

CERTIFICATION REPORT

**The certification of the mass concentration of As, Cd, Co, Cu,
Mn, Mo, Ni and Pb, and density in seawater:
ERM[®]- CA403**



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Abstract

This report describes the production of ERM[®]-CA403, a seawater material certified for the density and the mass concentrations of As, Cd, Co, Cu, Mn, Mo, Ni, and Pb. The material was produced following ISO Guide 34:2009. The starting material was 1500 L of seawater collected at Southern Bight just inside of Belgian territorial waters. The sample was filtered, acidified and spiked before filling into 500 mL high density polyethylene (HDPE) bottles which were placed into an aluminised PET/M (metallized polyethylene terephthalate) sachets. The material was sterilised by gamma irradiation. Between unit-homogeneity was quantified and stability during dispatch and storage were assessed in accordance with ISO Guide 35:2006. Due to the inherent homogeneity of filtered water samples, determination of minimum sample intake (within-unit heterogeneity) was not required. The material was characterised by an inter-comparison among laboratories of demonstrated competence and adhering to ISO/IEC 17025:2005. Technically invalid results were removed but no outlier was eliminated on statistical grounds only. Uncertainties of the certified values were calculated in compliance with the Guide to the Expression of Uncertainty in Measurement (GUM) and include uncertainties related to possible inhomogeneity, and instability and to characterisation. The material is intended for the 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 bottles containing 500 mL of seawater. The CRM was accepted as European Reference Material (ERM[®]) after peer evaluation by the partners of the European Reference Materials consortium.



CERTIFICATION REPORT

The certification of the mass concentration of As, Cd, Co, Cu, Mn, Mo, Ni and Pb, and density in seawater: ERM®- CA403

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Certain commercial equipment, instruments, and materials are identified in this paper to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the European Commission, nor does it imply that the material or equipment is necessarily the best available for the purpose.

Summary

This report describes the production of ERM[®]-CA403, a seawater material certified for the density and the mass concentrations of As, Cd, Co, Cu, Mn, Mo, Ni, and Pb. The material was produced following ISO Guide 34:2009 [1]. The starting material was 1500 L of seawater collected at Southern Bight just inside of Belgian territorial waters. The sample was filtered, acidified and spiked before filling into 500 mL high density polyethylene (HDPE) bottles which were placed into an aluminised PET/M (metallized polyethylene terephthalate) sachets. The material was sterilised by gamma irradiation.

Between unit-homogeneity was quantified and stability during dispatch and storage were 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 material was characterised by an inter-comparison among laboratories of demonstrated competence and adhering to ISO/IEC 17025:2005 [3]. Technically invalid results were removed but no outlier was eliminated on statistical grounds only.

Uncertainties of the certified values were calculated in compliance with the Guide to the Expression of Uncertainty in Measurement (GUM) [4] and include uncertainties related to possible inhomogeneity, and instability and to characterisation.

The material is intended for the 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 bottles containing 500 mL of seawater.

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

The following values were assigned:

	Density	
	Certified values ²⁾ [g/mL]	Uncertainty ³⁾ [g/mL]
Density (at 20 °C)	1.02352	0.00005
Mass concentration		
	Certified values ^{1,2)} [µg/L]	Uncertainty ³⁾ [µg/L]
As ¹	1.90	0.13
Cd ¹	0.094	0.011
Co ¹	0.074	0.011
Cu ¹	0.87	0.13
Mn ¹	2.47	0.11
Mo ¹	12.0	0.6
Ni ¹	1.04	0.16
Pb ¹	0.098	0.010

1) as obtained by measurement methods with quantification by Inductively Coupled Plasma Mass Spectrometry

2) Certified values are values that fulfil the highest standards of accuracy. The given values represent the 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).

3) The uncertainty is the expanded uncertainty of the certified value with a coverage factor, k, 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.

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Glossary

AFS	Atomic fluorescence spectrometry
ASTM international	ASTM international (formerly American Society for Testing and Materials)
ANOVA	Analysis of variance
b	Slope in the equation of linear regression $y = a + bx$
BCR [®]	One of the trademarks of CRMs owned by the European Commission; formerly Community Bureau of Reference
BIPM	Bureau International des Poids et Mesures (International Bureau of Weights and Measures)
CC	Collision cell
CCT	Collision cell technology
CEN	European Committee for Standardization
CI	confidence interval
CRM	Certified reference material
EC	European Commission
EN	European norm (standard)
EQS	Environmental quality standard
ERM [®]	Trademark of European Reference Materials
EU	European Union
GRP	Glass fibre reinforced plastic
GUM	Guide to the Expression of Uncertainty in Measurements [4]
HDPE	High density polyethylene
HEPA	High-efficiency particulate arrestance
HG-AFS	Hydride generation-atomic fluorescence spectrometry
ICP-OES	Inductively coupled plasma optical emission spectrometry
ICP-MS	Inductively coupled plasma-mass spectrometry
ICP-QMS	ICP-Quadrupole mass spectrometry
ICP-SFMS	ICP-Sector field mass spectrometry
ISO	International Organization for Standardization
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_r	Mean of squares between-run from an ANOVA
MS_{within}	Mean of squares within-unit from an ANOVA
MUMM	Management Unit of the North Sea Mathematical Models and the Scheldt estuary
N	Number of replicates per unit
N	Number of samples (units) analysed
n.a.	Not applicable
n.c.	Not calculated
n.d.	Not detectable
NIST	National Institute of Standards and Technology (USA)
NRC	National Research Council (Canada)
OD	Oscillating type density meter
P	Number of technically valid datasets
PET/M	Metallized polyethylene terephthalate
PFA	Perfluoroalkoxy copolymer resin
PP	Polypropylene
PTFE	Polytetrafluoroethylene
Pyc	Pycnometer (for density measurement)
QA	Quality assurance
QC	Quality control
rel	Index denoting relative figures (uncertainties etc.)
RM	Reference material
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 as appropriate
se	Standard error
SF-MS	Sector-field mass spectrometry
SI	International System of Units
s_r	Between-run standard deviation
s_{within}	Standard deviation within groups as obtained from ANOVA; an additional index "rel" is added as appropriate
s_{wb}	Within-unit standard deviation
T	Temperature

t	Time
t_i	Time point for each replicate
$t_{\alpha, df}$	Critical t -value for a t -test, with a level of confidence of $1-\alpha$ 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 inhomogeneity that could be hidden by method repeatability; an additional index "rel" is added as appropriate
u_{bb}	Standard uncertainty related to a possible between-unit inhomogeneity; an additional index "rel" is added as appropriate
u_c	combined standard uncertainty; an additional index "rel" is added as appropriate
u_{cal}	Standard uncertainty of calibration
u_{char}	Standard uncertainty of the material characterisation; an additional index "rel" is added as appropriate
u_{CRM}	Combined standard uncertainty of the certified value; an additional index "rel" is added as appropriate
U_{CRM}	Expanded uncertainty of the certified value; an additional index "rel" is added as 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 as appropriate
u_{meas}	Standard measurement uncertainty
U_{meas}	Expanded measurement uncertainty
u_{rec}	Standard uncertainty related to possible between-unit inhomogeneity modelled as rectangular distribution; an additional index "rel" is added as appropriate
u_{sts}	Standard uncertainty of the short-term stability; an additional index "rel" is added as appropriate
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
\bar{x}	Arithmetic mean
\bar{x}_{ns}	Arithmetic mean of all results of normal stock samples
\bar{x}_{ref}	Arithmetic mean of results of reference samples
α	significance level

Δ_{meas}	Absolute difference between mean measured value and the certified value
$\nu_{s,meas}$	Degrees of freedom for the determination of the standard deviation s_{meas}
$\nu_{MS_{within}}$	Degrees of freedom of MS_{within}

1 Introduction

1.1 Background

In the year 2000, the European Commission adopted the Water Framework Directive (WFD; [5]). Since then, a number of directives that provide the legislative framework for the protection of surface waters and other water resources have been added to the initial Directive.

The WFD constitutes a strategy against the chemical pollution of European water bodies (rivers, lakes, ground and coastal waters) and requires all member states to implement specific monitoring programmes covering the chemical status of surface waters and the assessment of significant, long-term pollution trends resulting from human activities. Directive 2013/39/EU [6] on environmental quality standards in the field of water policy contains a list of priority I substances, including cadmium, nickel, lead and their compounds for which maximum allowable concentrations and annual average values were set for surface waters (Table 1). In addition, the directive lists values for Zn, Cu, Cr, Se, As, Mo, and Co as priority II substances. The quality and comparability of analytical results generated by the Member States to perform water chemical monitoring should be ensured. This is guaranteed by Directive 2009/90/EC [7], which lays down the technical specifications for chemical analysis and monitoring of the water status. Among other criteria, the Directive 2009/90/EC establishes that EU laboratories shall ensure their competences in analysing relevant physico-chemical or chemical parameters by the analysis of available certified reference materials (CRMs) that are representative of collected samples which contain appropriate levels of concentrations in relation to relevant Environmental Quality Standards (EQS).

Table 1. Environmental quality standards for Cd, Pb and Ni.

	Annual average – EQS [$\mu\text{g/L}$]	Annual average – EQS [$\mu\text{g/L}$]	Maximum allowable concentration – EQS [$\mu\text{g/L}$]	Maximum allowable concentration – EQS [$\mu\text{g/L}$]
	Inland surface waters	Other surface waters	Inland surface waters	Other surface waters
Cd and its compounds (depending on water hardness classes)*	≤ 0.08 (Class 1) 0.08 (Class 2) 0.09 (Class 3) 0.15 (Class 4) 0.25 (Class 5)	0.20	≤ 0.45 (Class 1) 0.45 (Class 2) 0.60 (Class 3) 0.90 (Class 4) 1.5 (Class 5)	≤ 0.45 (Class 1) 0.45 (Class 2) 0.60 (Class 3) 0.90 (Class 4) 1.5 (Class 5)
Pb and its compounds	<u>1.2</u> [‡]	1.3	<u>14</u>	<u>14</u>
Ni and its compounds	<u>4</u> [‡]	8.6	<u>34</u>	<u>34</u>

*: Class 1: < 40 mg CaCO₃ /L, Class 2: 40 to < 50 mg CaCO₃ /L, Class 3: 50 to < 100 mg CaCO₃ /L, Class 4: 100 to < 200 mg CaCO₃ /L and Class 5: \geq 200 mg CaCO₃ /L.

[‡]: These EQS refer to bioavailable concentrations of the substances.

Moreover, the European Union has adopted two instruments, the EU Recommendation on Integrated Coastal Zone Management [8] and the Marine Strategy Framework Directive (2008/56/EC) [9] as complimentary tools to the protection of marine waters. The Marine

Strategy Framework Directive aims to achieve good environmental status of the EU's marine waters and to protect the resource base upon which marine-related economic and social activities depend. The Commission Decision on criteria and methodological standards on good environmental status of marine waters [10] contains a number of criteria and associated indicators for assessing good environmental status, in relation to the eleven descriptors of good environmental status laid down in Annex I of the Marine Strategy Framework Directive. Among the descriptors, contaminants, such as metals toxic at trace concentrations, are listed.

1.2 Choice of the material

ERM-CA403 was developed as replacement for the seawater-based certified reference material BCR[®]-403. The concentration levels that were targeted in the new material were based on those of the WFD and the water had to be spiked with Cd, Cr, Ni and Zn following assessment of the trace element composition of the raw material that was collected. The spiking aimed to increase the concentrations of the elements to around their respective EQS. The target uncertainties for the mass concentrations of the elements was below 20 %, to ensure that the material was suitable for the quality control of quantitative methods for measuring elements in seawater.

1.3 Design of the project

The certification of the element concentrations of ERM-CA403 was performed by interlaboratory comparison.

2 Participants

2.1 Project management and evaluation

European Commission, Joint Research Centre, 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, Geel (BE)
(accredited to ISO Guide 34 for production of certified reference materials, BELAC No. 268-RM)

2.3 Homogeneity study

European Commission, Joint Research Centre, Geel (BE)
(accredited to ISO Guide 34 for production of certified reference materials, BELAC No. 268-RM; measurements under the scope of ISO/IEC 17025 accreditation BELAC No. 268-TEST)

Agenzia Regionale per la Prevenzione e Protezione Ambientale del Veneto, Mestre (IT)
(measurements under the scope of ISO/IEC 17025 accreditation ACCREDIA No. 0838)

Laboratorios Tecnológicos del Levante, Paterna (ES)
(measurements under the scope of ISO/IEC 17025 accreditation ENAC No. 121/LE1782)

2.4 Stability study

Agenzia Regionale per la Prevenzione e Protezione Ambientale del Veneto, Mestre (IT)
(measurements under the scope of ISO/IEC 17025 accreditation ACCREDIA No. 0838)

Helmholtz Zentrum München – Forschungszentrum für Gesundheit und Umwelt GmbH, München (DE)
(measurements under the scope of ISO/IEC 17025 accreditation DACH; accreditation number DAC-PL-0141-01-10)

Laboratorios Tecnológicos del Levante, Paterna (ES)
(measurements under the scope of ISO/IEC 17025 accreditation ENAC No. 121/LE1782)

Reagecon Diagnostics Ltd, Shannon (IE)
(measurements under the scope of ISO/IEC 17025 accreditation NSAI, accreditation number 19.2769)

2.5 Characterisation

AGQ Labs & Technological Services S.L, Burguillos (ES)
(measurements under the scope of ISO/IEC 17025 accreditation ENAC; accreditation number 305/LE1322)

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

Agenzia Regionale per la Prevenzione e Protezione Ambientale del Veneto, Mestre (IT)
(measurements under the scope of ISO/IEC 17025 accreditation ACCREDIA No. 0838)

BEV - Bundesamt für Eich- und Vermessungswesen, Wien (AT)

Brooks Rand Labs L.L.C., Seattle (USA)
(measurements under the scope of ISO/IEC 17025 accreditation NELAP; accreditation number E87982)

EVANS Analytical group SAS, Tournefeuille (FR)
(measurements under the scope of ISO/IEC 17025 accreditation COFRAC; accreditation number E879821-1993)

Helmholtz Zentrum München – Forschungszentrum für Gesundheit und Umwelt GmbH, München (DE)
(measurements under the scope of ISO/IEC 17025 accreditation DACH; accreditation number DAC-PL-0141-01-10)

International Atomic Energy Agency - Marine Environmental Studies Laboratory (MC)

INM - National Institute of Metrology, Bucharest (RO)

Institut "Jozef Stefan", Ljubljana (SI)
(Measurements performed under ISO/IEC 17025 accreditation; Slovenska Akreditacija LP-090)

I.N.R.I.M - Istituto Nazionale di Ricerca Metrologica, Pavia (IT)
(measurements performed under the scope of ISO/IEC 17025 accreditation, BELAC, accreditation number 015-TEST)

INTA - Instituto Nacional de Técnica Aeroespacial "Esteban Terradas" (ES)
(measurements under the scope of ISO/IEC 17025 accreditation ENAC; accreditation number 16/LC10.007)

IPQ - Instituto Português da Qualidade, Caparica (PT)

Marine Institute, Cork (IE)
(measurements performed under the scope of ISO/IEC 17025 accreditation, INAB, accreditation number 130T)

Paragon Scientific Limited, Birkenhead (GB)
(measurements performed under the scope of ISO/IEC 17025 accreditation, UKAS, accreditation number 0640)

Reagecon Diagnostics Ltd, Shannon (IE)
(measurements under the scope of ISO/IEC 17025 accreditation NSAI, accreditation number 19.2769)

VSL - Dutch Metrology Institute, Delft (NL)
(measurements under the scope of ISO/IEC 17025 accreditation RvA, accreditation number K 999)

3 Material processing and process control

3.1 Origin of the starting material

The starting material for the seawater based reference material was collected during a sampling campaign from 18th to 21st October 2010 in the Southern Bight just inside of Belgian territorial waters in collaboration with Management Unit of the North Sea Mathematical Models and the Scheldt estuary (MUMM). The sample was pumped using an immersible pump, Kärcher DFP 14000, equipped with polytetrafluoroethylene (PTFE) tubing into three pre-cleaned vessels of 550 L each. The vessel wall is a sandwich construction and consists of GRP (glass fibre reinforced plastic) as outer providing structure, ruggedness and protection and a perfluoroalkoxy copolymer resin (PFA) as an inner liner. In this way all surfaces inside the drums are made of PFA which is a highly inert material that can resist harsh cleaning protocols with concentrated acids if necessary. Prior to pumping the seawater sample into the tanks, the tubing was rinsed with several litres of seawater. The final volume collected was 1500 L.

Upon arrival at the JRC facilities in Geel, the starting material was filtered using Versaflo capsule filters (0.8/0.45 µm, Pall corporation, Ann Arbor, Michigan USA), acidified to $1 < \text{pH} < 2$ with ultrapure hydrochloric acid (Merck) and stored at 4 °C.

3.2 Initial characterisation and spiking

An initial characterisation of the seawater based material was required to determine the concentration level of trace elements and to assess the need for spiking to reach target concentrations. The sample was analysed by inductively coupled plasma sector field mass spectrometry (ICP-SFMS) for all target elements (As, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Se and Zn). The seawater based material required spiking with Cd, Cr, Ni and Zn. Appropriate volumes of liquid reference materials (1000 mg/L, Merck) were added to the seawater base material. Prior to filling of the bottles the concentrations of Mn and Mo were checked by ICP-SFMS.

3.3 Processing

The CRM containers are 500 mL narrow-mouth HDPE bottles with polypropylene (PP) closure (Nalgene, Rochester, New York, USA). Before filling, they were washed in a clean-cell with high-efficiency particulate arrestance (HEPA) filtered air. Each bottle was filled with approximately 100 mL of 2 g/100 g nitric acid, and shaken for 60 minutes by a 3-dimensional mixer (Dynamix-CM 200, WAB, Basel, Switzerland). This was followed by two rinsing steps with ultrapure water (18.2 MΩ·cm, 0.053 µS·cm⁻¹, maximum of 50 µg L⁻¹ of total organic carbon, Merck Millipore, Billerica USA). The homogenisation of the seawater material was ensured by recirculating the water between three 550 L tanks before and during the filling into bottles using IWAKI FS-30HT2 inert bellow pumps (Tokyo, Japan). In total about 40 full mixing volumes were effected and the spike was added after 20 such cycles and subsequently mixed for another 20 cycles. A peristaltic pump (Watson-Marlow, Falmouth, UK) was used to pump the homogenised water from the three tanks simultaneously using PTFE tubing (Bohlander, Grünsfeld, DE) to a 20 L polycarbonate demijohn. Aliquots of 500 mL were filled into the cleaned HDPE bottles from the demijohn placed in a clean bench (Nuair 156, Plymouth, MN, USA). By manually opening the tap at the bottom of the demijohn water was flowing out by gravity into the sample bottle at sufficient flow rate. At regular intervals the demijohn was topped up by switching on the peristaltic pump. A total of 1513 bottles were filled, which were subsequently labelled, placed into aluminised PET/M sachets and dispatched for sterilisation by gamma irradiation (Isotron NV, Ede, NL) at 15 kGy. 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 Homogeneity

A key requirement for any reference material is the equivalence between the various units. In this respect, it is relevant whether the variation between units is significant compared to the uncertainty of the certified value. In contrast to that, it is not relevant if this variation between units is significant compared to the analytical variation. 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 inhomogeneity 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 inhomogeneity 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.

