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Agenda item 5: MEDPOL Proficiency Test on the Determination of Trace Elements in Sediment Sample (2019)

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REPORT

MEDPOL PROFICIENCY TEST ON THE DETERMINATION OF TRACE ELEMENTS IN SEDIMENT SAMPLE

2019

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1. INTRODUCTION

The primary goal of the International Atomic Energy Agency's Environment Laboratories (IAEA-NAEL), and in particular the Environment Laboratories (NAEL), is 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 UNEP 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 MED POL monitoring 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 sediment sample organised by the MESL in 2019 for the designated MED POL monitoring laboratories.

The IAEA officers responsible for this publication are S. Azemard, E. Vasilev, S. Sander. A. Trinkl from NAEL Terrestrial Laboratory was responsible for the management of the on-line reporting system.

SCOPE OF EXERCISE

In May 2019the MED POL Programme Officer contacted the National Focal Points of MED POL countries, requesting them to provide the names of the designated national laboratories, involved in MED POL monitoring activities. 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 July 2019.

The test material, named ***IAEA-MESL-2019-02-TE-MEDPOL-PT*** sample, was sent to 19 designated monitoring laboratories from 17 countries in August 2019. Figure 1 shows the distribution of PT samples in MED POL countries, and the distribution per countries of received results.

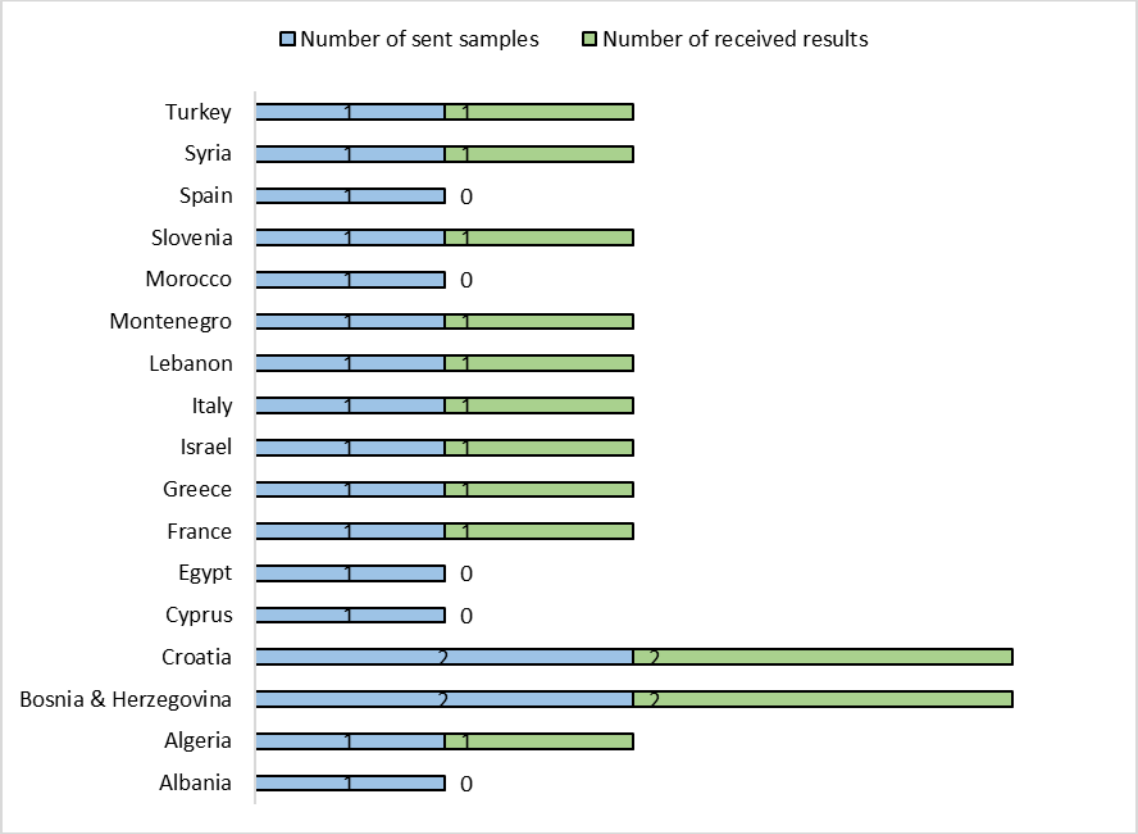


FIG. 1. Distribution per country of the MED POL PT sample

Participants were requested to apply their established analytical methods, usually used for MED POL monitoring studies, for the determination of total contents of the following IMAP EO9 mandatory (priority) elements: Cd, Hg and Pb as well as on some additional trace elements: Al, As, Co, Cr, Cu, Fe, Mn, Sr, V, and Zn in the test PT

sample (IAEA-MESL-2019-02-TE-MEPDOL-PT) as well as in one matrix matching quality control sample, sent to the MED POL laboratories together with the PT test sample.

The deadline for reporting the results back to the MESL was originally set to 31 October 2019. Finally, 14 from 19 (74%) monitoring laboratories proposed for participation in this proficiency sent their results back to the organisers in the requested deadlines.

Laboratories participating in the present exercise are listed in the Annex 1. Designated MED POL laboratories which didn't report the results are listed in the Annex 2.

2. MATERIAL

2.1. Preparation of the material

The sediment used for preparing IAEA-MESL-2019-02-TE-MEPDOL-PT sample was collected in a bay of the Caspian Sea; freeze dried, sieved at 100µm, mechanically homogenized and packed in amber glass bottles.

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

2.2. Assigned values and their uncertainties:

The assigned values and their associated uncertainties are presented in the Table 1.
The assigned values were calculated from the results reported by the participants in this PT and from the results obtained in the MESL with preliminary validated analytical methods. They were calculated according to the requirements of the ISO 17043 standard [2]. The robust statistics was applied as recommended in the ISO 13528 [3]. Kernel density was used as an appropriate method to represent the overall structure of the entire data set [4]. Several bimodality distributions were observed for Al, Cr, Cu, Mn and Pb, mainly connected to the incomplete digestion of the sediment sample. Therefore, only data reported with total digestion or non-destructive techniques were kept for derive the assigned values for above mentioned analytes. One laboratory reported negative results, rejected before starting the data treatment.

Expanded uncertainties were calculated according to the ISO standard 35 [1] applying the Eq. (1).

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

where:

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

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

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_{char} is the uncertainty of characterization, estimated according to the recommendations of the ISO 35 [1] using Eq. (2).

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

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

All assigned values and expanded uncertainties are presented in Table 1.

TABLE 1: ASSIGNED VALUES FOR TRACE ELEMENTS IN THE MED POL PT SAMPLE

Element	Assigned Value (mg kg^{-1})	U (*k*=2) (mg kg^{-1})
Al	68.0×10^3	5.0×10^3
As	10.0	1.0
Cd	0.162	0.026
Co	14.0	1.6
Cr	88.4	8.7
Cu	30.0	2.9
Fe	39.2×10^3	3.9×10^3
Hg	0.470	0.034
Mn	870	83
Pb	26.7	2.9
V	127	15
Zn	97.4	7.8

3. EVALUATION OF RESULTS

3.1. 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

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].:

	$\lvert z \text{ or Zeta} \rvert \leq 2$	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 mean of the laboratory and the assigned value in the same unit. *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, Zeta-score was not calculated.

3.2. Overview of the reported measurement results

14 laboratories provided 140 measurement results on the mass fractions of trace elements in the PT sample by the final deadline. Graphical presentations of z-score and Zeta-scores are presented in the Annex 3 together with a summary on the statistical evaluation of reported results for the respective trace element. Kernel density plots are presented in the Annex [4]. All results are reported by the laboratory code number only, to protect the Participants confidentiality. However, as agreed with the participants the laboratory codes will be shared with their MEDPOL National Focal Point as part of the capacity building and quality assurance programme of MEDPOL.

3.3. Laboratory results and scoring:

3.3.1 *z*-scores

The measurement performance of participating laboratories was assessed by *z*-scores. Obtained results are summarized in Table 2 and the z-scores are summarized in Table 4 and Figure 2. *z*-scores per element are presented in Table 5 and on Figure 3.

