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IMEP-40: Determination of trace elements in seawater

*Interlaboratory Comparison
Report*

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Abstract

Fifty-three participants from twenty-nine countries registered to the exercise. Seven participants did not report results. The test item used was a seawater sample containing the trace elements As, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Se and Zn. Laboratories with demonstrated experience in the field provided results to establish the assigned values (X_{ref}). The standard uncertainties associated to the assigned values (u_{ref}) were calculated according to ISO Guide 35. Laboratory results were rated with z- and zeta (ζ -) scores in accordance with ISO 13528. The standard deviation for the proficiency assessment, $\hat{\sigma}$, for all elements was based on the experience in the Water Framework Directive and was set at 25 %. The trace elements were present in very low concentration levels (low $\mu\text{g L}^{-1}$ range equal to natural contamination levels) and therefore many laboratories reported "lower than" values. The percentage of satisfactory z-scores ranged from 41 % (Cr, Fe) to 86 % (Mo). The low concentration levels of the trace elements in a difficult matrix (high saline content) need to be taken into consideration to understand the general low rate of satisfactory scores. Laboratories that score systematically too high should examine the cause of this positive bias.

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Executive summary

The Institute for Reference Materials and Measurements (IRMM) of the Joint Research Centre (JRC), a Directorate-General of the European Commission, operates the International Measurement Evaluation Programme (IMEP). It organises interlaboratory comparisons (ILC's) in support to European Union (EU) policies. This report presents the results of a proficiency test (PT), IMEP-40, on the determination of trace elements in seawater. The exercise was organised in support to the Water Framework Directive 2000/60/EC, which aims at achieving a long-term high level protection of the aquatic environment, covering lakes, ground water and coastal waters.

Fifty-three participants from twenty-nine countries registered to the exercise. Seven participants did not report results.

The test item was seawater containing the trace elements As, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Se and Zn; it was a candidate certified reference material (CRM) produced by IRMM under ISO Guide 34 accreditation and in line with ISO Guide 35. Laboratories with demonstrated experience in the field provided results to establish the assigned values (X_{ref}). The standard uncertainties associated to the assigned values (u_{ref}) were calculated according to the ISO Guide 35 by combining the uncertainty of the characterisation (u_{char}) with a contribution for homogeneity (u_{bb}) and for stability (u_{st}).

Laboratory results were rated with z- and zeta (ζ -) scores in accordance with ISO 13528. The standard deviation for the proficiency assessment, $\hat{\sigma}$, for all elements was based on previous experience in PTs in support to the Water Framework Directive and was set at 25 % of the respective assigned value.

The trace elements were present at very low concentration levels (low $\mu\text{g L}^{-1}$ range, to mimic natural contamination levels) and therefore many laboratories reported "lower than" values (i.e. lower than their limit of detection). A large fraction of the laboratories reported results with a significant positive bias. Only a limited number of laboratories was able to measure at these low concentration levels. The percentage of satisfactory z-scores ranged from 41 % (Cr, Fe) to 86 % (Mo). The low concentration levels of the trace elements in a difficult matrix (high saline content) need to be taken into consideration to understand the general low rate of satisfactory scores. Laboratories that score systematically too high should examine the cause of this positive bias.

1 Introduction

The IMEP-40 study was organised by the International Measurement Evaluation Programme (IMEP) and aimed to assess the world-wide performance of control laboratories on the determination of trace elements in seawater.

The PT supports the implementation of the Water Framework Directive 2000/60/EC (WFD) [1] which aims at achieving a long-term high level protection of the aquatic environment, covering lakes, ground water and coastal waters. With this aim the European Union legislation constitutes a strategy to minimise chemical pollution of surface waters, which includes seawater. The WFD established a List of Priority Substances. The daughter Directive 2013/39/EU [2] lays down the environmental quality standards (EQS) for priority substances and other pollutants with the aim of achieving good chemical status of surface waters. Regarding the trace elements investigated in this study, Maximum Allowable Concentrations in seawater are set for Cd ($0.45 \mu\text{g L}^{-1}$), Pb ($14 \mu\text{g L}^{-1}$) and Ni ($34 \mu\text{g L}^{-1}$) [2].

IMEP-40 was run in 2014 and made use of a candidate reference material (CRM) as test item containing As, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Se and Zn. The candidate reference material was produced under ISO Guide 34 accreditation and in line with the ISO Guide 35 standard [3,4]. Homogeneity and stability studies were carried out by the candidate CRM producer. Assigned values in this study were determined by expert laboratories. Fifty-three laboratories registered for the study of which 46 submitted results.

This report summarizes and evaluates the outcome of IMEP-40.

2 IMEP support to EU policy

IMEP is owned by the JRC – IRMM and provides support to the European measurement infrastructure in the following ways:

IMEP disseminates metrology from the highest level down to routine laboratories. These laboratories can benchmark their measurement result against the IMEP certified reference value which is established according to metrological best practice.

IMEP helps laboratories to assess their estimate of measurement uncertainty. Participants are invited to report the uncertainty on their measurement results. IMEP integrates the estimate into the scoring, and provides assistance for its interpretation.

IMEP supports EU policies by organising interlaboratory comparisons in the frame of specific EU legislation, or on request of a specific EC Directorate-General. IMEP-40 provided specific support to the following stakeholders:

- The European Cooperation for Accreditation (EA) in the frame of a Memorandum of Understanding on a number of metrological issues, including

the organisation of interlaboratory comparisons. National accreditation bodies were invited to nominate a limited number of laboratories for participation in IMEP-40. Mr Richard McFarlane from the United Kingdom Accreditation Service (UKAS) liaised between EA and IMEP for this ILC.

- The Asia Pacific Laboratory Accreditation Cooperation (APLAC) in the frame of collaboration with APLAC. Mrs Cynthia Chen (APLAC PT committee) liaised between APLAC and IMEP, announcing the exercise to the accreditation bodies in the APLAC network.
- The InterAmerican Accreditation Cooperation (IAAC). Mrs Barbara Belzer liaised between IAAC and IMEP, announcing the exercise to the accreditation bodies in the IAAC network.

3 Scope and aim

The scope of this PT was to assess the performance of laboratories world-wide in the determination and quantification of trace elements in seawater.

The assessment of the measurement results followed the administrative and logistic procedures of IMEP, which are accredited according to ISO 17043:2010 [5]. This PT is identified as IMEP-40.

4 Set-up of the exercise

4.1 Time frame

The exercise was announced on the IMEP webpage in June 2014 (Annex 1). Additionally, the exercise was announced to EA, to APLAC and to IAAC. These announcements were made on 5 June 2014 (Annexes 2-4).

Registration was open till 15 August 2014. The sample dispatch was done during the first half of September 2014. The deadline for reporting results was 31 October 2014.

4.2 Confidentiality

The following confidentiality statement was made to EA, IAAC and APLAC: "*Confidentiality of the participants and their results towards third parties is guaranteed.*" In the case of EA the following was added: "*However, IMEP will disclose details of the participants that have been nominated by EA to the EA working group for ILCs in Testing coordinator for this exercise. The EA accreditation bodies may wish to inform the nominees of this disclosure.*"

4.3 Distribution

Test items were dispatched on 8 September 2014. Each participant received one package containing:

- 1 bottle containing approximately 500 ml of the test material,
- The "*Sample accompanying letter*" (Annex 5),
- A "*Confirmation of Receipt*" form to be sent back to IRMM after receipt of the test item (Annex 6).

4.4 Instructions to participants

Participants were asked to perform two or three independent measurements, correct their measurements for recovery and report their calculated mean and its associated measurement uncertainty (u_{lab}).

Participants received an individual code to access the online reporting interface, to report their measurement results and to complete the related questionnaire. The questionnaire was used to extract relevant information related to measurements and laboratories (Annex 7).

Participants were requested that the procedure used for the analysis should resemble as closely as possible their respective routine procedures for this particular matrix, analyte and concentration level.

5 Test material

5.1 Preparation

The test material was a candidate CRM and was produced by IRMM. The raw material for the seawater based reference material was collected at Southern Bight outside the coast of Belgium (North Sea).

On arrival at IRMM, the three tanks with seawater were placed in a refrigerated container at 4 °C and acidified to pH < 2 with ultrapure hydrochloric acid. After acidification, the sample was filtered through a Versaflo 0.8/0.45 µm filter capsule (PALL, VWR, Belgium). The three vessels with filtered water were left to rest for four months in a cooled storage container at 4 °C.

After these four months the seawater was homogenised by re-circulation between holding tanks for several working days corresponding to about 40 full mixing cycles in total. Half-way through homogenisation the seawater base material was spiked with Cd, Cr, Ni and Zn. Liquid reference standards (1000 mg/L, Merck) were used for this purpose. After spiking, recirculation/homogenisation was carried out for another 20 cycles.

Units of 500 ml seawater were filled. The units were labelled according to fill-order. After bottle 0792 was filled, samples for IMEP-40 were filled in every fifth bottle and also labelled according to fill-order.

5.2 Homogeneity and stability studies

As the test item was a candidate CRM, homogeneity and stability studies were performed in line with the ISO Guide 35 standard [4]. Short-term stability data were used and expanded to cover the time between dispatch of the samples and reporting of results (8 weeks).

6 Reference values and their uncertainties

6.1 Assigned value X_{ref}

The assigned values were determined during the certification study of the candidate CRM by a number of expert laboratories. Not all expert laboratories reported results for all the analytes. The results of at least 3 expert laboratories were taken in order to assign the values in this PT. For Se a high variability was observed for both the group of the expert laboratories and the participants to the IMEP-40 study and therefore results for this trace element were not scored. The assigned values X_{ref} for the other trace elements are shown in the Table 1.

6.2 Associated uncertainty u_{ref}

The standard uncertainties (u_{ref}) of the assigned values were calculated combining the uncertainty of the characterization (u_{char}) with the contributions for homogeneity (u_{bb}) and stability (u_{st}) in compliance with ISO Guide 35 [4] Using Eq.1:

$$u_{ref} = \sqrt{u_{char}^2 + u_{bb}^2 + u_{st}^2} \quad \text{Eq. 1}$$

The u_{char} was calculated according to ISO Guide 35 [4]:

$$u_{char} = \frac{s}{\sqrt{p}} \quad \text{Eq. 2}$$

Where s refers to the standard deviation of the mean values obtained by the expert laboratories and p refers to the number of expert laboratories.

The assigned values (X_{ref}), the associated uncertainties (u_{ref}) and uncertainty contributions (u_{char} , u_{bb} , $u_{st,8weeks}$) are summarised in Table 1.

6.3 Standard deviation for the proficiency test assessment $\hat{\sigma}$

The standard deviation for the proficiency assessment, $\hat{\sigma}$, for all trace elements was set by the advisory board of this PT to 25 %, on the basis of the experience with similar measurands related to the EU Water Framework Directive.

Element	X_{ref}	u_{char}	u_{bb}	$u_{st,8weeks}$	u_{ref}	U_{ref}
As	1.89	0.051	0.020	0.062	0.083	0.17
Cd	0.096	0.005	0.001	0.004	0.007	0.013
Co	0.075	0.003	0.001	0.005	0.006	0.012
Cr	0.28	0.028	0.003	0.010	0.030	0.06
Cu	0.88	0.034	0.051	0.046	0.076	0.15
Fe	3.5	0.281	0.109	0.134	0.330	0.7
Mn	2.46	0.033	0.020	0.063	0.074	0.15
Mo	12.1	0.342	0.034	0.083	0.354	0.7
Ni	1.06	0.048	0.010	0.030	0.057	0.11
Pb	0.097	0.004	0.003	0.005	0.007	0.014
Zn	4.7	0.121	0.070	0.225	0.265	0.5

Table 1. Assigned values (X_{ref}), associated uncertainties (u_{ref}) and uncertainty contributions (u_{char} , u_{bb} , $u_{st,8weeks}$). All values are expressed in $\mu\text{g L}^{-1}$. The expanded uncertainty (U_{ref}) is calculated with a coverage factor $k=2$ corresponding to a level of confidence of about 95%.

7 Evaluation of results

7.1 Scores and evaluation criteria

Individual laboratory performance was expressed in terms of z - and ζ -scores in accordance with ISO 13528 [6]:

$$z = \frac{x_{lab} - X_{ref}}{\hat{\sigma}} \quad \text{Eq. 3}$$

$$\zeta = \frac{x_{lab} - X_{ref}}{\sqrt{u_{ref}^2 + u_{lab}^2}} \quad \text{Eq. 4}$$

The interpretation of the z - and ζ -score is done as follows (according to ISO/IEC 17043 [5]):

Satisfactory performance,	$ \text{score} \leq 2$	(green in Annexes 8-19)
Questionable performance,	$2 < \text{score} \leq 3$	(yellow in Annexes 8-19)
Unsatisfactory performance,	$ \text{score} > 3$	(red in Annexes 8-19)

The z-score compares the participant's deviation from the reference value with the standard deviation for proficiency assessment ($\hat{\sigma}$) used as common quality criterion. $\hat{\sigma}$ is defined by the PT organiser as the maximum acceptable standard uncertainty for the concerned measurands.

The ζ -score states if the laboratory result agrees with the assigned value within the respective uncertainty. The denominator is the combined uncertainty of the assigned value and the measurement uncertainty as stated by the laboratory. The ζ -score includes all parts of a measurement result, namely the expected value (assigned value), its uncertainty in the unit of the result as well as the uncertainty of the reported values. An unsatisfactory ζ -score can either be caused by an inappropriate estimation of the concentration or of its uncertainty or both.

The standard uncertainty of the laboratory (u_{lab}) was estimated by dividing the reported expanded uncertainty by the reported coverage factor, k . When no uncertainty was reported, it was set to zero ($u_{\text{lab}} = 0$). When k was not specified, the reported expanded uncertainty was considered as the half-width of a rectangular distribution; u_{lab} was then calculated by dividing this half-width by $\sqrt{3}$, as recommended by Eurachem and CITAC [7].

Uncertainty estimation is not trivial; therefore an additional assessment was provided to each laboratory reporting uncertainty, indicating how reasonable their uncertainty estimate is. The standard uncertainty from the laboratory (u_{lab}) is most likely to fall in a range between a minimum uncertainty (u_{min}), and a maximum allowed uncertainty (u_{max} , case "a"). u_{min} is set to the standard uncertainty of the reference value (u_{ref}). It is unlikely that a laboratory carrying out the analysis on a routine basis would measure the measurand with a smaller uncertainty than the expert laboratories chosen to establish the assigned value. u_{max} is set to the standard deviation ($\hat{\sigma}$) accepted for the PT assessment.

If u_{lab} is smaller than u_{min} (case "b") the laboratory may have underestimated its uncertainty. However, such a statement has to be taken with care as each laboratory reported only measurement uncertainty, whereas the uncertainty of the reference value also includes contributions of homogeneity and stability. If those are large, measurement uncertainties smaller than u_{min} (u_{ref}) are possible and plausible.

If u_{lab} is larger than u_{max} (case "c") the laboratory may have overestimated the uncertainty. An evaluation of this statement can be made when looking at the difference of the reported value and the assigned value: if the difference is small and the uncertainty is large, then overestimation is likely. If, however, the deviation is large but is covered by the uncertainty, then the uncertainty is properly assessed, but large. It should be pointed out that u_{max} is only a normative criterion if laid down by legislation.

7.2 General observations

Results were received from 46 of the 53 registered laboratories and 38 laboratories filled in the associated questionnaire. Not all laboratories reported results for all measurands. The total number of results received for the individual trace elements ranged from 36

(Mo) to 44 (Cu, Ni, Pb), including the "less than X" values (Table 2).

Analyte	Number of reported results	Number of reported values	Number of "less than X" values	Correct "less than X" values	Incorrect "less than X" values
As	43	36	7	4	3
Cd	43	25	18	16	2
Co	40	24	16	16	0
Cr	41	23	18	18	0
Cu	44	31	13	13	0
Fe	43	27	16	16	0
Mn	43	37	6	4	2
Mo	36	29	7	3	4
Ni	44	33	11	11	0
Pb	44	21	23	23	0
Se	37	20	17	--	--
Zn	43	33	10	10	0

Table 2. Total number of reported results, number of reported values, number of reported "less than X" values and number of correct and incorrect "less than X" values for each element

7.3 Laboratory results and scorings

Many of the elements were present at low concentrations equal to natural contamination levels. Therefore many laboratories reported "less than" values for the elements. Those reporting "less than X" values were not included in the evaluation. However, reported "less than" values were compared with the corresponding $X_{ref} - U_{ref}$. If the reported limit value "X" is lower than the corresponding $X_{ref} - U_{ref}$, this statement is considered incorrect, since the laboratory should have detected the respective element. Laboratories having been identified with such cases are indicated in red in Annexes 8-19. The number of correct and incorrect "less than" values is summarized in Table 2. It can be observed that for 7 out of the 11 scored trace elements all laboratories made a correct statement.

