CERTIFICATION REPORT

Certification of the Mass Concentrations of Arsenic, Cadmium, Iron, Lead, Manganese, Mercury and Nickel in Groundwater

Certified Reference Material ERM®-CA615

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The mission of the JRC-IRMM is to promote a common and reliable European measurement system in support of EU policies.

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Certified Reference Material ERM®-CA615

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Disclaimer

Summary

This report presents the preparation and certification of groundwater reference material ERM-CA615. All steps required for the production of this water-matrix reference material are described in detail, from the sampling of natural groundwater to the characterisation exercise that lead to the final assignment of the certified values, following ISO Guide 34:2009 [1] and ISO Guide 35:2006 [2].

Homogeneity and stability of the water material were investigated with dedicated studies and the certification campaign for the material characterisation was based on an inter-comparison involving several experienced laboratories.

IRMM organised and coordinated all phases of this project and carried out the evaluation of data.

The certified values were calculated as the unweighted mean of the laboratory means of the accepted sets of results for each parameter, as seen below. Uncertainties were calculated in compliance with the Guide to the Expression of Uncertainty in Measurement (GUM, ISO/IEC Guide 98-3:2008) [3]. The stated expanded uncertainties include contributions from characterisation, homogeneity and long-term stability.

GROUNDWATER

	Mass concentration	
	Certified value 2)	Uncertainty 3)
As	9.9 µg/L	0.7 µg/L
Cd	0.106 µg/L	0.011 µg/L
Fe	5.11 mg/L	0.26 mg/L
Hg1)	0.037 µg/L	0.004 µg/L
Mn	107 µg/L	5 µg/L
Ni	25.3 µg/L	1.1 µg/L
Pb	7.1 µg/L	0.6 µg/L

1) Mercury as obtained by cold vapor techniques

2) 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 values and their uncertainties are traceable to the International System of Units (SI).

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

Table of Contents

1. Introduction **4**

2. Participants **5**

3. Time schedule **6**

4. Sampling of the material **7**

5. Processing of the material **7**

5.1 Preparation steps *7*

5.2 Spiking, homogenisation and ampouling *8*

5.3 Sterilisation *9*

6. Homogeneity **9**

7. Minimum sample intake **13**

8. Stability studies **13**

8.1 Set-up of stability studies *13*

8.2 Results of stability studies *14*

9. Characterisation **16**

9.1 Study design *16*

9.2 Data evaluation and results *17*

10 Certified values and uncertainties **20**

11 Additional material information **21**

12 Metrological traceability **22**

13 Commutability **22**

14 Instructions for use and intended use **23**

14.1 Storage conditions *23*

14.2 Minimum sample intake *23*

14.3 Safety precautions *23*

14.4 Intended use *23*

14.5 Use of the certified value *23*

References **24**

Acknowledgments **25**

Annex 1 .... **26**

Annex 2 .... **29**

Annex 3 .... **30**

Annex 4 .... **37**

Glossary

ANOVA	analysis of variance
ASV	anodic stripping voltammetry
α	significance level
BCR	Community Bureau of Reference
CRM	certified reference material
CV-AFS	cold vapour atomic fluorescence spectrometry
Δ_{m}	absolute difference between mean measured value and certified value
DT	double Grubbs test
EDX	energy dispersive X-ray spectrometry
ET-AAS	electrothermal atomic absorption spectrometry
EQS	environmental quality standard
F-AAS	flame atomic absorption spectrometry
HG-AFS	hydride generation atomic fluorescence spectrometry
HG-ET-AAS	hydride generation electrothermal atomic absorption spectrometry
ICP-OES	inductively coupled plasma optical emission spectrometry
ICP-QMS	inductively coupled plasma quadrupole mass spectrometry
ICP-SFMS	inductively coupled plasma sector field mass spectrometry
IRMM	Institute for Reference Materials and Measurements
i.s.	internal standard
ISO	International Organization for Standardization
k	coverage factor
$MS_{between}$	mean square between-bottle from ANOVA
MS_{within}	mean square within-bottle from ANOVA
n	number of replicates per bottle
p	number of accepted datasets in the characterisation study
PTFE	polytetrafluoroethylene
QC	quality control
RSD	relative standard deviation
RSE	relative standard error (=RSD/√n)
s	standard deviation
s_{bb}	between-bottle standard deviation
SI	International System of Units
ST	single Grubbs test
s_{wb}	within-bottle standard deviation
$t_{\alpha,\text{df}}$	critical *t*-value for a *t*-test, with a level of confidence equal to 1-α and *df* degrees of freedom
u_{bb}	standard uncertainty related to possible between-bottle heterogeneity
u_{bb}^{*}	standard uncertainty of heterogeneity that can be hidden by method repeatability
u_{Δ}	combined standard uncertainty of measurement result and certified value
u_{char}	standard uncertainty related to characterisation
$7u_{\text{CRM}}$	combined standard uncertainty of a certified value
U_{CRM}	expanded uncertainty of a certified value
u_{lts}	standard uncertainty related to long-term stability
u_{m}	standard uncertainty of a measurement result
u_{rect}	standard uncertainty related to possible between-bottle heterogeneity modelled as rectangular distribution
x_i	time point of a stability study
$\overline{x}$	average of all time points of a stability study
$\overline{y}$	average of all results of the homogeneity study

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

1. Introduction

Groundwater is one of the most important natural resources. It is a crucial source of drinking water, supplying the water systems for about two-thirds of European Union citizens: its safety is therefore vital.

The legislative framework for its effective protection is established by the Water Framework Directive (WFD, 2000/60/EC) [4] which addresses inland surface waters, transitional waters, coastal waters and groundwater. The WFD consists of several steps of implementation, one of them being the mandatory monitoring of 33 Priority Substances since 2007 [5].

Recently, the priority substances were regulated to respect environmental quality standards (EQSs), threshold concentrations that should not be exceeded in order to protect human health and environment [6]. Among the 33 Priority Substances there are also four metals: nickel, lead, cadmium and mercury.

A Groundwater Daughter Directive (2006/118/EC) [7] was adopted (12th December 2006) by the European Parliament and Council which establishes specific measures as provided for in Article 17(1) and (2) of the WFD in order to prevent and control groundwater pollution; it will operate alongside the existing Groundwater Directive (80/68/EEC) [8] until its repeal in December 2013. This Directive sets for the first time groundwater quality standards (to be monitor and assess by the Member States) and introduces measures to prevent or limit inputs of pollutants into groundwater, including common criteria for the identification and reversal of significant and sustained upward trends in pollutant concentrations.

The compliance of the groundwater with good chemical status criteria is based on threshold values required to be decided by Member States for, among others, arsenic, cadmium, lead, mercury [7].

The WFD requires the establishment of monitoring programmes covering groundwater quantitative status, chemical status and the assessment of significant, long-term pollutant trends resulting from human activity. The confidence in any assessment of groundwater will depend on the quality in the context of measurement data. A continuous quality assurance system should be developed and implemented for each monitoring institution to ensure that the reported results meet assured target levels of precision and bias [9].

The availability of appropriate certified reference materials will therefore be an asset in the validation of analytical methods, ensuring accuracy and traceability of the measurement results [10].

ERM- CA615, the production of which was carried out by IRMM and described in this report, is intended to be used as a quality assurance and quality control tool especially by the laboratories involved in the mandatory monitoring prescribed under the WFD.

The parameters certified in ERM-CA615 are the following: arsenic, cadmium, iron, lead, manganese, mercury and nickel. The values are stated as mass concentrations, micrograms or milligrams per liter (µg/L or mg/L), because this is the most common way used by the "water analysis" community to express concentration of a parameter in water.

The target levels for nickel, lead, cadmium and mercury in the material were designed to reflect the recently enforced EQSs [6].

2. Participants

- Sampling and processing

European Commission, Joint Research Centre, Institute for Reference Materials and Measurements (IRMM), Geel, BE
(accredited to ISO Guide 34, Belac No 268-TEST)

- Homogeneity study

ALS Scandinavia AB, Luleå, SE
(accredited to ISO/IEC 17025 for measurements of metals in freshwater, SWEDAC No 07-213-51.1056)

- Stability studies

DVGW-Technologiezentrum Wasser, Karlsruhe, DE
(accredited to ISO/IEC 17025 for measurements of metals in groundwater, DACH DAC-PL-0142 -01-10)

- Characterisation analyses (in alphabetical order)

Bayer Antwerpen NV, Centraal Laboratorium, Antwerpen, BE
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Consiglio Nazionale delle Ricerche, Istituto di Ricerca Sulle Acque, UOS Brugherio, IT

DVGW-Technologiezentrum Wasser, Karlsruhe, DE
(accredited to ISO/IEC 17025 for measurements of metals in groundwater, DACH DAC-PL-0142 -01-10)

EPAL- Empresa Portuguesa das Águas Livres, S.A – Laboratório central, Lisboa, PT
(accredited to ISO/IEC 17025 for measurements of metals in drinking water, IPAC No L0242)

IWW Rheinisch-Westfälisches Institut für Wasser, Mülheim an der Ruhr, DE
(accredited to ISO/IEC 17025 for measurements of metals in groundwater, DGA DAC-PL-0170-02-01)

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- Project management and data evaluation

European Commission, Joint Research Centre, Institute for Reference Materials and Measurements (IRMM), Geel, BE
(accredited to ISO Guide 34, Belac No 268-TEST)

3. Time schedule

Sampling	April 2007
Processing	October 2007
Homogeneity	June 2008
Short-term stability	September 2008
Long-term stability	March 2010
Characterisation	August 2009

4. Sampling of the material

The site chosen for the sampling was a locked well located in Bree, North-East Limburg, Belgium. The place was carefully selected (with respect to water composition and discharge) through the Databank Ondergrond Vlaanderen, a database containing information on all wells belonging to the Flemish groundwater monitoring network, under the responsibility of the water division of Vlaamse Milieumaatschappij (VMM, Flemish Environment Agency).

The sampling was carried out by an IRMM team with the logistical support and under the supervision of representatives of the water division of VMM. The protocol of good water sampling as laid down by the Openbare Vlaamse Afvalstoffenmaatschappij (OVAM, Public Waste Agency of Flanders) was followed.

One pre-cleaned polyethylene drum of 200 L was filled with the aid of a frequency-regulated pump. The PTFE tubes and the in-line filter (Versaflow^{TM} Capsule containing a 0.45 µm Versapor® Membrane with pre-filter 8 µm PN 12131, Pall Corp, Port Washington, NY, US) were extensively flushed to avoid external contamination before starting with the water collection into the drum. The sampling depth was about 27 meters and the water was collected with a speed of about 5 L/min. The water bulk was acidified immediately upon collection with 200 mL concentrated HNO_3 (Suprapur, Merck, Darmstadt, DE) to pH ~2. The drum was then stored at +4 ºC in the dark at IRMM premises until further processing took place.

5. Processing of the material

5.1 Preparation steps

From the first container, the bulk water was pumped via an in-line filter (AcroPack^{TM} 1000, Supor® Membrane 0.8/0.2 µm PN 12992, Pall Corp, Port Washington, NY, US, offering also bacterial retention) to another pre-cleaned drum. The drum, the PTFE tubes and PTFE-paddle used for homogenisation were all previously washed with an in-house prepared solution ~2 % (volume fraction) of concentrated HNO_3 (Suprapur, Merck, Darmstadt, DE) and subsequently extensively rinsed with de-ionised water (18.2 µS/cm). For cleaning of the drum, a Turbula mixer (Turbula T-200, W.A.B, Basel, CH) was employed. The tubes and filter were also "conditioned" with the groundwater for few minutes, before starting the collection into the second drum intended to be used for spiking and homogenisation of the bulk water.