The number of selected units corresponds to approximately the cubic root of the total number of the produced units. Fourteen units (trace elements) and twelve units (density) were selected using a random stratified sampling scheme covering the whole batch for the between-unit homogeneity test. For this, the batch was divided into fourteen or twelve groups (with a similar number of units in each group) and one unit was selected randomly from each group. Three independent samples were taken from each selected unit, and analysed by the oscillating U-tube method (density) and by ICP-SFMS (trace elements). The set of fourteen units for the trace element measurements were also used for the short-term stability study as described in section 5.2.

The measurements were performed under repeatability conditions for density, and in a randomised manner to be able to separate a potential analytical drift from a trend in the filling sequence. The measurements for the trace elements were performed in a randomised block design due to instrumental constraints, as the number of individual measurements required could not be performed on a single measurement occasion. In this circumstance improved precision (measured as the within-unit standard deviation) was obtained using several short runs in a randomised block design, and applying 2-way ANOVA to account for between-run variance in addition to variances between-unit and within-unit. For three replicates on each of 14 units of ERM-CA403, the simplest randomised block design involves three measurement runs and each unit is measured once in random order. Runs were randomised individually in a manner to be able to separate a potential analytical drift from a trend in the production sequence. For selenium the results of the study on trace elements were unsatisfactory, as the multi-element method used did not have adequate sensitivity. Therefore, a dedicated study was conducted for selenium using the same samples tested for short-term stability. This study also included fourteen units and was performed under repeatability conditions on a single occasion (thus avoiding the need for 2-way ANOVA). The results of all studies are shown as graphs in Annex A.

Density

Regression analyses were performed to evaluate potential trends in the analytical sequence as well as trends in the filling sequence. No trends in the filling sequence or the analytical sequence were visible.

The dataset was tested for consistency using Grubbs outlier tests on a confidence level of 99 % on the individual results and the unit means. No outlying individual results and outlying unit means were detected.

Quantification of between-unit inhomogeneity was accomplished by analysis of variance (ANOVA), which can separate the between-unit variation (s_{bb}) from the 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 uni-modal distribution and results for each unit that follow uni-modal distributions with approximately the same standard deviations. Distribution of the unit means was visually tested using histograms and normal probability plots. Too few data are available for each unit to make a clear statement of the distribution of the individual results. Therefore, it was visually checked whether all individual data follow a uni-modal distribution using histograms and normal probability plots.

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 inhomogeneity that could be hidden by method repeatability, was calculated as described by Linsinger *et al.* [11]. u_{bb}^* is comparable to the limit of detection of an analytical method, yielding the maximum inhomogeneity 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:

$$s_{wb,rel} = \frac{\sqrt{MS_{within}}}{\bar{y}} \quad \text{Equation 1}$$

$$s_{bb,rel} = \frac{\sqrt{\frac{MS_{between} - MS_{within}}{n}}}{\bar{y}} \quad \text{Equation 2}$$

$$u_{bb,rel}^* = \frac{\sqrt{\frac{MS_{within}}{n}} \sqrt[4]{\frac{2}{v_{MS_{within}}}}}{\bar{y}} \quad \text{Equation 3}$$

- MS_{within} mean square within a unit from an ANOVA
- $MS_{between}$ mean squares between-unit from an ANOVA
- \bar{y} mean of all results of the homogeneity study
- n mean number of replicates per unit
- $v_{MS_{within}}$ degrees of freedom of MS_{within}

The results of the evaluation of the between-unit variation are summarised in Table 2. The resulting value from the above equation was converted into a relative uncertainty.

Table 2: Results of the homogeneity study for density.

Measurand	$s_{wb,rel}$ [%]	$s_{bb,rel}$ [%]	$u_{bb,rel}^*$ [%]	$u_{rec,rel}$ [%]	$u_{bb,rel}$ [%]
Density	0.0013	n.c.	0.0004	n.a.	0.0004

¹⁾ n.c.: cannot be calculated as $MS_{between} < MS_{within}$

²⁾ n.a.: not applicable

The homogeneity study showed no outlying unit means or trends in the filling sequence. The u_{bb}^* is adopted as uncertainty contribution to account for potential inhomogeneity.

Selenium

The homogeneity was evaluated by using the data of the short term stability study. The measurements were performed under repeatability conditions, and in a randomised manner to be able to separate a potential analytical drift from a trend in the filling sequence. The results are shown as graphs 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 (95 % confidence level) trends in the analytical sequence were visible for selenium, pointing at a signal drift in the analytical system. Correction of trends is therefore expected to improve the sensitivity of the subsequent statistical analysis through a reduction in analytical variation without masking potential between-unit heterogeneities. As the analytical sequence and the unit numbers were not correlated, trends significant on at least a 95 % confidence level were corrected as shown below:

$$\text{corrected result} = \text{measured result} - b \cdot i \quad \text{Equation 4}$$

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. No outlying individual results and outlying unit means were detected.

Quantification of between-unit inhomogeneity was again accomplished using ANOVA to separate the between-unit variation (s_{bb}) from the within-unit variation (s_{wb}). The statistical distribution was checked for normality as described above for the study on density.

Method repeatability ($s_{wb,rel}$), between-unit standard deviation ($s_{bb,rel}$) and $u_{bb,rel}^*$ were calculated as using the equations 1, 2 and 3.

The results of the evaluation of the between-unit variation are summarised in Table 3. The resulting value from the equation 3 was converted into a relative uncertainty.

Table 3: Results of the homogeneity study for selenium.

Measurand	$s_{wb,rel}$ [%]	$s_{bb,rel}$ [%]	$u_{bb,rel}^*$ [%]	$u_{rec,rel}$ [%]	$u_{bb,rel}$ [%]
Selenium	14.5	n.c.	4.3	n.a.	4.3

¹⁾ n.c.: cannot be calculated as $MS_{between} < MS_{within}$

²⁾ n.a.: not applicable

The homogeneity study showed no outlying unit means or trends in the filling sequence. The u_{bb}^* is adopted as uncertainty contribution to account for potential inhomogeneity.

Other trace elements

For all trace elements other than selenium, a two-way analysis of variance without replication was used because not all samples could be measured on the same occasion. Two-way analysis allowed us to estimate the within- and between-unit standard deviations independently of the between-run effect.

The data evaluation was performed in the following order:

1) Regression analyses to evaluate potential trends in each analytical run. Some significant (95 % confidence level) trends in the analytical sequence were visible for copper in run 1, for manganese in run 2 and for chromium and manganese in run 3, pointing at a signal drift in the analytical system.

2) Correction of dataset for significant analytical trend (95% confidence level). The correction of biases, even if they are statistically not significant, was found to combine the smallest uncertainty with the highest probability to cover the true value [12]. Correction of trends is therefore expected to improve the sensitivity of the subsequent statistical analysis through a reduction in analytical variation without masking potential between-unit heterogeneities. As the analytical sequence and the unit numbers were not correlated, trends significant on at least a 95 % confidence level were corrected as shown below:

$$x_T(r, i) = x(r, i) - b(r) \cdot i \quad \text{Equation 5}$$

- i position of the result in the analytical run
- r number of the analytical run from 1 to 3
- $b(r)$ slope of the linear regression for the analytical run r
- $x(r, i)$ measurement results on the position i in the analytical run r
- $x_T(r, i)$ corrected results for analytical trend on the position i in the analytical run r

3) The analytical trend-corrected dataset was evaluated for statistically significant difference between analytical runs (95 % confidence level) using one way ANOVA. A statistically significant difference between analytical runs was observed for all analytes on 95 % confidence level.

4) Normalisation of data showing statistically significant difference between analytical run (95 % confidence level). As it is assumed that run-effects and unit-effects are independent, differences between analytical runs on at least a 95 % confidence level were corrected as shown below:

$$x_R(r, i) = \frac{x_T(r, i)}{\bar{x}_T(r)} \quad \text{Equation 6}$$

- i position of the result in the analytical run
- r number of the analytical run from 1 to 3
- $\bar{x}_T(r)$ mean results of the analytical run r after correction for trend in analytical sequence (if necessary)
- $x_T(r, i)$ corrected results for analytical trend on the position i in the analytical run r
- $x_R(r, i)$ normalised results on the position i in the analytical run r

5) The normalised dataset was tested for consistency using Grubbs outlier tests on a confidence level of 99 % on the individual results and the unit means. The trend-corrected dataset was used to evaluate significant trends in the production sequence. Outliers were found for Cu and Fe, for the remaining elements no outlying individual results and outlying unit means were detected at the 99 % confidence level (See Table 4). Since no technical reason for the outliers could be found, all the data were retained for statistical analysis.

Table 4: Results of the statistical evaluation of the homogeneity studies at 95 % confidence level

Measurand	Trends		Outliers		Distribution	
	Analytical sequence	Filling sequence	Individual results	Unit means	Individual results	Unit means
Arsenic	no	no	none	none	normal/uni-modal	normal/uni-modal
Cadmium	no	no	none	none	normal/uni-modal	normal/uni-modal
Chromium	no	no	none	none	normal/uni-modal	normal/uni-modal
Cobalt	no	yes	none	none	normal/uni-modal	normal/uni-modal
Copper	yes	yes	1	1	normal/uni-modal	normal/uni-modal
Iron	yes	no	none	2	normal/uni-modal	normal/uni-modal
Lead	yes	yes	none	none	normal/uni-modal	normal/uni-modal
Manganese	yes	no	none	none	normal/uni-modal	normal/uni-modal
Molybdenum	yes	no	none	none	normal/uni-modal	normal/uni-modal
Nickel	no	no	none	none	normal/uni-modal	normal/uni-modal
Zinc	no	no	none	none	normal/uni-modal	normal/uni-modal

6) Quantification of between-unit inhomogeneity was accomplished using the analytical trend corrected dataset by two way ANOVA, which can separate the between-run variation (s_r), the between-unit variation (s_{bb}) and the within-unit variation (s_{wb}). The latter is equivalent to the method repeatability if the individual samples are representative of the whole unit.

Evaluation by ANOVA requires unit means which follow at least a uni-modal distribution and results for each unit that follow uni-modal distributions with approximately the same standard deviations. Distribution of the unit means was visually tested using histograms and normal probability plots. Minor deviations from uni-modality of the individual values were found but do not significantly affect the estimate of between-unit standard deviations (See Table 4).

Recall 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 inhomogeneity that could be hidden by method repeatability, was calculated as described by Linsinger *et al.* [11]. u_{bb}^* is comparable to the limit of detection of an analytical method, yielding the maximum inhomogeneity that might be undetected by the given study setup.

Analysis of variance applied to a randomised block design with one observation per unit per run leads to a between-run mean square MS_r together with a between-unit mean square $MS_{between}$, and a residual mean square MS_{within} . The analysis of variance table also includes associated degrees of freedom for each term. The residual mean square MS_{within} is an unbiased estimate of the repeatability variance s_r^2 . The results of two way ANOVA are given in Table 5.

Table 5: Two way ANOVA results. The two way ANOVA was performed on the results corrected only for analytical trends.

Measurand		Degrees of freedom	Mean square [(µg/L)]
Arsenic	Between run variation	2	$MS_r = 1.9 \cdot 10^{-2}$
	Between unit variation	13	$MS_{\text{Between}} = 4.2 \cdot 10^{-3}$
	Within unit variation	26	$MS_{\text{within}} = 4.5 \cdot 10^{-3}$
Cadmium	Between run variation	2	$MS_r = 3.0 \cdot 10^{-5}$
	Between unit variation	13	$MS_{\text{Between}} = 1.7 \cdot 10^{-5}$
	Within unit variation	26	$MS_{\text{within}} = 1.8 \cdot 10^{-5}$
Chromium	Between run variation	2	$MS_r = 3.0 \cdot 10^{-4}$
	Between unit variation	13	$MS_{\text{Between}} = 1.0 \cdot 10^{-6}$
	Within unit variation	26	$MS_{\text{within}} = 9.9 \cdot 10^{-5}$
Cobalt	Between run variation	2	$MS_r = 7.14 \cdot 10^{-6}$
	Between unit variation	13	$MS_{\text{Between}} = 2.4 \cdot 10^{-5}$
	Within unit variation	26	$MS_{\text{within}} = 3.0 \cdot 10^{-5}$
Copper	Between run variation	2	$MS_r = 3.16 \cdot 10^{-2}$
	Between unit variation	13	$MS_{\text{Between}} = 2.6 \cdot 10^{-3}$
	Within unit variation	26	$MS_{\text{within}} = 1.11 \cdot 10^{-3}$
Iron	Between run variation	2	$MS_r = 1.02 \cdot 10^{-1}$
	Between unit variation	13	$MS_{\text{Between}} = 1.4 \cdot 10^{-2}$
	Within unit variation	26	$MS_{\text{within}} = 6.5 \cdot 10^{-3}$
Lead	Between run variation	2	$MS_r = 1.9 \cdot 10^{-6}$
	Between unit variation	13	$MS_{\text{Between}} = 3.3 \cdot 10^{-5}$
	Within unit variation	26	$MS_{\text{within}} = 1.6 \cdot 10^{-5}$
Manganese	Between run variation	2	$MS_r = 7.4 \cdot 10^{-2}$
	Between unit variation	13	$MS_{\text{Between}} = 3.9 \cdot 10^{-3}$
	Within unit variation	26	$MS_{\text{within}} = 4.9 \cdot 10^{-3}$
Molybdenum	Between run variation	2	$MS_r = 1.8 \cdot 10^{-1}$
	Between unit variation	13	$MS_{\text{Between}} = 7.2 \cdot 10^{-3}$
	Within unit variation	26	$MS_{\text{within}} = 1.3 \cdot 10^{-2}$
Nickel	Between run variation	2	$MS_r = 8.6 \cdot 10^{-4}$
	Between unit variation	13	$MS_{\text{Between}} = 6.9 \cdot 10^{-4}$
	Within unit variation	26	$MS_{\text{within}} = 1.5 \cdot 10^{-5}$
Zinc	Between run variation	2	$MS_r = 7.6 \cdot 10^{-3}$
	Between unit variation	13	$MS_{\text{Between}} = 2.1 \cdot 10^{-2}$
	Within unit variation	26	$MS_{\text{within}} = 4.5 \cdot 10^{-2}$

With the exception of copper and lead, method repeatability ($s_{wb,rel}$), between–unit standard deviation ($s_{bb,rel}$) and $u_{bb,rel}^*$ were calculated as equations 1, 2 and 3 indicate.

However, a different approach was adopted for copper and iron for which outlying unit means were detected. In this case between-unit inhomogeneity was modelled as a rectangular distribution limited by the largest outlying unit mean, and the rectangular standard uncertainty of homogeneity was estimated by:

$$u_{rec} = \frac{|outlier - \bar{y}|}{\sqrt{3 \cdot \bar{y}}} \quad \text{Equation 7}$$

\bar{y} mean of all results of the homogeneity study

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

When a trend in the filling sequence was significant at least at 99 % confidence level, the uncertainty was assessed in a different way. This applies for lead. Here, u_{rec} was estimated using a rectangular distribution between the highest and lowest unit mean. The corrected uncertainty in those cases where there was a significant trend in the filling sequence is obtained by using equation 8:

$$u_{rec} = \frac{|highest\ result - lowest\ result|}{2 \cdot \sqrt{3} \cdot \bar{y}} \quad \text{Equation 8}$$

The results of the evaluation of the between-unit variation are summarised in Table 6. The resulting values from the above equations were converted into relative uncertainties.

Table 6: Results of the homogeneity study

Measurand	$s_{wb,rel}$ [%]	$s_{bb,rel}$ [%]	$u_{bb,rel}^*$ [%]	$u_{rec,rel}$ [%]	$u_{bb,rel}$ [%]
Arsenic	3.50	n.c.	1.06	n.a.	1.06
Cadmium	3.70	n.c.	1.12	n.a.	1.12
Chromium	3.93	0.21	1.20	n.a.	1.20
Cobalt	6.21	n.c.	1.89	n.a.	1.89
Copper	3.49	2.35	1.06	5.72	5.72
Iron	2.87	1.74	0.87	3.14	3.14
Lead	4.39	2.60	1.34	2.96	2.96
Manganese	2.69	n.c.	0.82	n.a.	0.82
Molybdenum	0.93	n.c.	0.28	n.a.	0.28
Nickel	3.09	n.c.	0.94	n.a.	0.94
Zinc	4.89	n.c.	1.49	n.a.	1.49

¹⁾ n.c.: cannot be calculated as $MS_{between} < MS_{within}$

²⁾ n.a.: not applicable

With the exception of copper, iron and lead, the homogeneity study showed no outlying unit means or trends in the filling sequence. 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. Outlying unit means were found for copper and iron, and a trend with filling was found for lead. However, the inhomogeneities quantified as u_{rec} were still sufficiently small to make the material suitable for its intended use. Therefore, u_{rec} was used as estimate of u_{bb} for these elements.

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.

ERM-CA403 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

2 mL were found to give acceptable repeatability for both density and element concentration measurement. This demonstrates that there is no intrinsic inhomogeneity or contamination when using sample intakes at this level.

5 Stability

Time, temperature and light were regarded as the most relevant influences on stability of the material. The influence of ultraviolet or visible radiation was minimised by the choice of the container and packaging which eliminates most of the incoming light. In addition, materials are stored and dispatched in the dark, thus eliminating practically the possibility of degradation by light. 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 under these conditions must be demonstrated if transport at ambient temperature will be applied.

The stability studies were carried out using an isochronous design [13]. 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). 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, units 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 units per storage time were selected using a random stratified sampling scheme. From each unit, three samples were measured by a high performance calibrated density meter (density), ICP-MS (selenium) and by ICP-SFMS (all other trace elements). The measurements were performed under repeatability conditions for density and selenium, whereas for the remaining trace elements were performed in a randomised block design because the number of replicates/analytes on all units cannot be included in a single run due to instrumental constraints (drift towards the end of a long run). In all the cases, the measurements were performed in a randomised sequence to be able to separate a potential analytical drift from a trend over storage time.

Density

Samples were measured using high performance calibrated density meter. The measurements were made in accordance with ASTM D4052-09 [14] which is the standard method for Density, Relative Density and API Gravity of Liquids by Digital Density Meter. The results of the measurements are shown in Annex B.

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 at 60 °C. As no technical reason for the outlier could be found the data point was retained for statistical analysis.

Furthermore, the data were evaluated against storage time and regression lines of density versus time were calculated. The slope of the regression line was tested for statistical significance (loss/increase due to shipping conditions). The slope of the regression line was not significantly different from zero (on 99 % confidence level) at both 18 °C and 60 °C.

None of the trends was statistically significant on a 99 % confidence level for any of the temperatures.

Selenium

The measurements were performed under repeatability conditions, and in a randomised manner. Regression analyses were performed to evaluate potential trends in the analytical sequence. Some significant (95 % confidence level) trends in the analytical sequence were found for selenium, pointing at a signal drift in the analytical system. Correction of trends is therefore expected to improve the sensitivity of the subsequent statistical analysis through a reduction in analytical variation without masking potential effect of the time and temperature. As the analytical sequence and the unit numbers were not correlated, trends significant on at least a 95 % confidence level were corrected as shown below:

$$\text{corrected result} = \text{measured result} - b \cdot i \quad \text{Equation 9}$$

b = slope of the linear regression

i = position of the result in the analytical sequence

The obtained trend-corrected data were evaluated individually for each temperature. The results were screened for outliers using the single and double Grubbs test. One outlier was found at 18 °C. As no technical reason for the outlier could be found the data point was retained for statistical analysis.

Furthermore, the data were evaluated against storage time and regression lines of concentration versus time were calculated. The slopes of the regression lines were tested for statistical significance (loss/increase due to shipping conditions). For selenium, the slopes of the regression lines were not significantly different from zero (on 99 % confidence level) at both 18 °C and 60 °C.

