whole batch. In this project, 12 units were selected by using random stratified sampling for each of the two participant laboratories. Homogeneity tests were carried out by measuring three sub-samples under repeatability conditions. The samples to be analyzed were introduced to the instruments by random order to find out any trend arising from analytical and/or filling sequences.

The data obtained by both laboratories were evaluated statistically by regression analysis for the presence of any trend in analytical and filling sequence at 99 % confidence level. Only analytical sequence trends were found for As, Co, Cu, Hg, Ni, Pb, Zn (for data by TÜBİTAK UME) and V (for both institutes) and data were not reprocessed to correct for these trends. Filling sequence was detected for Fe, but the relative uncertainty arose from this heterogeneity was found to be as low as 0.32 %. Grubbs test (one sided) was applied to all data for the presence of outlier at 99% confidence level and one outlier for Co, Fe and Mn were detected. Since no technical reason can be found to reject these data, all outliers were included in the homogeneity calculations. Data were visually checked whether all individual data follow a unimodal

distribution using histograms and normal probability plots. It was found that the distribution was normal and unimodal (except Cu by IJS). Minor deviations from unimodality of the individual values do not significantly affect the estimate of between-unit standard deviations. The results of all statistical evaluations are given in Table 3.

Table 3. Statistical Evaluation Results of Homogeneity for Soil

Parameter (Lab)	Any trend?		Any outlier?		Distribution
	Analytical sequence	Filling sequence	All data	Unit averages	All data
As (UME)	Yes	No	No	No	Normal/unimodal
As (IJS)	No	No	No	No	Normal/unimodal
Cd (UME)	No	No	No	No	Normal/unimodal
Cd (IJS)	No	No	No	No	Normal/unimodal
Co (UME)	Yes	No	Yes	No	Normal/unimodal
Co (IJS)	No	No	No	No	Normal/unimodal
Cr (UME)	No	No	No	No	Normal/unimodal
Cr (IJS)	No	No	No	No	Normal/unimodal
Cu (UME)	Yes	No	No	No	Normal/unimodal
Cu (IJS)	No	No	No	No	Not Normal/unimodal
Fe (UME)	No	Yes	Yes	No	Normal/unimodal
Fe (IJS)	nr	nr	nr	nr	nr
Hg (UME)	Yes	No	No	No	Normal/unimodal
Hg (IJS)	No	No	No	No	Normal/unimodal
Mn (UME)	No	No	Yes	No	Normal/unimodal
Mn (IJS)	No	No	No	No	Normal/unimodal
Ni (UME)	Yes	No	No	No	Normal/unimodal
Ni (IJS)	No	No	No	No	Normal/unimodal
Pb (UME)	Yes	No	No	No	Normal/unimodal
Pb (IJS)	nr	nr	nr	nr	nr
Sb (UME)	No	No	No	No	Normal/unimodal
Sb (IJS)	No	No	No	No	Normal/unimodal
V (UME)	Yes	No	No	No	Normal/unimodal
V (IJS)	Yes	No	No	No	Normal/unimodal
Zn (UME)	Yes	No	No	No	Normal/unimodal
Zn (IJS)	No	No	No	No	Normal/unimodal

nr: not reported by the laboratory.

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:

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

MS_{within} : Mean squares within-unit

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

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

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

n : Number of replicates per unit

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

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

$v_{MS_{within}}$: Degrees of freedom of MS_{within}

The occurrence of $MS_{between} < MS_{within}$ can be seen, if material heterogeneity is smaller than that can be detected by the analytical methodology used.

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} (Table 4). As a conservative approach, the uncertainty contribution for homogeneity, $u_{bb,rel}$ is accepted as the highest value of the two institute's results (except for Fe and Pb which were only measured by TÜBİTAK UME). Other exception was Cu result by IJS which was decided not to be used due to detected technical problem in the measurements.

Table 4. Results of the homogeneity study

Parameter (Lab)	$S_{wb,rel, \%}$	$S_{bb,rel, \%}$	$u^*_{bb,rel, \%}$	$u_{bb,rel, \%}$
As (UME)	2.85	$MS_{between} < MS_{within}$	0.88	0.88
As (IJS)	2.09	0.45	0.65	0.65
Cd (UME)	1.76	1.12	0.55	1.12
Cd (IJS)	1.68	0.71	0.52	0.71
Co (UME)	2.50	$MS_{between} < MS_{within}$	0.78	0.78
Co (IJS)	1.28	0.57	0.40	0.57
Cr (UME)	2.43	2.69	0.75	2.69
Cr (IJS)	2.77	0,78	0.86	0.86
Cu (UME)	2.45	$MS_{between} < MS_{within}$	0.76	0.76
Cu (IJS)	4.41	2.54	0.82	2.54*
Fe (UME)	0.90	0.32	0.28	0.32
Fe (IJS)	nr	nr	nr	nr
Hg (UME)	2.85	$MS_{between} < MS_{within}$	0.88	0.88
Hg (IJS)	2.96	1.17	0.92	1.17
Mn (UME)	0.68	0.34	0.21	0.34
Mn (IJS)	1.42	$MS_{between} < MS_{within}$	0.44	0.44
Ni (UME)	1.85	$MS_{between} < MS_{within}$	0.57	0.57
Ni (IJS)	1.73	1.08	0.54	1.08
Pb (UME)	1.39	$MS_{between} < MS_{within}$	0.43	0.43
Pb (IJS)	nr	nr	nr	nr
Sb (UME)	1.99	$MS_{between} < MS_{within}$	0.62	0.62
Sb (IJS)	3.15	1.22	0.98	1.22
V (UME)	2.12	$MS_{between} < MS_{within}$	0.66	0.66
V (IJS)	3.35	$MS_{between} < MS_{within}$	1,04	1.04
Zn (UME)	2.31	$MS_{between} < MS_{within}$	0.72	0.72
Zn (IJS)	1.17	0.38	0.36	0.38

* Technical problem was detected for the measurements

The between-unit variation for all elements is found to be low. Maximum allowed target uncertainty for homogeneity was 2 % and it was achieved (except Cr). The plotted data used for the evaluation of homogeneity can be found in Annex 3.

STABILITY

The stability studies were carried out using an isochronous design [6]. In this approach, samples are stored for a certain time at different temperature conditions. Afterwards, the samples are moved to conditions where further degradation can be assumed to be negligible ("reference conditions"), effectively "freezing" the degradation status of the materials. At the end of the isochronous storage, the samples are analyzed simultaneously under repeatability conditions. Analysis of the material (after various exposure times and temperatures) under repeatability conditions greatly improves the sensitivity of the stability tests.

For the Short Term Stability (STS) test, two different temperatures (18 °C and 60 °C) and 4 time points (0, 1, 2, and 4 weeks) were tested. Fourteen samples were randomly selected for each of the participating laboratories and 12 samples were subjected to the test temperatures for the specified time intervals.

Test samples were moved to +4 °C (reference temperature) after completion of the test time. All samples were analyzed at the same time. Three replicate measurements by IJS and two replicate measurements by TÜBİTAK UME for each unit were performed under the repeatability conditions.

The data for each temperature were first examined by single Grubbs test for both 95 % and 99 % confidence intervals to find out outliers. Number of detected outliers are given in the Table 5. Since no technical reason can be found to reject these data, all outliers were included in the STS calculations.

Values calculated for each time point were plotted against the time for the assessment of short term stability. The relationship between variables was analyzed in order to determine if any significant change exists with the testing time (regression analysis). It was found that the slopes were not significantly different than zero (except for Cd by TÜBİTAK UME at 60 °C in the 95% confidence interval) for all parameters in the 95 % and 99 % confidence intervals. Short term stability plots are presented in Annex 4.

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 outliers by applying the single 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 $\alpha = 0.05$ (95 % confidence level). The graphs are presented in Annex 4.

Outliers (shown in Table 5) 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 summarized in Table 5.

Uncertainty calculations are performed using Equation (4). Maximum time for transfer is chosen as four weeks.

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

where,

- RSD* : relative standard deviation of the points on the regression line,
t_i : time point for each replicate,
 \bar{t} : mean of all time points,
t : maximum time suggested for transfer (four weeks).

Results obtained from short term stability tests are presented in Table 5.

Table 5. Results of short term stability tests

Parameter (Lab)	18 °C	60 °C	Number of outliers in 95% confidence interval*		Number of outliers in 99% confidence interval*		Any significant trend in 95% confidence interval?		Any significant trend in 99% confidence interval?	
	<i>U_{sts,rel}</i> (%)	<i>U_{sts,rel}</i> (%)	18 °C	60 °C	18 °C	60 °C	18 °C	60 °C	18 °C	60 °C
As (UME)	1.12	1.48	-	-	-	-	No	No	No	No
As (IJS)	1.56	1.16	-	-	-	-	No	No	No	No
Cd (UME)	2.04	2.36	-	1	-	-	No	Yes	No	No
Cd (IJS)	0.80	0.72	1	1	1	1	No	No	No	No
Co (UME)	0.92	0.88	-	1	-	1	No	No	No	No
Co (IJS)	1.00	0.92	-	-	-	-	No	No	No	No
Cr (UME)	2.68	2.80	-	-	-	-	No	No	No	No
Cr (IJS)	2.56	2.28	-	-	-	-	No	No	No	No
Cu (UME)	0.80	1.08	-	1	-	1	No	No	No	No
Cu (IJS)	2.36	1.88	-	-	-	-	Yes	No	No	No
Fe (UME)	0.44	0.56	-	-	-	-	No	No	No	No
Fe (IJS)	nr	nr	nr	nr	nr	nr	nr	nr	nr	nr
Hg (UME)	5.12	4.80	-	-	-	-	No	No	No	No
Hg (IJS)	2.20	2.20	-	-	-	-	No	No	No	No
Mn (UME)	0.24	0.40	-	-	-	-	No	No	No	No
Mn (IJS)	0.60	0.64	-	-	-	-	No	No	No	No
Ni (UME)	1.46	1.28	-	1	-	-	No	No	No	No
Ni (IJS)	1.00	0.84	-	-	-	-	No	No	No	No
Pb (UME)	0.88	1.24	1	-	-	-	No	No	No	No
Pb (IJS)	nr	nr	nr	nr	nr	nr	nr	nr	nr	nr
Sb (UME)	1.48	1.32	-	-	-	-	No	No	No	No
Sb (IJS)	2.56	2.68	-	-	-	-	No	No	No	No
V (UME)	0.96	1.08	-	1	-	1	No	No	No	No
V (IJS)	1.68	1.68	-	-	-	-	No	No	No	No
Zn (UME)	1.00	1.04	1	-	-	-	No	No	No	No
Zn (IJS)	1.44	1.12	-	-	-	-	No	No	No	No

*SGT: Single Grubbs' Test, nr: not reported by the laboratory

As a conservative approach, the uncertainty contribution for short term stability, $u_{sts,rel}$ is accepted as the highest value obtained for the two test temperatures by two institute's (shown in bold, Table 4) except for Fe and Pb which were analyzed only by TÜBİTAK UME.

The material is found to be stable at 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 without applying any cooling elements.

Long Term Stability Results:

Shelf life of the CRM has been determined through long term stability measurements. For the measurements, four units for each of the months of 0, 3, 6 and 12 have been stored at +18 °C and transferred to reference temperature (+4 °C) after each period of time to be measured isochronously afterwards. Four units, designated as reference units, of the month 0 was stored at +4 °C.

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

No outlying data was detected by Grubbs' test. The graphs were plotted against time and the regression lines were calculated. The relative long term stability uncertainty, $u_{lts,rel}$ for each parameter is then calculated using Equation (5) for the required shelf life as [6]:

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

where

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

t_i : the time point for each replicate,

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

t : the proposed shelf life at 18 °C (12 months).

The uncertainty contribution u_{lts} was calculated for 12 months (t) at 18 °C. As a conservative approach, the relative uncertainty contribution for long term stability, $u_{lts,rel}$ is accepted as the highest value obtained by two institute's (shown in bold, Table 6). This uncertainty was one of the four parameters contributing to the overall uncertainty of the certified values. The results are given in Table 6. The graphs for long term stability are given in Annex 5.

Table 6. Results of the long-term stability tests for 12 months

Parameter (Lab)	Is the slope significantly different from zero at 18 °C?*	$u_{its,rel}$ [%] for shelf-life of 12 months at 18 °C
As (UME)	No	0.71
As (IJS)	No	0.98
Cd (UME)	No	1.24
Cd (IJS)	No	0.80
Co (UME)	No	0.54
Co (IJS)	No	1.36
Cr (UME)	No	5.83
Cr (IJS)	No	1.26
Cu (UME)	No	0,64
Cu (IJS)	No	0.85
Fe (UME)	No	1.02
Fe (IJS)	No	nr
Hg (UME)	No	1.84
Hg (IJS)	No	1.29
Mn (UME)	No	0.64
Mn (IJS)	No	0.98
Ni (UME)	No	1.35
Ni (IJS)	No	1.10
Pb (UME)	No	0.67
Pb (IJS)	No	nr
Sb (UME)	No	3.28
Sb (IJS)	No	1.36
V (UME)	No	1.31
V (IJS)	No	1.24
Zn (UME)	No	0.61
Zn (IJS)	No	0.57

*Data are evaluated at confidence level of 95 %,
nr: not reported by the laboratory

Based on the results obtained, 18 °C was found to be suitable to keep the samples for up to 12 months. In addition, to ensure stability beyond the initially determined shelf life, stability will be re-evaluated in certain periods, based on the results of post-certification monitoring.

CHARACTERIZATION

According to ISO 17034, the characterization and the value assignment can be carried out in different ways. In this project, the characterization of the material was carried out by an interlaboratory comparison exercise. The participating laboratories were partners of the EnvCRM project consortium [1]. The detailed information about the laboratories is given in the participants section. The participating laboratories used validated methods (including potentially primary methods such as ID ICP-MS and k_0 -INAA).

Each laboratory received two bottles of samples which were selected such from the whole set of samples that they represent the whole produced batch. The samples were selected randomly from the set of samples by the random stratified sampling technique. Each laboratory was asked to report at least six independent measurement results for two sample units, together with 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 the reported results.

If the laboratory provided results using more than one method, all results were taken into account during the assignment of the certified value. A list of laboratories with their abbreviations and their corresponding methodologies used for the measurements are summarized in Table 7. More details about the measurement methods are given in Annex 6.

Characterization standard uncertainty (u_{char}) is calculated using Equation (6) by taking into account the uncertainties and the standard deviation of the means reported by the participating laboratories except As and Sb. Characterization standard uncertainties for As and Sb are accepted as the uncertainty reported by IJS for the k_0 -INAA method. Graphs for characterization data are presented in Annex 7, where error bars represent expanded uncertainties reported by the laboratories.

$$u_{\text{char}} = \sqrt{\bar{u}_{\text{labs}}^2 + \left(\frac{SD}{\sqrt{n}}\right)^2} \quad (6)$$

where;

u_{char} : Standard uncertainty arising from characterization,

\bar{u}_{labs} : Arithmetic mean of standard uncertainties reported by the participating laboratories,

SD : Standard deviation of accepted means of participating laboratories,

n : Number of laboratories with accepted results.

Table 7. Techniques used by participating laboratories

Parameter	BAM	DMDM	IMBIH	IJS	NTUA	UME	UW
As	-	ICP-MS	-	1) ICP-MS 2) k_0 -INAA	1) ICP-MS 2) ICP-OES	ICP-MS	ICP-MS
Cd	ID ICP-MS	ICP-MS	-	ICP-MS	1) ICP-MS 2) ASV	ID ICP-MS	ICP-MS
Co	-	ICP-MS	MP-AES	1) ICP-MS 2) k_0 -INAA	1) ICP-MS 2) ICP-OES	ICP-MS	ICP-MS
Cr	ID ICP-MS	ICP-MS	MP-AES	1) ICP-MS 2) k_0 -INAA	1) ICP-MS 2) ICP-OES	ID ICP-MS	ICP-MS
Cu	ID TIMS	ICP-MS	MP-AES	ICP-MS	1) ICP-MS 2) ICP-OES 3) ASV	ICP-MS	ICP-MS
Fe	-	ICP-MS	MP-AES	1) ICP-MS 2) k_0 -INAA	-	1) ID ICP-MS 2) ICP-MS	AAS
Hg	ID ICP-MS	ICP-MS	-	1) CV-AAS; 2) k_0 -INAA	ICP-MS	ID ICP-MS	ICP-MS
Mn	-	ICP-MS	MP-AES	1) ICP-MS 2) k_0 -INAA	-	ICP-MS	ICP-MS
Ni	ID ICP-MS	ICP-MS	MP-AES	ICP-MS	1) ICP-MS 2) ICP-OES	ICP-MS	ICP-MS
Pb	ID TIMS	ICP-MS	MP-AES	-	1) ICP-MS 2) ICP-OES 3) ASV	ID ICP-MS	ICP-MS
Sb	-	ICP-MS	-	1) ICP-MS 2) k_0 -INAA	1) ICP-MS	ICP-MS	ICP-MS
V	-	ICP-MS	MP-AES	1) ICP-MS 2) k_0 -INAA	1) ICP-MS 2) ICP-OES	ICP-MS	ICP-MS
Zn	-	ICP-MS	MP-AES	1) ICP-MS 2) k_0 -INAA	1) ICP-MS 2) ICP-OES 3) ASV	ID ICP-MS	ICP-MS

AAS : Atomic Absorption Spectrometry
 ASV : Anodic Stripping Voltammetry
 CV-AAS : Cold Vapor Atomic Absorption Spectrometry
 ICP-MS : Inductively Coupled Plasma Mass Spectrometry
 ICP-OES : Inductively Coupled Plasma Optical Emission Spectrometry
 ID ICP-MS : Isotope Dilution ICP-MS
 ID TIMS : Isotope Dilution Thermal Ionization Mass Spectrometry
 k_0 -INAA : k_0 -Instrumental Neutron Activation Analysis
 MP-AES : Microwave Plasma Atomic Emission Spectrometry

PROPERTY VALUE AND UNCERTAINTY ASSIGNMENT

Datasets from participants were collected and robust statistics were applied. Summary of the results can be found in Table 7. The certified values are given in Table 7 as obtained from the characterization study as explained above. Certified values are calculated as the median of the laboratory means of the accepted data sets for Co, Cu, Mn, Ni, V and Zn.

For Cd, Cr, Fe, Hg and Pb certified values are assigned as the arithmetic mean of the applied reference methods (ID ICP-MS, k_0 -INAA).

For As and Sb certified values are calculated as the mean of the results of a single reference method (k_0 -INAA).

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

The different contributions to the CRM uncertainty are combined using Equation (7):

$$U_{CRM} = k \cdot \sqrt{u_{char}^2 + u_{bb}^2 + u_{lts}^2 + u_{sts}^2} \quad (7)$$

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 %. U_{CRM} values are presented as dashed lines in Annex 6.

The certified values and uncertainties are summarized in Table 8 and uncertainty contribution percentages are given in Table 9. Certified values and uncertainties are found to be in good agreement with the target values (Table 2).

Table 8. Summary of certified values and their uncertainties

Element	Certified Value (mg/kg)	U_{CRM} (mg/kg, $k=2$)	$U_{CRM,rel}$ (%, $k=2$)	$u_{char,rel}$ (%)	n_{char}	$u_{bb,rel}$ (%)	$u_{lts,rel}$ (%)	$u_{sts,rel}$ (%)
As	79.9	5.9	7.4	3.00	1	0.88	0.98	1.56
Cd	1.29	0.08	6.2	0.52	2	1.12	1.24	2.36
Co	42.0	4.5	10.7	5.02	6	0.78	1.36	1.00
Cr	115.6	16.9	14.6	2.03	2	2.69	5.83	2.80
Cu	63.5	8.2	12.9	5.96	6	0.76	0.85	2.36
Fe	26748	1761	6.6	3.06	2	0.32	1.02	0.56
Hg	0.315	0.047	14.9	4.53	3	1.17	1.84	5.12
Mn	674	70	10.4	5.01	5	0.44	0.98	0.64
Ni	51.7	7.1	13.7	6.43	6	1.08	1.35	1.68
Pb	64.1	2.1	3.3	0.71	2	0.43	0.67	1.24
Sb	1.81	0.19	10.5	2.76	1	1.22	3.28	2.68
V	76.2	10.1	13.3	6.14	6	1.04	1.31	1.68
Zn	150.6	26.7	17.7	8.69	6	0.72	0.61	1.44

Table 9. Percent contribution of each uncertainty component to U_{CRM} .

Element	u_{bb} (%)	u_{lts} (%)	u_{sts} (%)	u_{char} (%)
As	14	15	24	47
Cd	21	24	45	10
Co	10	17	12	61
Cr	20	44	21	15
Cu	8	8	24	60
Fe	6	21	11	62
Hg	9	14	41	36
Mn	6	14	9	71
Ni	10	13	16	61
Pb	14	23	39	24
Sb	12	33	27	28
V	10	13	17	60
Zn	6	5	13	76

INFORMATIVE VALUES

Information about the moisture content of the soil is given in Table 10.

Table 10. Moisture content of the soil CRM

Parameter	Measurement Result (% w/w)
Moisture	4.15 ± 0.18 ^[1] ($n = 4$)

[1] Value written with “±” sign represents standard deviation. Moisture content is determined after drying at 105 °C to constant weight by BAM, IMBIH, IJS and TÜBİTAK UME.

Aqua regia extractable element content information is given in Table 11.

Table 11. Informative values for extractable element content

Element	Measurement Result (Dry Mass Corrected ^[1] , mg/kg)
As ^[2]	70.3 ± 2.1
Cd ^[3]	1.29 ± 0.10
Co ^[4]	41.7 ± 3.2
Cr ^[4]	56.4 ± 17.6
Cu ^[5]	67.3 ± 7.9
Fe ^[6]	19189 ± 227
Hg ^[7]	0.310 ± 0.009

Element	Measurement Result (Dry Mass Corrected ^[1] , mg/kg)
Mn ^[6]	520 ± 7
Ni ^[4]	48.9 ± 8.8
Pb ^[5]	63.1 ± 11.6
Sb ^[8]	1.38 ± 0.28
V ^[2]	69.5 ± 2.3
Zn ^[5]	128.5 ± 11.7

* Values written with “±” sign represents standard deviation

[1] Assigned value is corrected for dry mass. Moisture content is determined at (103 ± 2) °C until constant weight.

[2] Unweighted mean of ICP-MS and ICP-OES means obtained by ISO 12914 method by NTUA.

[3] Unweighted mean of ICP-MS and ASV by ISO 12914 method by NTUA and ICP-MS means by ISO 11466 method by DMDM.

[4] Unweighted mean of ICP-MS and ICP-OES by ISO 12914 method by NTUA and ICP-MS means by ISO 11466 method by DMDM.

[5] Unweighted mean of ICP-MS, ICP-OES, ASV by ISO 12914 method by NTUA and ICP-MS means by ISO 11466 method by DMDM.

[6] Unweighted mean of ICP-MS means by ISO 11466 method by DMDM.

[7] Unweighted mean of ICP-MS means obtained by ISO 12914 method by NTUA.

[8] Unweighted mean of ICP-MS by ISO 12914 method by NTUA and ICP-MS means by ISO 11466 method by DMDM.

Informative values for total element content obtained by k_0 -INAA method are presented in Table 12.

Table 12. Informative values for total element content by IJS with k_0 -INAA method (long and short irradiation)

Element	Measurement Result (Dry Mass Corrected, mg/kg)*	n
Al**	58864 ± 4166	6
Ba	289 ± 20	20
Br	7.89 ± 0.56	14
Ca	88024 ± 5304	14
Cs	7.1 ± 0.5	14
Hf	3.97 ± 0.28	14
K	15774 ± 1114	20
Mg**	39008 ± 2840	6
Na	10130 ± 712	20
Rb	65.9 ± 4.6	14
Sr	461 ± 38	14
Ta	0.807 ± 0.056	14
Ti**	3854 ± 340	6
Zr	176 ± 14	14

* Values written with “±” sign represents expanded measurement uncertainty ($k = 2$).

** Results were obtained by short irradiation.

COMMUTABILITY

Commutability is defined as the equivalence of the mathematical relationships among the results of different measurement procedures for a reference material and for representative samples of the type intended to be measured [7]. The commutability of a CRM is important for its fitness for use and for the application of different measurement methods. When commutability of a CRM is not established, the results from routinely used methods cannot be compared with the certified value to determine the presence of a bias.

UME EnvCRM 03 was produced by blending the raw soil with eight elements spiked soil (details are given in Material Processing section and Annex 2). The analytical behavior is assumed to be similar for an anthropogenic contaminated soil. It should be noted that the extractability of the eight spiked elements (Cd, Co, Cu, Hg, Ni, Pb, Sb, Zn) from this CRM can be different to the extractability from an unspiked soil tested by the user's laboratory due to the possibility that these elements might exist in different chemical forms.