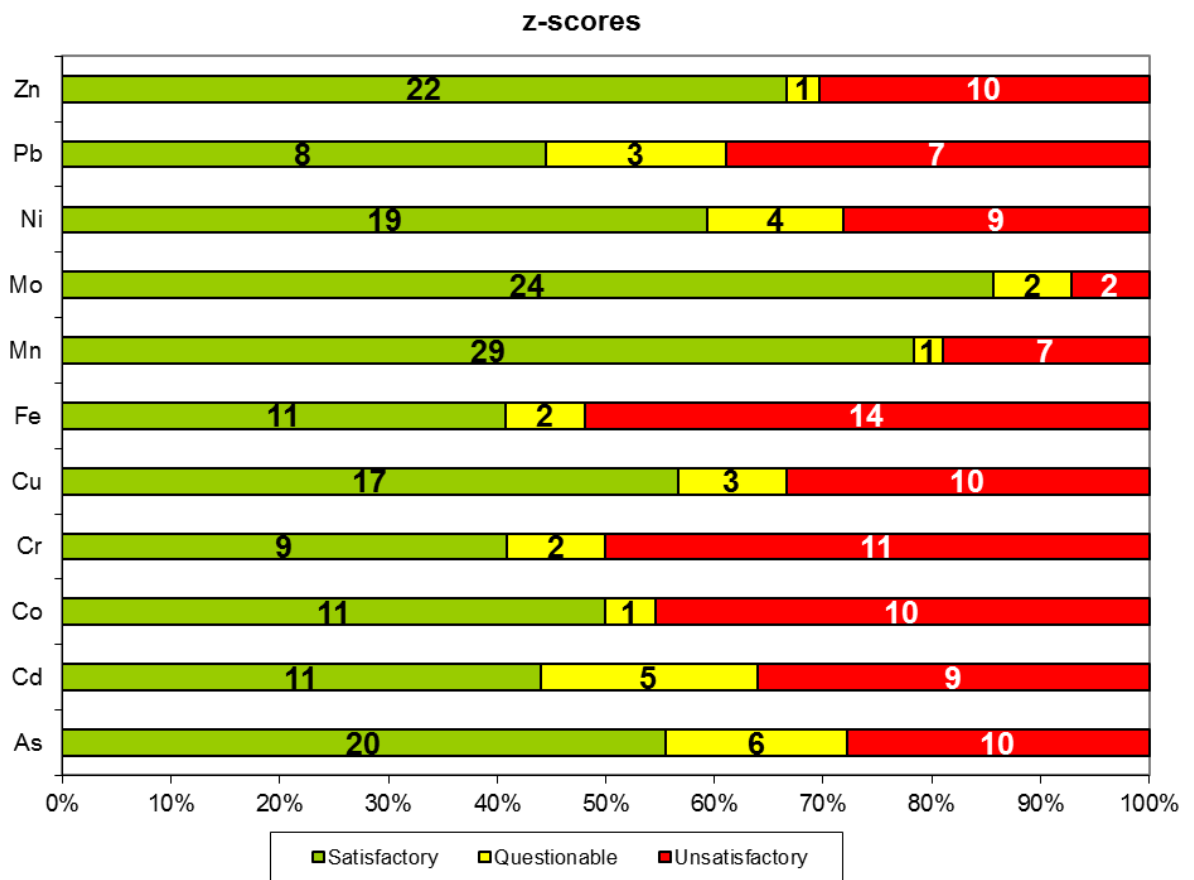
Three laboratories reported "0" values for some elements. These "0" values were not included in the evaluation for z- and ζ -scores.

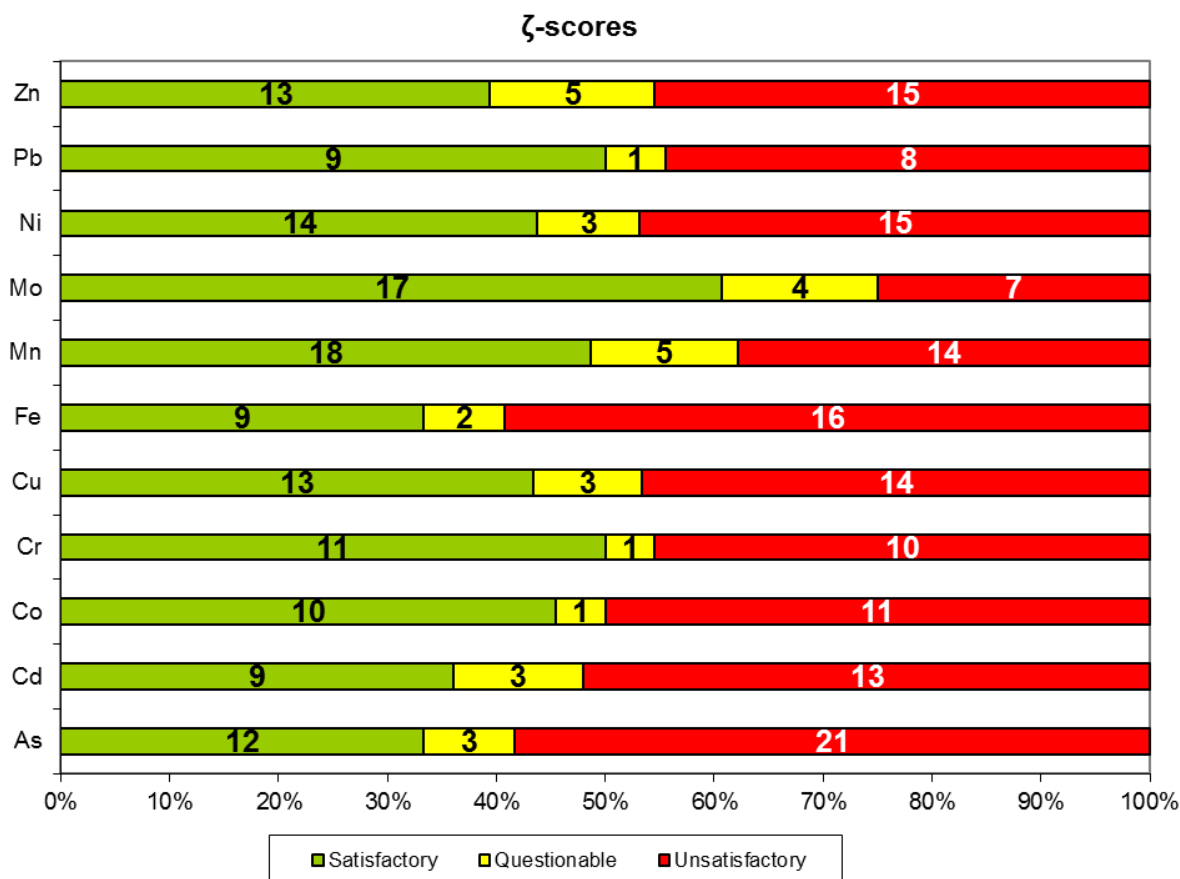
The overall performance of the participants regarding the z- and ζ -scores is summarized in Figure 1: for the determination of the 11 scored trace elements a range of 41 % (Cr, Fe) to 86 % (Mo) of satisfactory z-scores were obtained by the participants in this

exercise. Regarding ζ -scores, satisfactory ζ -scores were obtained by 33 % (As, Fe) to 61 % (Mo) of the participants.

The low concentration levels of the trace elements in a difficult matrix (high saline content), needs to be taken into consideration to understand the relatively low rate of satisfactory scores. Laboratories with a systematic positive bias should evaluate their methods in order to exclude any kind of interferences or contamination.

Figure 1. Number of evaluated laboratories with satisfactory, questionable and unsatisfactory z and ζ -scores. (The numbers on the bars correspond to the exact number of laboratories in a certain scoring category)





The reported results for the individual trace elements are presented in Annexes 8 to 19 in the form of a table and a graph. The table shows the reported X_{lab} , U_{lab} and k of the participants, the technique used by each participant, the obtained z and ζ -scores of each participant and an uncertainty assessment (a-b-c). The results are expressed in $\mu\text{g L}^{-1}$. One laboratory reported results in $\mu\text{g kg}^{-1}$. These results were converted into $\mu\text{g L}^{-1}$ using a density of $1.02352 \text{ g mL}^{-1}$ which was determined for this candidate CRM. The graph displays the measurement results and associated uncertainties of the participants and the assigned value X_{ref} with a reference interval and a target interval. In the graph σ_p stands for $\hat{\sigma}$. Furthermore, it includes a Kernel density plot which gives the probability density function of the reported measurement results together with the reference value X_{ref} . The Kernel density plot is used to check if there is a distribution different from normal of the measurement results (> 1 major peak). In this exercise a bimodal or even a multimodal distribution was found for some of the elements.

For the trace element Se, the variability on the results of the expert laboratories and the participants was very large. Therefore laboratories were not scored for this element (Annex 18).

7.4 Further information extracted from the questionnaire

The associated questionnaire was answered by 38 participating laboratories. According to those responses, 19 participants used a standardised method while 19 did not. The

method which was used the most (6 labs) was the "ISO 17294-2, Water quality - Application of inductively coupled plasma mass spectrometry (ICP-MS) - Part 2: Determination of 62 elements". When checking the overall performance of the laboratories using the ISO 17294-2 method, it was observed that this overall performance was better compared to the total population of participating laboratories: Table 3 shows that 69.8% of these laboratories obtained satisfactory z-scores (compared to 58.4% in the total population of laboratories) and only 13.2% obtained unsatisfactory z-scores (compared to 31.9% in the total population of laboratories). Three laboratories used the EPA 6020A method (ICP-MS, water and solid waste), one the EPA 6010C method (inductively coupled plasma atomic emission spectrometry-ICP-AES) and two labs the EPA 200.8 (ICP-MS, water and wastewater) method from the United States Environmental Protection Agency (EPA). The performance with these EPA methods is in line with the performance seen in the total population (Table 3). However, one observation is that the number of reported "less than X" values with these EPA methods is higher (46.2%) than in the total population (32.3%). The contrary is observed with the ISO 17294-2 method where only 19.7% of the reported results are "less than X" values.

A minority of the laboratories used a clean-up step (8 laboratories) or a pre-concentration technique (6 laboratories). None of these two steps seemed to contribute to a better performance: the laboratories using pre-concentration obtained only 46.2% of satisfactory z-scores (and 51.3% unsatisfactory) while laboratories using a clean-up step obtained only 27.0% satisfactory z-scores (and 63.5 % unsatisfactory). This may be related to the instrumental techniques coupled to these sample preparation techniques: in many cases not ICP-MS was used but other techniques like ICP-AES (or ICP-OES), atomic absorption spectrometry (AAS), electrothermal atomic absorption spectrometry (ET-AAS) or atomic fluorescence spectrometry (AFS). Indeed for all results measured with ICP-AES only 36.5% of satisfactory z-scores (and 55.8% of unsatisfactory z-scores) were obtained. Moreover 51.4% of the reported values obtained with ICP-AES were "less than X" values. One laboratory using pre-concentration combined with total reflection X-ray fluorescence (TXRF) obtained satisfactory z-scores for the 6 elements it analysed.

All laboratories except one had an ISO 17025 quality system in place.

Z-scores	Total population	ISO 17294-2	EPA	Pre-concentration	Clean-up step
Satisfactory	58.4%	69.8%	54.8%	46.2%	27.0%
Questionable	9.7%	17.0%	6.5%	2.6%	9.5%
Unsatisfactory	31.9%	13.2%	38.7%	51.3%	63.5%

Table 3. Percentage of satisfactory, questionable and unsatisfactory z-scores for results obtained using the ISO 17294-2 method, EPA method, pre-concentration and a clean-up step compared to the total population.

8 Conclusion

The mass concentrations of the 12 trace elements in the seawater sample were very low. Therefore many laboratories were not able to measure all the elements and reported "less than X" values. It was observed that the "less than" statements were correct in the majority of the cases: for 7 out of the 11 scored trace elements all laboratories reporting "less than X" values made a correct statement. When looking at the z-scores a range of 41 % (Cr, Fe) to 86 % (Mo) of satisfactory z-scores were obtained by the participants in this exercise. Some correlations with the methods and techniques used were observed: labs using the ISO 17294-2 method performed better than the total population of participating laboratories while laboratories using ICP-AES performed in general less satisfactorily. The low concentration levels of the trace elements in a difficult matrix (high saline content), needs to be taken into consideration to understand the general low rate of satisfactory scores. Laboratories with a systematic bias resulting in the overestimation of the mass fractions of the analytes should evaluate their methods in order to exclude interferences or contamination.

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US EPA, Region 4, SESD	UNITED STATES

10 Abbreviations

AAS	Atomic absorption spectroscopy
CITAC	Cooperation on international traceability in analytical chemistry
CV-AFS	Cold-vapour atomic fluorescence spectrometry
EA	European Cooperation for Accreditation
ET-AAS	Electrothermal atomic absorption spectrometry
EU	European Union
FI-HG-AAS	Flow injection hydride-generation atomic absorption spectrometry
GF-AAS	Graphite furnace atomic absorption spectrometry
HPLC-ICP-MS	High performance liquid chromatography inductively-coupled plasma mass spectrometry
ICP-AES	Inductively-coupled plasma atomic emission spectroscopy
ICP-MS	Inductively-coupled plasma mass spectrometry
ICP-OES	Inductively-coupled plasma optical emission spectroscopy
ICP-SFMS	Inductively-coupled plasma sector field mass spectrometry
ILC	Interlaboratory Comparison
IMEP	International Measurement Evaluation Programme
IRMM	Institute for Reference Materials and Measurements
ISO GUM	International Organisation for Standardisation – Guide to the expression of Uncertainty in Measurement
JRC	Joint Research Centre
LC-ICP-MS	Liquid chromatography inductively-coupled plasma mass spectrometry
PT	Proficiency testing
PTFE	
SS-CV-AAS	Solid sampling cold-vapour atomic absorption spectrometry

11 References

- [1] European Commission, Directive 2000//60/EC of the European Parliament and of the Council establishing a framework for Community action in the field of water policy, OJ Eur. Union L 327, 22.12.2000.
- [2] European Commission, Directive 2013/39/EU on environmental quality standards in the field of water policy, OJ Eur. Union L 226, 2013.
- [3] ISO Guide 34, issued by ISO-Geneva (CH), ISO-Geneva (CH).
- [4] ISO Guide 35 Reference Materials – general and statistical principles for certification (2006), issued by ISO-Geneva (CH), ISO-Geneva (CH).
- [5] ISO/IEC 17043:2010 "Conformity assessment – General requirements for proficiency testing", issued by the International Organisation for Standardization, Geneva
- [6] ISO 13528:2005 – "Statistical Methods for Use in Proficiency Testing by Interlaboratory Comparisons", issued by ISO-Geneva (CH), International Organisation for Standardization.
- [7] Eurachem/CITAC, "*Quantifying Uncertainty in Analytical Measurement*". <http://www.eurachem.org>, 3rd Ed., 2012.

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Annex 1: IRMM – IMEP web announcement

IMEP-40

Description	Determination of total As, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Se and Zn in seawater
Status	Ongoing
Year	2014
Type	Proficiency Test
Participation	Open to All
More	<p>The IMEP-40 exercise focuses on the analysis of the trace elements As, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Se and Zn in seawater. This PT is organised in support to the EU Water Framework Directive.</p> <p>IMEP-40 is open to all laboratories having experience in this kind of analyses. The concentrations of the trace elements in the test item are in the low $\mu\text{g L}^{-1}$ range. Laboratories whose analytical methods are not characterized by low limits of detection should not register to this exercise.</p> <p>The cost of this interlaboratory comparison is EUR 368 per registration.</p> <p>Test items and analytes</p> <p>The test item to be analysed is a seawater sample. Each participant will receive 1 sample. The measurands are the trace elements As, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Se and Zn in seawater.</p> <p>General outline of the exercise</p> <p>Participants are requested to perform 1 – 3 independent analyses using the method of their choice, and to report the mean, its expanded uncertainty and coverage factor k. Detailed instructions will be sent together with the sample.</p>
Registration URL	https://web.jrc.ec.europa.eu/ilcRegistrationWeb/registration/registration.do?sel...
Registration deadline	Friday, 15 August 2014
Sample dispatch	First half of September 2014
Reporting of results	Deadline 31/10/2014
Report to participants	End of December 2014
IL category	IMEP
Contact	jrc-irrm-imep@ec.europa.eu

Annex 2: Invitation letter to EA

Ref. Ares(2014)1837298 - 05/06/2014



EUROPEAN COMMISSION
DIRECTORATE-GENERAL
JOINT RESEARCH CENTRE
Directorate D - Institute for Reference Materials and Measurements
International Measurement Evaluation Program

Geel, 05 June 2014

UKAS
Richard Mc Farlane
21-47 High Street Feltham,
Middlesex TW13 4UN,
UK

IMEP-40: Interlaboratory comparison for the determination of trace elements in seawater

Dear Mr. Mc Farlane,

The Institute for Reference Materials and Measurements (IRMM) organises IMEP-40, an interlaboratory comparison for the "Determination of trace elements in seawater" in support to the EU Water Framework Directive. IMEP-40 focuses on the analysis of the trace elements As, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Se and Zn in seawater.

In the frame of the EA-IRMM collaboration agreement, IRMM kindly invites EA to nominate laboratories for free participation. They should hold (or be in the process of obtaining) an accreditation for this type of measurement and they should be competent to measure these analytes at the low $\mu\text{g L}^{-1}$ level. The concentrations of the trace elements in the test item are in the low $\mu\text{g L}^{-1}$ range. Laboratories whose analytical methods are not characterized by low limits of detection should not register to this exercise.

I suggest that you forward this invitation to the national EA accreditation bodies for its consideration. There are a limited number of samples at your disposal and the number of nominees should not exceed 5 laboratories per country.

Confidentiality of the participants and their results towards third parties is guaranteed. However, IMEP will disclose details of the participants that have been nominated by EA to the EA working group for ILCS in Testing coordinator for this exercise. The EA accreditation bodies may wish to inform the nominees of this disclosure.

Relesweg 111, B-2440 Geel - Belgium; Telephone: (32-14) 571 211
Telephone: direct line (32-14) 571 707; Fax: (32-14) 571 865

E-mail: jrc-irmm-imep@ec.europa.eu
Web site: <https://ec.europa.eu/jrc/institutes/irmm/>

The registration page for laboratories appointed by EA is open until 15 August 2014. Distribution of the samples is foreseen for the first half of September 2014. The deadline for submission of results is 31 October 2014.