The results of the measurements are shown in Annex B. A statistical outlier was detected for selenium, and this was retained for the estimation of u_{sts} . None of the trends was statistically significant on a 99 % confidence level for any of the temperatures.

Other trace elements

The measurements for the remaining trace elements were performed in a randomised block design because the number of replicates/analytes on all units cannot be included in a single run due to instrumental constraints (drift towards the end of a long run). In that circumstance better precision (measured as the within-unit standard deviation) can be obtained using several short runs in a randomised block design than the one obtained in a single run. In a randomised block design for three replicates on each of 14 units of ERM-CA403, the simplest randomised block design involves three measurement runs and each unit is measured once in random order. Runs were randomised individually. The results are shown as graphs in Annex B.

The obtained data were evaluated individually for each temperature. The data evaluation was performed in the following order:

- 1) Regression analyses to evaluate potential trends in each analytical run. Some significant (95 % confidence level) trends in the analytical sequence were visible for copper in run 1, for manganese in run 2 and for chromium and manganese in run 3, pointing at a signal drift in the measurement system.

- 2) Correction of dataset for significant analytical trend (95% confidence level). The correction of biases, even if they are statistically not significant, was found to combine the smallest uncertainty with the highest probability to cover the true value [12]. Correction of trends is therefore expected to improve the sensitivity of the subsequent statistical analysis through a

reduction in analytical variation without masking potential change over time. As the analytical sequence and the unit numbers were not correlated, trends significant on at least a 95 % confidence level were corrected as for the homogeneity study, using equation 5 (Section 4.1).

3) The analytical trend-corrected dataset was evaluated for significant difference between analytical runs (99 % confidence level) using one way ANOVA. A significant difference between analytical runs was observed on 99 % confidence level.

4) Normalisation of data showing significant difference between analytical run (95 % confidence level). As it is assumed that run effects and unit effects are independent, difference between analytical runs on at least a 99 % confidence level was corrected as for the homogeneity study, using equation 6 (Section 4.1).

5) The normalised dataset was tested for consistency using Grubbs outlier tests on a confidence level of 99 % on the individual results and the unit means. Outliers were found for some at the 99 % confidence level (See Table). Since no technical reason for the outliers could be found, all the data were retained for statistical analysis.

6) The normalised obtained data were evaluated individually for each temperature. Furthermore, the data were evaluated against storage time and regression lines of concentration versus time were calculated. 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 zero (on 95 % confidence level) at both 18 °C and 60 °C.

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 7.

Table 7: Results of the short-term stability tests

Measurand	Number of individual outlying results		Significance of the trend on a 95 % confidence level	
	18 °C	60 °C	18 °C	60 °C
Arsenic	1	0	no	no
Cadmium	2	1	no	no
Chromium	0	0	no	no
Cobalt	0	0	no	no
Copper	1	1	no	no
Iron	0	2	yes	no
Lead	0	0	no	no
Manganese	0	0	no	no
Molybdenum	2	0	no	no
Nickel	0	0	no	no
Zinc	0	0	no	no

Statistical outliers were detected for some of the analytes, and these were retained for the estimation of u_{sts} . None of the trends were statistically significant on a 99 % confidence level for any of the temperatures. However, the study on Fe at 18 °C showed a decrease with time significant at the 95 % confidence level. As this trend was not seen at the higher test temperature, and measurement variance was similar for both studies, the trend is considered to be a statistical artefact and not due to real degradation of Fe content.

Summary of short term stability:

Taken into account the results for all the analytes and the density, the material can be transported at ambient conditions without special conditions.

5.2 Long-term stability study

For the long-term stability study, samples were stored at 18 °C for 0, 4, 8, 12, 16 and 24 months. The reference temperature was set to 4 °C. Two samples per storage time were selected using a random stratified sampling scheme. From each sample, six replicates were measured by a high performance calibrated density meter (density) and by ICP-SFMS (all trace elements). The measurements were performed under repeatability conditions, in a random sequence to be able to separate any potential analytical drift from a trend over storage time.

Regression analyses were performed to evaluate potential trends in the analytical sequence. There were no statistically significant trends in the filling sequence or the analytical sequence.

The obtained data were evaluated. The results were screened for outliers using the single and double Grubbs test. Some outlying individual results were found for density (Table). 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 concentration versus time were calculated. The slope of the regression lines was tested for statistical significance (loss/increase due to storage conditions). For all elements, the slopes of the regression lines were not significantly different from zero (on 99 % confidence level) at 18 °C.

The results of the long term stability measurements are shown in Annex C. The results of the statistical evaluation of the long-term stability study are summarised in Table 8.

Table 8: Results of the long-term stability tests

Measurand	Number of individual outlying results	Significance of the trend on a 95 % confidence level
	18 °C	18 °C
Density	1	no
Arsenic	0	no
Cadmium	0	yes
Chromium	0	no
Cobalt	0	no
Copper	0	no
Iron	0	no
Lead	0	no
Manganese	1	no
Molybdenum	1	no
Nickel	0	no
Selenium	0	no
Zinc	0	no

The study on Cd showed an increase with time significant at the 95 % confidence level. Such an effect could only be possible if the matrix degraded or evaporated. However, as this trend was not seen for any other element, it is considered to be a statistical artefact and not due to real degradation of the sample. The material can therefore be stored at 18 °C.

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 $0 \pm x$ % per time".

Uncertainties of stability during dispatch and storage were estimated as described in [15] for the concentration of each element and for density. For this approach, the uncertainty of the linear regression line with a slope of zero is calculated. The uncertainty contributions u_{sts} and u_{lts} are calculated as the product of the chosen transport time/shelf life and the uncertainty of the regression lines as:

$$u_{sts,rel} = \frac{RSD}{\sqrt{\sum (x_i - \bar{x})^2}} \cdot t_{tt} \quad \text{Equation 12}$$

$$u_{lts,rel} = \frac{RSD}{\sqrt{\sum (x_i - \bar{x})^2}} \cdot t_{sl} \quad \text{Equation 13}$$

<i>RSD</i>	relative standard deviation of all results of the stability study
x_i	result at time point <i>i</i>
\bar{x}	mean results for all time points
t_{tt}	chosen transport time (1 week at 60 °C)
t_{sl}	chosen shelf life (36 months at 18 °C)

The following uncertainties were estimated:

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

The results of these evaluations are summarised in Table 9.

Table 9: Uncertainties of stability during dispatch and storage. $u_{sts,rel}$ was calculated for a temperature of 60 °C and 1 week; $u_{lts,rel}$ was calculated for a storage temperature of 18 °C and 3 years

Measurand	$u_{sts,rel}$ [%]		$u_{lts,rel}$ [%]
	At 18 °C	At 60 °C	At 18 °C
Density	0.00023	0.0030	0.0022
Arsenic	0.41	0.57	2.02
Cadmium	0.51	0.42	2.07
Chromium	0.44	0.57	1.88
Cobalt	0.85	0.77	4.80
Copper	0.65	0.69	1.76
Iron	0.48	0.45	6.91
Lead	0.63	0.74	2.19
Manganese	0.32	0.40	1.51
Molybdenum	0.085	0.14	1.54
Nickel	0.35	0.43	6.29
Selenium	1.81	1.85	8.46
Zinc	0.60	0.62	4.74

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

6 Characterisation

The material characterisation is the process of determining the property values of a reference material.

The material characterisation was based on an intercomparison of expert laboratories, i.e. 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

Laboratories were selected based on criteria that comprised both technical competence and quality management aspects. For density measurements 10 laboratories were selected and for trace element measurement, 9 laboratories. Each participant was required to operate a quality system and to deliver documented evidence of its laboratory proficiency in the field of density determination 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-CA403 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 necessary) and measurements had to be spread over at least two days to ensure intermediate precision conditions. An independent calibration was performed for each independent measurement.

For the trace elements, each participant received a sample of NASS-6 (NRC, National Research Council Canada, Canada) as a blinded quality control (QC) sample. The results for this sample were used to support the evaluation of the characterisation results.

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

Density

Two different methods without sample preparation were used to characterise the material. The combination of results from methods based on completely different principles mitigates undetected method bias.

All methods used during the characterisation study are summarised in Annex D. The laboratory code (e.g. L01) 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. L01) and abbreviation of the measurement method used (e.g. L01-OD for oscillating type density meter or L09-Pyc for the determination with pycnometer).

Trace elements

All laboratories used measurement methods based on ICP-MS, except for Se for which one laboratory used AFS.

As seen in Annex D, laboratories used different approaches to sample preparation, including dilution or pre-concentration. Each participating laboratory reported that their method was validated. Results from any validated method based on ICP-MS should be equivalent to the results used in characterisation of the material.

All methods used during the characterisation study are summarised in Annex D. The laboratory code (e.g. L01) is a random number and does not correspond to the order of laboratories in Section 2.

6.4 Evaluation of results

The characterisation campaign resulted in 10 datasets for density and 3 to 8 datasets for element concentrations. All individual results of the participants, grouped per analyte are displayed in tabular and graphical form in Annex E.

6.4.1 Technical evaluation

Density

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:

- appropriate validation of the measurement procedure
- compliance with the analysis protocol: measurements performed on two days, and the analytical sequence determination.

- measurement repeatability < 10%.

One dataset was rejected as not technically valid. Results provided by the laboratory L07 showed variance over 10 times higher than the mean variance of the other laboratories. This indicated that the results were not of the same quality as those from the other labs, and the dataset was not used in the evaluation.

Trace elements

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:

- appropriate validation of the measurement procedure
- compliance with the analysis protocol: sample preparations and measurements performed on two days, and the analytical sequence and water content determination
- no individual values given as below limit of detection or below limit of quantification
- agreement of the measurement results with the assigned value of the QC sample
- measurement repeatability < 50%
- results for Cd, Cr, Ni and Zn equal to or higher than the levels at which they were known to be present following spiking of the seawater for CA403

The QC sample was a CRM, NASS-6, which was re-bottled and supplied to participants as a blind sample. The assigned values were those certified, and the associated uncertainties were set taking into account the lower analyte concentrations of certain elements in this material. For As, Cr and Mo, which were present in similar concentration, the certificate uncertainty values were assigned. For Cd, Cu, Mn and Ni with concentrations of less than a third of those in CA403 and for Co, for which the value was not certified, 50 % uncertainty was assigned. For Fe, Pb and Zn with concentrations less than a sixth of those in CA403 and for Se, for which no value was available, no QC test was made.

Based on the above criteria, the following results were rejected as not technically valid:

L03: The laboratory's complete data set was not considered when calculating the certified values for the material, as the reported results for Cd, Ni and Zn were below the concentration added by spiking and QC test results for 3 of 8 elements did not agree. This strongly indicates poor performance in comparison to the other participating laboratories.

L05: The results for Co were rejected because measurement of the QC sample did not agree with the assigned value. In addition, results for Fe, Se, Cr and Zn were not used as they were reported as below their LOQ.

L06: The results for As, Cd, Cr and Cu were rejected as some individual values were below the method's respective LOQ.

L12: The results for Mn were rejected because measurement of the QC sample did not agree with the assigned value.

6.4.2 Statistical evaluation

Density

The datasets accepted based on technical reasons 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 10.

Table 10: Statistical evaluation of the technically accepted datasets for ERM-CA403. p : number of technically valid datasets

Analyte	p	Outliers		Normally distributed	Statistical parameters			
		Means	Variances		Mean [g/mL]	s [g/mL]	S_{between} [g/mL]	S_{within} [g/mL]
Density	9	no	yes	yes	1.02352	0.00003	0.00002	0.00002

The laboratory means follow normal distributions. None of the data contains outlying means, but some outlying variances were found. The outlying variances are not method dependent and therefore merely reflect the fact that both 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 density reported by the laboratories are slightly higher than 0.1 %. The datasets are therefore consistent and the mean of laboratory means is a good estimate of the true value. The uncertainty related to the characterisation is estimated as the standard error of the mean of laboratory means (Table).

Trace elements

The datasets accepted based on technical reasons 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 11.

Table 11: Statistical evaluation of the technically accepted datasets for ERM-CA403. p : number of technically valid datasets

Analyte	p	Outliers		Normally distributed	Statistical parameters			
		Means	Variances		Mean [$\mu\text{g/L}$]	s [$\mu\text{g/L}$]	S_{between} [$\mu\text{g/L}$]	S_{within} [$\mu\text{g/L}$]
As	5	0	1	yes	1.90	0.10	0.09	0.09
Cd	6	0	0	yes	0.0939	0.0123	0.0122	0.0049
Co	5	0	0	yes	0.0735	0.0081	0.0079	0.0040
Cr	3	0	0	$p < 4^*$	0.258	0.016	0.015	0.014
Cu	6	0	0	yes	0.875	0.093	0.092	0.028
Fe	3	0	1	$p < 4^*$	3.48	0.49	0.48	0.24
Mn	6	0	0	yes	2.47	0.08	0.07	0.09
Mo	5	0	1	yes	12.0	0.5	0.5	0.5
Ni	7	0	0	yes	1.04	0.11	0.11	0.07
Pb	7	1	1	yes	0.0984	0.0083	0.0078	0.0069
Se	2	n.a.	n.a.	$p < 4^*$	0.0771	0.0105	0.0102	0.0059
Zn	4	0	0	yes	4.59	0.25	0.25	0.14

* For $p < 4$ it is not possible to test Kurtosis

The statistical evaluation flags L05 as a high outlier for Pb. However, the difference between the mean values of laboratory L03 and the other results is less than the combined measurement uncertainty of laboratory L03 and the uncertainty of the dataset. As the mean of L03 agreed with the dataset, the value was retained. The outlying variances merely reflect

the fact that the method used has different intrinsic variability. As all measurement procedures were found technically valid, all results were retained.

For Cr, Fe and Se, the statistical tests cannot be considered reliable, as only 3 laboratories mean values were accepted for Cr and Fe, and only 2 for Se.

For the remaining elements, the laboratory means follow normal distributions. None of the data contains outlying means and variances. The datasets are therefore consistent and the mean of laboratory means is a good estimate of the true value. With the exception of Mn, standard deviations between laboratories are considerably larger than the standard deviation within laboratories, showing that confidence intervals of replicate measurements are unsuitable as estimate of measurement uncertainty.

In addition to the statistical tests, the agreement of individual laboratories' results with the dataset means was tested according to ERM Application Note 1.[16] As approaches to uncertainty estimation differ between laboratories, it is possible that not all sources of uncertainty are included in the budgets. In addition, labs L04, L05, L06 and L10 did not provide measurement uncertainties. Therefore, U_m of 20 % were assigned for all results for this test, as this was considered to represent an acceptable level of U_m for inclusion in the datasets. On this basis, all results agreed with the respective dataset means.

The uncertainty related to the characterisation is estimated as the standard error of the mean of laboratory means (Table 12).

Table 12: Uncertainty of characterisation for ERM-CA403

Analyte	p	Mean [g/mL]	s [g/mL]	u_{char} [g/mL]
Density	9	1.02352	$25 \cdot 10^{-6}$	$8.5 \cdot 10^{-6}$

Analyte	p	Mean [μ g/L]	s [μ g/L]	u_{char} [μ g/L]
As	5	1.90	0.10	0.04
Cd	6	0.0939	0.0123	0.0050
Co	5	0.0735	0.0072	0.0029
Cu	6	0.875	0.093	0.038
Mn	6	2.47	0.08	0.03
Mo	5	12.0	0.5	0.2
Ni	7	1.04	0.11	0.04
Pb	7	0.0984	0.0083	0.0031
Zn	4	4.59	0.25	0.13

7 Value Assignment

Certified, indicative and informative values were assigned.

Certified values are values that fulfil the highest standards of accuracy. Procedures at JRC Directorate F 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' [4] were established.

Indicative values are values where either the uncertainty is deemed too large or where too few independent datasets were available to allow certification. Uncertainties are evaluated according to the same rules as for certified values.

Additional material information refers to values that were obtained in the course of the study. For example, results reported from only one or two laboratories or in cases where individual measurement uncertainty is high, would fall under this category.

7.1 Certified values and their uncertainties

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

The assigned uncertainty consists of uncertainties related to characterisation, u_{char} (Section 6), potential between-unit inhomogeneity, u_{bb} (Section 4.1) and potential degradation during transport (u_{sts}) and long-term storage, u_{Its} (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:

$$U_{\text{CRM,rel}} = k \cdot \sqrt{u_{\text{char,rel}}^2 + u_{\text{bb,rel}}^2 + u_{\text{sts,rel}}^2 + u_{\text{Its,rel}}^2} \quad \text{Equation 14}$$

- u_{char} was estimated as described in Section 6
- u_{bb} was estimated as described in Section 4.1
- u_{sts} was estimated as described in section 5.3
- u_{Its} was estimated as described in Section 5.3.

For the concentrations of elements in CA403, the uncertainty contributions from potential degradation during transport (u_{sts}) were found to be insignificant, and were not retained in the combined uncertainty calculation.

Applying the Welch-Satterthwaite equation [4] to calculate the effective number of degrees of freedom yields between 11 and 38 for the elements As, Co, Mo and Zn, for which less than 6 characterisation datasets were obtained. Because of the sufficient numbers of the degrees of freedom of the different uncertainty contributions, a coverage factor k of 2 was applied for all elements, to obtain the expanded uncertainties.

The certified values and their uncertainties are summarised in Table 13.

Table 13: Certified values and their uncertainties for ERM-CA403

Analyte	Certified value [g/mL]	$u_{\text{char, rel}}$ [%]	$u_{\text{bb, rel}}$ [%]	$u_{\text{lbs, rel}}$ [%]	$u_{\text{sts, rel}}$ [%]	$U_{\text{CRM, rel}}$ [%]	U_{CRM} [g/mL] ¹⁾
Density (at 20 °C)	1.02352	0.0008	0.0004	0.0002	0.002	0.005	0.00005

Analyte	Certified value [µg/L]	$u_{\text{char, rel}}$ [%]	$u_{\text{bb, rel}}$ [%]	$u_{\text{lbs, rel}}$ [%]	$U_{\text{CRM, rel}}$ [%]	U_{CRM} [µg/L] ¹⁾
As	1.90	2.3	1.1	2.0	6	0.13
Cd	0.094	5.4	1.1	2.1	12	0.011
Co	0.074	4.9	1.9	4.8	14	0.011
Cu	0.87	4.3	5.7	1.8	15	0.13
Mn	2.47	1.3	0.8	1.5	4	0.11
Mo	12.0	1.9	0.3	1.5	5	0.6
Ni	1.04	4.1	0.9	6.3	15	0.16
Pb	0.098	3.2	3.0	2.2	10	0.010

¹⁾ Expanded with a factor $k=2$, and rounded uncertainty.

7.2 Indicative values and their uncertainties

An indicative value was assigned for the Zn concentration, as there were less than 5 accepted results. However, as the laboratories also provided results for the certified elements that agreed with the dataset means, the results were regarded as sufficiently trustworthy to assign an indicative value. Indicative values may not be used as certified values. The uncertainty budgets were set up as for the certified values and are listed together with the assigned values in Table 14.

Table 14: Indicative values and their uncertainties for ERM-CA403

Analyte	Indicative value [µg/L]	$u_{\text{char, rel}}$ [%]	$u_{\text{bb, rel}}$ [%]	$u_{\text{lbs, rel}}$ [%]	$U_{\text{CRM, rel}}$ [%]	U_{CRM} [µg/L] ¹⁾
Zn	4.6	2.8%	1.5%	4.7%	11%	0.6

¹⁾ Expanded with a factor $k=2$, and rounded uncertainty.