TRACEABILITY

The metrological traceability of the CRM was ensured by using SI traceable calibration standards and/or by using reference methods i.e. ID ICP-MS and k_0 -INAA by the laboratories participating to the interlaboratory comparison. The laboratories were asked to provide detailed information about the calibration standards and reference methods used in the measurements. The details about the measurement methods, calibration standards and quality control materials used by the participating laboratories are given in Annex 6.

INSTRUCTIONS FOR USE

Storage conditions

The material should be stored at (18 ± 4) °C in dark and clean environment. This material can be safely dispatched under conditions where the temperature do not exceed 60 °C for up to four weeks, i.e. at ambient temperature without applying any cooling elements. TÜBİTAK UME cannot be held responsible for changes that might happen to the material at customer's premises due to noncompliance with the instructions for use, and the storage conditions given.

Safety precautions

The usual laboratory safety measures apply as in the case of similar powders. It is strongly recommended that the material must be handled and disposed according to the safety guidelines where applicable. It is recommended to avoid inhalation of powder material and work under appropriate ventilation conditions. Please refer to the Safety datasheet (SDS) before any use of the material.

Minimum sample intake

During the measurements performed for homogeneity, characterization, long term and short term stability studies, the lowest amount used was 0.2 g for certified elements and no significant problem of heterogeneity have been observed. Therefore, this can be considered as the minimum sample amount to

be used in the analysis. Before opening and taking sample, bottle should be shaken to re-homogenize the content. After use, the bottle should be immediately and tightly recapped.

Use of Certified Value

All results should be corrected for dry mass content of the material. Moisture content might be determined on separate samples of about 1 g at (103 ± 2) °C until constant weight is achieved. For assessing the method performance, the measured values of the CRM are compared with the certified values [8]. The procedure can be described briefly as follows:

- Calculate the absolute difference between mean measured value and the certified value (Δ_m).
- Combine measurement uncertainty (u_{meas}) with the standard uncertainty of the certified value (u_{CRM}) using following equation:

$$u_{\Delta} = \sqrt{u_{meas}^2 + u_{CRM}^2} \quad (8)$$

- Calculate the expanded uncertainty (U_{Δ}) from the combined uncertainty (u_{Δ}) using a coverage factor of two ($k = 2$), corresponding to a confidence level of approximately 95 %.

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

An online application: CRM Result Evaluation-CRM RE to evaluate measurement results and automatically create quality control charts is available through the link: https://rm.ume.tubitak.gov.tr/en/crm_re/

ACKNOWLEDGMENTS

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REVISION HISTORY

Date	Remarks
22.03.2019	First issue.

Annex 1. Particle Size Analysis of Soil Samples

d(0.1): 2.664 um d(0.5): 25.757 um d(0.9): 95.228 um

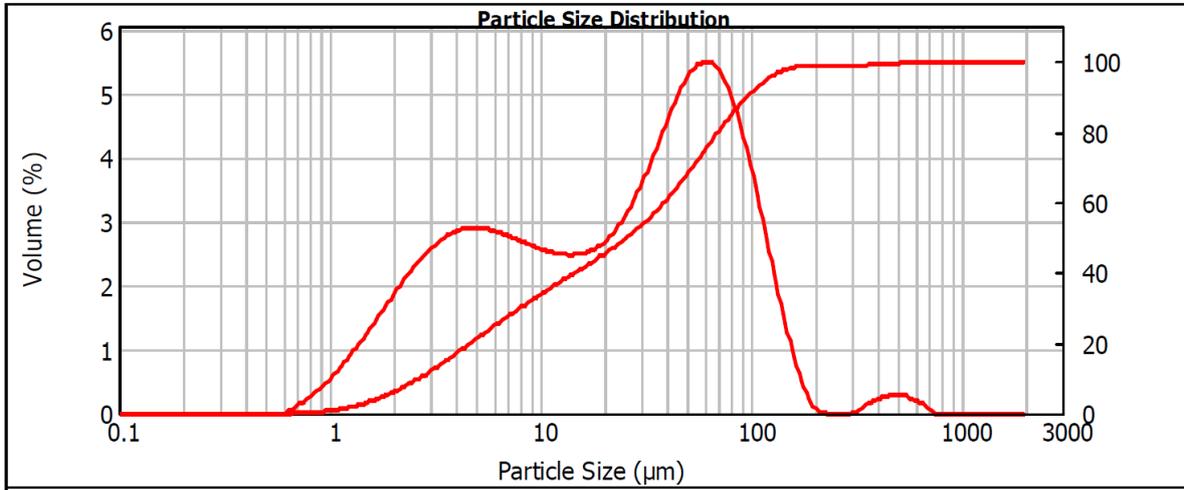


Figure A1.1. Particle size distribution analysis of original processed soil by laser diffraction

d(0.1): 3.027 um d(0.5): 26.598 um d(0.9): 81.468 um

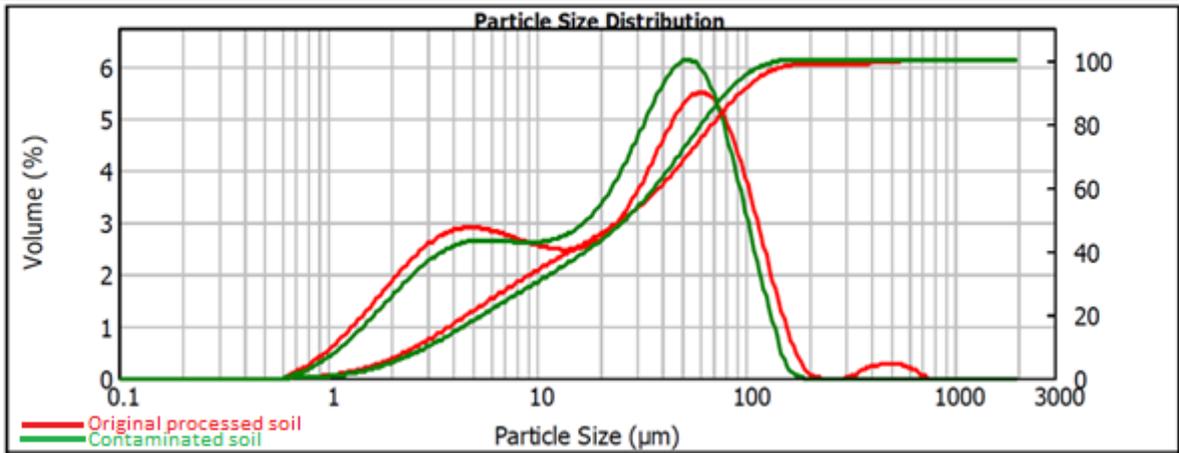
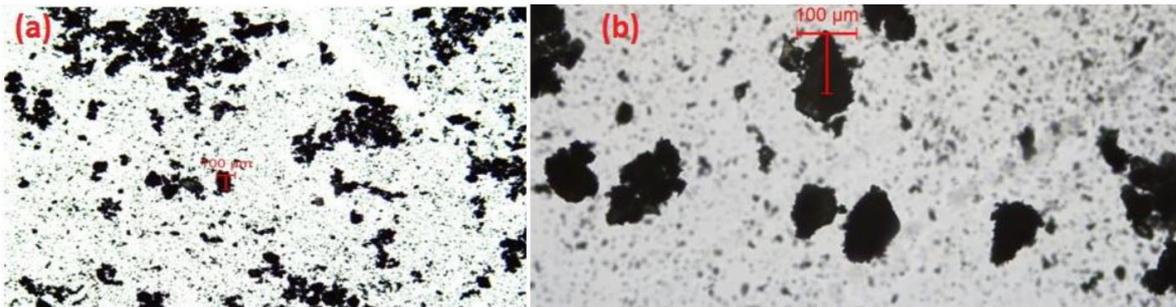


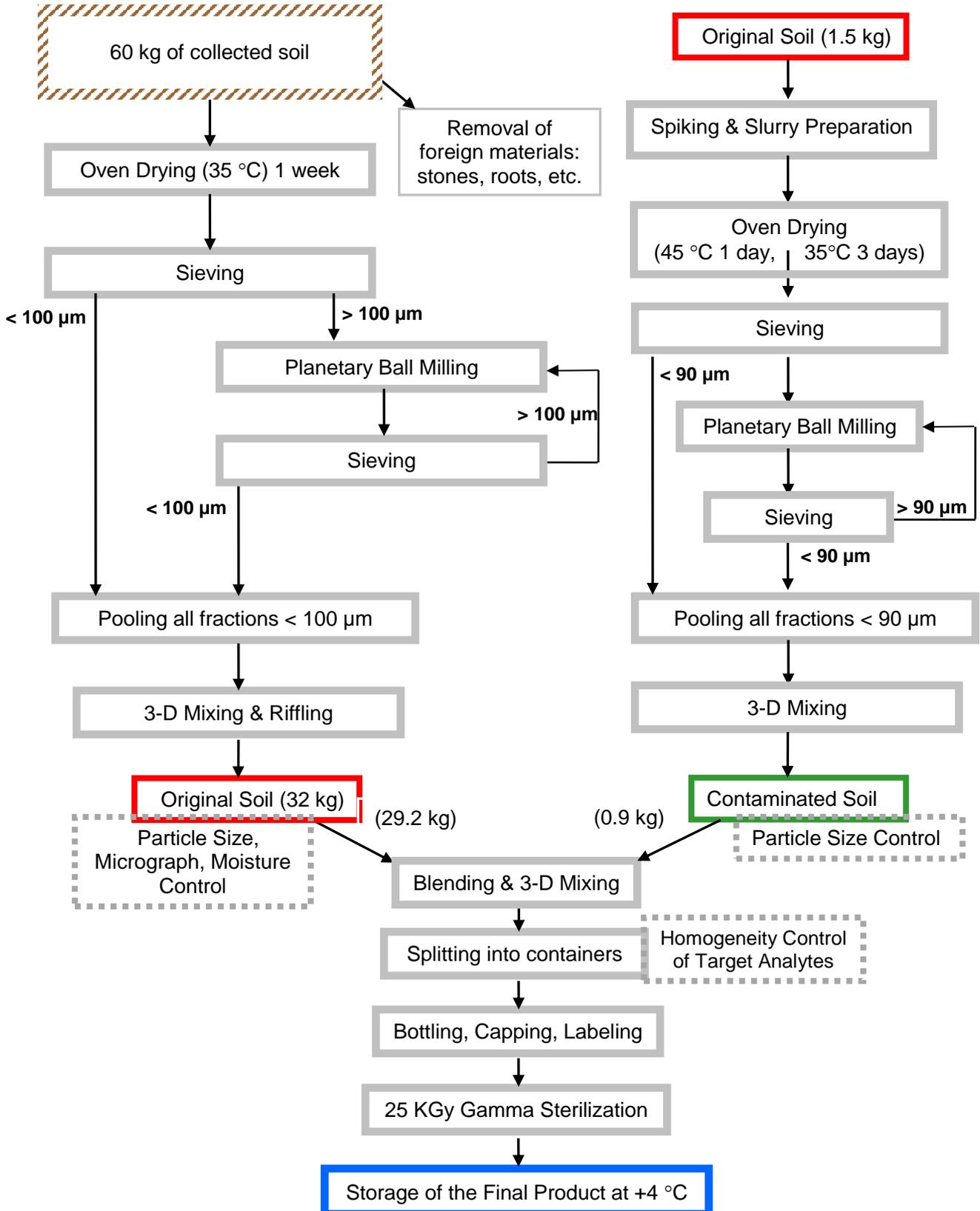
Figure A1.2. Comparative particle size distribution analysis of original processed soil and contaminated soil by laser diffraction



