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CERTIFICATION REPORT

The certification of the mass concentration of arsenic, cadmium, chromium, copper, iron, manganese, mercury, lead, nickel and selenium in wastewater: ERM®-CA713

Certified Reference Material ERM®- CA713

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The certification of the mass concentration of arsenic, cadmium, chromium, copper, iron, manganese, mercury, lead, nickel and selenium in wastewater: ERM®-CA713

Certified Reference Material ERM®- CA713

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Disclaimer

Summary

This report describes the production of ERM®-CA713, a wastewater material certified for the mass concentration of As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb and Se. The material was produced following ISO Guide 34:2009 [1].The starting material was 200 L of a wastewater effluent collected at a wastewater treatment facility in Belgium. The sample was filtered, acidified and spiked before filling into 100 mL borosilicate ampoules which were flame-sealed after filling. The material was sterilised by γ-irradiation.

Between unit-homogeneity and stability during dispatch and storage have been assessed in accordance with ISO Guide 35:2006 [2]. Due to the inherent homogeneity of filtered water samples, determination of minimum sample intake (within-unit heterogeneity) was not required.

The certified values were obtained by using a range of different analytical techniques. The material was characterised by an inter-comparison among laboratories of demonstrated competence and adhering to ISO/IEC 17025. Technically invalid results were removed but no outlier was eliminated for statistical reasons only.

Uncertainties of the certified values were calculated in compliance with the Guide to the Expression of Uncertainty in Measurement (GUM) [3] and include uncertainties related to possible heterogeneity, instability and characterisation.

The material is intended for quality control and assessment of method performance. As any reference material, it can also be used for control charts or validation studies. The certified reference material (CRM) is available in borosilicate ampoules containing 100 mL of wastewater with a headspace filled with argon.

The following values were assigned:

	Mass Concentration	
	Certified value 1) [µg/L]	Uncertainty 2) [µg/L]
As	10.8	0.3
Cd	5.09	0.20
Cr	20.9	1.3
Cu	101	7
Fe	445	27
Hg	1.84	0.11
Mn	95	4
Ni	50.3	1.4
Pb	49.7	1.7
Se	4.9	1.1

1) Unweighted mean value of the means of accepted sets of data, each set being obtained in a different laboratory and/or with a different method of determination. The certified value and its uncertainty are traceable to the International System of units (SI)

2) The certified uncertainty is the expanded uncertainty with a coverage factor *k* = 2 corresponding to a level of confidence of about 95 % estimated in accordance with ISO/IEC Guide 98-3, Guide to the Expression of Uncertainty in Measurement (GUM:1995), ISO, 2008.

Additional material information

Additional Material Information		
	Mass Concentration	
	Value[2)]	Unit
Zn[1)]	78	µg/L
1) Zinc was determined by using ICP-OES, ICP-QMS and ICP-SFMS 2) Unweighted mean value of the means of seven independent datasets.		

The CRM was accepted as European Reference Material (ERM®) after peer evaluation by the partners of the European Reference Materials consortium.

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Glossary

AAS	Atomic absorption spectrometry
AFS	Atomic fluorescence spectrometry
ANOVA	Analysis of variance
BCR$^{\circledR}$	One of the trademarks of CRMs owned by the European Commission; formerly Community Bureau of Reference
CC	Collision cell
CCT	Collision cell technology
CEN	European Committee for Standardization
CI	confidence interval
CRM	Certified reference material
CV-AAS	Cold vapour atomic absorption spectrometry
CV-AFS	Cold vapour atomic fluorescence spectrometry
EC	European Commission
EN	European norm (standard)
ERM$^{\circledR}$	Trademark of European Reference Materials
EU	European Union
ET-AAS	Electrothermal atomic absorption spectrometry
FAAS	Flame atomic absorption spectrometry
GUM	Guide to the Expression of Uncertainty in Measurements *[ISO/IEC Guide 98-3:2008]*
HG-AAS	Hydride generation atomic absorption spectrometry
HG-ICPSFMS	Hydride generation inductively coupled plasma sector field mass spectrometry
ICP	Inductively coupled plasma
ICPMS	Inductively coupled plasma mass spectrometry
ICPQMS	ICP-Quadrupole mass spectrometry
ICPSFMS	ICP-Sector field mass spectrometry
IRMM	Institute for Reference Materials and Measurements of the JRC
ISO	International Organization for Standardization
IU	International units
IUPAC	International Union of Pure and Applied Chemistry
JRC	Joint Research Centre of the European Commission
k	Coverage factor
LOD	Limit of detection
LOQ	Limit of quantification
MS	Mass spectrometry
MS_{between}	Mean of squares between-unit from an ANOVA

MS_{within}	Mean of squares within-unit from an ANOVA
n	Number of replicates per unit
N	Number of samples (units) analysed
n.a.	Not applicable
n.c.	Not calculated
n.d.	Not detectable
OES	Optical emission spectrometry
QA	Quality assurance
QC	Quality control
rel	Index denoting relative figures (uncertainties etc.)
RM	Reference material
RM Unit	Reference Materials Unit of the IRMM
RSD	Relative standard deviation
RSE	Relative standard error (=RSD/$\sqrt{n}$)
r^2	Coefficient of determination of the linear regression
s	Standard deviation
s_{bb}	Between-unit standard deviation; an additional index "rel" is added when appropriate
s_{between}	Standard deviation between groups as obtained from ANOVA; an additional index "rel" is added when appropriate
SF-MS	Sector field mass spectrometry
SI	International System of Units
s_{meas}	Standard deviation of measurement data; an additional index "rel" is added when appropriate
s_{ns}	Standard deviation of results of normal stock samples
STW	Sewage treatment works
s_{within}	Standard deviation within groups as obtained from ANOVA; an additional index "rel" is added when appropriate
s_{wb}	Within-unit standard deviation
T	Temperature
t	Time
t_i	Time point for each replicate
$t_{\alpha,\text{ df}}$	Critical t-value for a t-test, with a level of confidence of 1-α and df degrees of freedom
t_{sl}	Proposed shelf life
u	standard uncertainty
U	expanded uncertainty
u^*_{bb}	Standard uncertainty related to a maximum between-unit heterogeneity that could be hidden by method repeatability; an additional index "rel" is added when appropriate
u_{bb}	Standard uncertainty related to a possible between-unit heterogeneity; an

	additional index "rel" is added when appropriate
u_c	combined standard uncertainty; an additional index "rel" is added when appropriate
u_cal	Standard uncertainty of the calibration
u_char	Standard uncertainty of the material characterisation; an additional index "rel" is added when appropriate
u_CRM	Combined standard uncertainty of the certified value; an additional index "rel" is added when appropriate
U_CRM	Expanded uncertainty of the certified value; an additional index "rel" is added when appropriate
u_Δ	Combined standard uncertainty of measurement result and certified value
u_lts	Standard uncertainty of the long-term stability; an additional index "rel" is added when appropriate
u_m	Standard measurement uncertainty
U_meas	Expanded measurement uncertainty
u_rec	Standard uncertainty related to possible between-unit heterogeneity modelled as rectangular distribution; an additional index "rel" is added when appropriate
u_sts	Standard uncertainty of the short-term stability
u_t	Standard uncertainty of trueness
VIM	Vocabulaire International de Métrologie – Concepts Fondamentaux et Généraux et Termes Associés (International Vocabulary of Metrology – Basic and General Concepts and Associated Terms)*[ISO/IEC Guide 99:2007]*
WFD	Water Framework Directive
$\overline{x}$	Arithmetic mean
$\overline{x_\mathrm{ns}}$	Arithmetic mean of all results of normal stock samples
$\overline{x_\mathrm{ref}}$	Arithmetic mean of results of reference samples
α	significance level
Δm	Absolute difference between mean measured value and the certified value
ν_{smeas}	Degrees of freedom for the determination of the standard deviation s_meas
$\nu_{MSwithin}$	Degrees of freedom of MS_within

1 Introduction

1.1 Background: need for the CRM

A growing population and high standards of living result in increasing pressures on water resources. In 2000, the Water Framework Directive (WFD; [4]) was adopted and since then, the European Commission has issued a number of directives that provide the legislative framework for the protection of surface waters and other water resources. Directive 2008/105/EC on environmental quality standards in the field of water policy for instance contains a list of priority substances, including cadmium, mercury, nickel, lead and their compounds for which maximum allowable concentrations and annual average values were set for surface waters.

The WFD requires all member states to establish monitoring programmes covering the quantitative and chemical status of surface waters and the assessment of significant, long-term pollution trends resulting from human activities such as the direct discharge of wastewater effluents to surface and coastal waters. The requirement for the efficiency of the wastewater treatment was laid down in Commission Directive 91/271/EEC but the confidence in any assessment of the efficiency of the treatment process and the quality of the wastewater effluent will depend on the quality of measurement data. This is ensured by Directive 2009/60/EC, which lays down the technical specifications for chemical analysis and monitoring of the water status. The availability of appropriate certified reference materials (CRMs) will be an asset in meeting the minimum performance criteria that are stipulated in this legislation, such as the validation of analytical methods, ensuring accuracy and traceability of the measurement results [5].

ERM-CA713, the production of which was carried out by IRMM and is described in this report, is intended to be used as a quality assurance and quality control tool especially by laboratories responsible for the mandatory monitoring prescribed under the WFD.

1.2 Choice of the material

ERM-CA713 was developed as a replacement for three wastewater-based reference materials: BCR®-713, BCR®-714 and BCR®-715. It was decided to replace these materials because of changes in the legislation, in particular the requirement for the monitoring of Hg as a priority substance. IRMM recognises that the ERM-CA713 is not representative of all wastewater effluents. The concentration levels that were targeted were based on the certified values of the BCR-713 material and on the environmental quality standards set by the legislation 6.

1.3 Design of the project

The certification of ERM-CA713 was performed by interlaboratory comparison using more than one analytical method.

2 Participants

2.1 Project management and evaluation

European Commission, Joint Research Centre, Institute for Reference Materials and Measurements (IRMM), Geel, BE
(accredited to ISO Guide 34 for production of certified reference materials, BELAC No 268-RM)

2.2 Processing

European Commission, Joint Research Centre, Institute for Reference Materials and Measurements (IRMM), Geel, BE
(accredited to ISO Guide 34 for production of certified reference materials, BELAC No 268-RM)

2.3 Homogeneity study

DVGW -Technologiezentrum Wasser, Karlsruhe, DE
(measurements under the scope of ISO/IEC 17025 accreditation, DACH DAC-PL-0142-01-10)

2.4 Stability studies

DVGW -Technologiezentrum Wasser, Karlsruhe, DE
(measurements under the scope of ISO/IEC 17025 accreditation, DACH DAC-PL-0142-01-10)

IWW Rheinisch-Westfälisches Institut für Wasser Beratungs und Entwicklungsgesellschaft, Mülheim an der Ruhr, DE
(measurements under the scope of ISO/IEC 17025 accreditation, DGA DAC-PL-0170-02-10)

2.5 Characterisation

ALS Laboratory Group, ALS Czech Republic, Praha, CZ
(measurements under the scope of ISO/IEC 17025 accreditation, CAI, 521)

ALS Laboratory Group, ALS Scandinavia AB, Luleå, SE
(measurements under the scope of ISO/IEC 17025 accreditation, SWEDAC-1087)

Bundesanstalt für Materialforschung and -prüfung (BAM), Berlin, DE
(measurements under the scope of ISO/IEC 17025 accreditation, DAP-PL-2614.14)

Consiglio Nazionale delle Ricerce (CNR), Istituto di Ricerca sulle Acque, UOS Brugherio, IT

DVGW -Technologiezentrum Wasser, Karlsruhe, DE
(measurements under the scope of ISO/IEC 17025 accreditation, DACH DAC-PL-0142-01-10

Institute "Jozef Stefan" (JSI) Department for Environmental Sciences, Ljubljana, SI
(measurements under the scope of ISO/IEC 17025 accreditation, SA, LP-90)

IWW Rheinisch-Westfälisches Institut für Wasser Beratungs und Entwicklungsgesellschaft, Mülheim an der Ruhr, DE
(measurements under the scope of ISO/IEC 17025 accreditation, DGA DAC-PL-0170-02-10)

The James Hutton Institute, Analytical Group, Aberdeen, GB
(measurements under the scope of ISO/IEC 17025 accreditation, UKAS 1917)

Rijkswaterstaat, Ministerie van Verkeer en Waterstaat, Waterdienst, Lelystad, NL
(measurements under the scope of ISO/IEC 17025 accreditation, RvA, No L194)

VA SYD, Malmö, SE
(measurements under the scope of ISO/IEC 17025 accreditation, SWEDAC No 07-213-51.1056)

3 Material processing and process control

3.1 Origin of the starting material

The company Aquafin is responsible for the collection and treatment of wastewater in Flanders and was contacted for exploring the possibility of collecting a sample of treated wastewater effluent from one of their sewage treatment works (STW). Permission was granted to collect a sample of water from an installation of our choice on the condition that the exact location and the levels of the analytes would remain confidential. The Flemish Environment Agency (Vlaamse Milieumaatschappij or VMM) monitors the levels of As, Cr, Cu, Cd, Hg, Ni and Pb in the effluents discharged into surface waters on a monthly basis and publishes the data on the website (http://www.vmm.be/geoview/). For the purposes of our work, an assessment was made of the data on discharges made by various sewage treatment works throughout Flanders to select the most suitable for our needs. The data showed that trace element concentrations are all below the target concentrations in most STW in Flanders. As a consequence, it was decided to collect the sample in the local area.

The sample was collected on the 8th of July 2009 from a STW, which treats wastewater of mixed domestic and industrial origin. The exact location of sampling was a concrete-based channel about one meter wide and one meter deep, which conducts the treated wastewater from the STW to the discharge point in the local river. The depth of the water in the channel was approximately 20 cm. Prior to transferring the sample to the pre-cleaned polyethylene tank, the water was flushed through the tubing for several minutes to rinse the system. The final volume of the sample was 200 L.

Upon arrival at IRMM, the sample was filtered using Versaflow capsule filters (0.45 µm, Pall Corporation, Ann Arbor, Michigan, USA), acidified to a pH of 1.6 using ultrapure HNO_3 (Merck) and stored at 4 ^{o}C. The sample was allowed to rest for a period of 3 months, during which an initial characterisation of the material was carried out to determine trace element levels and to asses the need for spiking the material.

3.2 Initial characterisation and spiking

An initial characterisation of the wastewater base material was required to determine the concentration of trace elements and to assess the need for spiking to reach target concentrations. The sample was analysed by ICP-MS for all elements except Fe, which was analysed by ICP-OES, and Hg, which was analysed by CV-AAS. The sample was analysed without the need for specific sample pre-treatment. Based on the results of these analyses, it was decided to spike the material since the concentrations of most elements of interest were below the target concentrations with the exception of Fe and Mn. Following a three month resting period, the wastewater sample was filtered again to remove any precipitate (Versaflow filter capsule, 0.45 µm) and spiked accordingly with appropriate amounts of single element standards (Merck).

3.3 Processing

Borosilicate ampoules (Egilabo, Kontich, BE) were washed by rinsing with 2 % nitric acid (Merck), followed by two rinsing steps with reagent grade type I water (18.2 MΩ.cm, Millipore, Billerica, USA). The homogeneity of the wastewater sample was ensured by recirculating the water before and during the ampouling using a peristaltic pump (Watson-Marlow, Falmouth, UK) through PTFE tubing (Bohlender, Grünsfeld, DE). Aliquots of 100 mL were transferred to the ampoules using a R910/PA automatic ampouling machine (ROTA, Wehr/Baden, DE). Each individual ampoule was flushed with argon, filled with the wastewater material using a ceramic piston pump and flushed again with argon to ensure an inert atmosphere above the sample. Finally, the ampoule was sealed. A total of 1408 ampoules was obtained, which were subsequently labelled and dispatched for sterilisation by gamma irradiation (Isotron NV, Ede, NL) at 25 kGy. The high dosage of gamma radiation caused some (expected) discolouration of the glass ampoules, but no detrimental effect was expected on the material itself.

The residual bacterial activity was checked (in-house) after the irradiation of the material. The results confirmed that the material showed no residual bacterial activity.

4 Assessment of homogeneity

A key requirement for any reference material is the equivalence between the various units. In this respect, it is not relevant whether the variation between units is significant compared to the analytical variation, but whether this variation is significant to the certified uncertainty. Consequently, ISO Guide 34 requires RM producers to quantify the between unit variation. This aspect is covered in between-unit homogeneity studies.

The within-unit heterogeneity does not influence the uncertainty of the certified value when the minimum sample intake is respected, but determines the minimum size of an aliquot that is representative for the whole unit. Quantification of within-unit heterogeneity is therefore necessary to determine the minimum sample intake.