7.3 Additional material information

Three laboratories in the characterisation exercise provided accepted results for the Fe and Cr concentrations, and a single laboratory provided two results for the Se concentration, with one by an independent technique (Atomic Fluorescence Spectrometry in addition to ICP-MS). These were used to calculate approximate concentration ranges, and are listed in Table 15. These values must be regarded as informative only and can not be, in any case, used as certified or indicative values.

Table 15: Additional information values for ERM-CA403

Analyte	Additional information range [$\mu\text{g/L}$]
Cr	0.21 – 0.31
Fe	2.7 – 4.2
Se	0.060 – 0.094

8 Metrological traceability and commutability

8.1 Metrological traceability

Identity

Density is a clearly defined property 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.

The concentrations of the elements are method-defined measurands and can only be obtained by ICP-MS measurement. Adherence to this procedure was confirmed by agreement of the laboratories' results with the assigned values for the CRM that was used as quality control sample. The measurand is therefore operationally defined by method.

Quantity value

Traceability of the obtained results is based on the traceability of all relevant input factors. Instruments in individual laboratories were verified and calibrated with tools ensuring traceability to the International System of units (SI). Consistency in the interlaboratory comparison demonstrates that all relevant input factors were covered. As 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 Safety information

The usual laboratory safety measures apply.

9.2 Storage conditions

The material shall be stored at $18\text{ °C} \pm 5\text{ °C}$ 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 bottles.

9.3 Preparation and use of the material

The bottles shall be shaken by turning upside down for at least 2 min before opening to ensure material re-homogenisation.

9.4 Minimum sample intake

The minimum amount of sample to be used is 2 mL.

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.

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.

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 [16]).

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

Use in quality control charts

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

10 Acknowledgments

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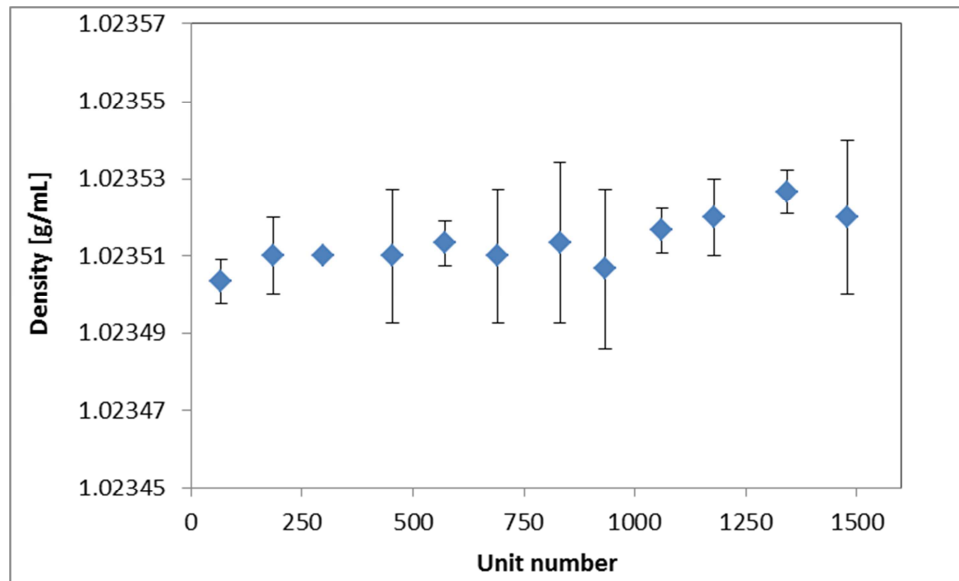
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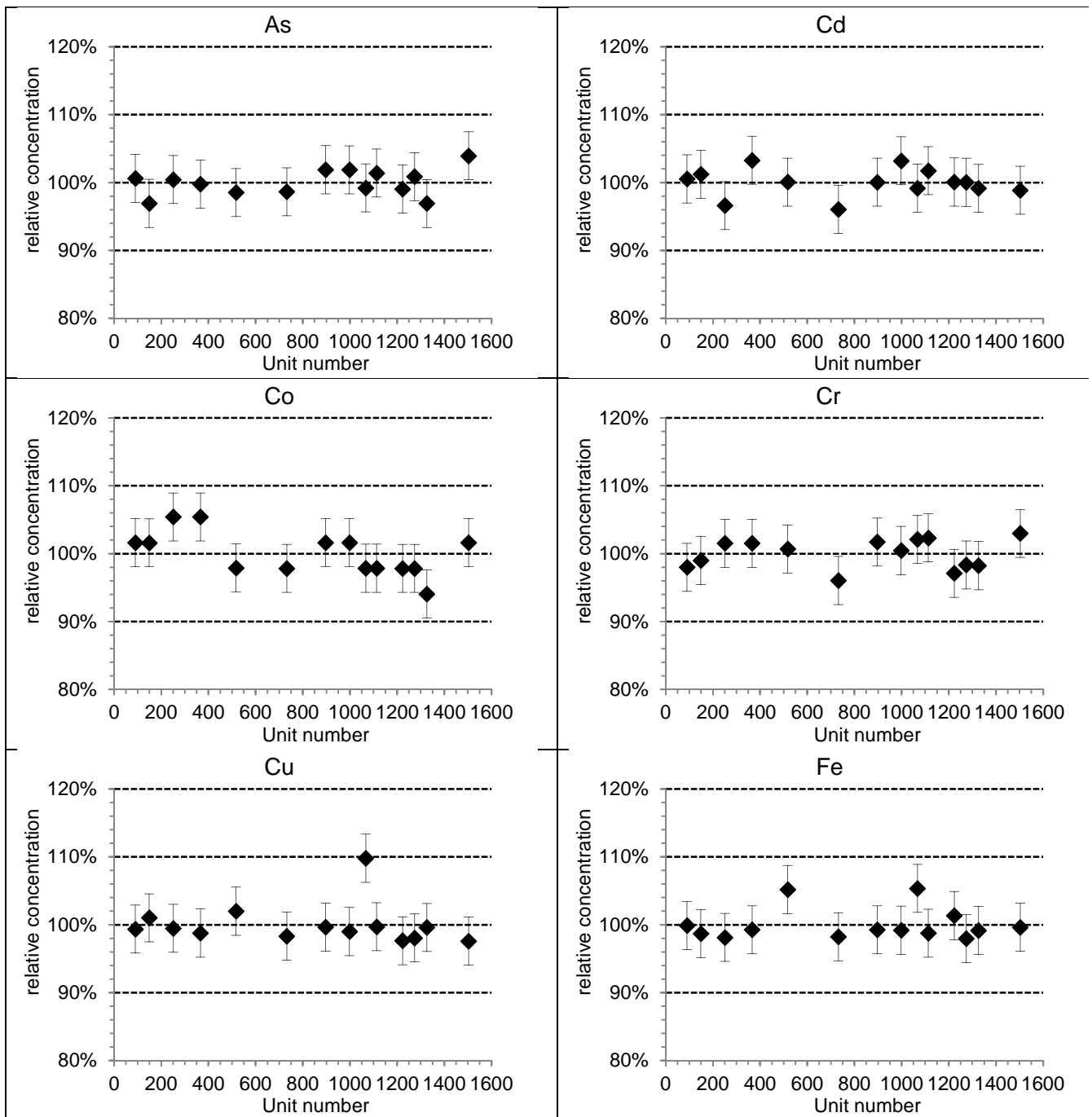
Annexes

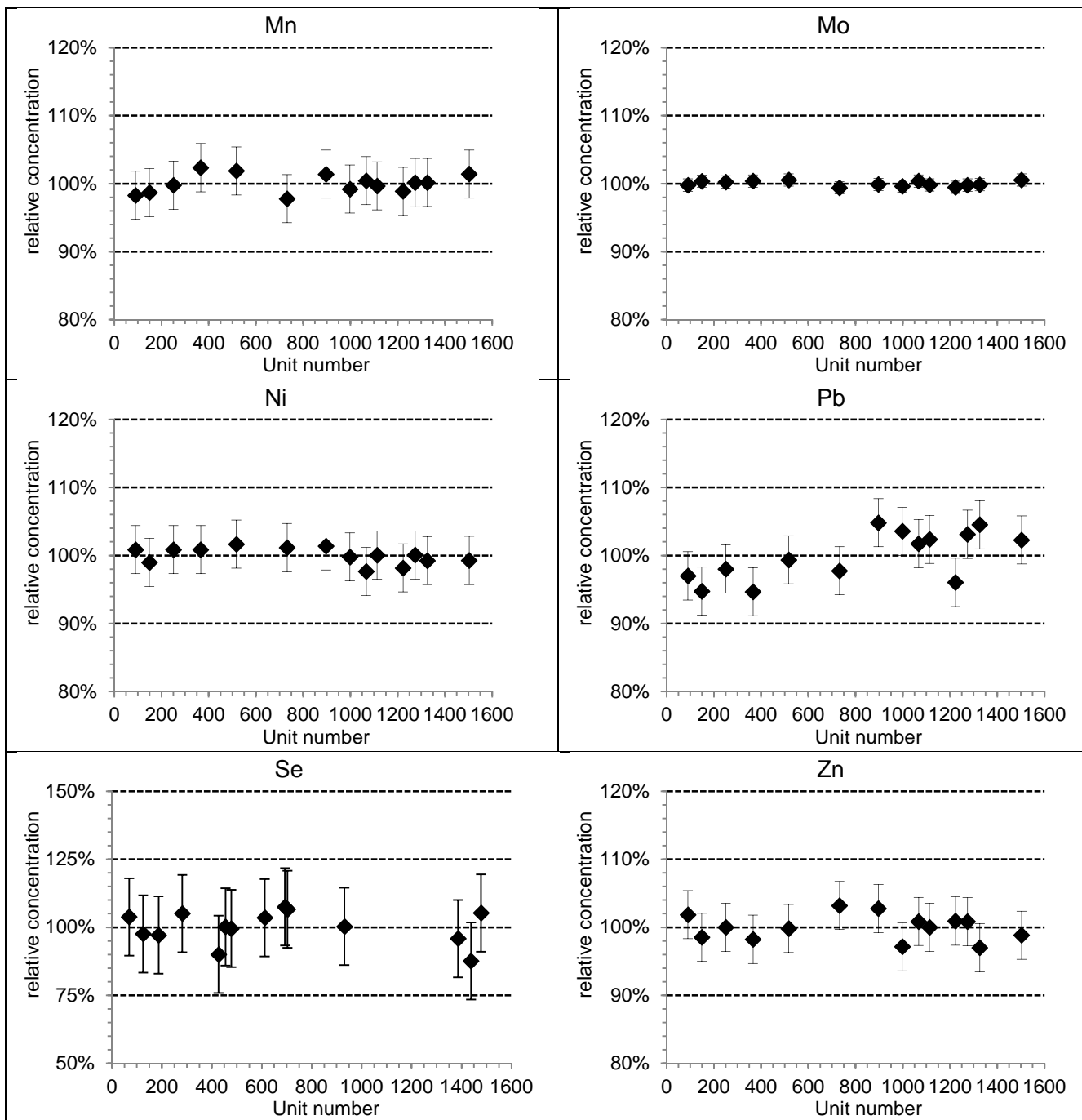
Annex A: Results of the homogeneity measurements for ERM-CA403 for density and trace elements as reported by the laboratories.

A1: Density results of the mean values against unit number. Vertical bars represent standard deviation of the three replicates.



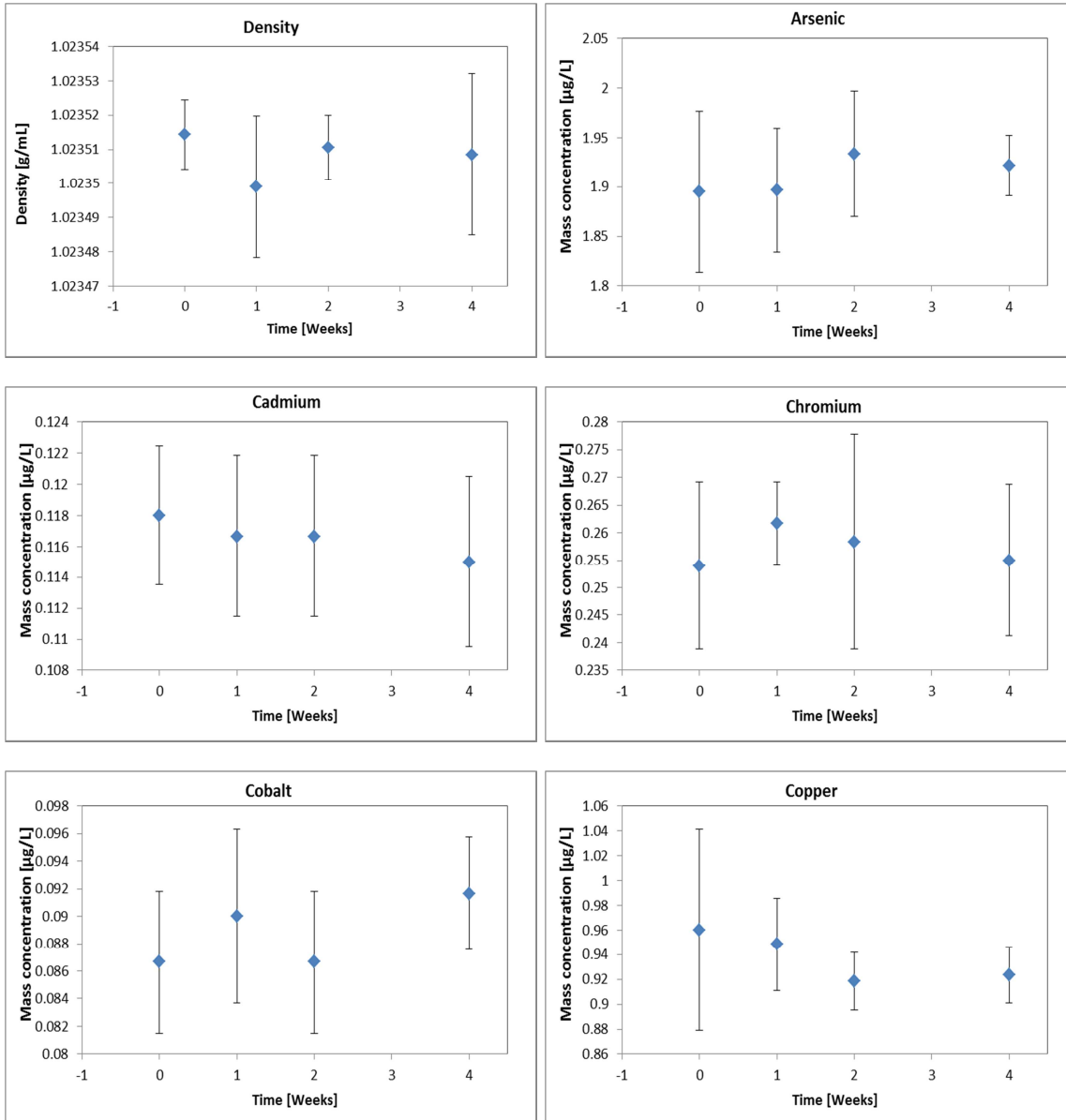
A2: Relative mass concentrations of elements against unit number. Points are normalised due to between-run effects and are relative to the mean of all points. Vertical bars are the 95 % confidence interval of measurement.

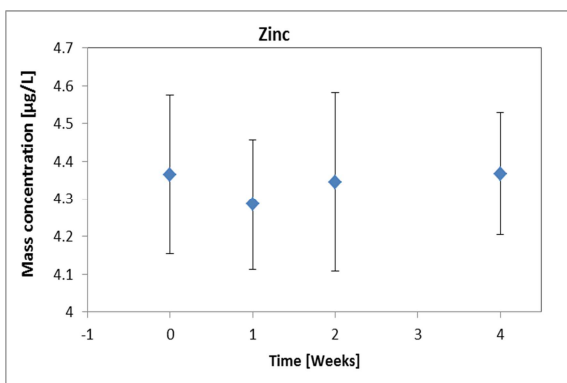
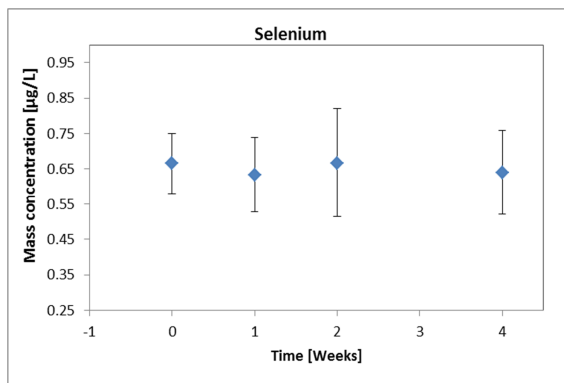
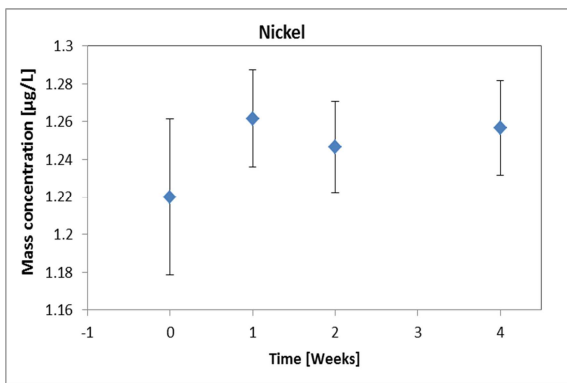
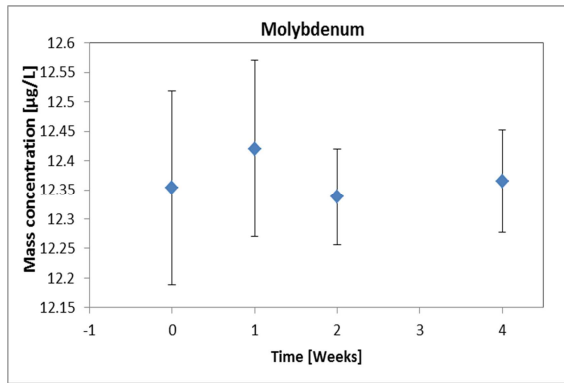
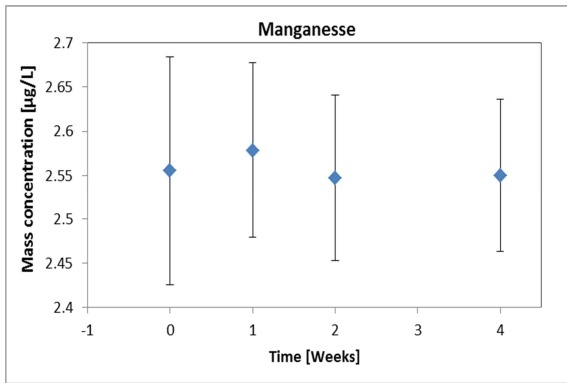
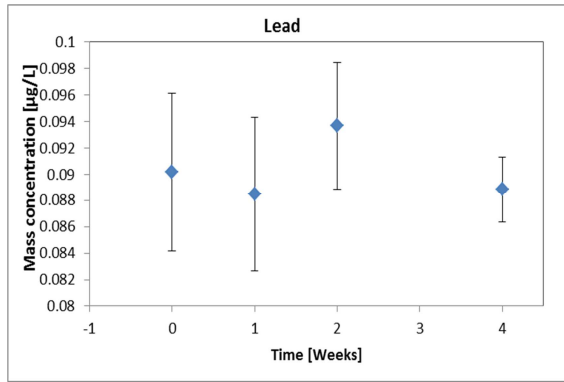
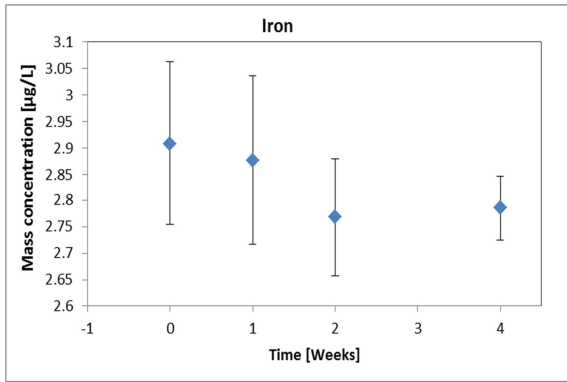




Annex B: Results of the short term stability measurements for ERM-CA403 for density and trace elements.