The hand-made borosilicate ampoules of 100 mL were checked for blank levels regarding the seven trace elements to be certified. The ampoules were left in contact with an in-house prepared solution ~2 % (volume fraction) of concentrated HNO_3 (Suprapur, Merck, Darmstadt, DE) for different periods of time (1, 7 and 25 days). The leaching solutions were measured in-house by ICP-QMS (Agilent 7500ce, Agilent Technologies, Santa Clara, USA) and showed a small contribution of lead (about 0.2 µg/L). The measurements of the acid solutions used for a simple rinsing of the ampoules (without any leach period) showed also comparable concentrations, leading to the conclusion that a simple short rinse would be sufficient to keep the possible contamination down to acceptable levels. To confirm this conclusion, ampoules were filled with an in-house prepared solution ~2 % (volume fraction) of concentrated HNO_3 (Suprapur, Merck, Darmstadt, DE), emptied after approximately 1 minute and left to dry overnight in a drying cabinet. The next day the ampoules were rinsed once again with freshly prepared solution ~2 % (volume fraction) of concentrated HNO_3 (Suprapur, Merck, Darmstadt, DE) and this rinse solution was analysed. The measured level of lead was about 0.08 µg/L, which was considered to be a negligible contribution to the envisaged target lead concentration of about 7 µg/L.

The ampoules to be used for ERM-CA615 were consequently first washed with an in-house prepared solution ~2 % (volume fraction) of concentrated HNO_3 (Suprapur, Merck, Darmstadt, DE), subsequently rinsed with ultra-pure water (18.2 µS/cm), dried overnight in a cabinet at 60 ºC (Elbanton, Kerkdriel, NL) and kept in the oven at 30 ºC until the filling with the groundwater took place.

5.2 Spiking, homogenisation and ampouling

A preliminary characterisation of the water, with regard to the parameters to be certified, was performed to find out if spiking was necessary to obtain the target levels of the analytes.

Following these preliminary analyses, spiking with the ICP Standards $Hg(NO_3)_2$, $Cd(NO_3)_2$ and $Pb(NO_3)_2$ (Certipur, Merck, Darmstadt, DE, solutions in HNO_3) was performed to increase the concentrations of Hg, Cd and Pb to about 0.04, 0.1 and 7 µg/L, respectively. These target levels were decided on the basis of the EQSs, which are set to 0.05 µg/L for Hg, 0.08 µg/L for Cd and 7.2 µg/L for Pb. The spiking was performed after the 0.8/0.2 µm filtration (see Section 5.1) and was followed by homogenisation with a PTFE-paddle for about five hours.

Quantities of about 97 mL of water were subsequently filled into 100 mL borosilicate glass ampoules. The head-space was flushed with argon before flame-sealing of the ampoules, using an automatic ampouling machine (ROTA R910/PA, Wehr-Baden, DE).

Subsequently, labelling of 1838 units took place.

During labelling, the presence of white flakes was noticed in some of the ampoules. They showed a maximum size of about 1 mm. The flakes were analysed at IRMM by means of electron microscopy, i.e. secondary electron imaging (Quanta 200/3D SEM/FIB, FEI Instruments, Eindhoven, NL) and X-ray Energy-Dispersive Spectrometry (EDX, INCA

Energy+ system, Oxford Instruments, Abingdon, UK). Based on the qualitative results acquired, C and O were the main elements detected in the flakes. The organic origin could also be deduced from the observed degradation due to the electronic beam. The comparison of the EDX spectra of a flake positioned on the C-tape substrate and of the substrate only could give an indication of presence of Cl, Ca, Si and Fe in the flake. None of the target elements were detected in the flakes, with the exception of Fe (which is anyway present in the water at the rather high concentration of ~5 mg/L). As additional information, the EDX detection limits quoted in literature (no validation of these limits was performed for the results presented here) vary form 0.05 to 0.2 % (mass fraction) for heavy elements, above the levels of all the target elements except Fe (~5 mg/L) and Mn (~100 µg/L).

It is not inconceivable that dissolved humic acids present in the water could precipitate upon acidification. The white flakes could therefore be precipitated humic acids. Since humic acids are known to be naturally occurring ligands for many elements, it could not be excluded that the flakes could have a negative impact on the homogeneity for some or even all target elements. Therefore it was decided to investigate the material homogeneity measuring non–filtered as well as filtered samples (see Section 6). The evaluation of the homogeneity data showed that the possible presence of flakes in the water did not lead to any undesirable effect. Nevertheless, it was decided later on to remove all ampoules with visible flakes from the batch available for distribution.

5.3 Sterilisation

The water in the closed ampoules of candidate certified reference material ERM-CA615 was sterilised by γ-irradiation with a ^{60}Co source, minimum dose 25 kGy. The irradiation caused the expected change in colour of the transparent borosilicate glass to amber. After this step, the ampoules were stored at 18 ºC in the dark.

6. Homogeneity

With the aim of checking the homogeneity of the material with regard to the parameters to be certified and because of the presence of flakes in a small fraction of the ampoules of the batch produced, 20 units (10 of which containing visible particles) were selected, taking care that the complete batch was covered. The samples were analysed in duplicate, filtered and unfiltered, for arsenic, cadmium, iron, lead, manganese, mercury and nickel. This was done to compare the results obtained with and without filtration, to find out any possible significant difference. The measurements were performed under repeatability conditions, i.e. during one analytical run and using validated methods and according to a random sequence to permit distinction between possible trends in the analytical sequence and in the filling order. Quality control (QC) samples and blank samples were analysed within the sequence. All measurements were performed by ICP-SFMS.

The average of the results after the filtration step and the average of the results without filtration were compared by mean of a *t*-test for significant difference, with $t_{\alpha,\mathrm{df}}$ being the critical *t*-value (two-tailed) for a significance level $\alpha = 0.05$ (95 % confidence interval). For Fe, As, Cd, Mn and Pb, the two means were not found to be significantly different and therefore it was decided to pool all results for the assessment of homogeneity. In the case of Ni and Hg, however, the two averages were found to be significantly different from each other. For these two elements, the datasets of unfiltered samples were chosen to be used for the evaluation of homogeneity because further contributions to the final uncertainty (from long-term stability and characterisation) will also be estimated on the samples analysed without filtration.

The 80 results of Fe, As, Cd, Mn and Pb and the 40 results of Ni and Hg were evaluated by one-way analysis of variance (ANOVA). The unimodal distribution of data is an important prerequisite in order to apply the statistical evaluation ANOVA, therefore the distributions of sample averages as well as individual results were checked both for normal distribution employing normal probability plots and for unimodality with histograms. For all analytes, the individual results and ampoule averages followed an approximately normal and unimodal distribution, with the exception of the ampoule averages for cadmium and the individual values for mercury, for which a slightly bimodal distribution could be discerned. This minor deviation from unimodality was judged not to grossly affect the estimate of the between-units standard deviation.

Data were also checked for presence of trends and outliers.

For nickel a trend towards lower values was observed in the filling sequence, both at 95 and 99 % confidence level.

One outlying individual result was found for arsenic (Grubbs single test at $\alpha = 0.05$ and 0.01) and for iron (Grubbs single test at $\alpha = 0.05$). Two outlying individual results were found for manganese (Grubbs double test at $\alpha = 0.05$).

One outlying sample average was found for lead (unit 1675) and one for nickel (unit 55), (for both Grubbs single test at $\alpha = 0.05$ and 0.01, see Annex 1) both caused by a single outlying measurement. This might be equally due to a measurement problem or to a heterogeneity issue.

Since no technical reasons were identified for the outlying results, all data were retained for statistical analysis.

In the case of presence of trends and of outlier averages, however, the evaluation by ANOVA could be not the most appropriate and therefore an alternative approach for the estimation of the heterogeneity was followed, see Equations (4) and (5) below.

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

$$s_{wb} = \sqrt{MS_{within}} \qquad \text{Equation (1)}$$

MS_{within} = mean squares within-bottle

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

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

$MS_{between}$ = mean squares between-bottle
n = number of replicates per bottle

When $MS_{between}$ is smaller than MS_{within}, s_{bb} can not be calculated. Instead, u^*_{bb}, the heterogeneity that can be hidden by the method repeatability, is calculated, according to the following expression [11]:

$$u^*_{bb} = \frac{s_{wb}}{\sqrt{n}} \sqrt[4]{\frac{2}{\nu_{MSwithin}}} \qquad \text{Equation (3)}$$

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

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

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

$\overline{y}$ = average of all results

For nickel, for which a trend in the filling sequence was detected as well, the between-bottle heterogeneity was modelled using the half-width of a rectangular distribution between the highest and lowest bottle average:

$$u_{rect} = \frac{|\text{highest result - lowest result}|}{2 \cdot \sqrt{3}}$$ Equation (5)

The very high u_{bb} estimated for nickel (16.0 % and 16.7 %, with Equations 4 and 5, respectively) raised concerns about the validity of these results. The presence of very high values in the data (e.g. measurements of 41.8 and 35.7 µg/L, see Annex 1) was further not observed either in the stability datasets (both short-term and long-term) or in the characterisation exercise.

For this reason it was decided to re-evaluate the homogeneity for nickel using the short-term stability data (a total of 42 results corresponding to 14 samples, analysed in triplicate, see Section 8.1). These data showed a trend both in the analytical and in the filling sequence towards lower values. Results were corrected for their trend in the analytical sequence as shown below:

corrected result = measured result – $(b \cdot i)$ Equation (6)

b = slope of the linear regression
i = position of the result in the analytical sequence

After correction for the trend in the analytical sequence still a trend in the filling sequence remained, therefore between-bottle heterogeneity was finally estimated using Equation (5) applied to the short-term stability data.

For the parameters for which ANOVA was applied, the larger value of s_{bb} or u^*_{bb} is taken as uncertainty contribution for homogeneity, u_{bb}. u_{rect} will be taken as u_{bb} for lead and nickel (Table 1).

Table 1. Results of the homogeneity study

	mean value	unit	$s_{wb,rel}$ [%]	$s_{bb,rel}$ [%]	$u^*_{bb,rel}$ [%]	$u_{rect,rel}$ [%]	$u_{bb,rel}$ [%]
arsenic	9.30	µg/L	3.1	$MS_{between}<MS_{within}$	0.7	-	0.7
cadmium	0.103	µg/L	3.8	0.6	0.8	-	0.8
iron	5.06	mg/L	3.2	$MS_{between}<MS_{within}$	0.7	-	0.7
lead	6.97	µg/L	-	-	-	2.2	2.2
manganese	108.4	µg/L	3.9	1.6	0.8	-	1.6
mercury	0.037	µg/L	6.1	4.5	2.4	-	4.5
nickel	24.6[1]	µg/L	-	-	-	0.5[1]	0.5

[1] mean value and u_{rect} calculated using the data from the short-term stability study

The relatively large spread observed for mercury, giving u_{bb} of 4.5 %, was nevertheless judged to be an acceptable contribution to the final uncertainty budget of the certified value. The occurrence of $MS_{between} < MS_{within}$ (for two analytes) could be an indication that material heterogeneity is smaller than it can be detected by the analytical methodology used. Even with retention of outliers, the between-unit variation is generally low (maximum around 2 %), with the mentioned exception of mercury. All data used for the evaluation of homogeneity can be found in Annex 1.

7. Minimum sample intake

The establishment of the minimum sample intake, *i.e.* the minimum subsample representative of the whole ampoule, was not specifically addressed due to the nature of the material itself (water). Even the heterogeneity of solutions is known to be very small if not negligible.

Nevertheless, minimum sample intake is defined as the smallest amount of sample for which homogeneity has been demonstrated through the obtainment of a technically valid set of results accepted for the characterisation. These amounts are the following: 20 µL for Ni, Mn, Pb, Cd and As, 50 µL for Fe and 6 mL for Hg.

8. Stability studies

8.1 Set-up of stability studies

Stability studies are conducted to establish both dispatch conditions (short-term stability) as well as storage conditions (long-term stability).