4.1 Between-unit homogeneity

The between-unit homogeneity was evaluated to ensure that the certified values of the CRM are valid for all units of the material, within the stated uncertainty.

Twelve units were selected using a random stratified sampling scheme covering the whole batch. The batch was divided into twelve groups (with similar number of units) and one unit was selected randomly from each group. The number of selected units corresponds to approximately the cubic root of the total number of produced units. Three independent samples were taken from each selected unit and analysed by ICPMS (As, Cd, Cr, Cu, Ni, Pb and Se), ICPOES (Fe and Mn) or CV-AFS (Hg) (five independent samples were taken for iron, lead and selenium). The measurements were performed under repeatability conditions and in a randomised manner to be able to separate potential analytical drift from a trend in the filling sequence. The results are shown as Tables in Annex A.

Regression analyses were performed to evaluate potential trends in the analytical sequence as well as trends in the filling sequence. Some significant (99 % confidence level) trends in the analytical sequence were found for cadmium, mercury, lead and selenium, pointing at drift of the analytical system. As the analytical sequence and the unit numbers were not correlated, correction for these trends can improve the sensitivity of the subsequent statistical analysis through a reduction in analytical variation without masking potential between-unit heterogeneities. Therefore, trends in the analytical sequence were corrected if the trend was significant on at least a 99 % confidence level as shown below.

$$corrected\,result = measured\,result - b \cdot i$$ **Equation 1**

b: slope of the linear regression

i: position of the result in the analytical sequence

The trend-corrected dataset was tested for consistency using Grubbs outlier tests on a confidence level of 99 % on the individual results and the unit means. Some outlying individual results and outlying unit means have been detected, in particular for arsenic, copper, manganese, mercury and lead (see Table 1). Since no technical reason for the outliers could be found, all the data were retained for statistical analysis.

Quantification of between-unit homogeneity is most easily done by analysis of variance (ANOVA), which can separate between-unit variation (s_{bb}) from within-unit variation (s_{wb}). The latter is equivalent to the method repeatability if the individual samples are representative for the whole unit.

Evaluation by ANOVA requires unit means which follow at least a unimodal distribution and results for each unit that follow unimodal distributions with approximately the same standard deviations. Distribution of the unit averages was tested using histograms and normal probability plots. Too few data are available for each unit to make a clear statement of the distribution of individual results. Therefore, it was visually checked whether all individual data follow a unimodal distribution using histograms and normal probability plots. 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 1.

Table 1: Results of the statistical evaluation

Measurand	Trends		Outliers		Distribution	
	Analytical sequence	Filling sequence	Individual results	Unit means	Individual results	Unit means
Arsenic	-	-	1	-	normal/unimodal	normal/unimodal
Cadmium*	yes	-	-	-	normal/unimodal	normal/unimodal
Chromium	-	-	-	-	normal/unimodal	normal/unimodal
Copper	-	-	-	2	normal/unimodal	normal/unimodal
Iron	-	-	-	-	normal/unimodal	normal/unimodal
Mercury*	yes		1	1	normal/unimodal	normal/unimodal
Manganese	-	-	1	-	normal/unimodal	normal/unimodal
Nickel	-	-	-	-	normal/unimodal	normal/unimodal
Lead*	yes	-	-	1	normal/unimodal	normal/unimodal
Selenium*	yes	-	-	-	normal/unimodal	normal/unimodal

* evaluation on re-sloped data

One has to bear in mind that $s_{bb,\ rel}$ and $s_{wb,\ rel}$ are estimates of the true standard deviations and therefore subject to random fluctuations. Therefore, the mean square between groups ($MS_{between}$) can be smaller than the mean squares within groups (MS_{within}), resulting in negative arguments under the square root used for the estimation of the between-unit variation, whereas the true variation cannot be lower than zero. In this case, u^*_{bb}, the maximum heterogeneity that could be hidden by method repeatability, was calculated as described by Linsinger *et al.* [7]. u^*_{bb} is comparable to the limit of detection of an analytical method, yielding the maximum heterogeneity that might be undetected by the given study setup.

Method repeatability ($s_{wb,\ rel}$), between–unit standard deviation ($s_{bb,\ rel}$) and $u^*_{bb,\ rel}$ were calculated as

$$s_{wb,rel} = \frac{\sqrt{MS_{within}}}{\overline{y}}$$ **Equation 2**

$$s_{bb,rel} = \frac{\sqrt{\frac{MS_{between} - MS_{within}}{n}}}{\overline{y}}$$ **Equation 3**

$$u^*_{bb,rel} = \frac{\sqrt{\frac{MS_{within}}{n}}\sqrt[4]{\frac{2}{\nu_{MSwithin}}}}{\overline{y}}$$ **Equation 4**

MS_{within}: mean square within a unit from an ANOVA

$MS_{between}$: mean squares between-unit from an ANOVA

$\overline{y}$: average of all results of the homogeneity study

n: average number of replicates per unit

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

However, a different approach was adopted for copper, mercury and lead for which outlying unit averages were detected. In this case between-unit heterogeneity was modelled as a rectangular distribution limited by the largest outlying unit average, and the rectangular standard uncertainty of homogeneity was estimated as given by

$$u_{rec} = \frac{\left|outlier - \overline{y}\right|}{\sqrt{3} \cdot \overline{y}}$$ **Equation 5**

$\overline{y}$: average of all results of the homogeneity study

It should be mentioned that the outlying unit averages are a result of presence of outlying individual values and do not necessarily reflect the real distribution of these elements in the material.

The results of the evaluation of the between-unit variation are summarised in Table 2. In most cases, the uncertainty contribution for homogeneity was determined by the method repeatability.

Table 2: Results of the homogeneity study; n.c.: cannot be calculated as $MS_{between} < MS_{within}$

	$s_{wb,rel}$ [%]	$s_{bb,rel}$ [%]	$u^*_{bb,rel}$ [%]	$u_{rec,rel}$ [%]	$u_{bb,rel}$ [%]
Arsenic	0.8	0.6	0.26	-	0.6
Cadmium	0.6	0.2	0.2	-	0.2
Chromium	0.4	1.3	0.1	-	1.3
Copper	-	-	-	1.0	1.0
Iron	0.8	0.8	0.2	-	0.8
Mercury	-	-	-	0.5	0.5
Manganese	0.6	n.c.	0.19	-	0.19
Nickel	0.4	n.c.	0.13	-	0.13
Lead	-	-	-	0.9	0.9
Selenium	1.2	0.6	0.22	-	0.6

The homogeneity study showed no outlying unit means or trends in the filling sequence for cadmium, chromium, iron, manganese and nickel. Therefore the between-unit standard deviation can be used as estimate of u_{bb}. As u^*_{bb} sets the limits of the study to detect inhomogeneity, the larger value of s_{bb} and u^*_{bb} is adopted as uncertainty contribution to account for potential inhomogeneity.

For the elements copper, lead and mercury the study found one or two outlying unit means. However, taking these extreme values into account, the heterogeneity as quantified as u_{rec} is still sufficiently small to make the material useful. Therefore, u_{rec} was used as estimate of u_{bb}.

4.2 Within-unit homogeneity and minimum sample intake

The within-unit homogeneity is closely correlated to the minimum sample intake. Due to this correlation, individual aliquots of a material will not contain the same amount of analyte. The minimum sample intake is the minimum amount of sample that is representative for the whole unit and thus can be used in an analysis. Sample sizes equal or above the minimum sample intake guarantee the certified value within its stated uncertainty.

The minimum sample intake for ERM-CA713 was not specifically addressed. The material is a true solution and is not expected to have any relevant heterogeneity. This assumption was confirmed by the characterisation study, where sample intakes as low as e.g. 0.02 mL were found to give acceptable repeatability, demonstrating that there is no intrinsic heterogeneity or contamination at a sample intake of 0.02 mL for Cr and Mn; 0.04 mL for As, Cd, Cu and Pb; 0.05 mL for Ni; 0.5 mL for Hg and Se, and 1 mL for Fe.

5 Stability

Time, temperature and radiation were regarded as the most relevant influences on stability of the materials. The influence of ultraviolet or visible radiation was minimised by storing and dispatching the material in the dark, thus practically eliminating the possibility of radiative degradation. Therefore, only the influences of time and temperature needed to be investigated.

Stability testing is necessary to establish conditions for storage (long-term stability) as well as conditions for dispatch to the customers (short-term stability). During transport, especially in summer time, temperatures up to 60 °C could be reached and stability against these conditions must be demonstrated if transport at ambient temperature will be applied.

The stability studies were carried out using an isochronous design [8]. In that 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 analysed 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.

5.1 Short-term stability study

For the short-term stability study, samples were stored at 18 °C and 60 °C for 0, 1, 2 and 4 weeks (at each temperature). The reference temperature was set to 4 °C. Two samples per storage time were selected using a random stratified sampling scheme. From each unit, three samples were measured by ICPMS, ICPOES and CV-AFS. The measurements were performed under repeatability conditions in a randomised sequence to be able to separate a potential analytical drift from a trend over storage time.

The obtained data were evaluated individually for each temperature. The results were screened for outliers using the single and double Grubbs test. One outlier was found for mercury. As no technical reason was found for excluding the outlier, the data point was retained for further statistical analysis (see Table 3).

Furthermore, the data were plotted against storage time in order to calculate regression lines of mass concentration versus time. The slopes of the regression lines were tested for statistical significance (loss/increase due to shipping conditions). For all elements, the slopes of the regression lines were not significantly different from 0 (on 99 % confidence level) at 18 °C. However, at 60 °C a significant trend was found for chromium at the 99% confidence level. A second set of samples was sent for analysis of chromium and the resulting data set showed no outliers and no trends at either temperature. Nevertheless, due to the possible degradation measured in the first set of samples and the presence of a negative trend in the long-term stability data (see 5.2), the outcome of the stability studies is inconclusive. Further testing will be carried out to assess the stability of chromium in ERM-CA713 in the post certification monitoring. Pending the findings of such further tests, the material will be dispatched under cooled conditions.

The results of the measurements are shown in Annex B. The results of the statistical evaluation of the short-term stability are summarised in Table 3.

Table 3: Results of the short-term stability tests

Measurand	Number of individual outlying results		Significance of the trend on a 99% confidence level	
	18 °C	60 °C	18 °C	60 °C
Arsenic	-	-	no	no
Cadmium	-	-	no	no
Chromium	-	-	no	yes
Chromium - repeat	-	-	no	no
Copper	-	-	no	no
Manganese	-	-	no	no
Nickel	-	-	no	no
Iron	-	-	no	no
Mercury	-	one	no	no
Lead	-	-	no	no
Selenium	-	-	no	no

5.2 Long-term stability study

For the long-term stability study, study samples were stored at 18 °C for 0, 8, 16 and 24 months. The reference temperature for both schemes was set to 4 °C.

Twelve samples per storage time were selected using a random stratified sampling scheme. From each storage time, two samples were selected randomly and five replicates in each sample were measured by ICP-OES (Fe and Mn), CV-AFS (Hg) and ICP-MS (all other elements). The measurements were performed under repeatability conditions, and in a randomised manner to be able to separate a potential analytical drift from a trend over storage time.

Regression analyses were performed to evaluate potential trends in the analytical sequence. Some significant (99 % confidence level) trends in the analytical sequence were found for cadmium, chromium, copper, iron, mercury, manganese, nickel and lead, pointing at drift of the analytical system. As the analytical sequence and the unit numbers were not correlated, correction for these trends can improve the sensitivity of the subsequent statistical analysis through a reduction in analytical variation without masking potential between-unit heterogeneities. Therefore, trends in the analytical sequence were corrected if the trend was significant on at least a 99 % confidence level as shown below.

$$corrected \quad result = measured \quad result - b \cdot i$$ **Equation 6**

b = slope of the linear regression

i = position of the result in the analytical sequence

The trend-corrected datasets were evaluated individually for each temperature. The results were screened for outliers using the single and double Grubbs test. One outlying individual result was found for cadmium and two for arsenic, copper and iron (see Table 4). As no technical reason for the outliers could be found all data were retained for statistical analysis.

Furthermore, the data were plotted against storage time and linear regression lines of mass concentration versus time were calculated. The slope of the regression lines was tested for statistical significance (loss/increase due to storage conditions). For most elements, the slopes of the regression lines were not significantly different from 0 (on 99 % confidence level) for 18 °C. A significant trend was found for chromium, copper, iron and lead (see Annex C), however this appears largely due to an initial degradation in the first period of 0 to 8 months, after which the concentrations remain stable. For this reason the uncertainty of the degradation has been included in the calculation of the u_{lts}. The characterisation study of ERM-CA713 was carried out after the initial degradation of the material. To ensure the validity of the certified value of Cr, Cu, Fe and Pb, the absence of further degradation will be evaluated further in the post-certification monitoring (three years after the certification study).

The results of the measurements are shown in Annex C. The results of the statistical evaluation of the long-term stability study are summarised in Table 4.

Table 4: Results of the long-term stability tests

Measurand	Number of individual outlying results	Significance of the trend on a 99% confidence level
	18 ºC	18 ºC
Arsenic	Two (double Grubbs test)	no
Cadmium*	one	no
Chromium*	none	yes
Copper*	Two (double Grubbs test)	yes
Manganese*	none	no
Nickel*	none	no
Iron*	Two (double Grubbs test)	yes
Mercury*	none	no
Lead*	none	yes
Selenium	none	no

* evaluation on re-sloped data

5.3 Estimation of uncertainties

Due to the intrinsic variation of measurement results no study can rule out degradation of materials completely, even in the absence of statistically significant trends. It is therefore necessary to quantify the potential degradation that could be hidden by the method repeatability, i.e. to estimate the uncertainty of stability. This means, even under ideal conditions, the outcome of a stability study can only be "degradation is 0 ± x % per time".

Uncertainties of stability during dispatch and storage were estimated as described in [9] for each analyte. For this approach, the uncertainty of the linear regression line with a slope of zero is calculated. The uncertainty contribution (u_{sts} and u_{lts}) is then calculated as the product of the chosen shelf life and the uncertainty of the regression lines as:

$$u_{sts,rel} = \frac{RSD}{\sqrt{\sum (x_i - \bar{x})^2}} \cdot t_{tt}$$

Equation 7

$$u_{lts,rel} = \frac{RSD}{\sqrt{\sum (x_i - \bar{x})^2}} \cdot t_{sl}$$

Equation 8

RSD	relative standard deviation of all results of the stability study
x_{i}:	time point for each replicate
$\bar{x}$:	mean results for all time points
t_{tt}	chosen transport time (1 week at 60 °C)
t_{sl}:	proposed shelf life (36 months at 18 °C in this case)

For Cr, Cu, Fe and Pb in which a significant trend was observed, the uncertainty contribution (u_{lts}) is then calculated as:

$$u_{lts,rel} = \frac{\sqrt{u_b{}^2 + u_{\deg}{}^2} \cdot t_{sl}}{\bar{y}} \cdot 100$$

Equation 9

$\bar{y}$:	mean results for all measurements
t_{sl}:	proposed shelf life (36 months at 18 °C in this case)

With $u_{\deg} = \frac{b \cdot t_{sl}}{\sqrt{3}}$ and $u_b{}^2 = \frac{\frac{\sum y_i - \hat{y}_i}{N-2}}{\sum (x_i - \bar{x})^2}$

b:	slope of the regression line
x_{i}:	time point for each replicate
$\bar{x}$:	mean results for all time points
y_i:	individual result *i* for the time point x_i
$\hat{y}_i$:	estimated result from the regression line at time point x_i

The following uncertainties were estimated:

- $u_{\mathrm{sts,\,rel}}$, the uncertainty of degradation during dispatch. This was estimated from the 60 °C studies for a time of 0.25 months (1 week). The uncertainty therefore describes the possible change during a dispatch at 60 °C lasting for one week.
- $u_{\mathrm{lts,\,rel}}$, the stability during storage. This uncertainty contribution was estimated from the 18 °C study. The uncertainty contribution therefore describes the possible degradation for 36 months at 18 °C.

The results of these evaluations are summarised in Table 5.

Table 5: Uncertainties of stability during storage and dispatch. $u_{\text{sts, rel}}$ was calculated for a temperature of 18 °C and 1 week; $u_{\text{lts, rel}}$ was calculated for a storage temperature of 18 °C and 3 years.

Measurand	$u_{\text{sts, rel}}$ [%]		$u_{\text{lts, rel}}$ [%]
	At 18 ^{o}C	At 60 ^{o}C	At 18 ^{o}C
Arsenic	0.10	0.08	0.4
Cadmium	0.11	0.15	0.6
Chromium	0.15	0.4	2.1
Copper	0.14	0.10	2.9
Iron	0.09	0.07	1.4
Mercury	0.15	0.20	1.1
Manganese	0.07	0.07	0.5
Nickel	0.13	0.12	0.3
Lead	0.14	0.17	1.0
Selenium	0.25	0.23	0.8

The uncertainty of stability during dispatch is negligible for all elements relative to the overall uncertainty. The results of the two data sets of the short term stability study were inconclusive for chromium. For this reason it is recommended to transport ERM-CA713 with cooling elements.