In order to register, laboratories must:

1. Enter their details online:

<https://web.jrc.ec.europa.eu/ilcRegistrationWeb/registration/registration.do?selComparis on=1281>

2. Print the completed form when the system asks to do so and clearly indicate on the printed form that they have been appointed by the European Cooperation for Accreditation to take part in this exercise **otherwise the laboratory will be invoiced 368 € for participation** as charged to the non-appointed laboratories.

3. Send the printout to both the IMEP-40 and the EA-IMEP-40 coordinators:

IMEP-40 coordinator
Dr. Pieter Dehouck
Fax +32 14 571 252
E-mail jrc-irmm-imep@ec.europa.eu

EA-IMEP-40 coordinator
Richard Mc Farlane
E-mail Richard.McFarlane@ukas.com

Please contact me if you have any questions or comments. We are looking forward to our cooperation!

With kind regards

Pieter Dehouck
IMEP-40 Coordinator

Relesweg 111, B-2440 Geel - Belgium; Telephone: (32-14) 571 211
Telephone: direct line (32-14) 571 707; Fax: (32-14) 571 865

E-mail: jrc-irmm-imep@ec.europa.eu
Web site: <https://ec.europa.eu/jrc/institutes/irmm/>

Annex 3: Invitation letter to APLAC

Ref. Ares(2014)1838912 - 05/06/2014



Geel, 05 June 2014

To: Cynthia Chen
APLAC PT Committee

IMEP-40: Interlaboratory comparison for the determination of trace elements in seawater

Dear Mrs Chen,

The Institute for Reference Materials and Measurements (IRMM) organises IMEP-40, an interlaboratory comparison for the "Determination of trace elements in seawater", in support to the EU Water Framework Directive. IMEP-40 focuses on the analysis of the trace elements As, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Se and Zn in seawater.

IRMM kindly invites APLAC to nominate 10 laboratories for free participation. However, they should hold (or be in the process of obtaining) an accreditation for this type of measurement and they should be competent to measure these analytes at the low $\mu\text{g L}^{-1}$ level. The concentrations of the trace elements in the test item are in the low $\mu\text{g L}^{-1}$ range. Laboratories whose analytical methods are not characterized by low limits of detection should not register to this exercise. I suggest that you forward this invitation to a selection of specialised laboratories in this area.

In addition to the 10 laboratories above mentioned, other laboratories may take part in IMEP-40 paying a registration fee of 368 €.

Confidentiality of the participants and their results towards third parties is guaranteed.

The registration page is open until **15 August 2014**. Distribution of the samples is foreseen for the first half of September 2014. The deadline for submission of results is **31 October 2014**.

Releseweg 111, B-2440 Geel - Belgium. Telephone: (32-14) 571 211
Telephone direct line (32-14) 571 767; Fax: (32-14) 571 866
E-mail: icc-irmm-imep@ec.europa.eu
Web site: <https://ec.europa.eu/irc/institutes/irmm/>

In order to register, laboratories must:

1. Enter their details online:
<https://web.irc.ec.europa.eu/iccRegistrationWeb/registration/registration.do?selComparison=1281>
2. Print the completed form when the system asks to do so and clearly indicate on the printed form that they have been appointed by APLAC to take part in this exercise **otherwise the laboratory will be invoiced 368 € for participation** as charged to the non-appointed laboratories.
3. Send the printout to both the IMEP-40 and the APLAC coordinators:

IMEP-40 coordinator Dr. Pieter Dehouck Fax: +32 14 571 252 E-mail: irc-irmm-imep@ec.europa.eu	APLAC coordinator Cynthia Chen E Mail: cynthia.chen@iafw.org
---	--

Please contact me if you have any questions or comments. We are looking forward to our cooperation!

With kind regards

Pieter Dehouck
IMEP-40 Coordinator

Releseweg 111, B-2440 Geel - Belgium. Telephone: (32-14) 571 211
Telephone direct line (32-14) 571 767; Fax: (32-14) 571 866
E-mail: icc-irmm-imep@ec.europa.eu
Web site: <https://ec.europa.eu/irc/institutes/irmm/>

Annex 4: Invitation letter to IAAC

1. Enter their details online:

<https://web.jrc.ec.europa.eu/iaacRegistrationWeb/registration/registration.do?selComparisOn=1281>

2. Print the completed form when the system asks to do so and clearly indicate on the printed form that they have been appointed by IAAC to take part in this exercise otherwise the laboratory will be invoiced 368 € for participation as charged to the non-appointed laboratories.

3. Send the printout to both the IMEP-40 and the IAAC coordinators:

IMEP-40 coordinator Dr. Pieter Dehouck Fax +32 14 571 252 E-mail: jrc-irmm-imep@ec.europa.eu	IAAC coordinator Barbara Belzer E-Mail: secretariat@iaac.org.mx
--	---

Please contact me if you have any questions or comments. We are looking forward to our cooperation!

With kind regards

Pieter Dehouck
IMEP-40 Coordinator

Reïseweg 111, B-2440 Geel - Belgium. Telephone: (32-14) 571 211
Telephone: direct line (32-14) 571 787. Fax: (32-14) 571 865

E-mail: jrc-irmm-imep@ec.europa.eu
Web site: <https://ec.europa.eu/irmm/index.html>

2

Ref. Ares(2014)1837010 - 05/08/2

 EUROPEAN COMMISSION
DIRECTORATE-GENERAL
JOINT RESEARCH CENTRE
Directorate D - Institute for Reference Materials and Measurements
International Measurement Evaluation Program



Geel, 05 June 2014

To: Barbara Belzer
IAAC Lab Committee

IMEP-40: Interlaboratory comparison for the determination of trace elements in seawater

Dear Mrs Belzer,

The Institute for Reference Materials and Measurements (IRMM) organises IMEP-40, an interlaboratory comparison for the "Determination of trace elements in seawater" in support to the EU Water Framework directive. IMEP-40 focuses on the analysis of the trace elements As, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Se and Zn in seawater.

IRMM kindly invites IAAC to nominate 10 laboratories for free participation. However, they should hold (or be in the process of obtaining) an accreditation for this type of measurement and they should be competent to measure these analytes at the $\mu\text{g L}^{-1}$ level. The concentrations of the trace elements in the test item are in the low $\mu\text{g L}^{-1}$ range. Laboratories whose analytical methods are not characterized by low limits of detection should not register to this exercise. I suggest that you forward this invitation to a selection of specialised laboratories in this area.

In addition to the 10 laboratories above mentioned, other laboratories may take part in IMEP-40 paying a registration fee of 368 €.

Confidentiality of the participants and their results towards third parties is guaranteed.

The registration page is open until 15 August 2014. Distribution of the samples is foreseen for the first half of September 2014. The deadline for submission of results is 31 October 2014.

In order to register, laboratories must:

Reïseweg 111, B-2440 Geel - Belgium. Telephone: (32-14) 571 211
Telephone: direct line (32-14) 571 787. Fax: (32-14) 571 865

E-mail: jrc-irmm-imep@ec.europa.eu
Web site: <https://ec.europa.eu/irmm/index.html>

Annex 5: Sample accompanying letter



EUROPEAN COMMISSION
DIRECTORATE-GENERAL
JOINT RESEARCH CENTRE
Directorate D - Institute for Reference Materials and Measurements
International Measurement Evaluation Program

Geel, 08 September 2014
JRC.D5/PD/acs/Ares(2014)2774710

«Title» «Firstname» «Surname»
«Organisation»
«Department»
«Address»
«Address2»
«Zip» «Town»
«Country»

Participation in IMEP-40, a proficiency test exercise for the determination of the trace elements As, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Se and Zn in seawater.

Dear «Title» «Surname»,

Thank you for participating in the IMEP-40 proficiency test for the determination of the trace elements As, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Se and Zn in seawater. This proficiency test (PT) exercise is organised in support to the EU Water Framework Directive.

Please keep this letter. You need it to report your results.

This parcel contains:

- a) One bottle containing approximately 500 ml of the test item
- b) A "Confirmation of Receipt" form
- c) This accompanying letter.

Please check whether the bottle containing the test item remained undamaged during transport. Then, send the "Confirmation of receipt" form back (fax: +32-14-571865, e-mail: JRC-IRMM-IMEP@ec.europa.eu). You should store the sample in a dark place at 4°C until analysis.

The measurands are As, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Se and Zn in seawater.

The procedure used for the analyses should resemble as closely as possible the one that you use in routine analyses.

Retieseweg 111, B-2440 Geel - Belgium. Telephone: +32-(0)14-571 211.
Telephone: direct line +32-(0)14-571 767, Fax: +32-(0)14-571 865.

E-mail: JRC-IRMM-IMEP@ec.europa.eu
Web site: <http://imm.jrc.ec.europa.eu>

Reporting of results

Please perform two or three independent measurements, correct the measurements results for recovery and report on the reporting website:

- the **mean** of your two or three measurement results,
- the associated expanded **uncertainty**,
- the **coverage factor** and
- the **technique** used.

The results should be reported in the same form (e.g. number of significant figures) as those normally reported to the customer.

The reporting website is <https://web.jrc.ec.europa.eu/ilcReportingWeb>

To access the webpage you need a personal password key, which is: «**Part_key**». The system will guide you through the reporting procedure. After entering your results, please complete also the relating questionnaire.

Do not forget to submit and confirm always when required.

Directly after submitting your results and the questionnaire information online, you will be prompted to print the completed report form. Please do so, **sign the paper version and return it to IRMM by fax (at +32-14-571-865) or by e-mail**. Check your results carefully for any errors before submission, since this is your last definitive confirmation.

The **deadline** for submission of results is **31/10/2014**.

Keep in mind that collusion is contrary to professional scientific conduct and serves only to nullify the benefits of proficiency tests to customers, accreditation bodies and analysts alike.

Your participation in this project is greatly appreciated. If you have any remaining questions, please contact me by e-mail: JRC-IRMM-IMEP@ec.europa.eu

With kind regards,

Pieter Dehouck (PhD)
IMEP-40 Coordinator

Cc: F. Ulberth (SFB HoU)

Retieseweg 111, B-2440 Geel - Belgium. Telephone: +32-(0)14-571 211.
Telephone: direct line +32-(0)14-571 767, Fax: +32-(0)14-571 866.

E-mail: JRC-IRMM-IMEP@ec.europa.eu
Web site: <http://irmm.jrc.ec.europa.eu>

Annex 6: "Confirmation of Receipt" form



EUROPEAN COMMISSION

DIRECTORATE-GENERAL
JOINT RESEARCH CENTRE

Directorate D - Institute for Reference Materials and Measurements
International Measurement Evaluation Program

This document is an attachment to
JRC.D5/PD/acs/ Ares(2014)2774710

«Title» «Firstname» «Surname»
«Organisation»
«Address»
«Address2»
«Zip» «Town»
«Country»

IMEP-40

Determination of the trace elements As, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Se and Zn in seawater

Confirmation of receipt of the samples

*Please return this form at your earliest convenience.
This confirms that the sample package arrived.
In case the package is damaged,
please state this on the form and contact us immediately.*

ANY REMARKS

Date of package arrival

Signature

Please return this form to:

Pieter Dehouck (PhD)

IMEP-40 Coordinator
EC-JRC-IRMM
Retieseweg 111
B-2440 GEEL, Belgium

Fax : +32-14-571865

e-mail: JRC-IRMM-IMEP@ec.europa.eu

Retieseweg, 111, B-2440 Geel - Belgium. Telephone: (32-14) 571 211
Telephone: direct line (32-14) 571 767, Fax: (32-14) 571 865

E-mail: jrc-irmm-imep@ec.europa.eu

Web site: <http://irmm.jrc.ec.europa.eu>

Annex 7: Questionnaire

Submission Form

1. Have you corrected your results for recovery?

- a) Yes
 b) No

1.1. If yes, how did you determine the recovery factor? By

- a) adding a known amount of the same analyte (spiking)
 b) using a certified reference material
 c) Other

1.1.1. If other, please specify

1.2. If no, why not?

1.3. Please enter the correction factors and the LODs of your methods.

Correction Factors and LODs

Questions/Response Table	Correction Factor	LOD
As		
Cd		
Cr		
Co		
Cu		
Fe		
Mn		
Mo		
Ni		
Pb		
Se		
Zn		

2. Experimental details for the analysis

2.1. Does your laboratory use reference material for this type of analysis?

- a) Yes
 b) No

2.1.1. If yes, which one?

2.1.2. The reference material was used for: (multiple answers are possible)

- the calibration of instruments
 the validation of the procedure

2.2. Did you use an official method?

- a) Yes
 b) No

2.2.1. If yes, which one?

2.3. Did you use a pre-concentration technique?

- a) Yes
 b) No

2.3.1. If yes, which one?

2.4. Did you use a clean-up step?

- a) Yes
 b) No

2.4.1. If yes, which one?

2.5. Does your laboratory carry out this type of analysis on a regular basis? (samples per year)

2.6. Additional remarks/comments on the method(s) of analysis.

3. What is the basis of your uncertainty estimate (multiple answers are possible)?

- a) Uncertainty budget (ISO-GUM)
- b) Known uncertainty of the standard method (ISO 21748)
- c) Uncertainty of the method (in-house validation)
- d) Measurement of replicates (precision)
- e) Estimation based on Judgment
- f) Use of intercomparison data
- g) Other

3.1. If other, please specify

4. What is the level of confidence (in %) reflected by the coverage (k) assigned to your reported uncertainty

5. Do you usually provide an uncertainty statement to your customers for this type of analysis?

- a) Yes
- b) No

6. Does your laboratory have a quality system in place?

- a) Yes
- b) No

6.1. If yes, which one?

- a) ISO 17025
- b) ISO 9000 series
- c) Other

6.1.1. If other, please specify

7. Does your laboratory take part in interlaboratory comparison scheme for this type of analysis?

- a) Yes
- b) No

7.1. If yes, which one(s)?

8. Do you have any comments? Please let us know: ...

Annexes 8-19: Results for the different trace elements

The table shows the reported x_{lab} , U_{lab} and k of the participants, the technique used by each participant, the obtained z and ζ -scores of each participant and an uncertainty assessment. Results are expressed in $\mu\text{g L}^{-1}$. Results reported in $\mu\text{g kg}^{-1}$ were converted using a density factor of $1.02352 \text{ g mL}^{-1}$. A satisfactory result is green, a questionable result is yellow and an unsatisfactory result is red in annexes 9 to 20. No scores are given when $<$ values were reported. In these cases any incorrect statement is indicated in red.

a: $U_{min}(U_{ref}) \leq U_{lab} \leq U_{max}(\hat{\sigma})$; b: $U_{lab} < U_{min}$; c: $U_{lab} > U_{max}(\hat{\sigma})$

The graph shows the measurement results and associated uncertainties of the participants, the reference value X_{ref} with a reference interval and a target interval. In the graph σ_p stands for $\hat{\sigma}$.

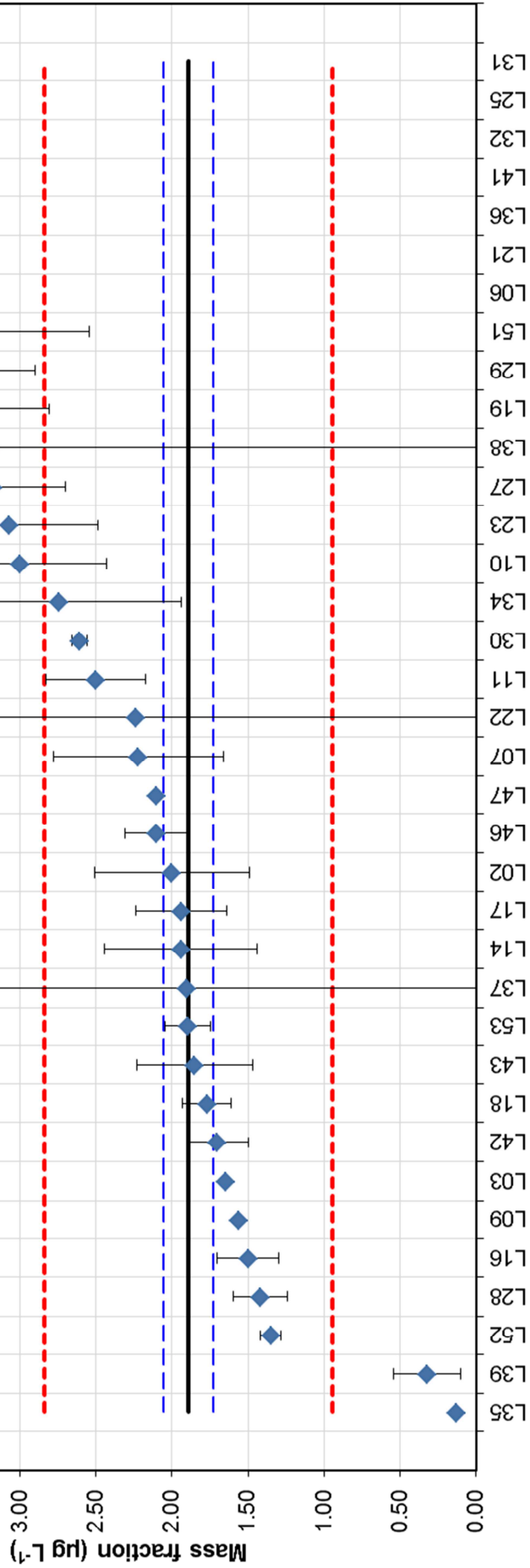
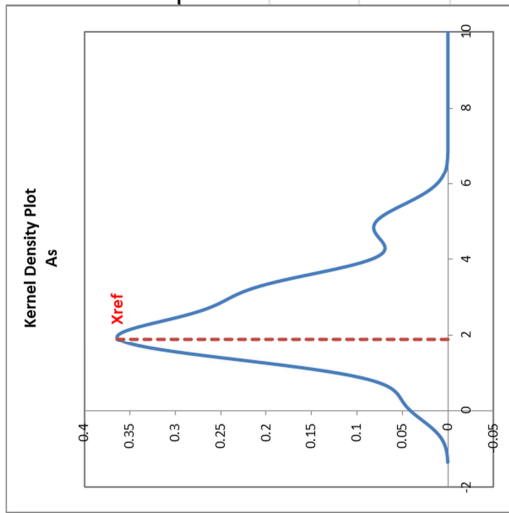
Annex 8: Results for As