A total 135 *z*-scores were calculated. Overall 81% of reported measurement results were assessed as satisfactory, 2.2% as questionable and 17% as unacceptable. From 14 participating laboratories, 6 laboratories (43%) reported 100% of their measurement results with $|z| \leq 3$ and 5 laboratories (36%) were able to report 100% of their measurement results with $|z| \leq 2$. On the other hand, 2 laboratories reported less than 40% of their results with $|z| \leq 2$. This fact is probably reflecting the existing of unresolved analytical problems in those laboratories.

Extreme z-scores >7 have been obtained for about 8% of reported results. Some have been identified as unit error (laboratory 1), while some have been obtained for understandable negative results (laboratory 7).

3.3.2 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.

Obtained in this PT Zeta-score results are summarized in Table 3. Zeta-scores per participant are summarized in Table 6 and on Figure 4. Zeta-score per element are presented in Table 7 and in Figure 5.

About 66% of measurement results were reported with uncertainties. Zeta-scores were calculated for 9 of participating laboratories (64%), 5 of participating laboratories didn't report measurement uncertainties, which made the calculation of Zeta score impossible. One participant (laboratory code 2) did report only expanded uncertainty and *k* factor and for the for calculation of Zeta scores, expanded uncertainties were divided by the reported *k* factor in order to obtained combined uncertainty.

Eleven participants have evaluated uncertainties but only 9 laboratories, effectively reported results with their uncertainties. Different approaches were reported to estimate measurement uncertainties: 4 participants applied single validation approach, 2 laboratories used modelling approach, 2 laboratories were reporting measurement uncertainties, obtained via Nordtest approach, and 1 participant didn't provide the information on how it estimates uncertainties.

86.5% of the calculated Zeta-scores are considered as satisfactory and 4 laboratories reported 100% of their measurement results with Zeta-scores below 2. Two participating laboratories received satisfactory Zeta-score for less than 50% of reported results.

Overall, obtained results show that there are still remaining problems with the realistic estimation of the combined measurement uncertainty. Some laboratories have reported wrong information for the measurement uncertainties: Laboratory 1 reported very similar values for u and U and Laboratory 17 reported u and U in % instead of mg kg^{-1} (as requested).

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

Laboratory Code	Al	As	Cd	Co	Cr	Cu	Fe	Hg	Mn	Pb	V	Zn
1	-7.99	15.05	18.16	-0.51	-3.79	-1.61	-7.99	0.49	-7.30	5.45		-0.98
2		-1.85	0.02	0.03	-3.20	-1.73		-1.62	-0.18	-0.83	-3.75	-0.52
5		0.54	1.70	0.93	-0.77	0.05		-3.10	-0.11	-0.66	-0.03	0.65
7	-4.28		-4843.42		-5.70	-1.77	-0.96		-0.35	-13.13		
8	-0.26	-1.76	-0.56		0.10	0.19	-0.14	1.74	-0.20	0.14		-0.70
9	0.22	0.47	-1.23	0.76	-0.09	0.28	0.09	0.38	-0.31	0.46	-0.44	0.35
10	-0.28	0.39	0.49	0.32	0.04	-0.94	-0.46	0.03	-0.49	0.19	0.45	-0.23
11		20.37	-5.02	-1.01	-3.90	-1.50	-1.05	-0.51	-0.29	1.33	-5.12	-0.92
12	-0.06		-1.55	0.48	-0.11	-1.09	-0.60	0.22	-0.60	0.46	-0.83	-0.25
14	-7.30	-0.30	9.00	0.19	1.93	0.70	1.90	-2.11	1.24	-0.56	-0.08	1.59
15		-0.27	-0.28	-0.21	0.52	0.28	0.08	0.67	0.35	0.70		0.00
17	0.57	-1.13		-3.28	1.04	-1.53	0.00		-0.09	-0.85	5.11	-1.74
18			0.40		-2.71	2.38	1.09		1.29			-0.23
19			-0.81					0.30		-3.34		

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

Laboratory Code	Al	As	Cd	Co	Cr	Cu	Fe	Hg	Mn	Pb	V	Zn
1	-27.04	0.65	0.70	-0.07	-0.90	-0.25	-19.84	0.06	-9.15	0.41		-0.14
2	-2.55		0.01	0.03	-4.45	-2.33		-1.89	-0.25	-0.99	-5.20	-0.64
5												
7												
8	-0.28	-2.37	-0.57		0.13	0.23	-0.19	2.35	-0.16	0.16		-0.96
9	0.40	0.75	-1.64	1.12	-0.16	0.42	0.14	0.63	-0.54	0.76	-0.68	0.59
10	-0.34	0.46	0.54	0.42	0.06	-1.37	-0.66	0.03	-0.69	0.24	0.56	-0.28
11												
12	-0.05		-1.91	0.62	-0.15	-1.70	-0.50	0.32	-0.89	0.30	-1.14	-0.31
14												
15		-0.44	-0.41	-0.23	1.03	0.62	0.15	0.28	0.66	1.08		0.00
17	1.94	-0.21		-0.80	1.64	-0.85	-0.01		-0.24	-0.42	9.60	-3.56
18												
19			-1.05					0.42		-6.75		

TABLE 4: SUMMARY OF OBTAINED z-SCORES PER LABORATORY

Laboratory Code	Number of results	$\lvert z \rvert \geq 3$	$2 < \lvert z \rvert < 3$	$\lvert z \rvert \leq 2$
1	11	64%	0%	36%
2	10	20%	0%	80%
5	10	10%	0%	90%
7	7	57%	0%	43%
8	10	0%	0%	100%
9	12	0%	0%	100%
10	12	0%	0%	100%
11	11	36%	0%	64%
12	11	0%	0%	100%
14	12	17%	8%	75%
15	10	0%	0%	100%
17	10	20%	0%	80%
18	6	0%	33%	67%
19	3	33%	0%	67%

TABLE 5: SUMMARY OF OBTAINED z-SCORES PER ELEMENT

Element	Participation	$\lvert z \rvert \geq 3$	$2 < \lvert z \rvert < 3$	$\lvert z \rvert \leq 2$
Al	93%	38%	0%	63%
As	57%	20%	0%	80%
Cd	57%	31%	0%	69%
Co	93%	10%	0%	90%
Cr	93%	31%	8%	62%
Cu	71%	0%	8%	92%
Fe	79%	9%	0%	91%
Hg	71%	9%	9%	82%
Mn	79%	8%	0%	92%
Pb	93%	23%	0%	77%
V	93%	38%	0%	63%
Zn	86%	0%	0%	100%