After the certification campaign, the material will be subjected to IRMM's regular stability monitoring programme to control its further stability.

6 Characterisation

The material characterisation was based on an intercomparison of expert laboratories. The properties of the material were determined in different laboratories that applied different measurement procedures to demonstrate the absence of a measurement bias. This approach aims at randomisation of laboratory bias, which reduces the combined uncertainty.

6.1 Selection of participants

Eleven laboratories were selected based on criteria that comprised both technical competence and quality management aspects. Each participant was required to operate a quality system and to deliver documented evidence of its laboratory proficiency in the field of element measurements in relevant matrices by submitting results for intercomparison exercises or method validation reports. Having a formal accreditation was not mandatory, but meeting the requirements of ISO/IEC 17025 was obligatory. Where measurements are covered by the scope of accreditation, the accreditation number is stated in the list of participants (Section 2).

6.2 Study setup

Each laboratory received two units of ERM-CA713 and was requested to provide six independent results, three replicates per unit. The units for material characterisation were selected using a random stratified sampling scheme and covered the whole batch. The sample preparations (if applicable) and measurements had to be spread over at least two days to ensure intermediate precision conditions. An independent calibration was performed for each result.

Each participant received a sample of BCR-713 as a blind quality control (QC) sample. The results for this sample were used to support the evaluation of the characterisation results for all measurands except mercury (the QC sample is not certified for this element).

Laboratories were also requested to give estimations of the expanded uncertainties of the mean value of the six results. No approach for the estimation was prescribed. i.e. top-down and bottom-up were regarded as equally valid procedures.

6.3 Methods used

A variety of different quantification steps, with or without sample preparation, were used to characterise the material. The combination of results from methods based on completely different principles virtually rule out undetected method bias.

All methods used during the characterisation study are summarised in Annex D. The laboratory code is a random number and does not correspond to the order of laboratories in Section 2. The lab-method code consists of a number assigned to each laboratory (e.g. L1) and abbreviation of the measurement method used (e.g. L12-ET-AAS).

6.4 Evaluation of results

The characterisation campaign resulted in 4 to 10 datasets depending on the element. All individual results of the participants, grouped per element, are displayed in tabular and graphical form in Annex E.

6.4.1 Technical evaluation

The obtained data were first checked for compliance with the requested analysis protocol and for their validity based on technical reasons. The following criteria were considered during the evaluation:

- compliance with the analysis protocol: sample preparations and measurements performed on two days, and the sequence of analysis;
- validity of the measurement procedure;
- absence of values given as below limit of detection or below limit of quantification;
- method performance, i.e. agreement of the measurement results with the assigned value of the QC sample;
- method performance measured in terms of repeatability;

Based on the above criteria, some datasets were rejected as not technically valid (see Table 6):

L2: the results for Fe were rejected because measurement of the QC sample did not yield the certified value. The results for Cr and Cu were rejected because the RSD on the measurements were higher than that requested in the technical specifications. The result for Hg did not conform with quality management system of IRMM.

L4: the results for Ni were rejected because the RSD on the measurements were higher than that requested in the technical specifications. The results for Se were rejected because measurement of the QC sample did not match the certified value.

Datasets from L6 and L12 were rejected entirely because during the evaluation of the data it became apparent that the results of more than half of all the analytes measured did not conform to the above criteria.

Table 6: Datasets that showed non-compliances with the analysis protocol and technical specifications, and action taken.

Property measured	Lab-method code	Description of problem	Action taken
As	L12-ET-AAS	High RSD (>5%)	not used for evaluation
Cd	L6-ICP-MS	High RSD	not used for evaluation
Cr	L2-ICP-MS	High RSD	not used for evaluation
	L6-ICP-MS	High RSD	not used for evaluation
	L12-ET-AAS	High RSD	not used for evaluation
Cu	L2-ICP-MS	QC failed (RSD>5%)	not used for evaluation
	L12-ET-AAS	QC failed	not used for evaluation
Fe	L2-ICP-MS	QC failed	not used for evaluation
	L6-ICP-MS	QC failed	not used for evaluation
Hg	L2-ICP-MS	Non-conformity with IRMM quality management system	not used for evaluation
Mn	L6-ICP-MS	QC failed	not used for evaluation
	L12-ET-AAS	High RSD	not used for evaluation
Ni	L4-ICP-MS	High RSD	not used for evaluation
Se	L4-HG-AAS	QC failed	not used for evaluation
	L6-ICP-MS	QC failed	not used for evaluation

6.4.2 Statistical evaluation

The datasets accepted on technical grounds were tested for normality of dataset means using kurtosis/skewness tests and normal probability plots and were tested for outlying means using the Grubbs test and using the Cochran test for outlying standard deviations (both at a 99 % confidence level). Standard deviations within (s_{within}) and between (s_{between}) laboratories were calculated using one-way ANOVA. The results of these evaluations are shown in Table 7.

Table 7: Statistical evaluation of the technically accepted datasets for ERM-CA713. p: number of technically valid datasets

Measurand	p	Outliers		Normally distributed	Statistical parameters			
		Means	Variances		Average [µg/L]	s [µg/L]	s_{between} [µg/L]	s_{within} [µg/L]
As	8	no	no	yes	10.8	0.3	0.3	0.2
Cd	9	no	no	yes	5.09	0.3	0.3	0.1
Cr	9	no	no	yes	20.9	1.0	1.0	0.5
Cu	9	no	no	yes	101	2.0	1.9	2.0
Fe	8	no	yes	yes	445	28	31	11
Hg	8	no	yes	yes	1.84	0.2	0.2	0.1
Mn	10	no	yes	yes	956	5.1	5.0	2.3
Ni	9	no	no	yes	50.3	1.9	1.9	0.8
Pb	10	no	yes	yes	49.7	1.6	1.4	1.5
Se	7	no	no	yes	4.9	0.5	0.5	0.3

The laboratory averages follow normal distributions. None of the data contains outlying means, but some outlying variances were found, in particular for Mn, Fe, Hg and Pb. The outlying variances are not method dependent and therefore merely reflect the fact that different methods have different intrinsic variability. As all measurement procedures were found technically valid, all results were retained. Moreover, closer scrutiny of the data shows that the standard deviations on the mean mass concentrations reported for these elements by the laboratories are within 5 % that was required in the technical specifications. The datasets are therefore consistent and the mean of laboratory means is a good estimate of the true value. The uncertainty on the characterisation is estimated as the standard error of the laboratory means (see Table 8).

7 Value Assignment

Certified values are values that fulfil the highest standards of accuracy. Procedures at IRMM require generally pooling of not less than 6 datasets to assign certified values. Full uncertainty budgets in accordance with the Guide to the Expression of Uncertainty in Measurement [3] must be established.

7.1 Certified values and their uncertainties

The unweighted mean of the means of the accepted datasets as shown in Table 7 was assigned as certified value for each element.

The assigned uncertainty consists of uncertainties related to characterisation, u_{char} (see Section 6), potential between-unit heterogeneity, u_{bb} (see Section 4) and potential degradation during transport (u_{sts}) and long-term storage, u_{lts} (see Section 5). These different contributions were combined to estimate the expanded, relative uncertainty of the certified value ($U_{\text{CRM, rel}}$) with a coverage factor k as

$$U_{\text{CRM,rel}} = k \cdot \sqrt{u^2_{\text{char,rel}} + u^2_{\text{bb,rel}} + u^2_{\text{sts,rel}} + u^2_{\text{lts,rel}}} \qquad \textbf{Equation 10}$$

- u_{char} was estimated as described in Section 6.
- u_{bb} was estimated as described in Section 4.
- u_{sts} was estimated as described in section 5.3. The uncertainty of degradation during dispatch is negligible compared to the other uncertainty contributions.
- u_{lts} was estimated as described in Section 5.3.

Table 8: Certified values and their uncertainties for ERM-CA713

Property	Certified value [µg/L]	$u_{\text{char, rel}}$ [%]	$u_{\text{bb, rel}}$ [%]	$u_{\text{lts, rel}}$ [%]	$U_{\text{CRM, rel}}$ [%]	U_{CRM} [µg/L]
As	10.8	1.0	0.6	0.4	2.4	0.3
Cd	5.09	1.9	0.2	0.6	3.8	0.20
Cr	20.9	1.7	1.3	2.1	5.8	1.3
Cu	101	0.7	1.0	2.9	6.1	7
Fe	445	2.6	0.8	1.4	6.2	27
Hg	1.84	2.8	0.5	1.1	6.0	0.11
Mn	95	1.7	0.19	0.5	3.6	4
Ni	50.3	1.3	0.13	0.3	2.7	1.4
Pb	49.7	1.0	0.9	1.0	3.3	1.7
Se	4.9	10.4	0.8	0.8	20.9	1.1

Because of the sufficient numbers of the degrees of freedom of the different uncertainty contributions, a coverage factor *k* of 2 was applied, to obtain the expanded uncertainties.

For Se, one laboratory reported results for which the mean and the expanded uncertainty were not covered by the U_{CRM} (see Annex E). This element is however very important so the decision was made to calculate the uncertainty for Se by modelling the data as a rectangular distribution, using the following formula:

$$u_{rec} = \frac{\left| outlier - \overline{y} \right|}{\sqrt{3} \cdot \overline{y}}$$ **Equation 11**

$\overline{y}$: average of all results of the homogeneity study

The certified values and their uncertainties are summarised in Table 8.

7.2 Additional material information

The data provided in this section should be regarded as informative only on the general composition of the material and can not be, in any case, used as certified or indicative value.

Seven laboratories (L1, L2, L3, L4, L7, L8 and L11), participating in the characterisation study, also provided results on Zinc in the material by using ICP-OES, ICP-QMS and ICP-SFMS.

The long term stability of Zinc mass fraction in ERM-CA713 was found uncertain and the value may change over time. This result, which is reported in Table 9, can only be considered as an informative value.

Table 9: Additional material information for ERM-CA713

Additional Material Information		
Total content	Mass fraction	
	Value [2)]	Unit
Zn [1)]	78	µg/L

1) Zinc was determined by using ICP-OES, ICP-QMS and ICP-SFMS
2) Unweighted mean value of the means of seven independent datasets.

8 Metrological traceability and commutability

8.1 Metrological traceability

Identity

Arsenic, cadmium, chromium, copper, iron, mercury, manganese, lead, nickel and selenium are clearly defined analytes that can be measured with high specificity. The participants used different methods for the sample preparation as well as for the final determination, demonstrating absence of measurement bias. The measurands are therefore structurally defined and independent of the measurement method.

Quantity value

Only validated methods were used for the determination of the assigned values. Different calibrants of specified traceability of their assigned values were used and all relevant input parameters were calibrated. The individual results are therefore traceable to the SI, as it is also confirmed by the agreement among the technically accepted datasets. Since the assigned values are combinations of agreeing results individually traceable to the SI, the assigned quantity values themselves are traceable to the SI as well.

9 Instructions for use

9.1 Storage conditions

The materials shall be stored at 18 °C ± 5 °C in the dark.

Please note that the European Commission cannot be held responsible for changes that happen during storage of the material at the customer's premises, especially of opened samples.

9.2 Safety and protection for the environment

The usual laboratory safety measures apply.

9.3 Preparation and use of the material

The units shall be shaken by turning upside down for at least 2 min before opening to ensure material re-homogenisation. To open the ampoule safely, score the neck of the ampoule with a diamond cutter and break off the tip. As a precautionary measure, wrap some paper around the tip to protect your hands.

9.4 Minimum sample intake

The minimum sample intake is 0.02 mL for Cr and Mn; 0.04 mL for As, Cd, Cu and Pb; 0.05 mL for Ni; 0.5 mL for Hg and Se and 1 mL for Fe.

9.5 Use of the certified value

The main purpose of this material is to assess method performance, i.e. for checking accuracy of analytical results/calibration. As any reference material, it can also be used for control charts or validation studies.

Comparing an analytical result with the certified value

A result is unbiased if the combined standard uncertainty of measurement and certified value covers the difference between the certified value and the measurement result (see also ERM Application Note 1, www.erm-crm.org [10]).

For assessing the method performance, the measured values of the CRMs are compared with the certified values. The procedure is described here in brief:

- Calculate the absolute difference between mean measured value and the certified value (Δ_m).
- Combine measurement uncertainty (u_m) with the uncertainty of the certified value (u_{CRM}): $u_\Delta = \sqrt{u_m^2 + u_{CRM}^2}$
- Calculate the expanded uncertainty (U_Δ) from the combined uncertainty ($u_{\Delta.}$) using an appropriate coverage factor, corresponding to a level of confidence of approximately 95 %.
- If $\Delta_m \leq U_\Delta$ no significant difference between the measurement result and the certified value, at a confidence level of about 95 % exists.

Use as a calibrant

It is not recommended to use this matrix material as calibrant. If used nevertheless, the uncertainty of the certified value shall be taken into account in the estimation of the measurement uncertainty.

Use in quality control charts

The materials can be used for quality control charts. Different CRM-units will give the same result as heterogeneity was included in the uncertainties of the certified values.

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Annexes

Annex A: Results of the homogeneity measurements for ERM-CA713 for Cd, Cr, Cu, Mn and Ni as reported by the laboratory.

Nº	**Cd [µg/L]**			**Cr [µg/L]**			**Cu [µg/L]**		
	Rep 1	**Rep 2**	**Rep 3**	**Rep 1**	**Rep 2**	**Rep 3**	**Rep 1**	**Rep 2**	**Rep 3**
15	4.70	4.55	4.57	21.3	21.2	21.3	95.7	94.8	94.7
121	4.63	4.62	4.54	20.7	20.8	20.9	94.7	94.3	94.5
263	4.67	4.64	4.64	20.4	20.4	20.6	94.9	94.3	94.7
382	4.61	4.61	4.56	20.6	20.7	20.5	97	96.1	95.9
484	4.63	4.61	4.61	20.4	20.6	20.7	94.3	94.2	94.6
602	4.65	4.65	4.57	21.2	21.2	21	96.5	96.4	95.9
713	4.63	4.64	4.62	20.5	20.4	20.4	94.8	94.1	94.4
827	4.63	4.57	4.61	20.4	20.5	20.4	94.8	94.5	94.2
954	4.63	4.67	4.62	20.8	20.8	20.9	94.1	94.3	94.5
1066	4.63	4.60	4.61	20.7	20.8	20.8	94.2	94.1	94.3
1207	4.64	4.63	4.58	20.7	20.8	20.7	94.9	94.4	94
1330	4.60	4.61	4.61	21	20.8	21	94.9	94	94.7

Nº	**Mn [µg/L]**			**Ni [µg/L]**		
	Rep 1	**Rep 2**	**Rep 3**	**Rep 1**	**Rep 2**	**Rep 3**
15	94.1	92.3	92.8	47	46.6	46.5
121	92.5	92.6	93.5	46.9	46.3	46.6
263	93.2	93	93	46.8	46.5	46.9
382	93.1	92.3	93.3	47	46.8	46.5
484	93	92.8	92.5	46.8	46.7	46.9
602	93.1	92.7	92.3	46.9	47	46.5
713	92.8	92.3	92.4	46.8	46.4	46.7
827	92.9	92.5	92.7	46.7	46.7	46.7
954	93.4	92.7	93.4	46.6	46.6	46.8
1066	92.7	92.4	94.7	46.5	46.5	46.7
1207	93.1	92.5	93.2	46.9	46.9	46.7
1330	93.3	93	93.2	46.7	46.4	46.6

Annex A - continued: Results of the homogeneity measurements as reported by the laboratory

Nº	Cd [µg/L]			Cr [µg/L]			Cu [µg/L]		
	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3
15	4.70	4.55	4.57	21.3	21.2	21.3	95.7	94.8	94.7
121	4.63	4.62	4.54	20.7	20.8	20.9	94.7	94.3	94.5
263	4.67	4.64	4.64	20.4	20.4	20.6	94.9	94.3	94.7
382	4.61	4.61	4.56	20.6	20.7	20.5	97	96.1	95.9
484	4.63	4.61	4.61	20.4	20.6	20.7	94.3	94.2	94.6
602	4.65	4.65	4.57	21.2	21.2	21	96.5	96.4	95.9
713	4.63	4.64	4.62	20.5	20.4	20.4	94.8	94.1	94.4
827	4.63	4.57	4.61	20.4	20.5	20.4	94.8	94.5	94.2
954	4.63	4.67	4.62	20.8	20.8	20.9	94.1	94.3	94.5
1066	4.63	4.60	4.61	20.7	20.8	20.8	94.2	94.1	94.3
1207	4.64	4.63	4.58	20.7	20.8	20.7	94.9	94.4	94
1330	4.60	4.61	4.61	21	20.8	21	94.9	94	94.7