$X_{ref} = 1.89$; $U_{Ref} (k=2) = 0.17$; $s_p = 0.473 (\mu\text{g L}^{-1})$

Lab Code	X_{lab}	U_{lab}	k	Technique	u_{lab}	z-score	ζ -score	uncert.
2	2	0.51	2	ICP-MS	0.255	0.23	0.41	a
3	1.648			ICP-MS	0	-0.51	-2.94	b
4	< 5	30		ICP-MS				
5	< 5			AFS				
6	3.6			Colorimetry	0	3.61	20.63	b
7	2.22	0.56	2	ICP-MS	0.28	0.70	1.13	a
8	< 7.5			ICP-MS				
9	1.56	0	0	HG-AAS	0	-0.70	-4.00	b
10	3	0.57	2	ICP-MS	0.285	2.35	3.74	a
11	2.5	0.33	2	ICP-MS	0.165	1.29	3.30	a
14	1.94	0.5	2	ICP-MS	0.25	0.10	0.19	a
15	< 0.2			HG-ICP-OES				
16	1.5	0.2	2	HG-AAS	0.1	-0.83	-3.01	a
17	1.94	0.3	2	ICP-MS	0.15	0.10	0.28	a
18	1.77	0.16	2	AFS	0.08	-0.26	-1.05	b
19	3.28	0.47	2	ICP-MS	0.235	2.94	5.57	a
21	4.7	0.9	2	ICP-MS	0.45	5.94	6.14	a
22	2.24	23	2	ICP-MS	11.5	0.74	0.03	c
23	3.071	0.583	2	ICP-OES	0.2915	2.50	3.89	a
25	32.9	0.6	3.182	ICP-OES	0.188561	65.59	150.56	a
27	3.18	0.477	2	ICP-MS	0.2385	2.73	5.10	a
28	1.42	0.18	2	ICP-MS	0.09	-1.00	-3.85	a
29	3.3	0.4	2	ICP-MS	0.2	2.98	6.51	a
30	2.609	0.049	$\sqrt{3}$	ICP-MS	0.02829	1.52	8.20	b
31	192.5	28.3	2	ICP-OES	14.15	403.16	13.47	c
32	5.3	0.8	2	ETAAS	0.4	7.21	8.34	a
33	< 1.0		2	ICP-MS				
34	2.74	0.8	2	ICP-MS	0.4	1.80	2.08	a
35	0.13			ICP-AES	0	-3.73	-21.26	b
36	4.7	1.2	2	ICP-MS	0.6	5.94	4.64	c
37	1.9	25	2	ICP-MS	12.5	0.02	0.00	c
38	3.2	11.69	2	ICP-MS	5.845	2.77	0.22	c
39	0.32	0.22	2	ICP-OES	0.11	-3.32	-11.41	a
41	4.9			ICP-MS	0	6.36	36.32	b
42	1.7	0.2	2.26	ICP-MS	0.088496	-0.40	-1.58	a
43	1.85	0.38	2	ICP-MS	0.19	-0.09	-0.20	a
44	< 0.5			ICP-OES				
46	2.1	0.21	$\sqrt{3}$	ICP-MS	0.121244	0.44	1.42	a
47	2.1			ICP-MS	0	0.44	2.52	b
48	< 50			ICP-OES				
51	3.39	0.85	2	ICP-MS	0.425	3.17	3.46	a
52	1.35	0.07	2	HG-ICP-MS	0.035	-1.14	-6.02	b
53	1.897	0.149	2	ICP-MS	0.0745	0.01	0.05	b

IMEP-40: As in seawater

$X_{\text{ref}} = 1.89$; $U_{\text{Ref}} (k=2) = 0.17$; $\sigma_p = 0.473$ ($\mu\text{g L}^{-1}$)



5.3
32.9
192.5

Laboratory Code

Measurement results and associated uncertainties (reported uncertainties shown).
Reference value (X_{Ref}): solid black line; Reference interval ($X_{\text{Ref}} \pm U_{\text{Ref}}$): dashed blue lines; Target interval ($X_{\text{Ref}} \pm 2\sigma_p$): dotted red lines.

Annex 9: Results for Cd

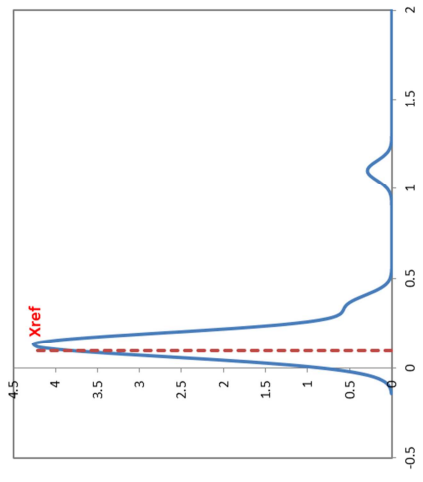
$X_{ref} = 0.096$; $U_{Ref} (k=2) = 0.013$; $s_p = 0.022$ ($\mu\text{g L}^{-1}$)

Lab Code	X_{lab}	U_{lab}	k	Technique	U_{lab}	z-score	ζ -score	uncert.
3	0.024			ICP-MS	0	-3.00	-10.94	b
4	< 0.2	35		ICP-MS				
5	< 0.2			ICP-AES				
6	< 6			AAS				
7	0.12	0.03	2	ICP-MS	0.015	1.02	1.49	a
8	0.144	0.069	$\sqrt{3}$	ICP-MS	0.039837	2.03	1.20	c
9	< 0.5			ETAAS				
10	0.101	0.0253	2	ICP-MS	0.01265	0.23	0.38	a
11	0.127	0.016	2	ICP-MS	0.008	1.32	3.04	a
14	< 0.05			ICP-MS				
15	< 5			ICP-OES				
17	0.319	0.1	2	ICP-MS	0.05	9.36	4.43	c
18	0.099	0.043	2	ICP-MS	0.0215	0.14	0.15	a
19	0.37	0.12	2	ICP-MS	0.06	11.49	4.55	c
21	0.2	0.03	2	ICP-MS	0.015	4.37	6.38	a
22	0.101	27	2	ICP-MS	13.5	0.23	0.00	c
23	0.16	0.042	2	ICP-OES	0.021	2.70	2.93	a
25	77.7	0.4	3.182	ICP-OES	0.125707	3249.13	616.51	c
27	0.128	0.019	2	ICP-MS	0.0095	1.36	2.81	a
28	0.054	0.008	2	ICP-MS	0.004	-1.74	-5.42	b
29	0.15	0.02	2	ICP-MS	0.01	2.28	4.56	a
30	< 0.1			ICP-MS				
31	293.8	57.7	2	ICP-OES	28.85	12296.75	10.18	c
32	1.1	0.2	2	ETAAS	0.1	42.05	10.02	c
33	< 0.1		2	ICP-MS				
34	< 0.01			ICP-MS				
35	9.35			ICP-AES	0	387.46	1414.84	b
36	< 1			ICP-MS				
37	< 0.2			ICP-MS				
38	< 0.15			ICP-MS				
39	0.14	0.15	2	ICP-OES	0.075	1.86	0.59	c
40	0.2	0.02	2	ETAAS	0.01	4.37	8.74	a
41	< 0.5			ICP-MS				
42	0.2	0.1	2.26	ICP-MS	0.044248	4.37	2.34	c
43	0.113	0.022	2	ICP-MS	0.011	0.73	1.36	a
44	< 0.5			ICP-OES				
45	< 1			ICP-MS				
46	< 0.2			ICP-MS				
47	< 0.13			ICP-MS				
48	< 10			ICP-OES				
51	0.104	0.026	2	ICP-MS	0.013	0.35	0.58	a
52	0.167	0.041	2	ICP-MS	0.0205	2.99	3.32	a
53	0.103	0.014	2	ICP-MS	0.007	0.31	0.78	a

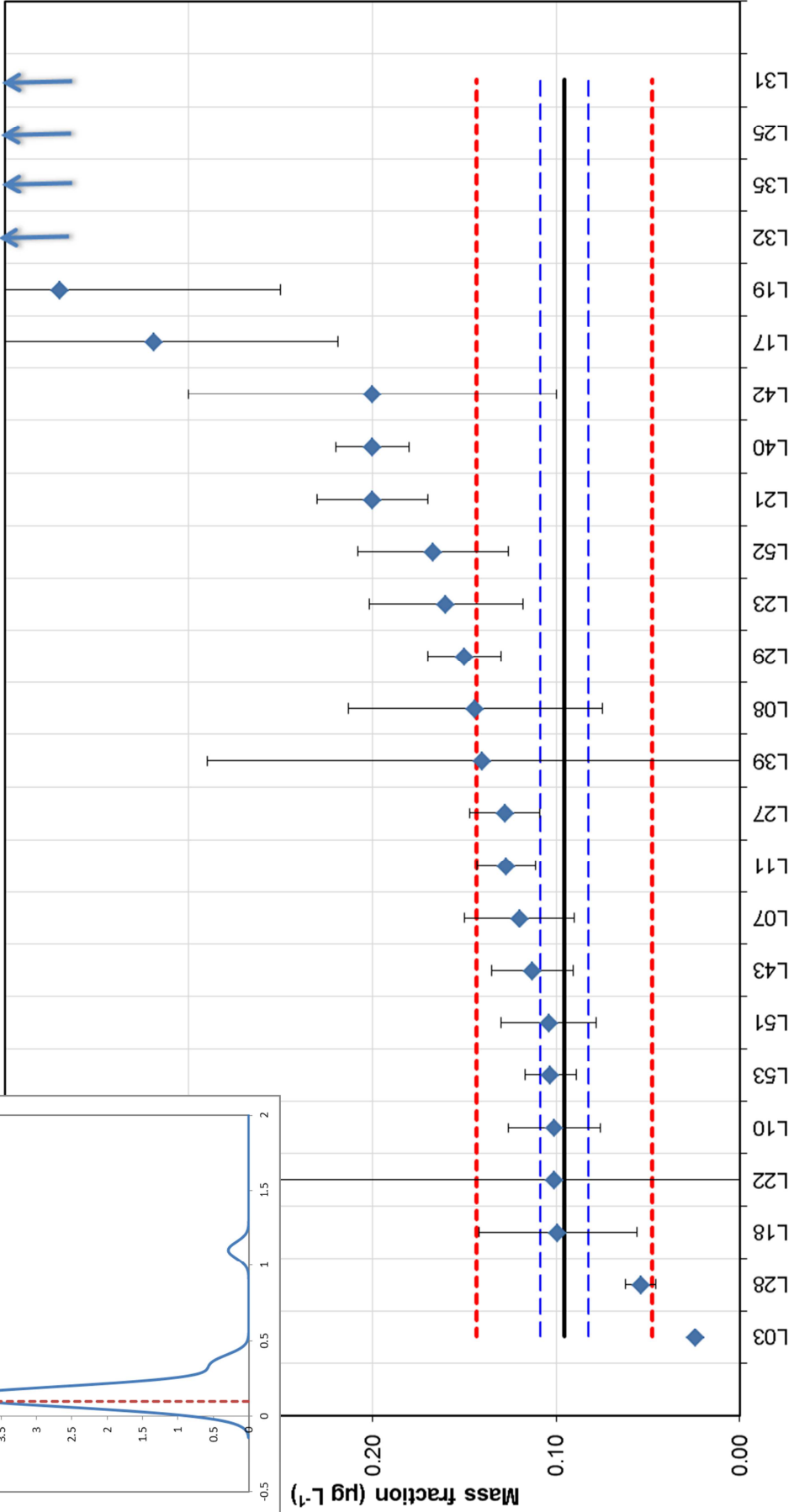
IMEP-40: Cd in seawater

$X_{\text{Ref}} = 0.096$; $U_{\text{Ref}} (k=2) = 0.013$; $\sigma_p = 0.022$ ($\mu\text{g L}^{-1}$)

Kernel Density Plot
Cd



1.1
9.35
77.7
293.8



Laboratory Code

Measurement results and associated uncertainties (reported uncertainties shown).
Reference value (X_{Ref}): solid black line; Reference interval ($X_{\text{Ref}} \pm U_{\text{Ref}}$): dashed blue lines; Target interval ($X_{\text{Ref}} \pm 2\sigma_p$): dotted red lines.

Annex 10: Results for Co

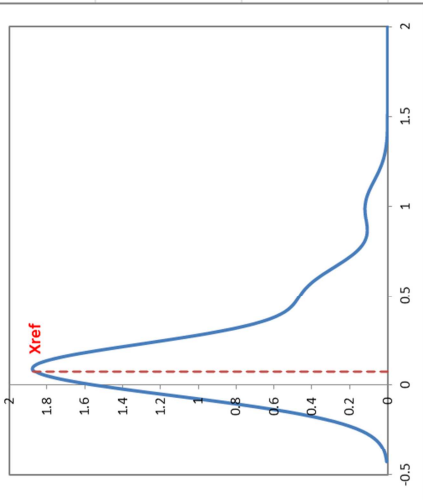
$X_{ref} = 0.075$; $U_{Ref} (k=2) = 0.012$; $s_p = 0.019$ ($\mu\text{g L}^{-1}$)

Lab Code	X_{lab}	U_{lab}	k	Technique	u_{lab}	z-score	ζ -score	uncert.
3	0.133			ICP-MS	0	3.10	9.49	b
4	< 1			ICP-MS				
5	< 1			ICP-AES				
6	212			AAS	0	11314.71	34617.94	b
7	< 0.5			ICP-MS				
8	< 5			ICP-OES				
9	< 5			ETAAS				
10	0	0	2	ICP-MS				
11	< 0.1			ICP-MS				
14	0.07	0.03	2	ICP-MS	0.015	-0.26	-0.30	a
15	< 5			ICP-OES				
17	0.108	0.1	2	ICP-MS	0.05	1.77	0.66	c
18	0.059	0.021	2	ICP-MS	0.0105	-0.85	-1.31	a
19	0.17	0.06	2	ICP-MS	0.03	5.08	3.11	c
21	0.1	0.02	2	ICP-MS	0.01	1.34	2.14	a
22	0.072	30	2	ICP-MS	15	-0.16	0.00	c
23	0.399	0.072	2	ICP-OES	0.036	17.30	8.87	c
25	< 1.3			ICP-OES				
27	0.0988	0.05	2	ICP-MS	0.025	1.27	0.93	c
28	0.065	0.011	2	ICP-MS	0.0055	-0.53	-1.21	b
29	0.12	0.02	2	ICP-MS	0.01	2.41	3.84	a
30	< 1			ICP-MS				
31	< 0.4			ICP-OES				
32	0.5	0.1	2	ETAAS	0.05	22.70	8.44	c
33	< 0.1		2	ICP-MS				
34	0.58	0.1	2	ICP-MS	0.05	26.97	10.03	c
35	0			ICP-AES				
36	< 1			ICP-MS				
37	< 0.25			ICP-MS				
39	0.22	0.28	2	ICP-OES	0.14	7.75	1.04	c
41	4.8			ICP-MS	0	252.27	771.84	b
42	1	0.2	2.26	ICP-MS	0.088496	49.39	10.43	c
43	0.561	0.12	2	ICP-MS	0.06	25.95	8.06	c
44	< 2			ICP-OES				
46	< 0.5			ICP-MS				
47	0.077			ICP-MS	0	0.11	0.34	b
48	< 10			ICP-OES				
51	0.09	0.023	2	ICP-MS	0.0115	0.81	1.16	a
52	0.0797	0.0091	2	ICP-MS	0.00455	0.26	0.63	b
53	0.096	0.002	2	ICP-MS	0.001	1.13	3.40	b