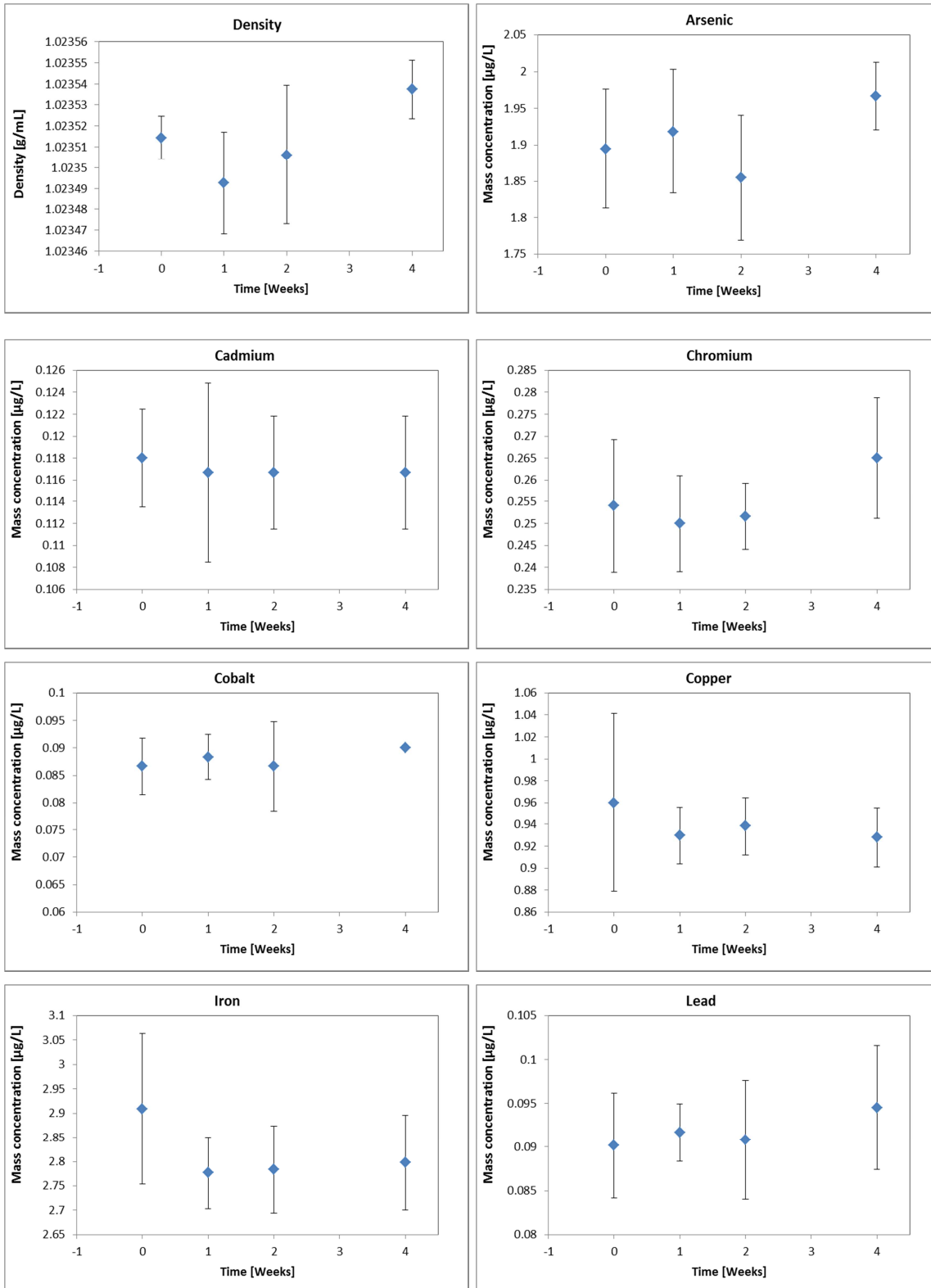
The data for the short-term stability study at 18 °C. the graphs report unit averages per time point and the standard deviation of the measurements per time as reported by the laboratories.

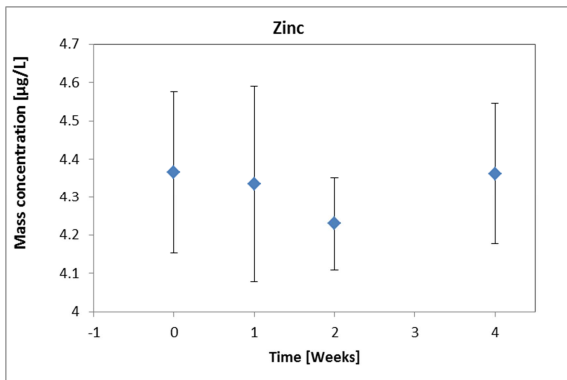
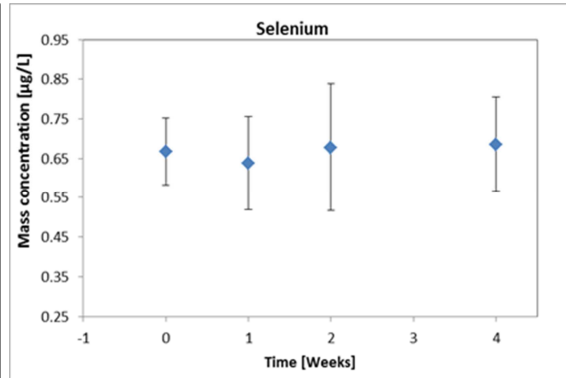
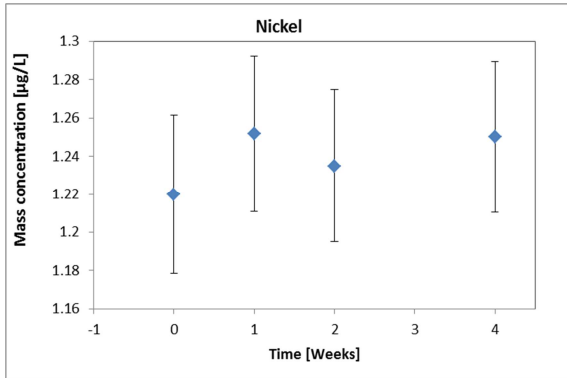
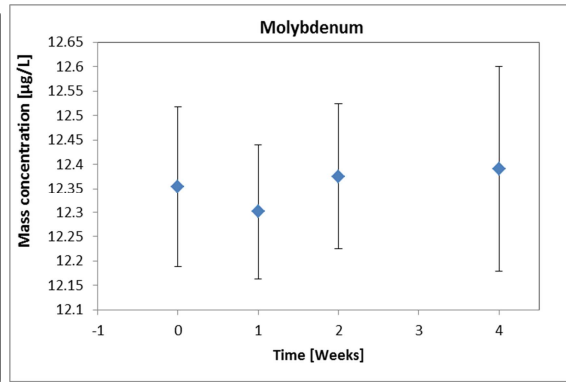
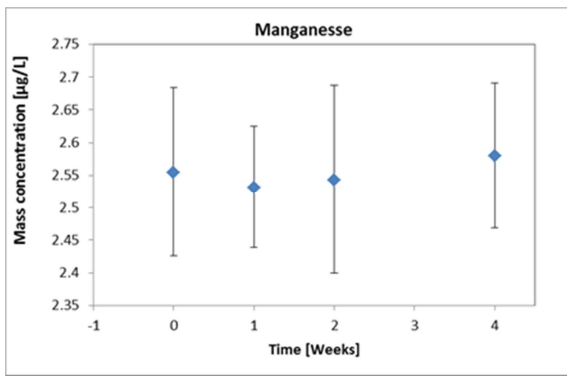




Annex B – Continued: Results of the short term stability measurements for ERM-CA403 for density and trace elements.

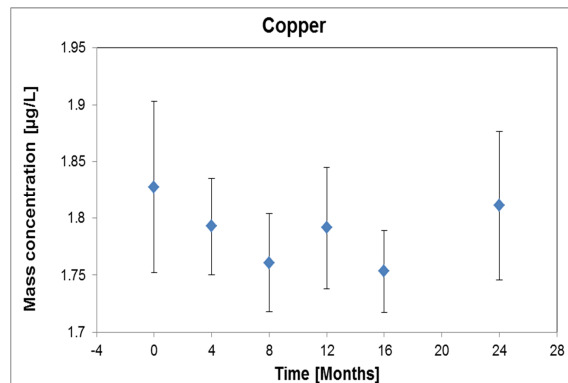
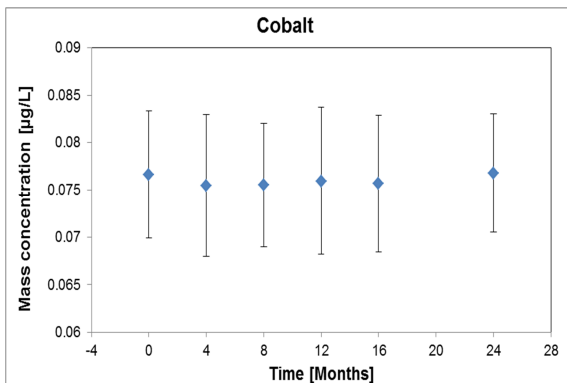
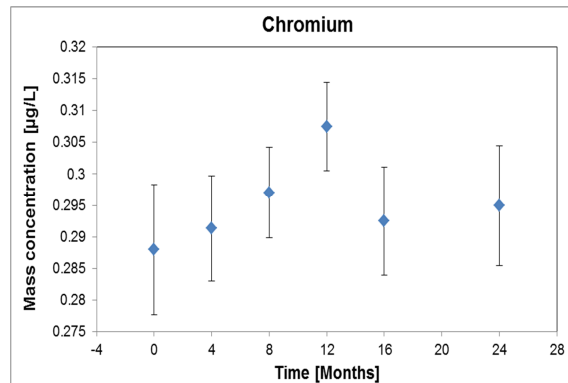
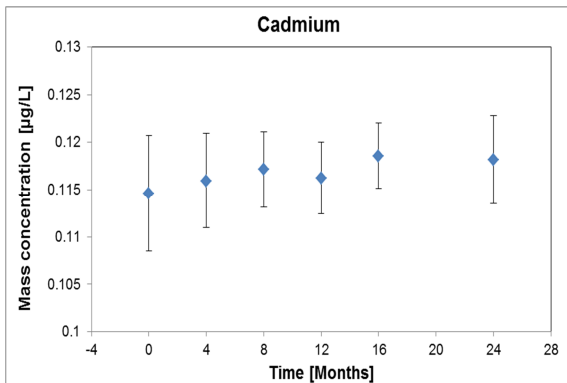
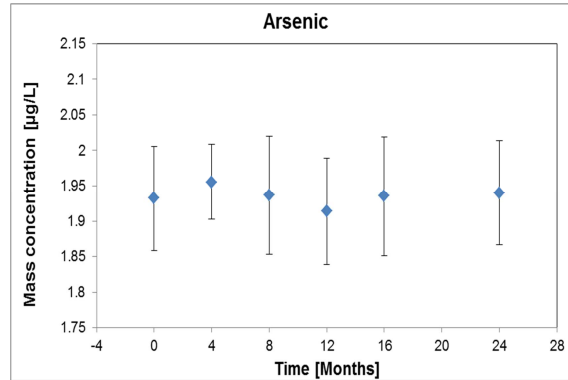
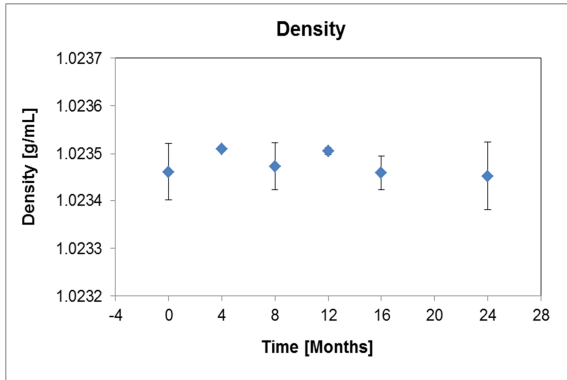
The data for the short-term stability study at 60 °C. the graphs report unit averages per time point and the standard deviation of the measurements per time as reported by the laboratories.

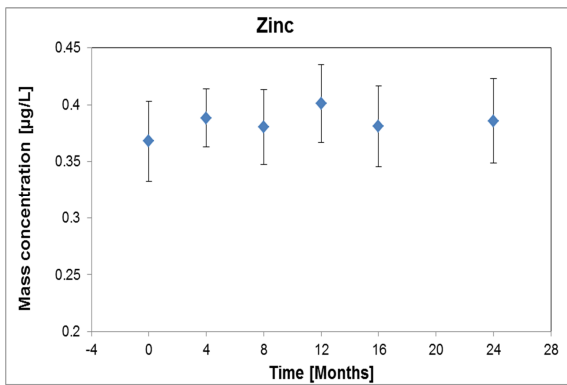
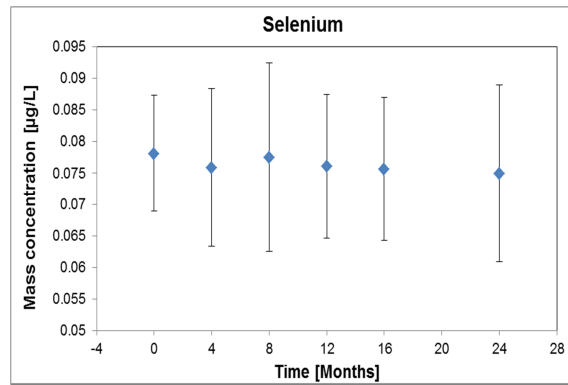
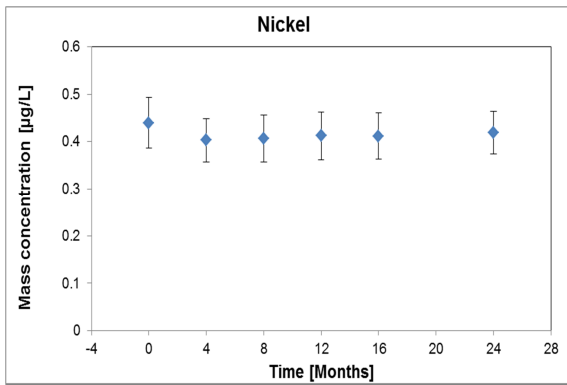
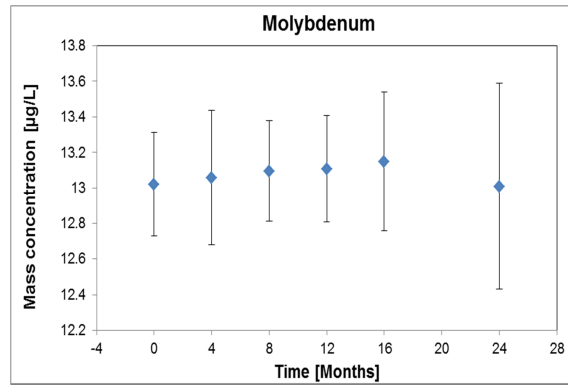
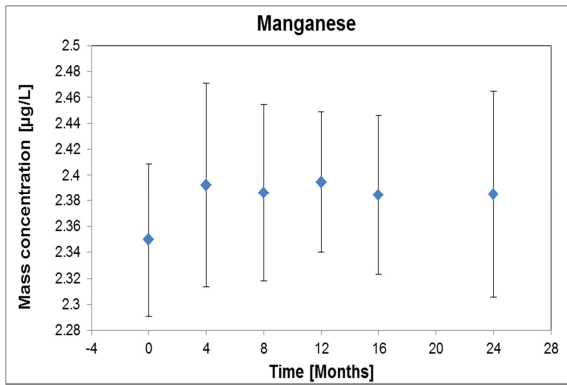
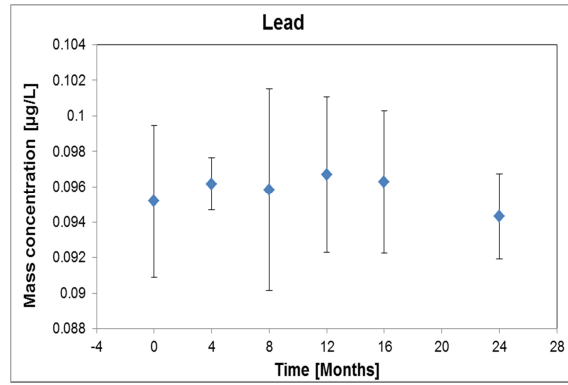
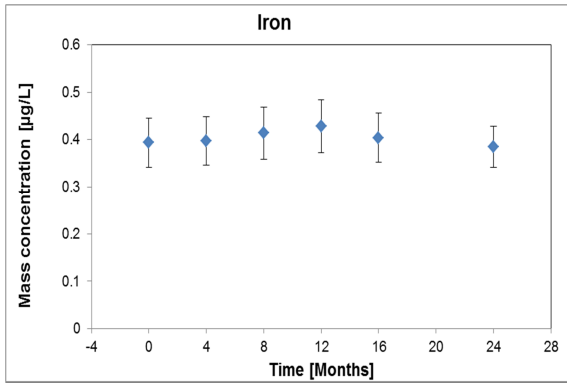




Annex C: Results of the long-term stability measurements for ERM-CA403 for density and trace elements.