Nº	Mn [µg/L]			Ni [µg/L]		
	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3
15	94.1	92.3	92.8	47	46.6	46.5
121	92.5	92.6	93.5	46.9	46.3	46.6
263	93.2	93	93	46.8	46.5	46.9
382	93.1	92.3	93.3	47	46.8	46.5
484	93	92.8	92.5	46.8	46.7	46.9
602	93.1	92.7	92.3	46.9	47	46.5
713	92.8	92.3	92.4	46.8	46.4	46.7
827	92.9	92.5	92.7	46.7	46.7	46.7
954	93.4	92.7	93.4	46.6	46.6	46.8
1066	92.7	92.4	94.7	46.5	46.5	46.7
1207	93.1	92.5	93.2	46.9	46.9	46.7
1330	93.3	93	93.2	46.7	46.4	46.6

Nº	Fe [mg/L]				
	Rep 1	Rep 2	Rep 3	Rep 4	Rep 5
73	0.429	0.423	0.428	0.426	0.426
195	0.426	0.419	0.42	0.422	0.427
312	0.423	0.422	0.42	0.417	0.42
395	0.433	0.426	0.423	0.425	0.433
542	0.425	0.425	0.424	0.422	0.426
629	0.423	0.419	0.423	0.421	0.422
755	0.412	0.42	0.422	0.421	0.424
864	0.419	0.418	0.421	0.417	0.421
991	0.437	0.422	0.428	0.426	0.428
1124	0.429	0.422	0.426	0.426	0.426
1255	0.424	0.429	0.426	0.426	0.431
1348	0.425	0.422	0.426	0.422	0.425

Annex A - continued: Results of the homogeneity measurements as reported by the laboratory

Nº	Pb [µg/L]				
	Rep 1	**Rep 2**	**Rep 3**	**Rep 4**	**Rep 5**
73	46.1	45.5	45.1	44.8	44.5
195	45.3	45	44.6	44.2	44.2
312	45.5	45.1	44.3	44.4	43.9
395	45.1	44.6	44.6	43.9	44
542	45.9	45	44.5	44.2	44
629	45.2	44.6	44.3	44	43.7
755	45.1	44.3	44.1	44.2	43.6
864	45.1	44.5	44.4	44	43.9
991	45.4	45	44.6	44.4	44
1124	45	44.3	44.4	44.1	43.9
1255	45.3	44.8	44.6	43.8	44.1
1348	45.1	44.8	44.4	44.1	43.7

Nº	Se [µg/L]				
	Rep 1	**Rep 2**	**Rep 3**	**Rep 4**	**Rep 5**
106	4.91	4.932	4.963	4.921	4.906
229	4.921	4.799	4.956	4.846	4.809
341	4.93	4.914	4.912	4.862	4.927
463	4.861	4.876	4.824	4.857	4.844
552	4.98	4.988	4.921	4.735	4.783
682	4.96	4.915	4.901	4.908	4.822
814	4.88	4.835	4.845	4.825	4.877
938	4.913	4.835	4.782	4.869	4.649
1050	4.832	4.813	4.996	4.825	4.848
1170	4.903	4.908	4.777	4.855	4.842
1279	4.871	4.799	4.825	4.8	4.776
1388	4.801	4.857	4.93	4.799	4.903

Nº	**As [µg/L]**			**Hg [µg/L]**		
	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3
106	11.11	10.74	10.84	2.01	2.07	2.076
229	10.78	10.87	10.72	2.035	2.044	2.062
341	10.66	10.64	10.6	2.036	2.052	2.037
463	10.76	10.71	10.85	2.034	2.059	2.061
552	10.82	10.81	10.63	1.856	2.049	2.07
682	10.77	10.69	10.73	1.998	2.058	2.053
814	10.8	10.81	10.69	2.052	2.044	2.075
938	10.75	10.67	10.8	2	2.06	2.079
1050	10.7	10.61	10.75	2.029	2.052	2.072
1170	10.63	10.79	10.53	2.04	2.057	2.061
1279	10.66	10.53	10.59	1.98	2.066	2.061
1388	10.72	10.67	10.66	1.919	2.054	2.047

Annex B: Short term stability data as reported by the laboratory

Time (weeks)	Cd [µg/L]			Cr [µg/L]		
	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3
Reference						
0	4.70	4.68	4.71	20.22	20.18	20.43
0	4.67	4.64	4.70	20.47	20.52	20.80
18 °C						
1	4.70	4.66	4.72	19.91	20.10	20.26
1	4.60	4.67	4.67	19.94	20.31	20.34
2	4.63	4.77	4.73	20.44	20.05	20.25
2	4.70	4.80	4.80	20.38	20.49	20.50
4	4.65	4.64	4.64	19.82	19.80	20.03
4	4.69	4.66	4.64	20.20	20.11	20.26
60 °C						
1	4.60	4.64	4.73	20.42	20.24	20.40
1	4.66	4.71	4.77	20.20	20.26	20.38
2	4.73	4.70	4.74	19.80	19.77	19.87
2	4.74	4.83	4.72	19.97	20.22	20.16
4	4.66	4.66	4.65	19.90	20.21	20.26
4	4.74	4.75	4.80	19.92	19.88	19.94

Time (weeks)	Cu [µg/L]			Mn [µg/L]		
	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3
Reference						
	100.6	100.4	100.8	91.04	91.01	91.54
	100.6	99.9	100.8	90.83	90.88	91.95
18 °C						
1	99.6	100.8	101.0	90.91	91.12	92.15
1	101.5	102.5	103.4	90.51	90.85	91.49
2	101.1	100.7	101.7	90.98	91.15	91.44
2	99.7	101.9	102.6	90.85	91.56	91.88
4	100.2	100.4	101.4	91.22	91.51	92.16
4	99.3	101.6	100.1	91.02	91.34	91.60
60 °C						
1	100.4	101.2	102.1	90.72	90.98	91.59
1	100.2	100.2	101.4	91.18	91.16	91.63
2	100.6	101.3	101.4	90.79	91.15	91.55
2	101.1	99.9	100.9	91.25	91.71	91.41
4	99.5	100.0	99.5	90.15	90.80	90.62
4	101.0	102.4	100.8	91.41	91.50	91.79

Annex B - continued: Short term stability data as reported by the laboratory

Time (weeks)	**Ni [µg/L]**		
	Rep 1	**Rep 2**	**Rep 3**
Reference			
	48.16	47.26	47.86
	47.51	47.52	48.59
18 ^{o}C			
1	47.60	47.60	48.09
1	48.08	49.01	48.58
2	48.05	48.46	47.90
2	48.20	48.11	48.66
4	48.31	47.41	48.33
4	48.35	47.59	47.78
60 ^{o}C			
1	47.57	47.55	47.94
1	47.38	47.74	47.77
2	47.48	47.94	48.18
2	48.10	47.96	48.64
4	47.24	47.38	47.96
4	48.40	48.29	47.74

Time (weeks)	**Fe [mg/L]**			**Pb [µg/L]**		
	Rep 1	**Rep 2**	**Rep 3**	**Rep 1**	**Rep 2**	**Rep 3**
Reference						
	0.428	0.428	0.432	48.92	47.69	48.60
	0.426	0.426	0.431	48.69	49.00	49.65
18 ^{o}C						
1	0.424	0.427	0.430	48.55	48.88	49.18
1	0.426	0.431	0.435	49.16	48.67	49.14
2	0.425	0.428	0.428	48.46	49.04	49.20
2	0.428	0.429	0.430	48.54	48.88	48.37
4	0.425	0.426	0.432	48.81	49.44	49.73
4	0.426	0.426	0.428	49.44	48.50	49.71
60 ^{o}C						
1	0.425	0.426	0.431	49.17	48.98	49.26
1	0.427	0.427	0.429	49.03	49.00	49.40
2	0.426	0.429	0.430	50.31	49.20	48.69
2	0.427	0.428	0.429	49.05	49.80	49.37
4	0.423	0.426	0.428	48.30	47.97	49.88
4	0.428	0.428	0.429	49.51	48.45	49.01

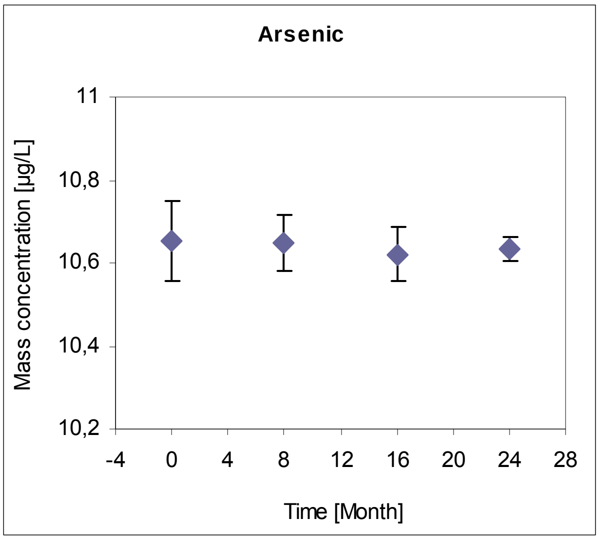
Annex B - continued: Short term stability data as reported by the laboratory

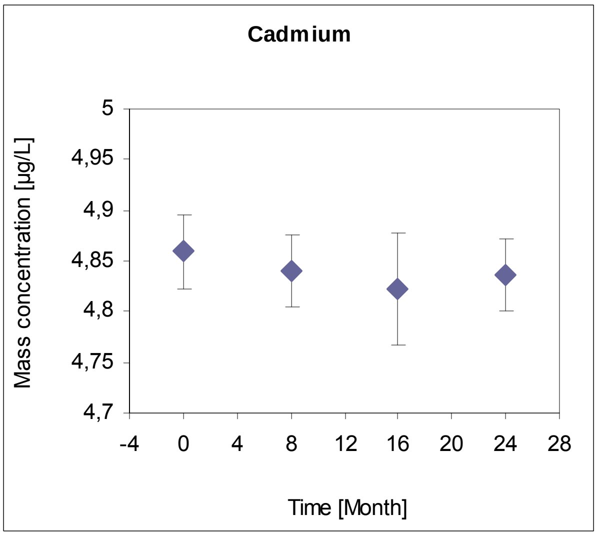
Time (weeks)	**As [µg/L]**			**Hg [µg/L]**		
	Rep 1	**Rep 2**	**Rep 3**	**Rep 1**	**Rep 2**	**Rep 3**
Reference samples						
	10.72	10.75	10.76	2.006	2.00	1.999
	10.72	10.64	10.65	1.991	2.00	1.977
18 °C						
1	10.62	10.68	10.75	1.982	2.008	2.021
1	10.68	10.55	10.47	1.992	2.021	1.991
2	10.69	10.63	10.72	1.96	2.038	2.021
2	10.71	10.61	10.54	1.985	1.989	1.965
4	10.65	10.70	10.72	2.031	2.004	1.987
4	10.51	10.55	10.72	1.958	1.983	1.997
60 °C						
1	10.75	10.74	10.67	1.99	2.033	2.029
1	10.65	10.55	10.67	2.038	2.03	2.016
2	10.66	10.62	10.70	2.028	1.996	2.037
2	10.74	10.72	10.73	2.00	2.05	2.032
4	10.64	10.72	10.71	1.917	2.021	2.003
4	10.64	10.62	10.60	2.006	2.011	2.016

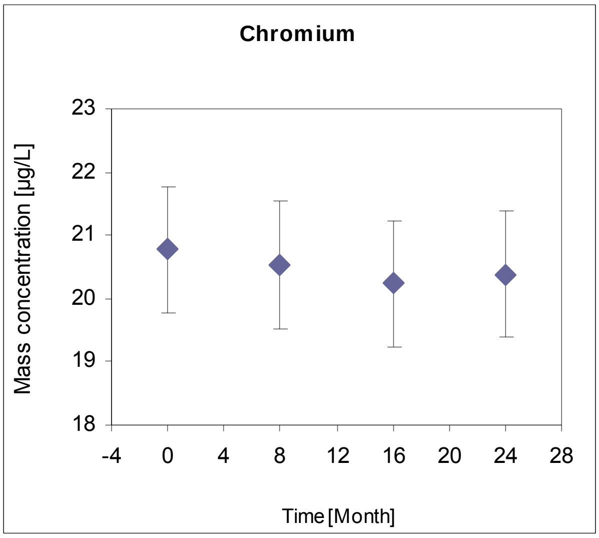
Time (weeks)	**Se [µg/L]**		
	Rep 1	**Rep 2**	**Rep 3**
Reference samples			
	4.9	4.881	4.877
	4.92	4.836	4.748
18 °C			
1	4.882	4.932	4.702
1	4.927	4.777	4.602
2	4.885	4.758	4.798
2	4.883	4.717	4.724
4	4.857	4.767	4.68
4	4.868	4.879	4.755
60 °C			
1	4.837	4.819	4.855
1	4.876	4.935	4.821
2	4.818	4.864	4.781
2	4.893	4.621	4.784
4	4.846	4.897	4.88
4	4.861	4.684	4.73

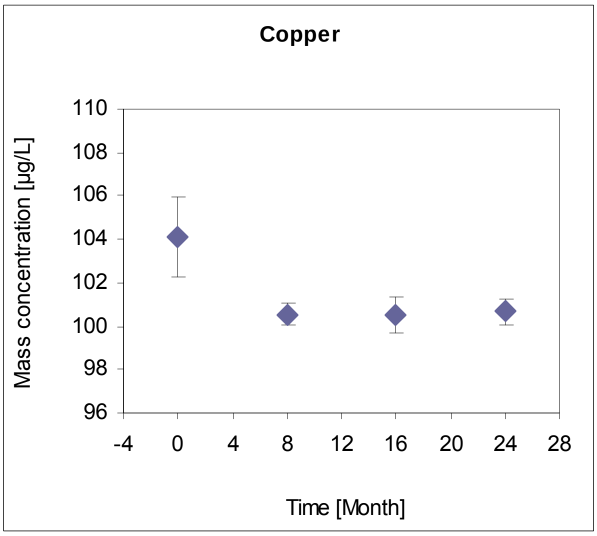
Annex C. Results of the long term stability data

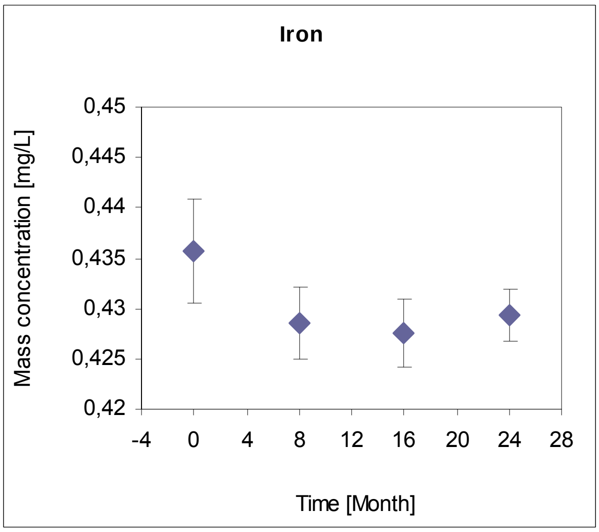
The data for the long-term stability study at 18 °C. The graphs report unit averages per time point and the standard deviation of the measurements per time.