The two principal means of stabilisation of the water for long-term perspective were the creation of an inert atmosphere by flushing argon within the ampoule just before flame sealing and the sterilisation by exposing the ampoules to an autoclaving process (see Section 5.3).

For performing the stability studies according to the planned tested temperatures and time points, 28 ampoules were required for the short-term stability (14 for Hg measurements and 14 for the remaining parameters) and 16 ampoules were required for the long-term stability schemes, selected by random stratified sampling from the entire batch produced. For the stability studies, it was decided not to ask for measurements of filtered samples with the intention to establish certified values valid for the water analysed without any filtration step. This is also specified in the "Instructions for use and intended use" section of the certificate.

The measurements were performed by ICP-QMS for arsenic, cadmium, lead and nickel, by ICP-OES for iron and manganese and by CV-AFS for mercury, using standardised and in-house validated methods. The set-up of the studies followed an isochronous scheme [12] as described below:

- Short-term stability

Two ampoules were kept at +18 °C and +60 °C for 1, 2 and 4 weeks, respectively. After these time periods, they were put at +4 °C, the temperature at which two "reference" ampoules were stored. Three analyses per ampoule (non-filtered) were performed under repeatability conditions *i.e.,* all analyses were included in the same analytical run according to a prescribed random sequence.

- Long-term stability

Two ampoules were kept at +18 °C for 4, 8, and 12 months, respectively (1st scheme) and for 8, 16 and 24 months, respectively (2nd scheme). The reference temperature was also +4 °C. Three independent measurements per ampoule (non-filtered) were performed under repeatability conditions.

8.2 Results of stability studies

The results were first grouped and evaluated for each time point and temperature.

Results were screened for single and double outliers by applying the Grubbs test at confidence levels of 95 % and 99 %, respectively. Data were plotted against time and the regression lines were calculated to check for significant trends possibly indicating degradation of the material. The observed slopes were tested for significance using a *t*-test, with $t_{\alpha,df}$ being the critical *t*-value (two-tailed) for a significance level α = 0.05 (95 % confidence interval).

The results for the short-term stability at +18 °C and +60 °C are summarised in Table 2.

Table 2. Short-term stability

	18 °C			**60 °C**		
	outliers	slope significance	$u_{sts,rel}$[%] /week	outliers	slope significance	$u_{sts,rel}$[%] /week
arsenic	-	no	0.2	One (ST, 95 %)	no	0.2
cadmium	-	no	0.7	-	no	0.7
iron	-	no	0.1	-	no	0.1
lead	One (ST, 95 and 99 %)	no	0.1	Two (DT, 95 %)	no	0.2
manganese	-	no	0.1	-	no	0.1
mercury	One (ST, 95 %)	no	0.7	One (ST, 95 and 99 %)	no	0.5
nickel	One (ST, 95 and 99 %)	no	0.2	One (ST, 95 %)	no	0.2

ST = single Grubbs test
DT = double Grubbs test

Outliers were detected at 18 °C and/or at 60 °C for lead, mercury and nickel while for arsenic only one outlying value was found at 60 °C. These were all individual results. No technical reason for exclusion of the outliers could be found, therefore they were retained leading to a conservative estimate of the short-term stability uncertainty. The resulting uncertainty contributions for short-term stability were calculated according to Linsinger *et al.* [13] and were negligible for all analytes (maximum 0.7 % for one week at 60 °C). Because the potential degradation during transport can be considered negligible if compared to the uncertainty of the final certified value, the uncertainty contribution from the short-term stability will not be considered in the final uncertainty budget.

Since no significant slope was observed for any of the elements in the tested conditions, the transport of the material will occur under normal conditions.

The results of the two long-term stability studies at +18 °C (1st scheme lasting 12 months and 2nd scheme lasting 24 months) were combined and evaluated together to obtain more confidence about the assessment of the stability. Since the two datasets (1st scheme and 2nd scheme) were obtained at different points in time, a correction had to be applied. For all parameters, the correction factor was between 1.00 and 1.07. The results are summarised in Table 3 (graphical depictions of the data can be found in Annex 2). The outliers (single values) detected for arsenic, iron, manganese and mercury were kept for the statistical evaluation, in absence of any technical reason justifying their rejection. A tentative removal of these outliers did not result in a significant trend of the data, which means that the estimate of u_{lts} is conservative.

The uncertainty of stability u_{lts} due to storage at 18 °C is estimated for a shelf-life of 2 years and calculated as uncertainty of the slope of the regression line multiplied with the chosen shelf life [13]:

$$u_{lts} = \frac{s}{\sqrt{\sum \left(x_i - \overline{x}\right)^2}} \cdot t_{sl} \qquad \text{Equation (7)}$$

with s being the standard deviation of all 48 individual results of the stability studies, x_i being the time point for each replicate, $\overline{x}$ being the average of all time points and t_{sl} being the pre-defined shelf life (24 months).

For all analytes, the standard uncertainty introduced by the long-term stability at +18 °C (recommended storage temperature of the material) for 2 years is low, between 0.2 and 1.6 %.

u_{lts} is included as one of the three contributions to the final uncertainty budget of the certified value. The material will be included in IRMM's regular stability monitoring programme and the shelf life of the material will be confirmed based on these results.

Table 3. Long-term stability

	18 °C		
	outliers	slope significance	$u_{lts,rel}$[%] (2 years)
arsenic	One (ST, 95)	no	0.6
cadmium	-	no	1.6
iron	One (ST, 95 and 99 %)	no	0.2
lead	-	no	1.0
manganese	One (ST, 95)	no	0.2
mercury	One (ST, 95)	no	1.3
nickel	-	no	1.0

ST = single Grubbs test

9. Characterisation

9.1 Study design

The characterisation of the material was carried out by a laboratory intercomparison exercise. Laboratories were selected on the basis of expertise in water analysis (with supporting documentation on their measurement capabilities), quality requirements criteria (e.g. successful participation in proficiency testing schemes for the relevant parameters and/or previous characterisation exercises), with accreditation for the specific analysis to be performed considered as an asset. Laboratories were only allowed to use validated methods. Most participating laboratories are accredited to ISO/IEC 17025, and where measurements are covered by the scope of accreditation, the accreditation number is stated in the list of participants (see Section 2). The non-accredited laboratories were asked to provide separate evidences supporting the compliance of their measurements to the quality requirements described in ISO/IEC 17025.

In order to prevent biased results, a number of precautionary measures were taken:

- when possible, completely different and independent analytical methodologies were chosen for the determination of the same parameter (aiming to at least 2 laboratories per method), thus being able to demonstrate the absence of method bias.

- six independent measurements per laboratory were required, meaning that a new sample preparation had to be performed for each measurement. These measurements were prescribed to be spread over two days, to ensure within-laboratory reproducibility conditions.
- to further demonstrate the accuracy and traceability of their data, laboratories were asked to report results of QC samples analysed together with the characterisation samples and were asked to insert blanks in the measuring sequence.
- samples for the characterisation study covered the whole batch produced and were selected using a random stratified sampling scheme.

The two quality control samples received by the laboratories were the certified reference materials BCR-610 (re-labelled as QC1, certified for the mass fraction of As, Cd and Pb) and ORMS-4, National Research of Canada (re-labelled as QC2, certified for mass fraction of Hg).

Laboratories were also asked to provide an estimate of their measurement uncertainty and to describe the approach used to derive the uncertainty budget.

Laboratories received two or three (one additional unit was dispatched to the laboratories analysing mercury) ampoules of candidate certified reference material ERM-CA615: six independent results per each parameter were to be returned. Additionally they received one or two (laboratories analysing mercury) quality control materials, as explained before, for which three replicates were to be provided.

In the guidelines for characterisation measurements, an approximate concentration range for the parameters to be analysed was provided for helping the laboratories in establishing the correct calibration curve.

9.2 Data evaluation and results

A detailed overview of the analytical techniques used by the laboratories for the characterisation of ERM-CA615 is presented in Annex 3, listed per parameter.

Evidences of non-compliance regarding contract review and method validation for one of the laboratories (tags L3 and L12) was obtained between commissioning and receipt of results. Therefore, the results of this laboratory were excluded on quality management grounds regardless of their compliance or non-compliance with the criteria applied in the technical evaluation (see below).

Upon receipt of the datasets, the results were subject to technical evaluation. The results of the QC samples could be directly used to check for presence of significant bias.

Datasets were rejected whenever the laboratory reported a technical problem, when one or both quality control samples results did not agree with the certified values (according to ERM Application Note 1 [15]) and/or the RSD of the measurement results reported for ERM-CA615 exceeded 12 % (quality criterion set considering the required trueness asked in the technical specifications of the characterisation study and the repeatability claimed by the laboratories). A summary of the data evaluation is presented in Table 4.

The following datasets were discarded:

L0: measurement results of mercury rejected because the QC sample result did not agree with the certified value.

L1: measurement results of arsenic rejected because the QC sample result did not agree with the certified value.

L2: measurement results of arsenic rejected because the QC sample result did not agree with the certified value and because the RSD (12.6 %) exceeded the set quality criterion.

L5: measurement results of cadmium rejected because the RSD (15.1 %) exceeded the quality criterion.

L7: measurement results of arsenic rejected because the QC sample result did not agree with the certified value.

L9: measurement results of lead rejected because the QC sample result did not agree with the certified value, measurement results of nickel and mercury rejected because of too high RSD (13.1 and 26.5 %, respectively).

L11: measurement results of arsenic rejected because the QC sample result did not agree with the certified value.

Table 4. Summary of the technical evaluation

	arsenic	cadmium	iron	lead	manganese	mercury	nickel
L0						Discarded QC2 out	
L1	Discarded QC1 out					-	
L2	Discarded QC1 out RSD 12.6 %		-		-	-	-
L4		-		-		-	
L5		Discarded RSD 15.1 %					
L6		-				-	
L7	Discarded QC1 out					-	
L8	-	-		-			
L9				Discarded QC1 out		Discarded RSD 26.5 %	Discarded RSD 13.1 %
L10							
L11	Discarded QC1 out	-				-	
L13	-	Discarded QC1 out	-	-	-	Discarded QC2 out	-
L14	-	-	-	-	-		-
L15	-	-	-	-	-		-
L16	-	-	-	-	-	Discarded RSD 36 %	-
L17	-	-	-	-		-	-

- parameter not analysed

L13: measurement results of mercury and cadmium rejected because the QC sample results did not agree with the certified value.
L16: measurement results of mercury rejected because of too high RSD (36 %).

After this technical scrutiny, all remaining datasets were accepted for further statistical assessment. Eleven datasets from 10 laboratories were accepted for manganese, 10 datasets were accepted for iron, 9 datasets were accepted for nickel, 8 datasets were accepted for lead, 6 datasets were accepted for arsenic and cadmium, 5 datasets were accepted for mercury.

The datasets accepted on technical grounds were tested for outliers using Dixon, Grubbs and Nalimov *t*-test, for normality of means distribution using kurtosis/skewness tests and for outlying variances using Cochran test.

Table 5 shows a summary of the statistical analysis for ERM-CA615, where *s* stands for standard deviation of the distribution of laboratories' means.

Table 5. Statistical evaluation of technically accepted datasets

	number of individual results	outlier mean	normal distribution	*s*	unit
arsenic	36	-	n.a.*	0.72	µg/L
cadmium	39	L2	n.a.*	0.012	µg/L
iron	63	-	yes	0.39	mg/L
lead	51	-	yes	0.53	µg/L
manganese	69	L4	yes	4.91	µg/L
mercury	30	L15	n.a.*	0.001	µg/L
nickel	57	-	yes	1.30	µg/L

* too few datasets for a meaningful outcome

For three of the analysed parameters (cadmium, manganese and mercury), at least one laboratory was flagged as outlying mean result. No technical reason was found for excluding these results. In addition, when considering the associated measurement uncertainty reported by the concerned laboratories, the measured values were found to be not significantly different from the certified value. For these reasons the results were retained for the calculation of the mean and uncertainty of characterisation (u_{char}).