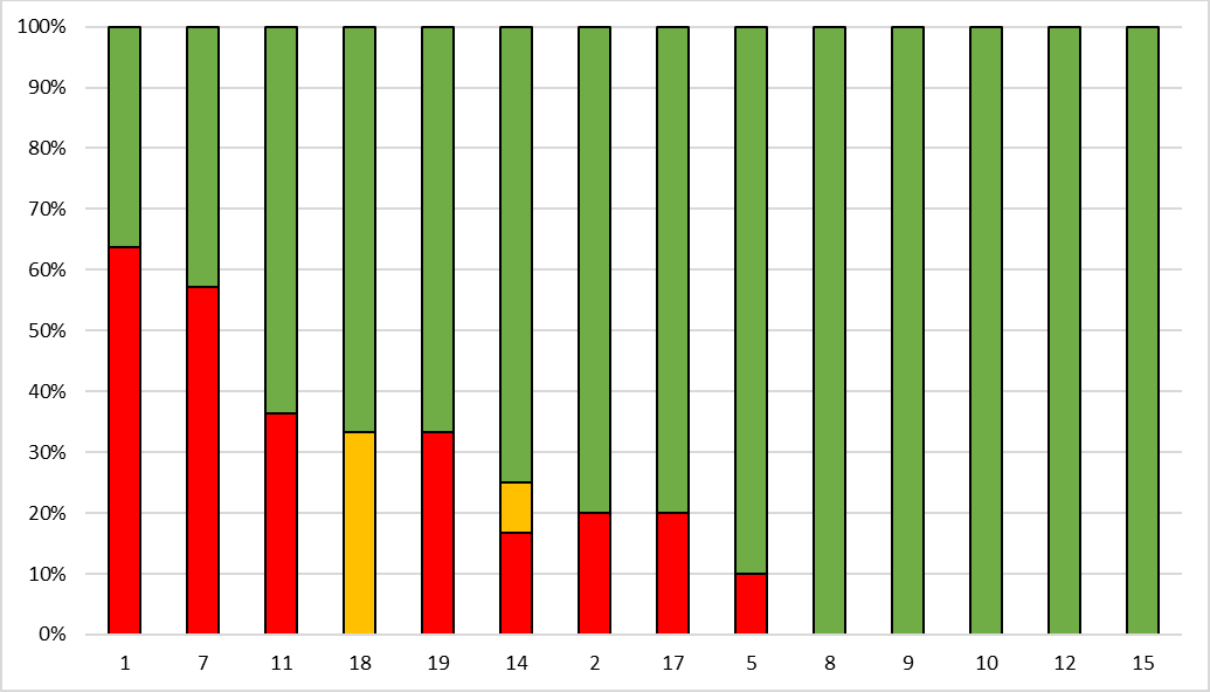


FIG. 2. Summary of obtained z-scores per participant

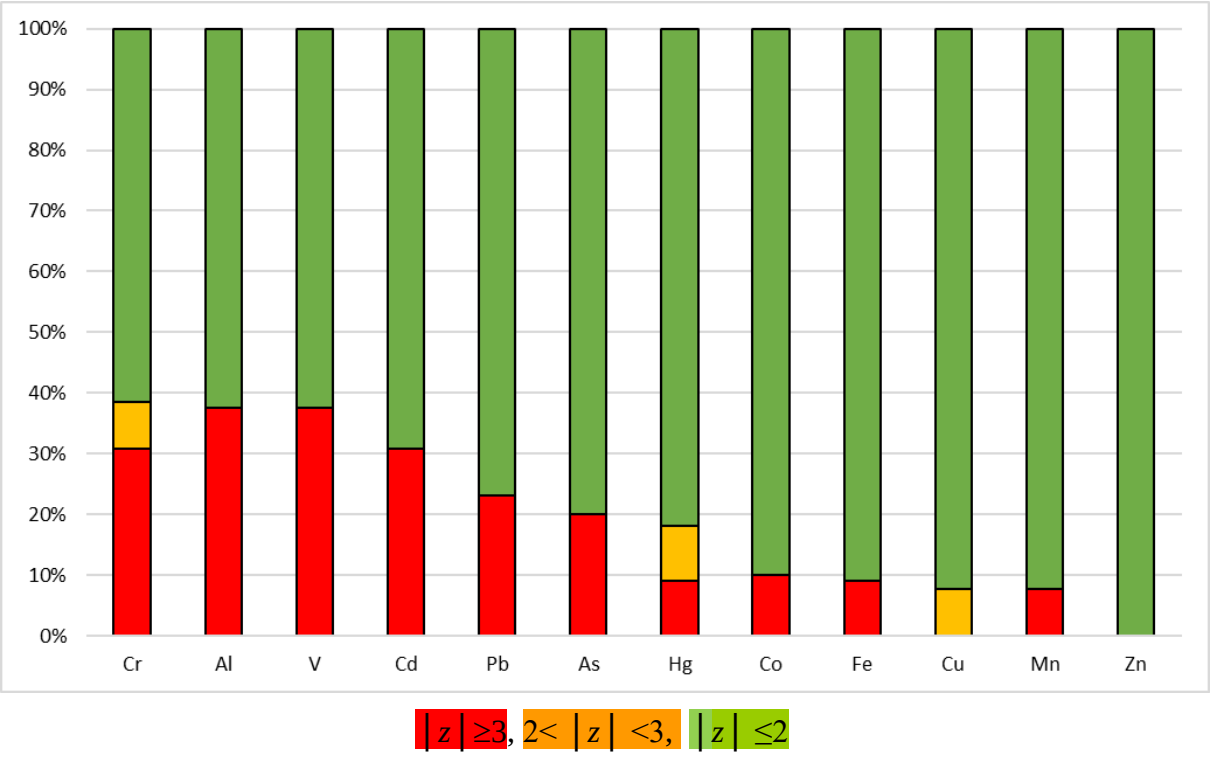


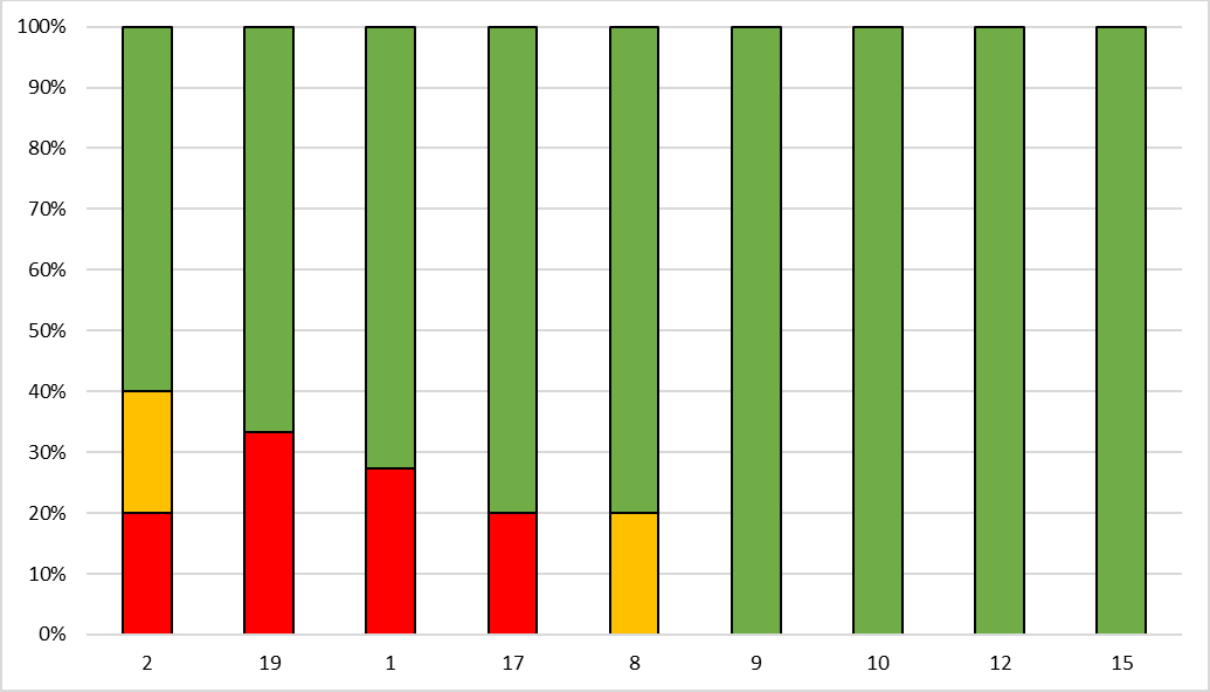
FIG. 3. Summary of obtained z-scores per element

TABLE 6: SUMMARY OF OBTAINED ZETA-SCORES PER LABORATORY

Laboratory Code	Number of results	|Zeta| ≥3	2< |Zeta| <3	|Zeta| ≤2
1	11	27%	0%	73%
2	10	20%	20%	60%
5				
7				
8	10	0%	20%	80%
9	12	0%	0%	100%
10	12	0%	0%	100%
11				
12	11	0%	0%	100%
14				
15	10	0%	0%	100%
17	10	20%	0%	80%
18				
19	3	33%	0%	67%