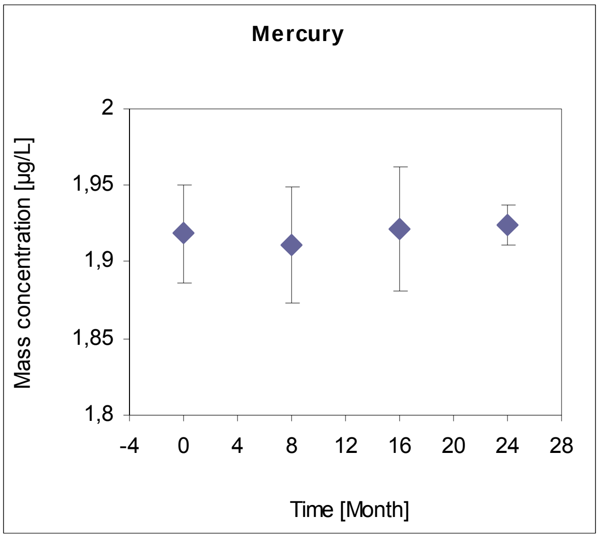




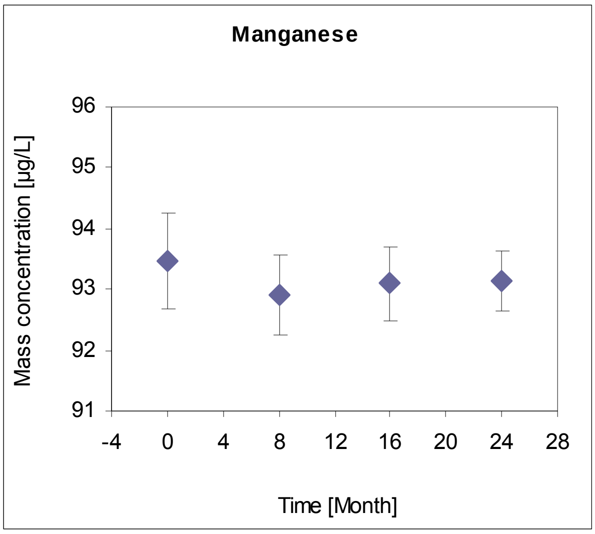


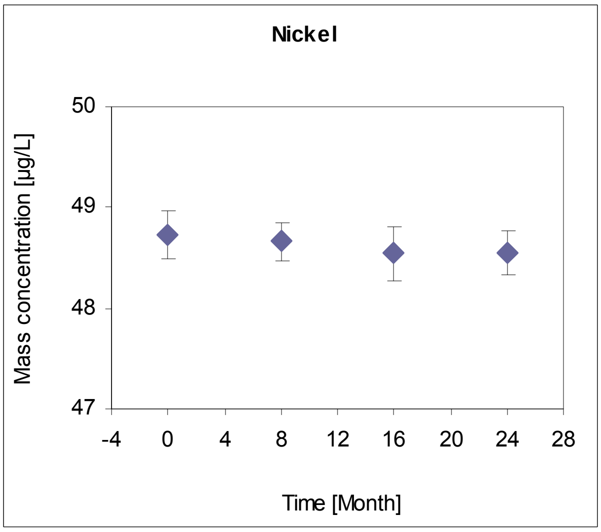


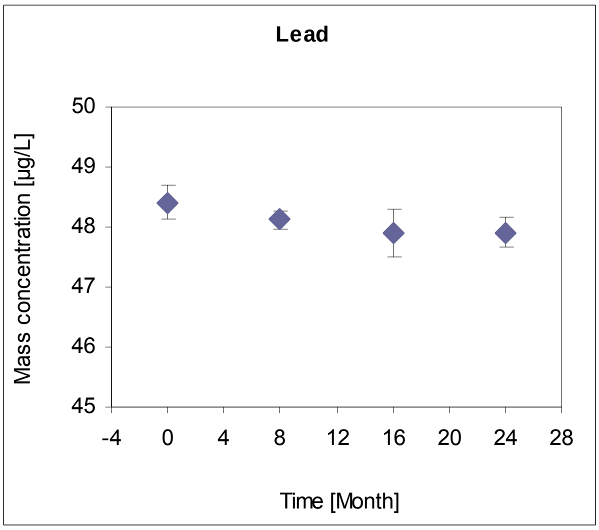


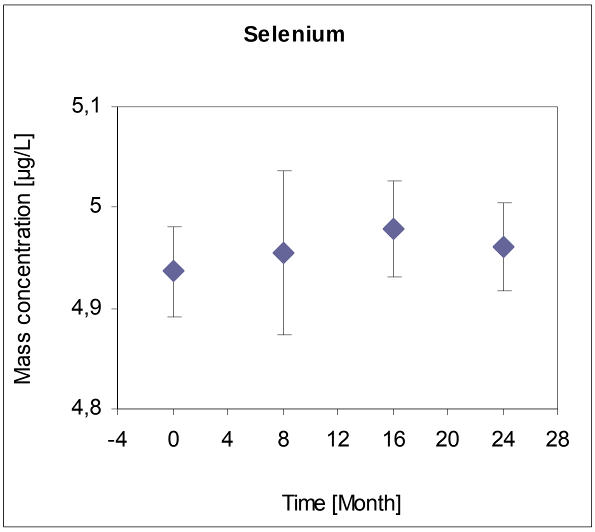


Annex C - continued: Results of the long term stability data









Annex D. Summary of analytical techniques used in the characterisation of ERM-CA713 as reported by the laboratories

D.1 Mass concentration of As

Lab	Sample pretreatment	Sample intake	Analytical method	Calibration	LOQ
L1	none	1 mL	ICP-SFMS In as internal standard	External: 0 - 10 µg/L two point calibration checked against synthetic QC sample at ½ max concentration	0.005 µg/L
L2	Dilution and acidification to 10% HNO_3	2 mL	ICP-QMS He collision mode Ge as internal standard	External: 1/ 2/ 5/ 10/ 20/ 50/ 100 µg/L	0.25 µg/L
L3	Addition of KI, ascorbic acid and HCl as reducing agent	0.5 mL	HG-AAS Flow injection $NaBH_4$ as reducing agent	External: 0.5/ 1.0/ 2.5/ 5.0/ 7.5/ 10.0 µg/L	0.5 µg/L
L4	none	0.04 mL	ET-AAS Pd and Mg as modifier	External, non-linear: 3.125/ 6.25/ 12.50/ 18.75/ 25.00 µg/L	1 µg/L
L7	Preservation by HNO_3; Digestion at 95 °C	15 mL	HG-ICP-SFMS	Linear; one point: 0 and 2 µg/L	0.1 µg/L
L8	none	5 mL	ICP-QMS Collision cell with He Ge, In, Lu as internal standards	External, linear through zero: 1/ 20/ 50/ 100 µg/L	0.44 µg/L
L10	Acidification to 1 % HNO_3	5 mL	ICP-QMS Collision cell with He/H_2 Ge as internal standard	Matrix matched: 0/ 10/ 25/ 48/ 101 µg/L	0.2 µg/L
L11	Dilution and acidification with HNO_3	1.5 mL	ICP-QMS Collision cell in He mode Ge as internal standard	External calibration: 0.1/ 0.5/ 1/ 5/ 10/ 20/ 50 µg/L	0.03 µg/L
Not used in certification					
L6	Dilution 1:1 to 2M HNO_3	1.1 mL	ICP-QMS	Linear calibration: 0/ 100/ 200/ 300/ 400/ 500 µg/L	0.2 µg/L
L12	none	0.02 mL	ETAAS Zeeman correction	Non-linear calibration: 0/ 25/ 50/ 100 µg/L	0.1 µg/L (LOD)

D.2 Mass concentration of Cd

Lab	Sample pretreatment	Sample intake	Analytical method	Calibration	LOQ
L1	none	1 mL	ICP-SFMS In as internal standard	External: 0 - 10 µg/L two point calibration checked against synthetic QC sample at ½ max concentration	0.0002 µg/L
L2	Dilution and acidification to 10% HNO_3	2 mL	ICP-QMS He collision mode Ge as internal standard	External: 1/ 2/ 5/ 10/ 20/ 50/ 100 µg/L	0.01 µg/L
L3	none	8 mL	ICP-OES	External: 0.5/ 1/ 2/ 5/ 10/ 25/ 50/ 100 µg/L	0.2 µg/L
L4	none	10 mL	ICP-QMS Rh as internal standard	External: 1/ 10/ 100 µg/L	0.5 µg/L
L5	none	0.04 mL	ET-AAS	External, non-linear: 0.5/ 1/ 1.5/ 1.75/ 2 µg/L	Not reported
L7	Preservation HNO_3; digestion 95 °C for 2 h	15 mL	ICP-SFMS RH as internal standard Mass resolution >400	External, linear 1 point: 0/ 10 µg/L	0.05 µg/L
L8	none	5 mL	ICP-QMS Collision cell with He Ge, In, Lu as internal standards	External, linear through zero: 0.1/ 2/ 5/ 10 µg/L	0.05 µg/L
L10	Acidification to 1 % HNO_3	5 mL	ICP-QMS Collision cell with He/H_2 Rh as internal standard	Matrix matched: 0/ 10/ 25/ 48/ 101 µg/L	0.04 µg/L
L11	Dilution and acidification with HNO_3	1.5 mL	ICP-QMS Collision cell in He mode In as internal standard	External calibration: 0.1/ 0.5/ 1/ 5/ 10/ 20/ 50 µg/L	0.015 µg/L
Not used in certification					
L6	Dilution 1:1 to 2M HNO_3	1.1 mL	ICP-QMS	Linear calibration: 0/ 100/ 200/ 300/ 400/ 500 µg/L	0.009 µg/L
L12	none	0.02 mL	ETAAS Zeeman correction	Non-linear calibration: 0/ 2.5/ 5 µg/L	0.01 µg/L (LOD)

D.3 Mass concentration of Cr

Lab	Sample pretreatment	Sample intake	Analytical method	Calibration	LOQ
L1	none	1 mL	ICP-SFMS In as internal standard	External: 0 - 10 µg/L two point calibration checked against synthetic QC sample at ½ max concentration	0.005 µg/L
L3	none	8 mL	ICP-OES	External: 2/ 4/ 10/ 20/ 50/ 100/ 200 µg/L	1 µg/L
L4	none	10 mL	ICP-QMS Rh as internal standard	External: 1/ 10/ 100 µg/L	0.5 µg/L
L5	none	0.02 mL	ET-AAS	External, non-linear: 2/ 4/ 6/ 8/ 10 µg/L	Not reported
L7	Preservation HNO_3; digestion 95 °C for 2 h	15 mL	ICP-SFMS Ge as internal standard Mass resolution >4000	External, linear 1 point: 0/ 10 µg/L	0.5 µg/L
L8	none	5 mL	ICP-QMS Collision cell with He Ge, In, Lu as internal standards	External, linear through zero: 1/ 20/ 50/ 100 µg/L	0.298 µg/L
L9	none	5 mL	ICP-OES	External, linear: 0/ 1/ 5 µg/L	0.01 mg/L
L10	Acidification to 1 % HNO_3	5 mL	ICP-QMS Collision cell with He/H_2 Ge as internal standard	Matrix matched: 0/ 10/ 25/ 48/ 101 µg/L	0.9 µg/L
L11	Dilution and acidification with HNO_3	1.5 mL	ICP-QMS Collision cell in He mode Sc as internal standard	External calibration: 0.1/ 0.5/ 1/ 5/ 10/ 20/ 50 µg/L	0.012 µg/L
Not used in certification					
L2	Dilution and acidification to 10% HNO_3	2 mL	ICP-QMS He collision mode Ge as internal standard	External: 0.1/ 0.2/ 0.5/ 1/ 2/ 5/ 10/ 20 µg/L	0.2 µg/L
L6	Dilution 1:1 to 2M HNO_3	1.1 mL	ICP-QMS	Linear calibration: 0/ 200/ 400/ 600/ 800/ 1000 µg/L	0.03 µg/L
L12	none	0.02 mL	ETAAS Zeeman correction	Non-linear calibration forced through zero: 5/ 10/ 20 µg/L	0.2 µg/L (LOD)

D.4 Mass concentration of Cu

Lab	Sample pretreatment	Sample intake	Analytical method	Calibration	LOQ
L1	none	1 mL	ICP-SFMS In as internal standard	External: 0 - 10 µg/L two point calibration checked against synthetic QC sample at ½ max concentration	0.005 µg/L
L3	none	8 mL	ICP-OES	External: 4/ 10/ 20/ 40/ 100/ 200/ 500 µg/L	2 µg/L
L4	none	10 mL	ICP-QMS Rh as internal standard	External: 1/ 10/ 100 µg/L	0.5 µg/L
L5	none	0.04 mL	ET-AAS	External, non-linear: 5/ 10/ 15/ 17.5/ 20 µg/L	Not reported
L7	Preservation HNO_3; digestion 95 °C for 2 h	15 mL	ICP-SFMS Ge as internal standard Mass resolution >4000	External, linear 1 point: 0/ 10 µg/L	0.5 µg/L
L8	none	5 mL	ICP-QMS Collision cell with He Ge, In, Lu as internal standards	External, linear through zero: 10/ 200/ 500/ 1000 µg/L	2.24 µg/L
L9	none	5 mL	ICP-OES	External, linear: 0/ 1/ 5 µg/L	0.01 mg/L
L10	Acidification to 1 % HNO_3	5 mL	ICP-QMS Collision cell with He/H_2 Ge as internal standard	Matrix matched: 0/ 10/ 25/ 48/ 101 µg/L	0.9 µg/L
L11	Dilution and acidification with HNO_3	1.5 mL	ICP-QMS Collision cell in He mode Sc as internal standard	External calibration: 0.1/ 0.5/ 1/ 5/ 10/ 20/ 50 µg/L	0.012 µg/L
Not used in certification					
L2	Dilution and acidification to 10% HNO_3	2 mL	ICP-QMS He collision mode Ge as internal standard	External: 0.1/ 0.2/ 0.5/ 1/ 2/ 5/ 10/ 20 µg/L	0.4 µg/L
L6	Dilution 1:1 to 2M HNO_3	1.1 mL	ICP-QMS	Linear calibration: 0/ 200/ 400/ 600/ 800/ 1000 µg/L	0.04 µg/L
L12	none	0.02 mL	ETAAS Zeeman correction	Non-linear calibration forced through zero: 12.5/ 25/ 50 µg/L	0.2 µg/L (LOD)

D.5 Mass concentration of Hg

Lab	Sample pretreatment	Sample intake	Analytical method	Calibration	LOQs
L0	None	0.5 mL	Amalgamation AAS	11 point calibration: 0.25/ 0.50/ 0.75/ 1.0/ 2.0/ 2.5/ 5.0/ 10.0/ 15.0/ 20.0/ 25.0	0.1 µg/L
L1	none	20 mL	CV-AFS	External: 0 - 0.2 µg/L two point calibration checked against synthetic QC sample at ½ max concentration	0.002 µg/L
L3	none	1 mL	CV-AAS	External: 0.05/ 0.1/ 0.25/ 0.5/ 0.75/ 1.0 µg/L	0.1 µg/L
L7	Preservation/digestion with Br_2	15 mL	CV-AFS	External, linear 1 point: 0/ 0.04 µg/L	0.005 µg/L
L8	Digestion with HNO_3, $KMnO_4$ and $K_2S_2O_8$ in ultrasonic at 50 °C for 30 minutes	5 mL	CV-AFS With enrichment on AU/Pt net	External: 0.05/ 0.10/ 0.25/ 0.5/ 0.75/ 1 µg/L	0.032µg/L
L9	Dilution	12 or 25 mL	CV-AFS	External: 0/ 0.5/ 1/ 2 µg/L	0.05µg/L
L10	Acidification to 1 % HNO_3	5 mL	ICP-QMS Collision cell with He/H_2 Ho as internal standard	Matrix matched: 0/ 10/ 25/ 48/ 101 µg/L	0.8 µg/L
L11	Digestion with HCl and BrCl in UV for 3h, addition of $NH_2OH.HCl$ before analysis	5 mL	CV-AAS Reduction with $SnCl_2$ Pre-concentration on Au trap	External: 0/ 0.0005/ 0.001/ 0.002/ 0.004 µg/L	0.0005 µg/L
Not used in certification					
L2	Dilution and acidification to 10% HNO_3	8 mL	ICP-QMS He collision mode Lu as internal standard	External: 0.1/ 0.2/ 0.3/ 0.4/ 0.5/ 1/ 2/ 5 µg/L	0.1 µg/L
L6	Dilution 1:1 to 2M HNO_3	1.1 mL	ICP-QMS	Linear calibration: 0/ 2/ 4/ 6/ 8/ 10 µg/L	0.1 µg/L

D.6 Mass concentration of Fe

Lab	**Sample pretreatment**	**Sample intake**	**Analytical method**	**Calibration**	**LOQs**
L1	none	1 mL	ICP-SFMS In as internal standard	External: 0 - 20 µg/L two point calibration checked against synthetic QC sample at ½ max concentration	0.01 µg/L
L3	none	8 mL	ICP-OES	External: 20/ 50/ 100/ 200/ 500/ 1000/ 2500/ 5000/ 10000 µg/L	10 µg/L
L4	none	10 mL	ICP-QMS Rh as internal standard Isobaric overlap correction	External: 10/ 100/ 1000 µg/L	10 µg/L
L7	Preservation HNO_3; digestion 95 °C for 2 h	15 mL	ICP-SFMS Ge as internal standard Mass resolution >4000	External, linear 1 point: 0/ 10 µg/L	50 µg/L
L8	none	5 mL	ICP-OES Yb as internal standard	External, linear through zero: 0.1/ 1/ 2/ 5 µg/L	0.004 µg/L
L9	none	5 mL	ICP-OES	External, linear: 0/ 1/ 5 µg/L	0.01 mg/L
L10	Acidification to 1 % HNO_3	5 mL	ICP-QMS Collision cell with He/H_2 Ge as internal standard	Matrix matched: 0/ 10/ 25/ 48/ 101 µg/L	0.8 µg/L
L11	Dilution and acidification with HNO_3	1.5 mL	ICP-QMS Collision cell in He mode Sc as internal standard	External calibration: 0.1/ 0.5/ 1/ 5/ 10/ 20/ 50 µg/L	0.18 µg/L
Not used in certification					
L2	Dilution and acidification to 10% HNO_3	2 mL	ICP-QMS He collision mode Ge as internal standard	External: 1/ 2/ 5/ 10/ 20/50/ 100/ 200 µg/L	0.89 µg/L
L6	Dilution 1:1 to 2M HNO_3	1.1 mL	ICP-QMS	Linear calibration: 0/ 2000/ 4000/ 6000/ 8000/ 10000 µg/L	2 µg/L
L12	none	2 mL	FAAS Deuterium background correction	Non-linear calibration: 0/ 500/ 1000/ 2000 µg/L	26 µg/L

