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Agenda item 5: MEDPOL Proficiency Test on the Determination of Trace Elements in Fish Sample (2020)

UNEP/MAP
Athens, 2021

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REPORT

MEDPOL PROFICIENCY TEST
ON THE DETERMINATION OF TRACE ELEMENTS
IN FISH SAMPLE
IAEA-MEL-2020-TE MEDPOL

2020

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1. INTRODUCTION

The International Atomic Energy Agency's Environment Laboratories (IAEA-NAEL), and in particular the Environment Laboratories (NAEL), continues to help Member States understand, monitor and protect the marine environment. Relevant activities comprise the organization of global inter-laboratory comparison, regional proficiency tests, the production of marine certified reference materials and development of recommended analytical methods for trace elements and organic pollutants analysis in marine samples. The Marine Environmental Studies Laboratory (MESL) of NAEL is actively assisting Member States with the organization of inter-laboratory comparisons and provision of certified reference materials.

The IAEA has a long collaboration with UN Environment Programme/Mediterranean Action Plan (UNEP/ MAP) and its Program for the Assessment and Control of Pollution in the Mediterranean region (MED POL) which was initiated as the environmental assessment component of the Mediterranean Action Plan (MAP).

The MESL provides assistance to the designated IMAP competent laboratories via training (trace element, petroleum hydrocarbons and organochlorine compounds), provision of certified reference materials and organisation of targeted proficiency tests (PTs) on matrices of relevance to the marine monitoring studies.

The periodic external assessments of measurement performances of monitoring laboratories via interlaboratory comparisons (ILCs) and targeted proficiency tests (PTs) are of crucial interest for laboratories as they provide clear information of their measurement capabilities. These exercises are designed not only to monitor and demonstrate the performance and analytical capabilities of the participating laboratories, but also to identify gaps and problem areas where further development is needed.

This report describes the results of the PT on the determination of selected trace elements in fish sample organised by the MESL in 2020 for the designated IMAP Pollution Cluster competent laboratories. In line with the conclusions of the Meeting of the Ecosystem Approach Correspondence Group on Pollution Monitoring (April, 2019), this report is complemented with the individual evaluation reports for each specific laboratory that participated in 2020 PT, as well as the national reports. The individual reports have been shared by MESL with the laboratories, while the National

Reports for all 2020/2021 activities will be prepared for submission to MEDPOL Focal Points respectively to designated IMAP laboratories in November 2021.

The IAEA officers responsible for this publication are S. Azemard, E. Vasileva, Mr. A. Trinkl from NAEL Terrestrial Laboratory was responsible for the management of the on-line reporting system. This report has also been revised by the MED POL Monitoring and Assessment Officer, Jelena Knezevic and IAEA Scientific Secretary, Sylvia Sander.

2. SCOPE OF EXERCISE

In July 2020 the MED POL Monitoring and Assessment Officer contacted MEDPOL Focal Points of the Contracting Parties of Barcelona Convention that are eligible for participation in Proficiency Testing for IMAP CI 17, according to procedures of IAEA-MESL, requesting them to provide the names of the designated national laboratories, involved in implementation of IMAP CI 17. The final list of designated national laboratories, respectively participants in the organised by MESL targeted proficiency test for trace elements in marine environment, was established at the end of August 2020.

The test material, named ***IAEA-MEL-2020-TE MEDPOL*** sample, was sent to 18 designated monitoring laboratories from 15 countries. Figure 1 shows the distribution of PT samples in MED POL countries, and the distribution per countries of received results.

Participating laboratories, thereafter, also called participants received together with the sample an information sheet (see Annex 3) with information on expected concentration range of analytes, protocol for determination of moisture and explanation on expected reported results and information., Participants were requested to use their established analytical methods usually applied for IMAP /MED POL monitoring studies, for the determination of total contents of the mandatory elements: Cd, Hg and Pb and additional elements: As, Co, Cr, Cu, Fe, Mn, MeHg, Ni, and Zn in IAEA-MESL-2020-TE-MEPDOL-PT sample, as well as in one matrix matching quality control sample.

The deadline for reporting the results back to the MESL was originally set to 2 November 2020, but deadline was extended to 1st December. Finally, 15 out of 18

(83%) participating laboratories proposed for participation in this proficiency testing sent their results in the requested deadlines.

Laboratories participating in the present exercise are listed in the

Annex 1:

List of participants

Designated IMAP Competent laboratories that sent results

1. Designated IMAP competent laboratories which did not report the results are listed in the Annex 2.

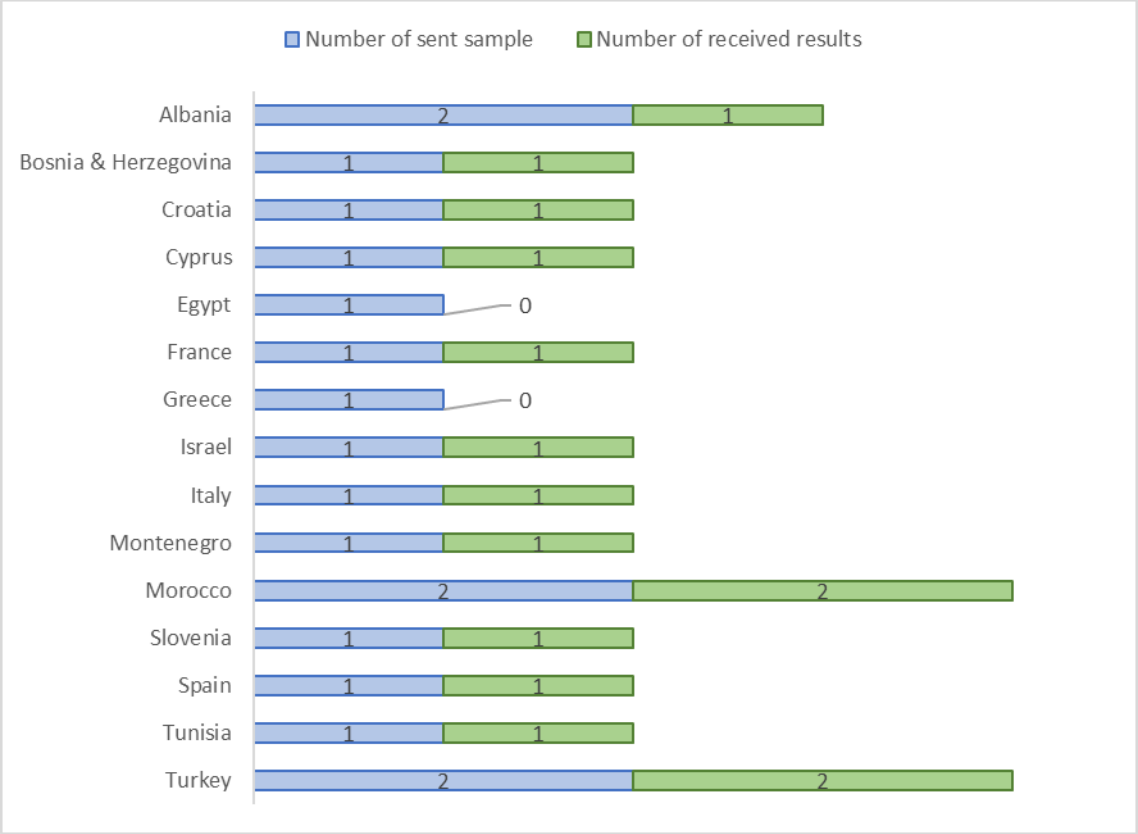


FIG. 1. Distribution per country of the MED POL PT sample

3. MATERIAL

3.1. Preparation of the material

Fish flesh homogenate from North Sea was used for preparing IAEA-MESL-2020-TE-MEPDOL-PT test sample The Fish flesh homogenate was freeze dried, sieved at 250µm, mechanically homogenized and packed in plastic sealed containers.

Homogeneity tests were performed at the MESL following the requirements ISO 35 guidelines [1], using preliminary validated in MESL's trace elements laboratories analytical methods.

3.2. Assigned values and their uncertainties

The assigned values for the trace element mass fractions of IAEA-MESL-2020-TE-MEPDOL-PT sample were calculated according to the requirements of the ISO 17043 standard [2]. The assigned values were calculated as Robust mean (ISO 13528 [3]) from the results reported by the participants in this PT and results obtained in the MESL with preliminarily validated analytical methods.

To ensure the best possible estimate of the assigned values, the following criteria have been set before applying robust statistics:

- Rejection of data reported without QC;
- Visual inspection of results, kernel density plot [4] to evaluate potential bimodality of distribution;
- Comparison with IAEA values as expert laboratory;
- Review of data based on technical validity.

As a results of dataset evaluation, some reported data have been excluded before applying robust statistics; details are shown in the table 1.

Table 1: REPORTED VALUES REJECTED BEFORE CALCULATION OF ROBUST MEANS

ANALYTE	LAB CODE	Comments
ALL	3	No QC, rejected all data before calculation of assigned values
As	13	Appears like extreme outlier, rejected
Co	8	Expected mass fraction (from IAEA) is < reported LOD
Pb	8, 14, 16	Bimodality Based on IAEA values the first mode is kept, and three values are rejected before applying robust statistics.

Expanded uncertainties of assigned values for trace element mass fractions were calculated according to the ISO standard 35 [1], using equation (Eq1).

$$U = k \times \sqrt{u_{char}^2 + u_{stab}^2 + u_{hom}^2} \qquad (1)$$

where:

k: coverage factor, *k* = 2, representing level of confidence of about 95%

u_{char} is the uncertainty of characterization, estimated according to the recommendations of the ISO 35 [1] using Eq. (2); u_{stab} is the standard uncertainty, due to long term stability of the sample. Based on our experience u_{stab} component was considered to have negligible contribution and was set at 1%;

u_{hom} is the standard uncertainty, due to between unit inhomogeneity, evaluated by ANOVA [1].

$$u_{char} = 1.25 \times \frac{s^*}{\sqrt{n}} \quad (2)$$

Where: s^* is the robust standard deviation and n the number of measurement results.

All assigned values (Xass) of trace element mass fractions, expanded uncertainties (U) and the standard deviation for the proficiency assessment (also called target standard deviation, see 4.2)), obtained in this study are presented in Table 2. For Cr expanded uncertainty was beyond 20%, therefore the value is given for information only and was not used for the evaluation of measurement performances of laboratories, participating in this PT.

TABLE 2: ASSIGNED VALUES FOR TRACE ELEMENTS IN THE PT SAMPLE

	Xass - Assigned Values (mg kg^{-1})	U (mg kg^{-1}) (k=2)	Target standard deviation(mg kg^{-1})
As	4.7	0.4	0.6
Cd	0.78	0.06	0.1
Co	0.063	0.009	0.008
Cr	*0.7*	*0.2*	*0.09*
Cu	3.9	0.2	0.5
Fe	137	16	17
Hg	0.115	0.009	0.014
Mn	6	0.4	0.8
Ni	0.6	0.12	0.07
Pb	0.051	0.007	0.006
Zn	103	4	13

4. EVALUATION OF RESULTS

4.1. Data Reporting

Data were reported through the IAEA on-line reporting system. Participants were asked to report data for trace elements ((as listed in information sheet) and to fill a questionnaire (see Annex 3)

All participants were able to download their draft preliminary evaluation report (reporting assigned values, reported values z and Zeta-scores) at the middle of December 2020 through the online portal.