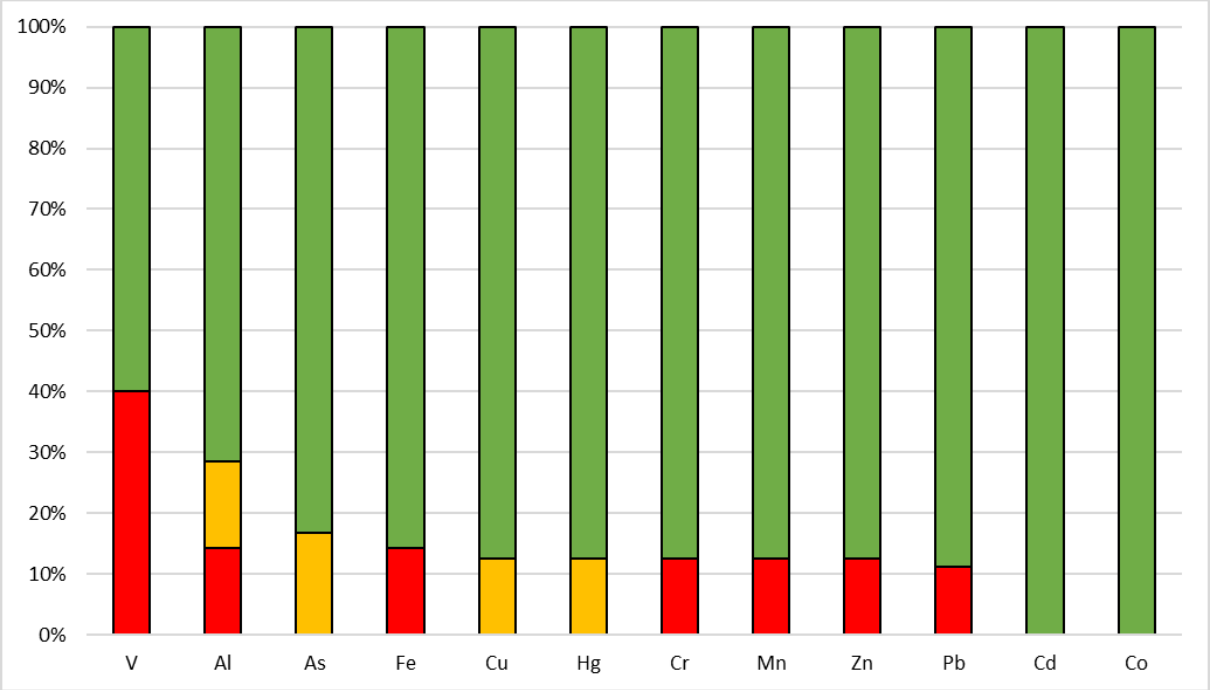
TABLE 7: SUMMARY OF OBTAINED ZETA-SCORE PER ELEMENT

Element	Participation	|Zeta| ≥3	2< |Zeta| <3	|Zeta| ≤2
Al	36%	14%	14%	71%
As	50%	0%	17%	83%
Cd	43%	0%	0%	100%
Co	50%	0%	0%	100%
Cr	57%	13%	0%	88%
Cu	57%	0%	13%	88%
Fe	57%	14%	0%	86%
Hg	57%	0%	13%	88%
Mn	57%	13%	0%	88%
Pb	64%	11%	0%	89%
V	57%	40%	0%	60%
Zn	50%	13%	0%	88%



| Zeta | ≥3, 2< | Zeta | <3, | Zeta | ≤2

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



| Zeta | ≥3, 2< | Zeta | <3, | Zeta | ≤2

FIG. 5. Summary of obtained Zeta-scores per element

3.4. Sample treatment, use of CRM and recovery correction:

Most of participating in the MEDPOL PT laboratories applied microwave digestion, using mainly mixture of acid. Hydrofluoric acid is required for decomposition of the silicate lattice of a sediment matrix. Without the use of HF, the dissolution of a sediment sample will be incomplete, resulting in the observation of negatively biased concentrations for certain refractory elements, such as Al, Cr, and V (Figure 3 and Annex 3). Only 8 laboratories participating in the MED POL PT have used hydrofluoric acid in their sample preparation step. 6 participants were not using total digestion procedure and despite that 4 of them (1, 2, 7 and 11) have reported results for refractory elements (Al, Cr and V), unsurprisingly with unsatisfactory low biased results (i.e. z scores < - 3) for the mass fractions of Al, Cr and V.

For the total mercury determination 36% of laboratories used solid mercury analyser and didn't applied any sample preparation before the instrumental measurement. One laboratory has used XRF without any sample digestion before, except for the determination of Al and Fe mass fractions in the PT sample.

Freeze drying step was a part of sample processing procedure for the MEDPOL 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 letter, describing details on the MED POL PT exercise. Oven drying for a separate portion of sediment sample at 110°C until constant weight was the recommended procedure for moisture determination. Only 3 participating laboratories have respected it, while the remaining participants applied in house developed protocol or didn't report the information on moisture content. The moisture content reported by the laboratories was in the range from 0.4 to 5%.

In order to provide traceable results and to confirm the validation of the methods used, designated MED POL 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 in the PT exercise designated laboratories, were generally selected according to the above described criteria: similar matrix and concentration range of the analytes of interest.

Out of the 14 data sets received, 5 laboratories didn't include quality control (QC) results in the reporting form, despite the fact that some of them are reporting the use of CRM in their

quality procedures. It should be noted that 2 participating laboratories, claiming to be accredited for this type of analyses didn't report any quality control results and evidences.

Nine laboratories reported recoveries, but only 4 of them claimed implementing correction for recovery for all, or part of reported trace elements mass fraction. Most participants have calculated recovery rates by using CRMs and few of them have used spike solution for the analytes of interest. Interestingly, a considerably high proportion of laboratories that didn't 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%.

3.5. Analytical techniques used by participants:

Abbreviations of the instrumental techniques used in this exercise are given in Table 8. As it can be seen from Figure 6, ICP-MS is the most used instrumental technique, followed by AAS and ICP-OES.

TABLE 8: ANALYTICAL TECHNIQUES ABBREVIATIONS

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

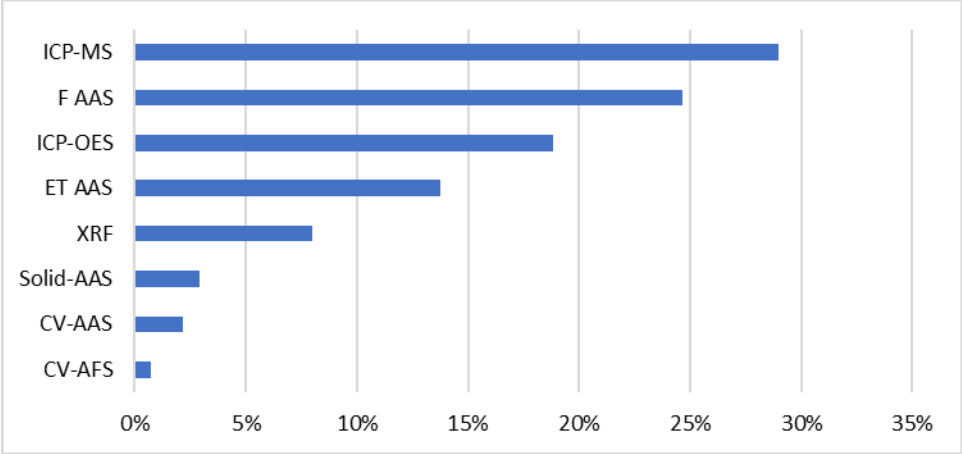


FIG. 6. Graphical distribution of instrumental techniques, applied in the present PT

3.6. Answer to the provided questionnaire:

Four laboratories didn't report any information in the questionnaire.

Nine laboratories claimed to be accredited, however 4 of them didn't report measurement uncertainties, which should be part of a result provided by an accredited laboratory.

Nine laboratories applied preliminary validated methods, while 11 participants declared to have quality system in place. Nine participants declare to be accredited, but only 2 of them are accredited for the analytes and matrix of this PT.

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

4. CONCLUSIONS AND RECOMMENDATIONS

Participation in MEDPOL proficiency test is considered as an educational 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.

In order to obtain a real estimation of laboratory performance, the proficiency test sample should be treated in exactly the same way as any routine test sample. Examples of 'poor practice' include:

- Getting the PT samples analysed by the most experienced analyst

- Reporting results considered to be the ‘best’ ones.

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 in order to prevent the problem to reoccur. This is one of the requirements for laboratories accredited according to the ISO/IEC 17025 standard.

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

Five laboratories didn’t provide results for the use of CRMs in their analytical procedure, which means that the internal quality control in those laboratories is not in place.

Uncertainty of the measurement results in the MED POL PT exercise was calculated from 64% 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 desirable.

Five (26%) from 19 designated by the MED POL laboratories didn’t send the requested in the frame of MED POL PT results, which make the evaluation of their measurement performance impossible. One of them didn’t receive the test sample due to problem with transportation.