D.7 Mass concentration of Mn

Lab	Sample pretreatment	Sample intake	Analytical method	Calibration	LOQs
L1	none	1 mL	ICP-SFMS In as internal standard	External: 0 - 20 µg/L two point calibration checked against synthetic QC sample at ½ max concentration	0.002 µg/L
L2	Dilution and acidification to 10% HNO_3	2 mL	ICP-QMS He collision mode Ge as internal standard	External: 1/ 2/ 5/ 10/ 20/ 50/ 100 µg/L	0.1 µg/L
L3	none	8 mL	ICP-OES	External: 10/ 25/ 50/ 100/ 250/ 500/ 1250/ 2500/ 5000 µg/L	10 µg/L
L4	none	10 mL	ICP-QMS Rh as internal standard	External: 1/ 10/ 100 µg/L	0.5 µg/L
L5	none	0.02 mL	ET-AAS	External, non-linear: 7.5/ 10/ 12.50/ 18.75/ 25 µg/L	Not reported
L7	Preservation HNO_3; digestion 95 °C for 2 h	15 mL	ICP-SFMS Ge as internal standard Mass resolution >9000	External, linear 1 point: 0/ 100 µg/L	10 µg/L
L8	none	5 mL	ICP-OES Yb as internal standard	External, linear through zero: 0.05/ 0.2/ 0.5/ 1 µg/L	0.006 µg/L
L9	none	5 mL	ICP-OES	External, linear: 0/ 1/ 5 µg/L	0.01 mg/L
L10	Acidification to 1 % HNO_3	5 mL	ICP-QMS Collision cell with He/H_2 Ge as internal standard	Matrix matched: 0/ 10/ 25/ 48/ 101 µg/L	0.05 µg/L
L11	Dilution and acidification with HNO_3	1.5 mL	ICP-QMS Collision cell in He mode Sc as internal standard	External calibration: 0.1/ 0.5/ 1/ 5/ 10/ 20/ 50 µg/L	0.03 µg/L
Not used in certification					
L6	Dilution 1:1 to 2M HNO_3	1.1 mL	ICP-QMS	Linear calibration: 0/ 2000/ 4000/ 6000/ 8000/ 10000 µg/L	0.1 µg/L
L12	none	0.02 mL	ETAAS Zeeman correction	Non-linear calibration forced through zero: 0/ 5/ 10/ 20 µg/L	0.5 µg/L

D.8 Mass concentration of Ni

Lab	Sample pretreatment	Sample intake	Analytical method	Calibration	LOQs
L1	none	1 mL	ICP-SFMS In as internal standard	External: 0 - 10 µg/L two point calibration checked against synthetic QC sample at ½ max concentration	0.0005 µg/L
L2	Dilution and acidification to 10% HNO_3	2 mL	ICP-QMS He collision mode Ge as internal standard	External: 1/ 2/ 5/ 10/ 20/ 50/ 100 µg/L	0.13 µg/L
L3	none	8 mL	ICP-OES	External: 2/ 4/ 10/ 20/ 50/ 100/ 200 µg/L	2 µg/L
L5	none	0.05 mL	ET-AAS	External, non-linear: 5/ 10/ 15/ 20/ 25 µg/L	Not reported
L7	Preservation HNO_3; digestion 95 °C for 2 h	15 mL	ICP-SFMS Ge as internal standard Mass resolution >4000	External, linear 1 point: 0/ 10 µg/L	1 µg/L
L8	none	5 mL	ICP-QMS Collision cell with He Ge, In, Lu as internal standards	External, linear through zero: 1/ 20/ 50/ 100 µg/L	0.324 µg/L
L9	none	5 mL	ICP-OES	External, linear: 0/ 1/ 5 µg/L	0.01 mg/L
L10	Acidification to 1 % HNO_3	5 mL	ICP-QMS Collision cell with He/H_2 Ge as internal standard	Matrix matched: 0/ 10/ 25/ 48/ 101 µg/L	0.3 µg/L
L11	Dilution and acidification with HNO_3	1.5 mL	ICP-QMS Collision cell in He mode Sc as internal standard	External calibration: 0.1/ 0.5/ 1/ 5/ 10/ 20/ 50 µg/L	0.09 µg/L
Not used in certification					
L4	None	10 mL	ICP-QMS Isobaric overlap correction Rh as internal standard	Linear calibration: 1/ 10/ 100 µg/L	0.5 µg/L
L6	Dilution 1:1 to 2M HNO_3	1.1 mL	ICP-QMS	Linear calibration: 0/ 200/ 400/ 600/ 800/ 1000 µg/L	0.02 µg/L
L12	none	0.02 mL	ETAAS Zeeman correction	Non-linear calibration forced thorugh zero: 25/ 50 µg/L	0.4 µg/L (LOD)

D.9 Mass concentration of Pb

Lab	Sample pretreatment	Sample intake	Analytical method	Calibration	LOQs
L1	none	1 mL	ICP-SFMS In as internal standard	External: 0 - 10 µg/L two point calibration checked against synthetic QC sample at ½ max concentration	0.0005 µg/L
L2	Dilution and acidification to 10% HNO_3	2 mL	ICP-QMS He collision mode Ge as internal standard	External: 1/ 2/ 5/ 10/ 20/ 50/ 100 µg/L	0.04 µg/L
L3	none	8 mL	ICP-OES	External: 2/ 4/ 10/ 20/ 50/ 100 200 µg/L	2 µg/L
L4	none	10 mL	ICP-QMS Rh as internal standard	External: 1/ 10/ 100 µg/L	0.5 µg/L
L5	none	0.04 mL	ET-AAS	External, non-linear: 9.375/ 15.625/ 18.75/ 21.875/ 25.00 µg/L	Not reported
L7	Preservation HNO_3; digestion 95 ^{o}C for 2 h	15 mL	ICP-SFMS Re as internal standard Mass resolution >4000	External, linear 1 point: 0/ 10 µg/L	0.5 µg/L
L8	none	5 mL	ICP-QMS Collision cell with He Ge, In, Lu as internal standards	External, linear through zero: 1/ 20/ 50/ 100 µg/L	0.234 µg/L
L9	none	5 mL	ICP-OES	External, linear: 0/ 1/ 5 µg/L	0.01 mg/L
L10	Acidification to 1 % HNO_3	5 mL	ICP-QMS Collision cell with He/H_2 Ho as internal standard	Matrix matched: 0/ 10/ 25/ 48/ 101 µg/L	0.04 µg/L
L11	Dilution and acidification with HNO_3	1.5 mL	ICP-QMS Bi as internal standard	External calibration: 0.1/ 0.5/ 1/ 5/ 10/ 20/ 50 µg/L	0.03 µg/L
Not used in certification					
L6	Dilution 1:1 to 2M HNO_3	1.1 mL	ICP-QMS	Linear calibration: 0/ 200/ 400/ 600/ 800/ 1000 µg/L	0.03 µg/L
L12	none	0.02 mL	ETAAS Zeeman correction	Non-linear calibration forced through zero: 20/ 40/ 60 µg/L	0.1 µg/L (LOD)

D.10 Mass concentration of Se

Lab	Sample pretreatment	Sample intake	Analytical method	Calibration	LOQs
L1	none	1 mL	ICP-SFMS In as internal standard	External: 0 - 20 µg/L two point calibration checked against synthetic QC sample at ½ max concentration	0.01 µg/L
L2	Dilution and acidification to 10%with HNO_3	2 mL	ICP-QMS H_2 reaction mode Ge as internal standard	External: 1/ 2/ 5/ 10/ 20/ 50/ 100 µg/L	0.3 µg/L
L3	Addition of KI, ascorbic acid and HCl as reducing agent	0.5 mL	HG-AAS Flow injection $NaBH_4$ as reducing agent	External: 0.5/ 1.0/ 2.5/ 5.0/ 7.5/ 10.0 µg/L	0.5 µg/L
L7	Preservation in HNO_3; digestion at 95 ^{o}C for 2 h	15 mL	HG-ICP-SFMS Mass resolution >9000	External, linear one point: 0 and 1 µg/L	0.1 µg/L
L8	None	5 mL	ICP-QMS Collision cell with He Ge, In, Lu as internal standards	External, linear through zero: 1/ 20/ 50/ 100 µg/L	0.303 µg/L
L10	Acidification to 1 % HNO_3	5 mL	ICP-QMS Collision cell with He/H_2 Ge as internal standard	Matrix matched: 0/ 10/ 25/ 48/ 101 µg/L	0.3 µg/L
L11	Dilution and acidification with HNO_3	1.5 mL	ICP-MS Collision cell in He mode Ge as internal standard	External calibration: 0.1/ 0.5/ 1/ 5/ 10/ 20/ 50 µg/L	0.27µg/L
Not used in certification					
L4	None	0.04 mL	ETAAS Pd and Mg modifier	Non-linear calibration: 30/ 22.5/ 15/ 7.5/ 3.75 µg/L	0.5 µg/L
L6	Dilution 1:1 to 2M HNO_3	1.1 mL	ICP-QMS	Linear calibration: 0/ 100/ 200/ 300/ 400/ 500 µg/L	0.9 µg/L

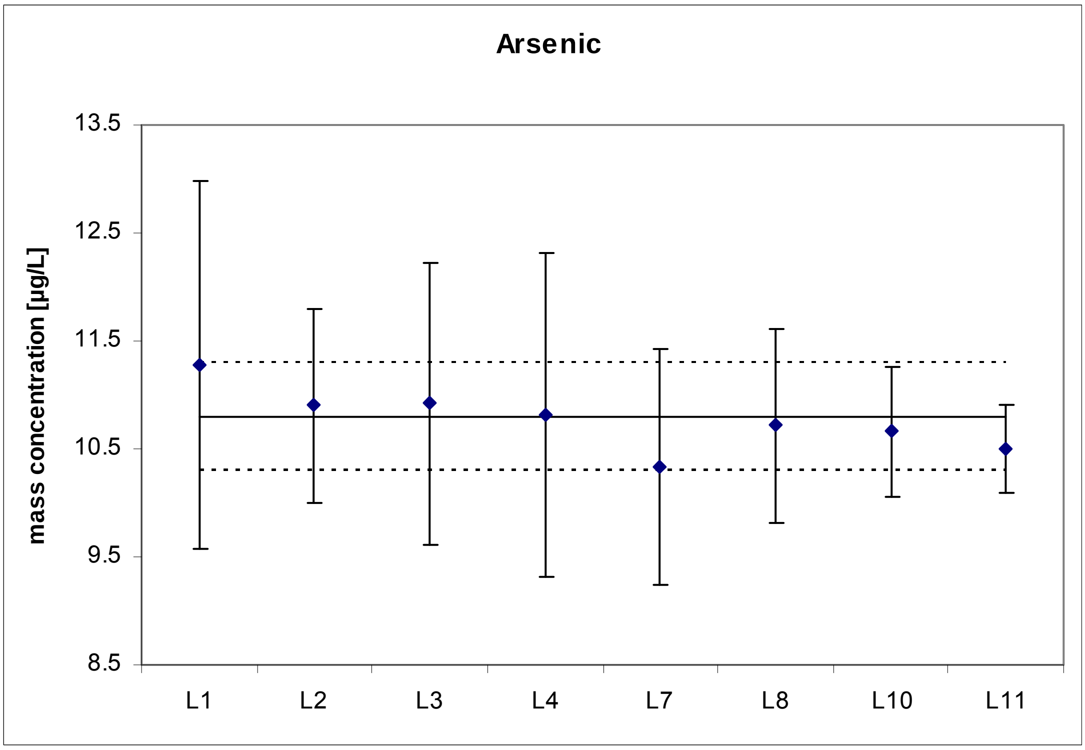
Annex E. Results of the characterisation study

The tables in this annex also contain the data sets that were discarded for technical reasons. These data sets are highlighted in italics and are given for information purposes only. They are not included in the graphs.

Error bars represent expanded uncertainties as reported by participating laboratories. The solid line represents the certified values (the mean of laboratory means), while the broken lines represent the expanded uncertainty of the certified value.

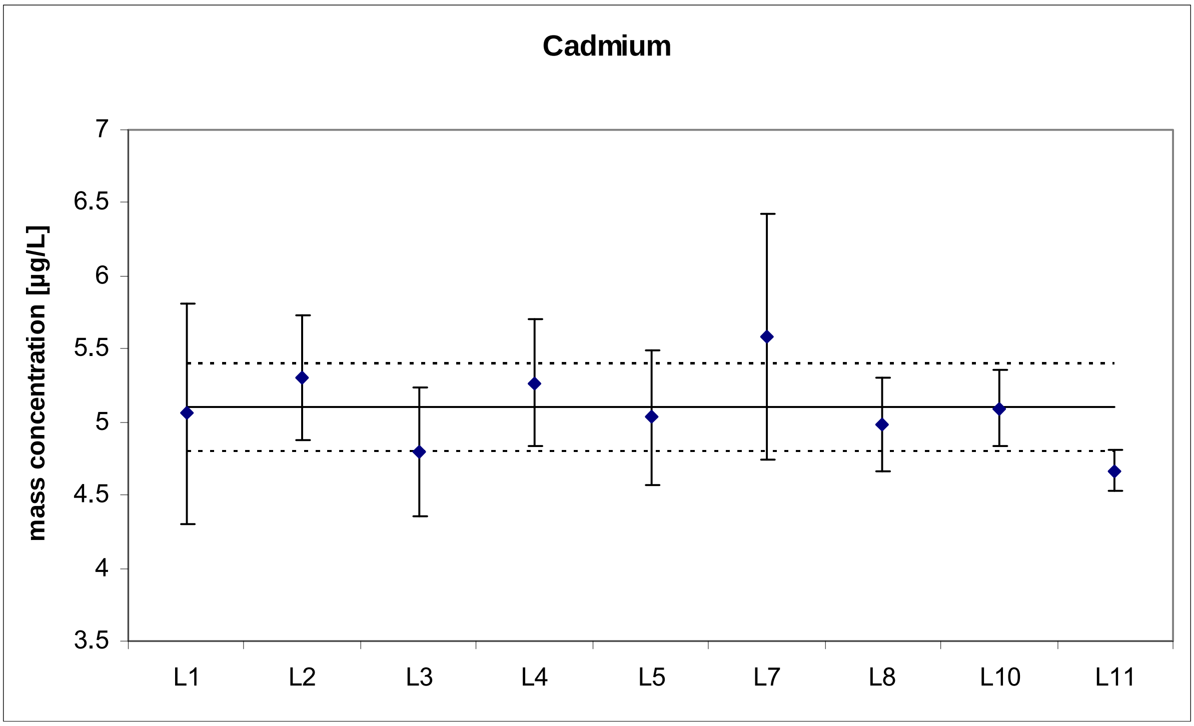
E.1 Mass concentration of As [µg/L]

Lab code	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Mean	U
L1	11.0	11.5	11.3	11.2	11.4	11.3	11.3	1.7
L2	11.06	11.08	10.87	10.72	10.72	10.95	10.90	0.87
L3	10.76	10.90	10.72	11.08	11.07	10.97	10.92	1.31
L4	10.95	10.65	10.93	10.87	10.76	10.68	10.81	1.41
L7	10.24	10.27	10.13	10.4	10.54	10.42	10.33	1.03
L8	10.89	10.78	10.69	10.50	10.73	10.71	10.72	0.81
L10	10.62	10.63	10.68	10.79	10.65	10.63	10.66	0.53
	10.64	10.48	10.66	10.85	10.78	10.52		
L11	10.6	10.4	10.5	10.6	10.5	10.4	10.5	0.4
Results not used in certification								
L6	*11.0*	*11.5*	*11.3*	*11.2*	*11.4*	*11.3*	*12.0*	*1.53*
L12	*9.49*	*10.11*	*10.69*	*9.67*	*11.05*	*10.68*	*10.28*	*0.17*