All datasets followed normal distributions. Average and standard deviations were considered therefore as meaningful estimators for the expected value and its variation.

In Table 6 the characterisation results of the groundwater material, expressed as the mean of means of the accepted datasets, are presented. The relative standard error of the mean is used as an estimation of the uncertainty contribution of the characterisation exercise ($u_{\mathrm{char,rel}}$).

Table 6. Characterisation results

	Mean of means	unit	p	$\mathrm{RSD}_{\mathrm{average}}$ [%]	$\mathrm{RSE}_{\mathrm{average}}$ [%] $u_{\mathrm{char,rel}}$
arsenic	9.92	µg/L	6	7.3	3.0
cadmium	0.1057	µg/L	6	11.4	4.7
iron	5.107	mg/L	10	7.7	2.4
lead	7.110	µg/L	8	7.5	2.6
manganese	107.4	µg/L	11	4.6	1.4
mercury	0.0368	µg/L	5	3.7	1.6
nickel	25.27	µg/L	9	5.2	1.7

p = number of accepted datasets

10 Certified values and uncertainties

The certified values of groundwater ERM-CA615 were calculated as the unweighted mean of the means of the accepted datasets (see Table 6). It has to be underlined that the certified values are only applicable to the analysis of the unfiltered material, since all data used for their establishment were gathered from the sample analysed without prior filtration.

The relative combined uncertainty of the certified values of the CRM consists of uncertainties related to characterisation (u_{char}), between bottle heterogeneity (u_{bb}) and long-term storage (u_{lts}) [14].

- u_{char} was estimated as the standard deviation of laboratory means, i.e. $s/\sqrt{p}$ with s and p taken from Table 5 and Table 6.
- u_{bb} was estimated as the larger value of the standard deviation between-units (s_{bb}) and the maximum heterogeneity potentially hidden by method repeatability (u_{bb}^*), or as u_{rect} in the case of lead and nickel (see Table 1).
- u_{lts} was estimated from the combination of 1-year and 2-years long-term stability results at 18 °C projected for a shelf life of 2 years (see Table 3).

These uncertainties were combined quadratically to estimate the relative combined standard uncertainty of the certified value $u_{\mathrm{CRM,rel}}$ according to:

$$u_{CRM,rel} = \sqrt{u_{bb,rel}^2 + u_{lts,rel}^2 + u_{char,rel}^2} \qquad \text{Equation (8)}$$

The relative expanded uncertainty $U_{\mathrm{CRM,rel}}$ is given by the following expression, where $k = 2$ is chosen as coverage factor to provide a confidence level of approximately 95 %:

$$U_{CRM,rel} = k \cdot u_{CRM,rel} \qquad \text{Equation (9)}$$

The absolute expanded uncertainty U_{CRM} is then calculated by rounding up the value obtained multiplying the certified value with the relative expanded uncertainty $U_{\mathrm{CRM,rel}}$.

The various uncertainty contributions, the expanded uncertainties and the certified values are summarised in Table 8.

Annex 4 summarises the results of the characterisation exercise and presents as well a graphical depiction of the assigned values, together with averages and uncertainties of the individual laboratories for arsenic, cadmium, iron, lead, manganese, mercury and nickel with the participating laboratories encrypted by codes.

Table 8. Certified values and uncertainty budget for arsenic, cadmium, iron, lead, manganese, mercury and nickel in ERM-CA615

	$u_{\mathrm{bb,rel}}$ [%]	$u_{\mathrm{lts,rel}}$ [%]	$u_{\mathrm{char,rel}}$ [%]	$U_{\mathrm{CRM,rel}}$ (k=2) [%]	Certified value	U_{CRM} (k=2)	unit
arsenic	0.7	0.6	3.0	6.2	9.9	0.7	µg/L
cadmium	0.8	1.6	4.7	10.0	0.106	0.011	µg/L
iron	0.7	0.2	2.4	5.1	5.11	0.26	mg/L
lead	2.2	1.0	2.6	7.1	7.1	0.6	µg/L
manganese	1.6	0.2	1.4	4.3	107	5	µg/L
mercury	4.5	1.3	1.6	10.0	0.037	0.004	µg/L
nickel	0.5	1.0	1.7	4.0	25.3	1.1	µg/L

11 Additional material information

An additional characterisation for the mass concentration of a number of major components and for pH was performed on ERM-CA615. The results are presented in Table 9 (3 replicates on 3 units in repeatability conditions) and are reported for information purposes only.

Table 9. Additional material information

	Mean value	*s*	unit	Method of determination
ammonium	0.067	0.002	mg/L	Photometry
calcium	32.20	0.08	mg/L	ICP-OES
chloride	40.99	0.14	mg/L	Ion chromatography
magnesium	8.676	0.021	mg/L	ICP-OES
ortho-phosphate	0.053	0.004	mg/L	Photometry
potassium	4.154	0.012	mg/L	ICP-OES
sodium	30.30	0.09	mg/L	ICP-OES
sulfate	33.35	1.23	mg/L	Ion chromatography
pH (20 °C)	1.931	0.002	-	Potentiometry

12 Metrological traceability

Laboratories quantified the analytes using different and independent analytical methodologies, both regarding sample preparation as well as detection principles, with the exception of mercury, for which only cold vapour techniques were used.

The calibrants employed were available pure standards, in-house gravimetrically prepared and/or CRMs, all traceable to the SI. For arsenic, cadmium, iron, lead, manganese and nickel, the agreement between the results confirms absence of any significant method bias and demonstrates the identity of the analytes. For mercury, which characterisation measurements were all based on a single technique, there is no confirmation of absence of method bias, leading to its classification as operationally defined measurand (as obtained by cold vapour techniques).

Only validated methods were used. Agreement with the certified values of the quality control materials further proved absence of significant bias, correctness of the calibration curves and proper calibration of all relevant input parameters.

The realisation of the above-mentioned conditions demonstrates that the certified values are traceable to the International System of Units (SI).

13 Commutability

ERM-CA615 is a natural spiked groundwater. Moreover, the laboratories participating in the characterisation study have been selected such as to provide a large variety of analytical methods, regarding sample preparation, calibration and detection. The agreement between the results obtained, leading to the certification of several parameters, shows that ERM-

CA615 exhibits the same behaviour as a typical laboratory sample and confirms its commutability.

14 Instructions for use and intended use

14.1 Storage conditions

The material shall be stored at +18 °C ± 5 °C in the dark. However, the European Commission cannot be held responsible for changes that happen during storage of the material at the customer's premises, especially of open samples.

14.2 Minimum sample intake

The minimum amount of sample to be used is 20 µL for Ni, Mn, Pb, Cd and As, 50 µL for Fe and 6 mL for Hg.

14.3 Safety precautions

The usual laboratory safety measures apply.

14.4 Intended use

ERM-CA615 is intended for method validation and quality control purposes. The sample must be used without applying any filtration step.

14.5 Use of the certified value

For assessing the trueness of an analytical method, the CRM is analysed by the laboratory and the result is compared to the certified value as described in ERM Application Note 1 [15]. A result is unbiased if the combined uncertainty of measurement and certified value covers the difference between the certified value and the measurement result:

- Calculate the absolute difference between the mean of the CRM measurement results and the certified value (Δ_m).
- Convert the expanded uncertainty of the certified value U_{CRM} into a standard uncertainty (u_{CRM}) by dividing U_{CRM} with the coverage factor $k = 2$.
- Combine the standard uncertainty of the measurement result (u_m) with the uncertainty of the certified value (u_{CRM}) as follows:

$$u_\Delta = \sqrt{u_m^2 + u_{CRM}^2} \qquad \text{Equation (10)}$$

If $\Delta_m < 2 \cdot u_\Delta$, there is no significant difference between the measurement result and the certified value, at a confidence level of about 95 %.

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Annex 1

Homogeneity data for arsenic, cadmium, iron in ERM-CA615

Ampoule number	**Arsenic** (µg/L)				**Cadmium** (µg/L)				**Iron** (mg/L)			
	anal.1	anal.2	anal.3	anal.4	anal.1	anal.2	anal.3	anal.4	anal.1	anal.2	anal.3	anal.4
55	9.35	9.12	9.31	9.39	0.101	0.103	0.104	0.105	5.19	5.06	5.08	5.14
116	9.5	9.43	9.48	9	0.106	0.104	0.107	0.1	4.87	5.28	5.15	5.09
233	9.34	8.95	9.15	9.05	0.11	0.108	0.102	0.106	5.14	4.91	4.95	5.17
299	10.1	9.54	9.53	9.38	0.108	0.105	0.106	0.102	5.37	4.9	4.97	5.2
350	9.48	8.92	9.39	9.24	0.108	0.1	0.107	0.102	5.2	4.99	5.03	4.92
475	9.34	8.77	9.12	9.55	0.102	0.105	0.103	0.107	4.97	5.2	5.08	5.15
585	9.33	9.36	9.37	9.51	0.104	0.107	0.101	0.103	4.92	4.78	4.87	5.09
710	9.16	9.21	9.41	9.29	0.104	0.0986	0.0982	0.101	5.09	4.66	4.94	5.43
778	9.37	8.84	9.28	9.73	0.102	0.0975	0.102	0.108	5.15	5.01	5.16	5.15
890	9.32	8.86	9.18	9.8	0.102	0.102	0.103	0.109	4.98	5.05	4.95	5.08
955	9.27	9.16	9.47	9.49	0.105	0.107	0.109	0.105	5.09	4.94	5.25	5.13
1081	9.58	9.13	9.37	9.39	0.105	0.104	0.106	0.0967	5.11	5.14	5.02	5.18
1130	9.47	9.43	9.5	9.39	0.104	0.104	0.105	0.101	5.02	5.04	5.16	4.9
1187	9.32	9.14	9.32	9.33	0.0996	0.101	0.102	0.0967	4.92	5.06	5.1	5.03
1311	9.44	8.9	9.44	9.41	0.103	0.103	0.11	0.0947	5.15	5.1	4.8	5.37
1430	8.96	9.51	9.34	9.14	0.106	0.107	0.107	0.103	5.1	5.24	5.27	5.24
1554	9.34	9.02	9.32	8.16	0.102	0.1	0.105	0.0928	4.86	5.12	5.16	4.57
1615	9.39	8.41	9.5	9.58	0.106	0.0952	0.107	0.11	5.08	5.07	5.03	5.33
1675	9.59	9.22	9.41	8.56	0.106	0.0997	0.101	0.0938	5.22	4.99	5.12	4.7
1795	9.4	9.6	9.66	9.48	0.104	0.0965	0.112	0.105	4.88	5.24	5.09	4.97

Annex 1 (continued)