All results disseminated in this report are only referring to a laboratory code number, to protect the Participants confidentiality. However, as agreed with the participants the laboratory codes will be shared with UNEP/MAP – MEDPOL and respective MEDPOL Focal Point as part of the capacity building and quality assurance programme of MEDPOL.

4.2. Evaluation criteria

Individual laboratory performance was evaluated with *z* and Zeta scores as recommended in the ISO guide 17043 [2]

$$z = \frac{x_{lab} - X_{ass}}{\sigma_p} \quad (3)$$

$$\text{zeta} = \frac{x_{lab} - X_{ass}}{\sqrt{u_{lab}^2 + u_{ass}^2}} \quad (4)$$

Where:

x_{lab} is the measurement result reported by participant;

X_{ass} is the assigned value of mass fractions for TEs in PT sample;

σ_p is the target standard deviation or standard deviation for proficiency assessment;

U_{ass} is the standard uncertainty of the assigned value;

u_{lab} is the standard uncertainty reported by participant.

The interpretation of a laboratory's performance was according to the following generally accepted criteria [2].:

$|z \text{ or Zeta}| \leq 2$ Satisfactory

2<	$\lvert z \text{ or Zeta} \rvert < 3$	Questionable
	$\lvert z \text{ or Zeta} \rvert \geq 3$	Unsatisfactory

***z*-score:** This score expresses the difference between the reported mass fraction of the laboratory and the assigned mass fraction in the same unit for each analyte. *z*-score represents a simple method of giving each participant a normalized performance score for the measurement bias of the respective measurement result. The standard deviation for the proficiency assessment (also called target standard deviation), σ_p, was set to be fit for purpose and was fixed to 12.5 % of the assigned values. The determination of target standard deviation was done on the basis of the outcome of previous ILCs organised by the MESL for the same population of laboratory. The appropriateness of this level of tolerated variability of results was confirmed by calculation of the robust standard deviation of the participants' results and the uncertainty of the assigned values for the respective measurements.

Zeta-Score: This score state if the participant result agrees with the assigned value within the respective uncertainties. The denominator of equation 4 is the combined uncertainty of the assigned value and the measurement uncertainty reported by the participant. When the uncertainties were not reported by participating laboratories, Zeta-score was not calculated.

4.3. Overview of the reported measurement results

15 laboratories provided results for the analysis of the PT sample by the final deadline, comprising 114 measurement results. Graphical presentations of z-score and Zeta-scores are presented in Annex 2 with a summary on the statistical evaluation of reported results for the respective trace element. Kernel density plots [4] are also presented in Annex 2.

4.4. Laboratory results and scoring

4.4.1 *z*-scores

The measurement performance of participating laboratories was assessed by *z*-scores. Obtained results are summarized in Table 3 and on Figure 2 and 3. The number of evaluated analytes per participant is displayed in Figure 2.

A total 104 *z*-scores were calculated. Overall, 87% of reported measurement results were assessed as satisfactory, 2% as questionable and 12% as unsatisfactory. From 15 participating laboratories, 8 laboratories (53%) reported 100% of their measurement results with $|z| \leq 2$ and all laboratories except 1 could report at least half of their results evaluated as satisfactory. Extreme z-scores >7 have been obtained for about 7% of reported results.

Nickel, lead and cobalt are analytes with higher percentage of unsatisfactory z scores probably reflecting unresolved analytical problems with those analytes at low levels.

4.4.2 Zeta-scores

The Zeta-score shows if the laboratory result agrees with the assigned value within the respective combined uncertainty. It should be mentioned that an unsatisfactory Zeta-score can be caused either by an incorrect measurement result or by an inappropriate estimation of the respective measurement uncertainty, or by both.

Zeta-score results obtained in this PT are summarized in Table 4 and presented in in Figure 4 and 5. The number of evaluated analytes per participant is displayed in Figure 4.

About 67% of measurement results were reported with uncertainties. Zeta-scores were calculated for 10 of participating laboratories (66%), 5 of participating laboratories (33%) did not report measurement uncertainties, which made the calculation of Zeta score impossible. It should be noted that 2 out of 5 laboratories that did not provide uncertainties claim to be accredited against ISO 17025.

74% of the calculated Zeta-scores are considered as satisfactory but only 2 laboratories reported 100% of their results with Zeta-scores below 2. The results show that there are still remaining problems with the realistic estimation of the combined measurement uncertainty. Some laboratories have reported unrealistically small uncertainties (i.e less than 2.5%)

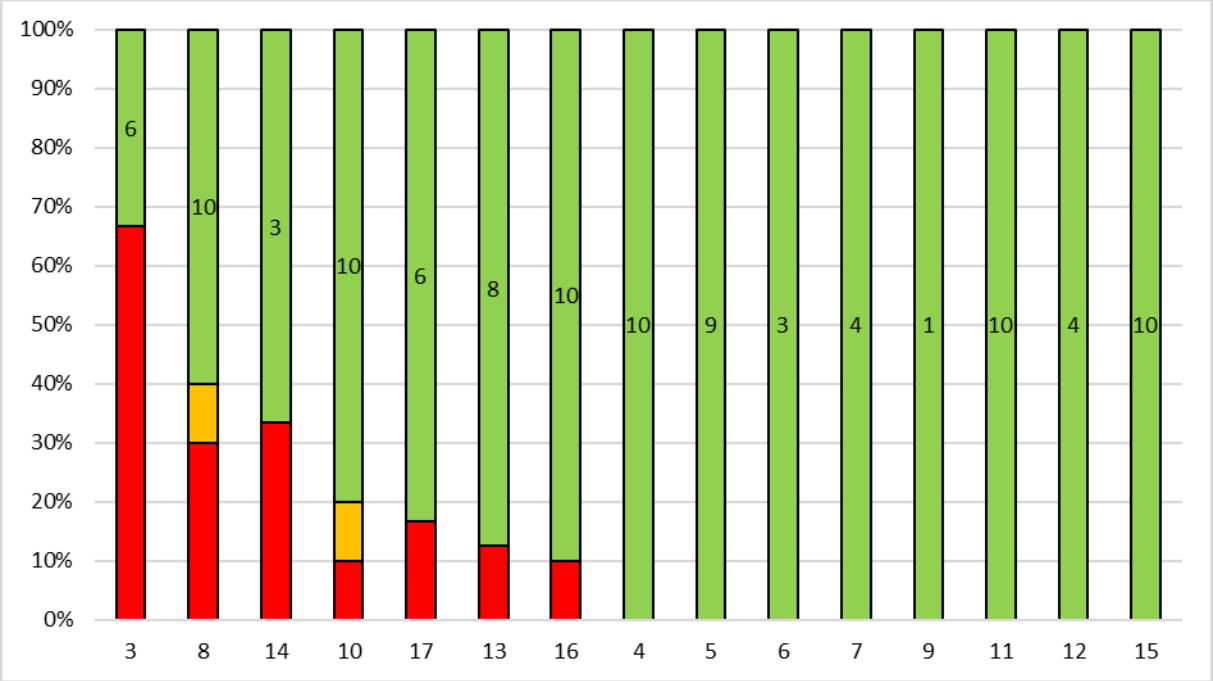
It should be mentioned here that an unsatisfactory Zeta-score can also be caused by an inappropriate evaluation of the mass fraction of the respective trace element.

TABLE 3: ALL CALCULATED z-SCORES. Blue fonts are z-scores 2< | *z* | <3, and red highlighted fields being z-scores | *z* |>3.

Lab. Code	As	Cd	Co	Cu	Fe	Hg	Mn	Ni	Pb	Zn
3		17.79	515.17	-3.54	-0.04		0.00			-3.59
4	-1.45	0.28	-0.38	0.13	-0.54	0.33	0.21	1.83	1.20	-0.13
5	1.86	0.67	-1.02	0.14	0.53		1.42	-0.71	-0.99	1.51
6		0.99				0.93			-0.43	
7	-0.04	-0.63				-0.31			1.22	
8	1.30	0.07	12.28	0.41	-0.06	2.43	0.09	-4.13	25.99	-0.16
9						-0.70				
10	-0.10	-0.20	1.06	-0.26	2.82	-0.35	-0.01	9.73	0.05	-0.08
11	0.42	0.61	-1.09	-0.57	0.31	1.23	-0.09	0.23	-0.05	0.13
12					-0.90	-0.30	-0.96			0.58
13	-6.11	-0.17		1.75	-0.11	-1.02	-0.60		-1.27	0.24
14		-1.75				-0.28			37.33	
15	-0.14	-0.48	0.72	-0.08	-0.66	0.09	0.30	-0.76	0.52	0.26
16	-1.41	-0.24	-0.63	0.27	-0.13	-1.76	0.18	1.13	28.55	-0.86
17		-3.03		-0.31	0.05	1.67	-0.56			-0.26

TABLE 4: ALL CALCULATED ZETA –SCORES. Blue fonts are Zeta-scores 2< │Zeta│ <3, and red highlighted fields being Zeta-scores │Zeta│>3.