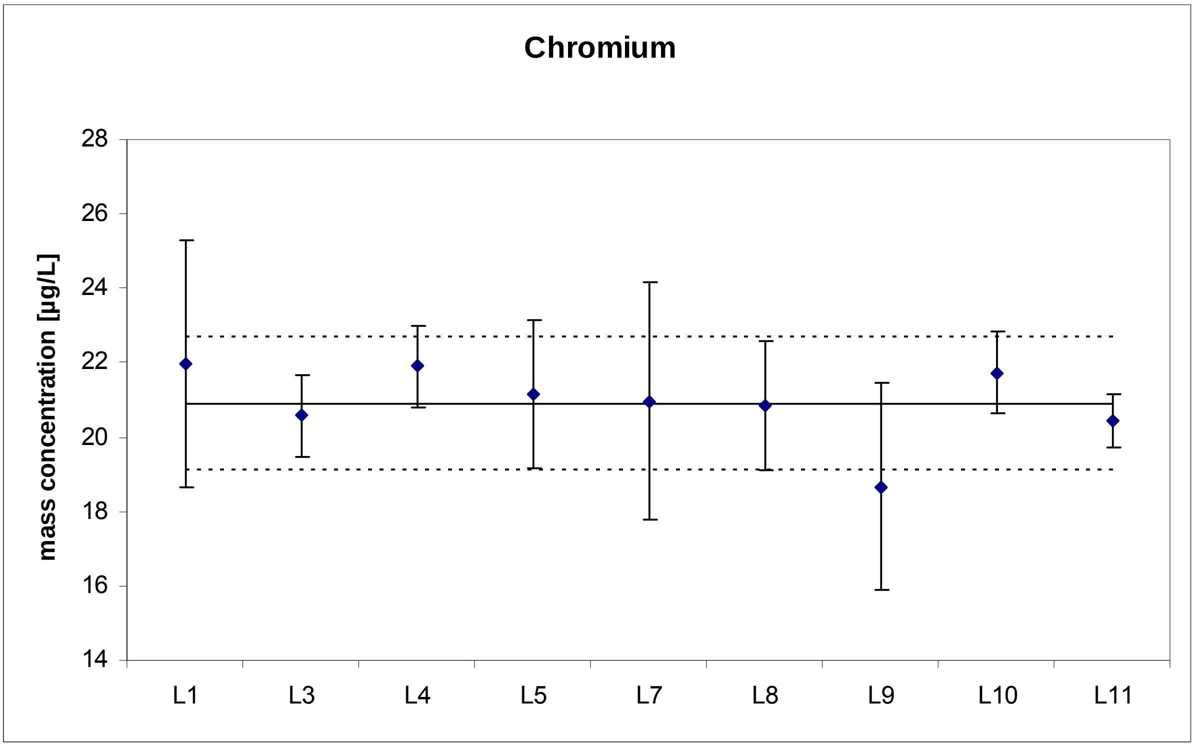
E.2 Mass concentration of Cd [µg/L]

Lab code	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Mean	U
L1	5.13	5.10	4.99	5.07	5.07	4.98	5.06	0.76
L2	5.18	5.30	5.45	5.21	5.47	5.21	5.30	0.43
L3	4.72	4.79	4.82	4.71	4.89	4.81	4.79	0.44
L4	5.3	5.30	5.25	5.30	5.20	5.26	5.27	0.43
L5	5.05	4.99	5.01	5.06	5.08	5.02	5.04	0.46
L7	5.673	5.713	5.545	5.668	5.483	5.454	5.589	0.839
L8	4.970	5.009	5.006	4.947	4.964	4.994	4.982	0.314
L10	5.157	5.215	5.060	5.022	5.098	5.137	5.096	0.255
	5.200	5.018	5.175	5.139	5.049	4.880		
L11	4.70	4.68	4.65	4.66	4.64	4.67	4.67	0.14
Results not used in certification								
L6	*5.4*	*5.7*	*5*	*4.766*	*4.938*	*3.774*	*4.93*	*0.38*
L12	*4.66*	*4.48*	*5.06*	*4.82*	*4.82*	*5.12*	*4.83*	*0.06*



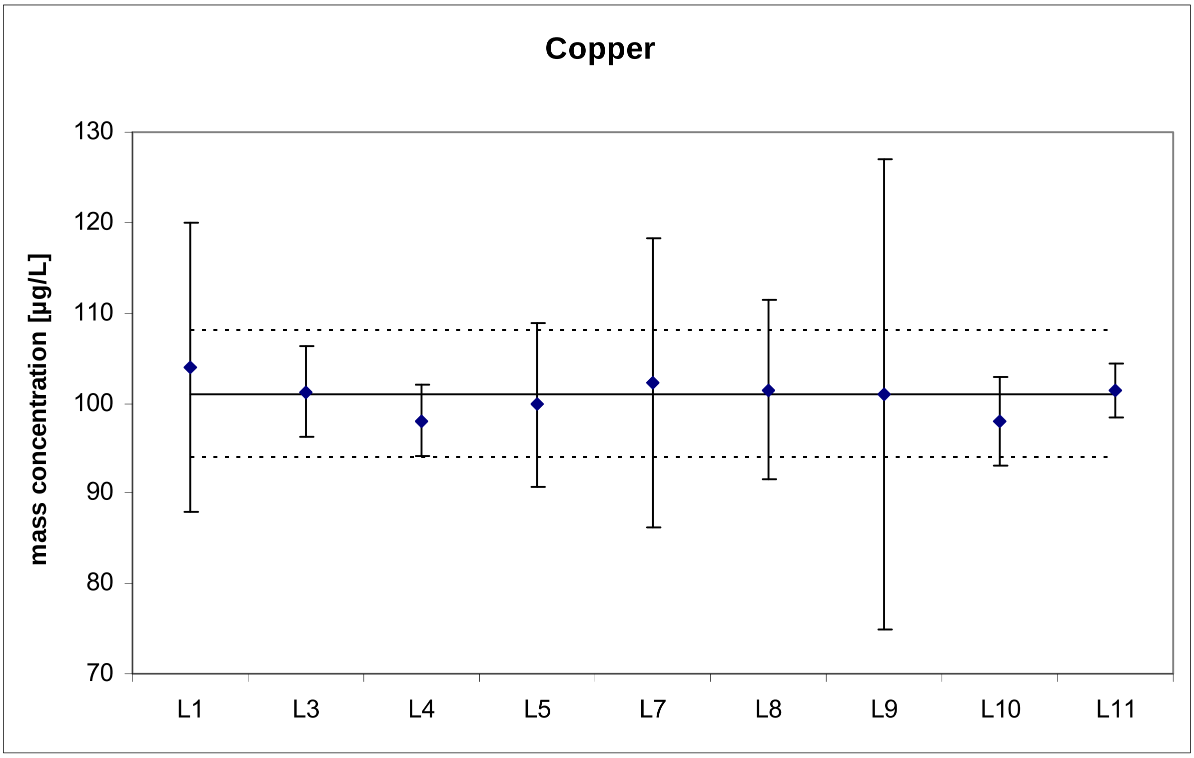
E.3 Mass concentration of Cr [µg/L]

Lab codes	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Mean	U
L1	22.3	21.8	22.1	22.3	21.5	21.8	22.0	3.3
L3	20.2	20.5	20.8	20.5	20.8	20.7	20.6	1.1
L4	22.3	22.7	21.2	22.5	21.6	21.1	21.9	1.1
L5	20.67	20.56	21.56	20.44	21.77	21.84	21.14	1.9
L7	20.88	21.11	20.98	21.22	20.75	20.88	20.97	3.15
L8	20.61	20.99	20.96	20.47	21.05	21.10	20.86	1.74
L9	19	19	19	19	18	18	19	3
L10	22.39	21.84	21.24		22.03	22.32	21.72	2.80
	21.53	20.93	21.19	22.18	21.68	21.56		
L11	20.0	20.2	19.9	20.8	20.9	20.8	20.43	0.62
Results not used in certification								
L2	*24.57*	*24.90*	*25.40*	*26.01*	*26.28*	*25.03*	*25.36*	*2.03*
L6	*25.29*	*22.69*	*25.92*	*25.29*	*26.32*	*22.65*	*24.69*	*4.15*
L12	*19.4*	*20.0*	*16.4*	*19.7*	*17.6*	*15.3*	*18.1*	*0.17*



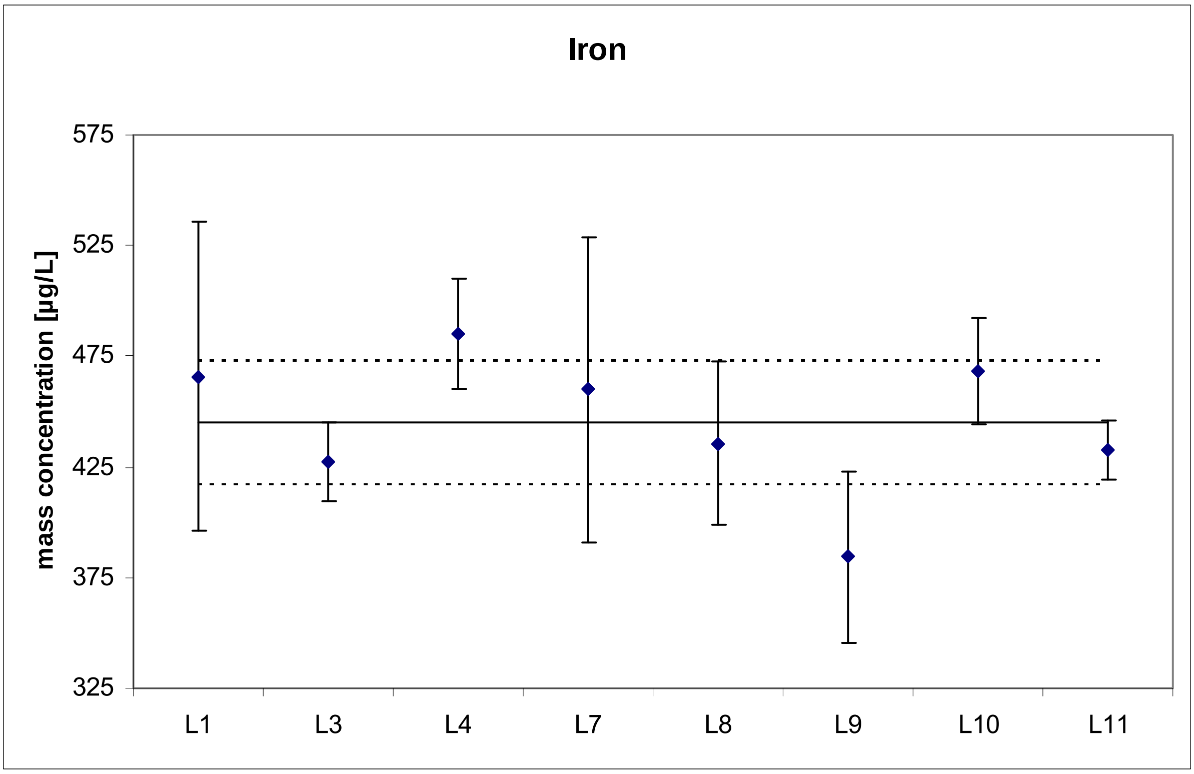
E.4 Mass concentration of Cu [µg/L]

Lab codes	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Mean	U
L1	105	105	105	103	104	102	104	16
L3	100.1	101.2	103.9	99.87	100.9	101.7	101.3	4.1
L4	100.7	101.0	94.9	100.8	94.9	95.9	98.0	3.5
L5	101.5	101.3	100.6	98.08	100.7	96.73	99.82	8.99
L7	102.6	102.1	102.8	101.9	101.0	103	102.2	15.4
L8	99.74	100.4	105.7	105.6	98.45	98.9	101.5	9.5
L9	99	102	102	100	102	101	101	26
L10	98.64	97.90	98.67	99.57	98.50	98.97	97.98	4.90
	98.91	9394	98.85	98.77	98.85	94.21		
L11	101	102	102	100	103	100	101	3
Results not used in certification								
L2	*111.02*	*108.53*	*108.73*	*112.47*	*115.29*	*114.78*	*111.8*	*8.9*
L6	*105.5*	*99.32*	*101.1*	*112.4*	*104.5*	*101.1*	*104.0*	*17.1*
L12	*111*	*103*	*94*	*105*	*90*	*94*	*99.5*	*2.4*



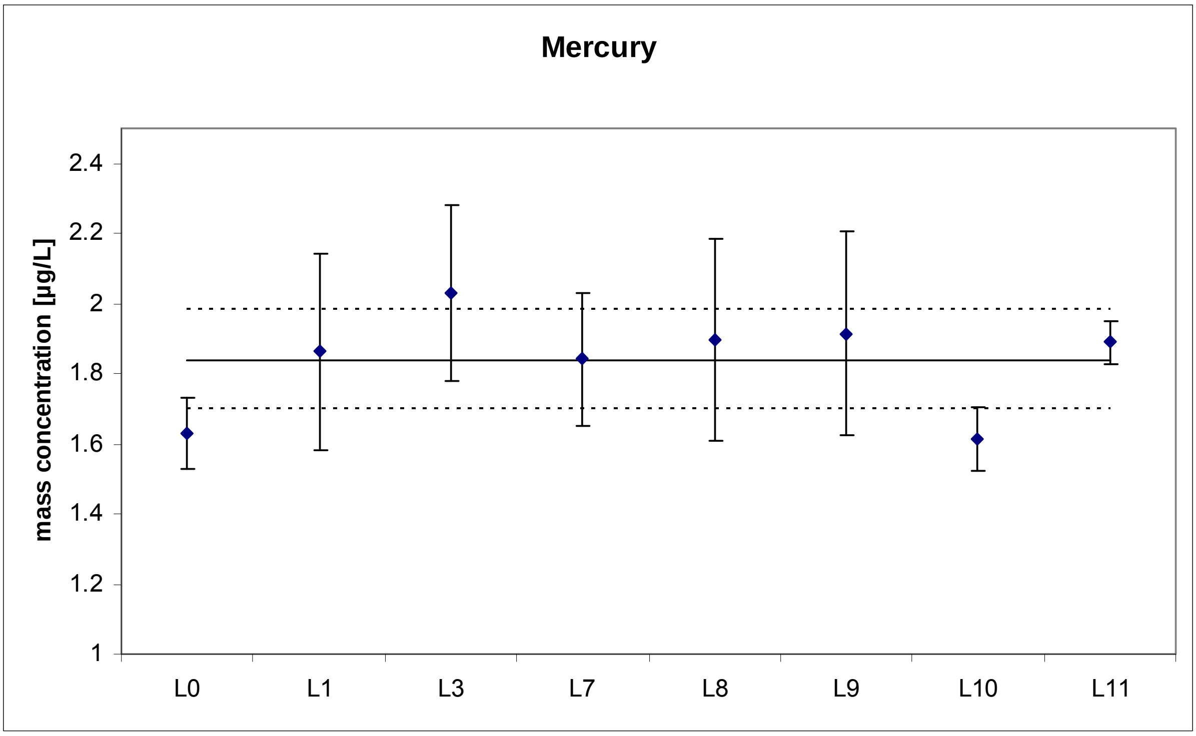
E.5 Mass concentration of Fe [µg/L]

Lab codes	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Mean	U
L1	465	459	459	472	474	467	466	70
L3	423.9	424.3	433.6	424.4	430.1	429.0	427.6	17.1
L4	505.7	501.4	461.5	501.1	474.6	467.8	485.4	24.3
L7	459	469	458	463	456	454	460	69
L8	441.4	432.3	435.3	439.0	430.5	434.2	435.5	36.6
L9	385	393	377	389	382	379	384	39
L10	460.1	467.8	459.0	500.3	457.2	471.9	468.4	23.5
	464.7	458.8	458.8	489.0	458.7	473.9		
L11	431	428	431	432	440	434	433	13
Results not used in certification								
L2	*537.53*	*533.35*	*543.66*	*552.08*	*507.10*	*506.48*	*530.03*	*42.4*
L6	*1403*	*1185*	*1209*	*1368*	*1379*	*1180*	*1287*	*146*
L12	*424*	*419*	*436*	*414*	*433*	*434*	*427*	*27*