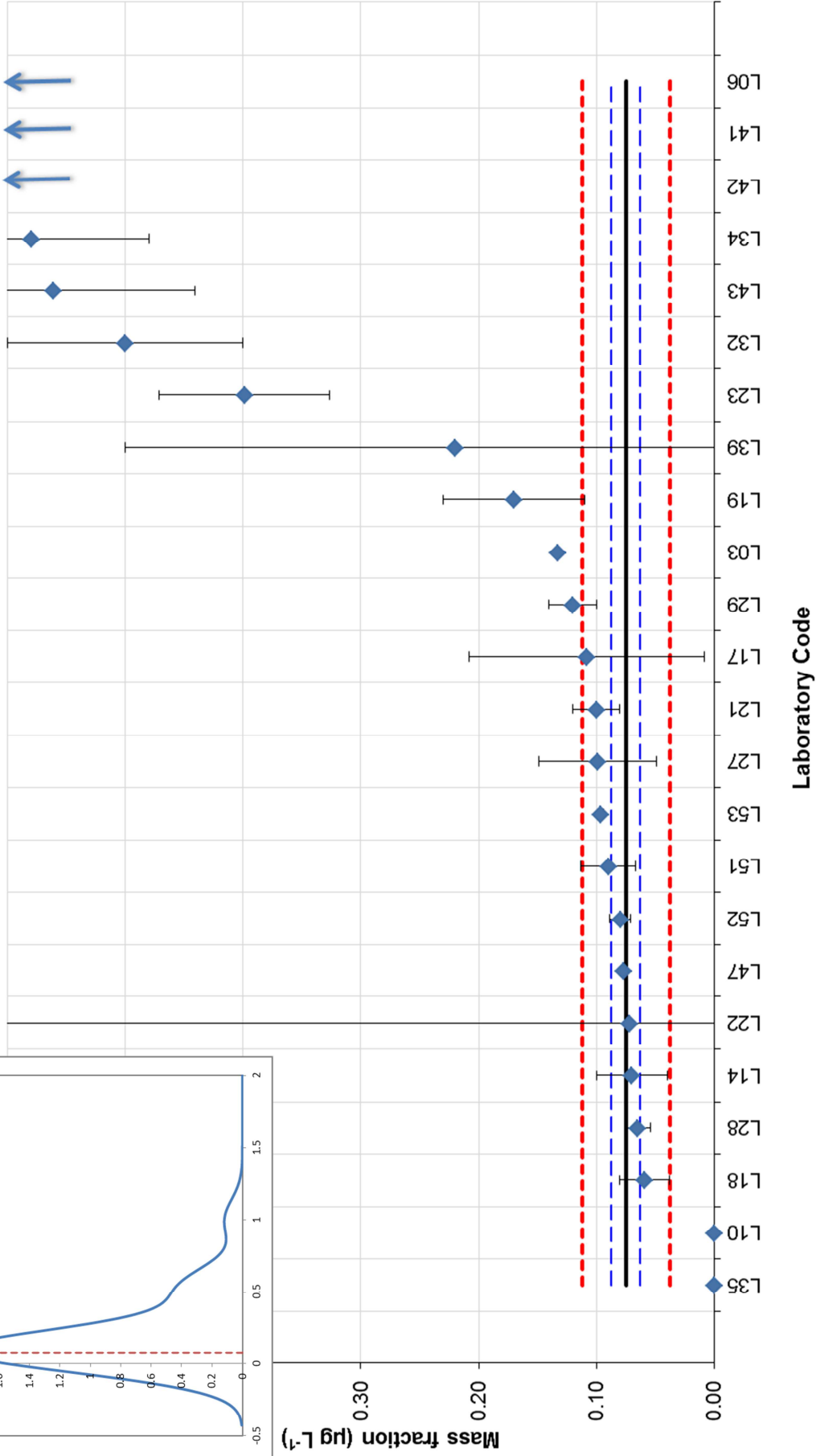
IMEP-40: Co in seawater

$X_{\text{ref}} = 0.075$; $U_{\text{Ref}} (k=2) = 0.012$; $\sigma_p = 0.019$ ($\mu\text{g L}^{-1}$)

Kernel Density Plot
Co



1
4.8
212



Laboratory Code

Measurement results and associated uncertainties (reported uncertainties shown).

Reference value (X_{Ref}): solid black line; Reference interval ($X_{\text{Ref}} \pm U_{\text{Ref}}$): dashed blue lines; Target interval ($X_{\text{Ref}} \pm 2\sigma_p$): dotted red lines.

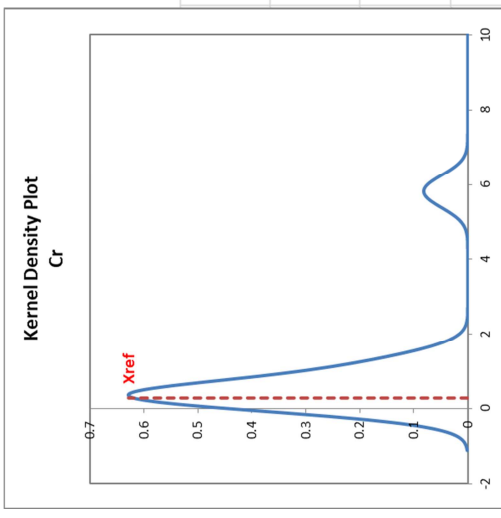
Annex 11: Results for Cr

$X_{\text{ref}} = 0.28$; $U_{\text{Ref}} (k=2) = 0.06$; $s_p = 0.063$ ($\mu\text{g L}^{-1}$)

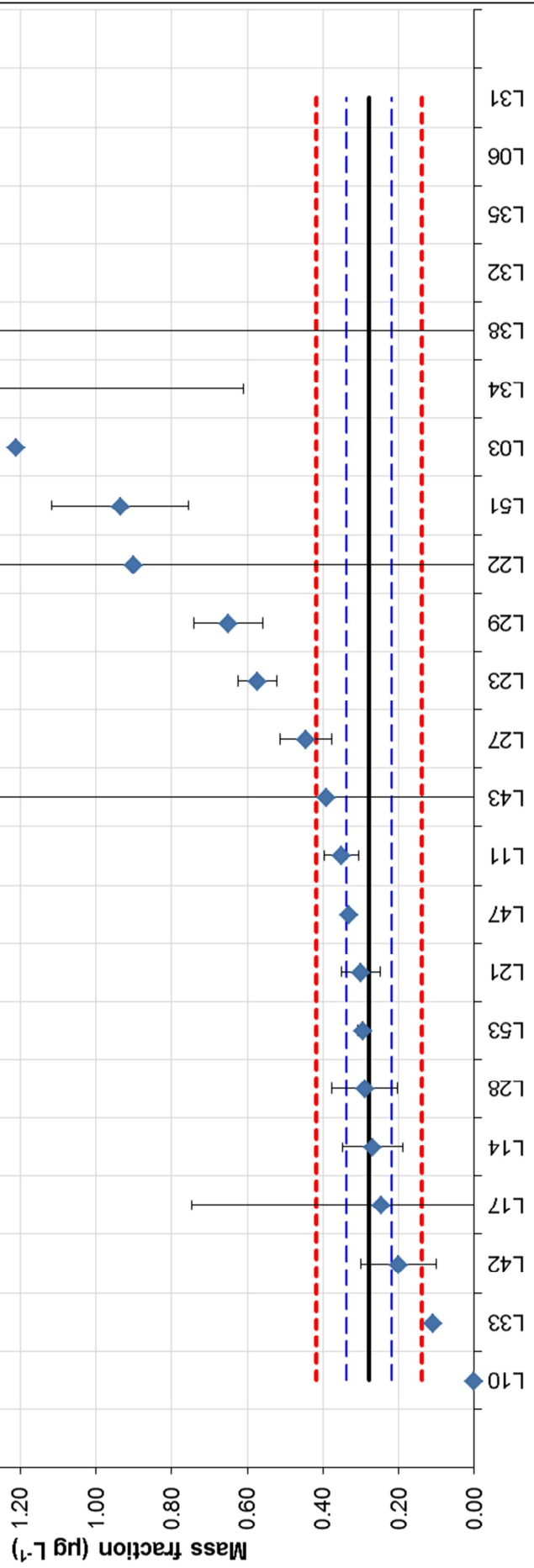
Lab Code	X_{lab}	U_{lab}	k	Technique	U_{lab}	z-score	ζ -score	uncert.
3	1.21			ICP-MS	0	13.33	30.97	b
4	< 1			ICP-MS				
5	< 1			ICP-MS				
6	35			AAS	0	497.35	1155.33	b
7	< 2			ICP-MS				
8	< 5			ICP-MS				
9	< 4			ETAAS				
10	0	0	2	ICP-MS				
11	0.351	0.046	2	ICP-MS	0.023	1.03	1.90	b
14	0.268	0.08	2	ICP-MS	0.04	-0.16	-0.22	a
15	< 5			ICP-OES				
17	0.247	0.5	2	ICP-MS	0.25	-0.46	-0.13	c
19	< 0.68			ICP-MS				
21	0.3	0.05	2	ICP-MS	0.025	0.30	0.53	b
22	0.9	29	2	ICP-MS	14.5	8.89	0.04	c
23	0.573	0.052	2	ICP-OES	0.026	4.21	7.39	b
25	< 1.3			ICP-OES				
27	0.445	0.067	2	ICP-MS	0.0335	2.37	3.68	a
28	0.289	0.087	2	ICP-MS	0.0435	0.14	0.18	a
29	0.65	0.09	2	ICP-MS	0.045	5.31	6.85	a
30	< 5			ICP-MS				
31	517.8	142.3	2	ICP-OES	71.15	7413.05	7.27	c
32	6	0.3	2	ETAAS	0.15	81.95	37.40	c
33	0.110		2	ICP-MS	0	-2.43	-5.65	b
34	1.33	0.72	2	ICP-MS	0.36	15.05	2.91	c
35	14.85			ICP-AES	0	208.71	484.84	b
36	< 1			ICP-MS				
37	< 1			ICP-MS				
38	5.62	6	2	ICP-MS	3	76.50	1.78	c
39	< 0.29	0.27	2	ICP-OES				
41	< 0.5			ICP-MS				
42	0.2	0.1	2.26	ICP-MS	0.044248	-1.14	-1.48	a
43	0.39	20	2	ICP-MS	10	1.59	0.01	c
44	< 3			ICP-OES				
45	< 1			ICP-MS				
46	< 2			ICP-MS				
47	0.33			ICP-MS	0	0.73	1.69	b
48	< 50			ICP-OES				
51	0.936	0.18	2	ICP-MS	0.09	9.41	6.92	c
52	< 0.5			ICP-MS				
53	0.293	0.015	2	ICP-MS	0.0075	0.20	0.44	b

IMEP-40: Cr in seawater

$X_{\text{Ref}} = 0.28$; $U_{\text{Ref}} (k=2) = 0.06$; $\sigma_p = 0.063$ ($\mu\text{g L}^{-1}$)



517.8
35
14.85
6
5.62



Laboratory Code

Measurement results and associated uncertainties (reported uncertainties shown).
Reference value (X_{Ref}): solid black line; Reference interval ($X_{\text{Ref}} \pm U_{\text{Ref}}$): dashed blue lines; Target interval ($X_{\text{Ref}} \pm 2\sigma_p$): dotted red lines.

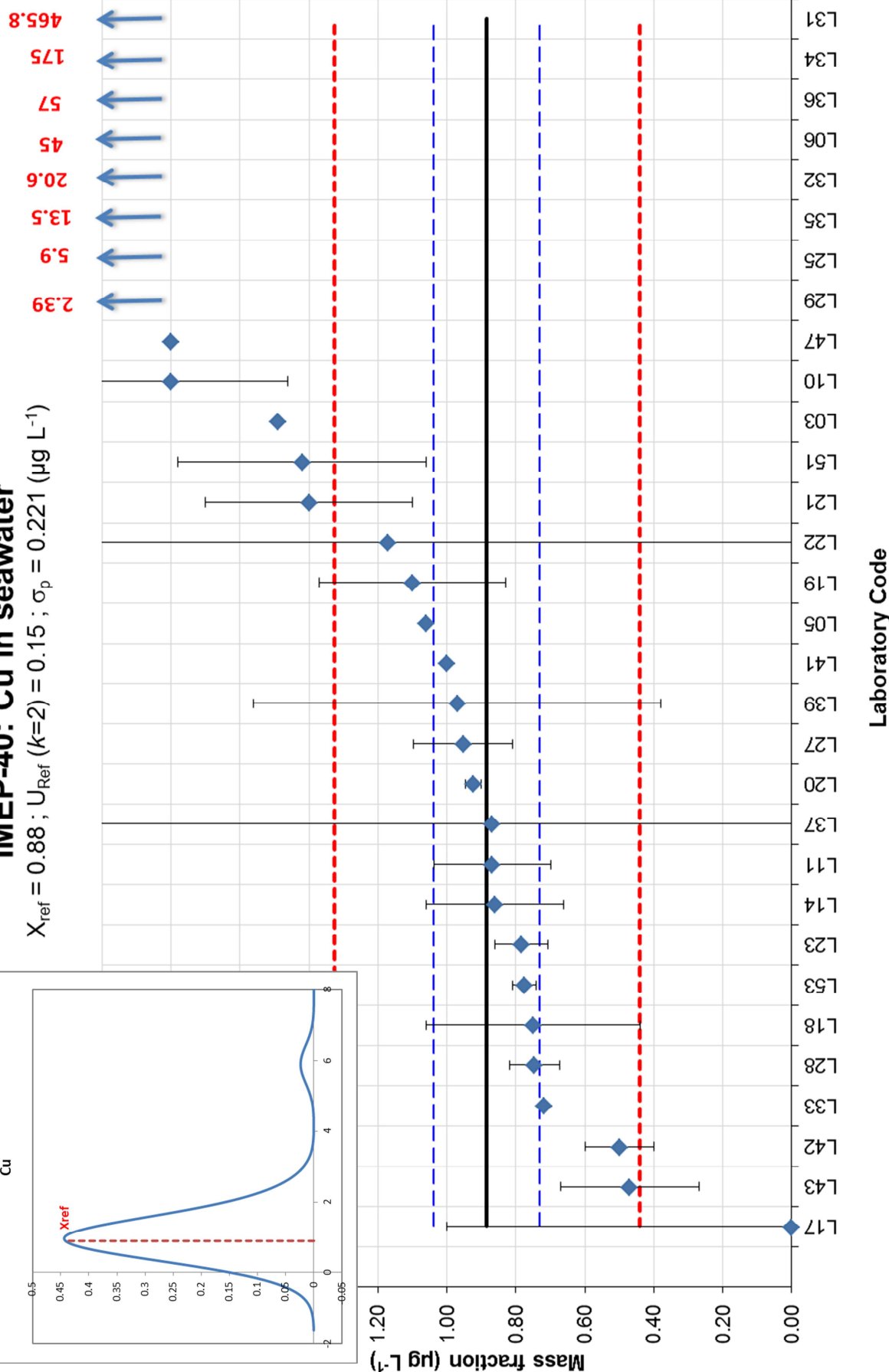
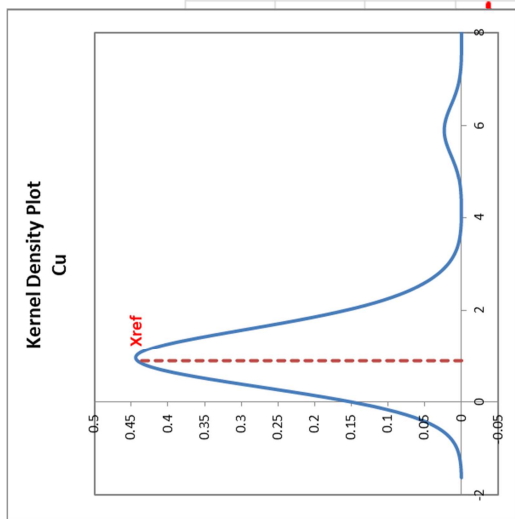
Annex 12: Results for Cu

$X_{ref} = 0.88$; $U_{Ref} (k=2) = 0.15$; $s_p = 0.221$ ($\mu\text{g L}^{-1}$)

Lab Code	X_{lab}	U_{lab}	k	Technique	U_{lab}	z-score	ζ -score	uncert.
3	1.49			ICP-MS	0	2.74	7.92	b
4	< 5			ICP-MS				
5	1.06			ICP-AES	0	0.79	2.30	b
6	45			AAS	0	199.51	576.98	b
7	< 2			ICP-MS				
8	< 5			ICP-MS				
9	< 5			ETAAS				
10	1.8	0.34	2	ICP-MS	0.17	4.14	4.91	a
11	0.868	0.169	2	ICP-MS	0.0845	-0.07	-0.14	a
14	0.861	0.2	2	ICP-MS	0.1	-0.11	-0.19	a
15	< 5			ICP-OES				
17	0	1	2	ICP-MS				
18	0.75	0.31	2	ICP-MS	0.155	-0.61	-0.78	a
19	1.1	0.27	2	ICP-MS	0.135	0.97	1.39	a
20	0.924	0.023	2	TXRF	0.0115	0.18	0.51	b
21	1.4	0.3	2	ICP-MS	0.15	2.33	3.06	a
22	1.17	29	2	ICP-MS	14.5	1.29	0.02	c
23	0.784	0.078	2	ICP-OES	0.039	-0.45	-1.17	b
25	5.9	0.8	3.182	ICP-OES	0.251414	22.68	19.09	c
27	0.953	0.143	2	ICP-MS	0.0715	0.31	0.65	b
28	0.746	0.073	2	ICP-MS	0.0365	-0.63	-1.63	b
29	2.39	0.29	2	ICP-MS	0.145	6.81	9.18	a
30	< 10			ICP-MS				
31	465.8	128	2	ICP-OES	64	2102.57	7.26	c
32	20.6	0.5	2	AAS	0.25	89.16	75.41	c
33	0.719		2	ICP-MS	0	-0.75	-2.16	b
34	175	41	2	ICP-MS	20.5	787.43	8.49	c
35	13.5			ICP-AES	0	57.05	165.00	b
36	57	11	2	ICP-MS	5.5	253.78	10.20	c
37	0.87	30	2	ICP-MS	15	-0.07	0.00	c
38	< 1			ICP-MS				
39	0.97	0.59	2	ICP-OES	0.295	0.39	0.28	c
40	< 5			ETAAS				
41	1			ICP-MS	0	0.52	1.51	b
42	0.5	0.1	2.26	ICP-MS	0.044248	-1.74	-4.35	b
43	0.47	0.2	2	ICP-MS	0.1	-1.87	-3.29	a
44	< 4			ICP-OES				
45	< 1			ICP-MS				
46	< 1			ICP-MS				
47	1.8			ICP-MS	0	4.14	11.97	b
48	< 10			ICP-OES				
51	1.42	0.36	2	ICP-MS	0.18	2.42	2.74	a
52	< 1			ICP-MS				
53	0.776	0.034	2	ICP-MS	0.017	-0.49	-1.38	b

IMEP-40: Cu in seawater

$X_{\text{ref}} = 0.88$; $U_{\text{Ref}} (k=2) = 0.15$; $\sigma_p = 0.221$ ($\mu\text{g L}^{-1}$)



Laboratory Code

Measurement results and associated uncertainties (reported uncertainties shown).