5. REFERENCES

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[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 MEDPOL designated participants that sent results

ALGERIA

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Observatoire National de l'Envirnnement et du Développement Durable
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BOSNIA & HERZEGOVINA

Institut for Water
(Institut Za Vode Doo)
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76300 Bijeljina

Institute for Public Health FB&H
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88000 Mostar

CROATIA

Public Health Institute of County of Istra
Nazorova 23
52100 Pula

Institute of Public Health
Ljudevita Posavskog 7A
23000 Zadar

FRANCE

Laboratoire de Biogéochimie des Contaminants Métalliques
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Bliss St Hamra
PO Box 11.0236 Riad El Solh
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MONTENEGRO

Centre for Ecotoxicological Research Podgorica
Bulevar Sarla de Gola 2
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SLOVENIA

National Laboratory of Health
Environment and Food
Prvomajska Ulica 1
2000 Maribor

SYRIA

Central Laboratories
Ministry of Local Administration and Environment
Kafar sosah- 17 Nesaan Street
po box 3773
963 Damascus

TURKEY

Çevre Referans Laboratuvarı
National Environmental Reference Laboratory
Haymana Yolu 5. Km.
Gölbaşı-Ankara

Annex 2: List of MEDPOL designated particpants that did not send results

ALBANIA

Agjencia Kombetare e Mjedisit
National Environment Agency (NEA)
Rruga Sami Frasheri nr 23 godina nr 4
Tirana

CYPRUS

State General Laboratory
44 Kimonos Str.
Stovolos
1451 Nicosia

EGYPT

Institute of Graduate Studies and Research
Alexandria University
163 El Horreya Avenue
Alexandria

NOTE : Did not received sample

MOROCCO

Laboratoire National des Etudes et de Surveillance de la Pollution
Av. Mohamed Ben Abdellah Erregragui Madinat
Al-Irfane
Rabat

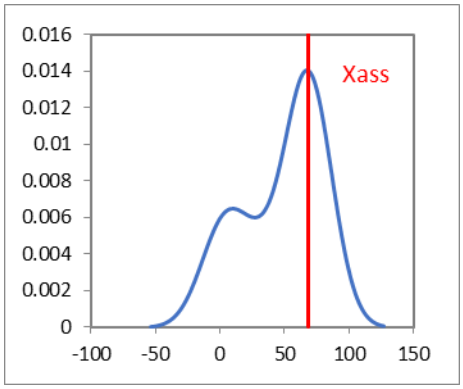
SPAIN

Instituto Espanol de Oceanografia (IEO)
Centro Oceanografico de Murcia
c/Varadero, 1
30740 San Pedro del Pinatar

Annex 3: Graphical representation

Reported data for Al in the IAEA-MESL-2019-02-TE

Kernel density Plot



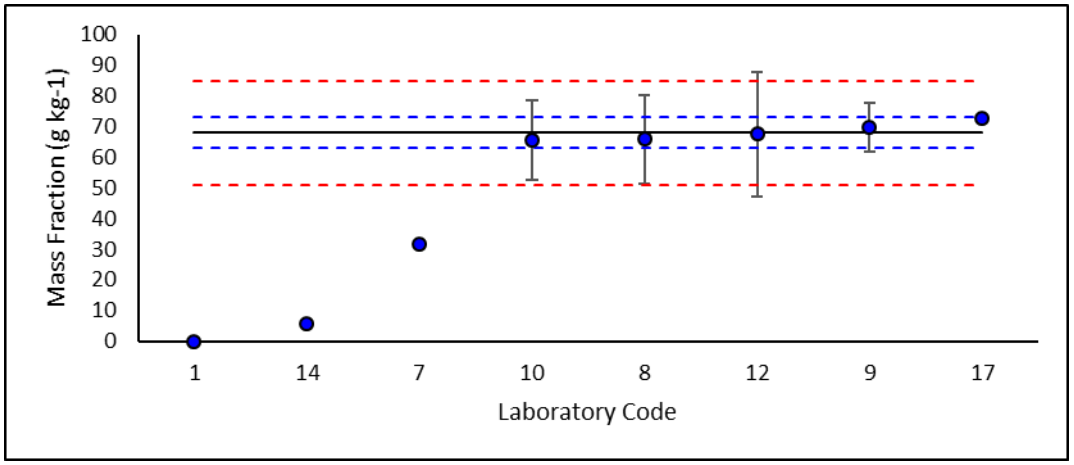
Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	63%	0%	38%
Zeta-score	71%	14%	14%

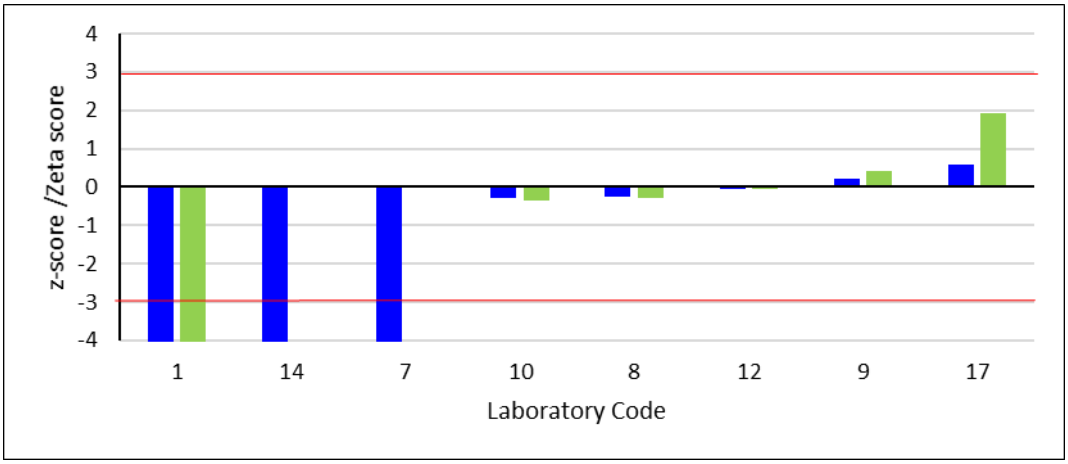
X_{Ass} g kg^{-1}	68.0
U_{Ass} (k=2) g kg^{-1}	5.0[1]
2σ_p g kg^{-1}	17.0
Number of results:	8
Number of methods:	4

Reported results and expanded uncertainties:

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

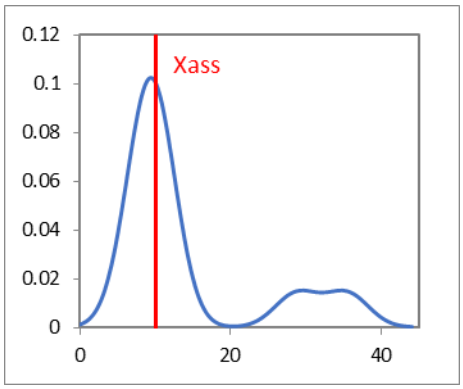


Performance evaluation: z-score Zeta-score



Reported data for As in the IAEA-MESL-2019-02-TE

Kernel density Plot



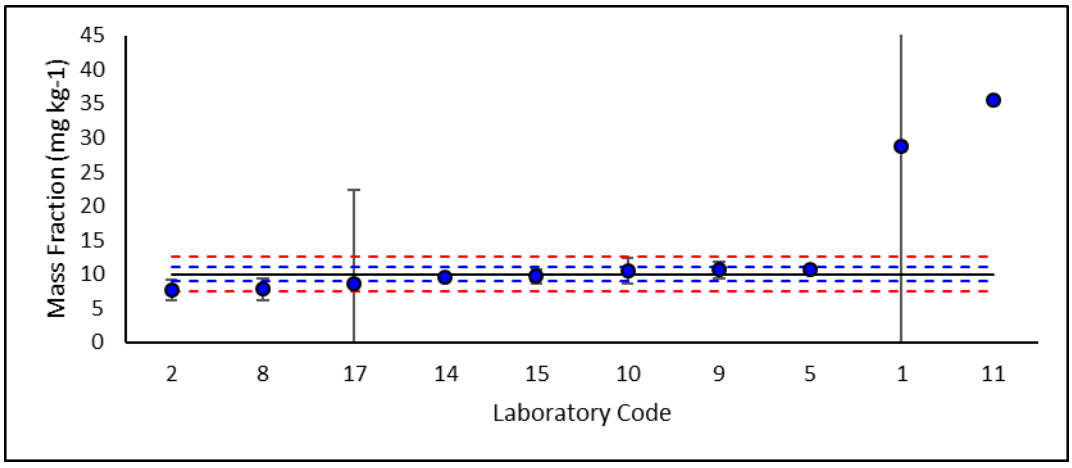
Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	80%	0%	20%
Zeta-score	83%	17%	0%