Lab. Code	As	Cd	Co	Cu	Fe	Hg	Mn	Ni	Pb	Zn
3										
4										
5	3.10	1.27	-1.60	0.30	0.84		2.62	-0.81	-1.42	3.03
6		1.54				1.65			-0.41	
7										
8	2.71	0.22	21.62	1.79	-0.12	7.83	0.33	-4.90	15.38	-0.55
9						-2.45				
10	-0.15	-0.22	1.03	-0.40	2.34	-0.51	-0.02	5.10	0.05	-0.10
11	1.05	1.09	-1.71	-2.06	0.52	2.28	-0.24	0.26	-0.06	0.42
12										
13	-12.08	-0.22		2.18	-0.12	-1.25	-1.02		-1.38	0.45
14		-4.45				-0.29			17.50	
15	-0.28	-1.01	1.13	-0.21	-1.27	0.21	0.78	-0.87	0.67	0.68
16										
17		-7.45		-0.61	0.08	1.07	-1.14			-0.54



c. Summary of obtained z-scores per participant, number are total number of evaluated analytes

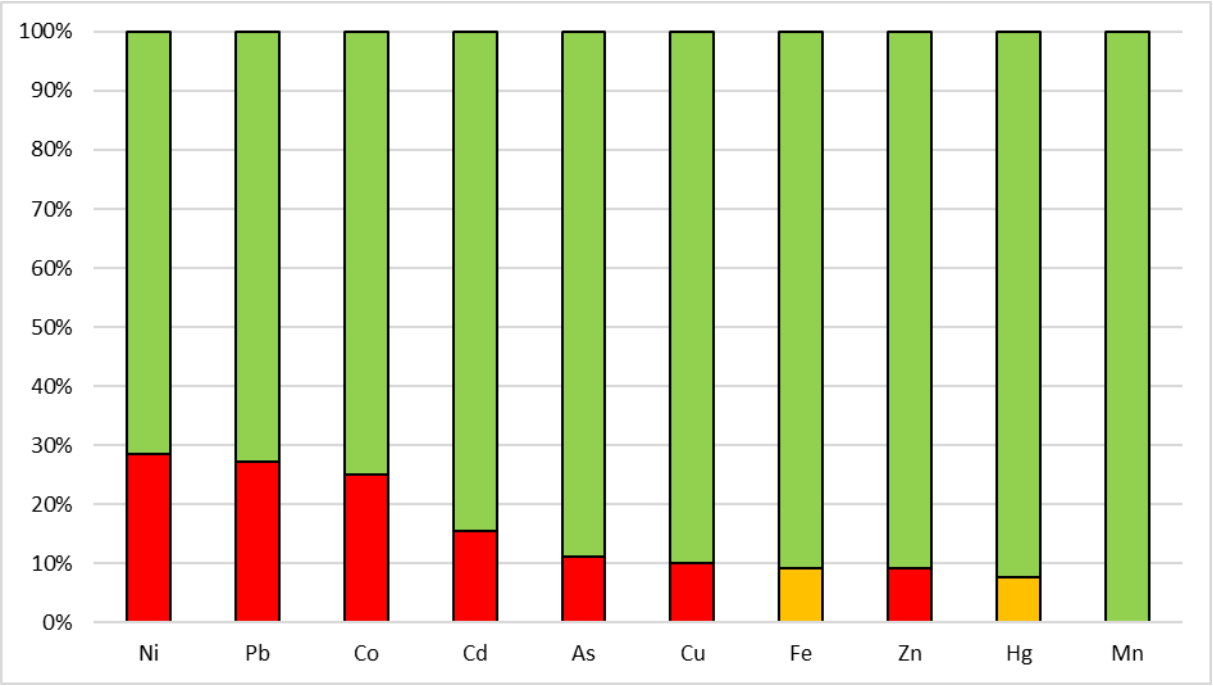


FIG. 2. Summary of obtained z-scores per element

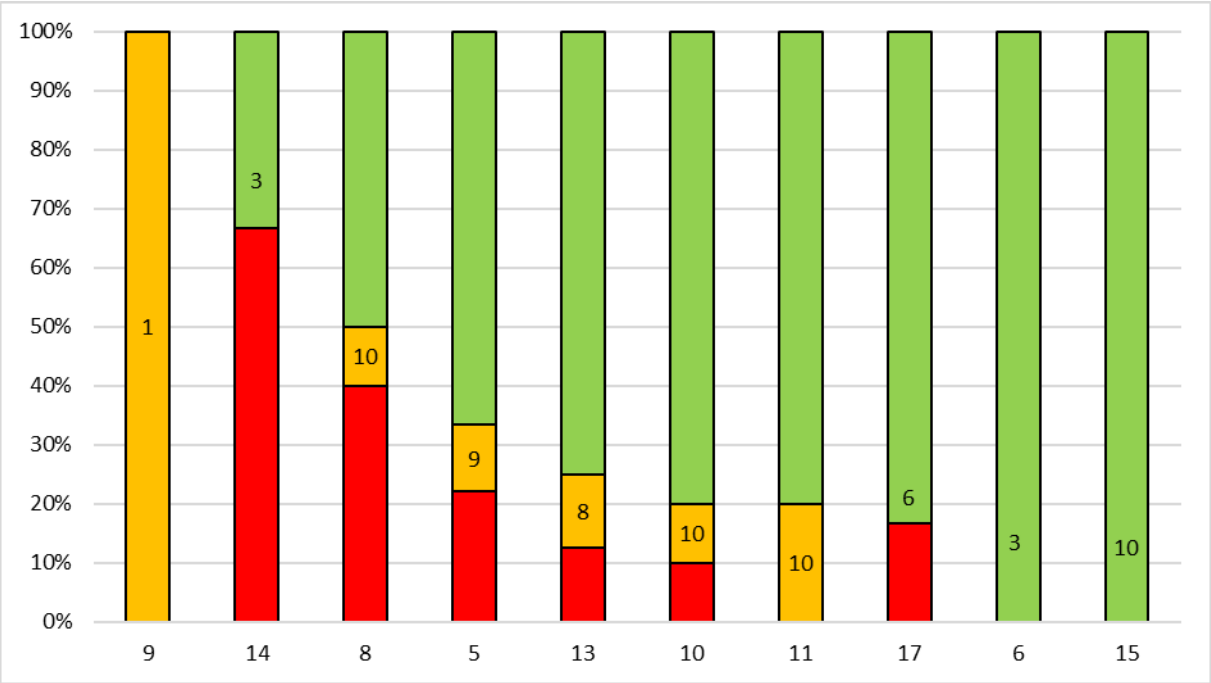


FIG. 3. Summary of obtained Zeta-scores per participants number are total number of evaluated analytes

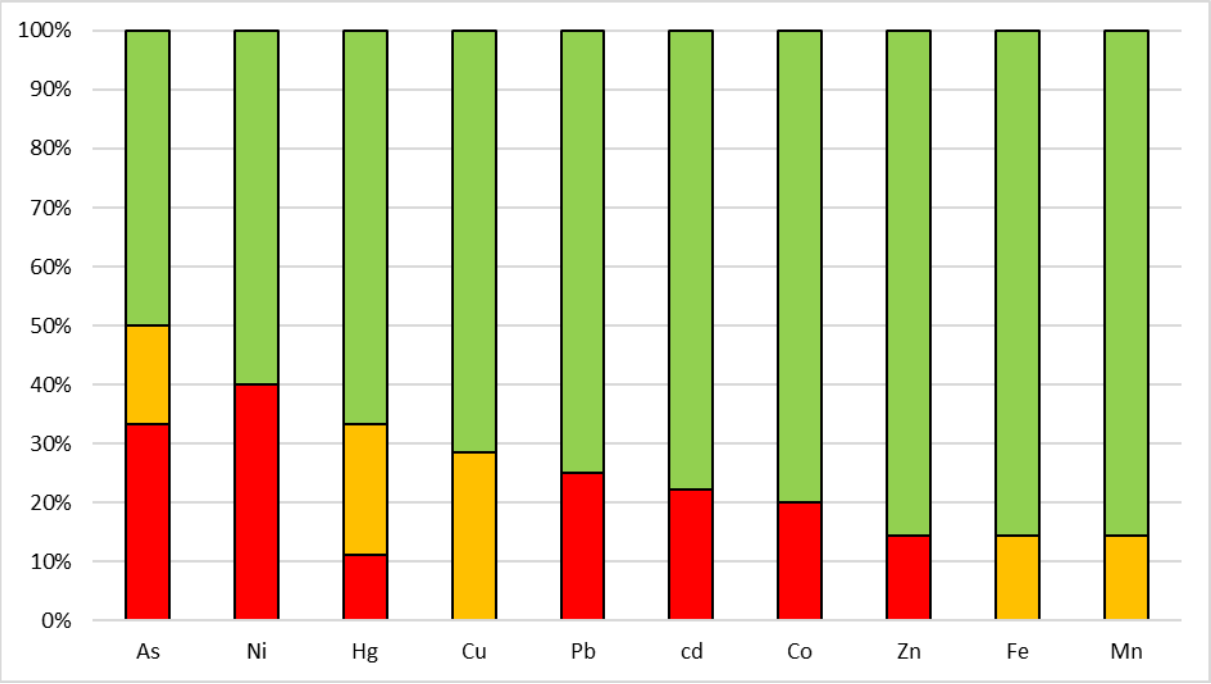


FIG. 4. Summary of obtained Zeta-scores per element

4.5. Sample treatment, use of CRM and recovery correction

All participating IMAP competent laboratories applied microwave digestion, using nitric acid with or without addition of hydrogen peroxide. For total mercury determination 46% of laboratories used solid mercury analyser and did not apply any sample preparation before the instrumental measurement.

Freeze drying step was a part of sample processing procedure for the IAEA-MESL-2020-TE-MEPDOL-PT sample. Depending on local storage and humidity conditions, the PT sample might absorb water from the laboratory environment. As the moisture is an operationally dependent parameter, the procedure for moisture content determination in the PT sample was carefully developed and provided in the information sheet, describing details on the MED POL/MESL PT exercise. Oven drying for a separate portion of sediment sample at 85°C until constant weight was the recommended procedure for moisture determination. Only 5 participating laboratories have respected this procedure, while most of the remaining participants applied in house developed protocol. One participant declared not to correct for moisture. The moisture content reported by the laboratories was in the range from 1 to 9%.

In order to provide traceable results and to confirm the validation of the methods used, designated IMAP competent laboratories have been systematically requested to analyse a CRM with a matrix and concentration range similar to the PT sample. CRMs used from the participating laboratories in the PT exercise, were generally selected accordingly. Out of the 15 data sets received, only 1 participant (laboratory 3) did not include quality control (QC) results in the reporting form.

Eight laboratories reported recoveries, but only 1 of them claimed implementing correction for recovery for all, or part of reported trace elements mass fraction. Interestingly, a considerably high proportion of laboratories that did not correct for recovery obtained satisfactory scorings. This is an indication that the laboratories have correctly estimated that the recoveries achieved with the used analytical procedures were not significantly different from 100%.

4.6. Analytical techniques used by participants:

Abbreviations of the instrumental techniques used in this exercise are given in Table 5. As it can be seen from Figure 6, ICP-MS is the most used instrumental technique, followed by ICP-OES. Solid mercury analyser represents about half of reported results for mercury.