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 D: Summary of analytical techniques used in the characterisation of ERM-CA403 as reported by the laboratories (which may not be in line with VIM)

D.1 Density

Lab-method code	Sample pretreatment	Analytical method	Calibrant	Instrument
L01-OD	None	Oscillating type density meter in accordance with ASTM D4052-09	Air, purified water and dodecane	Anton Paar DMA5000M
L02-OD	None	Oscillating type density meter	Distilled water	Anton Paar DMA5000
L04-OD	Temperature stabilisation	Oscillating type density meter	Air, distilled water and dodecane	Anton Paar DMA5000
L05-Pyc	Temperature stabilisation	Gravimetric density determination with pycnometer	The volume of the pycnometer was calibrated with primary density standard (water) by hydrostatic weighing	Pycnometer made with glass
L06-OD	Temperature stabilisation (24 hours)	Oscillating type density meter		Anton Paar DMA5000
L08-OD	None	Oscillating type density meter	2,2,4 trimethyl pentane, dodecan, lube oil 8,pure water and dimethyl phalate	Anton Paar DMA5000
L09-Pyc		Gravimetric density determination with pycnometer in accordance with ASTM D1480		Bingham Pycnometers
L10-OD	None	Oscillating type density meter	Air and ultra-pure water	Anton Paar DMA5000
Not used in certification				
L03-OD	Samples were stirred during 30 minutes at 150 rpm before collecting one subsample	Oscillating type density meter	Air and ultra-pure water	Anton Paar DMA5000

L07-OD	The samples were homogenized by shaking and adjusted at 20°C	Oscillating type density meter	None	Portable Density Meter Densito 30PX, Mettler Toledo
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D.2 Mass concentration of As

Lab-method code	Sample pretreatment	Analytical method	Calibration	LOQ
L01-ICP-SFMS	Acidification with 1 mL ultra high-purity HNO ₃ per 100 mL of sample.	ICP-SFMS In as internal standard.	External: 0/ 2/ 10 µg/L. Matrix matched.	0.5 µg/L
L02-ICP-MS	Dilution and acidification with ultrapure 0.5 % HNO ₃ .	ICP-MS Collision cell mode. Ge as internal standard.	Linear, two points: 0.12/ 5.12 µg/L. Matrix matched.	0.12 µg/L
L04-ICP-MS	None	ICP-MS He collision mode. Ge as internal standard.	External: 0/ 0.05/ 0.10/ 0.5/ 1.00/ 2.50/ 5.00/ 10.0/ 25.0 µg/L.	0.05 µg/L
L12-ICP-MS	Dilution 1:2 with Milli-Q purified water	ICP-MS Sc, Ge, Y, Rh, In as internal standards	External	1 µg/L
L13-ICP-MS	10 g sample is introduced in SeaFAST matrix separation and pre-concentration system and retained elements eluted with 200 µl 2% HNO ₃	ICP-MS in collision reaction mode	External with gravimetrically diluted multi-elemental standards, recovery correction with NASS-6; SLEW-3 or CASS-5.	0.3 ng/L
Not used in certification				
L03-ICP-SFMS	Dilution 1:5 with 1 % HNO ₃ solution.	ICP-SFMS In as internal standard	Standard addition, two points: 5/ 10 µg/L.	0.5 µg/L

L05-ICP-MS	Pre-concentration step with resin chelex-100. Elution with 5 mL of HNO ₃ 2 mol/L.	ICP-MS Y as internal standard.	External: 0/ 0.05/ 0.10/ 0.5/ 1.00/ 2.50/ 5.00/ 10.0/ 20.0 µg/L.	not supplied
L06-ICP-MS	Reductive precipitation by pH adjustment with 0.2% (v/v) HNO ₃ then prepared according to EPA Method 1640.	ICP-MS Sc, Ge, In, Tm as internal standards	External, 8 calibration points	Varies, reported per sample

D.3 Mass concentration of Cd

Lab-method code	Sample pretreatment	Analytical method	Calibration	LOQ
L01-ICP-SFMS	Acidification with 1 mL ultra high-purity HNO ₃ per 100 mL of sample.	ICP-SFMS In as internal standard.	External: 0/ 2/ 10 µg/L. Matrix matched.	0.03 µg/L
L02-ICP-MS	Dilution and acidification with ultrapure 0.5 % HNO ₃ .	ICP-MS Collision cell mode. Rh as internal standard.	Linear, two points: 0.005/ 5.005 µg/L. Matrix matched.	0.005 µg/L
L04-ICP-MS	None	ICP-MS He collision mode. In as internal standard.	External: 0/ 0.05/ 0.10/ 0.5/ 1.00/ 2.50/ 5.00/ 10.0/ 25.0 µg/L.	0.05 µg/L
L05-ICP-MS	Pre-concentration step with resin Chelex [®] -100. Elution with 5 mL of HNO ₃ 2 mol/L.	ICP-MS Y as internal standard.	External: 0/ 0.05/ 0.10/ 0.5/ 1.00/ 2.50/ 5.00/ 10.0/ 20.0 µg/L.	
L10-ICP-MS	column chelation after adjustment to 1% (v/v) HNO ₃	ICP-MS In internal standard	External, 7 calibration points	Varies, reported per sample

L13-ICP-MS	10 g sample is introduced in SeaFAST matrix separation and pre-concentration system and retained elements eluted with 200 µl 2% HNO ₃	ICP-SFMS in low resolution mode	External with gravimetrically diluted multi-elemental standards, recovery correction with NASS-6; SLEW-3 or CASS-5.	0.06 ng/L
Not used in certification				
L03-ICP-SFMS	Dilution 1:5 with 1 % HNO ₃ solution.	ICP-SFMS In as internal standard	Standard addition, two points: 0.05/ 0.10 µg/L.	0.01 µg/L
L06-ICP-MS	Reductive precipitation by pH adjustment with 0.2% (v/v) HNO ₃ then prepared according to EPA Method 1640.	ICP-MS Sc, Ge, In, Tm as internal standards	External, 8 calibration points	Varies, reported per sample

D.4 Mass concentration of Co

Lab-method code	Sample pretreatment	Analytical method	Calibration	LOQ
L01-ICP-SFMS	Acidification with 1 mL ultra high-purity HNO ₃ per 100 mL of sample.	ICP-SFMS In as internal standard.	External: 0/ 2/ 10 µg/L. Matrix matched.	0.03 µg/L
L02-ICP-MS	Dilution and acidification with ultrapure 0.5 % HNO ₃ .	ICP-MS Collision cell mode. Ge as internal standard.	Linear, two points: 0.01/ 5.01 µg/L. Matrix matched.	0.01 µg/L
L04-ICP-MS	None	ICP-MS He collision mode. Ge as internal standard.	External: 0/ 0.05/ 0.10/ 0.5/ 1.00/ 2.50/ 5.00/ 10.0/ 25.0 µg/L.	
L10-ICP-MS	column chelation after adjustment to 1% (v/v) HNO ₃	ICP-MS In internal standard	External, 7 calibration points	Varies, reported per sample

L13-ICP-MS	10 g sample is introduced in SeaFAST matrix separation and pre-concentration system and retained elements eluted with 200 µl 2% HNO ₃	ICP-SFMS in low resolution mode	External with gravimetrically diluted multi-elemental standards, recovery correction with NASS-6; SLEW-3 or CASS-5.	0.1 ng/L
Not used in certification				
L03-ICP-SFMS	Dilution 1:5 with 1 % HNO ₃ solution.	ICP-SFMS In as internal standard	Standard addition, two points: 5/ 10 µg/L.	0.01 µg/L
L05-ICP-MS	Pre-concentration step with resin chelex-100. Elution with 5 mL of HNO ₃ 2M.	ICP-MS Y as internal standard.	External: 0/ 0.05/ 0.10/ 0.5/ 1.00/ 2.50/ 5.00/ 10.0/ 20.0 µg/L.	

D.5 Mass concentration of Cr

Lab-method code	Sample pretreatment	Analytical method	Calibration	LOQ
L01-ICP-SFMS	Acidification with 1 mL ultra high-purity HNO ₃ per 100 mL of sample.	ICP-SFMS In as internal standard.	External: 0/ 2/ 10 µg/L. Matrix matched.	0.15 µg/L
L02-ICP-MS	Dilution and acidification with ultrapure 0.5 % HNO ₃ .	ICP-MS Collision cell mode. Ge as internal standard.	Linear, two points: 0.01/ 5.01 µg/L. Matrix matched.	0.10 µg/L
L04-ICP-MS	None	ICP-MS He collision mode. Y as internal standard.	External: 0/ 0.05/ 0.10/ 0.5/ 1.00/ 2.50/ 5.00/ 10.0/ 25.0 µg/L.	0.05 µg/L
Not used in certification				
L03-ICP-SFMS	Dilution 1:5 with 1 % HNO ₃ solution.	ICP-SFMS	Standard addition, two points: 5/ 10 µg/L.	0.02 µg/L

		In as internal standard		
L06-ICP-MS	Reductive precipitation by pH adjustment with 0.2% (v/v) HNO ₃ then prepared according to EPA Method 1640.	ICP-MS Sc, Ge, In, Tm as internal standards	External, 8 calibration points	Varies, reported per sample

D.6 Mass concentration of Cu

Lab-method code	Sample pretreatment	Analytical method	Calibration	LOQ
L01-ICP-SFMS	Acidification with 1 mL ultra high-purity HNO ₃ per 100 mL of sample.	ICP-SFMS In as internal standard.	External: 0/ 2/ 10 µg/L. Matrix matched.	0.3 µg/L
L02-ICP-MS	Dilution and acidification with ultrapure 0.5 % HNO ₃ .	ICP-MS Collision cell mode. Ge as internal standard.	Linear, two points: 0.05/ 5.05 µg/L. Matrix matched.	0.05 µg/L
L04-ICP-MS	None	ICP-MS He collision mode. Ge as internal standard.	External: 0/ 0.05/ 0.10/ 0.5/ 1.00/ 2.50/ 5.00/ 10.0/ 25.0 µg/L.	0.10µg/L
L05-ICP-MS	Pre-concentration step with resin chelex-100. Elution with 5 mL of HNO ₃ 2 mol/L.	ICP-MS Y as internal standard.	External: 0/ 0.05/ 0.10/ 0.5/ 1.00/ 2.50/ 5.00/ 10.0/ 20.0 µg/L.	
L10-ICP-MS	column chelation after adjustment to 1% (v/v) HNO ₃	ICP-MS In internal standard	External, 7 calibration points	Varies, reported per sample
L13-ICP-MS	10 g sample is introduced in SeaFAST matrix separation and pre-concentration system and retained elements eluted with 200 µl 2% HNO ₃	ICP-SFMS in low resolution mode	External with gravimetrically diluted multi-elemental standards, recovery correction with NASS-6; SLEW-3 or CASS-5.	0.0167 µg/L

Not used in certification				
L03-ICP-SFMS	Dilution 1:5 with 1 % HNO ₃ solution.	ICP-SFMS In as internal standard	Standard addition, two points: 5/ 10 µg/L.	0.02 µg/L
L06-ICP-MS	Reductive precipitation by pH adjustment with 0.2% (v/v) HNO ₃ then prepared according to EPA Method 1640.	ICP-MS Sc, Ge, In, Tm as internal standards	External, 8 calibration points	Varies, reported per sample

D.7 Mass concentration of Fe

Lab-method code	Sample pretreatment	Analytical method	Calibration	LOQ
L01-ICP-SFMS	Acidification with 1 mL ultra high-purity HNO ₃ per 100 mL of sample.	ICP-SFMS In as internal standard.	External: 0/ 2/ 10 µg/L. Matrix matched.	1.5 µg/L
L02-ICP-MS	Dilution and acidification with ultrapure 0.5 % HNO ₃ .	ICP-MS Collision cell mode. Ge as internal standard.	Linear, two points: 0.14/ 5.14 µg/L. Matrix matched.	0.14 µg/L
L10-ICP-MS	column chelation after adjustment to 1% (v/v) HNO ₃	ICP-MS In internal standard	External, 7 calibration points	Varies, reported per sample
Not used in certification				
L03-ICP-SFMS	Dilution 1:5 with 1 % HNO ₃ solution.	ICP-SFMS In as internal standard	Standard addition, two points: 0.25/ 0.50 µg/L.	0.05 µg/L

D.8 Mass concentration of Mn

Lab-method code	Sample pretreatment	Analytical method	Calibration	LOQ
L01-ICP-SFMS	Acidification with 1 mL ultra high-purity HNO ₃ per 100 mL of sample.	ICP-SFMS In as internal standard.	External: 0/ 2/ 10 µg/L. Matrix matched.	0.3 µg/L
L02-ICP-MS	Dilution and acidification with ultrapure 0.5 % HNO ₃ .	ICP-MS Collision cell mode. Ge as internal standard.	Linear, two points: 0.26/ 5.26 µg/L. Matrix matched.	0.26 µg/L
L04-ICP-MS	None	ICP-MS He collision mode. Ge as internal standard.	External: 0/ 0.05/ 0.10/ 0.5/ 1.00/ 2.50/ 5.00/ 10.0/ 25.0 µg/L.	
L05-ICP-MS	Dilution 1:10.	ICP-MS Y as internal standard.	External: 0/ 0.05/ 0.10/ 0.5/ 1.00/ 2.50/ 5.00/ 10.0/ 20.0 µg/L.	
L10-ICP-MS	column chelation after adjustment to 1% (v/v) HNO ₃	ICP-MS In internal standard	External, 7 calibration points	Varies, reported per sample
L13-ICP-MS	10 g sample is introduced in SeaFAST matrix separation and pre-concentration system and retained elements eluted with 200 µl 2% HNO ₃	ICP-SFMS in low resolution mode	External with gravimetrically diluted multi-elemental standards, recovery correction with NASS-6; SLEW-3 or CASS-5.	0.8 ng/L
Not used in certification				
L03-ICP-SFMS	Dilution 1:5 with 1 % HNO ₃ solution.	ICP-SFMS In as internal standard	Standard addition, two points: 5/ 10 µg/L.	0.05 µg/L
L12-ICP-MS	Dilution 1:2 with Milli-Q purified water	ICP-MS Sc, Ge, Y, Rh, In as internal standards	External	1 µg/L

D.9 Mass concentration of Mo

Lab-method code	Sample pretreatment	Analytical method	Calibration	LOQ
L01-ICP-SFMS	Acidification with 1 mL ultra high-purity HNO ₃ per 100 mL of sample.	ICP-SFMS In as internal standard.	External: 0/ 2/ 10 µg/L. Matrix matched.	0.15 µg/L
L02-ICP-MS	Dilution and acidification with ultrapure 0.5 % HNO ₃ .	ICP-MS Collision cell mode. Rh as internal standard.	Linear, two points: 0.98/ 5.98 µg/L. Matrix matched.	0.98 µg/L
L05-ICP-MS	Dilution 1:10.	ICP-MS Y as internal standard.	External: 0/ 0.05/ 0.10/ 0.5/ 1.00/ 2.50/ 5.00/ 10.0/ 20.0 µg/L.	
L12-ICP-MS	Dilution 1:2 with Milli-Q purified water	ICP-MS Sc, Ge, Y, Rh, In as internal standards	External	1 µg/L
L13-ICP-MS	10 g sample is introduced in SeaFAST matrix separation and pre-concentration system and retained elements eluted with 200 µl 2% HNO ₃	ICP-SFMS in low resolution mode	External with gravimetrically diluted multi-elemental standards, recovery correction with NASS-6; SLEW-3 or CASS-5.	0.01298 µg/L
Not used in certification				
L03-ICP-SFMS	Dilution 1:5 with 1 % HNO ₃ solution.	ICP-SFMS In as internal standard	Standard addition, two points: 5/ 10 µg/L.	0.05 µg/L

D.10 Mass concentration of Ni

Lab-method code	Sample pretreatment	Analytical method	Calibration	LOQ
L01-ICP-SFMS	Acidification with 1 mL ultra high-purity HNO ₃ per 100 mL of sample.	ICP-SFMS In as internal standard.	External: 0/ 2/ 10 µg/L. Matrix matched.	0.3 µg/L
L02-ICP-MS	Dilution and acidification with ultrapure 0.5 % HNO ₃ .	ICP-MS Collision cell mode. Ge as internal standard.	Linear, two points: 0.03/ 5.03 µg/L. Matrix matched.	0.03 µg/L
L04-ICP-MS	None	ICP-MS He collision mode. Ge as internal standard.	External: 0/ 0.05/ 0.10/ 0.5/ 1.00/ 2.50/ 5.00/ 10.0/ 25.0 µg/L.	0.05 µg/L
L05-ICP-MS	Pre-concentration step with resin chelex-100. Elution with 5 mL of HNO ₃ 2M.	ICP-MS Y as internal standard.	External: 0/ 0.05/ 0.10/ 0.5/ 1.00/ 2.50/ 5.00/ 10.0/ 20.0 µg/L.	
L06-ICP-MS	Reductive precipitation by pH adjustment with 0.2% (v/v) HNO ₃ then prepared according to EPA Method 1640.	ICP-MS Sc, Ge, In, Tm as internal standards	External, 8 calibration points	Varies, reported per sample
L10-ICP-MS	column chelation after adjustment to 1% (v/v) HNO ₃	ICP-MS In internal standard	External, 7 calibration points	Varies, reported per sample
L13-ICP-MS	10 g sample is introduced in SeaFAST matrix separation and pre-concentration system and retained elements eluted with 200 µl 2% HNO ₃	ICP-SFMS in low resolution mode	External with gravimetrically diluted multi-elemental standards, recovery correction with NASS-6; SLEW-3 or CASS-5.	5.3 ng/L

Not used in certification				
L03-ICP-SFMS	Dilution 1:5 with 1 % HNO ₃ solution.	ICP-SFMS In as internal standard	Standard addition, two points: 0.25/ 0.50 µg/L.	0.05 µg/L

D.11 Mass concentration of Pb

Lab-method code	Sample pretreatment	Analytical method	Calibration	LOQ
L01-ICP-SFMS	Acidification with 1 mL ultra high-purity HNO ₃ per 100 mL of sample.	ICP-SFMS Lu as internal standard.	External: 0/ 2/ 10 µg/L. Matrix matched.	0.03 µg/L
L02-ICP-MS	Dilution and acidification with ultrapure 0.5 % HNO ₃ .	ICP-MS Collision cell mode. Rh as internal standard.	Linear, two points: 0.005/ 5.005 µg/L. Matrix matched.	0.005 µg/L
L04-ICP-MS	None	ICP-MS He collision mode. Bi as internal standard.	External: 0/ 0.05/ 0.10/ 0.5/ 1.00/ 2.50/ 5.00/ 10.0/ 25.0 µg/L.	0.1 µg/L
L05-ICP-MS	Dilution 1:10.	ICP-MS Y as internal standard.	External: 0/ 0.05/ 0.10/ 0.5/ 1.00/ 2.50/ 5.00/ 10.0/ 20.0 µg/L.	
L06-ICP-MS	Reductive precipitation by pH adjustment with 0.2% (v/v) HNO ₃ then prepared according to EPA Method 1640.	ICP-MS Sc, Ge, In, Tm as internal standards	External, 8 calibration points	Varies, reported per sample
L10-ICP-MS	column chelation after adjustment to 1% (v/v) HNO ₃	ICP-MS In internal standard	External, 7 calibration points	Varies, reported per sample

L13-ICP-MS	10 g sample is introduced in SeaFAST matrix separation and pre-concentration system and retained elements eluted with 200 µl 2% HNO ₃	ICP-SFMS in low resolution mode	External with gravimetrically diluted multi-elemental standards, recovery correction with NASS-6; SLEW-3 or CASS-5.	0.3 ng/L
Not used in certification				
L03-ICP-SFMS	Dilution 1:5 with 1 % HNO ₃ solution.	ICP-SFMS In as internal standard	Standard addition, two points: 0.05/ 0.10 µg/L.	0.01 µg/L

D.12 Mass concentration of Se

Lab-method code	Sample pretreatment	Analytical method	Calibration	LOQ
L01-ICP-SFMS	Acidification with 1 mL ultra high-purity HNO ₃ per 100 mL of sample.	ICP-SFMS In as internal standard.	External: 0/ 2/ 10 µg/L. Matrix matched.	0.3 µg/L
L11-AFS	Dilution 1:5 with 1 % HNO ₃ solution.	AFS according to SS-EN ISO 17852:2008		0.03 µg/L
Not used in certification				
L03-ICP-SFMS	Dilution 1:5 with 1 % HNO ₃ solution.	ICP-SFMS In as internal standard	Standard addition, two points: 0.05/ 0.10 µg/L.	0.01 µg/L