a) 4 x magnified view, b) 10 x magnified view

Figure A3. Micrograph of original processed soil

Annex 2. Flow Diagram for the Preparation of the Soil CRM



Annex 3. Graphs for Homogeneity Studies

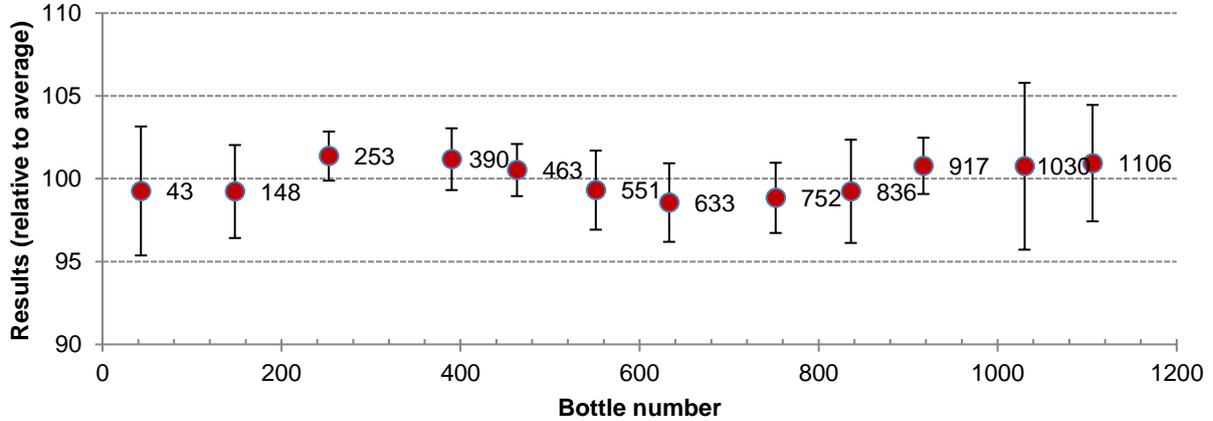


Figure A3.1. Homogeneity plot for As by UME

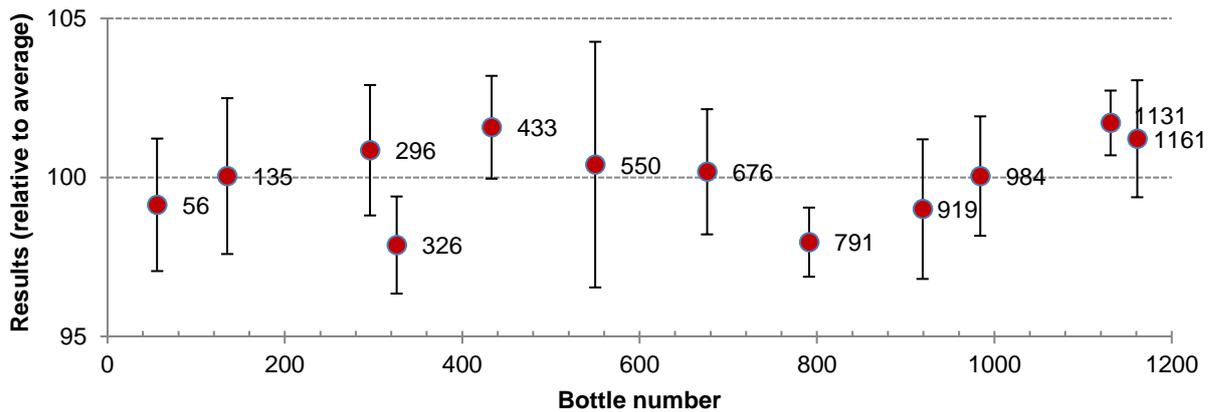


Figure A3.2. Homogeneity plot for As by IJS

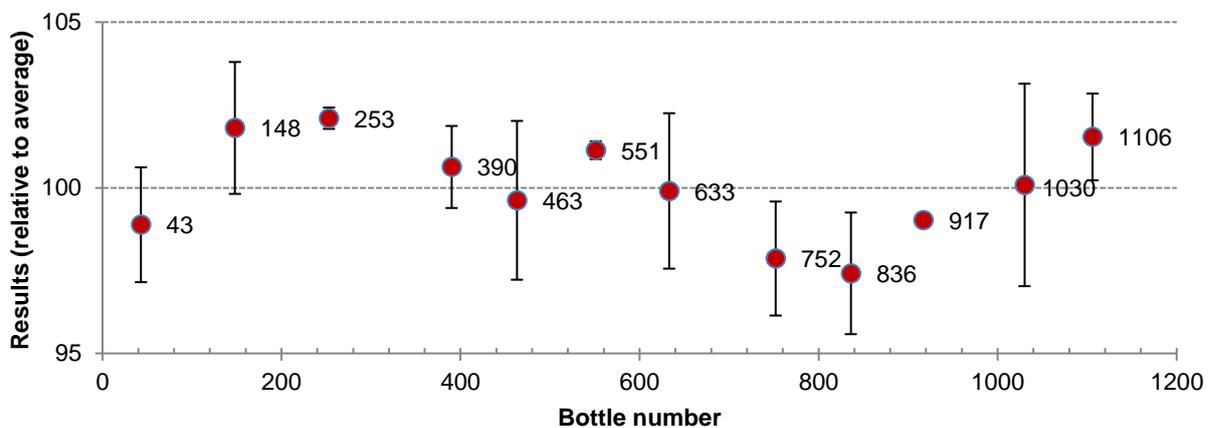


Figure A3.3. Homogeneity plot for Cd by UME

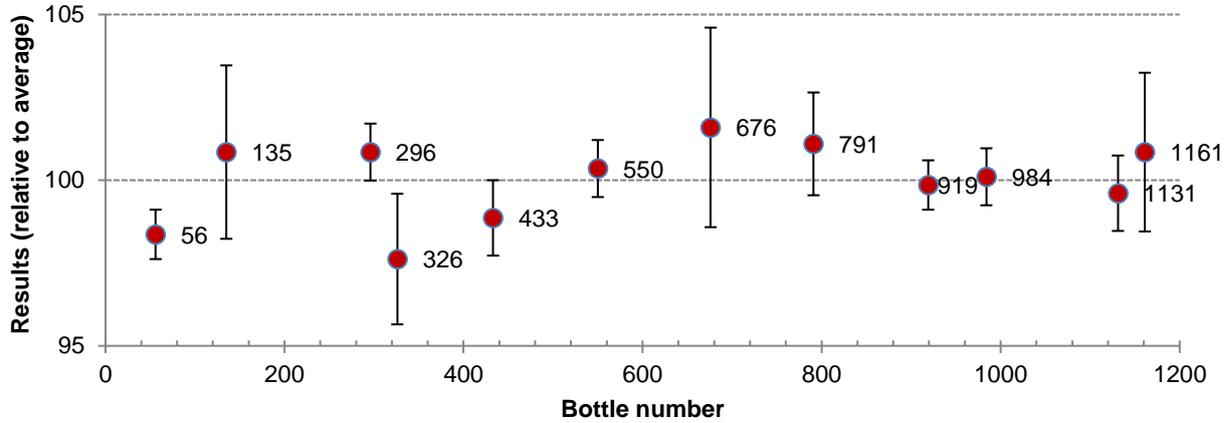


Figure A3.4. Homogeneity plot for Cd by IJS

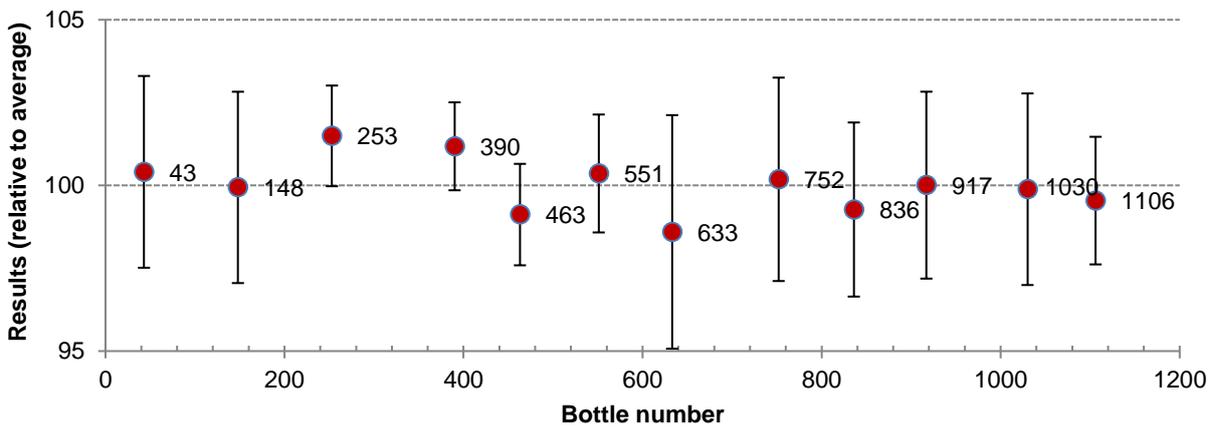


Figure A3.5. Homogeneity plot for Co by UME

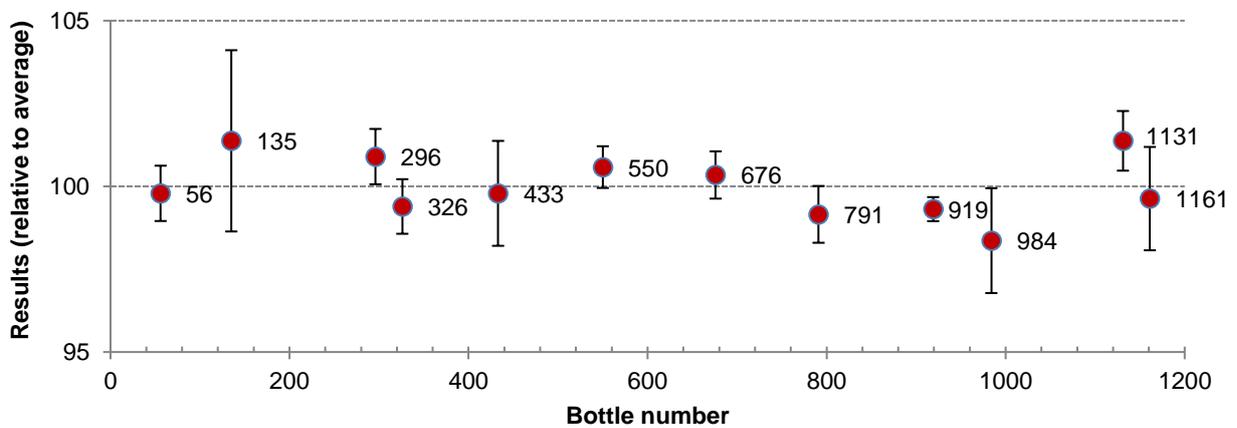


Figure A3.6. Homogeneity plot for Co by IJS

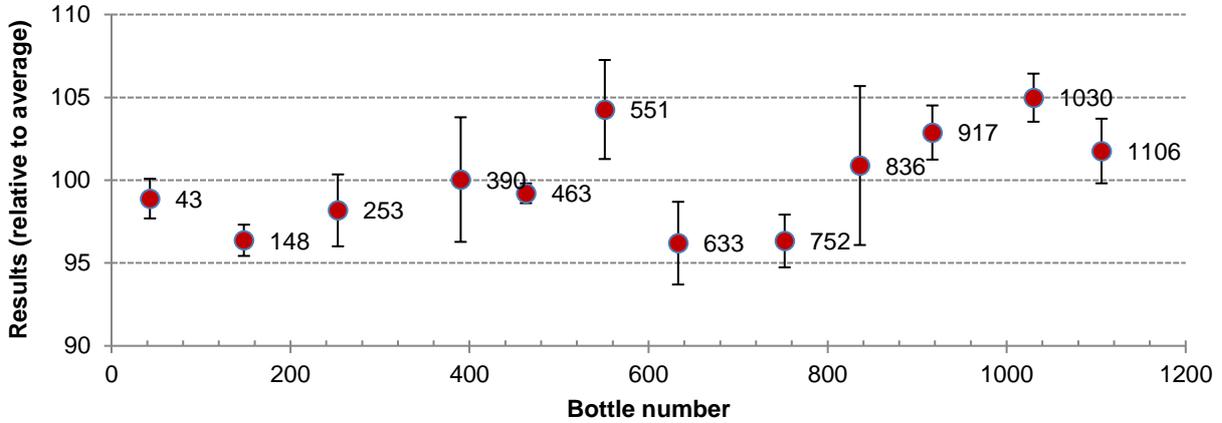


Figure A3.7. Homogeneity plot for Cr by UME

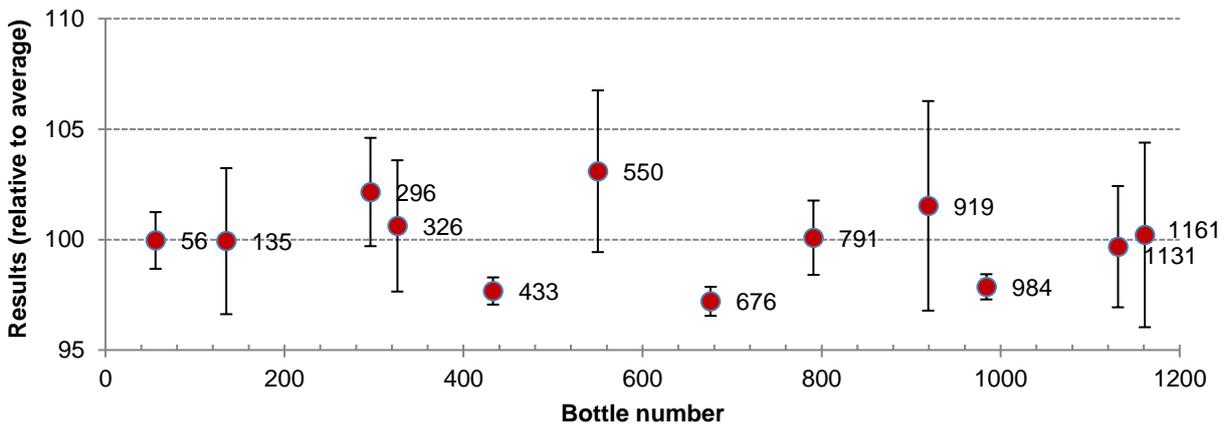


Figure A3.8. Homogeneity plot for Cr by IJS

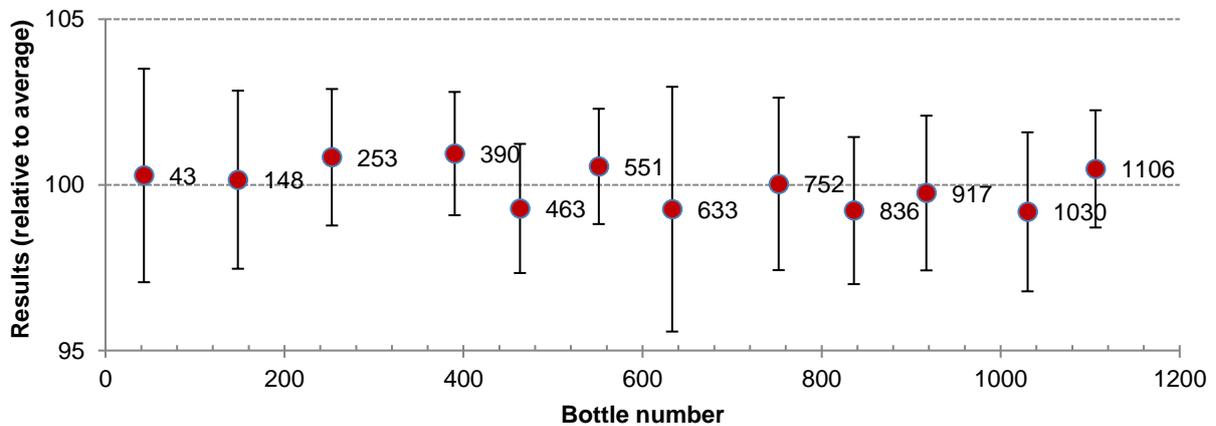


Figure A3.9. Homogeneity plot for Cu by UME

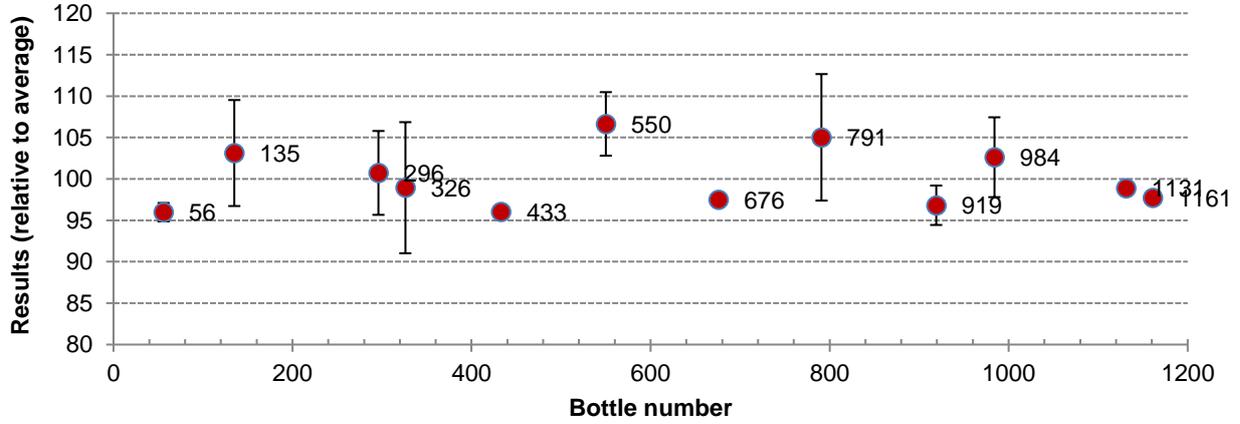


Figure A3.10. Homogeneity plot for Cu by IJS

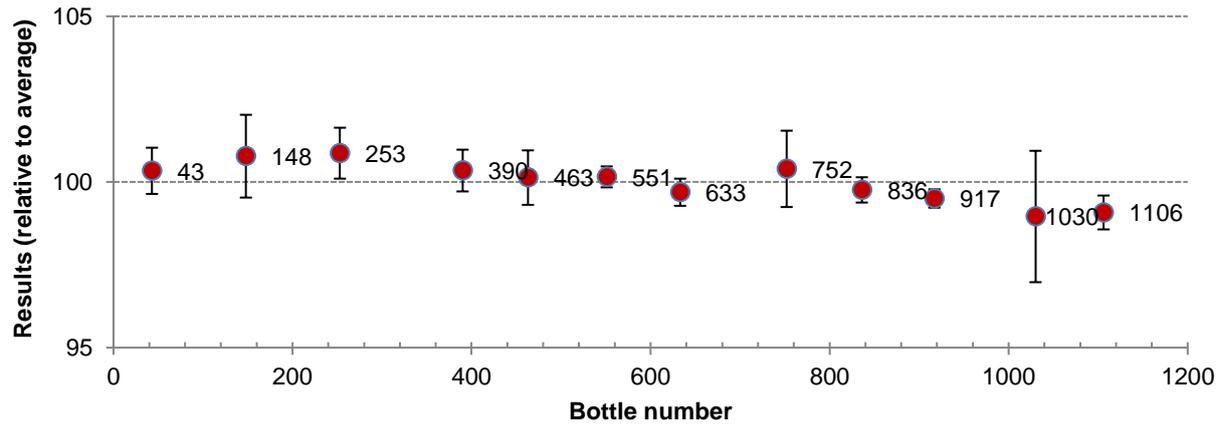


Figure A3.11. Homogeneity plot for Fe by UME

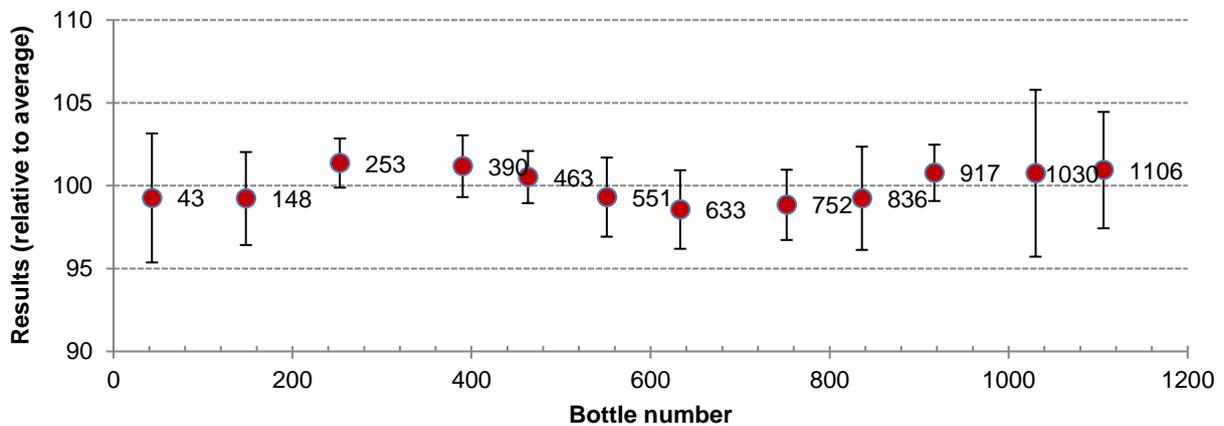


Figure A3.12. Homogeneity plot for Hg by UME

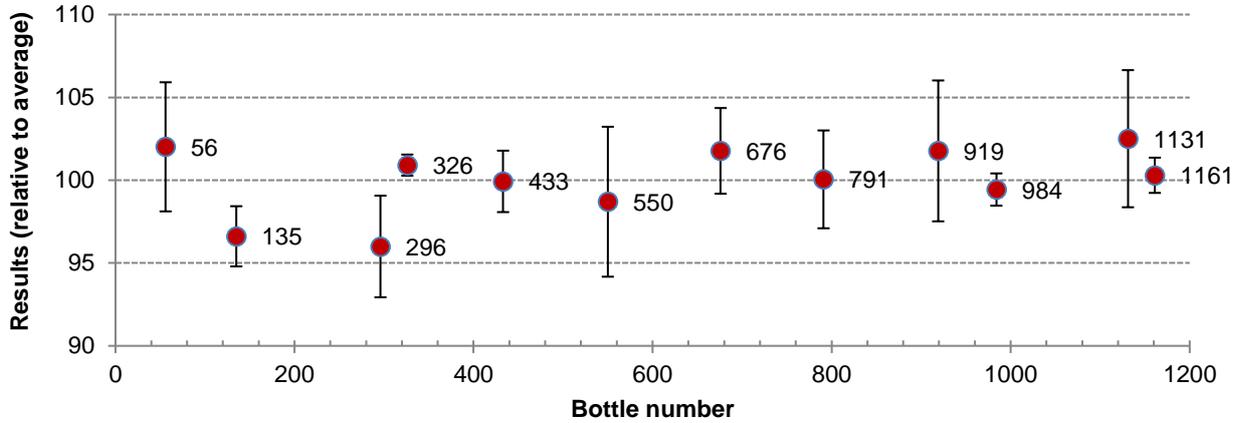


Figure A3.13. Homogeneity plot for Hg by IJS

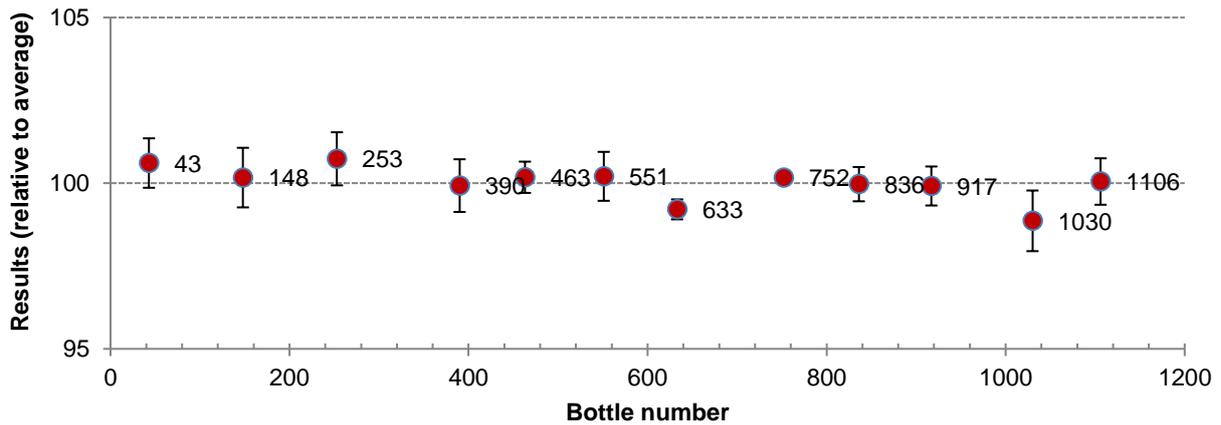


Figure A3.14. Homogeneity plot for Mn by UME

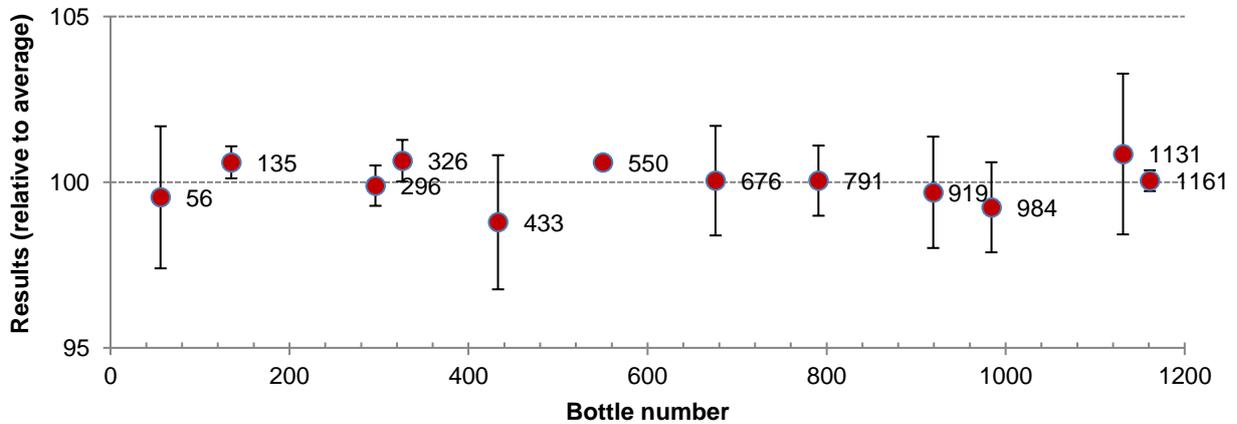


Figure A3.15. Homogeneity plot for Mn by IJS

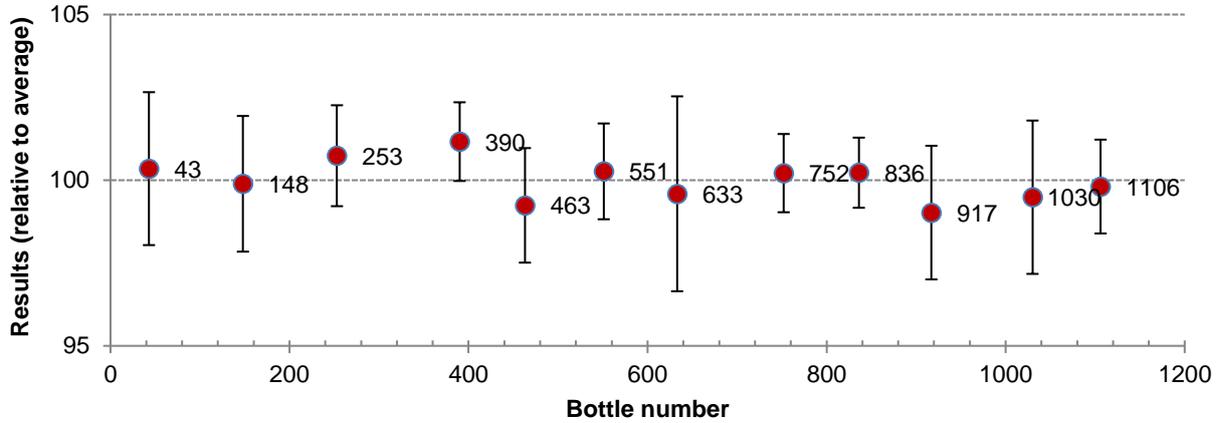


Figure A3.16. Homogeneity plot for Ni by UME

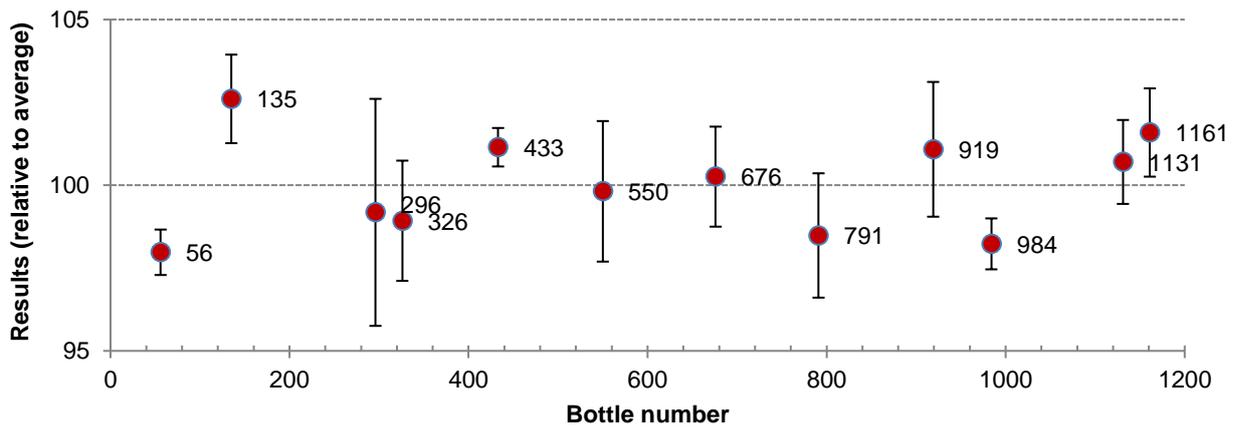


Figure A3.17. Homogeneity plot for Ni by IJS

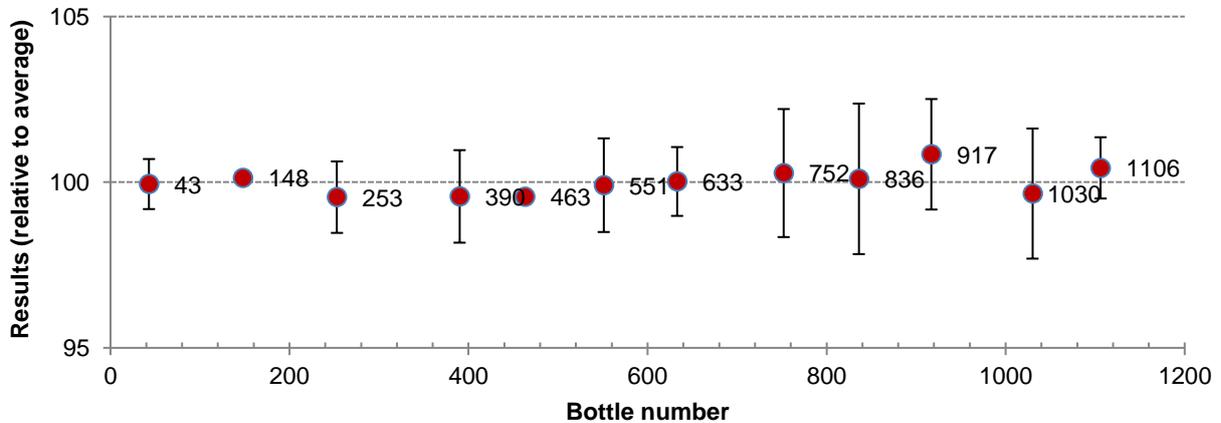


Figure A3.18. Homogeneity plot for Pb by UME

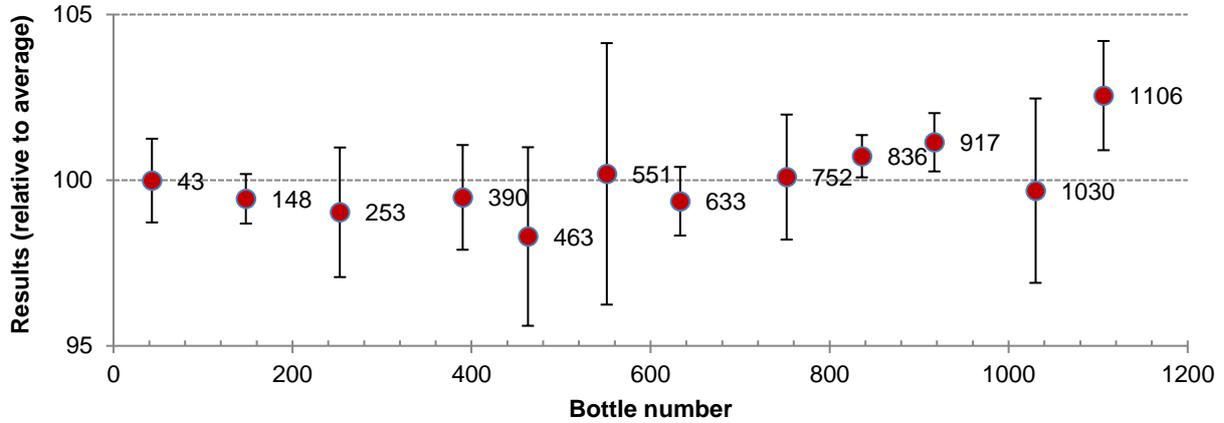


Figure A3.19. Homogeneity plot for Sb by UME

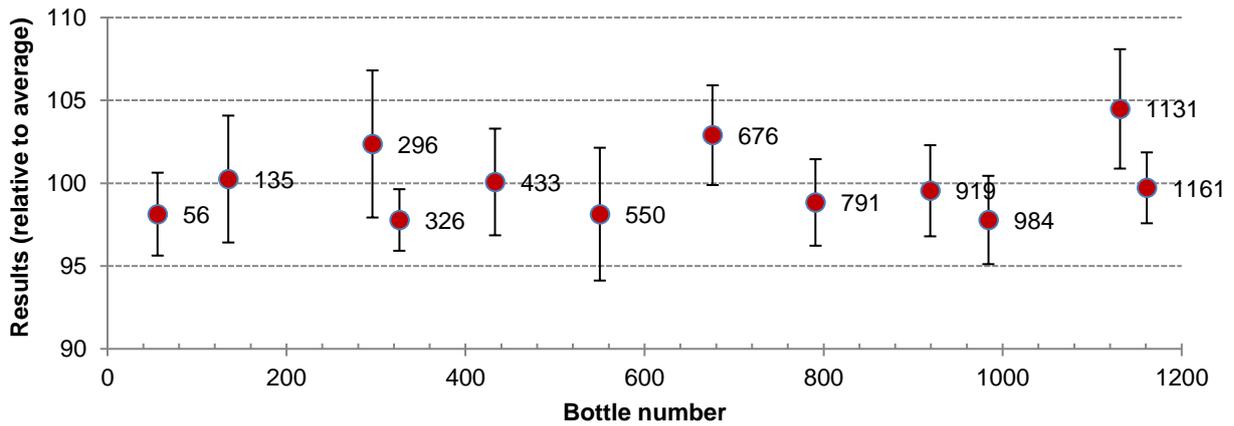


Figure A3.20. Homogeneity plot for Sb by IJS

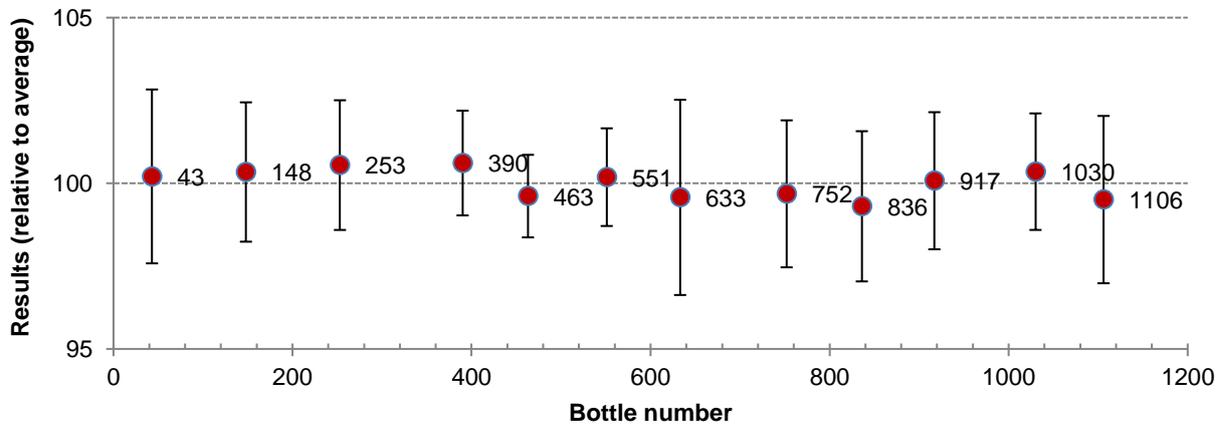


Figure A3.21. Homogeneity plot for V by UME

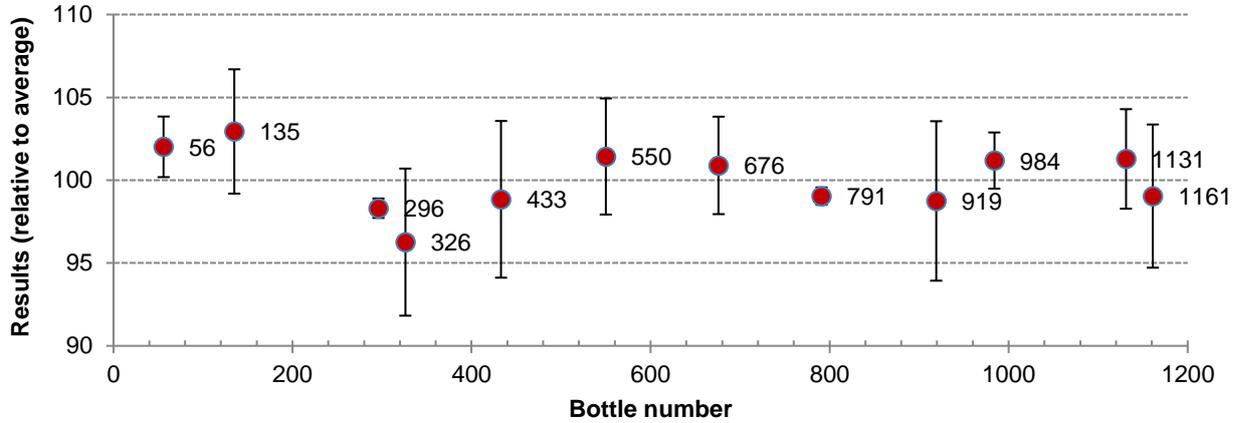


Figure A3.22. Homogeneity plot for V by IJS

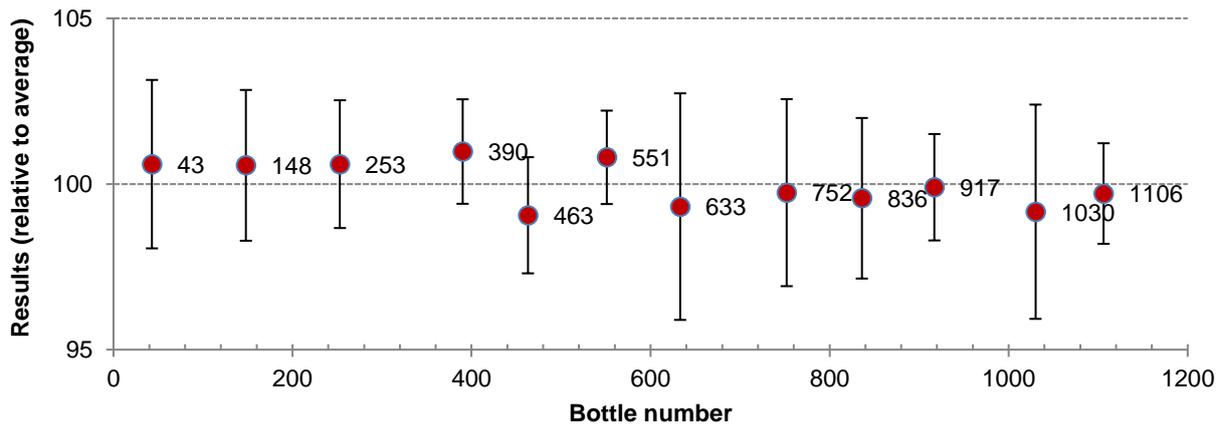


Figure A3.23. Homogeneity plot for Zn by UME

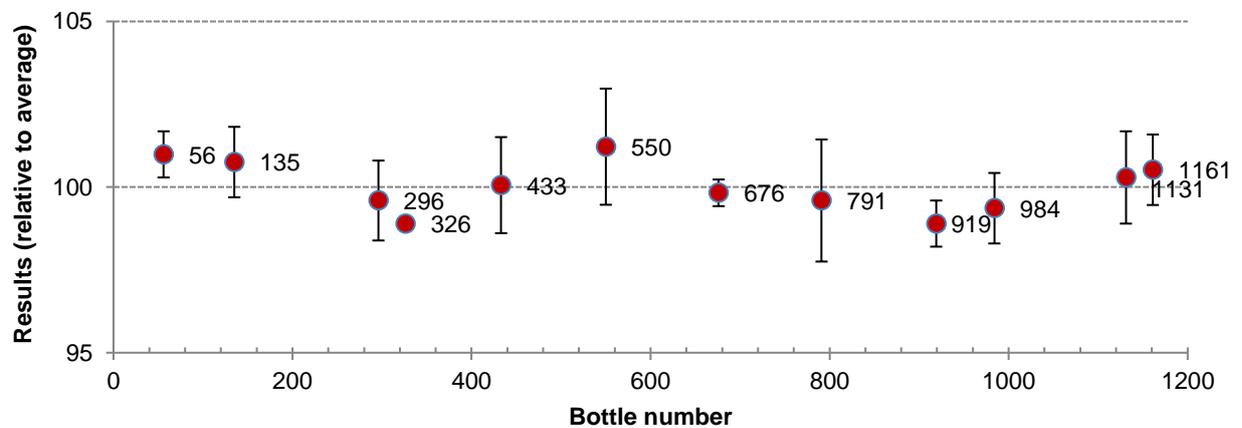


Figure A3.24. Homogeneity plot for Zn by IJS

Annex 4. Graphs for Short Term Stability Studies

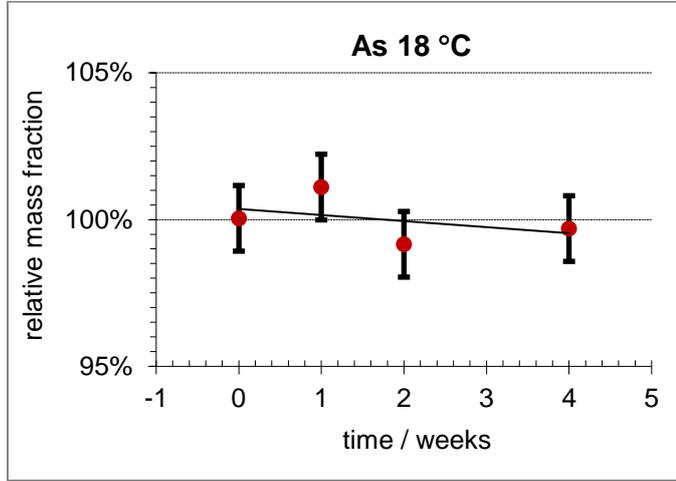


Figure A4.1. STS plot for As at 18 °C by UME

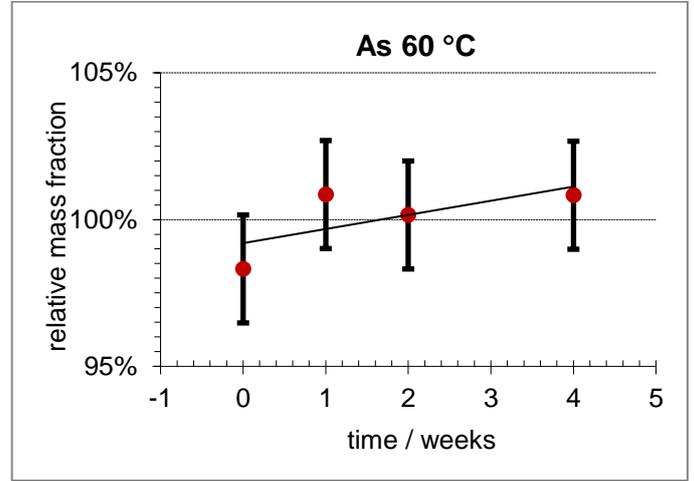


Figure A4.4. STS plot for As at 60 °C by IJS

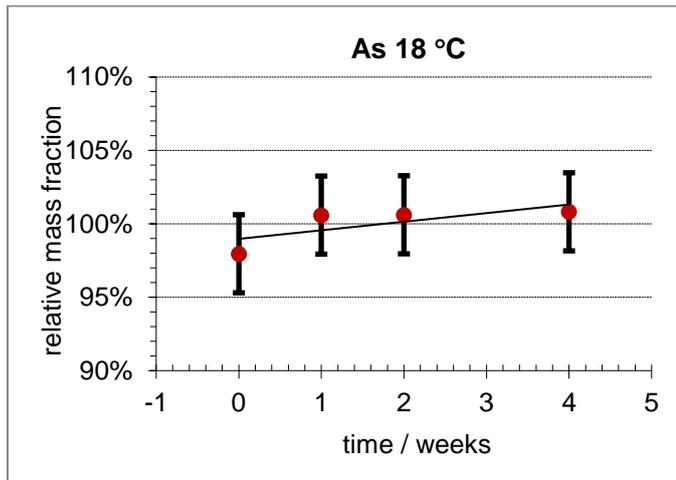


Figure A4.2. STS plot for As at 18 °C by IJS

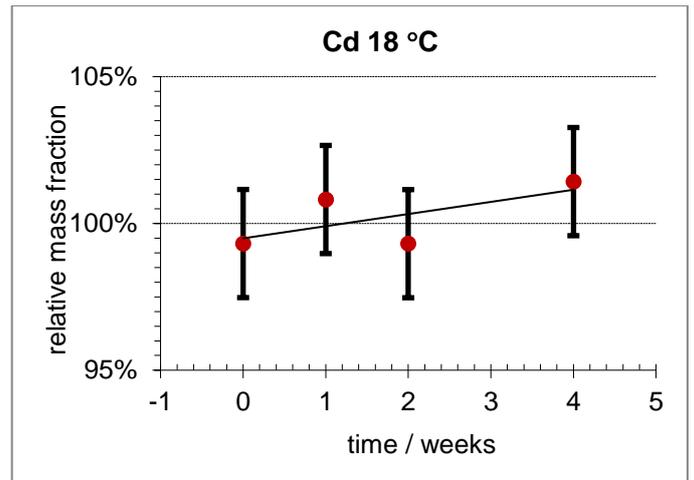


Figure A4.5. STS plot for Cd at 18 °C by UME

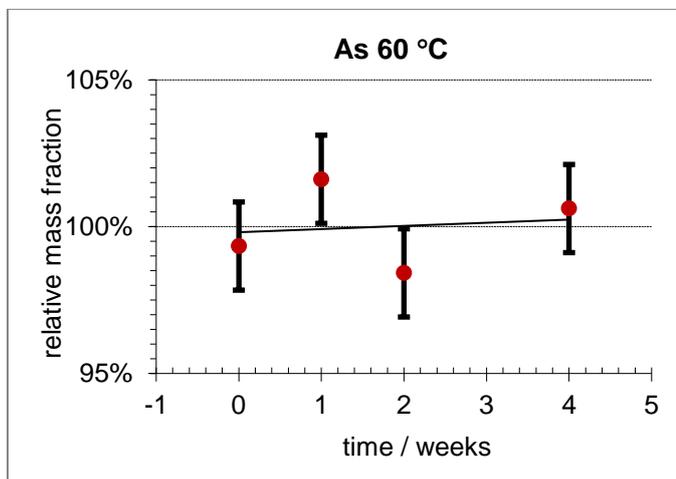


Figure A4.3. STS plot for As at 60 °C by UME

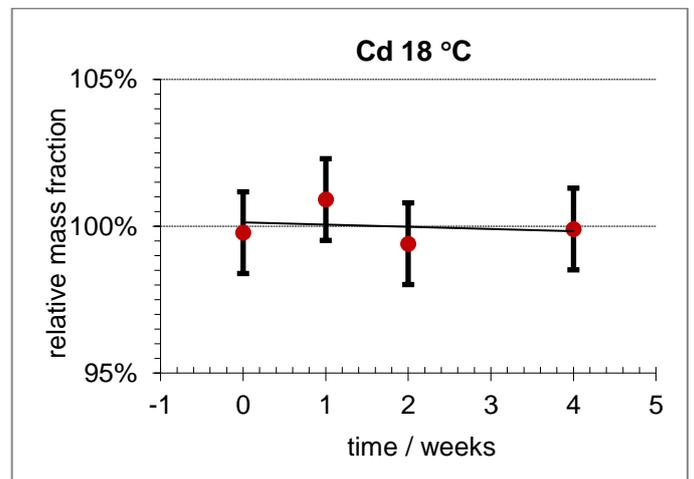


Figure A4.6. STS plot for Cd at 18 °C by IJS

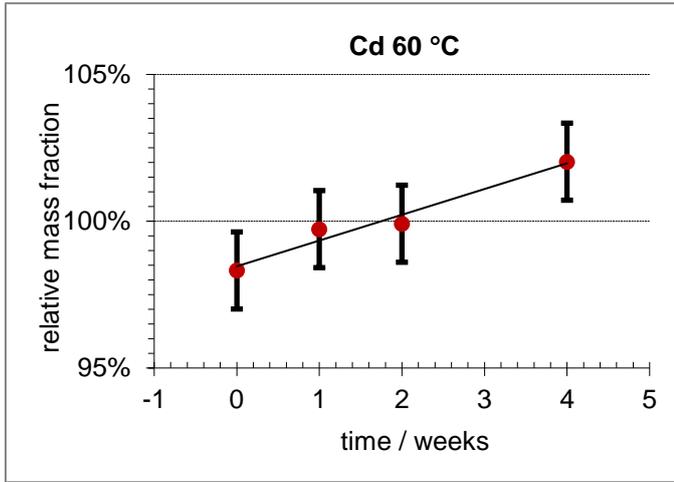


Figure A4.7. STS plot for Cd at 60 °C by UME

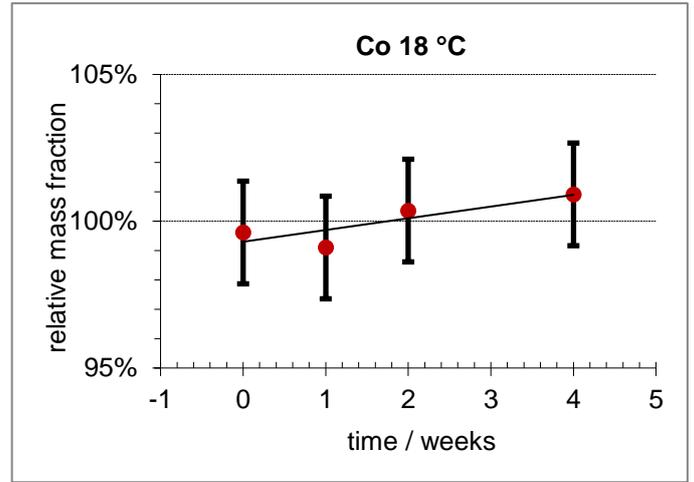


Figure A4.10. STS plot for Co at 18 °C by IJS

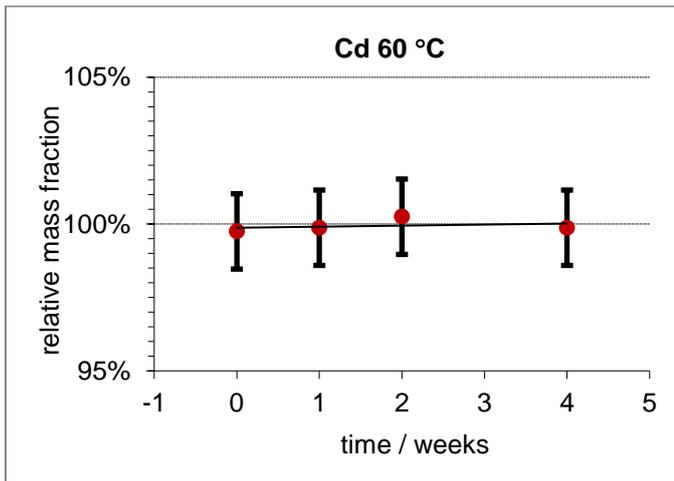


Figure A4.8. STS plot for Cd at 60 °C by IJS

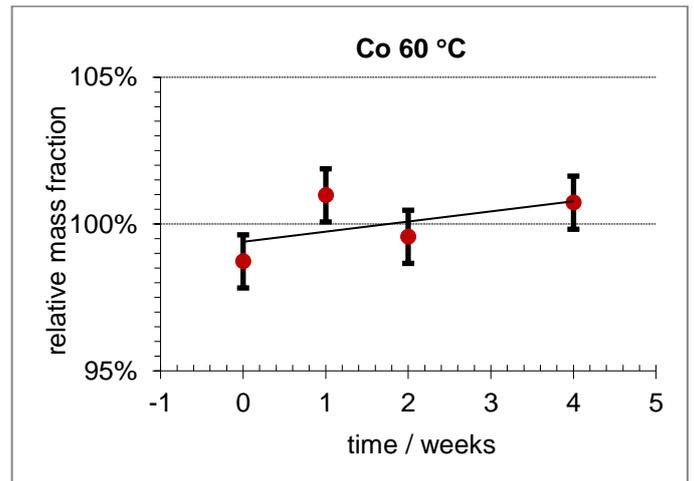


Figure A4.11. STS plot for Co at 60 °C by UME

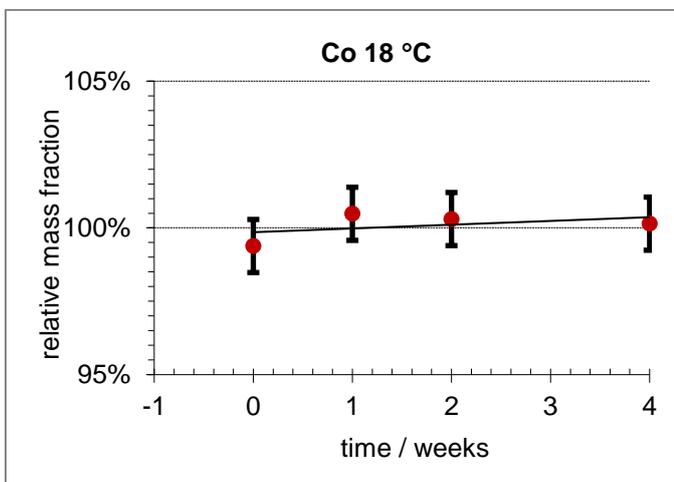


Figure A4.9. STS plot for Co at 18 °C by UME

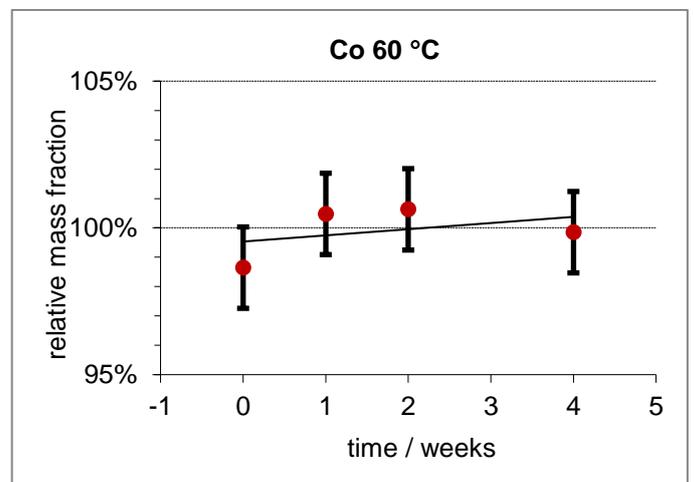


Figure A4.12. STS plot for Co at 60 °C by IJS