TABLE 5: ANALYTICAL TECHNIQUES ABBREVIATIONS

Method Code	Instrumental Technique
AAS	Atomic Absorption Spectrometry
AFS	Atomic Fluorescence Spectrometry
F	Flame
ET	Graphite Furnace
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
CV	Cold Vapour
MP-AES	Microwave Plasma Atomic Emission Spectrometry

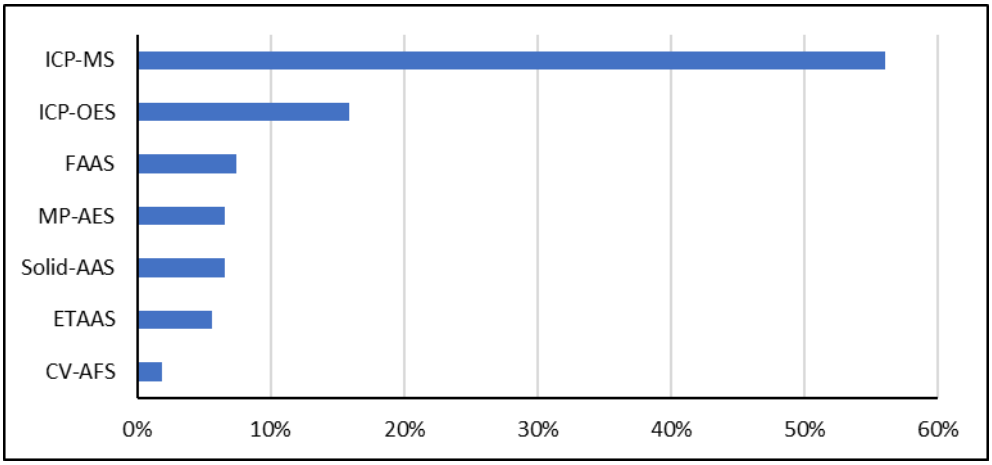


FIG. 5. Graphical distribution of instrumental techniques, applied in the present PT

4.7. Answer provided to the questionnaire

As mentioned in 4.1, participants were requested to answer a questionnaire (Annex 3), to reply to questions on analytical methods used and quality assurance measured taken to assure the traceability of their results. Two laboratories did not report any information in the questionnaire.

Seven laboratories claimed to be accredited, however 2 of them were not reporting measurement uncertainties and also did not claim using a validated method, both of which should be part of a result provided by an accredited laboratory. Two out of the seven accredited laboratories are however not accredited for biological matrix, while one is accredited only for Hg.

Ten laboratories applied preliminary validated methods, and 10 participants declared to have quality system in place. Out of seven laboratories not reporting their limits of detection and quantification, three claimed to use validated methods which should imply the estimation of those parameters.

Four participants did not explain how they have assured the traceability of obtained results.

5. CONCLUSIONS AND RECOMMENDATIONS

The MEDPOL/MESL proficiency tests is part of the capacity building activity for IMAP competent laboratories. To make the most of this activity, participants are advised to review their data element-by-element, especially in the cases where the *z*-score or/and Zeta-score are above 2. The use of the *z*-scores will help to identify systematic errors in the measurement results (e.g. from calibration or reagent contamination) and should ultimately improve data quality.

To get a realistic estimation of the laboratory's performance, the proficiency test sample should be treated in exactly the same way as any routine test sample. Examples of 'poor practice' include:

- Having the PT samples analysed by the most experienced analyst;
- Reporting only the 'best' results, rather than all.

In the case of unsatisfactory performance each laboratory should carefully investigate the cause of the unsatisfactory scores (i.e. $|z| > 3$) and put in place the necessary corrective actions to prevent the problem reoccurring. This is one of the requirements for laboratories accredited according to the ISO/IEC 17025 standard.

The concept of recovery is still not implemented in several laboratories and consequently the validation of the analytical methods, used by them is often questionable.

All except one laboratory provided results for the use of CRMs in their analytical procedure, which means that the internal quality control in those laboratories is in place.

In the MED POL PT exercise the uncertainty of measurement results was calculated from 67% of the participants. Considering the Zeta-scores reported, we can conclude that the way of calculation and application of uncertainty concept is still questionable for some of the laboratories participating in the MEDPOL PT and further training on uncertainty of measurement results is highly recommended.

Three (16%) from 18 designated MED POL laboratories did not send the PT results by the deadline, which make the evaluation of their measurement performance impossible.

Two national laboratory mission visits were conducted in early 2020 by MESL experts. The focus of the gap-finding visits was aimed at the identification of technical (e.g. acquisition of laboratory equipment) and knowledge needs to strengthen the understanding for applying the analytical methods and good laboratory practices in line with the requirements of IMAP Common Indicator 17.

6. REFERENCES

[1] INTERNATIONAL ORGANISATION FOR STANDARDISATION, Guide *35 (2005), Reference Materials-General and statistical principles for certification, ISO, Geneva, Switzerland.*

[2] INTERNATIONAL ORGANISATION FOR STANDARDISATION, Guide *17043 (2010), Conformity assessment, general requirements for proficiency testing, ISO, Geneva, Switzerland.*

[3] INTERNATIONAL ORGANISATION FOR STANDARDISATION, Guide *13528 (2005), Statistical Methods for Use in Proficiency Testing by Interlaboratory Comparisons, ISO, Geneva, Switzerland.*

[4] ROYAL SOCIETY OF CHEMISTRY, Statistical Subcommittee of the Analytical Methods Committee (AMC), AMC Technical Brief: Representing data distributions with Kernel density estimates" 2006, www.rsc.org/amc.

Annex 1:

List of participants

Designated IMAP Competent laboratories that sent results

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TUBITAK Gebze Yerleskesi Marmara Arastirma Merkeri
Cevre ve Temiz Uretim Enstitusu
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Ministry of Environment and Urbanization
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Tirana

EGYPT

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Alexandria

GREECE

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Institute of Oceanography
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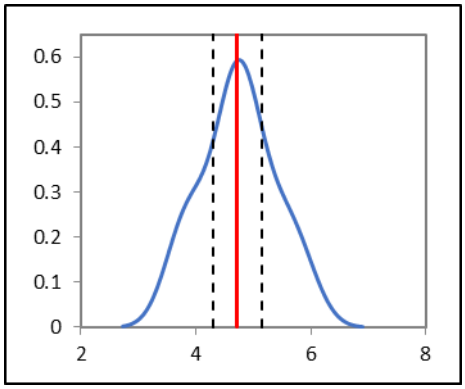
PO Box 712
19013
Anavyssos

Annex 2:

Graphical representation

Reported data for As in IAEA-MESL-2020-TE-MEPDOL-PT

Kernel density Plot



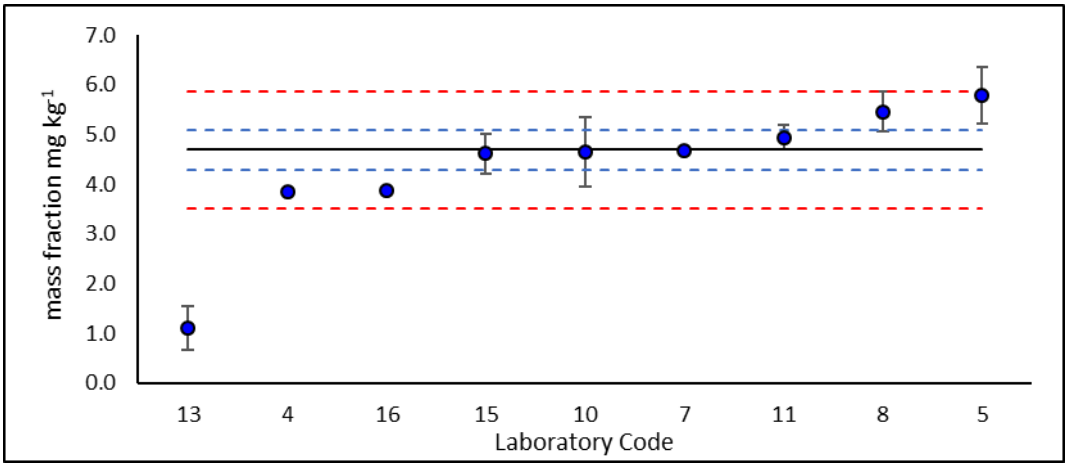
Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	89%	0%	11%
Zeta-score	50%	17%	33%

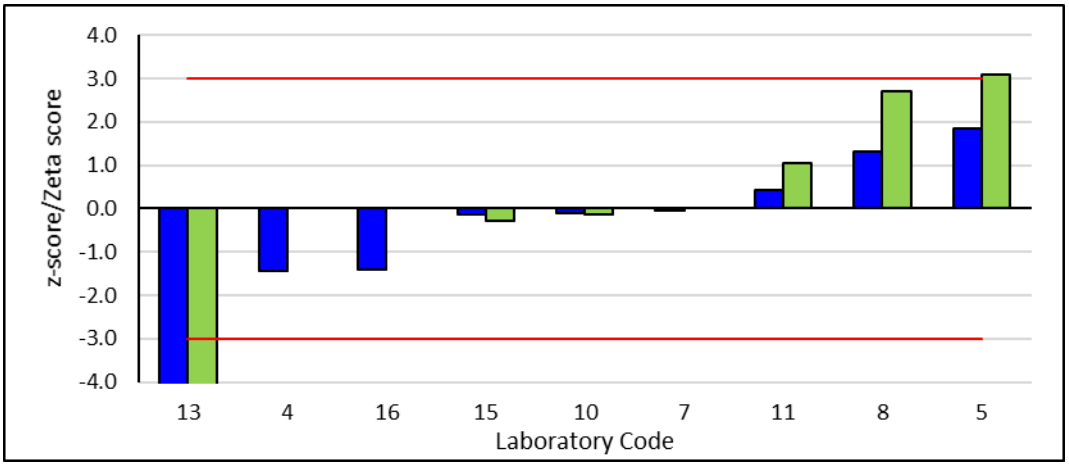
X_{Ass} mg kg^{-1}	4.7
U_{Ass} (k=2) mg kg^{-1}	0.4
$2\sigma_p$ mg kg^{-1}	1.2
Number of results:	9
Number of methods:	3

Reported results and expanded uncertainties:

— X_{Ass} ; $X_{lab} \pm U_{lab}$; ---- $X_{Ass} \pm 2\sigma_p$; ---- $X_{Ass} \pm U_{Ass}(k=2)$

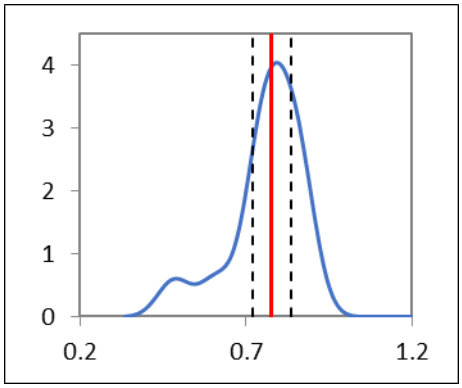


Performance evaluation: z-score Zeta-score



Reported data for Cd in the IAEA-MESL-2020-TE-MEPDOL-PT

Kernel density Plot



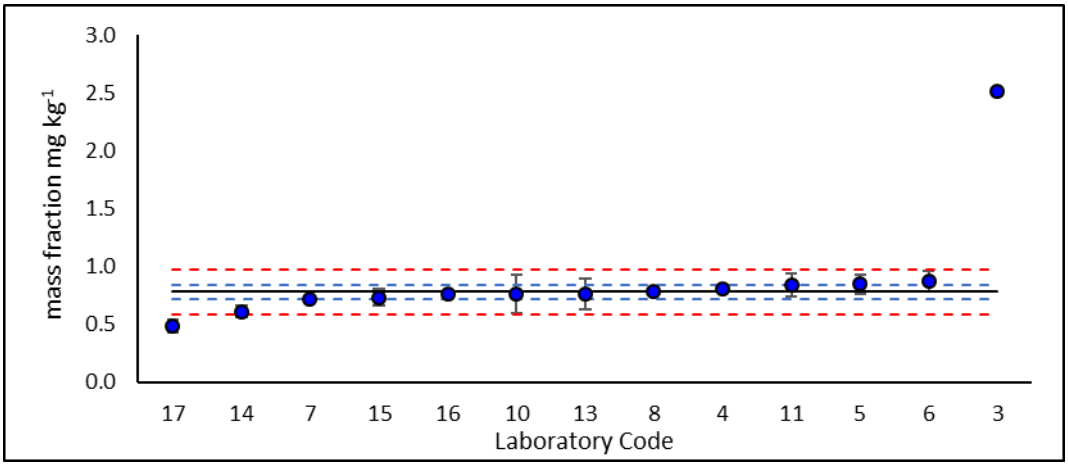
Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	85%	0%	15%
Zeta-score	78%	0%	22%