Reference value (X_{Ref}): solid black line; Reference interval ($X_{\text{Ref}} \pm U_{\text{Ref}}$): dashed blue lines; Target interval ($X_{\text{ref}} \pm 2\sigma_p$): dotted red lines.

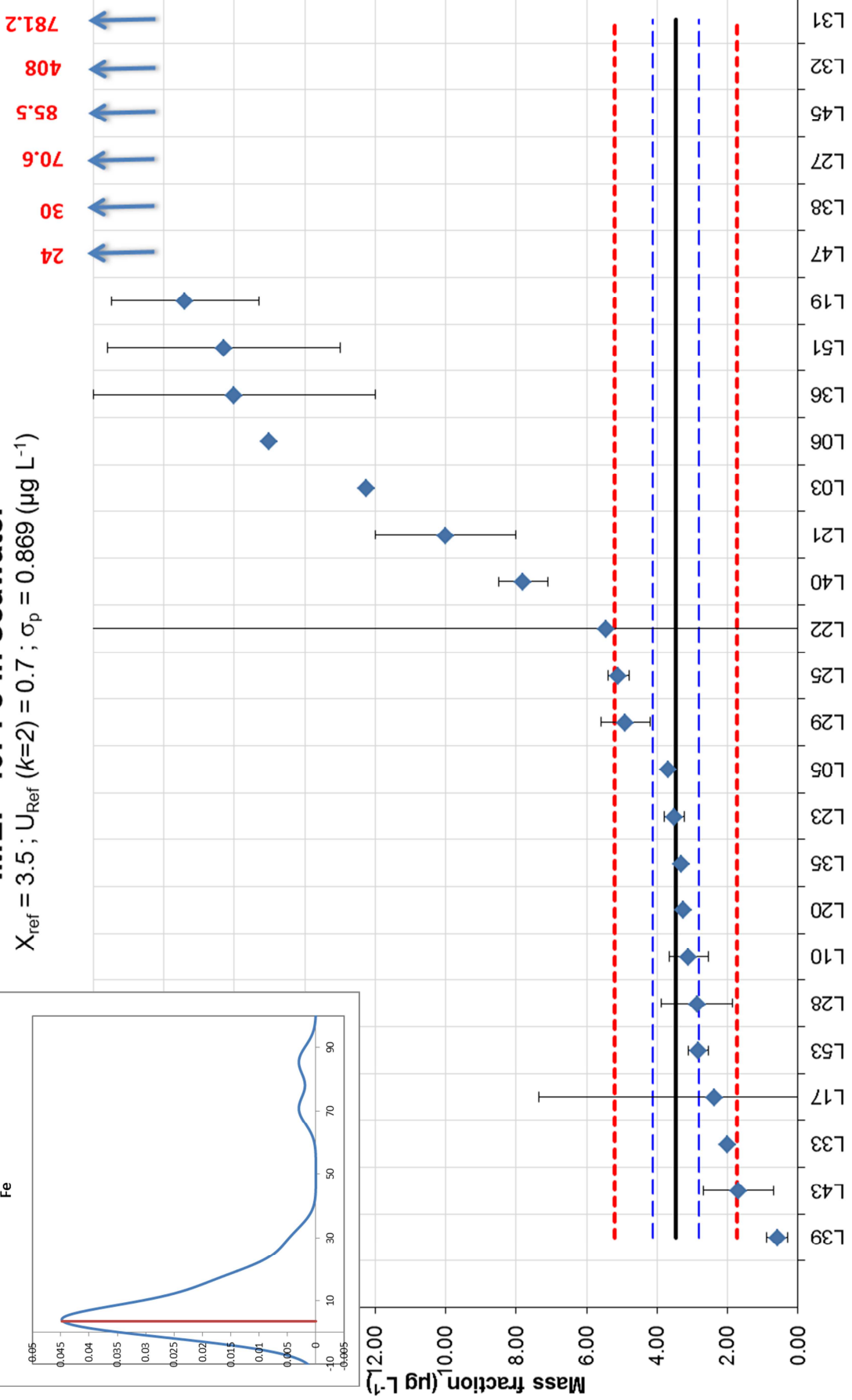
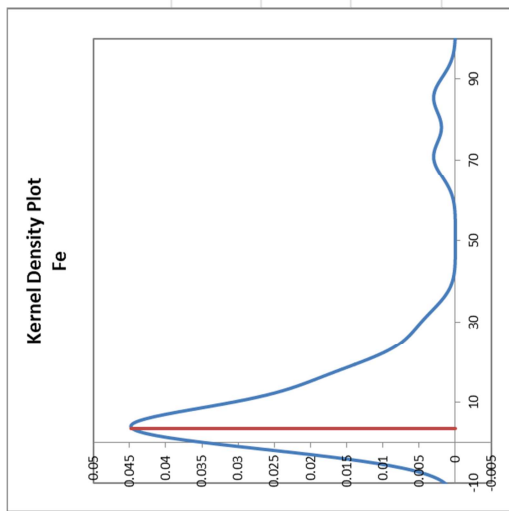
Annex 13: Results for Fe

$X_{ref} = 3.5$; $U_{Ref} (k=2) = 0.7$; $s_p = 0.869$ ($\mu\text{g L}^{-1}$)

Lab Code	X_{lab}	U_{lab}	k	Technique	u_{lab}	z-score	ζ -score	uncert.
3	12.26			ICP-MS	0	10.10	26.65	b
4	< 10			ICP-AES				
5	3.69			ICP-AES	0	0.24	0.64	b
6	15			AAS	0	13.25	34.96	b
7	< 10			ICP-MS				
8	< 10			ICP-OES				
9	< 50			UV-VIS				
10	3.1	0.56	2	ICP-MS	0.28	-0.43	-0.87	b
11	< 5			ICP-MS				
14	< 4			ICP-MS				
15	< 5			ICP-OES				
17	2.36	5	2	ICP-MS	2.5	-1.29	-0.44	c
19	17.4	2.09	2	ICP-MS	1.045	16.01	12.71	c
20	3.244	0.0059	2	TXRF	0.00295	-0.27	-0.71	b
21	10	2	2	ICP-MS	1	7.50	6.19	c
22	5.45	29	2	ICP-MS	14.5	2.27	0.14	c
23	3.52	0.28	2	ICP-OES	0.14	0.05	0.12	b
25	5.1	0.3	3.182	ICP-OES	0.09428	1.87	4.73	b
27	70.6	10.6	2	ICP-MS	5.3	77.20	12.64	c
28	2.87	1	2	ICP-MS	0.5	-0.70	-1.01	a
29	4.9	0.7	2	ICP-MS	0.35	1.64	2.96	a
30	< 200			ICP-OES				
31	781.2	214.6	2	ICP-OES	107.3	894.50	7.25	c
32	408	17	2	AAS	8.5	465.27	47.56	c
33	2.00		2	ICP-MS	0	-1.70	-4.50	b
34	< 25			ICP-MS				
35	3.3			ICP-AES	0	-0.20	-0.54	b
36	16	4	2	ICP-MS	2	14.40	6.18	c
37	< 10			ICP-MS				
38	30	4.64	2	ICP-MS	2.32	30.50479	11.31837	c
39	0.59	0.29	2	ICP-OES	0.145	-3.32	-8.02	b
40	7.8	0.7	2	Flame AAS	0.35	4.97	8.99	a
41	< 20			ICP-MS				
42	< 5			ICP-MS				
43	1.7	1	2	ICP-OES	0.5	-2.04	-2.97	a
44	< 4			ICP-OES				
45	85.5			ICP-MS	0	94.34	248.89	b
46	< 50			ICP-MS				
47	24			ICP-MS	0	23.60	62.27	b
48	< 100			ICP-OES				
51	16.3	3.3	2	ICP-MS	1.65	14.75	7.62	c
52	< 10			ICP-MS				
53	2.827	0.291	2	ICP-MS	0.1455	-0.75	-1.81	b

IMEP-40: Fe in seawater

$X_{\text{ref}} = 3.5$; $U_{\text{Ref}} (k=2) = 0.7$; $\sigma_p = 0.869$ ($\mu\text{g L}^{-1}$)



Laboratory Code

Measurement results and associated uncertainties (reported uncertainties shown).
 Reference value (X_{ref}): solid black line; Reference interval ($X_{\text{ref}} \pm U_{\text{Ref}}$): dashed blue lines; Target interval ($X_{\text{ref}} \pm 2\sigma_p$): dotted red lines.

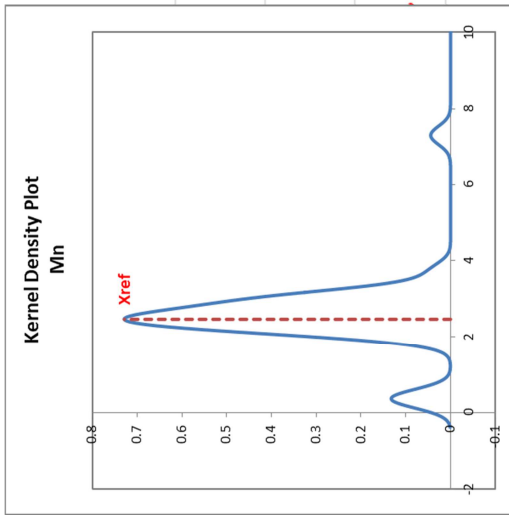
Annex 14: Results for Mn

$X_{ref} = 2.46$; $U_{Ref} (k=2) = 0.15$; $s_p = 0.615 (\mu\text{g L}^{-1})$

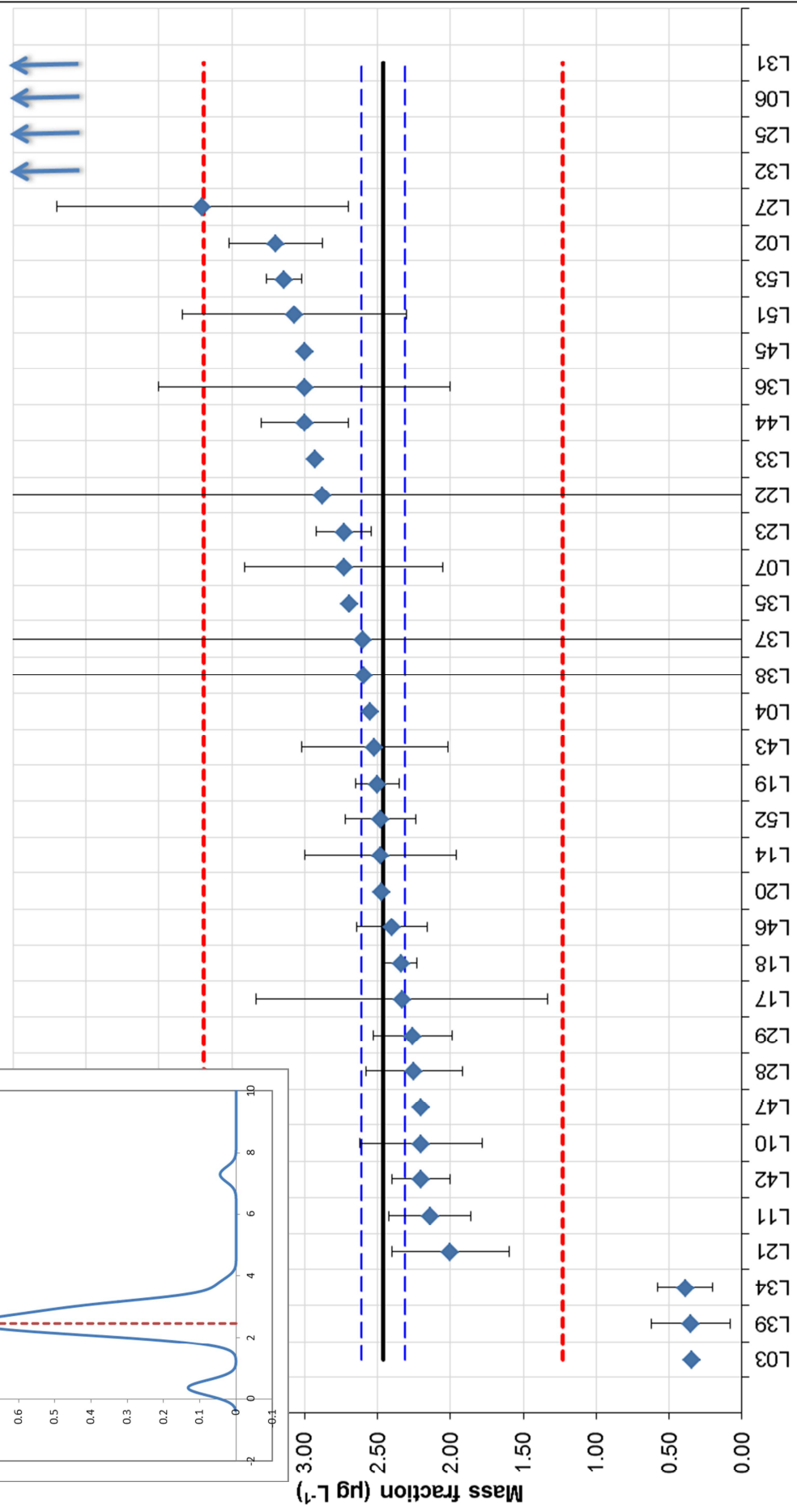
Lab Code	X_{lab}	U_{lab}	k	Technique	U_{lab}	z-score	ζ -score	uncert.
2	3.2	0.32	2	ICP-MS	0.16	1.20	4.20	a
3	0.344			ICP-MS	0	-3.44	-28.70	b
4	2.55			ICP-MS	0	0.15	1.21	b
5	< 1			ICP-AES				
6	36			AAS	0	54.53	454.78	b
7	2.73	0.68	2	ICP-MS	0.34	0.43826	0.774852	a
8	< 10			ICP-OES				
10	2.2	0.42	2	ICP-MS	0.21	-0.42	-1.17	a
11	2.14	0.28	2	ICP-MS	0.14	-0.52	-2.02	a
14	2.48	0.52	2	ICP-MS	0.26	0.03	0.07	a
15	< 5			ICP-OES				
17	2.33	1	2	ICP-MS	0.5	-0.21	-0.26	a
18	2.34	0.11	2	ICP-MS	0.055	-0.20	-1.31	b
19	2.5	0.15	2	ICP-MS	0.075	0.06	0.38	a
20	2.471	0.013	2	TXRF	0.0065	0.02	0.14	b
21	2	0.4	2	ICP-MS	0.2	-0.75	-2.16	a
22	2.88	26	2	ICP-MS	13	0.68	0.03	c
23	2.73	0.19	2	ICP-OES	0.095	0.44	2.24	a
25	13.3	0.1	3.182	ICP-OES	0.031427	17.62	135.21	b
27	3.7	1	2	ICP-MS	0.5	2.02	2.45	a
28	2.25	0.33	2	ICP-MS	0.165	-0.34	-1.16	a
29	2.26	0.27	2	ICP-MS	0.135	-0.33	-1.30	a
30	< 100			ICP-OES				
31	84.4	14.1	2	ICP-OES	7.05	133.21	11.62	c
32	7.3	0.2	2	AAS	0.1	7.867873	38.9492	a
33	2.93		2	ICP-MS	0	0.76	6.33	b
34	0.39	0.19	2	ICP-MS	0.095	-3.37	-17.22	a
35	2.69			ICP-AES	0	0.37	3.11	b
36	3	1	2	ICP-MS	0.5	0.88	1.07	a
37	2.6	20	2	ICP-MS	10	0.23	0.01	c
38	2.59	4.15	2	ICP-MS	2.075	0.21	0.06	c
39	0.35	0.27	2	ICP-OES	0.135	-3.43	-13.72	a
41	< 0.5			ICP-MS				
42	2.2	0.2	2.26	ICP-MS	0.088496	-0.42	-2.26	a
43	2.52	0.5	2	ICP-MS	0.25	0.10	0.23	a
44	3	0.3	2	ICP-OES	0.15	0.88	3.23	a
45	3			ICP-MS	0	0.88	7.32	b
46	2.4	0.24	$\sqrt{3}$	ICP-MS	0.138564	-0.10	-0.38	a
47	2.2			ICP-MS	0	-0.42	-3.53	b
48	< 50			ICP-OES				
51	3.07	0.77	2	ICP-MS	0.385	0.99	1.56	a
52	2.48	0.24	2	ICP-MS	0.12	0.03	0.14	a
53	3.14	0.12	2	ICP-MS	0.06	1.10	7.15	b

IMEP-40: Mn in seawater

$X_{\text{ref}} = 2.46$; $U_{\text{Ref}} (k=2) = 0.15$; $\sigma_p = 0.615$ ($\mu\text{g L}^{-1}$)



7.3
13.3
36
84.4



Laboratory Code

Measurement results and associated uncertainties (reported uncertainties shown).
 Reference value (X_{Ref}): solid black line; Reference interval ($X_{\text{Ref}} \pm U_{\text{Ref}}$): dashed blue lines; Target interval ($X_{\text{Ref}} \pm 2\sigma_p$): dotted red lines.