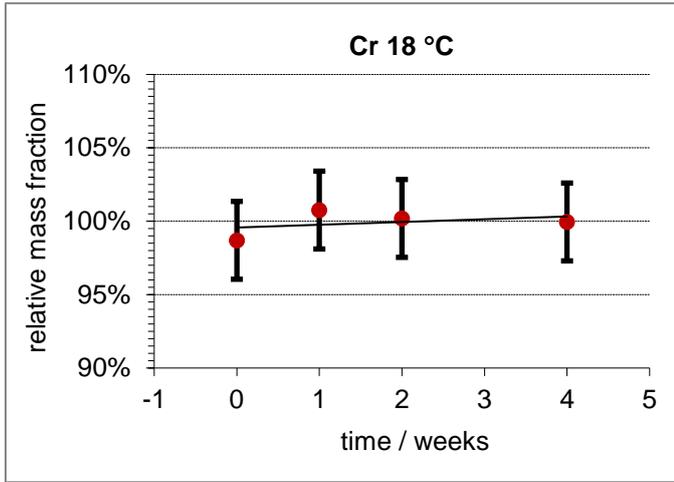


Figure A4.13. STS plot for Cr at 18 °C by UME

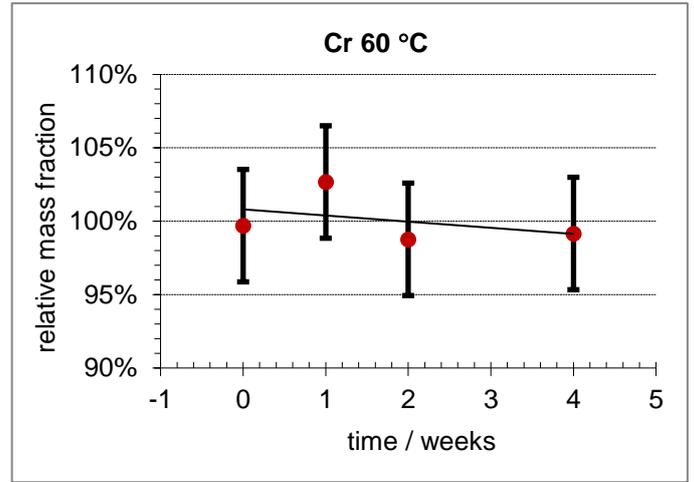


Figure A4.16. STS plot for Cr at 60 °C by IJS

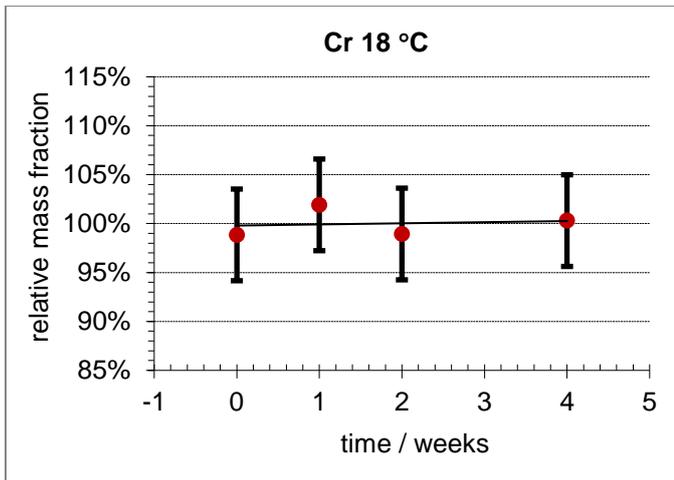


Figure A4.14. STS plot for Cr at 18 °C by IJS

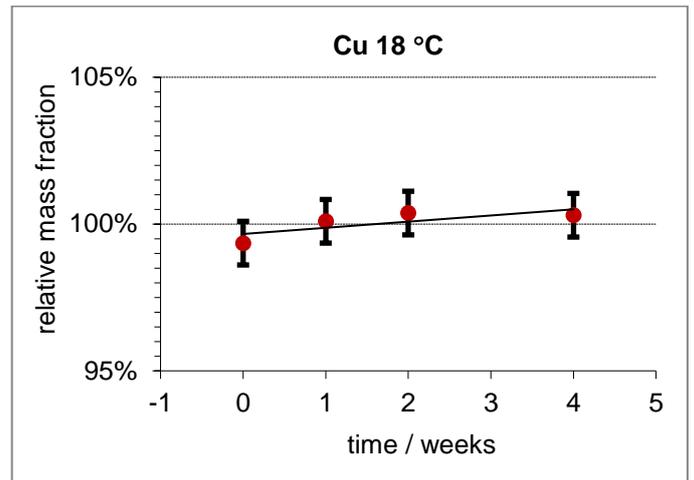


Figure A4.17. STS plot for Cu at 18 °C by UME

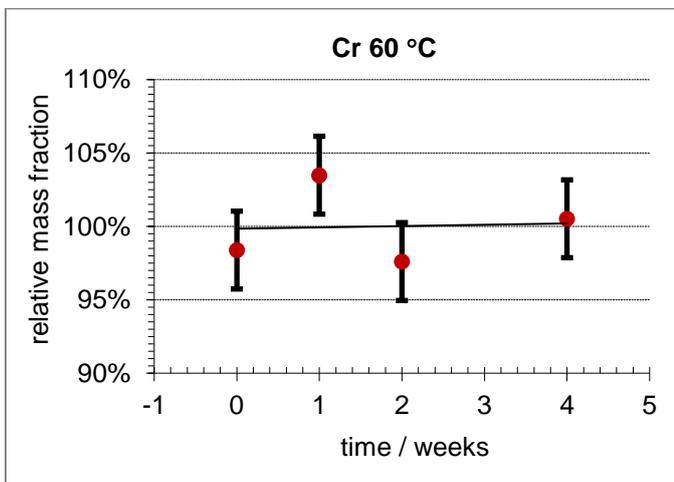


Figure A4.15. STS plot for Cr at 60 °C by UME

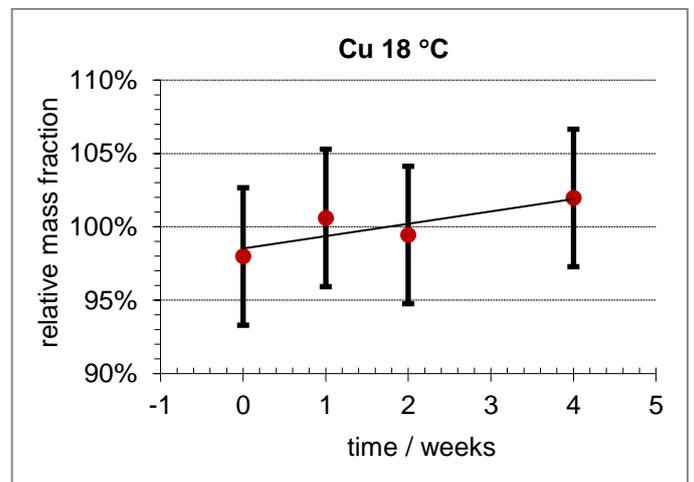


Figure A4.18. STS plot for Cu at 18 °C by IJS

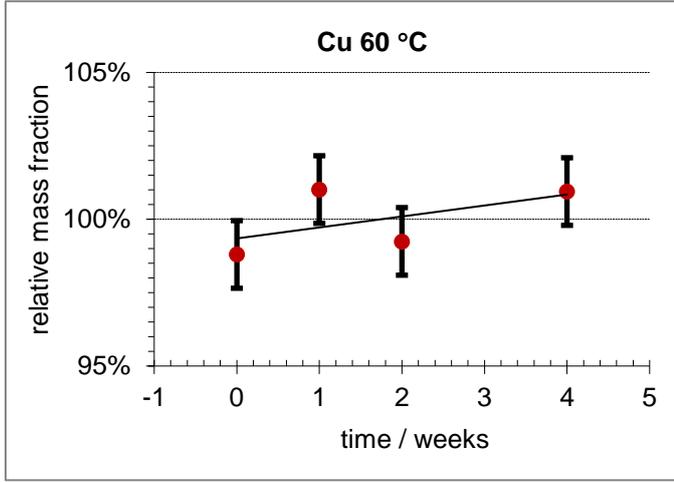


Figure A4.19. STS plot for Cu at 60 °C by UME

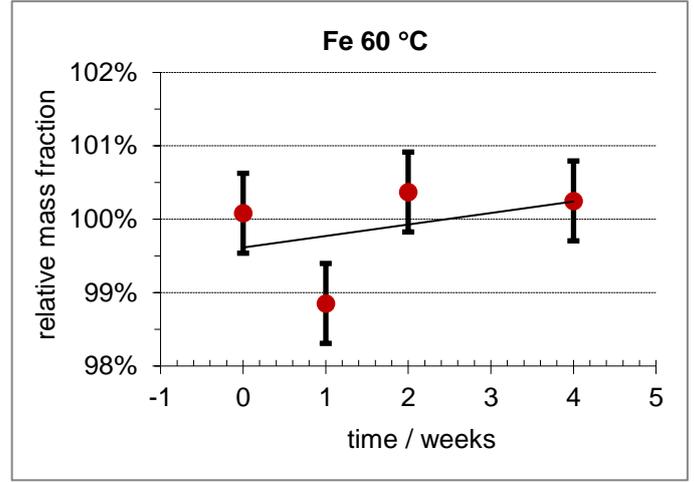


Figure A4.22. STS plot for Fe at 60 °C by UME

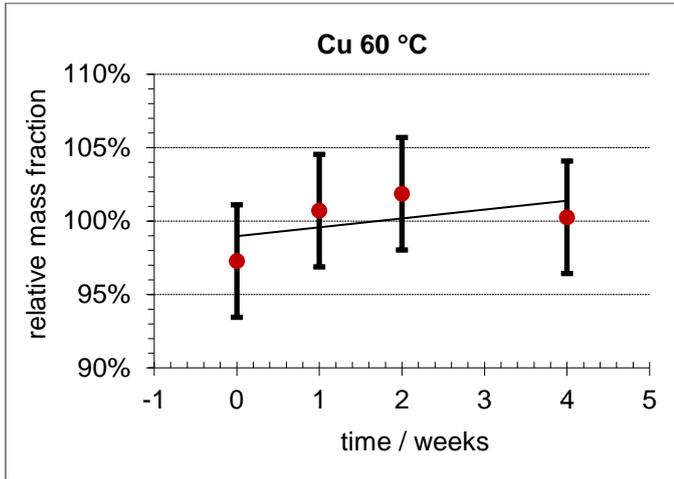


Figure A4.20. STS plot for Cu at 60 °C by IJS

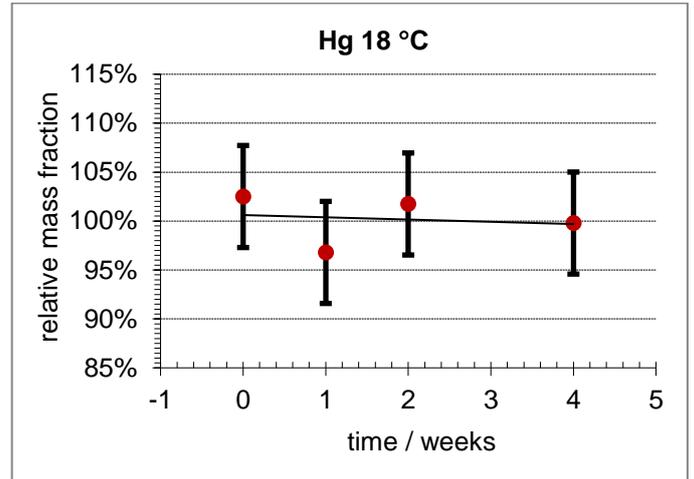


Figure A4.23. STS plot for Hg at 18 °C by UME

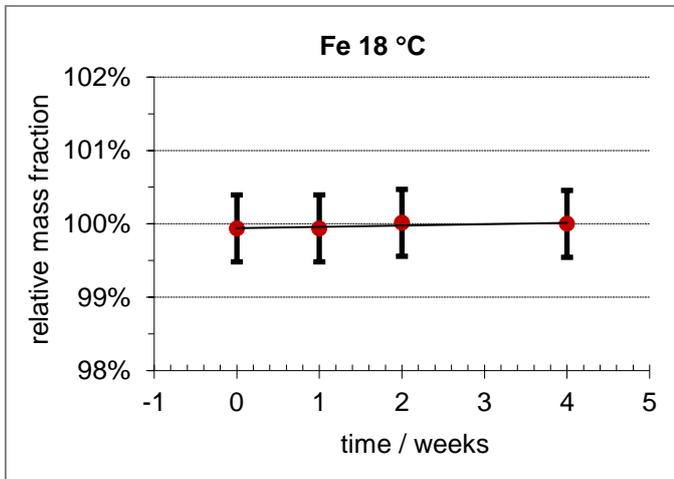


Figure A4.21. STS plot for Fe at 18 °C by UME

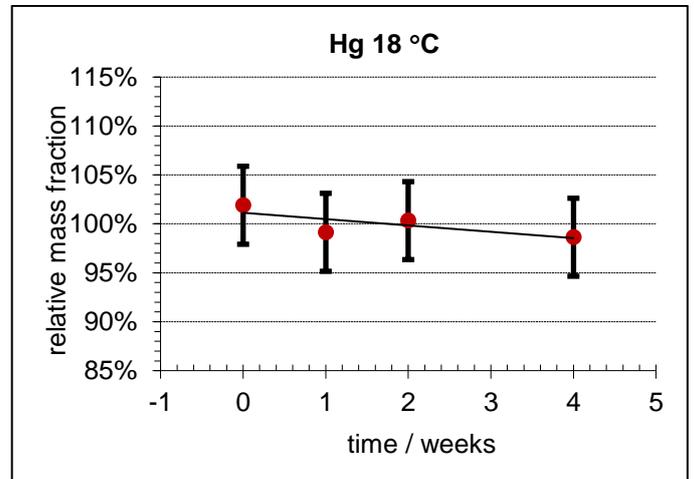


Figure A4.24. STS plot for Hg at 18 °C by IJS

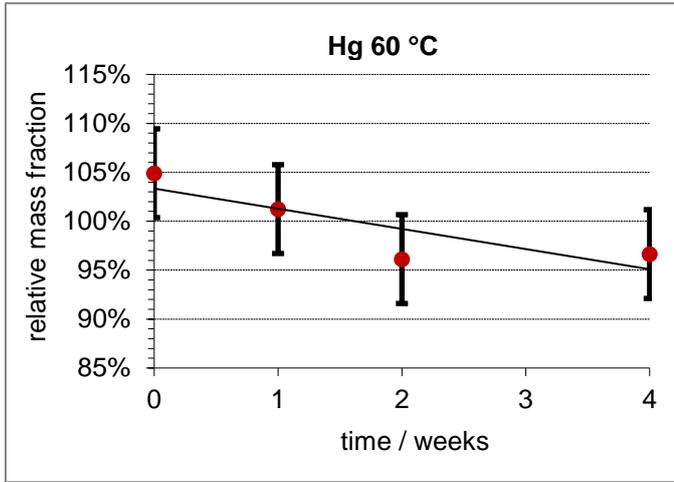


Figure A.25. STS plot for Hg at 60 °C by UME

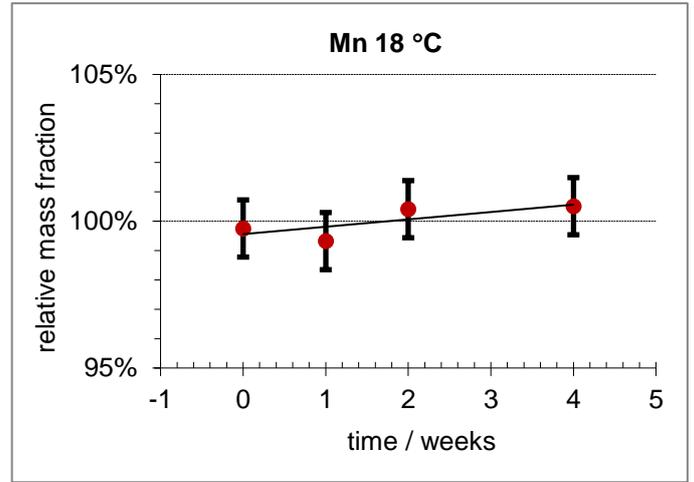


Figure A4.28. STS plot for Mn at 18 °C by IJS

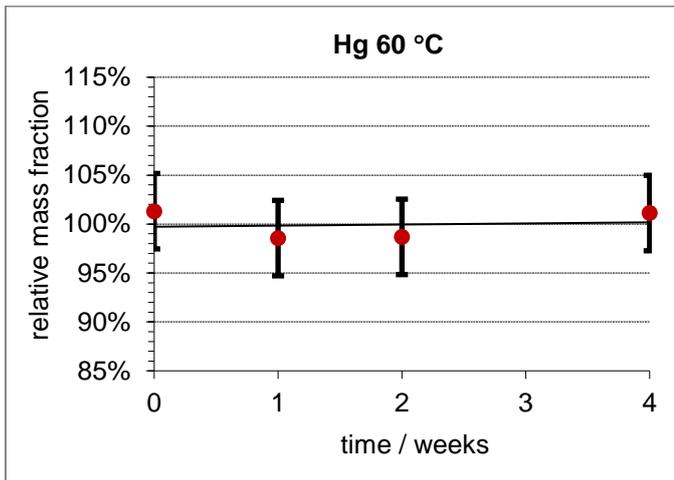


Figure A4.26. STS plot for Hg at 60 °C by IJS

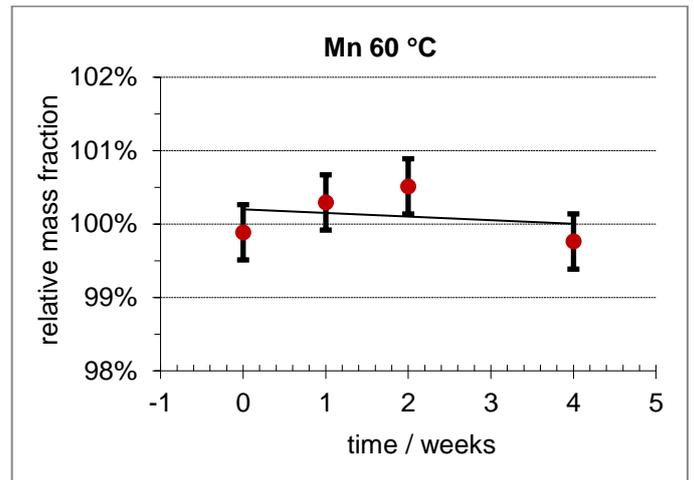


Figure A4.29. STS plot for Mn at 60 °C by UME

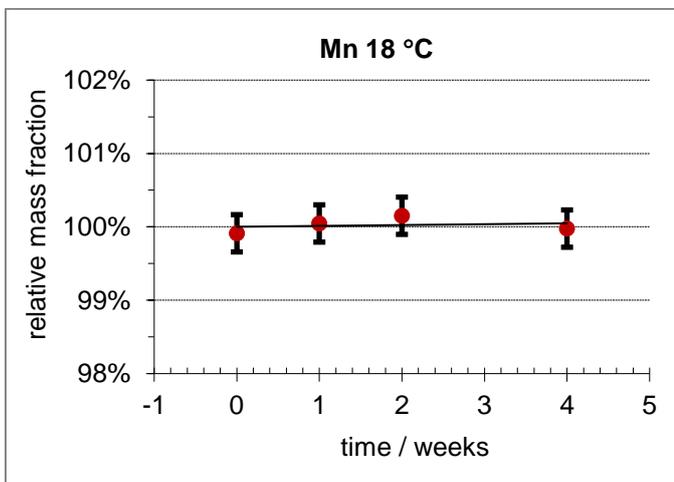


Figure A4.27. STS plot for Mn at 18 °C by UME

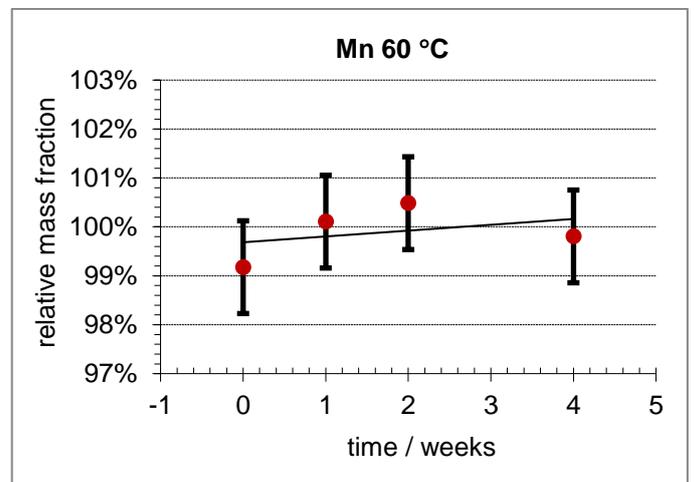


Figure A4.30. STS plot for Mn at 60 °C by IJS

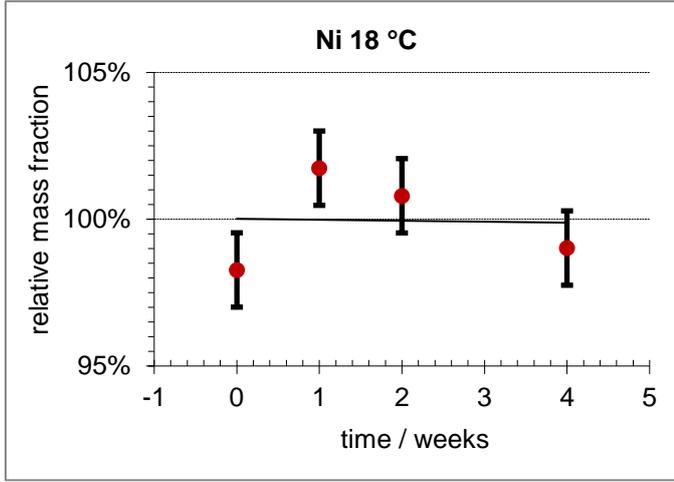


Figure A4.31. STS plot for Ni at 18 °C by UME

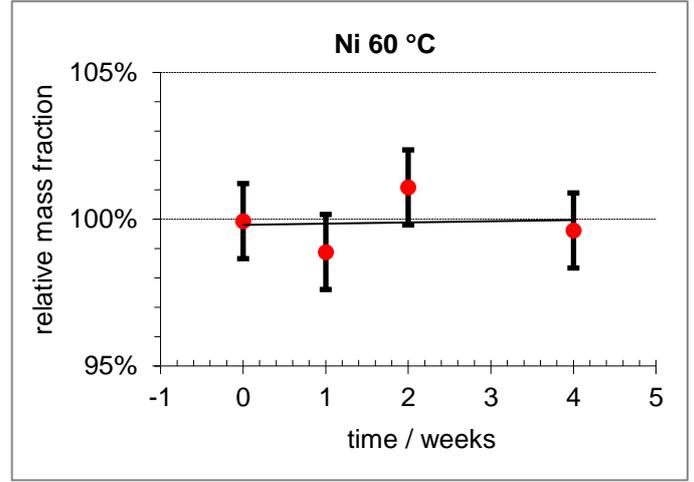


Figure A4.34. STS plot for Ni at 60 °C by IJS

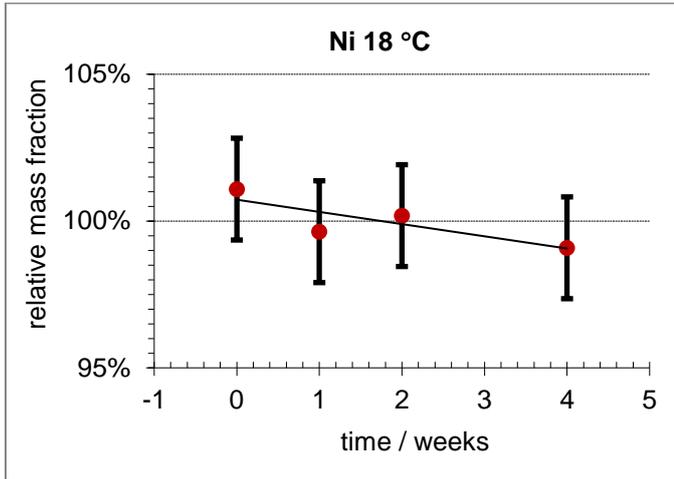


Figure A4.32. STS plot for Ni at 18 °C by IJS

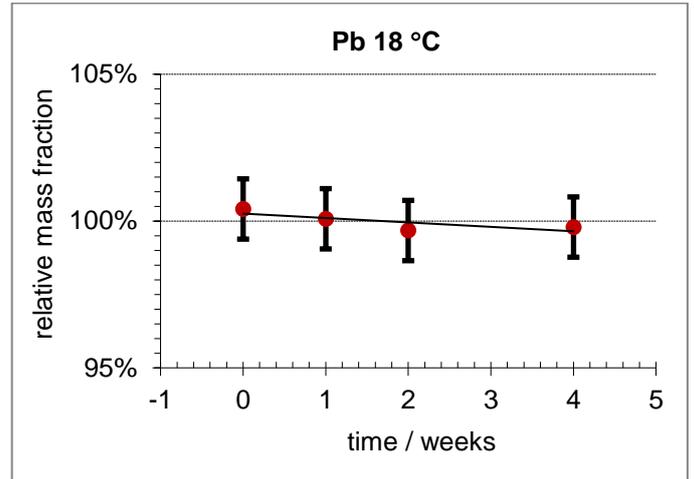


Figure A4.35. STS plot for Pb at 18 °C by UME

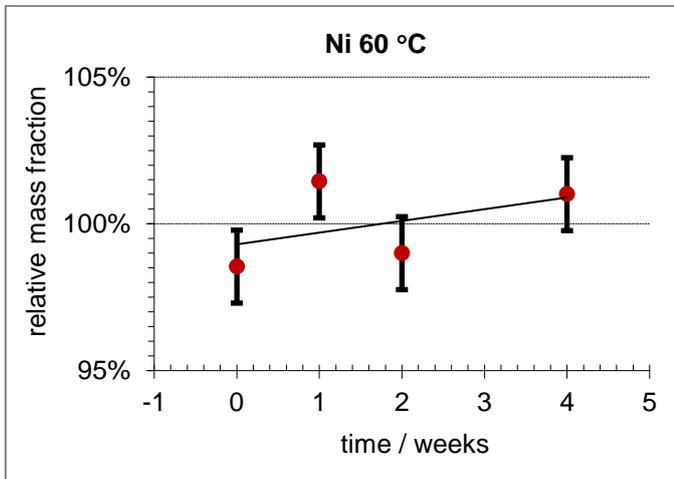


Figure A4.33. STS plot for Ni at 60 °C by UME

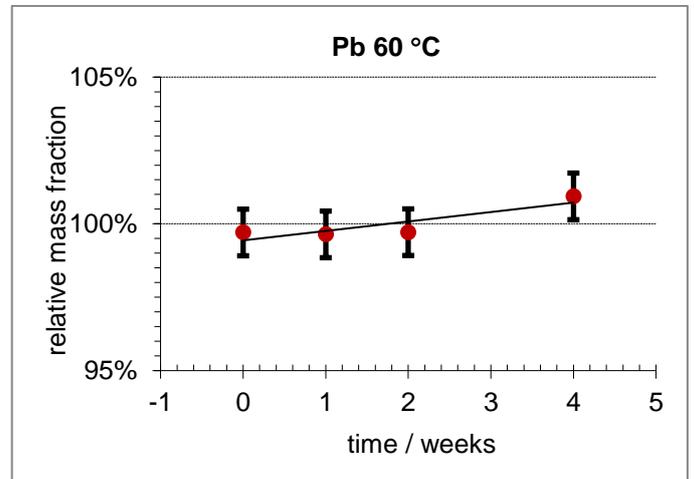


Figure A4.36. STS plot for Pb at 60 °C by UME

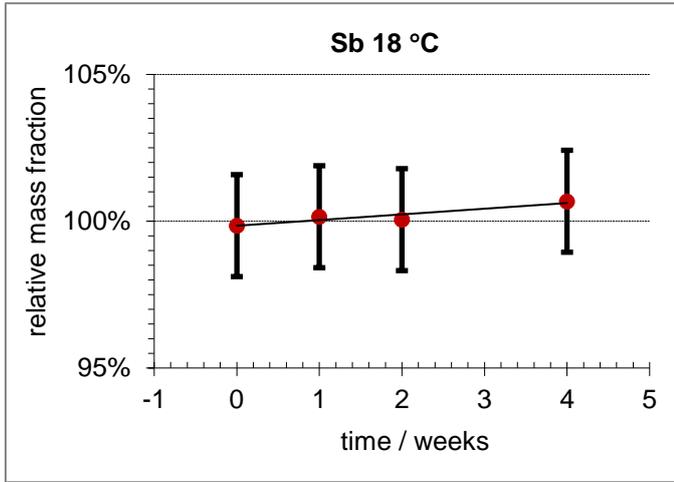


Figure A4.37. STS plot for Sb at 18 °C by UME

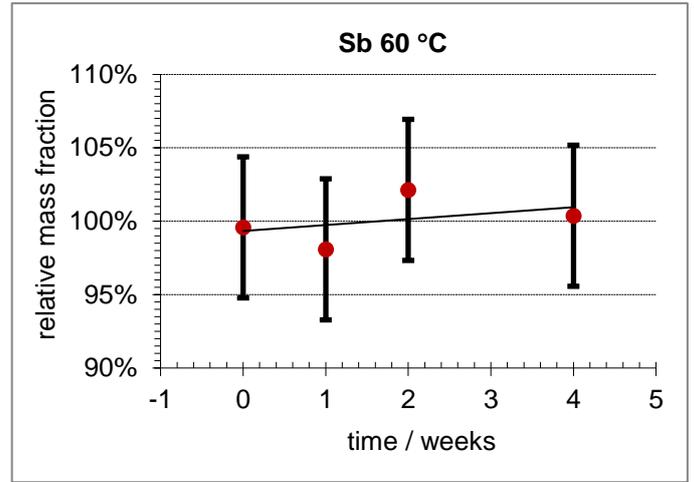


Figure A4.40. STS plot for Sb at 60 °C by IJS

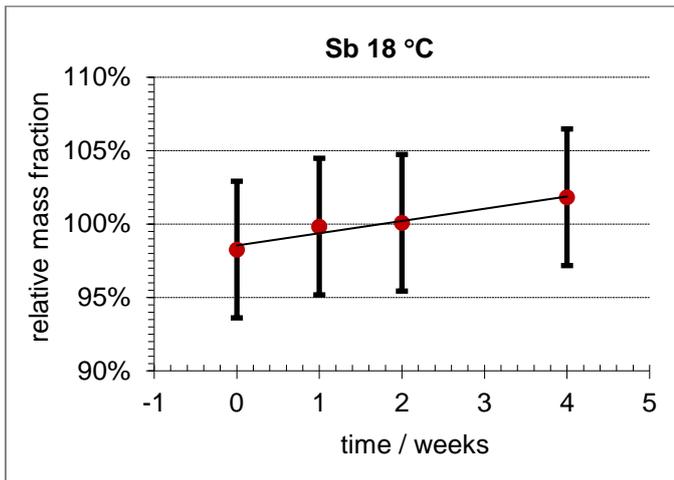


Figure A4.38. STS plot for Sb at 18 °C by IJS

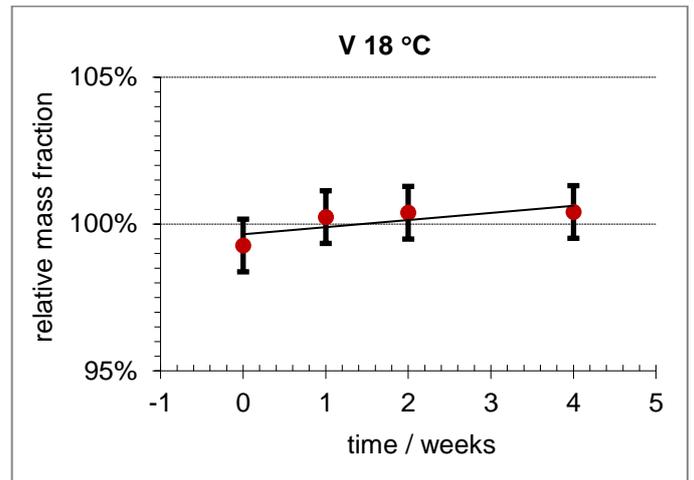


Figure A4.41. STS plot for V at 18 °C by UME

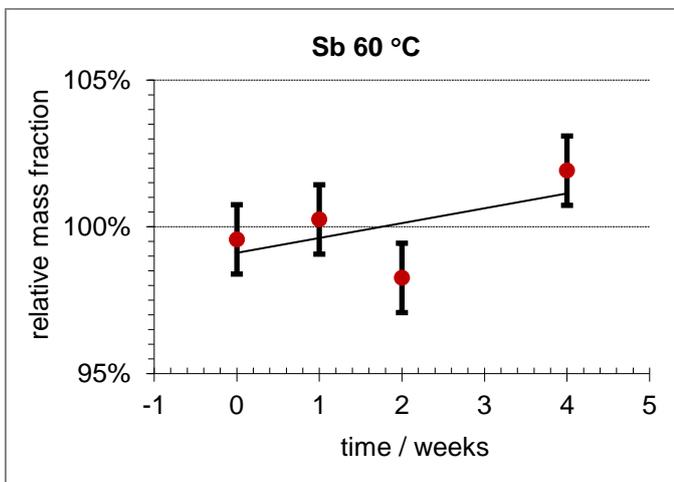


Figure A4.39. STS plot for Sb at 60 °C by UME

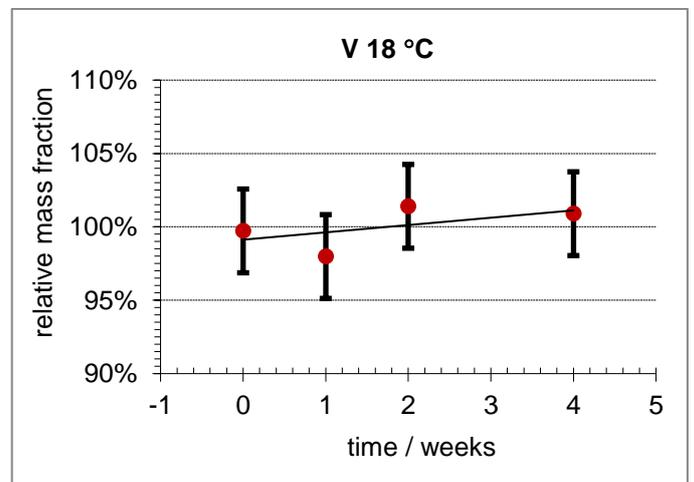


Figure A4.42. STS plot for V at 18 °C by IJS

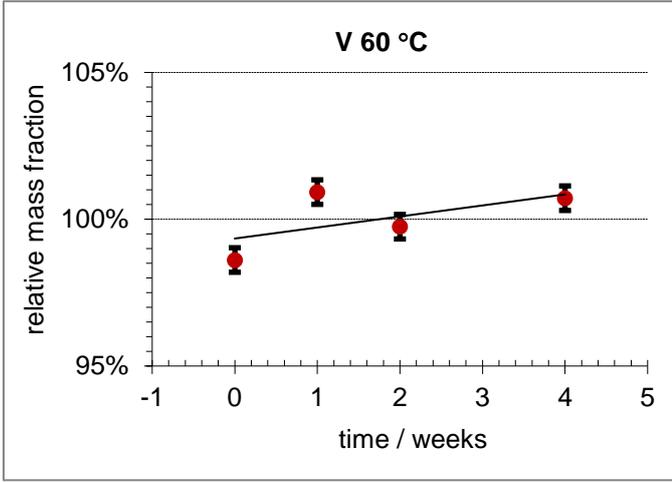


Figure A4.43. STS plot for V at 60 °C by UME

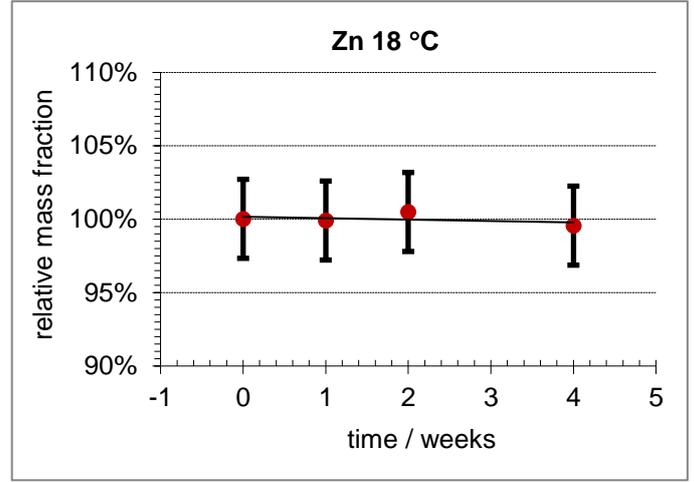


Figure A4.46. STS plot for Zn at 18 °C by IJS

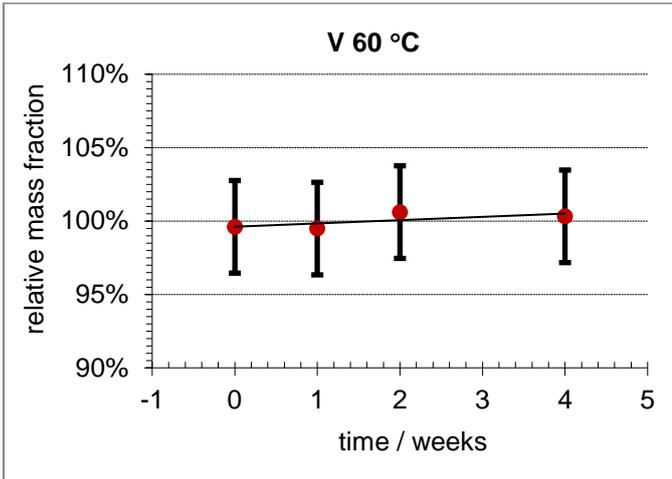


Figure A4.44. STS plot for V at 60 °C by IJS

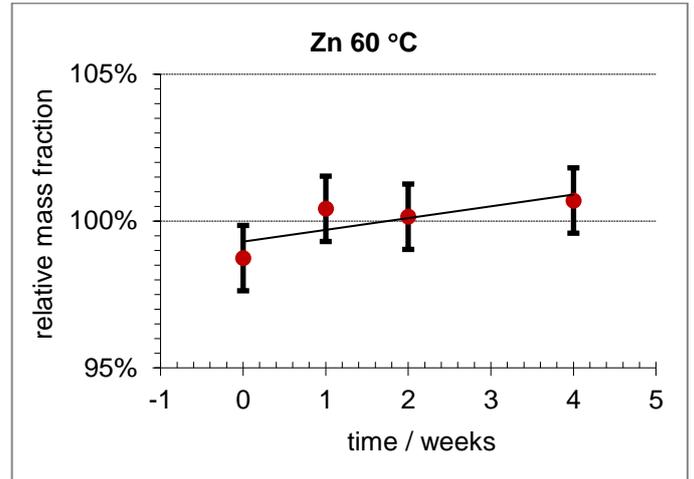


Figure A4.47. STS plot for Zn at 60 °C by UME

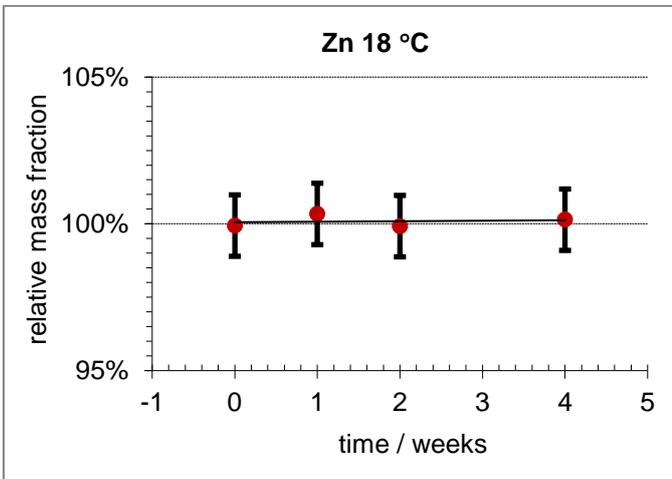


Figure A4.45. STS plot for Zn at 18 °C by UME

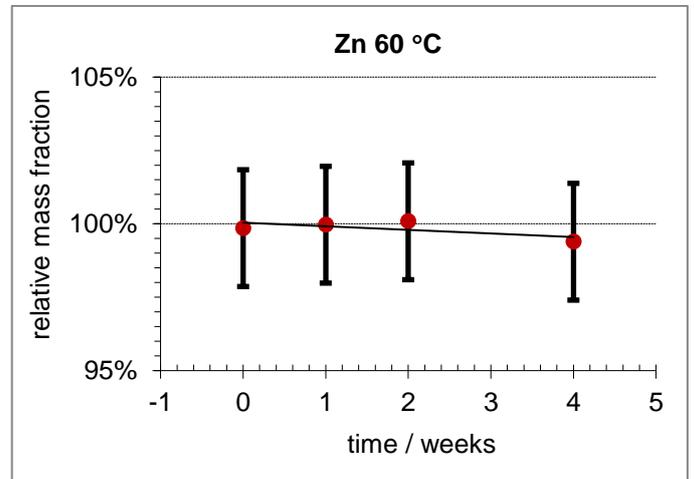


Figure A4.48. STS plot for Zn at 60 °C by IJS

Annex 5. Graphs for Long Term Stability Studies

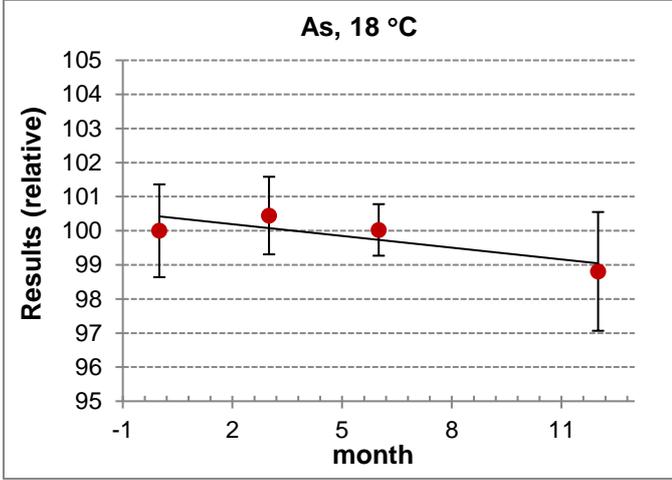


Figure A5.1. LTS plot for As at 18 °C by UME

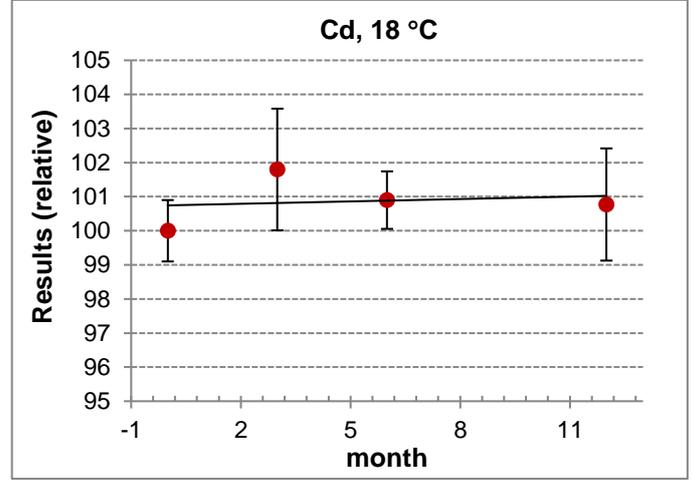