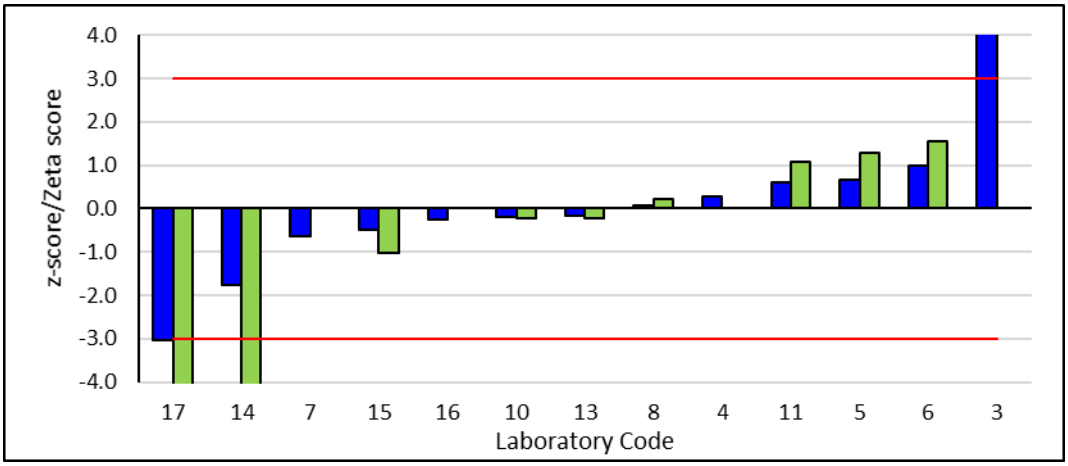
X_{Ass} mg kg^{-1}	0.78
U_{Ass} (k=2) mg kg^{-1}	0.06
$2\sigma_p$ mg kg^{-1}	0.19
Number of results:	13
Number of methods:	5

Reported results and expanded uncertainties:

— X_{Ass} ; $X_{lab} \pm U_{lab}$; ---- $X_{Ass} \pm 2\sigma_p$; ---- $X_{Ass} \pm U_{Ass}(k=2)$

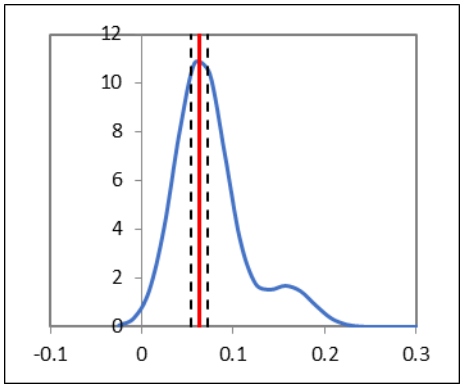


Performance evaluation: z-score Zeta-score



Reported data for Co in the IAEA-MESL-2020-TE-MEPDOL-PT

Kernel density Plot



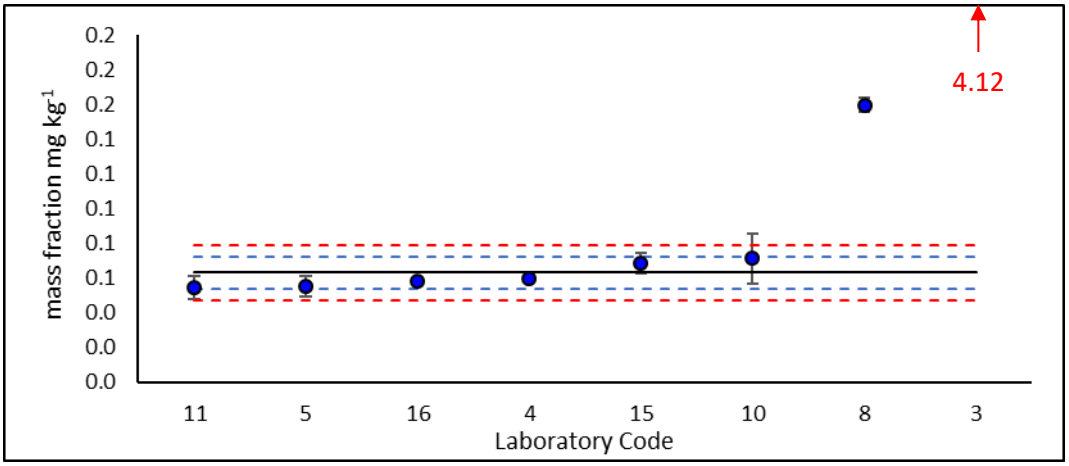
Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	75%	0%	25%
Zeta-score	80%	0%	20%

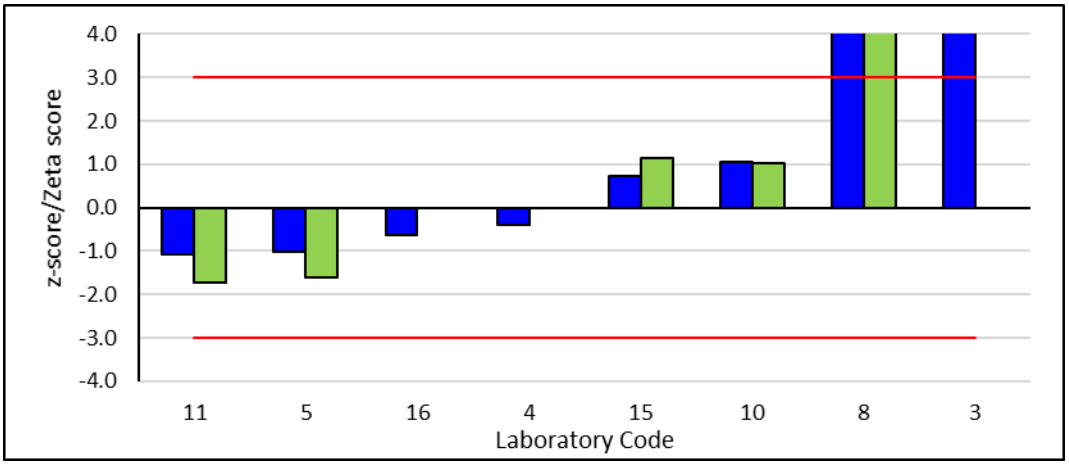
X_{Ass} mg kg^{-1}	0.063
U_{Ass} (k=2) mg kg^{-1}	0.009
$2\sigma_p$ mg kg^{-1}	0.016
Number of results:	8
Number of methods:	3

Reported results and expanded uncertainties:

— X_{Ass} ; $X_{lab} \pm U_{lab}$; ---- $X_{Ass} \pm 2\sigma_p$; ---- $X_{Ass} \pm U_{Ass}$ (k=2)

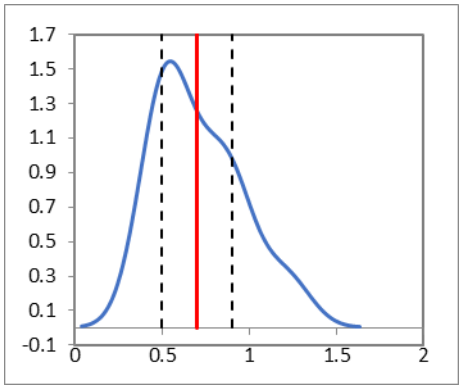


Performance evaluation: z-score Zeta-score



Reported data for Cr in the IAEA-MESL-2020-TE-MEPDOL-PT

Kernel density Plot

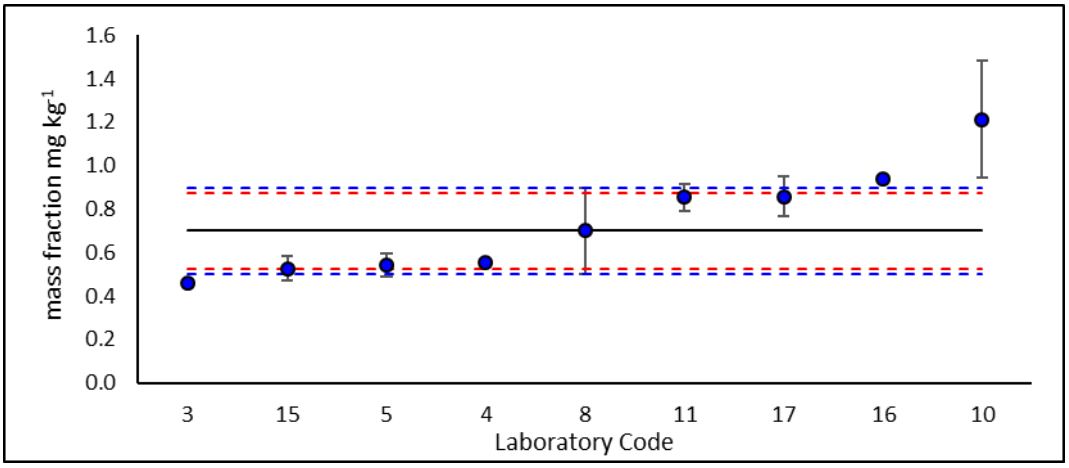


Summary of results:

X_{info} mg kg^{-1}	0.7
U_{Info} (k=2) mg kg^{-1}	0.2
$2\sigma_p$ mg kg^{-1}	0.16
Number of results:	9
Number of methods:	3

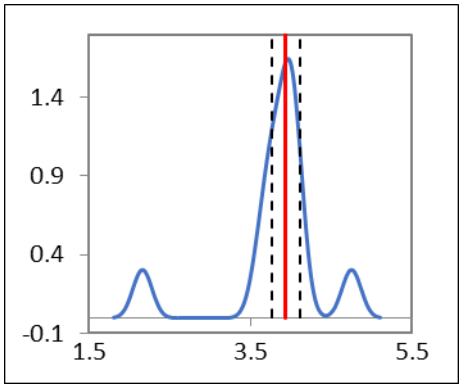
Reported results and expanded uncertainties:

— X_{info} ; $X_{lab} \pm U_{lab}$; ---- $X_{info} \pm 2\sigma_p$; ---- $X_{info} \pm U_{info}(k=2)$



Reported data for Cu in the IAEA-MESL-2020-TE-MEPDOL-PT

Kernel density Plot



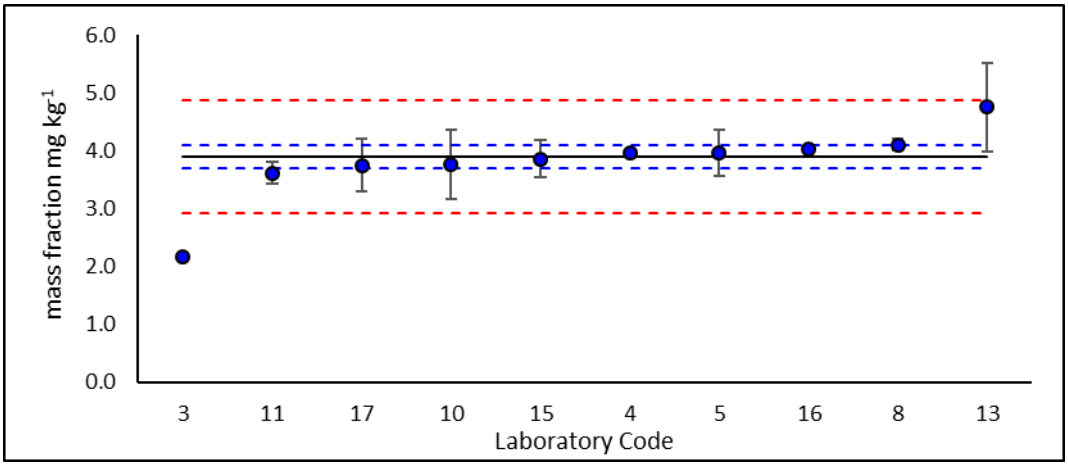
Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	90%	0%	10%
Zeta-score	71%	29%	0%

X_{Ass} mg kg^{-1}	3.9
U_{Ass} (k=2) mg kg^{-1}	0.2
$2\sigma_p$ mg kg^{-1}	0.1
Number of results:	10
Number of methods:	4

Reported results and expanded uncertainties:

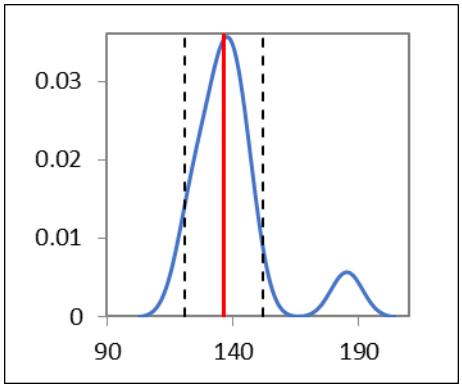
— X_{Ass} ; $X_{lab} \pm U_{lab}$; ---- $X_{Ass} \pm 2\sigma_p$; ---- $X_{Ass} \pm U_{Ass}$ (k=2)



Performance evaluation: z-score Zeta-score

Reported data for Fe in the IAEA-MESL-2020-TE-MEPDOL-PT

Kernel density Plot



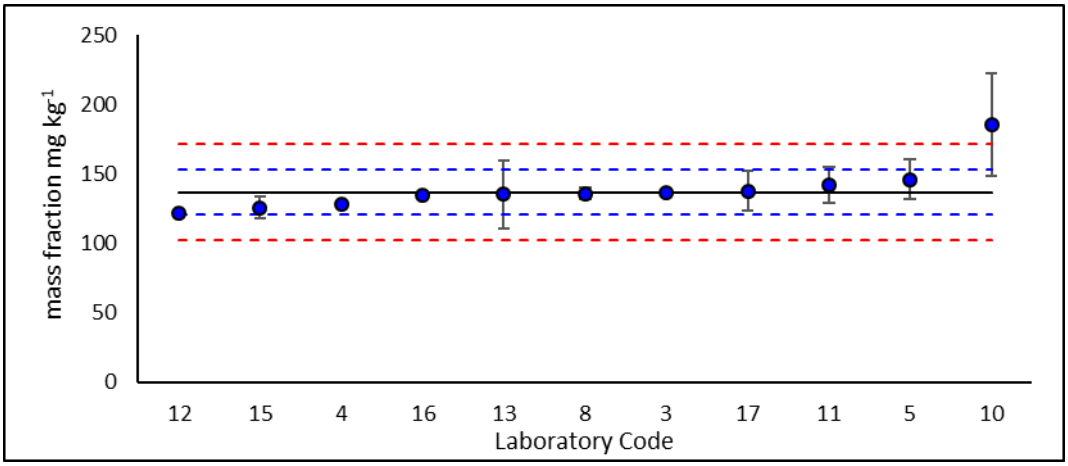
Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	91%	9%	0%
Zeta-score	86%	14%	0%

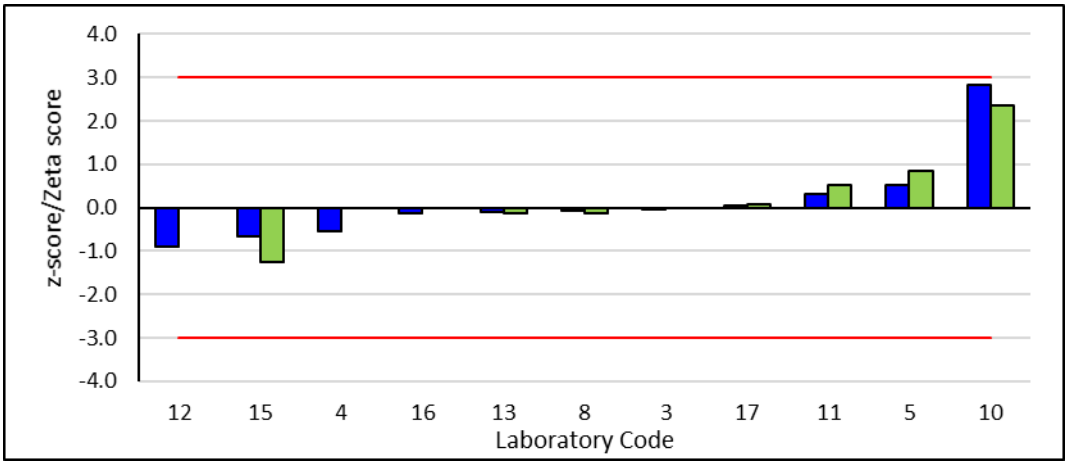
X_{Ass} mg kg^{-1}	137
U_{Ass} (k=2) mg kg^{-1}	16
$2\sigma_p$ mg kg^{-1}	34
Number of results:	11
Number of methods:	4

Reported results and expanded uncertainties:

— X_{Ass} ; $X_{lab} \pm U_{lab}$; ---- $X_{Ass} \pm 2\sigma_p$; ---- $X_{Ass} \pm U_{Ass}$ (k=2)

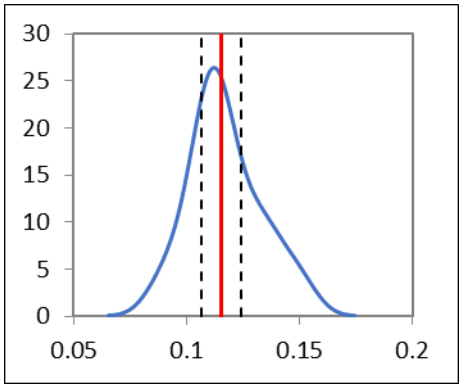


Performance evaluation: z-score Zeta-score



Reported data for Hg in the IAEA-MESL-2020-TE-MEPDOL-PT

Kernel density Plot



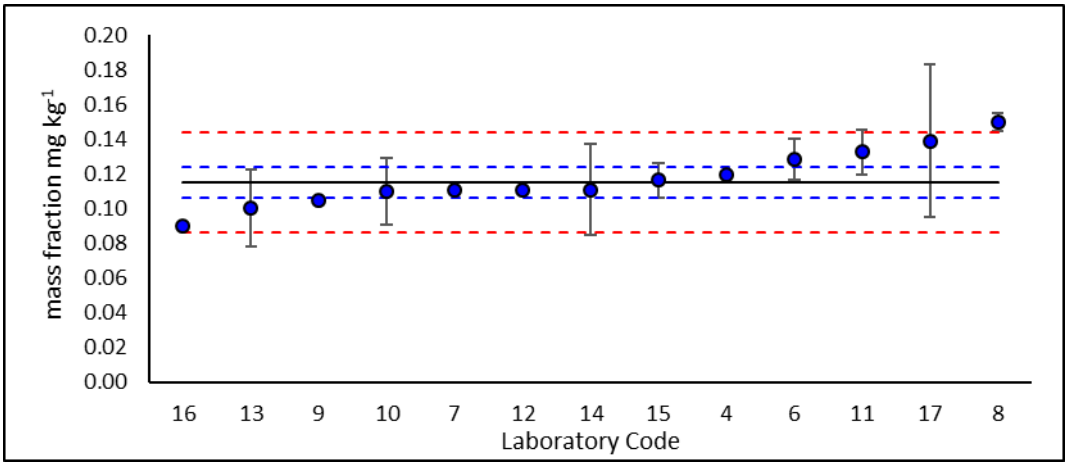
Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	92%	8%	0%
Zeta-score	67%	22%	11%

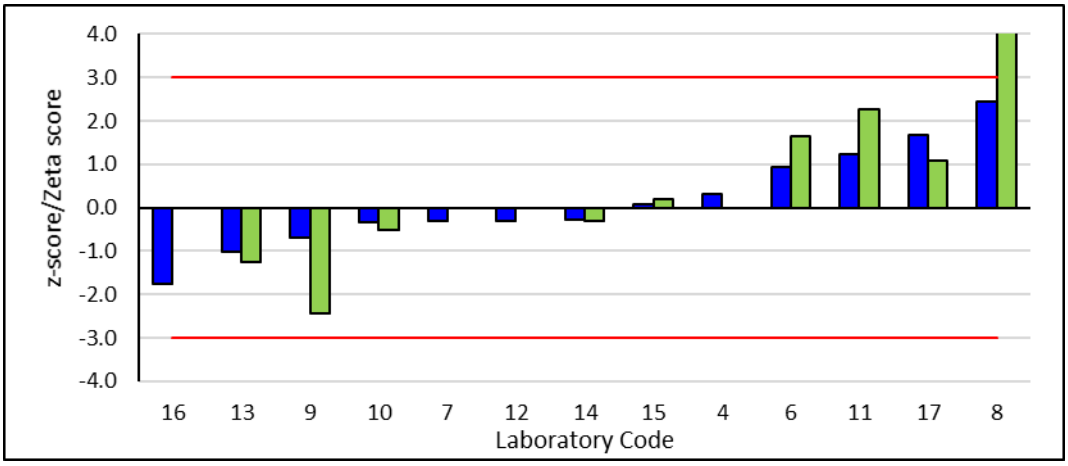
X_{Ass} mg kg^{-1}	0.115
U_{Ass} (k=2) mg kg^{-1}	0.009
$2\sigma_p$ mg kg^{-1}	0.029
Number of results:	13
Number of methods:	4