Homogeneity data for lead, manganese, mercury and nickel in ERM-CA615

Ampoule number	**Lead** (µg/L)				**Manganese** (µg/L)				**Mercury** (µg/L)		**Nickel** (µg/L)	
	anal. 1	anal.2	anal.3	anal.4	anal.1	anal.2	anal.3	anal.4	anal.1	anal.2	anal.1	anal.2
55	6.92	6.79	6.79	6.91	110	112	110	107	0.031	0.038	30	41.8
116	7.08	6.81	7.01	7.01	114	112	110	106	0.04	0.038	35.7	28.2
233	6.94	6.8	6.8	6.9	110	111	104	111	0.04	0.039	27.2	26.4
299	7.16	6.88	6.9	6.97	114	101	108	108	0.037	0.037	35.7	27.6
350	7.29	7.19	6.94	7	107	105	115	108	0.04	0.038	26.3	26.9
475	6.83	7.07	6.91	7.09	109	117	106	120	0.036	0.037	26	31
585	6.85	6.88	7.01	7.19	108	97.3	110	111	0.037	0.038	30.7	28.5
710	7.22	7.16	7.1	7.11	109	94.4	108	109	0.043	0.043	26.8	25.7
778	6.86	6.97	6.89	7.53	110	100	100	105	0.038	0.036	27.2	26.3
890	6.8	7.08	7	7.08	110	115	105	108	0.037	0.038	26.5	26.5
955	6.78	7.02	7.06	7.04	108	108	110	107	0.039	0.039	27.3	27.1
1081	6.9	6.94	6.93	6.91	107	109	106	108	0.037	0.039	26.4	33.3
1130	6.83	6.93	6.89	7.13	104	105	112	107	0.032	0.035	26.1	26.8
1187	6.97	6.89	6.78	6.86	109	109	105	107	0.039	0.037	26.5	25.7
1311	7.01	7.14	6.83	7.15	110	115	115	113	0.038	0.04	27.5	28.1
1430	6.87	7.24	7.12	7.19	113	107	105	118	0.036	0.032	27.4	28.1
1554	7.02	7.08	7.02	6.45	103	102	104	98.6	0.038	0.04	26.9	26.7
1615	6.99	6.75	7.07	7.22	110	105	112	111	0.032	0.038	27.4	26.1
1675	6.95	6.91	6.84	6.1	110	113	111	104	0.036	0.037	27.1	25.6
1795	6.76	7.13	6.9	6.88	107	110	114	106	0.038	0.03	25.9	27.1

Annex 1 (continued)

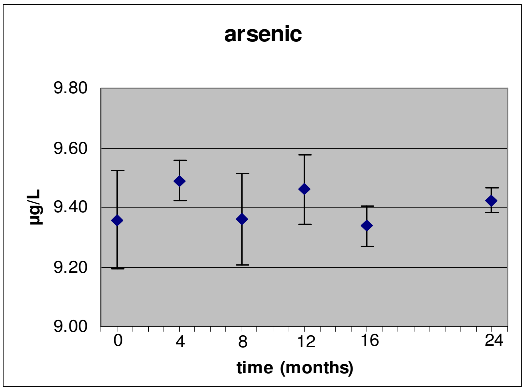
Short-term stability data used for the homogeneity evaluation of nickel in ERM-CA615

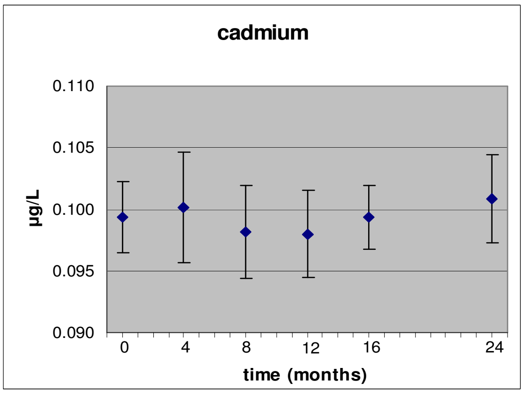
Ampoule number	**Nickel** (µg/L)		
	anal.1	anal.2	anal.3
467	24.7	24.8	25
533	24.8	24.8	24.6
600	24.5	25.4	24.3
671	24.5	24.5	24.7
722	25.3	23.8	24.5
843	24.5	24.5	24.7
856	25.3	23.9	24.8
1429	24.6	24.4	24.7
1448	24.3	24.5	24.6
1508	24.5	24.5	24.7
1618	24.3	24.4	24.6
1666	24.6	24.5	24.5
1737	24.5	24.5	24.6
1762	24.3	24.5	24.5

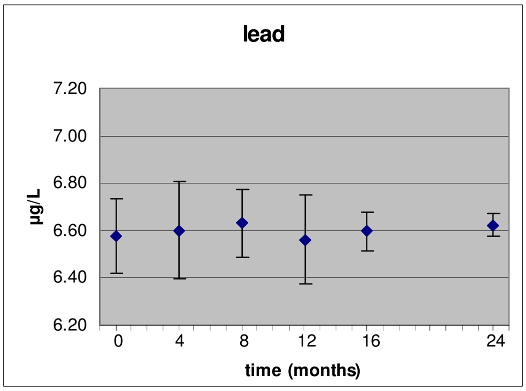
Annex 2

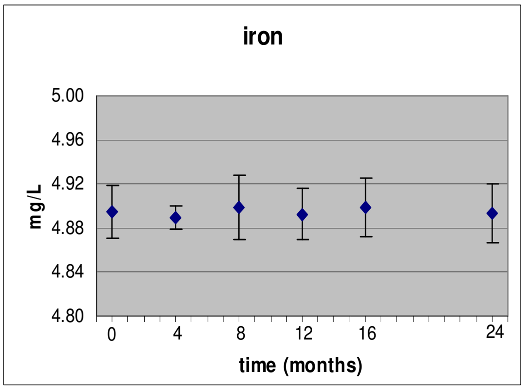
Graphical depictions of long-term stability data for arsenic, cadmium, iron, lead, manganese, mercury and nickel in ERM-CA615

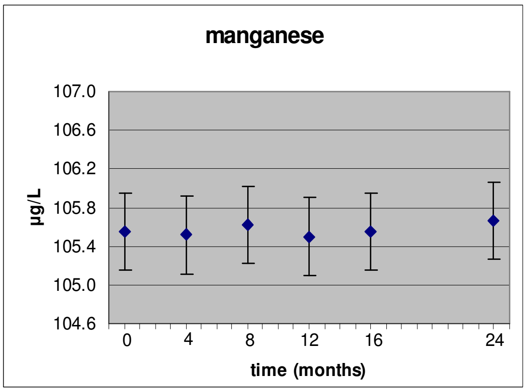
The graphs report ampoule averages per time point and their 95 % confidence intervals based on the standard deviations of the measurements per time (12 for points 0 and 8 months, 6 for points 4, 12, 16 and 24 months).

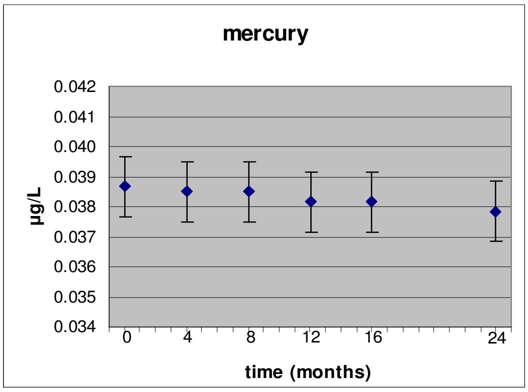


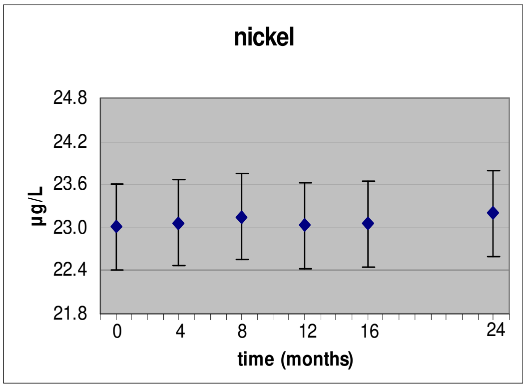












Annex 3
Detailed description of the analytical techniques used in the characterization of ERM-CA615

Arsenic

Lab	*Sample pre-treatment*	*Sample intake*	*Analytical method and determination*	*Calibration: type, points, calibrant*	*LOQ*
L0	none	5 mL	ICP-QMS Collision cell with He Addition of i.s. solution: Ge 20 mg/L, In and Lu 3 mg/L	Linear through zero 1, 20, 50 100 µg/L High purity standard	0.67 µg/L
L3	none	20 µL	ET-AAS Matrix modifier: Pd/$Mg(NO_3)_2$ (2.5 µg / 1.0 µg)	External 0, 5, 10, 15, 20 µg/L Commercially available As_2O_3	1.8 µg/L
L4	25 mL sample+25 mL HCl conc., 1 h reflux. Addition of 10 mL H_2O_2 (30 %) and KI. Making up to 100 mL with MilliQ water	25 mL	HG-ET-AAS Hydride generation with $NaBH_4$/HCl	External 2, 5, 8, 10, 12, 15 µg/L Commercially available H_2AsO_4	0.002 µg/L
L5	none	1.5 mL	ICP-QMS Collision cell with He	External calibration 1, 2, 3, 4, 5, 10, 20 µg/L Commercially available ICP As standard	1 µg/L
L6	Dilution 50x	0.2 mL	ICP-QMS Poliatomics of chlorides correction Use of Y, In and Bi as i.s.	Linear 0.050, 0.100, 0.150, 0.250, 0.350, 0.400 µg/L Commercially available solution	0.050 µg/L
L9	Dilution 2x	1 g	ICP-QMS No interferences detected	External 0.1, 0.5, 1, 5, 10, 50 µg/L Commercially available standard	0.1 µg/L
L10	Acidification with HNO_3 and addition of i.s.	~5 mL	ICP-SFMS High resolution mode m/Δm 10000	Linear 0, 10 µg/L (checking of linear range with control sample of 50 µg/L) Commercially available multi element standard	0.05 µg/L
L12	10 mL aliquot was made up to 25 mL with 50 % KI, 10 % ascorbic acid and 3 M HCl	10 mL	HG-AFS Pre-reduction of As(V) to As (III), hydride generation by 0.7 % $NaBH_4$/0.1 M NaOH	External 0, 1, 2, 3, 4, 5 µg/L Commercially available As_2O_3	0.6 µg/L

Cadmium

Lab	*Sample pre-treatment*	*Sample intake*	*Analytical method and determination*	*Calibration: type, points, calibrant*	*LOQ*
L0	none	5 mL	ICP-QMS Collision cell with He i.s. solution: Ge 20 mg/L, In and Lu 3 mg/L	Linear through zero 0.1, 2.5, 10 µg/L High purity standard	0.1 µg/L
L1	none	20 µL	ET-AAS Matrix modifier: $NH_4H_2PO_4$+$Mg(NO_3)_2$	Linear 0, 2.5, 5 µg/L Commercially available mixed standard	0.03 µg/L
L2	UV digestion of the acidified sample (HCl 0.01 M)	Between 4.03 and 8.14 g	ASV Mercury drop electrode	Internal standard addition 3 points (2, 3 and 4 times the initial Cd concentration) Commercial available solution	0.003 µg/L
L3	none	20 µL	ET-AAS Matrix modifier: Pd/NH_4NO_3 mixture (2.5 µg / 25 µg)	Linear 0, 0.5, 1, 1.5, 2 µg/L $Cd(NO_3)_2$	0.06 µg/L
L7	none	2 mL	ICP-SFMS Low resolution mode I.s. solution: In 1 µg /L	External linear 0, 10, 20, 50, 100, 250, 500, 750, 1000 ng/L Commercially available multi-element standard solution	0.1 ng/L
L9	Dilution 2x	3 g	ICP-QMS No interferences detected	External 0.1, 0.5, 1, 5, 10, 50 µg/L Commercially available standard	0.004 µg/L
L10	Acidification with HNO_3 and addition of i.s.	~5 mL	ICP-SFMS Low resolution mode m/Δm 400	Linear 0, 10 µg/L (checking of linear range with control sample of 50 µg/L) Commercially available multi element standard	0.05 µg/L