Figure A5.4. LTS plot for Cd at 18 °C by IJS

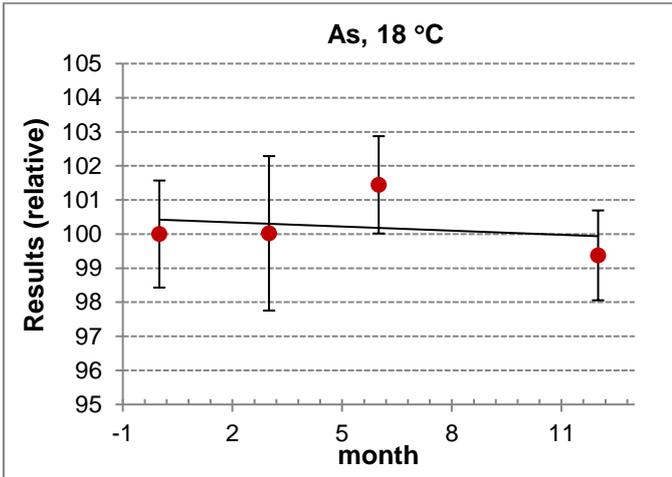


Figure A5.2. LTS plot for As at 18 °C by IJS

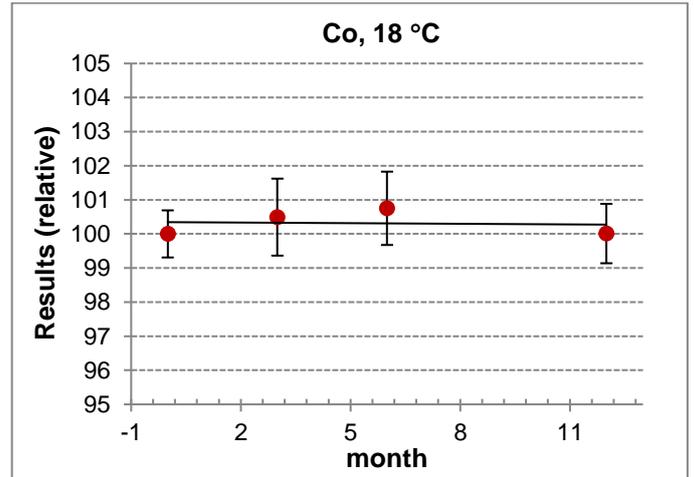


Figure A5.5. LTS plot for Co at 18 °C by UME

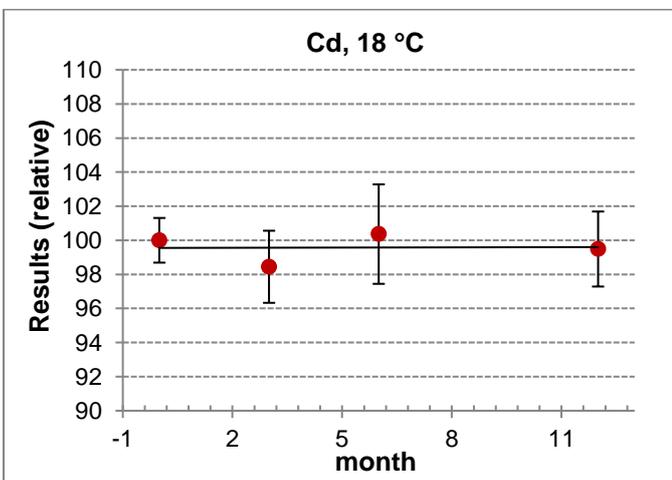


Figure A5.3. LTS plot for Cd at 18 °C by UME

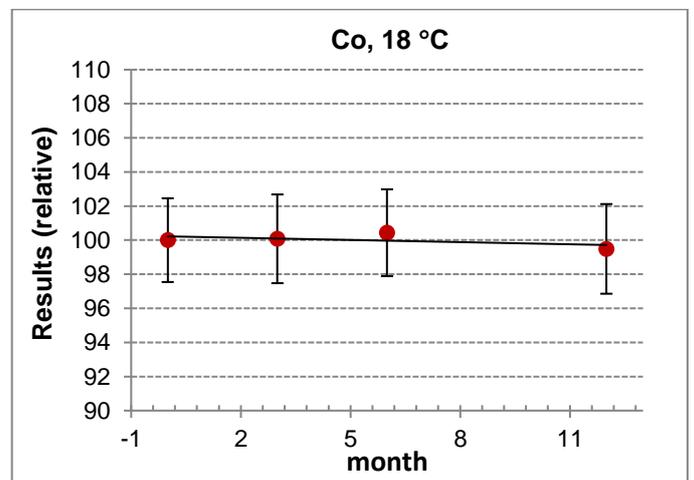


Figure A5.6. LTS plot for Co at 18 °C by IJS

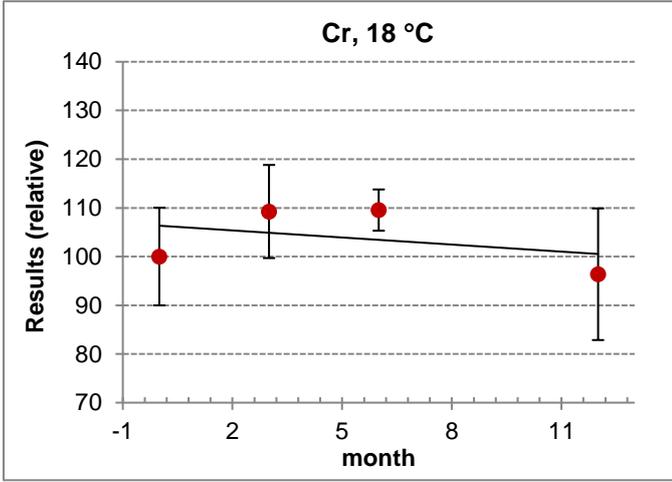


Figure A5.7. LTS plot for Cr at 18 °C by UME

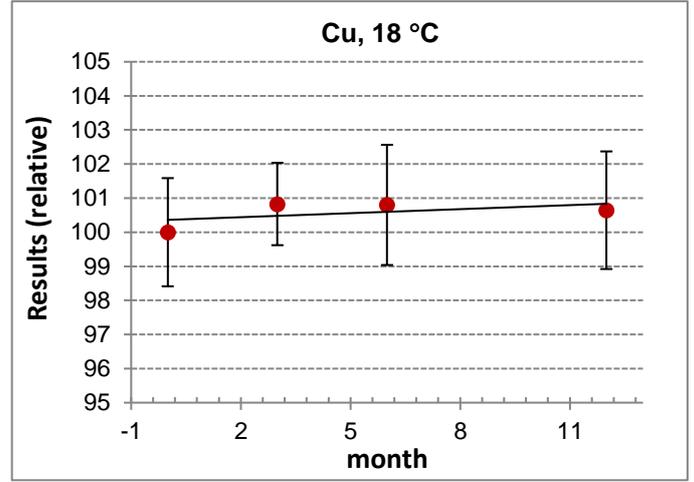


Figure A5.10. LTS plot for Cu at 18 °C by IJS

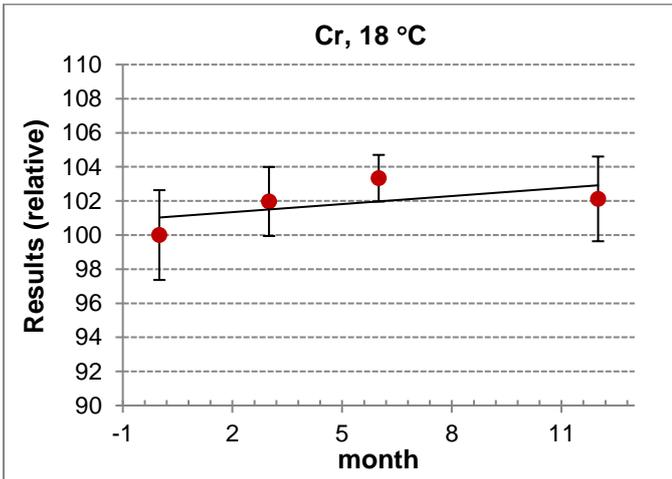


Figure A5.8. LTS plot for Cr at 18 °C by IJS

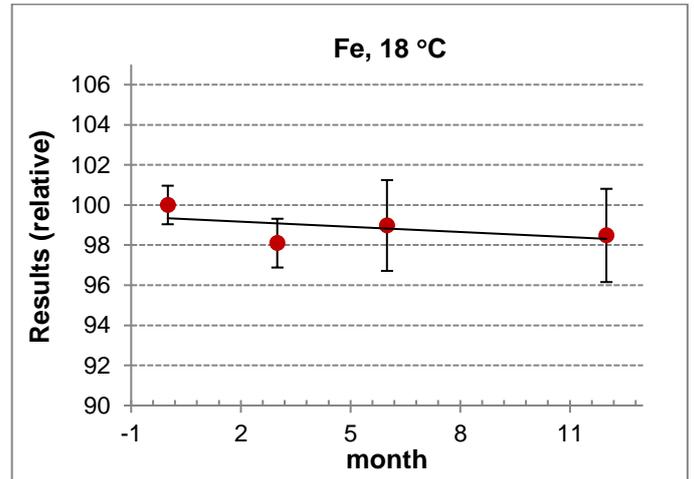


Figure A5.11. LTS plot for Fe at 18 °C by UME

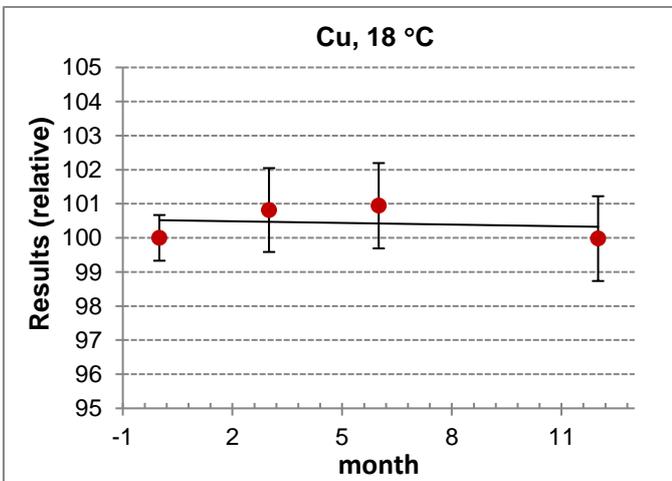


Figure A5.9. LTS plot for Cu at 18 °C by UME

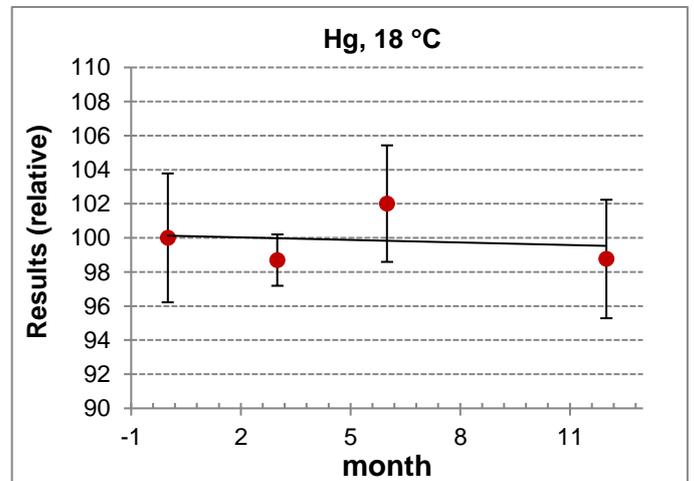


Figure A5.12. LTS plot for Hg at 18 °C by UME

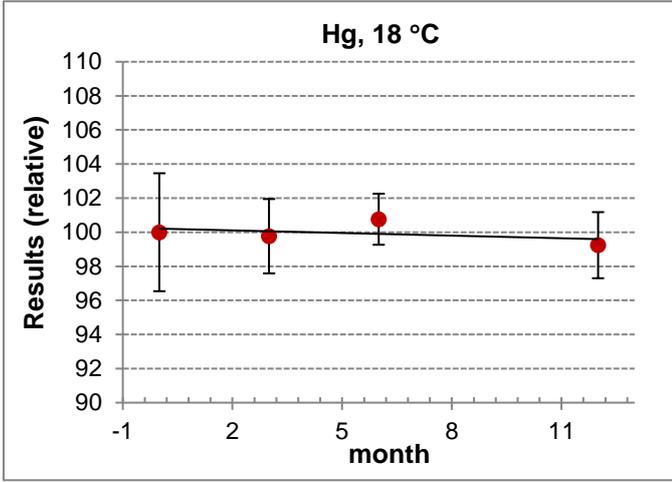


Figure A5.13. LTS plot for Hg at 18 °C by IJS

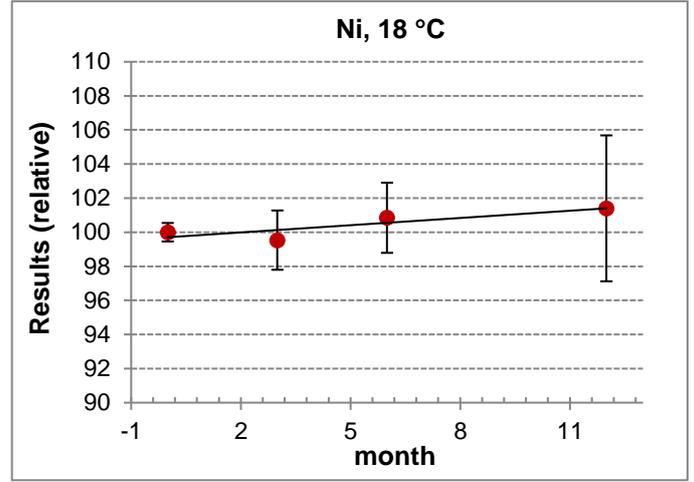


Figure A5.16. LTS plot for Ni at 18 °C by UME

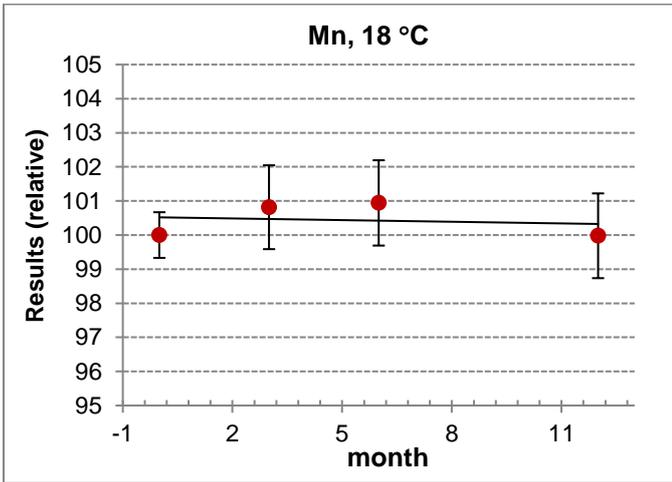


Figure A5.14. LTS plot for Mn at 18 °C by UME

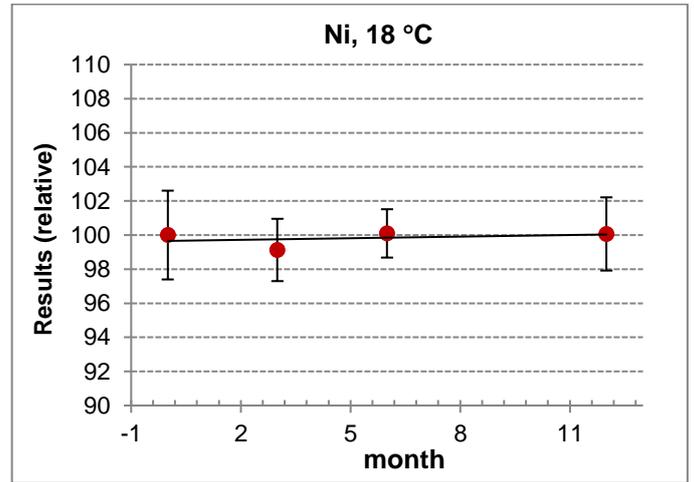


Figure A5.17. LTS plot for Ni at 18 °C by IJS

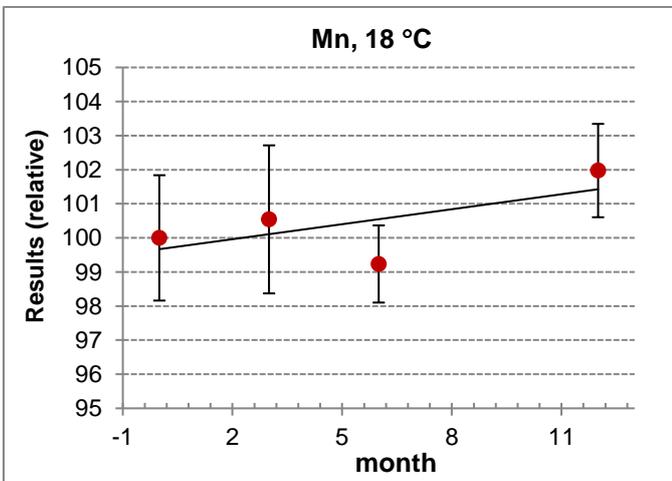


Figure A5.15. LTS plot for Mn at 18 °C by IJS

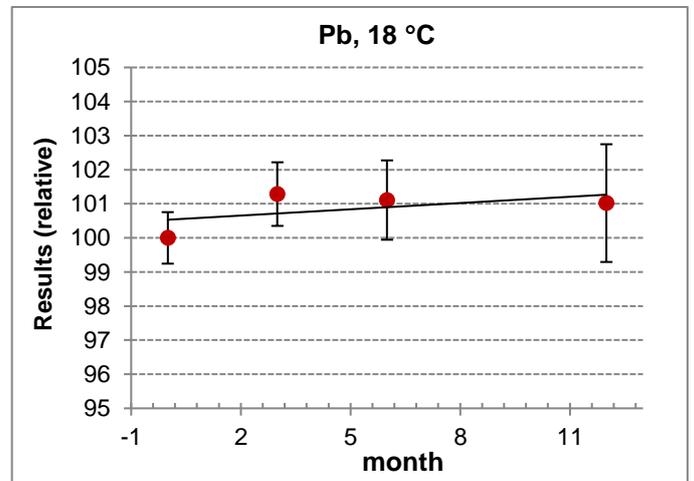


Figure A5.18. LTS plot for Pb at 18 °C by UME

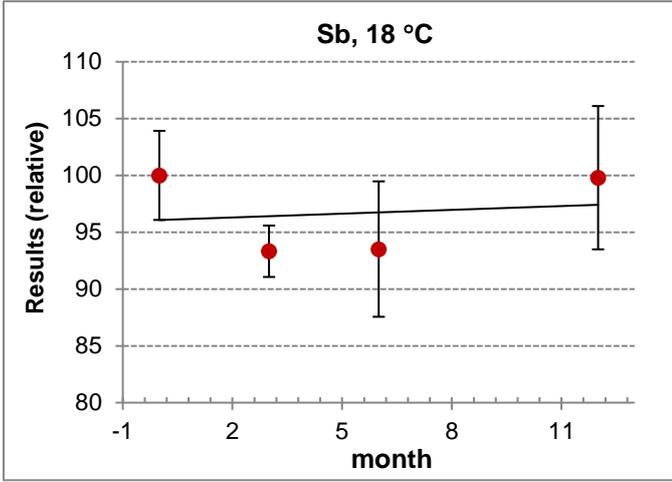


Figure A5.19. LTS plot for Sb at 18 °C by UME

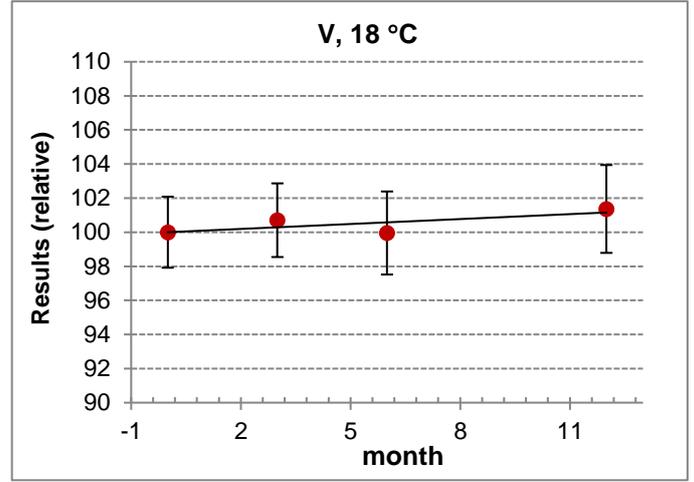


Figure A5.22. LTS plot for V at 18 °C by IJS

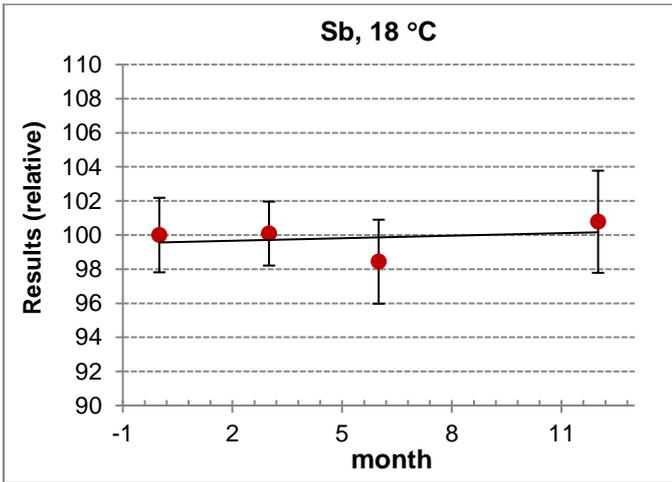


Figure A5.20. LTS plot for Sb at 18 °C by IJS

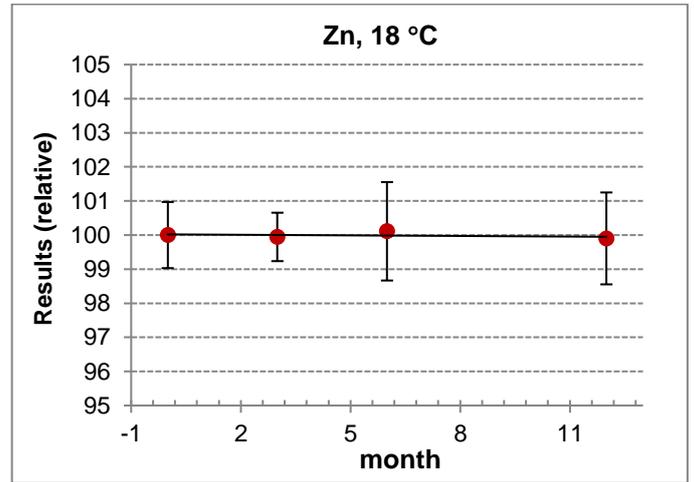


Figure A5.23. LTS plot for Zn at 18 °C by UME

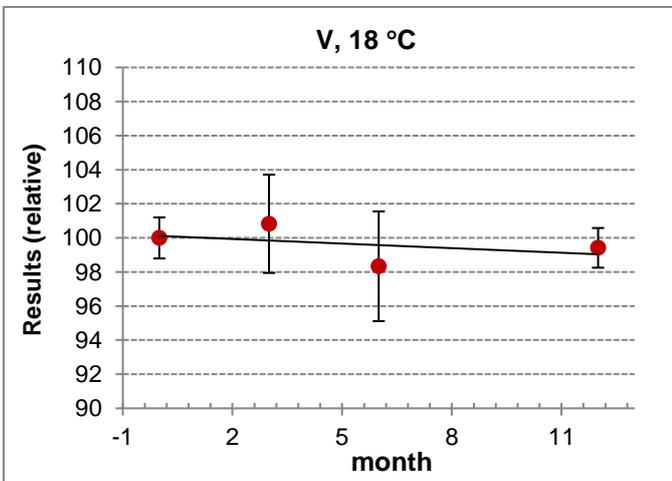


Figure A5.21. LTS plot for V at 18 °C by UME

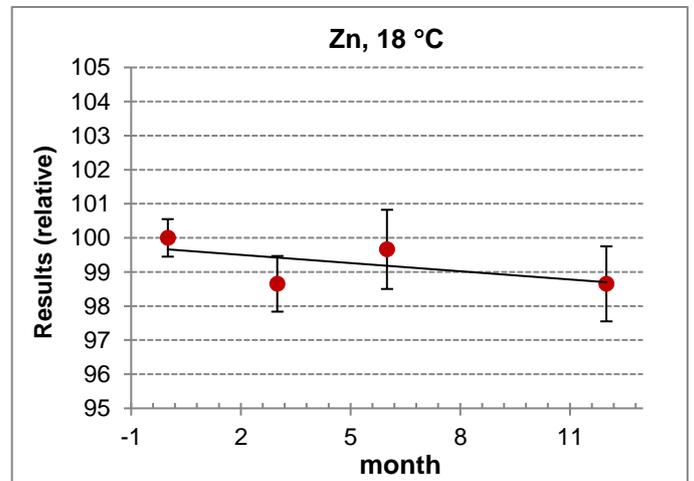


Figure A5.24. LTS plot for Zn at 18 °C by IJS

Annex 6. Information About the Methods Used for the Characterisation Study

Laboratory	Analytes	Sample Preparation	Calibration Strategy	Method/ Technique	CRM(s) for Calibration and QC
BAM	Cd, Hg, Ni	Dry mass determination was carried out at 105°C in a drying oven over 3 days on 4 samples each with ≈ 0.9 g. In parallel the samples for the IDMS measurements were weighed and spiked with ⁶¹ Ni, ¹¹³ Cd and spike solutions. Then a closed digestion with HNO ₃ (6 mL), HCl (2 mL) and HF (3 mL) using a microwave with T _{max} ≈ 200°C and p _{max} ≈ 20 bar (duration 20 min). Samples were split and matrix separation was carried out using an AG 1X8 resin for Cd and Hg (plus cystein); Ni was separated using the Ni Spec resin (Eichrom).	Isotope dilution mass spectrometry with isotopically enriched standards, which were calibrated with inhouse produced primary calibration solutions	ID-ICP-MS	BAM primary assays were used to calibrate the spike solutions
	Cr	Dry mass determination was carried out at 105°C in a drying oven over 3 days on 4 samples each with ≈ 0.9 g. In parallel the samples for the IDMS measurements were weighed and spiked with the ⁵³ Cr solution. Then a closed digestion with HNO ₃ and H ₂ O ₂ using a high pressure asher with T _{max} ≈ 320 °C and p _{max} ≈ 130 bar (duration 4 h). Samples were filtered, the filter and solid precipitate was ashed in a Pt crucible and the ash was digested with HF, the HF (and the formed SiF ₄) was evaporated; the solid residuum was combined with the filtrate from before, evaporated to dryness; then a fusion melt with Na ₂ CO ₃ was carried out; the solid material was dissolved in water and matrix separation was carried out using an AG 1X8 resin for Cr..			