Reported results and expanded uncertainties:

— X_{Ass} ; $X_{lab} \pm U_{lab}$; ---- $X_{Ass} \pm 2\sigma_p$; ---- $X_{Ass} \pm U_{Ass}$ (k=2)

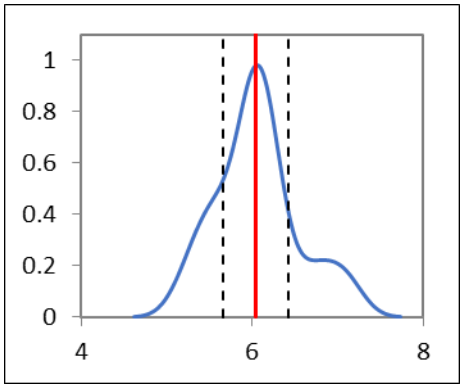


Performance evaluation: z-score Zeta-score



Reported data for Mn in the IAEA-MESL-2020-TE-MEPDOL-PT

Kernel density Plot



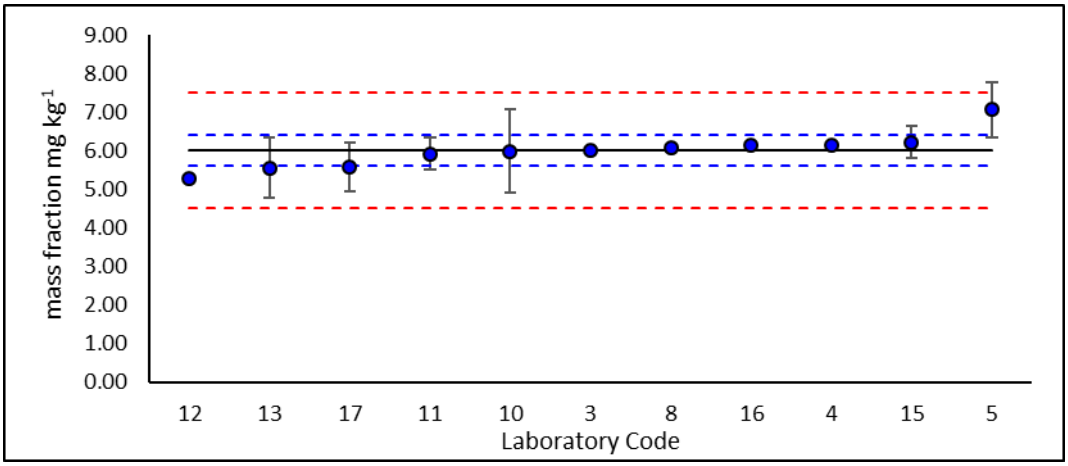
Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	100%	0%	0%
Zeta-score	86%	14%	0%

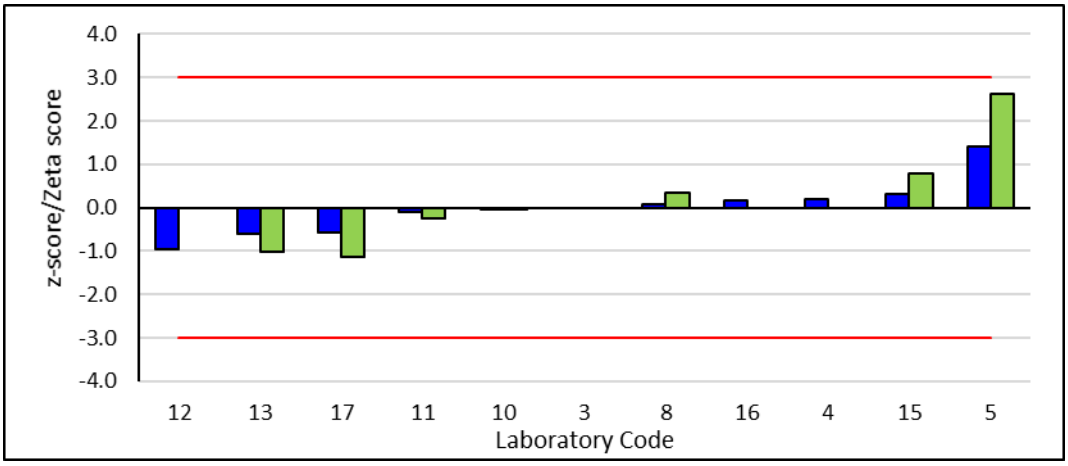
X_{Ass} mg kg^{-1}	6.0
U_{Ass} (k=2) mg kg^{-1}	0.4
$2\sigma_p$ mg kg^{-1}	1.5
Number of results:	11
Number of methods:	4

Reported results and expanded uncertainties:

— X_{Ass} ; $X_{lab} \pm U_{lab}$; ---- $X_{Ass} \pm 2\sigma_p$; ---- $X_{Ass} \pm U_{Ass}$ (k=2)

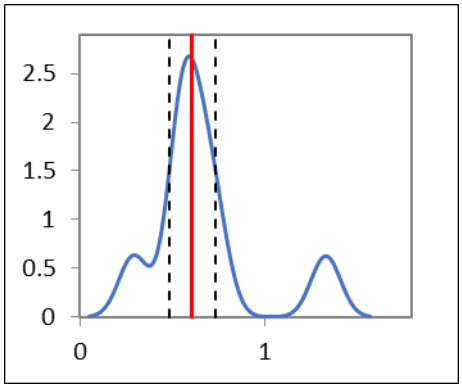


Performance evaluation: z-score Zeta-score



Reported data for Ni in the IAEA-MESL-2020-TE-MEPDOL-PT

Kernel density Plot



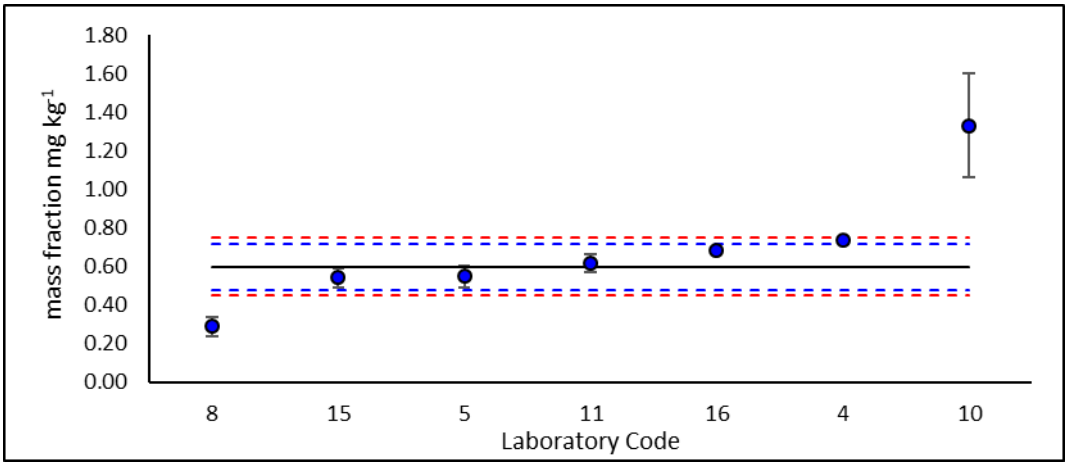
Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	71%	0%	29%
Zeta-score	60%	0%	40%

X_{Ass} mg kg^{-1}	0.60
U_{Ass} (k=2) mg kg^{-1}	0.12
$2\sigma_p$ mg kg^{-1}	0.15
Number of results:	7
Number of methods:	2

Reported results and expanded uncertainties:

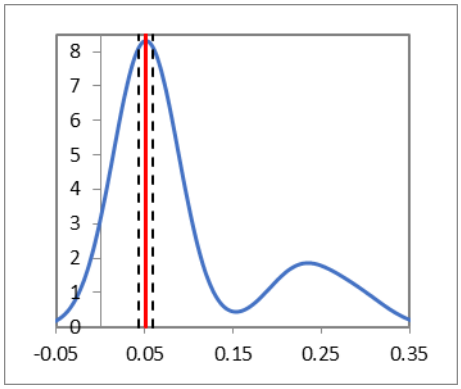
— X_{Ass} ; $X_{lab} \pm U_{lab}$; ---- $X_{Ass} \pm 2\sigma_p$; ---- $X_{Ass} \pm U_{Ass}$ (k=2)



Performance evaluation: z-score Zeta-score

Reported data for Pb in the IAEA-MESL-2020-TE-MEPDOL-PT

Kernel density Plot



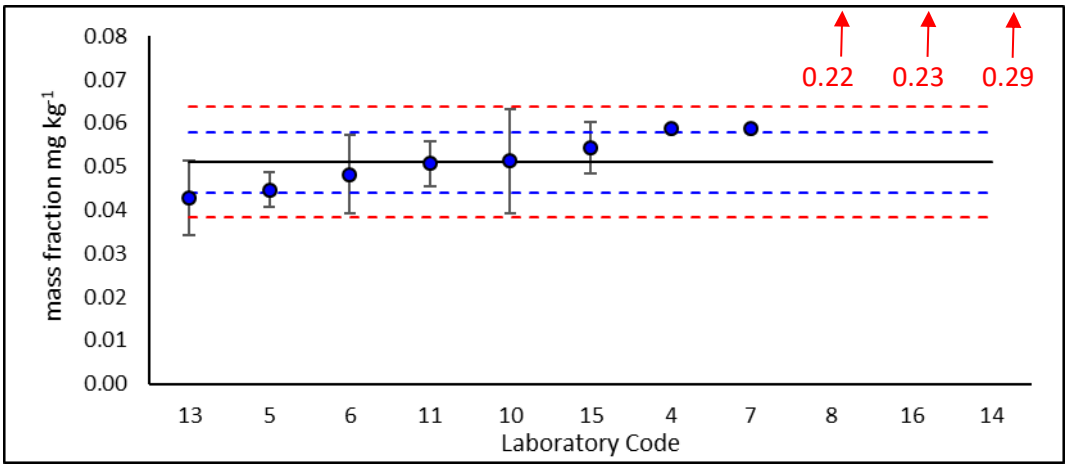
Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	73%	0%	27%
Zeta-score	75%	0%	25%