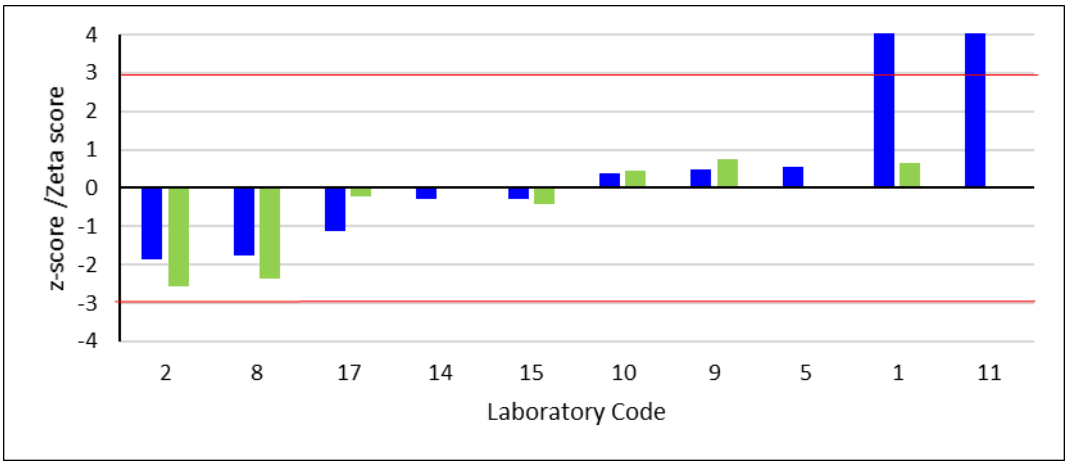
X_{Ass} mg kg^{-1}	10.0
U_{Ass} (k=2) mg kg^{-1}	1.0
$2\sigma_p$ mg kg^{-1}	2.5
Number of results:	10
Number of method:	4

Reported results and expanded uncertainties:

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

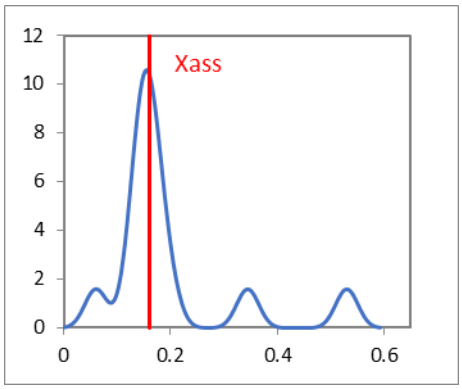


Performance evaluation: *z*-score Zeta-score



Reported data for Cd in the IAEA-MESL-2019-02-TE

Kernel density Plot



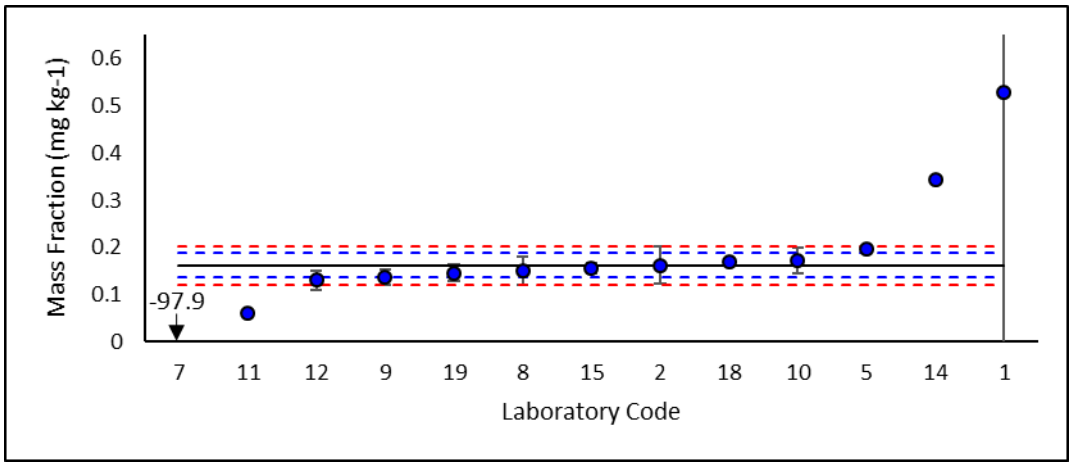
Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	69%	0%	31%
Zeta-score	100%	0%	0%

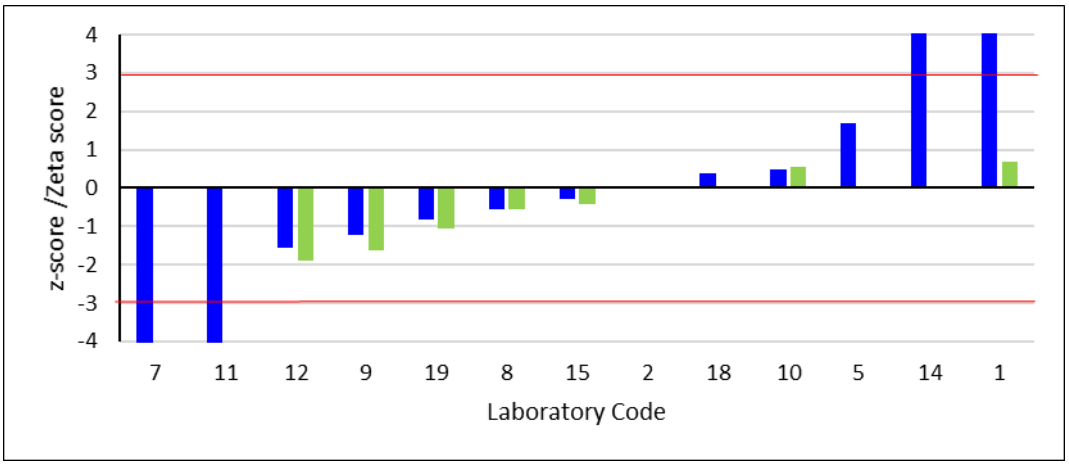
X_{Ass} mg kg^{-1}	0.162
U_{Ass} (k=2) mg kg^{-1}	0.026
$2\sigma_p$ mg kg^{-1}	0.040
Number of results:	13
Number of method:	3

Reported results and expanded uncertainties:

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

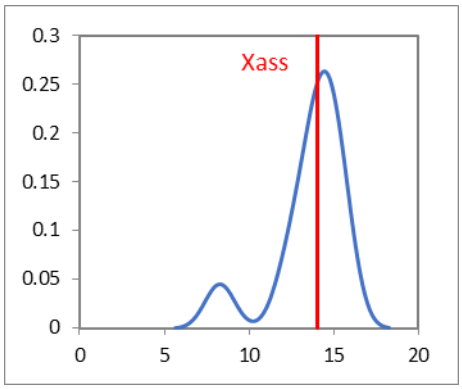


Performance evaluation: *z*-score Zeta-score



Reported data for Co in the IAEA-MESL-2019-02-TE

Kernel density Plot



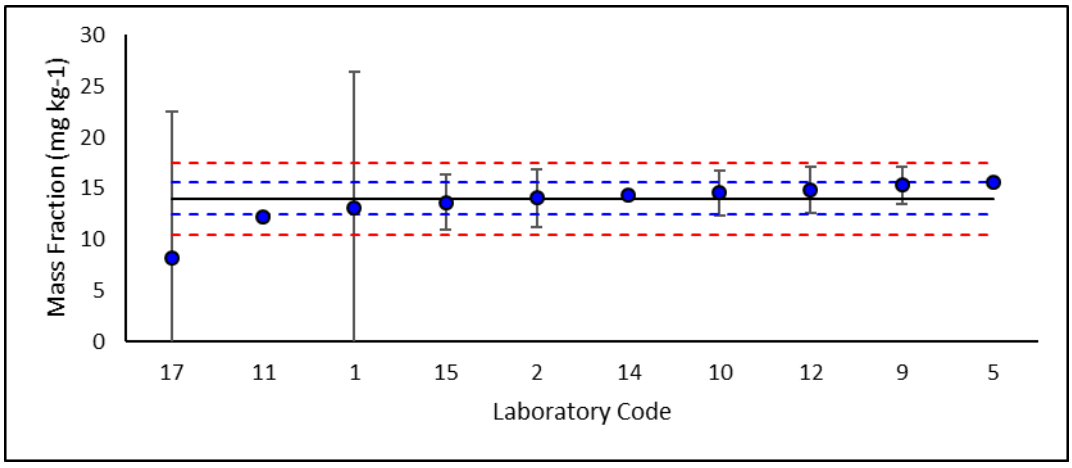
Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	90%	0%	10%
Zeta-score	100%	0%	0%