	Cu, Pb	Dry mass determination was carried out at 105°C in a drying oven over 3 days on 4 samples each with ≈ 0.9 g. In parallel the samples for the IDMS measurements were weighed and spiked with ⁶⁵ Cu and ²⁰⁶ Pb spike solutions. Then a closed digestion with HNO ₃ (6 mL), HCl (2 mL) and HF (3 mL) using a microwave with T _{max} ≈ 200 °C and p _{max} ≈ 20 bar (duration 20 min). CaF ₂ precipitate was separated by centrifugation. The resulting solutions were split and matrix separation was carried out using a MP1 resin for Cu ; Pb was separated using the Pb Spec resin; (Eichrom)		ID-TIMS	

Laboratory	Analytes	Sample Preparation	Calibration Strategy	Method/ Technique	CRM(s) for Calibration and QC
DMDM	As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sb, V, Zn (Aqua Regia Extractable)	The sample is dried at 105 °C to constant weight. 3.0 g of sample accurately weighed, is added into glass container together with 21 mL of concentrated HCl and 7 mL of concentrated HNO ₃ (aqua regia) + 15 mL concentrated HNO ₃ in absorbing dish. Reaction dish (glass container) and absorbing dish are joined together, and sample is left on room temperature within 16 hours and then boiled at 105 °C for 2 hours. After cooling, sample is filtrated trough 0.2 µm filter and diluted up to 1 L.	Calibration standards were prepared from multi element certified reference materials using gravimetric method for preparation.	ICP-MS	Multi element standard. Traceable to NIST standards
IMBIH	Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V, Zn	The sample is dried at 105 °C to constant weight. Microwave digestion: 0.5 g of sample + 6 ml HCl + 2 ml HNO ₃ + 1 ml HF. The digestion program was: 150 °C; 10 min 180 °C; 10 min 200 °C; 5 min 210 °C; 10 min. The digest brought to a 50 mL final volume. Samples were prepared in triplicate.	Calibration standards were prepared from single element certified reference materials using gravimetric method for preparation	MP-AES	Accu Standard- single element certified reference materials
IJS	As, Cd, Co, Cr, Cu, Mn, Ni, Sb, V, Zn	Approximately 0.25 g of sample 4 mL of HNO ₃ , 2 mL of HF, 1 mL of HCl, 2 mL of H ₂ O ₂ and 12.5 mL of boric acid were added. The samples were subjected to closed microwave digestion. All acid used were suprapure grade.	For calibration external calibration via calibration curve was applied. The standards were prepared in the same mixtures of acids as were used for digestion. Measured isotopes: ⁷⁵ As, ¹¹¹ Cd, ⁵⁹ Co, ⁵² Cr, ⁶³ Cu, ⁵⁵ Mn, ⁶⁰ Ni, ¹²¹ Sb, ⁵¹ V, ⁶⁶ Zn. Internal standards used: ⁷² Ge, ¹⁰³ Rh, ¹¹⁵ In, ¹⁹³ Ir.	ICP-MS	For As (3103a), Cd (3108), Cr (3112a), Cu (3114), Ni (3136) and Zn (3168a) NIST calibration standards were used. For other elements Merck-Millipore single element standard solutions were used. ERM-CC141 Loam soil used for validation and quality control of the method