D.13 Mass concentration of Zn

Lab-method code	Sample pretreatment	Analytical method	Calibration	LOQ
L01-ICP-SFMS	Acidification with 1 mL ultra high-purity HNO ₃ per 100 mL of sample.	ICP-SFMS In as internal standard.	External: 0/ 2/ 10 µg/L. Matrix matched.	1.5 µg/L
L02-ICP-MS	Dilution and acidification with ultrapure 0.5 % HNO ₃ .	ICP-MS Collision cell mode. Ge as internal standard.	Linear, two points: 0.07/ 5.07 µg/L. Matrix matched.	0.07 µg/L
L10-ICP-MS	column chelation after adjustment to 1% (v/v) HNO ₃	ICP-MS In internal standard	External, 7 calibration points	Varies, reported per sample
L13-ICP-MS	10 g sample is introduced in SeaFAST matrix separation and pre-concentration system and retained elements eluted with 200 µl 2% HNO ₃	ICP-SFMS in low resolution mode	External with gravimetrically diluted multi-elemental standards, recovery correction with NASS-6; SLEW-3 or CASS-5.	4.8 ng/L
Not used in certification				
L03-ICP-SFMS	Dilution 1:5 with 1 % HNO ₃ solution.	ICP-SFMS In as internal standard	Standard addition, two points: 0.25/ 0.50 µg/L.	0.25 µg/L

Annex E: Results of the characterisation study

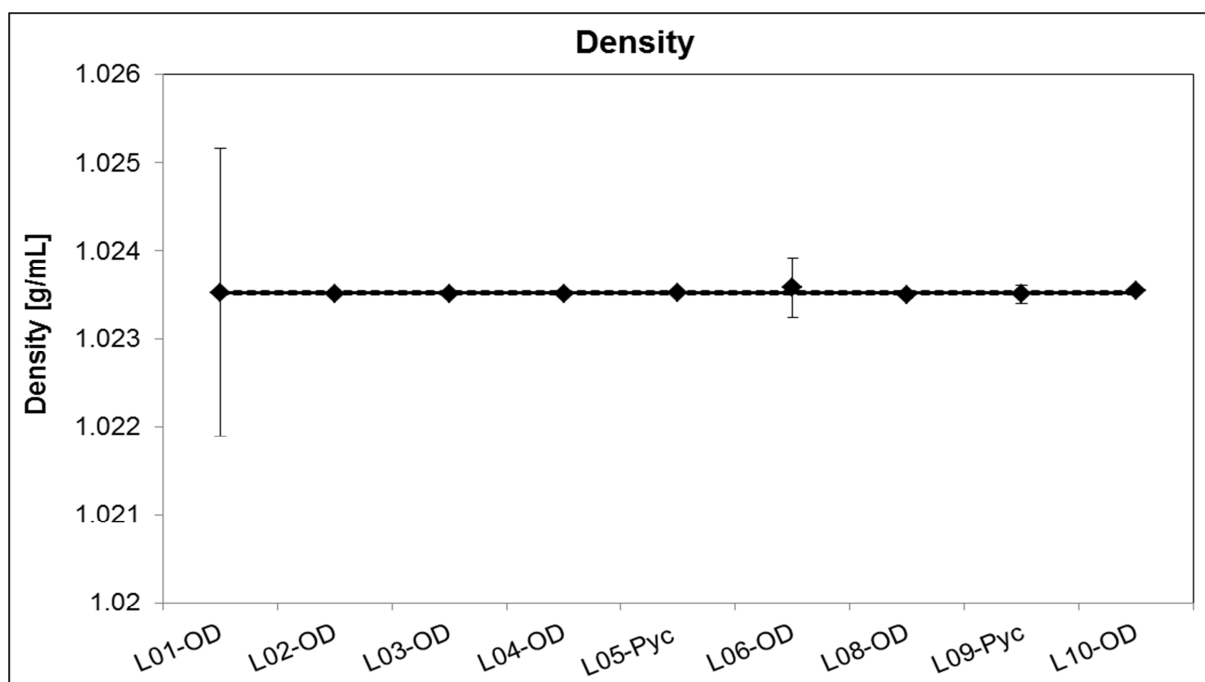
The tables in this annex also contain the data sets that were discarded for technical reasons. These data sets are highlighted in italics and are given for information purposes only. They are not included in the graphs.

Error bars represent expanded uncertainties as reported by participating laboratories. The solid line represents the certified values (the mean of the laboratory means), while the broken lines represent the expanded uncertainty of the certified value. For the trace element measurements, Labs L04, L05, L06 and L10 did not provide uncertainties. For these results, an indicative measurement uncertainty of 20 % was assigned, as described in section 6.4.2.

Approaches to number rounding differed between participants. Values presented in this annex were rounded to assist document formatting.

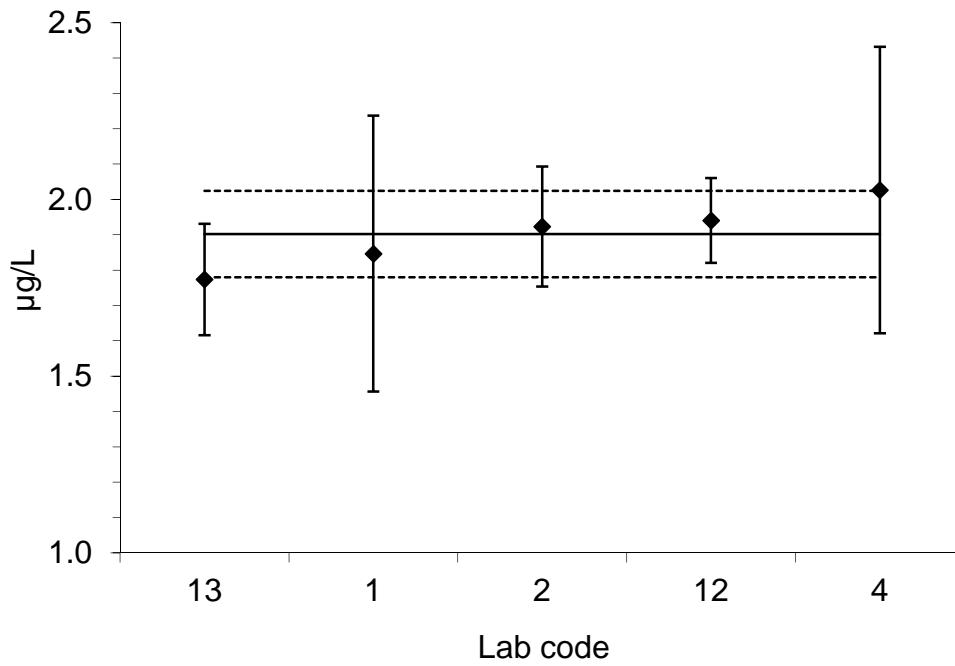
E.1 Density [g/mL]

Lab code	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Mean	U [%]
<i>L01-OD</i>	1.023528	1.023526	1.023520	1.023528	1.023512	1.023522	1.023523	0.16
<i>L02-OD</i>	1.023507	1.023507	1.023506	1.023508	1.023509	1.023510	1.023508	0.003
<i>L03-OD</i>	1.023506	1.023514	1.023507	1.023504	1.023507	1.023512	1.023508	0.003
<i>L04-OD</i>	1.023511	1.023509	1.023510	1.023509	1.023507	1.023509	1.023509	0.0010
<i>L05-Pyc</i>	1.023523	1.023524	1.023522	1.023525	1.023521	1.023523	1.023523	0.002
<i>L06-OD</i>	1.023500	1.023620	1.023620	1.023560	1.023520	1.023640	1.023577	0.03
<i>L08-OD</i>	1.023490	1.023481	1.023487	1.023494	1.023492	1.023485	1.023488	0.003
<i>L09-Pyc</i>	1.023520	1.023510	1.023520	1.023510	1.023510	1.023460	1.023505	0.010
<i>L10-OD</i>	1.023538	1.023553	1.023518	1.023573	1.023522	1.023519	1.023537	0.002
Results not used in the certification								
<i>L07-OD</i>	1.0236	1.0238	1.0237	1.024	1.0239	1.0239	1.023817	



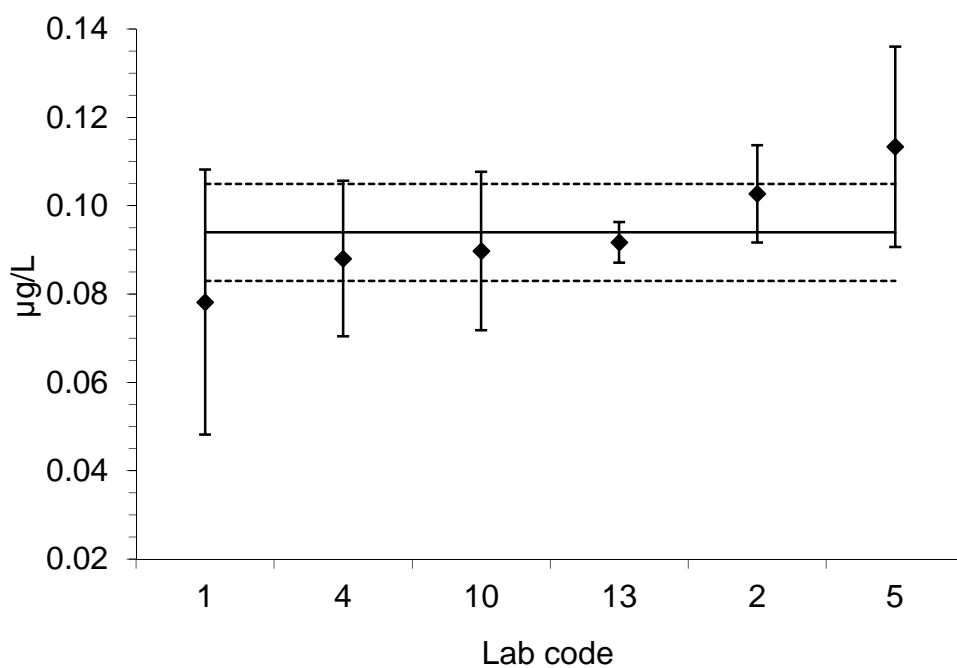
E.2 As mass concentration [$\mu\text{g/L}$]

Lab code	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Mean	U
L01	1.930	1.780	1.870	1.780	1.840	1.880	1.847	0.390
L02	1.900	1.870	1.850	1.940	1.880	2.100	1.923	0.170
L04	1.743	2.173	2.080	1.961	2.161	2.042	2.027	
L12	1.940	1.990	1.930	1.940	1.910	1.930	1.940	0.120
L13	1.780	1.830	1.770	1.740	1.780	1.740	1.773	0.158
Results not used in the certification								
L03	1.953	1.999	1.976	1.891	1.908	1.899	1.938	0.082
L06	1.730	1.590	1.770	1.480	1.930	1.830	1.722	



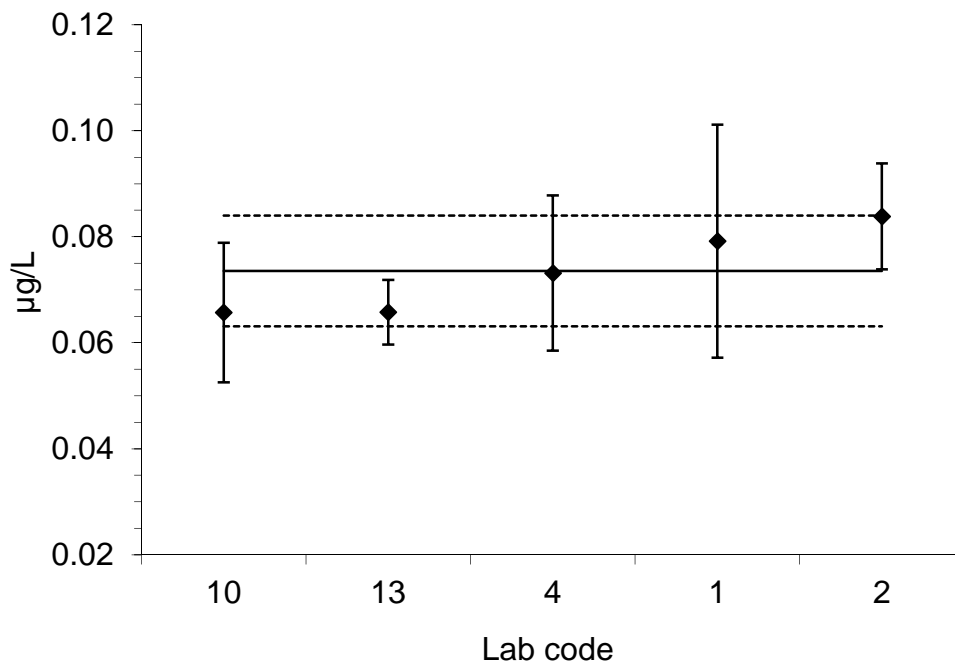
E.3 Cd mass concentration [$\mu\text{g/L}$]

Lab code	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Mean	U
L01	0.0830	0.0720	0.0820	0.0710	0.0740	0.0870	0.0782	0.0300
L02	0.1050	0.1040	0.0990	0.1050	0.0970	0.1060	0.1027	0.0110
L04	0.0900	0.0850	0.0920	0.0980	0.0810	0.0820	0.0880	
L05	0.1200	0.1100	0.1100	0.1200	0.1100	0.1100	0.1133	
L10	0.0884	0.0875	0.0946	0.086	0.0913	0.0906	0.0897	
L13	0.0907	0.0903	0.0895	0.0925	0.0923	0.0950	0.0917	0.0046
Results not used in the certification								
L03	0.0619	0.0505	0.0589	0.0569	0.0558	0.0545	0.0564	0.0071
L06	0.0990	0.0940	0.1160	0.0800	0.1100	0.1090	0.1013	



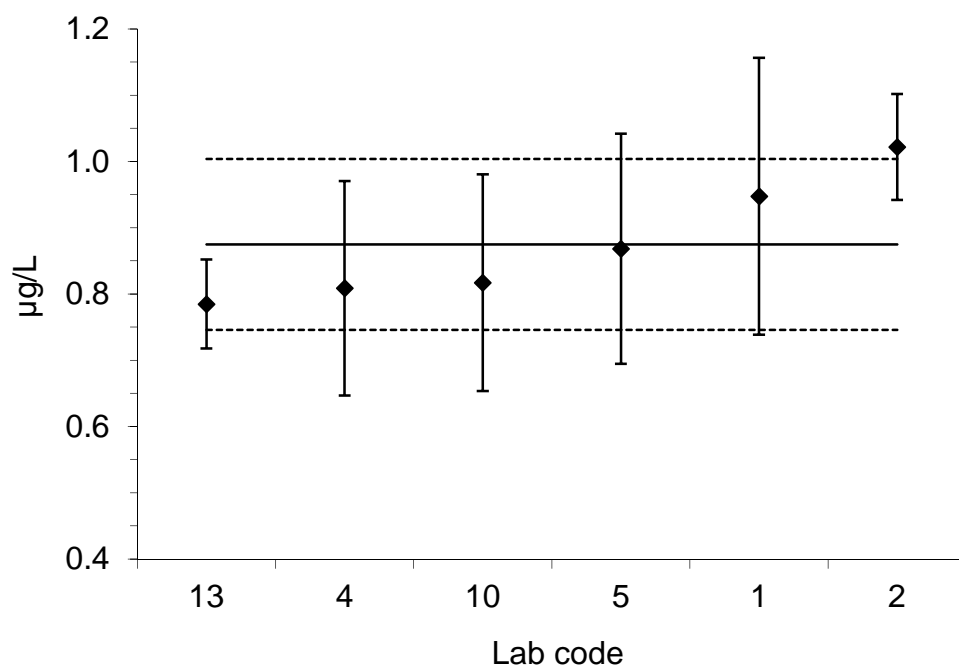
E.4 Co mass concentration, [$\mu\text{g/L}$]

Lab code	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Mean	U
L01	0.0820	0.0810	0.0780	0.0740	0.0800	0.0800	0.0792	0.0220
L02	0.0800	0.0790	0.0930	0.0830	0.0790	0.0890	0.0838	0.0100
L04	0.0670	0.0720	0.0720	0.0800	0.0700	0.0780	0.0732	
L10	0.0675	0.0681	0.0649	0.0685	0.0630	0.0622	0.0657	
L13	0.0644	0.0643	0.0632	0.0657	0.0690	0.0681	0.0658	0.0061
Results not used in the certification								
L03	0.0717	0.0753	0.0695	0.0765	0.0741	0.0692	0.0727	0.0056
L05	0.1200	0.1600	0.1300	0.0900	0.0900	0.1200	0.1183	



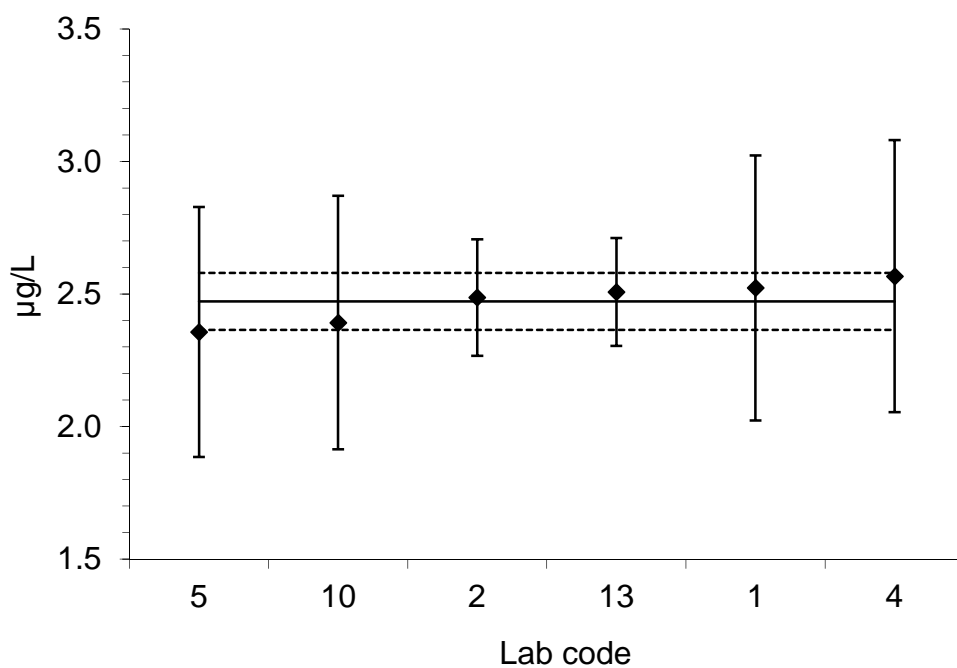
E.5 Cu mass concentration [$\mu\text{g/L}$]

Lab code	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Mean	U
L01	0.923	0.968	0.944	0.923	0.950	0.977	0.948	0.209
L02	0.994	1.022	1.051	1.019	1.031	1.015	1.022	0.080
L04	0.757	0.810	0.790	0.842	0.833	0.820	0.809	
L05	0.870	0.910	0.870	0.800	0.880	0.880	0.868	
L10	0.839	0.833	0.829	0.833	0.777	0.791	0.817	
L13	0.758	0.780	0.749	0.798	0.805	0.819	0.785	0.067
Results not used in the certification								
L03	1.852	1.919	1.810	1.822	1.914	1.868	1.864	0.083
L06	0.840	0.770	0.920	0.670	0.940	0.920	0.843	