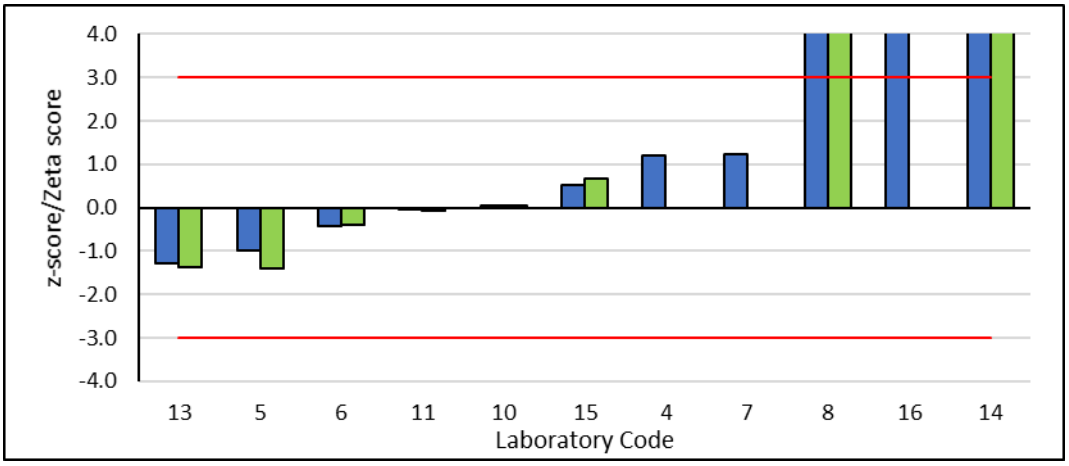
X_{Ass} mg kg^{-1}	0.051
U_{Ass} (k=2) mg kg^{-1}	0.007
$2\sigma_p$ mg kg^{-1}	0.013
Number of results:	11
Number of methods:	3

Reported results and expanded uncertainties:

— X_{Ass} ; $X_{lab} \pm U_{lab}$; ---- $X_{Ass} \pm 2\sigma_p$; ---- $X_{Ass} \pm U_{Ass}$ (k=2)

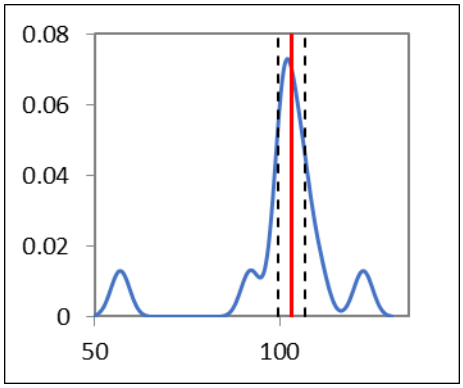


Performance evaluation: z-score Zeta-score



Reported data for Zn in the IAEA-MESL-2020-TE-MEPDOL-PT

Kernel density Plot



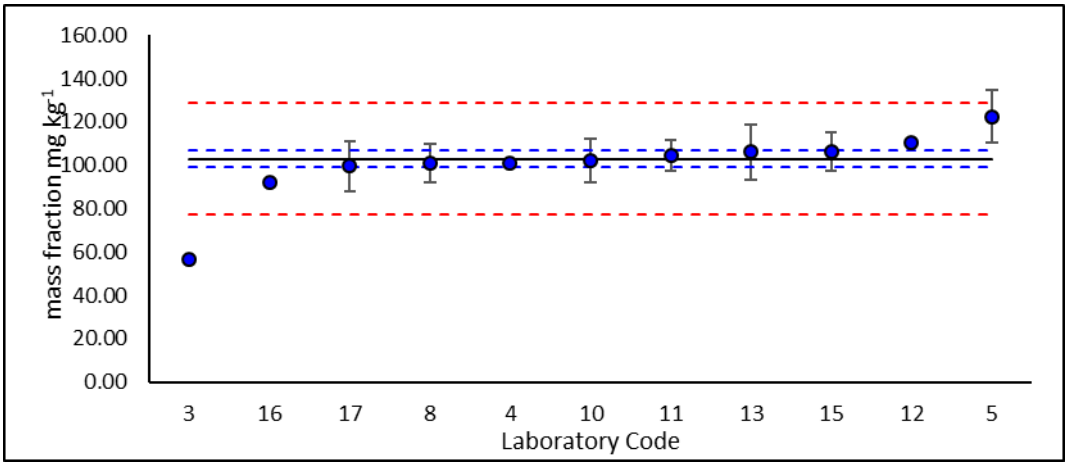
Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	91%	0%	9%
Zeta-score	86%	0%	14%

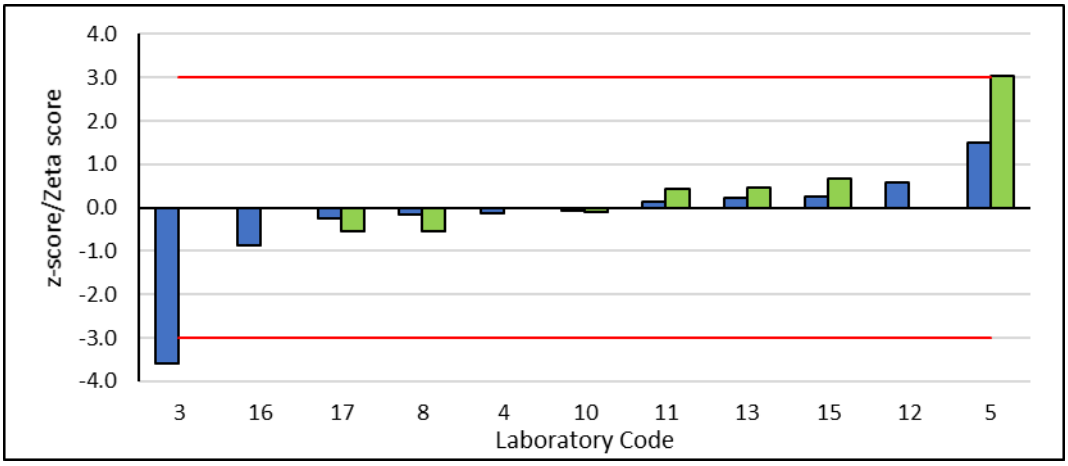
X_{Ass} mg kg^{-1}	103
U_{Ass} (k=2) mg kg^{-1}	4
$2\sigma_p$ mg kg^{-1}	26
Number of results:	11
Number of methods:	4

Reported results and expanded uncertainties:

— X_{Ass} ; $X_{lab} \pm U_{lab}$; ---- $X_{Ass} \pm 2\sigma_p$; ---- $X_{Ass} \pm U_{Ass}$ (k=2)



Performance evaluation: z-score Zeta-score



Annex 3:

Document sent to participants

INFORMATION SHEET: IAEA-MESL-2021-01-ILC-TE-BIOTA

TRACE ELEMENTS IN FISH

PLEASE READ THIS INFORMATION CAREFULLY BEFORE STARTING THE ANALYSES AND FILLING IN THE ONLINE DATA REPORTING FORM!

The present exercise is specifically organized for the determination of **trace elements in fish sample: IAEA-MESL-2021-01-ILC-TE-BIOTA**

Description of the material

IAEA-MESL-2021-01-ILC-TE-BIOTA is a fish flesh homogenate sample from North Sea; freeze dried, sieved at 250µm, mechanically homogenized and packed in plastic sealed containers.

Moisture content

The material can easily pick up moisture during storage. It is therefore necessary that the water content of the material is determined at the time of analysis in a separate sub-sample (i.e., not that taken for analysis) by **drying to a constant weight at 85˚C** (usually at least 24 hours).

PLEASE NOTE THAT ALL RESULTS ARE TO BE REPORTED ON A DRY MASS BASIS.

Instruction for use:

The sample should be kept in original bottle and mixed well before each use. A minimum sample of 0.3g should is required for analytical determination of all trace elements except mercury were subsamples of 0.05 g can be use.

Elements to be determined

Participants are requested to use their established analytical methods for the determination of **total contents** of the **mandatory** elements: **Cd, Hg and Pb** in IAEA-MESL-2020-TE-MEPDOL-PT sample.

In addition, when possible IAEA MESL will also evaluate results for some additional analytes, As, Co, Cr, Cu, Fe, MeHg, Mn, Ni and Zn.

Expected range of concentration:

- Fe, Zn: > 50 mg kg^{-1}
- Co, Cr, Cu, Mn, Ni: <10 mg kg^{-1}
- Cd, Hg, MeHg, Pb: < 1 mg kg^{-1}

Analytical quality control

Procedures of quality control and laboratory quality assurance are recommended to be applied.

The results of the analyses of a matrix matching quality control (QC) sample **must be reported** together with the results from the PT sample.

Reporting of results

1. Participants **MUST** report results together with a short **description of the method** and their **QA/QC procedures** using the IAEA on-line reporting system. User name, password and instructions for the on-line reporting will be sent to participant by email about 2 weeks before the deadline.

2. The participants are requested to make **three independent determinations** for each element in the PT sample.

3. The participant **MUST** answer to all questions during the reporting:

    - Moisture determination procedure
    - Sample preparation procedure
    - Instrumental method used for the quantitative determination of requested elements
    - Information on the validation of the method used
    - Statement on traceability of obtained measurement results (standards, reference material used, etc.)
    - Calculation of results and combined uncertainty
    - Recovery and correction for recovery
    - Quality control procedures (control charts, etc.).

4. For **each** element the participants **MUST** report:

    - **The results of each independent determination**; reported as net values (i.e., after correcting for blanks, etc.), leaving as many significant figures as

justified by the precision of the method used. **The results should be reported using the unit specified on the reporting form on a dry mass basis**.

- Uncertainties (standard combined and expanded) **in the same specified unit**
- Coverage factor
- The result of the matrix matching QC sample
- The recovery
- The detection and quantification limit in the **specified unit**

OTHER NOTES

1. If an element is not detected by the method used, it should not be reported but associated results of QC material, detection and quantification limits **must be** to allow evaluation of less than values by MESL. If not, the analyte will be evaluated as not determined by participant in the final evaluation report.

2. One report containing the results and statistical evaluation of the proficiency test data will be issued and sent to participants after the finalization of the exercise. Each participant or working group will be identified with a code number and the identity of this number will be revealed only to the respective participant, and, since this activity is part of the MED POL quality assurance of monitoring data program, their respective MEDPOL National Focal Point.

3. Two weeks before the deadline, the organizers of the Proficiency Test will send to all participating laboratories a deadline reminder and further instructions for the on-line submission of results by email.

Questionnaire:

- Description of sample preparation
- Description of calibration strategy
- Did you apply recovery correction?
- How did you calculate recovery?
- Do you usually report uncertainties?
- If yes, what is your coverage factor?
- How did you estimate uncertainties?
- How do you assure traceability of your results?
- Did you correct your results for moisture?
- Description of protocol used for determination of moisture content
- If you did not correct for moisture explain why
- Did you used validated method?
- Did you used CRM for validation?
- Did you used CRM for calibration?
- Do you have a quality system in place?
- If yes, please describe
- Are you accredited?
- If yes, please provide details of your accreditation
- Do you have further comments?