Iron

Lab	*Sample pre-treatment*	*Sample intake*	*Analytical method and determination*	*Calibration: type, points, calibrant*	*LOQ*
L0	none	5 mL	ICP-OES i.s. solution: Yb 100 mg/L	Linear through zero 0.05, 1, 5, 10 mg/L Fe(III)nitrate in nitric acid Suprapur®	0.012 mg/L
L1	none	2 mL	F-AAS	Linear 0, 2, 5, 10 mg/L Commercially available solution	0.078 mg/L
L4	none	5 mL	ICP-OES	External, linear, 4 points including blank 2, 4, 8 mg/L $Fe(NO_3)_2$	0.025 mg/L
L5	none	1.5 mL	ICP-QMS Collision cell with He	External calibration 100, 200, 300, 400, 500, 1000, 2000 µg/L (checking of linear range with control sample of 10000 µg/L) Commercially available ICP Fe standard	60 µg/L
L6	Dilution 50x	1 mL	ICP-OES	Linear 0.0200, 0.0400, 0.0600, 0.0800, 0.1200, 0.160 mg/L Commercially available solution	0.020 mg/L
L7	none	2 mL	ICP-SFMS Medium resolution mode, $m/\Delta m > 4000$ i.s. solution: In 1 µg /L	External linear 0, 0.1, 0.2, 0.5, 1, 2.5, 5, 7.5, 10 µg /L Commercially available multi-element standard solution	2.3 µg/L
L8	Dilution 5x	12 mL	ICP-OES	External 0, 2.5 mg/L Commercially available custom-made standard	0.006 mg/L
L9	Dilution 100x	0.1 g	ICP-QMS Collision cell	External calibration 5, 10, 50, 100 µg/L Commercially available standard	0.08 µg/L
L10	Acidification with HNO_3 and addition of i.s.	~5 mL	ICP-SFMS Medium resolution mode, $m/\Delta m$ 4000	Linear 0, 1000 µg/L (checking of linear range with control sample of 5000 µg/L) Commercially available multi element standard	10 µg/L
L11	Acidification with 0.3 ml HNO_3 (65 % suprapur) per 15 mL sample	0.05 mL	ICP-OES	2nd order 0.02, 0.05, 0.1, 0.2, 0.5, 1, 2.5, 5, 10 mg/L Commercially available standard	0.010 mg/L

Lead

Lab	*Sample pre-treatment*	*Sample intake*	*Analytical method and determination*	*Calibration: type, points, calibrant*	*LOQ*
L0	none	5 mL	ICP-QMS Collision cell with He i.s. solution: Ge 20 mg/L, In and Lu 3 mg/L	Linear through zero 1, 20, 50, 100 µg/L High purity standard	0.37 µg/L
L1	none	20 µL	ET-AAS Matrix modifier: $NH_4H_2PO_4$+$Mg(NO_3)_2$	Linear 0, 20, 40 µg/L Commercially available mixed standard	0.3 µg/L
L2	UV digestion of the acidified sample (HCl 0.01 M)	Between 4.03 and 8.14 g	ASV Mercury drop electrode	Internal standard addition 3 points (2, 3 and 4 times the initial Pb concentration) Commercial available solution	0.02 µg/L
L5	none	1.5 mL	ICP-QMS Collision cell with no gas	External calibration 2, 4, 6, 8, 10, 20, 40 µg/L Commercially available ICP Pb standard	2 µg/L
L6	Dilution 50x	0.2 mL	ICP-QMS Sum of ^{206}Pb, ^{207}Pb and ^{208}Pb isotopes Use of Y, In and Bi as i.s.	Linear 0.050, 0.100, 0.150, 0.250, 0.350, 0.400 µg/L Commercially available solution	0.050 µg/L
L7	none	2 mL	ICP-SFMS Low resolution mode I.s. solution: In 1 µg /L	External linear 0, 10, 20, 50, 100, 250, 500, 750, 1000 ng/L Commercially available multi-element standard solution	6.5 µg/L
L10	Acidification with HNO_3 and addition of i.s.	~5 mL	ICP-SFMS Low resolution mode m/Δm 400	Linear 0, 10 µg/L (checking of linear range with control sample of 50 µg/L) Commercially available multi element standard	0.5 µg/L
L11	Acidification with 1.0 mL HNO_3 (65 % Suprapur) per 100 mL sample	40 µL	ET-AAS	2nd order 0.005, 0.01, 0.02 mg/L Commercially available standard solution, Certipur	0.002 mg/L

Manganese

Lab	*Sample pre-treatment*	*Sample intake*	*Analytical method and determination*	*Calibration: type, points, calibrant*	*LOQ*
L0	none	5 mL	ICP-OES I.s. solution: Yb 100 mg/L	Linear through zero 0.05, 1, 2.5, 5 µg/L Mn(II)nitrate in nitric acid Suprapur®	0.7 µg/L
L1	none	2 mL	F-AAS	Linear 0, 0.5, 1, 2 mg/L Commercially available solution	0.024 mg/L
L4	none	5 mL	ICP-OES	External, linear, 4 points including blank 50, 100, 200 µg/L $Mn(NO_3)_2$	0.005 mg/L
L5	none	1.5 mL	ICP-QMS Collision cell with He	External calibration 100, 200, 300, 400, 500, 1000, 2000 µg/L Commercially available ICP Mn standard	50 µg/L
L6	Dilution 4x	3 mL	ICP-OES	Linear 0.00500, 0.0100, 0.0150, 0.0200, 0.0300, 0.0400 mg/L Commercially available solution	0.0050 mg/L
L7	none	2 mL	ICP-SFMS Medium resolution mode, m/Δm > 4000 I.s. solution: In 1 µg /L	External linear 0, 10, 20, 50, 100, 250, 500, 750, 1000 ng/L Commercially available multi-element standard solution	0.03 µg/L
L8	none	12 mL	ICP-OES	External 0, 2.5 mg/L Commercially available custom-made standard	0.2 µg/L
L9	Dilution 10x	1 g	ICP-QMS No interferences detected	External calibration 0.1, 0.5, 1, 5, 10, 50 µg/L Commercially available standard	0.09 µg/L
L10	Acidification with HNO_3 and addition of i.s.	~5 mL	ICP-SFMS High resolution mode, m/Δm 10000	Linear 0, 100 µg/L (checking of linear range with control sample of 500 µg/L) Commercially available multi element standard	5 µg/L
L11	Acidification	3 mL	ICP-QMS No interferences detected I.s. solution: In 0.1 mg /L	Linear 0.01, 0.02, 0.03, 0.04, 0.05, 0.075, 0.1, 0.15 mg/L Commercially available ICP multi element standard solution Certipur	6.16 µg/L
L17	Dilution 10x	20 µL	ET-AAS Matrix modifier: Pd+ $Mg(NO_3)_2$	Linear 0, 0.005, 0.010, 0.020 mg/L Commercially available mixed standard	0.0015 mg/L

Mercury

Lab	*Sample pre-treatment*	*Sample intake (mL)*	*Analytical method and determination*	*Calibration: type, points, calibrant*	*LOQ*
L5	Addition of 100 µL solution (40 g $K_2Cr_2O_7$/L 10 M HNO_3) to 10 mL sample	10 mL	CV-AAS no pre-concentration	External calibration 0.05, 0.25, 0.5 µg/L (blank included) Commercially available ICP Hg standard	0.01 µg/L
L8	Dilution 1/5 into a solution of 1 % HCl and 0.5 % BrCl reagent for digestion	10 mL	CV-AFS after amalgamation	0, 1, 2, 5, 10, 20 ng/L Commercially available Hg standard	1 ng/L
L10	Acidification with HNO_3, addition of Br_2 vapour, digestion at 45 °C for 2 hs. Removal of excess Br_2 by ascorbic acid. Conversion of ionic Hg to volatile Hg(0) by addition of $SnCl_2$ in a gas/liquid separator.	10 mL	CV-AFS after concentration of Hg(0) with a gold trap	Linear 0, 8, 16, 24, 32, 40 ng/L Commercially available Hg standard	0.5 ng/L
L14	Preservation, oxidation with BrCl solution, reduction with NH_2OH HCl and subsequently with $SnCl_2$ (EPA 1631)	6 mL	CV-AFS after concentration of Hg(0) with a gold trap	External 0, 0.01, 0.02, 0.03, 0.04, 0.05 µg/L Commercially available solution $Hg(NO_3)_2$ in HNO_3	0.005 µg/L
L15	Combined preservation and digestion. 15 mL conc. HCl and 2 mL KBr - $KBrO_3$ reagent is added per 100 mL of samples. Incubation for 30 min. Addition of 100 µL L-ascorbic acid and $SnCl_2$.	23 mL	CV-AFS no pre-concentration	Linear 0, 0.025, 0.050, 0.100 µg/L Commercially available standard	0.030 µg/L

Nickel

Lab	*Sample pre-treatment*	*Sample intake*	*Analytical method and determination*	*Calibration: type, points, calibrant*	*LOQ*
L0	none	5 mL	ICP-QMS Collision cell with He i.s. solution: Ge 20 mg/L, In and Lu 3 mg/L	Linear through zero 1, 20, 50, 100 µg/L High purity standard	0.46 µg/L
L1	none	20 µL	ET-AAS	Linear 0, 0.025, 0.050 mg/L Commercially available mixed standard	0.4 µg/L
L3	none	5 mL	ICP-OES	External 0, 5, 10, 20, 40, 60 µg/L Commercially available $Ni(NO_3)_2$	11.6 µg/L
L4	none	5 mL	ICP-OES	External, linear, 4 points including blank 20, 40, 80 µg/L $Ni(NO_3)_2$	10 µg/L
L5	none	1.5 mL	ICP-QMS Collision cell with He	External calibration 4, 8, 12, 16, 20, 40, 80 µg/L Commercially available ICP Ni standard	4 µg/L
L6	Dilution 50x	0.2 mL	ICP-QMS No interferences detected Use of Y, In and Bi as i.s.	Linear 0.100, 0.200, 0.300, 0.500, 0.700, 0.800 µg/L Commercially available solution	0.1 µg/L
L7	none	2 mL	ICP-SFMS Medium resolution mode, m/Δm > 4000 i.s. solution: In 1 µg /L	External linear 0, 10, 20, 50, 100, 250, 500, 750, 1000 ng/L Commercially available multi-element standard solution	0.022 µg/L
L8	none	12 mL	ICP-OES	External 0, 1 mg/L Commercially available custom-made standard	1 µg/L
L10	Acidification with HNO_3 and addition of i.s.	~5 mL	ICP-SFMS Medium resolution mode, m/Δm 4000	Linear 0, 10 µg/L (checking of linear range with control sample of 50 µg/L) Commercially available multi element standard	0.5 µg/L
L11	Acidification with 1.0 mL HNO_3 (65 % Suprapur) per 100 mL sample	40 µL	ET-AAS	2nd order 0.005, 0.01, 0.025, 0.05 mg/L Commercially available standard solution, Certipur	0.002 mg/L

Annex 4

Characterisation measurement results used in the certification of arsenic, cadmium, iron, lead, manganese, mercury and nickel in ERM-CA615

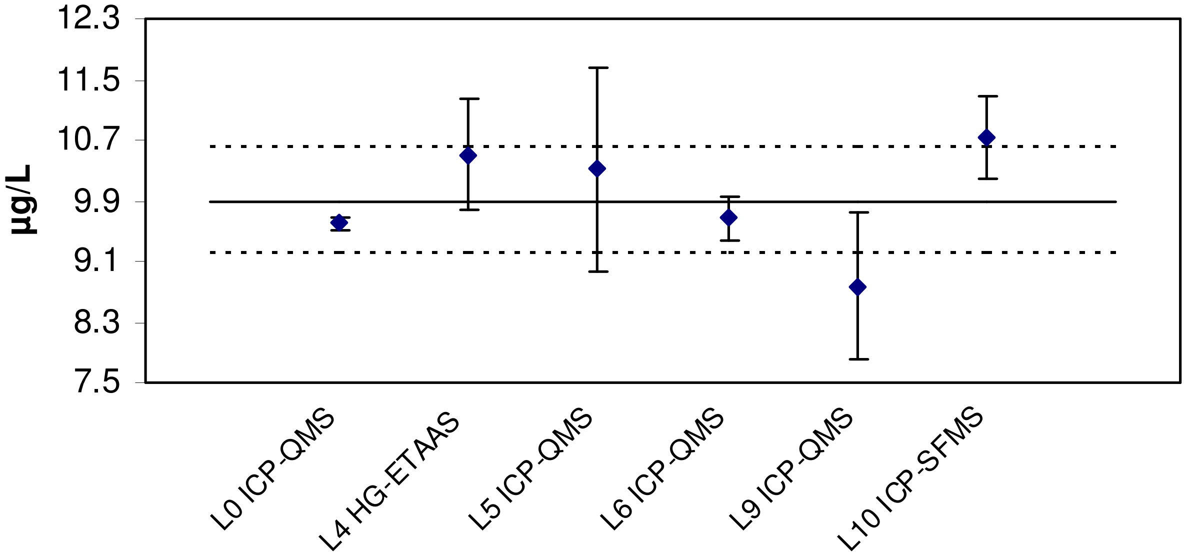
The tables in this annex contain also the datasets that were discarded for technical reasons. These data are presented in *italics* and are given for informative purposes only. They are not reported in the graphs.