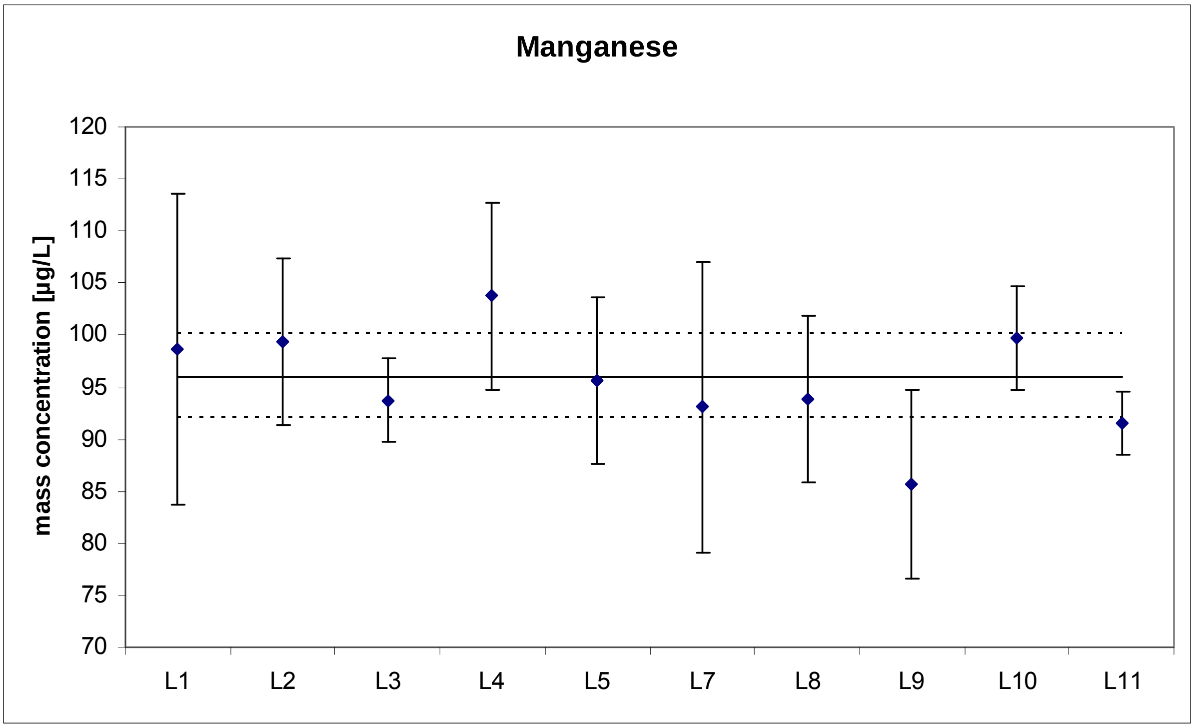
E.6 Mass concentration of Hg [µg/L]

Lab codes	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Mean	U
L0	1.63	1.64	1.66	1.57	1.64	1.64	1.63	0.10
L1	1.88	1.88	1.84	1.88	1.86	1.84	1.86	0.28
L3	2.023	2.037	2.049	2.010	2.013	2.057	2.03	0.25
L7	1.681	1.843	1.901	1.843	1.876	1.901	1.841	0.19
L8	1.912	1.909	1.889	1.910	1.872	1.884	1.896	0.29
L9	2.006	2.019	1.710	2.013	1.859	1.884	1.915	0.29
L10	1.655	1.559	1.563	1.706	1.602	1.589	1.612	0.09
	1.631	1.592	1.597	1.655	1.599	1.594		
L11	1.88	1.94	1.80	1.99	1.80	1.93	1.890	0.06
Results not used in certification								
L2	*1.30*	*1.31*	*1.30*	*1.37*	*1.36*	*1.36*	*1.33*	*0.11*
L6	*1.1*	*1.8*	*1.6*	*1*	*1*	*1.9*	*1.4*	*0.4*



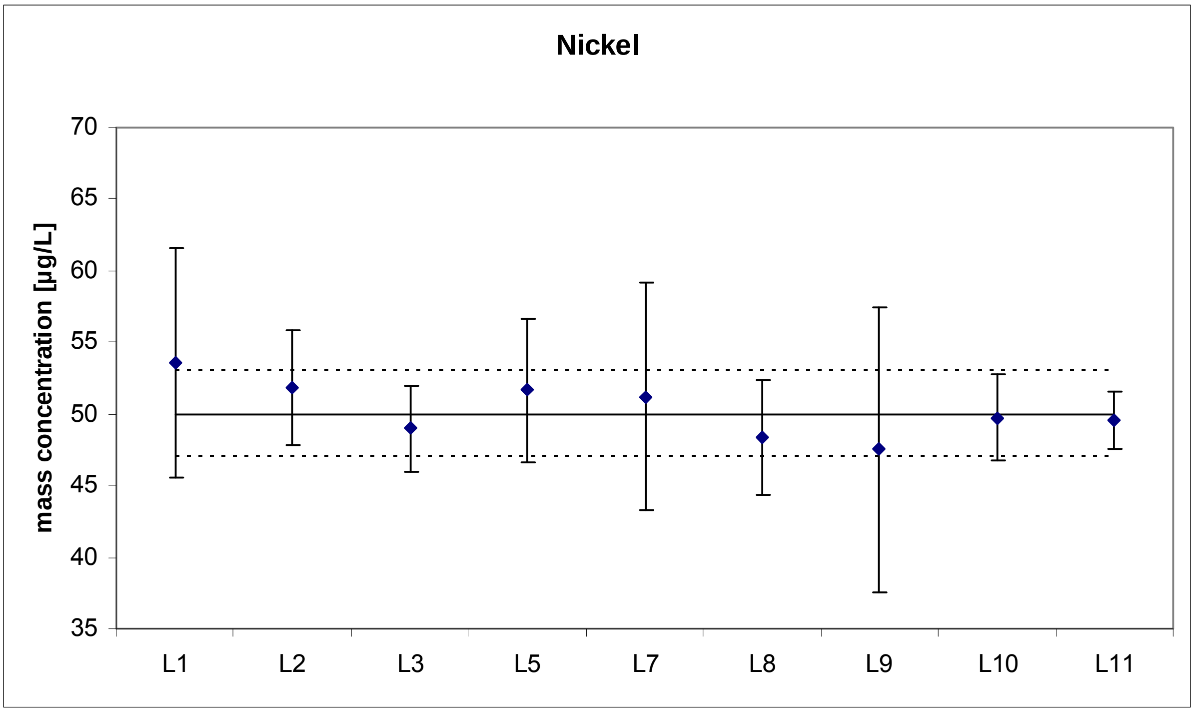
E.7 Mass concentration of Mn [µg/L]

Lab codes	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Mean	U
L1	99.5	96.0	101.0	98.0	99.3	98.0	98.6	14.8
L2	103.69	103.55	104.19	93.44	95.17	96.01	99.34	7.95
L3	92.7	92.8	94.7	93.2	94.3	94.8	93.8	8.3
L4	106.6	108.2	100.0	107.6	100.4	99.7	103.8	8.3
L5	95.53	97.42	94.53	96.17	94.13	95.60	95.56	7.65
L7	92.41	88.42	94.75	94.31	94.56	94.01	93.08	13.96
L8	94.96	92.86	93.65	95.01	92.61	93.80	93.82	7.79
L9	85	88	85	86	85	85	86	9
L10	98.78	99.50	100.25	99.32	99.61	100.22	99.73	4.99
	100.47	98.53	101.44	100.39	99.90	98.39		
L11	92.0	92.0	92.0	90.6	91.7	90.8	91.5	2.8
Results not used in certification								
L6	*116.5*	*123*	*109*	*119.8*	*112.2*	*113.8*	*115.7*	*12.6*
L12	*92.8*	*96.5*	*76.3*	*96.3*	*74.2*	*76.5*	*85.4*	*8.0*



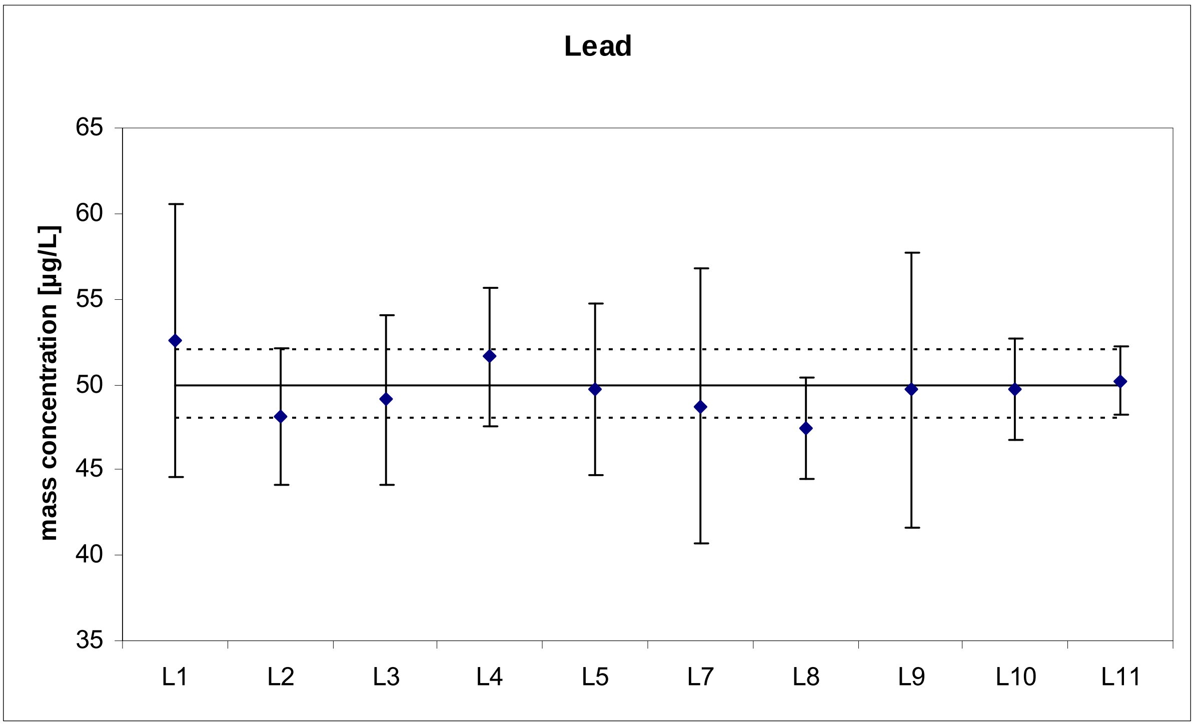
E.8 Mass concentration of Ni [µg/L]

Lab codes	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Mean	U
L1	54.0	53.5	53.6	53.5	53.6	53.0	53.5	8.0
L2	51.30	50.58	51.12	52.19	52.9	53.0	51.85	4.15
L3	49.0	48.8	49.3	49.0	48.9	49.1	49.0	2.5
L5	50.42	51.51	51.70	52.15	51.73	52.48	51.67	4.65
L7	51.23	51.06	51.24	52.36	50.71	50.74	51.22	7.68
L8	48.30	48.50	48.63	47.75	48.40	48.43	48.34	3.48
L9	47	48	48	47	47	48	47	10
L10	49.60	48.54	50.46	52.32	50.27	49.00	49.74	2.49
	49.51	47.63	50.84	50.53	49.94	48.27		
L11	48.8	49.3	50.0	49.5	50.7	49.3	49.6	1.5
Results not used in certification								
L4	*51.0*	*51.1*	*46.9*	*55.6*	*54.5*	*55.0*	*52.4*	
L6	*62.8*	*57.31*	*58.6*	*54.9*	*56.7*	*58.03*	*58.06*	*7.70*
L12	*43.1*	*45.0*	*45.4*	*44.0*	*44.5*	*43.8*	*44.3*	*1.2*



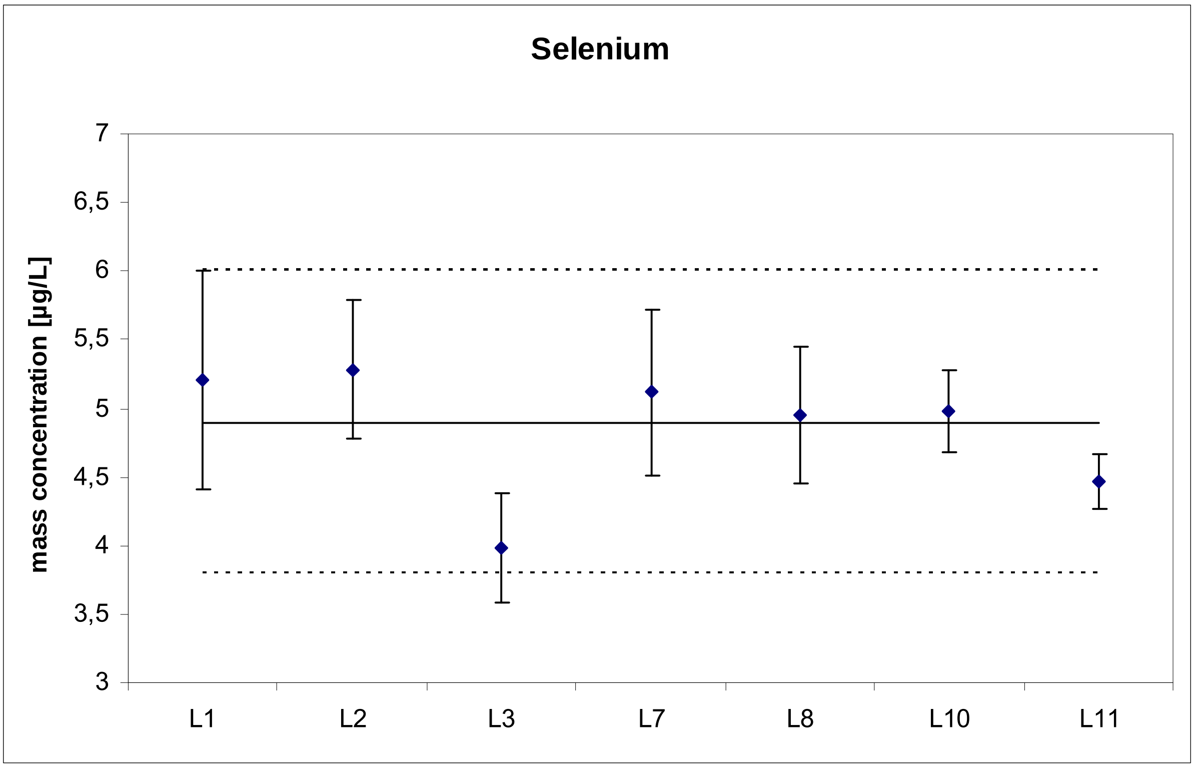
E.9 Mass concentration of Pb [µg/L]

Lab codes	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Mean	U
L1	53.8	53.8	50.6	53.6	51.6	51.9	52.6	7.9
L2	47.98	47.84	48.07	48.1	48.66	47.90	48.10	3.85
L3	47.6	48.5	49.9	48.8	49.8	50.0	49.1	4.5
L4	52.7	55.1	49.2	54.3	49.2	49.1	51.6	3.7
L5	48.79	49.10	50.17	49.64	50.40	50.25	49.73	4.48
L7	48.84	48.91	48.94	48.63	47.88	49.19	48.73	7.31
L8	47.54	47.62	47.73	47.70	47.07	46.98	47.44	2.85
L9	48	54	48	50	50	48	50	8
L10	50.20	53.24	50.40	48.56	49.62	52.44	49.67	2.49
	50.32	48.31	50.09	48.41	48.25	46.84		
L11	49.90	50.14	50.36	50.19	50.10	50.64	50.22	1.51
Results not used in certification								
L6	*55.51*	*55.68*	*54.09*	*55.11*	*56.65*	*57.59*	*55.77*	*8.25*
L12	*47.6*	*46.6*	*46.0*	*49.4*	*54.2*	*54.8*	*49.8*	*1.5*



E.10 Mass concentration of Se [µg/L]

Lab codes	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Mean	U
L1	5.02	5.04	5.42	5.20	5.21	5.33	5.20	0.8
L2	5.58	5.62	5.44	5.64	5.74	5.73	5.62	0.45
L3	3.84	3.83	4.06	3.80	4.180	4.18	3.98	0.4
L7	4.97	5.06	5.21	5.03	5.22	5.20	5.12	0.6
L8	4.899	5.008	4.965	4.894	4.972	4.972	4.952	0.5
L10	2.044	4.878	5.033	5.090	4.980	4.969	4.979	0.3
	5.054	4.819	5.098	5.013	5.006	4.764		
L11	4.46	4.43	4.48	4.47	4.47	4.46	4.462	0.2
Results not used in certification								
L4	*3.6*	*3.83*	*4.28*	*3.74*	*4.72*	*4.67*	*4.14*	*0.41*
L6	*5.3*	*4.8*	*4.3*	*4.6*	*4.9*	*5.1*	*4.8*	*0.9*



European Commission

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Abstract

The report describes the production and certification of the certified reference material ERM-CA713 Wastewater. The material was produced to replace the existing materials BCR-713, BCR-714 and BCR-715 because of changes in the legislation, in particular the requirement for the monitoring of Hg as a priority substance. The material is certified for As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb and Se. and will serve as a quality control tool for the laboratories involved in the mandatory monitoring of the Priority Substances prescribed under the Water Framework Directive (WFD, 2000/60/EC).

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