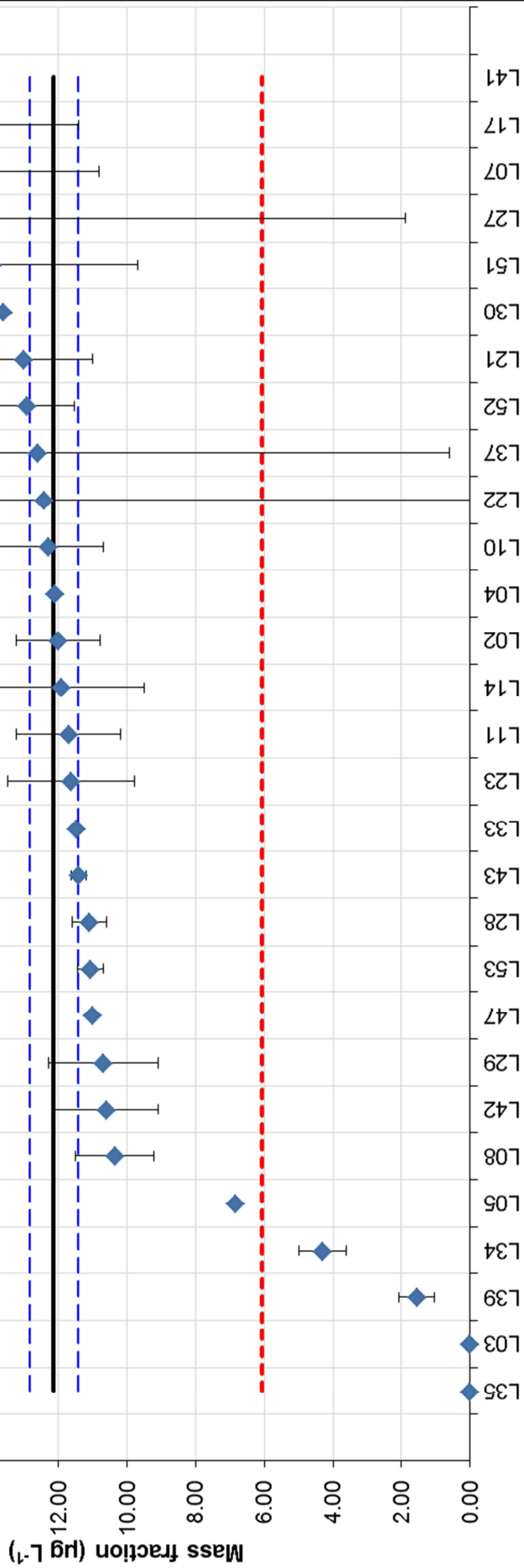
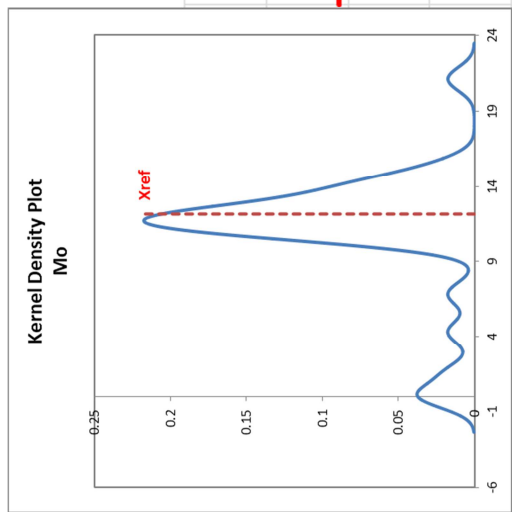
Annex 15: Results for Mo

$X_{\text{ref}} = 12.1$; $U_{\text{Ref}} (k=2) = 0.7$; $s_p = 3.034$ ($\mu\text{g L}^{-1}$)

Lab Code	X_{lab}	U_{lab}	k	Technique	U_{lab}	z-score	ζ -score	uncert.
2	12	1.21	2	ICP-MS	0.605	-0.05	-0.20	a
3	0.002			ICP-MS	0	-4.00	-34.32	b
4	12.1			ICP-MS	0	-0.01	-0.10	b
5	6.83			ICP-AES	0	-1.74897	-15.0095	b
6	< 600			AAS				
7	14.4	3.6	2	ICP-MS	1.8	0.75	1.23	a
8	10.35	1.14	$\sqrt{3}$	ICP-OES	0.658179	-0.59	-2.39	a
10	12.3	1.6	2	ICP-MS	0.8	0.05	0.19	a
11	11.7	1.52	2	ICP-MS	0.76	-0.14	-0.52	a
14	11.9	2.4	2	ICP-MS	1.2	-0.08	-0.19	a
15	< 5			ICP-OES				
17	15.4	4	2	ICP-MS	2	1.08	1.61	a
21	13	2	2	ICP-MS	1	0.28	0.81	a
22	12.4	21	2	ICP-MS	10.5	0.09	0.03	c
23	11.63	1.86	2	ICP-OES	0.93	-0.17	-0.51	a
25	< 5			ICP-OES				
27	14.2	12.3	2	ICP-MS	6.15	0.68	0.33	c
28	11.1	0.5	2	ICP-MS	0.25	-0.34	-2.39	b
29	10.7	1.6	2	ICP-MS	0.8	-0.47	-1.64	a
30	13.6	0.017	$\sqrt{3}$	ICP-MS	0.009815	0.48	4.14	b
31	< 0.4			ICP-OES				
33	11.5		2	ICP-MS	0	-0.22	-1.90	b
34	4.3	0.7	2	ICP-MS	0.35	-2.58	-15.75	b
35	0			ICP-AES				
37	12.6	12	2	ICP-MS	6	0.15	0.08	c
39	1.56	0.53	2	ICP-OES	0.265	-3.49	-23.94	b
41	21.1			ICP-MS	0	2.95	25.35	b
42	10.6	1.5	2.26	ICP-MS	0.663717	-0.51	-2.04	a
43	11.4	0.22	2	ICP-MS	0.11	-0.24	-1.99	b
44	< 4			ICP-OES				
46	< 20			ICP-MS				
47	11			ICP-MS	0	-0.37462	-3.21498	b
48	< 50			ICP-OES				
51	13.9	4.2	2	ICP-MS	2.1	0.58	0.83	a
52	12.9	1.37	2	ICP-MS	0.685	0.25	0.99	a
53	11.065	0.373	2	ICP-MS	0.1865	-0.35	-2.68	b

IMEP-40: Mo in seawater

$X_{ref} = 12.1$; $U_{Ref} (k=2) = 0.7$; $\sigma_p = 3.034$ ($\mu\text{g L}^{-1}$)



Laboratory Code

Measurement results and associated uncertainties (reported uncertainties shown).

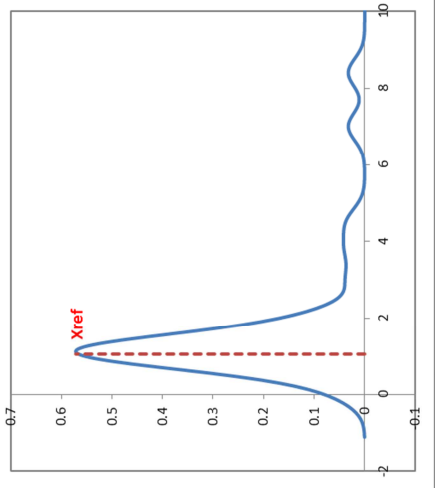
Reference value (X_{ref}): solid black line; Reference interval ($X_{ref} \pm U_{ref}$): dashed blue lines; Target interval ($X_{ref} \pm 2\sigma_p$): dotted red lines.

Annex 16: Results for Ni

$X_{ref} = 1.06$; $U_{Ref} (k=2) = 0.11$; $s_p = 0.264 (\mu\text{g L}^{-1})$

Lab Code	X_{lab}	U_{lab}	k	Technique	U_{lab}	z-score	ζ -score	uncert.
2	4.5	0.45	2	ICP-MS	0.225	13.05	14.84	a
3	0.92			ICP-MS	0	-0.51	-2.37	b
4	< 1			ICP-MS				
5	1.29			ICP-AES	0	0.89	4.11	b
6	< 30			AAS				
7	< 2			ICP-MS				
8	< 25			ICP-OES				
9	< 5			ETAAS				
10	0	0	2	ICP-MS				
11	1.23	0.16	2	ICP-MS	0.08	0.66	1.78	a
14	1	0.2	2	ICP-MS	0.1	-0.21	-0.48	a
15	< 5			ICP-OES				
17	1.39	0.4	2	ICP-MS	0.2	1.27	1.61	a
18	1.59	0.56	2	ICP-MS	0.28	2.03	1.87	c
19	< 2.98			ICP-MS				
20	1.191	0.015	2	TXRF	0.0075	0.51	2.35	b
21	0.9	0.2	2	ICP-MS	0.1	-0.59	-1.35	a
22	1.35	28	2	ICP-MS	14	1.12	0.02	c
23	1.47	0.15	2	ICP-OES	0.075	1.57	4.40	a
25	7	4.5	3.182	ICP-OES	1.414205	22.53	4.20	c
27	1.22	0.3	2	ICP-MS	0.15	0.62	1.03	a
28	0.767	0.078	2	ICP-MS	0.039	-1.09	-4.17	b
29	1	0.12	2	ICP-MS	0.06	-0.21	-0.67	a
30	< 5			ICP-MS				
31	110.9	12	2	ICP-OES	6	416.31	18.31	c
32	3.8	0.2	2	ETAAS	0.1	10.40	23.83	a
33	0.86		2	ICP-MS	0	-0.74	-3.43	b
34	8.4	1.4	2	ICP-MS	0.7	27.84	10.46	c
35	13.75			ICP-AES	0	48.11	222.33	b
36	3	1	2	ICP-MS	0.5	7.37	3.86	c
37	1.2	30	2	ICP-MS	15	0.55	0.01	c
38	2.14	7.9	2	ICP-MS	3.95	4.11	0.27	c
39	0.4	0.3	2	ICP-OES	0.15	-2.48	-4.08	a
41	1.8			ICP-MS	0	2.82	13.04	b
42	0.8	0.1	2.26	ICP-MS	0.044248	-0.97	-3.54	b
43	0.51	0.4	2	ICP-MS	0.2	-2.07	-2.62	a
44	< 4			ICP-OES				
45	2			ICP-MS	0	3.58	16.54	b
46	< 4			ICP-MS				
47	1.1			ICP-MS	0	0.17	0.78	b
48	< 20			ICP-OES				
51	1.37	0.34	2	ICP-MS	0.17	1.19	1.75	a
52	1.06	0.17	2	ICP-MS	0.085	0.02	0.04	a
53	0.987	0.034	2	ICP-MS	0.017	-0.26	-1.15	b

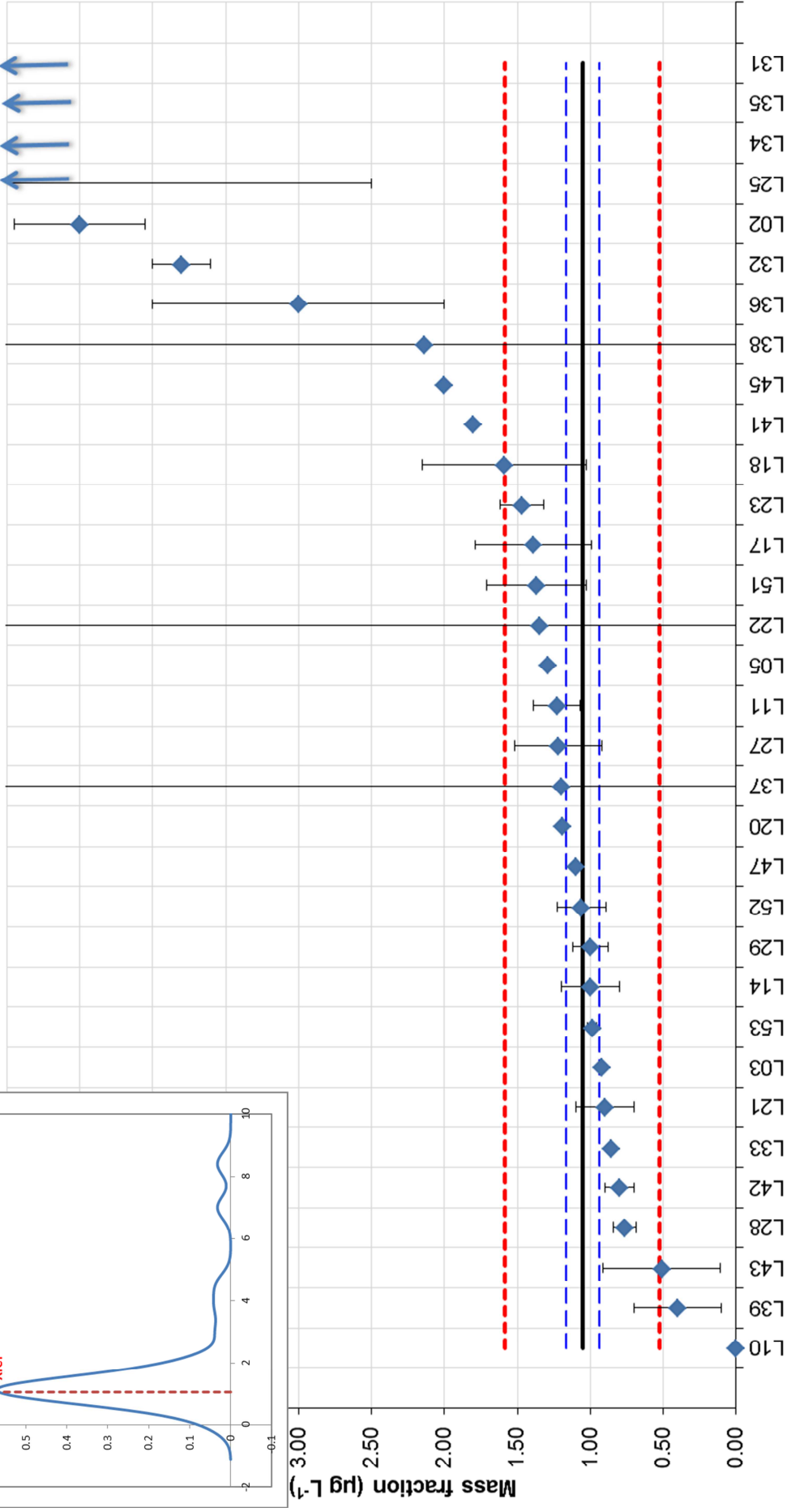
Kernel Density Plot
Ni



IMEP-40: Ni in seawater

$X_{ref} = 1.06$; $U_{Ref} (k=2) = 0.11$; $\sigma_p = 0.264$ ($\mu\text{g L}^{-1}$)

7
8.4
13.75
110.9



Laboratory Code

Measurement results and associated uncertainties (reported uncertainties shown).

Reference value (X_{Ref}): solid black line; Reference interval ($X_{Ref} \pm U_{Ref}$): dashed blue lines; Target interval ($X_{Ref} \pm 2\sigma_p$): dotted red lines.

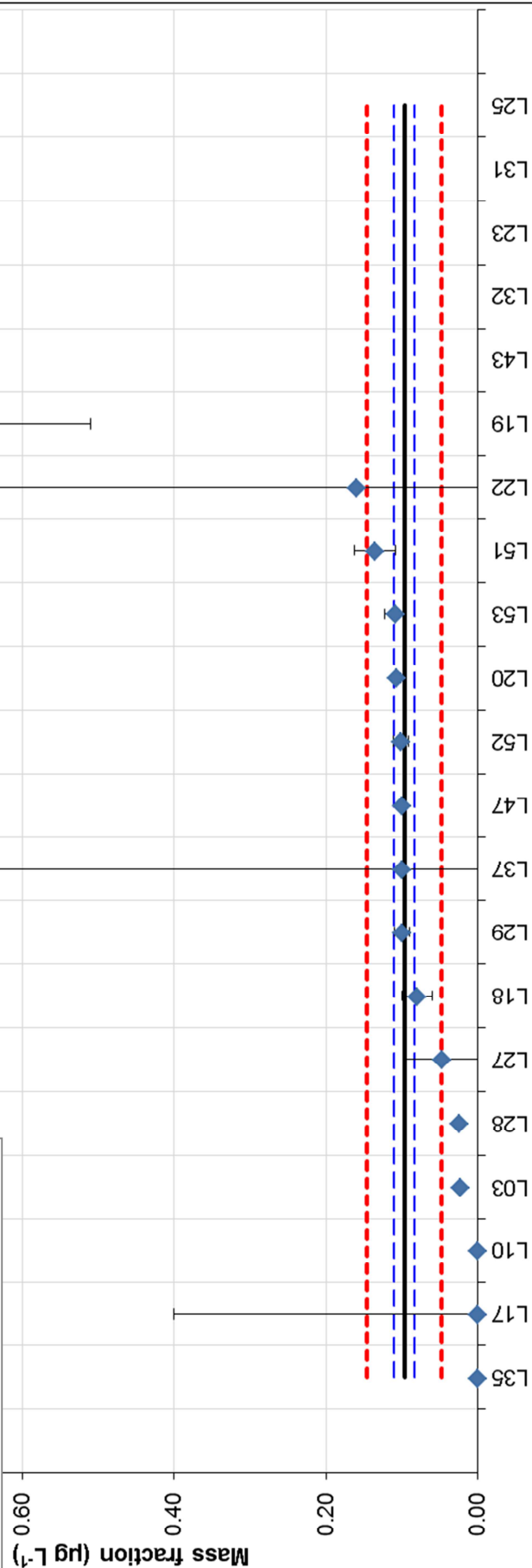
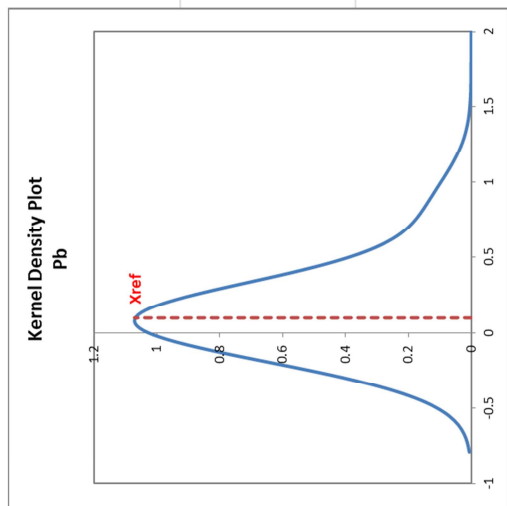
Annex 17: Results for Pb