Error bars in the graph represent expanded uncertainties as reported by the participating laboratories. Solid line represents the certified value (mean of laboratories' means). Broken lines represent the expanded uncertainty of the certified value.

Arsenic

lab code	Replicates [µg/L]									mean	*U*
L0	9.44	9.26	9.54	9.76	9.91	9.66	-	-	-	9.60	0.17
L1	*10.41*	*9.86*	*11.23*	*9.91*	*11.48*	*11.36*	-	-	-	*10.71*	*0.86*
L2	*6.12*	*6.51*	*6.62*	*6.97*	*7.52*	*8.6*	-	-	-	*7.06*	*0.36*
L4	10.1	10.6	10.8	10.2	10.7	10.3	-	-	-	10.5	1.5
L5	10.1	10.38	10.17	10.22	10.28	10.71	-	-	-	10.31	2.68
L6	9.26	9.74	9.93	9.36	9.77	9.98	-	-	-	9.67	0.58
L7	*12*	*10.9*	*11.2*	*11.9*	*11.3*	*11.4*	*11.7*	*11.6*	*11.3*	*11.5*	*0.8*
L9	7.67	8.26	9.46	7.85	9.72	9.66	-	-	-	8.8	2.0
L10	10.74	10.45	11.83	10.52	10.32	10.56	-	-	-	10.7	1.1
L11	*9.568*	*9.228*	*10.11*	*9.215*	*10.18*	*10.12*	-	-	-	*9.74*	*0.68*

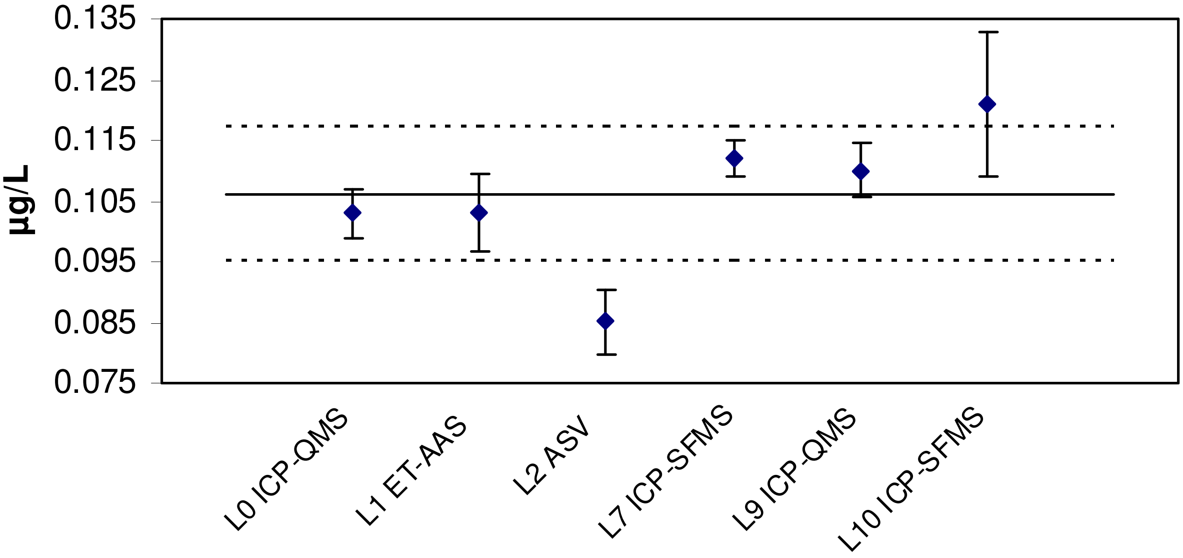
As certified value 9.9 µg/L



Cadmium

lab code	Replicates [µg/L]									mean	*U*
L0	0.105	0.094	0.099	0.096	0.108	0.114	-	-	-	0.103	0.008
L1	0.111	0.107	0.086	0.113	0.106	0.096	-	-	-	0.103	0.013
L2	0.097	0.088	0.076	0.087	0.088	0.075	-	-	-	0.085	0.011
L5	*0.11*	*0.12*	*0.12*	*0.11*	*0.16*	*0.12*	-	-	-	*0.12*	*0.03*
L7	0.115	0.114	0.112	0.114	0.111	0.112	0.112	0.112	0.108	0.112	0.006
L9	0.115	0.113	0.111	0.107	0.103	0.112	-	-	-	0.110	0.009
L10	0.12	0.116	0.126	0.121	0.123	0.119	-	-	-	0.121	0.024
L13	*0.105*	*0.106*	*0.108*	*0.107*	*0.114*	*0.111*	-	-	-	*0.109*	*0.003*

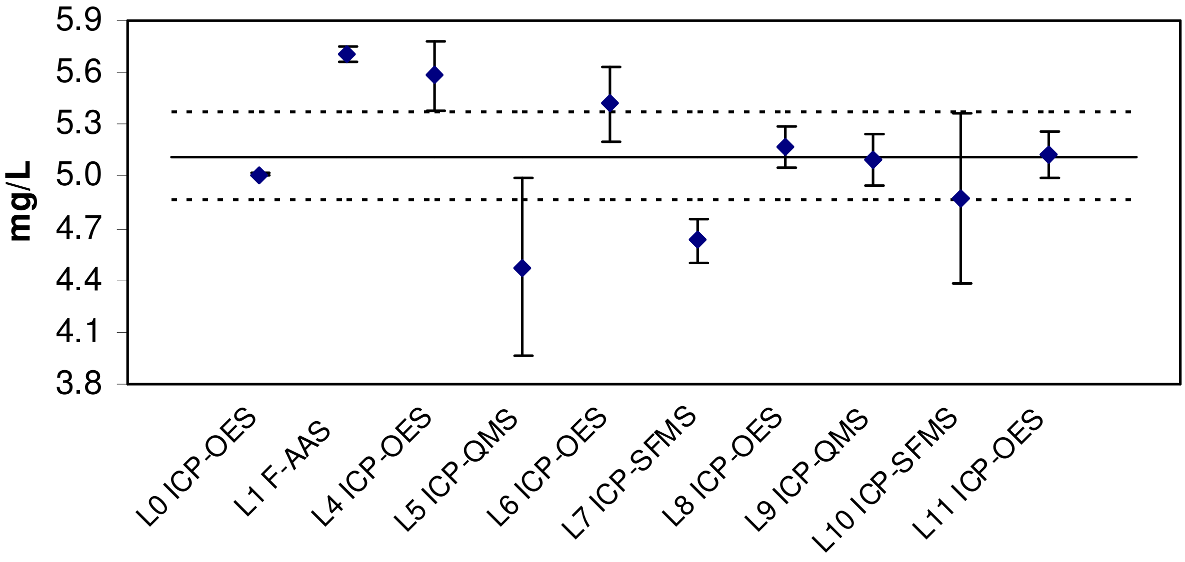
Cd certified value 0.106 µg/L



Iron

lab code	Replicates [mg/L]									mean	*U*
L0	5	5.02	5.01	5.03	4.99	5	-	-	-	5.01	0.02
L1	5.8	5.79	5.65	5.77	5.6	5.66	-	-	-	5.71	0.09
L4	5.58	5.57	5.6	5.59	5.59	5.57	-	-	-	5.58	0.39
L5	4.4	4.447	4.454	4.419	4.499	4.639	-	-	-	4.48	1.03
L6	5.375	5.46	5.37	5.51	5.37	5.415	-	-	-	5.42	0.43
L7	4.67	4.64	4.53	4.74	4.54	4.62	4.67	4.68	4.56	4.63	0.26
L8	5.24	5.23	5.09	5.21	5.11	5.13	-	-	-	5.17	0.23
L9	5.16	4.85	5.08	5.13	5.18	5.08	-	-	-	5.1	0.3
L10	4.978	5.011	4.702	4.828	4.897	4.794	-	-	-	4.87	0.98
L11	5.151	5.158	5.092	5.12	5.111	5.12				5.13	0.27

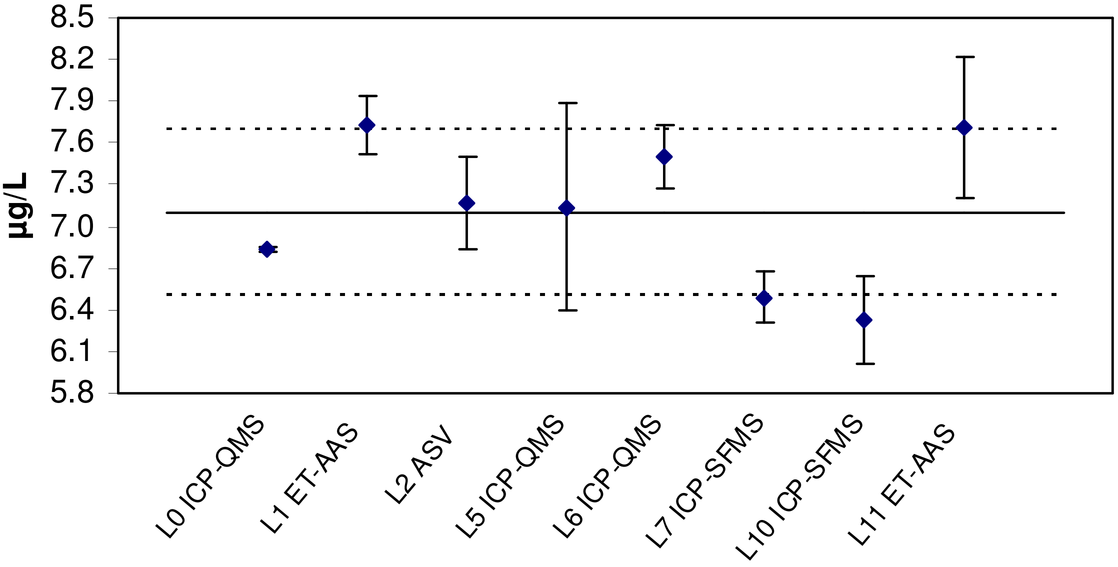
Fe certified value 5.11 mg/L



Lead

lab code	Replicates [µg/L]									mean	*U*
L0	6.8	6.82	6.79	6.85	6.87	6.82	-	-	-	6.83	0.04
L1	7.53	8.34	7.73	7.16	7.86	7.74	-	-	-	7.73	0.41
L2	8.09	7.54	6.71	7.39	6.34	6.95	-	-	-	7.17	0.67
L5	6.61	7.14	7.28	7.08	7.38	7.34	-	-	-	7.14	1.50
L6	7.58	7.58	7.41	7.58	7.36	7.47	-	-	-	7.50	0.45
L7	6.53	6.45	6.44	6.64	6.66	6.48	6.56	6.25	6.41	6.49	0.36
L9	*7.71*	*7.46*	*7.7*	*7.4*	*7.99*	*7.86*	-	-	-	*7.7*	*0.6*
L10	6.25	6.28	6.35	6.27	6.45	6.36	-	-	-	6.33	0.64
L11	7.241	7.558	8.19	7.303	8.008	7.938				7.71	1.01