	Hg	About 250 mg of sample was weighed directly in a Teflon digestion vessels. After addition of 5 mL of mixture HNO ₃ /HF (2:1) and 1 mL of HCl, the vessels were closed and the mixture was left to react at room temperature for an hour. Digestion was finished by heating at 100°C for 12 hours on a hot plate. When cooled, the samples were diluted with 5% H ₃ BO ₃ to the mark (25.8 mL). The same procedure (reagents without sample) was applied for blank sample.	CV AAS, calibration with NIST 3133	CV-AAS	ERM-CC141 – Loam soil

Laboratory	Analytes	Sample Preparation	Calibration Strategy	Method/ Technique	CRM(s) for Calibration and QC
IJS	As, Co, Cr, Fe, Hg, Mn, Sb, V, Zn	An aliquot varied from 0.20 to 0.21 g was sealed into a pure polyethylene ampoule. For determination of intermediate/ median and long-lived radionuclides an aliquot and standard Al-0.1%Au alloy (IRMM-530R) were stacked together, fixed in the polyethylene vial in sandwich form and irradiated for 12 hours in the carousel facility (CF) of the TRIGA reactor with a thermal neutron flux of $1.1E12 \text{ cm}^{-2} \text{ s}^{-1}$. 7 aliquots were taken in this study. For determination of short-lived radionuclides an aliquot and standard Al-0.1%Au alloy (IRMM-530R) were stacked together and irradiated 30 seconds in the CF of the TRIGA reactor. 3 aliquots were taken in this study. This technique is non-destructive.	k_0 -standardization method of INAA. Certified reference material used for calibration: IRMM-530R (Al-0.1%Au alloy)	k_0 -INAA	Certified reference material IRMM-530R (Al-0.1%Au alloy) BCR-320R Channel sediment used for validation and quality control of the method.
NTUA	As, Cd, Ni, Pb, Cr, Zn, Cu, Co, V, Sb, Hg	Total digestion : 0,2 g of the dry sample was placed in a Teflon vessel with 9 ml HCl, 3ml HNO ₃ , 1ml HF and 1ml H ₂ O ₂ . The vessels were heated in a microwave apparatus up to 200 °C within 20 min and remained at 200 °C for 20 min.	External calibration with internal standards, As 75 (IS Ge72), Cd 111 (IS In115), Ni 59 (IS Ge 72), Pb 206+207+208 (IS Ir199), Cr 52 (IS Ge72), Zn 66 (IS Ge 72), Cu 63 (IS Ge 72), Co 59 (IS Ge72), V 51 (IS Sc 45), Sb121 (IS In 115), Hg 202 (IS Ir 191).	ICP-MS	Multi element standard, NIST traceable. Validation was obtained using the ERM-CC 141 (Loam soil) reference material. This soil has certified values for As, Cd, Co, Cr, Cu, Hg, Ni, Pb, Zn but not for Sb and V. Hence, in case of Sb and V, the uncertainty of validation was calculated by recovery experiments.
	As, Co, Cr, Cu, Ni, Pb, V, Zn Aqua Regia Extractable)	The sample is dried at 105 °C overnight (to constant weight). 0.5 g of sample accurately weighed, is added into a Teflon vessel together with 9 mL of concentrated HCl and 3 mL of concentrated HNO ₃ (aqua regia). The vessel is secured and put into a temperature controlled microwave oven. The digestion program applied is heating up to 180 °C within 5.5 min and then hold at 180 °C for another 9.5 min. The solution obtained is diluted up to 25 mL, after cooling.	External calibration and standard addition method at the following wavelengths: Ni (231.604 nm), Pb (220.353 nm), As (193.696 nm), Cr (205.560 nm), Zn (213.857nm), Cu (324.752 nm), Co (238.892 nm), V (292.402 nm).	ICP-OES	
	As, Cd, Ni, Pb, Cr, Zn, Cu, Co, V, Sb, Hg (Aqua Regia Extractable)		External calibration with internal standard, As ⁷⁵ (IS Ge ⁷²), Cd ¹¹¹ (IS In ¹¹⁵), Ni ⁵⁹ (IS Ge ⁷²), Pb ²⁰⁶⁺²⁰⁷⁺²⁰⁸ (IS Ir ¹⁹⁹), Cr ⁵² (IS Ge ⁷²), Zn ⁶⁶ (IS Ge ⁷²), Cu ⁶³ (IS Ge ⁷²), Co ⁵⁹ (IS Ge ⁷²), V ⁵¹ (IS Sc ⁴⁵), Sb ¹²¹ (IS In ¹¹⁵), Hg ²⁰² (IS Ir ¹⁹¹).	ICP-MS	
	Cd, Cu, Pb, Zn (Aqua Regia Extractable)		Standard addition method according Metrohm VA App. Note No. V-83	ASV	