$X_{ref} = 0.097$; $U_{Ref} (k=2) = 0.014$; $s_p = 0.024 (\mu\text{g L}^{-1})$

Lab Code	X_{lab}	U_{lab}	k	Technique	U_{lab}	z-score	ζ -score	uncert.
3	0.024			ICP-MS	0	-3.01	-10.83	b
4	< 1	25		ICP-MS				
5	< 1			ICP-AES				
6	< 50			AAS				
7	< 1			ICP-MS				
8	< 8			ICP-OES				
9	< 5			ETAAS				
10	0	0	2	ICP-MS				
11	< 0.1			ICP-MS				
14	< 0.3			ICP-MS				
15	< 5			ICP-OES				
17	0	0.4	2	ICP-MS				
18	0.08	0.02	2	ICP-MS	0.01	-0.71	-1.43	a
19	0.65	0.14	2	ICP-MS	0.07	22.73	7.86	c
20	0.107	0.006	2	TXRF	0.003	0.40	1.31	b
21	< 0.1			ICP-MS				
22	0.16	29	2	ICP-MS	14.5	2.58	0.00	c
23	6.68	1.07	2	ICP-OES	0.535	270.70	12.30	c
25	474.3	5.6	3.182	ICP-OES	1.759899	19500.84	269.45	c
27	0.0472	0.05	2	ICP-MS	0.025	-2.06	-1.93	c
28	0.025	0.003	2	ICP-MS	0.0015	-2.97	-10.43	b
29	0.1	0.01	2	ICP-MS	0.005	0.11	0.32	b
30	< 1			ICP-MS				
31	78	14.5	2	ICP-OES	7.25	3203.63	10.75	c
32	4.1	0.5	2	ETAAS	0.25	164.61	16.01	c
33	< 0.1		2	ICP-MS				
34	< 1			ICP-MS				
35	0			ICP-AES				
36	< 1			ICP-MS				
37	0.1	30	2	ICP-MS	15	0.11	0.00	c
38	< 0.2			ICP-MS				
39	< 1.24	0.06	2	ICP-OES				
40	< 0.3			ETAAS				
41	< 1			ICP-MS				
42	< 0.1			ICP-MS				
43	0.862	0.18	2	ICP-MS	0.09	31.45	8.47	c
44	< 4			ICP-OES				
45	< 1			ICP-MS				
46	< 0.5			ICP-MS				
47	0.1			ICP-MS	0	0.11	0.40	b
48	< 10			ICP-OES				
51	0.136	0.027	2	ICP-MS	0.0135	1.59	2.56	a
52	0.102	0.01	2	ICP-MS	0.005	0.19	0.56	b
53	0.109	0.014	2	ICP-MS	0.007	0.48	1.20	a

IMEP-40: Pb in seawater

$X_{ref} = 0.097$; $U_{Ref} (k=2) = 0.014$; $\sigma_p = 0.024$ ($\mu\text{g L}^{-1}$)



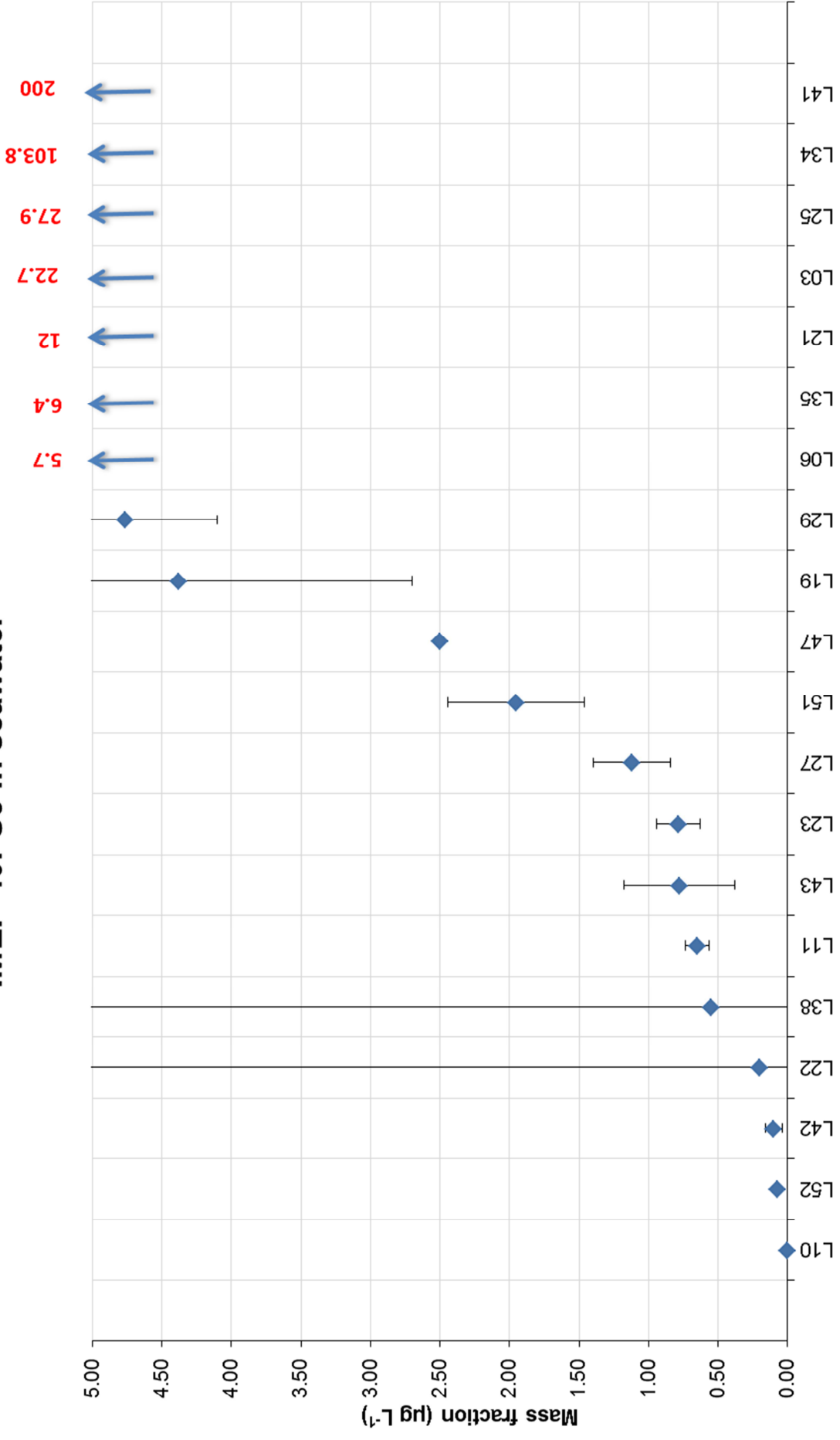
Laboratory Code

Measurement results and associated uncertainties (reported uncertainties shown).
 Reference value (X_{ref}): solid black line; Reference interval ($X_{ref} \pm U_{Ref}$): dashed blue lines; Target interval ($X_{ref} \pm 2\sigma_p$): dotted red lines.

Annex 18: Results for Se

Lab Code	X_{lab}	U_{lab}	k	Technique
3	22.7			ICP-MS
4	< 1			ICP-MS
5	< 5			AFS
6	5.7			HG-AAS
7	< 2			ICP-MS
8	< 3			ICP-MS
10	0	0	2	ICP-MS
11	0.653	0.085	2	ICP-MS
14	< 3			ICP-MS
15	< 0.2			HG-ICPI-OES
16	< 0.5			HG-AAS
19	4.38	1.68	2	ICP-MS
21	12	3	2	ICP-MS
22	0.205	30	2	ICP-MS
23	0.783	0.157	2	ICP-OES
25	27.9	13.1	3.182	ICP-OES
27	1.12	0.28	2	ICP-MS
29	4.76	0.66	2	ICP-MS
30	< 2			ICP-MS
31	< 1.5			ICP-OES
32	< 6			ETAAS
33	< 1		2	ICP-MS
34	103.8	16.94	2	ICP-MS
35	6.4			ICP-AES
37	< 5			ICP-MS
38	0.55	12.56	2	ICP-MS
39	< 2.6	0.44	2	ICP-OES
41	200			ICP-MS
42	0.1	0.06	2.26	ICP-MS
43	0.78	0.4	2	ICP-MS
44	< 0.5			ICP-OES
46	< 0.5			ICP-MS
47	2.5			ICP-MS
48	< 10			ICP-OES
51	1.95	0.49	2	ICP-MS
52	0.076	0.0061	2	HG-ICP-MS
53	< 0.694			ICP-MS

IMEP-40: Se in seawater



Laboratory Code

Measurement results and associated uncertainties (reported uncertainties shown).

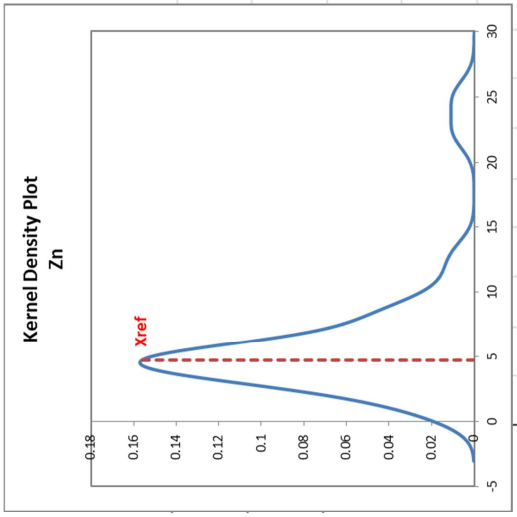
Annex 19: Results for Zn

$X_{ref} = 4.7$; $U_{Ref} (k=2) = 0.5$; $s_p = 1.172 (\mu\text{g L}^{-1})$

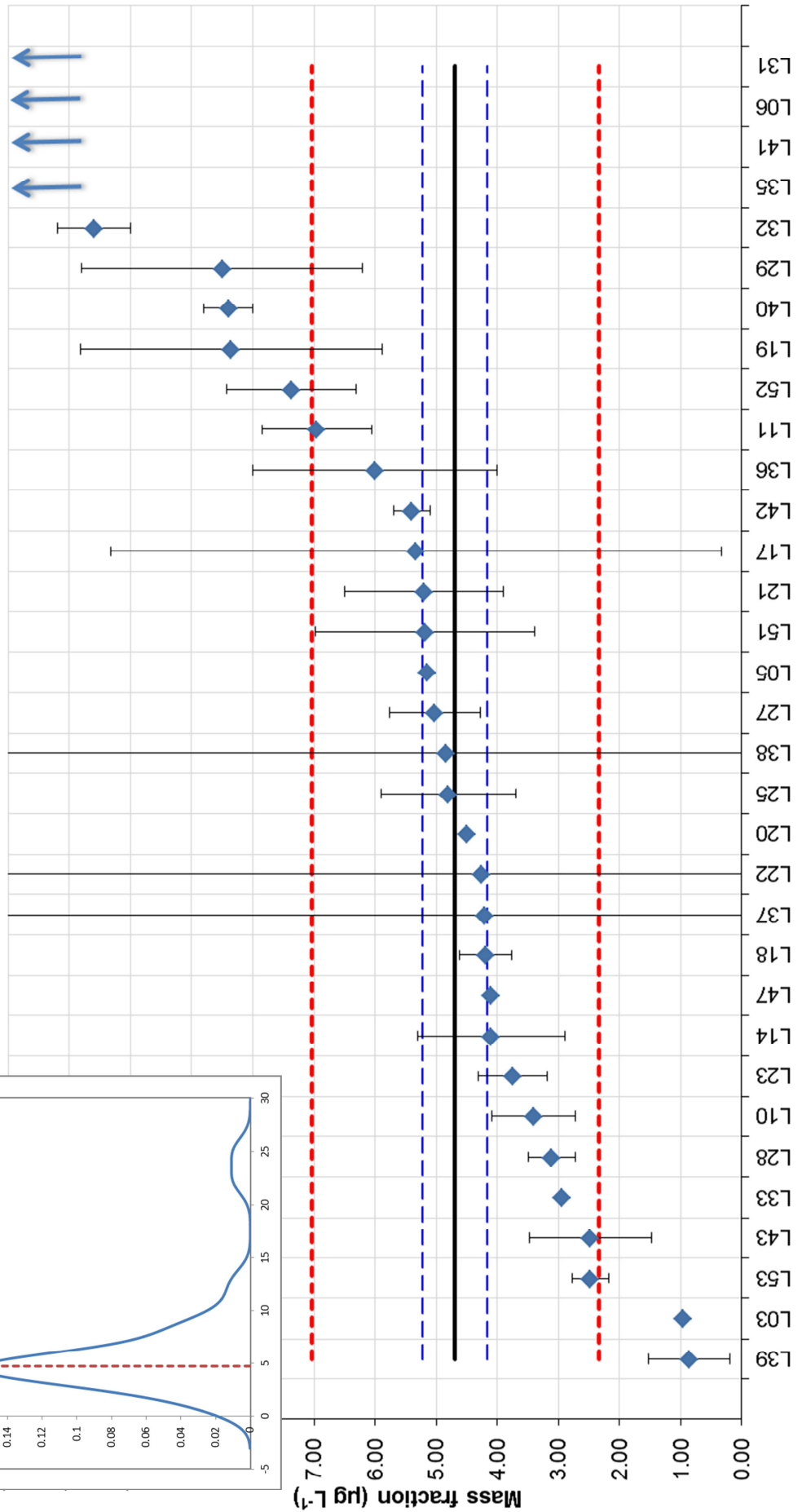
Lab Code	X_{lab}	U_{lab}	k	Technique	u_{lab}	z-score	ζ -score	uncert.
3	0.969			ICP-MS	0	-3.17	-14.03	b
4	< 10			ICP-MS				
5	5.15			ICP-AES	0	0.39	1.74	b
6	25			AAS	0	17.33	76.62	b
7	< 10			ICP-AES				
8	< 25			ICP-OES				
10	3.4	0.68	2	ICP-MS	0.34	-1.10	-2.99	a
11	6.95	0.903	2	ICP-MS	0.4515	1.93	4.32	a
14	4.1	1.2	2	ICP-MS	0.6	-0.50	-0.90	a
15	< 5			ICP-OES				
17	5.33	5	2	ICP-MS	2.5	0.55	0.26	c
18	4.19	0.43	2	ICP-MS	0.215	-0.43	-1.46	b
19	8.35	2.47	2	ICP-MS	1.235	3.12	2.90	c
20	4.494	0.0039	2	TXRF	0.00195	-0.17	-0.74	b
21	5.2	1.3	2	ICP-MS	0.65	0.44	0.73	a
22	4.26	30	2	ICP-MS	15	-0.37	-0.03	c
23	3.75	0.563	2	ICP-OES	0.2815	-0.80	-2.43	a
25	4.8	1.1	3.182	ICP-OES	0.345695	0.09	0.26	a
27	5.02	0.75	2	ICP-MS	0.375	0.28	0.72	a
28	3.11	0.38	2	ICP-MS	0.19	-1.35	-4.84	b
29	8.5	2.3	2	ICP-MS	1.15	3.25	3.23	a
30	< 10			ICP-MS				
31	78	10.7	2	ICP-OES	5.35	62.54	13.69	c
32	10.6	0.6	2	AAS	0.3	5.04	14.77	a
33	2.95		2	ICP-MS	0	-1.49	-6.57	b
34	< 10			ICP-MS				
35	12.74			ICP-AES	0	6.87	30.37	b
36	6	2	2	ICP-MS	1	1.12	1.27	a
37	4.2	30	2	ICP-MS	15	-0.42	-0.03	c
38	4.84	7.38	2	ICP-MS	3.69	0.13	0.04	c
39	0.86	0.66	2	ICP-OES	0.33	-3.27	-9.05	a
40	8.4	0.4	2	Flame AAS	0.2	3.17	11.18	b
41	22.3			ICP-MS	0	15.02	66.44	b
42	5.4	0.3	2.26	ICP-MS	0.132743	0.61	2.40	b
43	2.48	1	2	ICP-MS	0.5	-1.88	-3.90	a
44	< 5			ICP-OES				
45	< 25			ICP-MS				
46	< 50			ICP-MS				
47	4.1			ICP-MS	0	-0.50	-2.22	b
48	< 50			ICP-OES				
51	5.18	1.8	2	ICP-MS	0.9	0.42	0.52	a
52	7.36	1.06	2	ICP-MS	0.53	2.28	4.51	a
53	2.477	0.3	2	ICP-MS	0.15	-1.89	-7.26	b

IMEP-40: Zn in seawater

$X_{\text{ref}} = 4.7$; $U_{\text{Ref}} (k=2) = 0.5$; $\sigma_p = 1.172$ ($\mu\text{g L}^{-1}$)



12.74
22.3
25
78



Laboratory Code

Measurement results and associated uncertainties (reported uncertainties shown).
 Reference value (X_{Ref}): solid black line; Reference interval ($X_{\text{Ref}} \pm U_{\text{Ref}}$): dashed blue lines; Target interval ($X_{\text{Ref}} \pm 2\sigma_p$): dotted red lines.

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