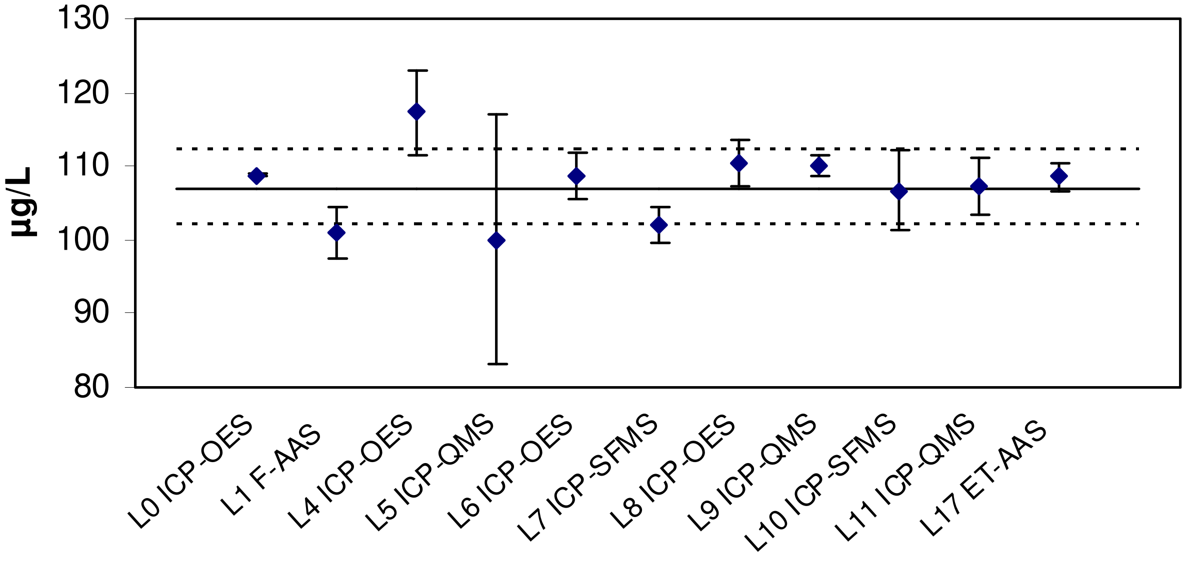
Pb certified value 7.1 µg/L



Manganese

lab code	Replicates [µg/L]									mean	*U*
L0	108.5	109.3	108.6	109	108.4	108.9	-	-	-	108.8	0.5
L1	105	111	98	106	95	93	-	-	-	101	7
L4	118.1	117.2	116.7	118	116.7	117.3	-	-	-	117.3	11.7
L5	97.54	98.87	99.62	98.28	101.2	104.4	-	-	-	99.99	34.00
L6	110.16	108.2	105.92	109.28	108.6	109.84	-	-	-	108.7	6.5
L7	103	102	100	104	103	103	103	102	99	102	5
L8	111.8	111.9	108.6	111.9	109.5	108.9	-	-	-	110.4	6.3
L9	108.9	112.4	110.5	109.5	109	110.9				110	3
L10	107.6	106.7	110.3	107.4	102.5	105.4	-	-	-	106.7	10.7
L11	108	108.6	107.6	106.2	106.7	106.7				107.3	7.5
L17	109.1	107.8	111.8	108	111.1	103				108.5	4.1

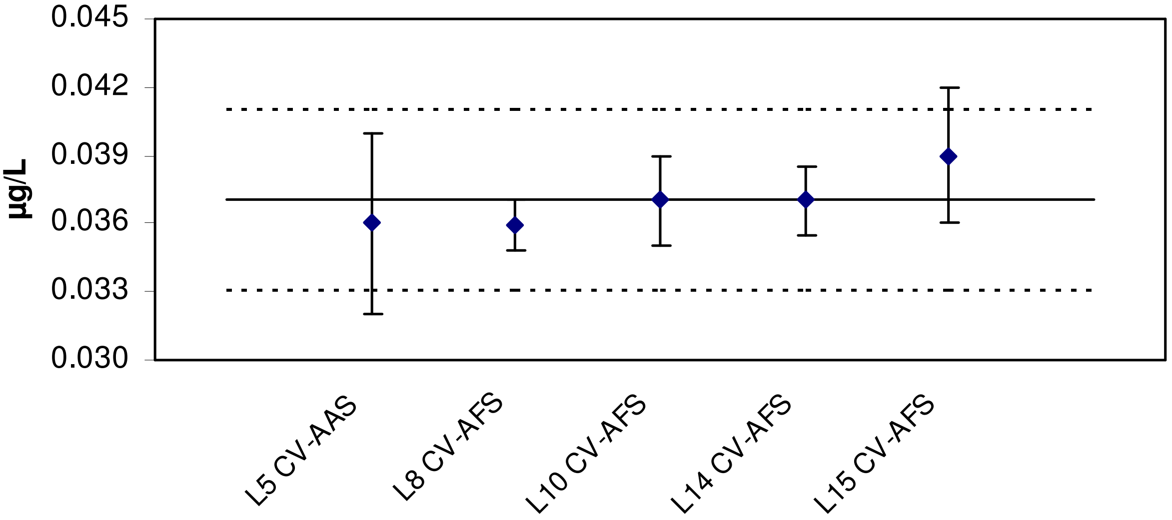
Mn certified value 107 µg/L



Mercury

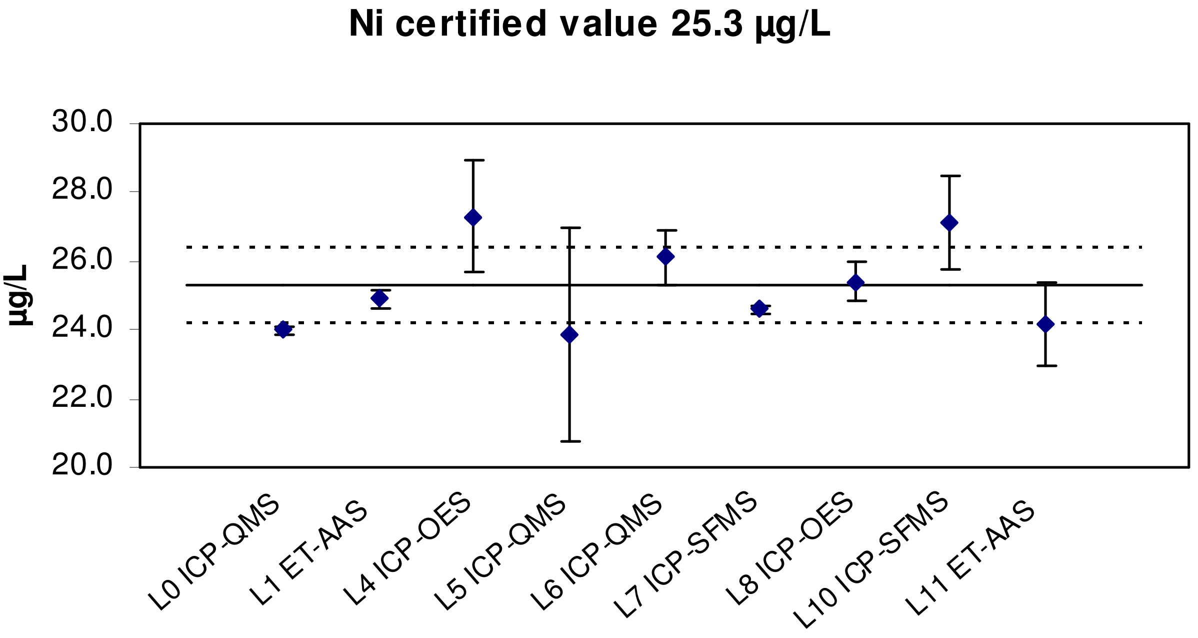
lab code	Replicates [µg/L]						mean	*U*
L0	*0.043*	*0.043*	*0.044*	*0.04*	*0.037*	*0.039*	*0.041*	*0.003*
L5	0.038	0.037	0.034	0.035	0.034	0.035	0.036	0.008
L8	0.0355	0.0342	0.0361	0.0356	0.0369	0.0368	0.0359	0.0022
L9	*0.022*	*0.029*	*0.045*	*0.03*	*0.028*	*0.0405*	*0.03*	*0.02*
L10	0.038	0.038	0.036	0.038	0.035	0.035	0.037	0.004
L13	*0.042*	*0.041*	*0.045*	*0.043*	*0.044*	*0.044*	*0.043*	*0.002*
L14	0.0362	0.0371	0.0364	0.0357	0.0363	0.0405	0.0370	0.0030
L15	0.0393	0.0402	0.0379	0.0399	0.0379	0.0385	0.0390	0.0059
L16	*0.03*	*0.024*	*0.046*	*0.021*	*0.051*	*0.048*	*0.037*	*0.022*

Hg certified value 0.037 µg/L



Nickel

lab code	Replicates [µg/L]									mean	*U*
L0	24.3	24.2	24.1	23.8	23.9	23.8	-	-	-	24.0	0.2
L1	24	24.8	24.9	25.2	24.7	25.5	-	-	-	24.9	0.5
L4	28.2	27.9	27	27.8	26.5	26.6	-	-	-	27.3	3.3
L5	23.2	23.24	23.87	23.19	25.11	24.42	-	-	-	23.84	6.20
L6	25.8	25.8	26.6	25.8	26.2	26.1	-	-	-	26.1	1.6
L7	25.4	24.6	24.2	25.4	24.1	24.7	25.2	24.5	23.6	24.6	0.3
L8	25.3	25.9	25.1	25.8	25.1	25.2	-	-	-	25.4	1.1
L9	*31.85*	*31.7*	*38.5*	*31.4*	*28.3*	*26.5*	-	-	-	*31*	*7*
L10	26.4	26.6	27.6	25.8	28.6	27.6				27.1	2.7
L11	24.6	24.23	23.92	24.26	23.84	24.28				24.19	2.42



European Commission

EUR 24508 EN – Joint Research Centre – Institute for Reference Materials and Measurements
Title: Certification of the Mass Concentrations of Arsenic, Cadmium, Iron, Lead, Manganese, Mercury and Nickel in Groundwater, Certified Reference Material ERM®-CA615
Author(s): M. Ricci, E. de Vos, J. Charoud-Got, H. Emteborg, A. Held
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Abstract

This report presents the preparation and certification of groundwater reference material ERM-CA615. All steps required for the production of this water-matrix reference material are described in detail, from the sampling of natural groundwater to the characterisation exercise that lead to the final assignment of the certified values, following ISO Guide 34:2009 [1] and ISO Guide 35:2006 [2].
Homogeneity and stability of the water material were investigated with dedicated studies and the certification campaign for the material characterisation was based on an inter-comparison involving several experienced laboratories.
IRMM organised and coordinated all phases of this project and carried out the evaluation of data.
The certified values were calculated as the unweighted mean of the laboratory means of the accepted sets of results for each parameter, as seen below. Uncertainties were calculated in compliance with the Guide to the Expression of Uncertainty in Measurement (GUM, ISO/IEC Guide 98-3:2008) [3]. The stated expanded uncertainties include contributions from characterisation, homogeneity and long-term stability.

GROUNDWATER		
	Mass concentration	
	Certified value 2)	Uncertainty 3)
As	9.9 µg/L	0.7 µg/L
Cd	0.106 µg/L	0.011 µg/L
Fe	5.11 mg/L	0.26 mg/L
Hg 1)	0.037 µg/L	0.004 µg/L
Mn	107 µg/L	5 µg/L
Ni	25.3 µg/L	1.1 µg/L
Pb	7.1 µg/L	0.6 µg/L

1) as obtained by cold vapor techniques

2) 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 values and their uncertainties are traceable to the International System of Units (SI).

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

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