Laboratory	Analytes	Sample Preparation	Calibration Strategy	Method/ Technique	CRM(s) for Calibration and QC
UME	As, Cu, Co, Fe, Mn, Ni, Sb, V	0.5 g of sample weighed and mixed with 8 mL of HNO ₃ , 5 mL of HCl and 1 mL of HF. After 1 hour predigestion program 1 was applied: Ramp to 180 °C in 20 min. Keep 10 min and ramp to 200 °C in 10 min. Keep at 200 °C for 30 min and cool down. Vessels opened and 1 mL HCl and 0.5 mL HF added. Program 2 was applied: Ramp to 200 °C in 20 min and keep for 30 min. Cool down and dilute the contents to 25 mL with 18 MΩ·cm deionized water. All the sample dilutions for analysis were done with 1% (v/v) HNO ₃ .	Standard addition method NIST SRM 31XX series certified reference materials for calibration	ICP-MS	NIST SRM 31XX series CRMs were used for calibration. NIST SRM 2711a Montana Soil was used for method development and validation.
	Cd, Cr, Fe, Hg, Pb, Zn		Isotope dilution mass spectrometry with isotopically enriched standards	ID-ICP-MS	
UW	As, Co, Cr, Cu, Cd, Hg, Mn, Ni, Sb, V, Zn, Pb	Closed vessels system UltraWave Milistone for digestion was used. Digestion was performed for around 0.2 g of material with addition of 4 mL 65% HNO ₃ and 1 mL 40% HF. After digestion samples were diluted till 30 mL with deionized water. Digestion program was as followed: 250 °C within 20 min and then hold at 60 °C for another 15 min.	External calibration curves were used. For the preparation of standard solutions multielemental stock solution was appropriate diluted by 1% HNO ₃	ICP-MS	
	Fe			AAS	

Annex 7. Graphs for Characterization Study

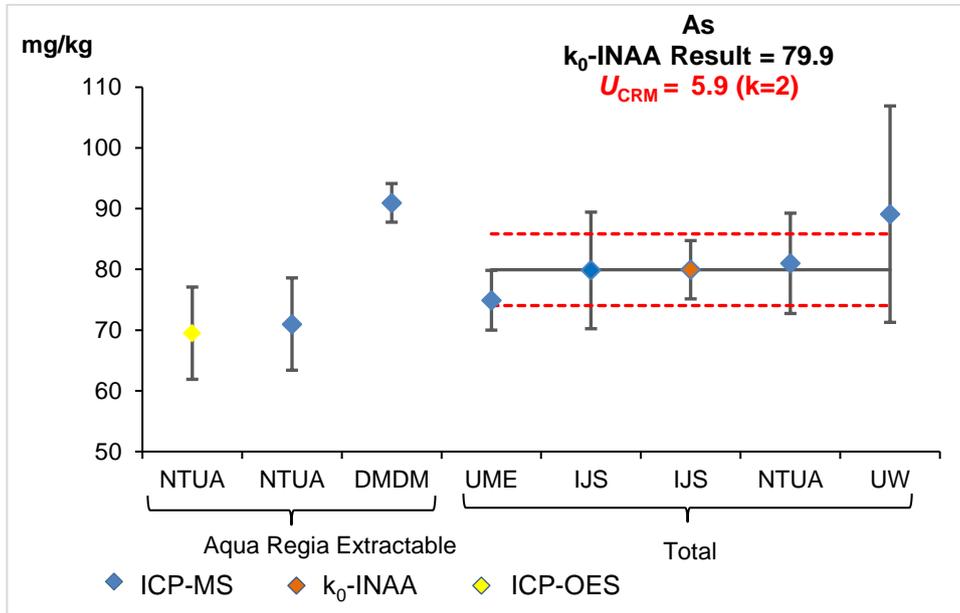


Figure A7.1. Characterization Study Plot for As

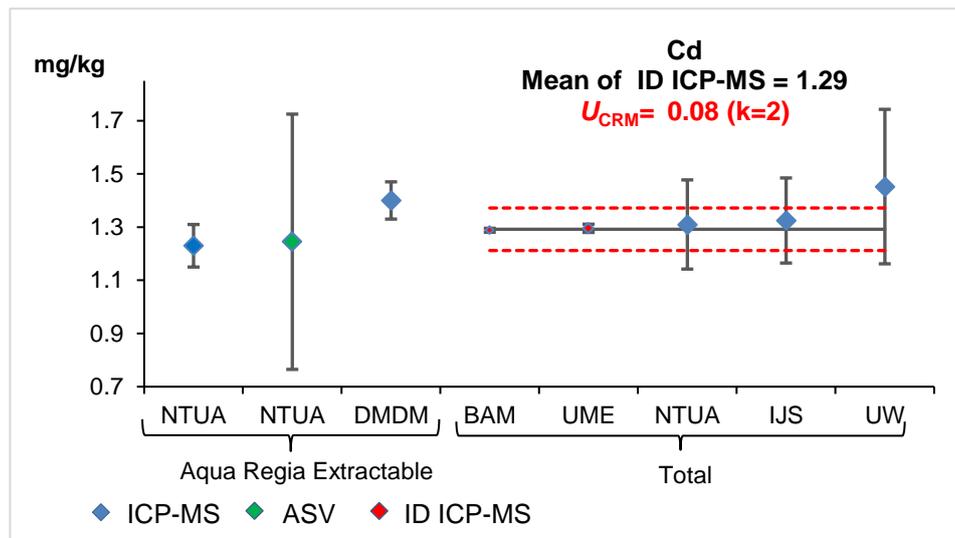


Figure A7.2. Characterization Study Plot for Cd

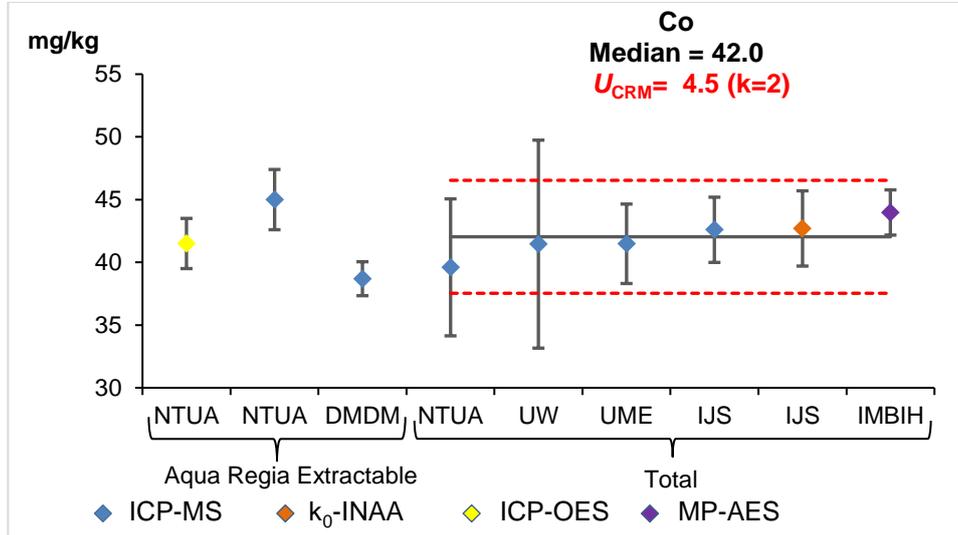


Figure A7.3. Characterization Study Plot for Co

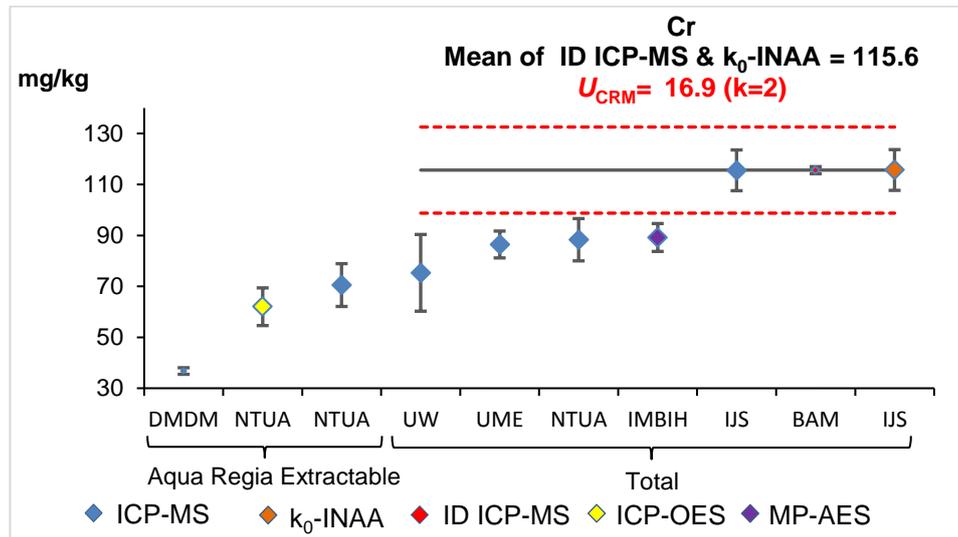


Figure A7.4. Characterization Study Plot for Cr

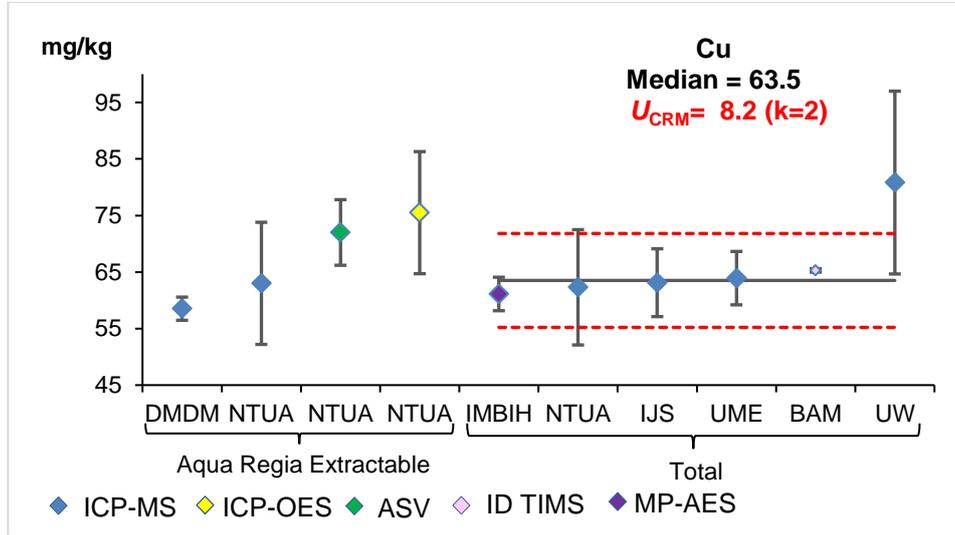


Figure A7.5. Characterization Study Plot for Cu

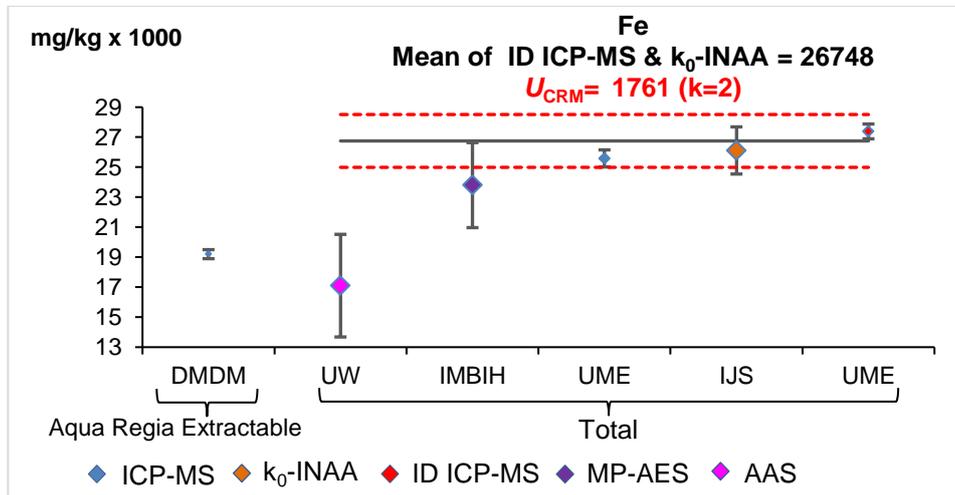


Figure A7.6. Characterization Study Plot for Fe

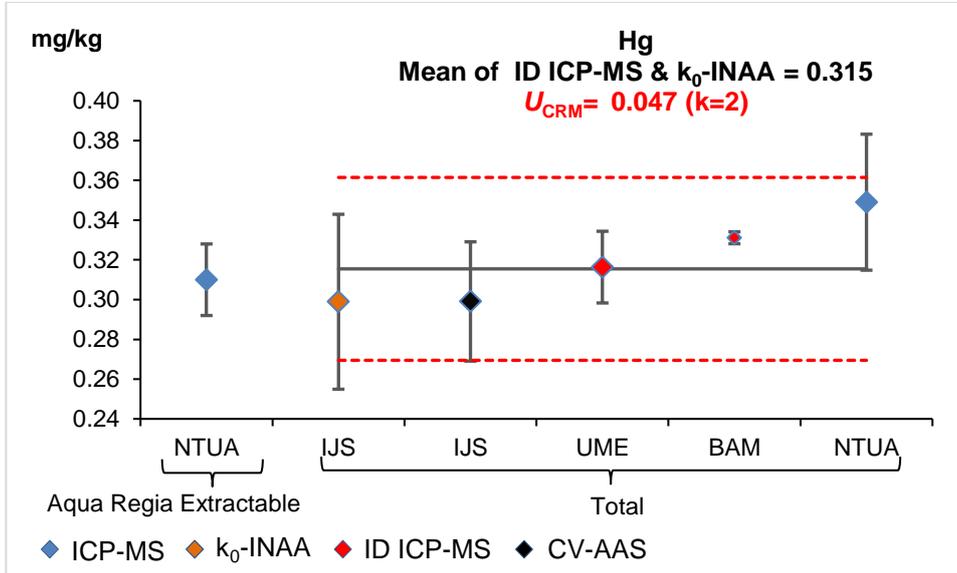


Figure A7.7. Characterization Study Plot for Hg

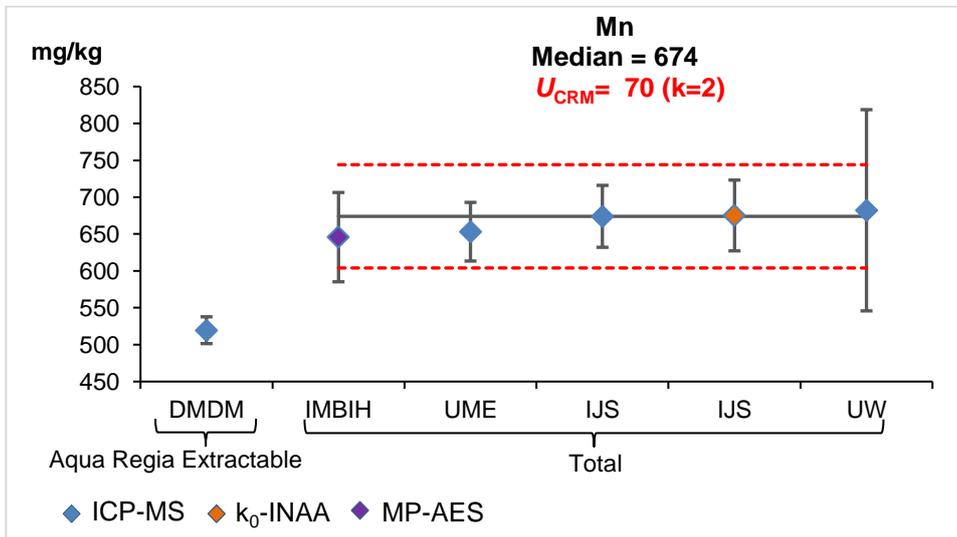


Figure A7.8. Characterization Study Plot for Mn

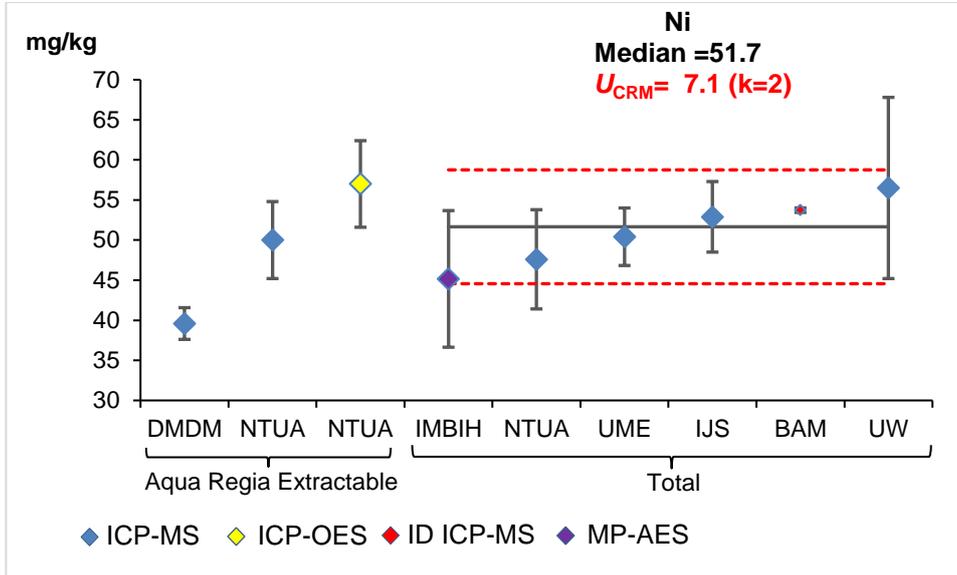


Figure A7.9. Characterization Study Plot for Ni

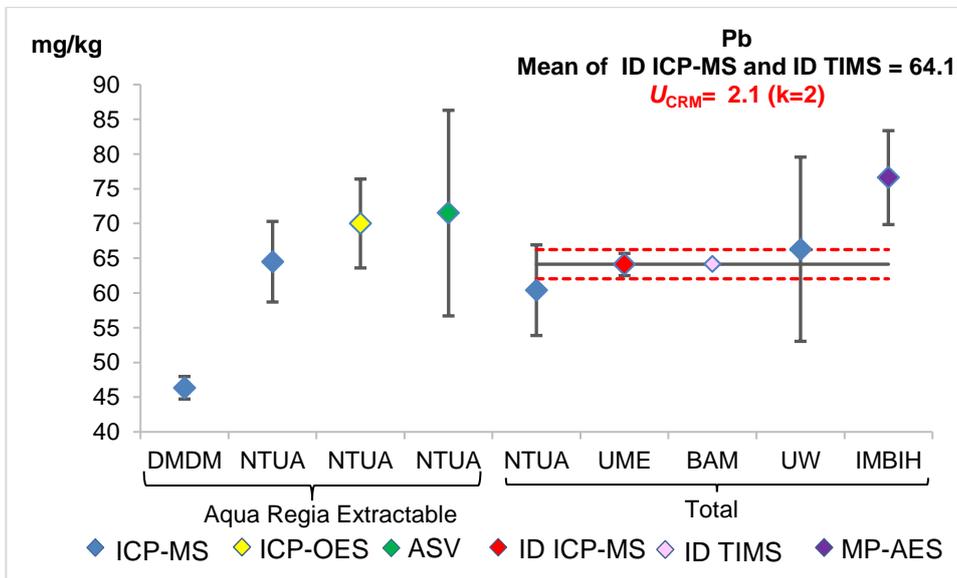


Figure A7.10. Characterization Study Plot for Pb

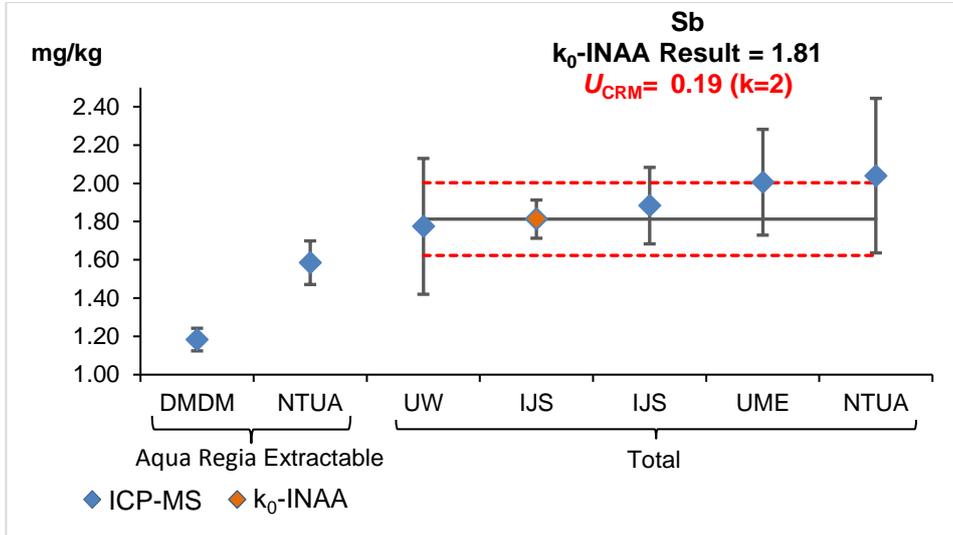


Figure A7.11. Characterization Study Plot for Sb

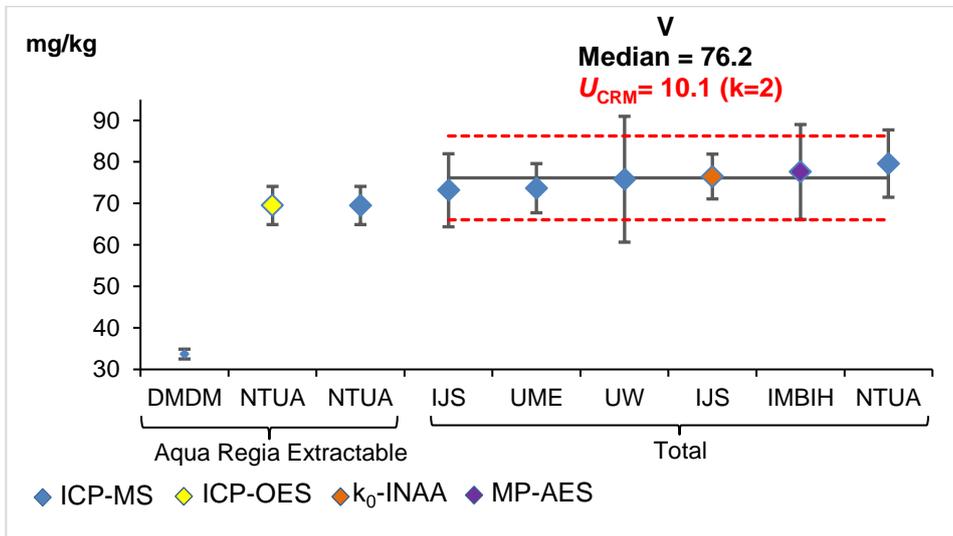


Figure A7.12. Characterization Study Plot for V

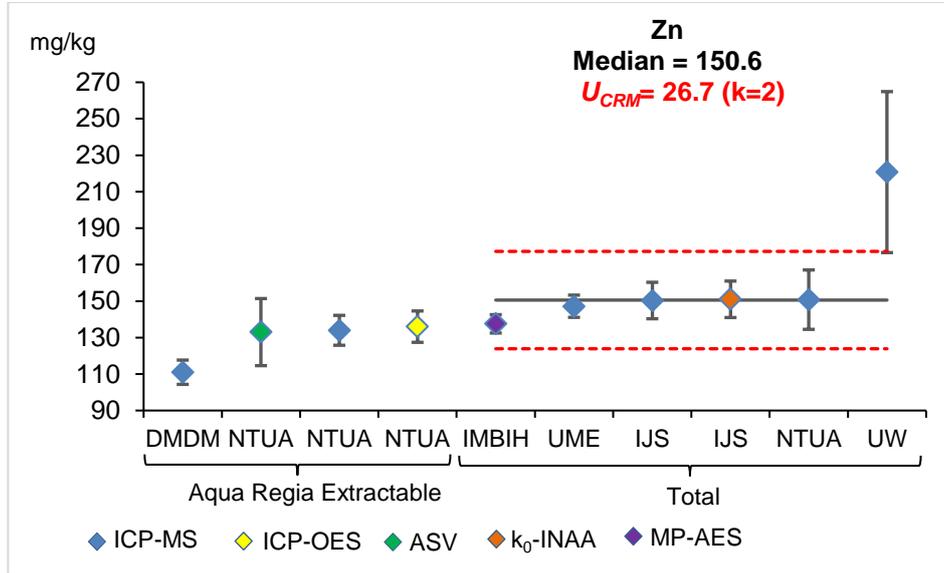


Figure A7.13. Characterization Study Plot for Zn