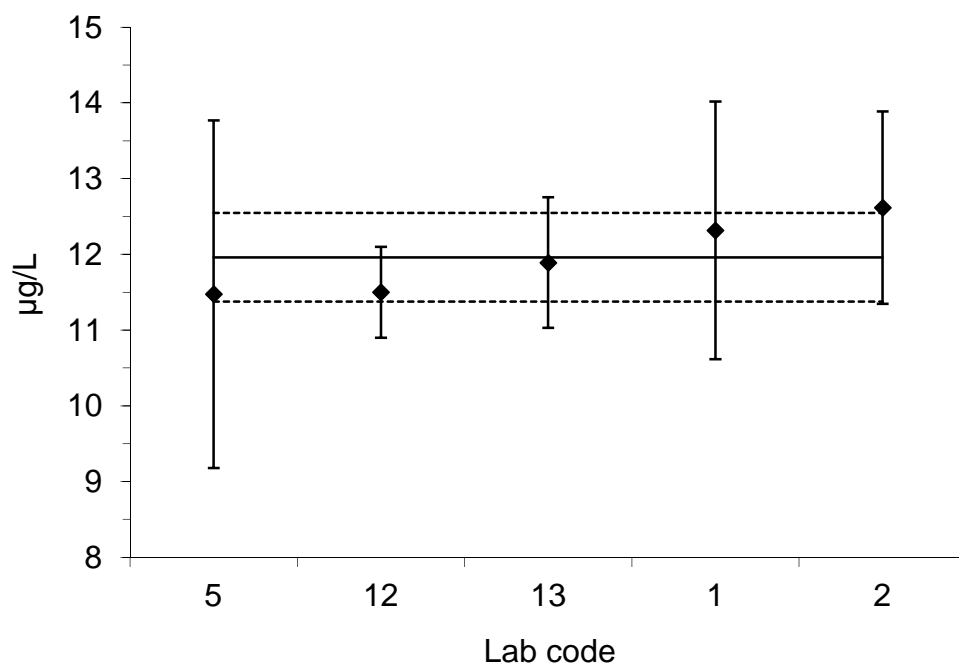
E.6 Mn mass concentration [$\mu\text{g/L}$]

Lab code	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Mean	U
L01	2.558	2.521	2.464	2.552	2.484	2.559	2.523	0.500
L02	2.500	2.370	2.720	2.470	2.350	2.510	2.487	0.220
L04	2.387	2.657	2.575	2.718	2.436	2.628	2.567	
L05	2.350	2.400	2.300	2.360	2.380	2.350	2.357	
L10	2.370	2.370	2.500	2.370	2.350	2.390	2.392	
L13	2.445	2.420	2.399	2.568	2.570	2.642	2.508	0.204
Results not used in the certification								
L03	2.468	2.435	2.416	2.449	2.431	2.428	2.438	0.034
L12	3.200	3.160	3.520	3.170	3.300	3.320	3.278	0.180



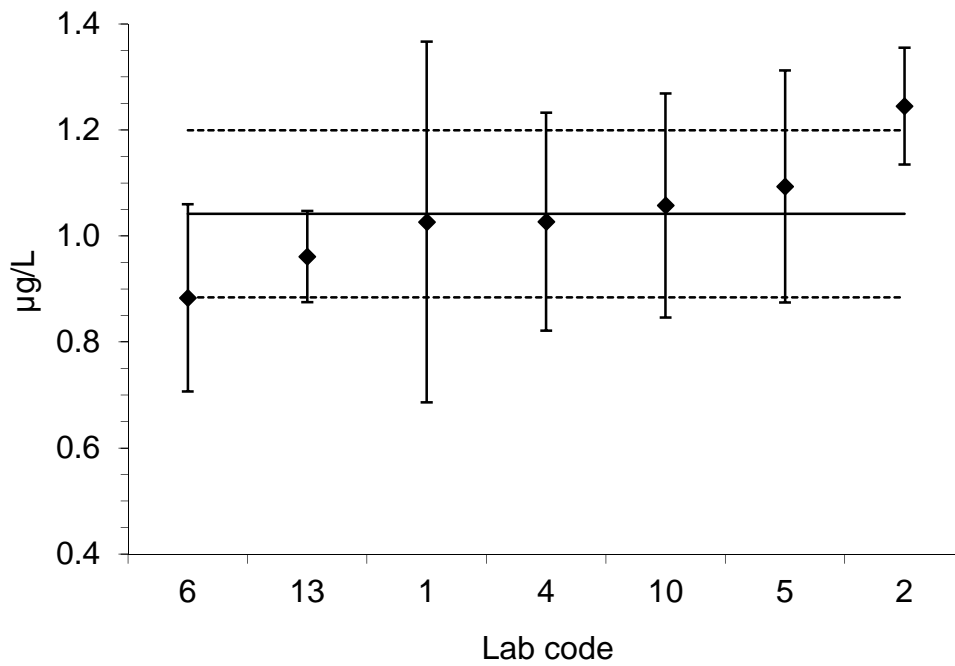
E.7 Mo mass concentration [$\mu\text{g/L}$]

Lab code	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Mean	U
L01	12.20	12.70	11.60	12.60	12.00	12.80	12.32	1.70
L02	12.65	12.42	12.73	12.61	12.74	12.56	12.62	1.27
L05	11.25	11.30	11.50	11.40	11.80	11.60	11.48	
L12	11.60	11.50	11.70	11.50	11.10	11.60	11.50	0.60
L13	12.31	12.89	11.71	12.15	12.08	10.19	11.89	0.86
Results not used in the certification								
L03	8.33	7.79	7.68	8.38	9.70	8.82	8.45	1.36



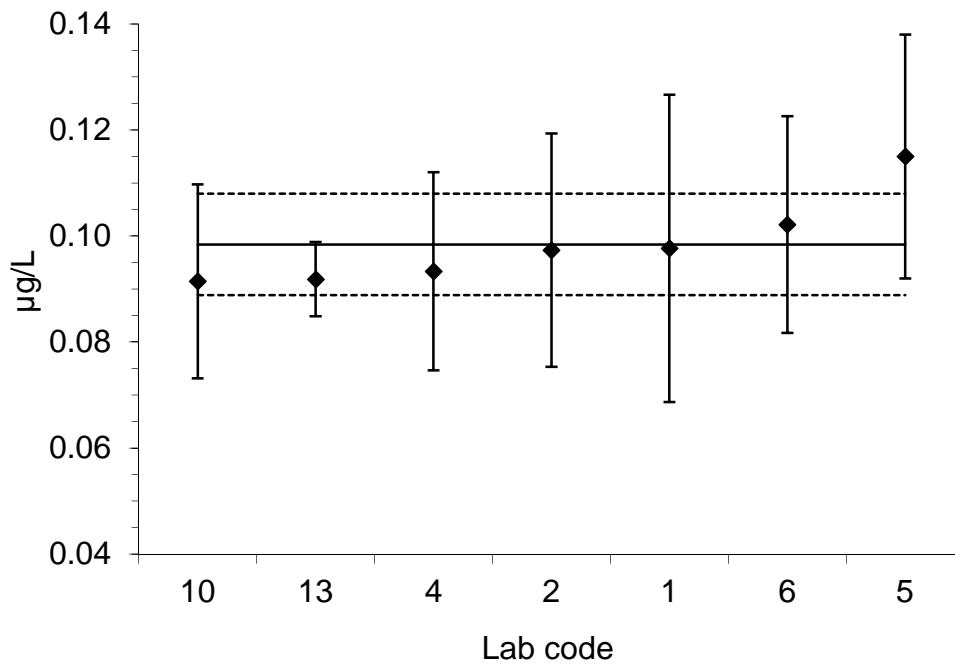
E.8 Ni mass concentration [$\mu\text{g/L}$]

Lab code	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Mean	U
L01	1.060	0.986	1.060	1.030	0.902	1.120	1.026	0.340
L02	1.240	1.200	1.280	1.240	1.170	1.340	1.245	0.110
L04	0.972	1.066	0.988	1.068	0.990	1.078	1.027	
L05	1.050	1.190	1.150	1.120	1.020	1.030	1.093	
L06	0.910	0.900	0.880	0.680	1.030	0.900	0.883	
L10	1.110	1.120	1.040	1.110	0.972	0.993	1.058	
L13	0.954	0.902	0.932	1.006	0.975	0.996	0.961	0.086
Results not used in the certification								
L03	0.429	0.422	0.429	0.431	0.367	0.422	0.417	0.045



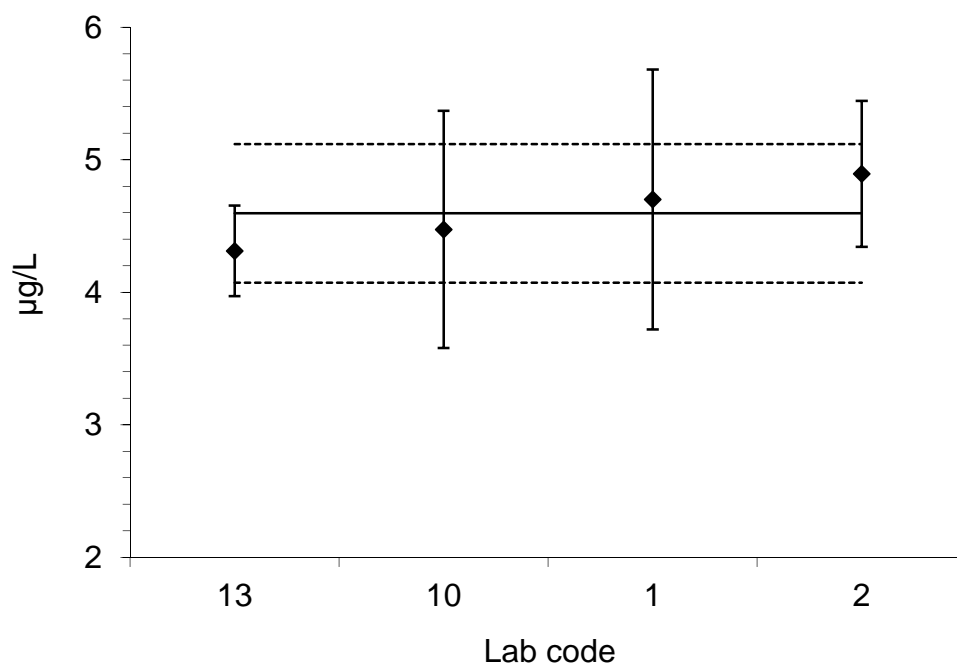
E.9 Pb mass concentration [$\mu\text{g/L}$]

Lab code	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Mean	U
L01	0.104	0.091	0.097	0.093	0.101	0.100	0.098	0.029
L02	0.100	0.109	0.090	0.100	0.080	0.105	0.097	0.022
L04	0.096	0.090	0.091	0.093	0.091	0.099	0.093	
L05	0.120	0.110	0.120	0.120	0.110	0.110	0.115	
L06	0.103	0.093	0.114	0.100	0.086	0.117	0.102	
L10	0.092	0.091	0.094	0.091	0.091	0.090	0.091	
L13	0.092	0.093	0.094	0.086	0.092	0.092	0.092	0.007
Results not used in the certification								
L03	0.082	0.077	0.097	0.085	0.091	0.071	0.084	0.017



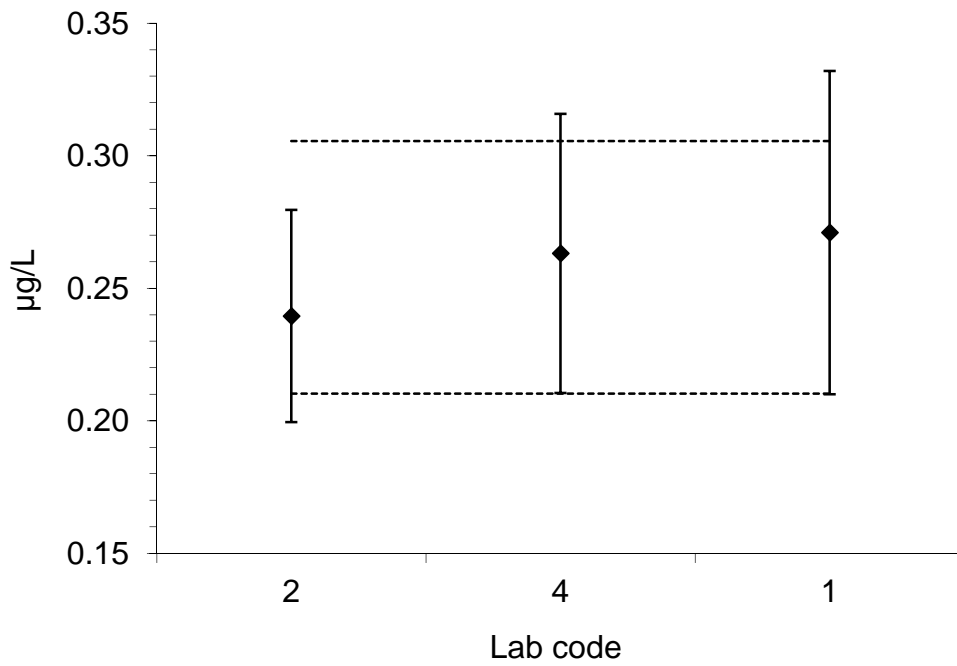
E.10 Zn mass concentration, indicative value [$\mu\text{g/L}$]

Lab code	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Mean	U
L01	4.92	4.53	4.78	4.59	4.5	4.88	4.70	0.98
L02	4.84	4.71	4.98	4.94	5.00	4.89	4.89	0.55
L10	4.34	4.37	4.68	4.42	4.48	4.55	4.47	
L13	4.23	4.19	4.18	4.37	4.41	4.50	4.31	0.34
Results not used in the certification								
L03	0.37	0.43	0.33	0.34	0.47	0.34	0.38	0.11
L05	<2	<2	<2	<2	<2	<2		



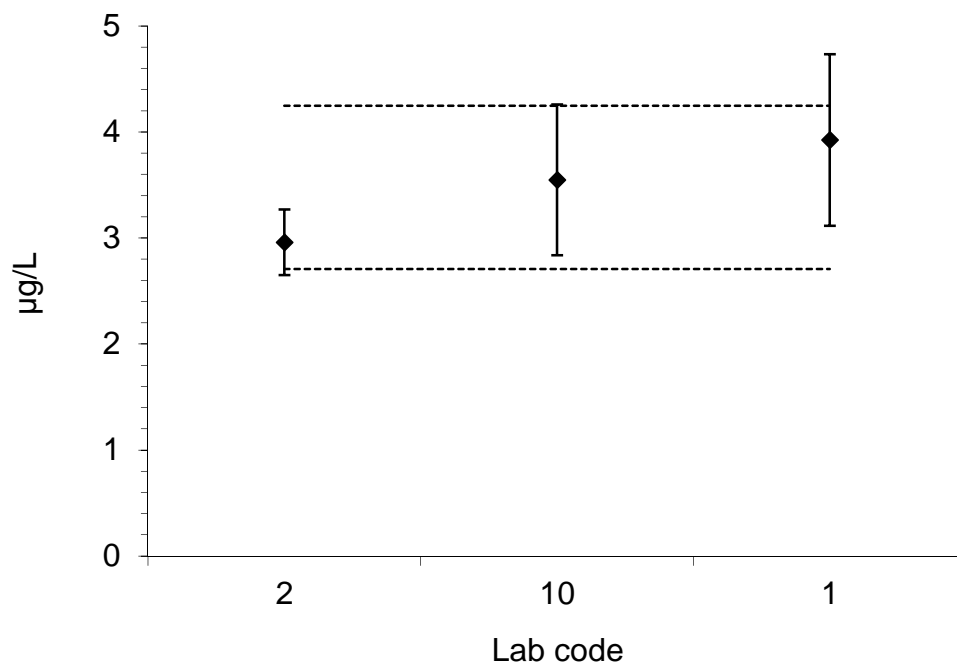
E.11 Cr mass concentration, additional information value [$\mu\text{g/L}$]

Lab code	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Mean	U
L01	0.286	0.280	0.262	0.278	0.267	0.253	0.271	0.061
L02	0.242	0.270	0.228	0.235	0.218	0.244	0.240	0.040
L04	0.260	0.277	0.266	0.259	0.248	0.269	0.263	
Results not used in the certification								
L03	0.410	0.424	0.417	0.358	0.394	0.329	0.389	0.068
L05	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5		
L06	0.155	0.163	0.374	0.149	0.291	0.272	0.234	



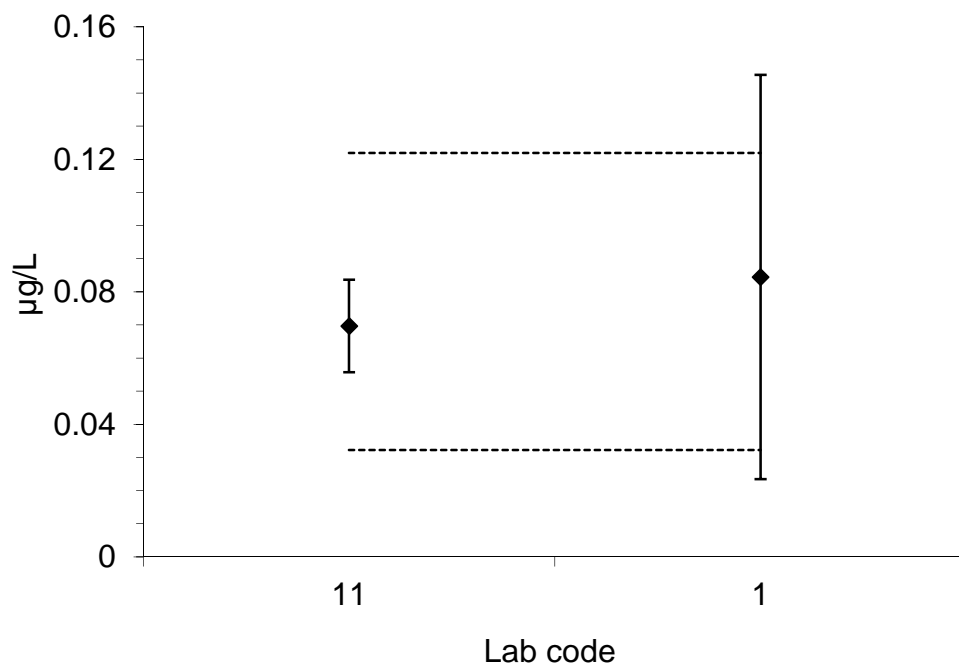
E.12 Fe mass concentration, additional information value [$\mu\text{g/L}$]

Lab code	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Mean	U
L01	4.060	3.810	3.740	3.990	3.860	4.090	3.925	0.810
L02	2.930	3.100	2.890	2.920	3.010	2.910	2.960	0.310
L10	3.580	3.560	3.380	3.390	4.250	3.130	3.548	
Results not used in the certification								
L03	0.503	0.547	0.554	0.439	0.483	0.414	0.490	0.103
L05	<1	<1	<1	<1	<1	<1		



E.13 Se mass concentration, additional information value [$\mu\text{g/L}$]

Lab code	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Mean	U
L01	0.084	0.077	0.085	0.087	0.088	0.086	0.085	0.061
L10	0.0654	0.0729	0.0718	0.0804	0.0687	0.0589	0.070	
Results not used in the certification								
L03	0.08	0.08	0.08	0.08	0.08	0.07	0.078	0.009
L05	<1	<1	<1	<1	<1	<1		



European Commission

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Title: **CERTIFICATION REPORT: The certification of the mass concentration of As, Cd, Co, Cu, Mn, Mo, Ni and Pb, and density in seawater: ERM®- CA403**

Author(s): R. Sánchez, E. de Vos, J. Snell, H. Emteborg, A. Held

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