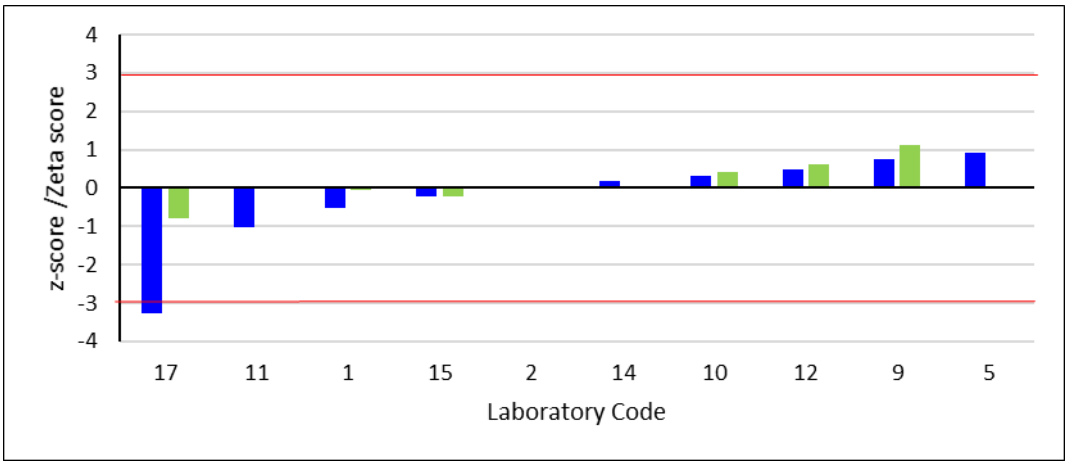
X_{Ass} mg kg^{-1}	14.0
U_{Ass} (k=2) mg kg^{-1}	1.6
$2\sigma_p$ mg kg^{-1}	3.5
Number of results:	10
Number of method:	5

Reported results and expanded uncertainties:

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

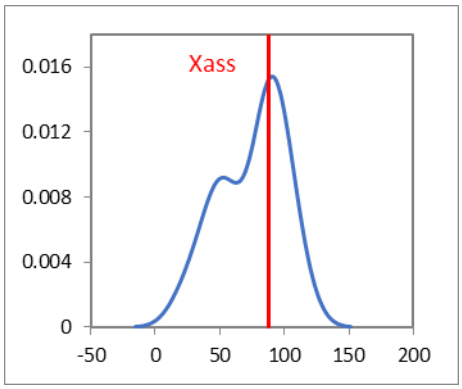


Performance evaluation: *z*-score Zeta-score



Reported data for Cr in the IAEA-MESL-2019-02-TE

Kernel density Plot



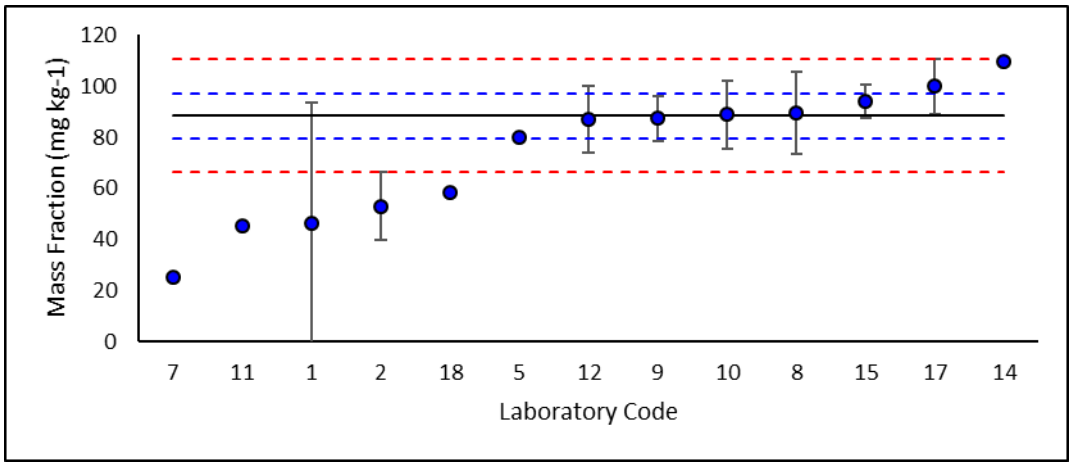
Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	62%	8%	31%
Zeta-score	88%	0%	13%

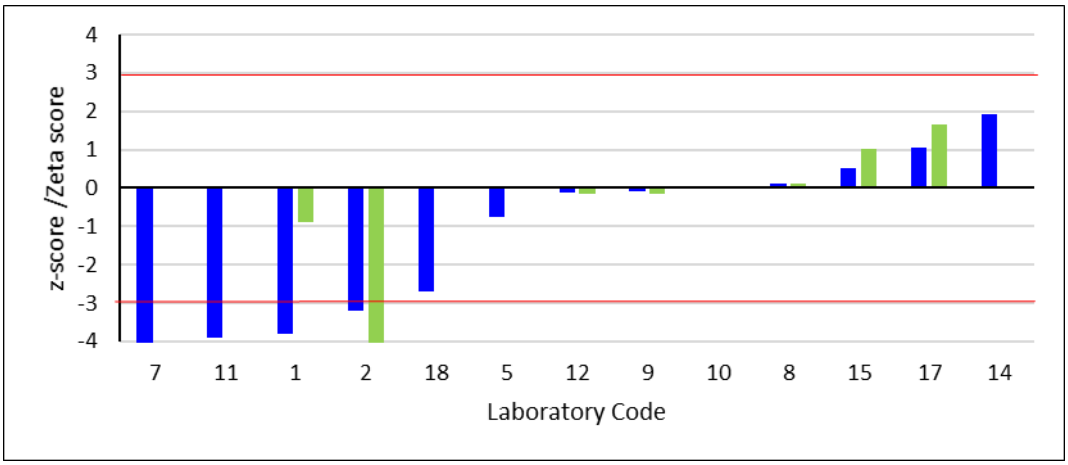
X_{Ass} mg kg^{-1}	88.4
U_{Ass} (k=2) mg kg^{-1}	8.7
$2\sigma_p$ mg kg^{-1}	22.1
Number of results:	13
Number of method:	5

Reported results and expanded uncertainties:

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

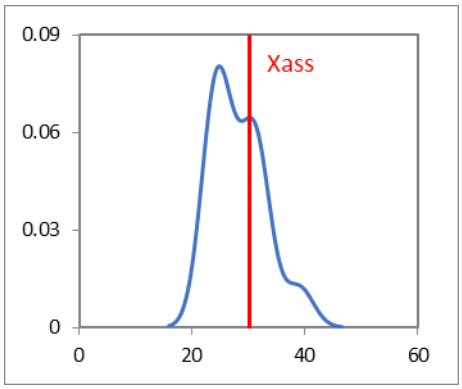


Performance evaluation: *z*-score Zeta-score



Reported data for Cu in the IAEA-MESL-2019-02-TE

Kernel density Plot



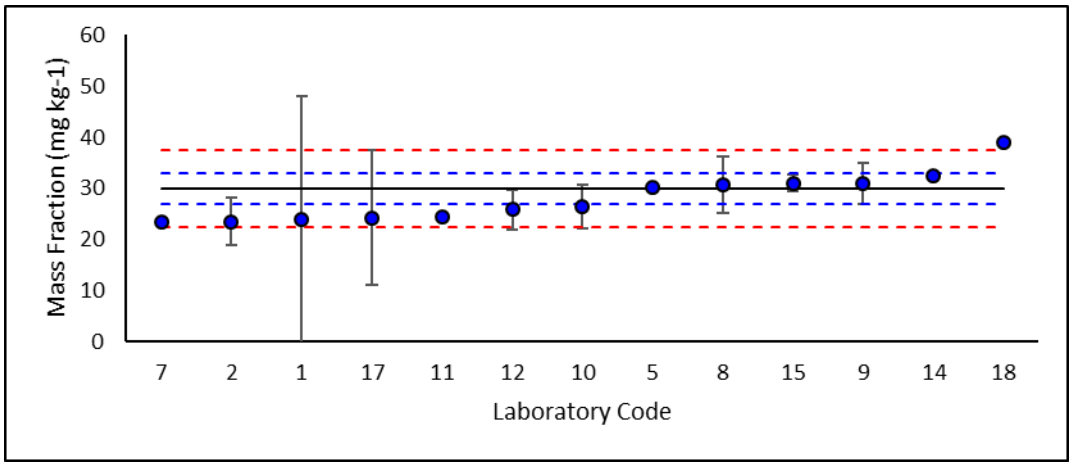
Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	92%	8%	0%
Zeta-score	88%	13%	0%

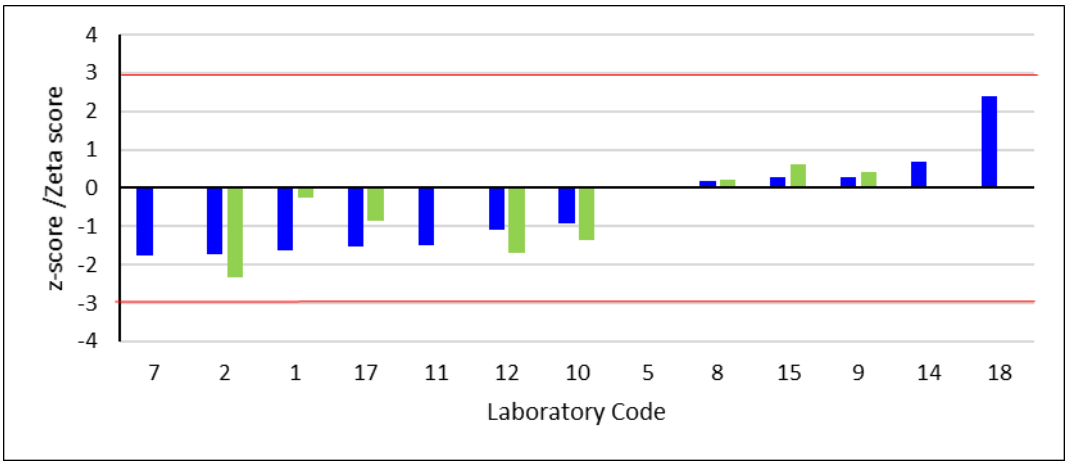
X_{Ass} mg kg^{-1}	30.1
U_{Ass} (k=2) mg kg^{-1}	2.9
$2\sigma_p$ mg kg^{-1}	7.5
Number of results:	13
Number of method:	5

Reported results and expanded uncertainties:

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

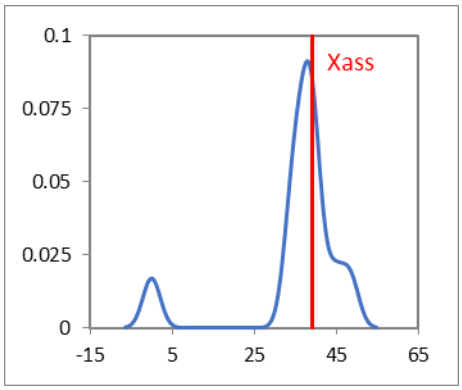


Performance evaluation: *z*-score Zeta-score



Reported data for Fe in the IAEA-MESL-2019-02-TE

Kernel density Plot



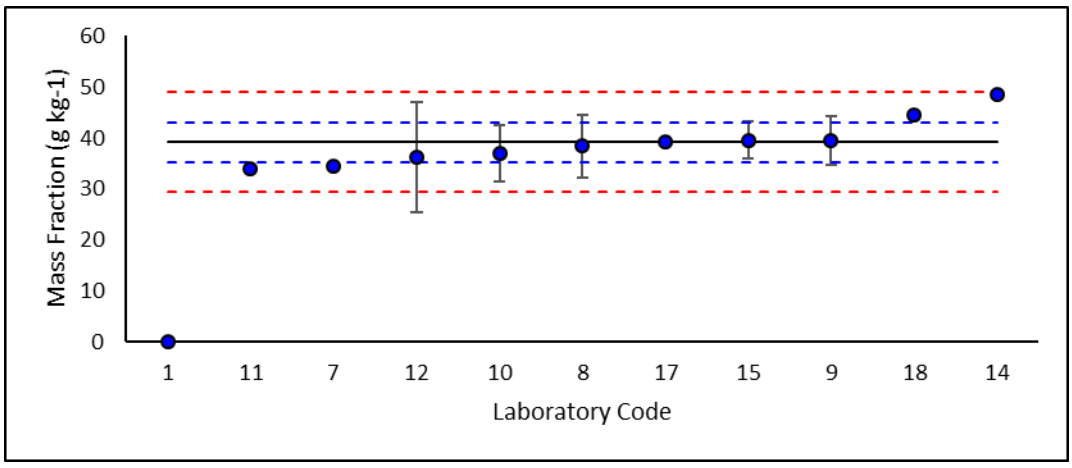
Summary of results:

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

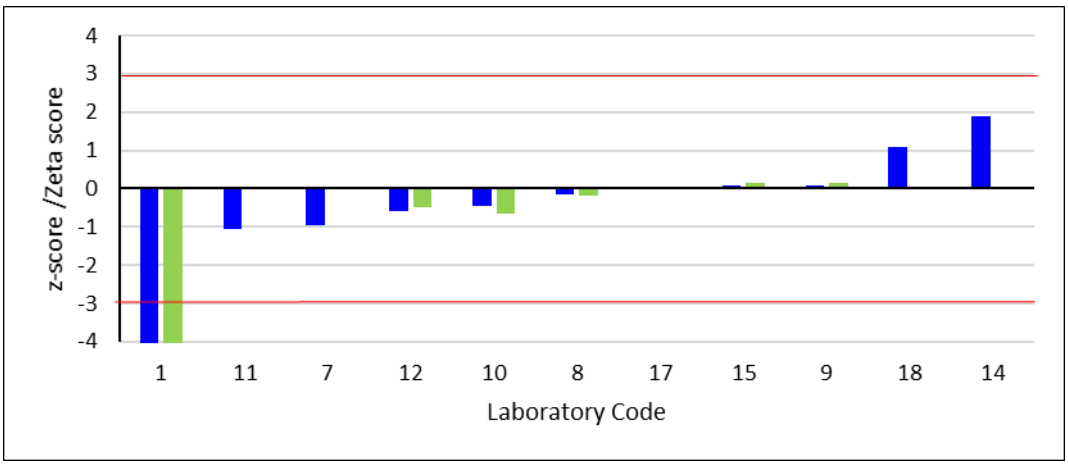
X_{Ass} g kg^{-1}	39.2
U_{Ass} (k=2) g kg^{-1}	3.9
$2\sigma_p$ g kg^{-1}	9.8
Number of results:	11
Number of method:	4

Reported results and expanded uncertainties:

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

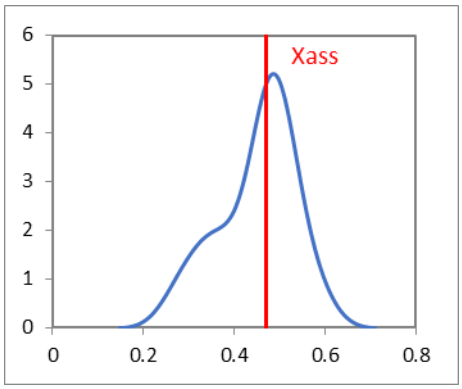


Performance evaluation: *z*-score Zeta-score



Reported data for Hg in the IAEA-MESL-2019-02-TE

Kernel density Plot



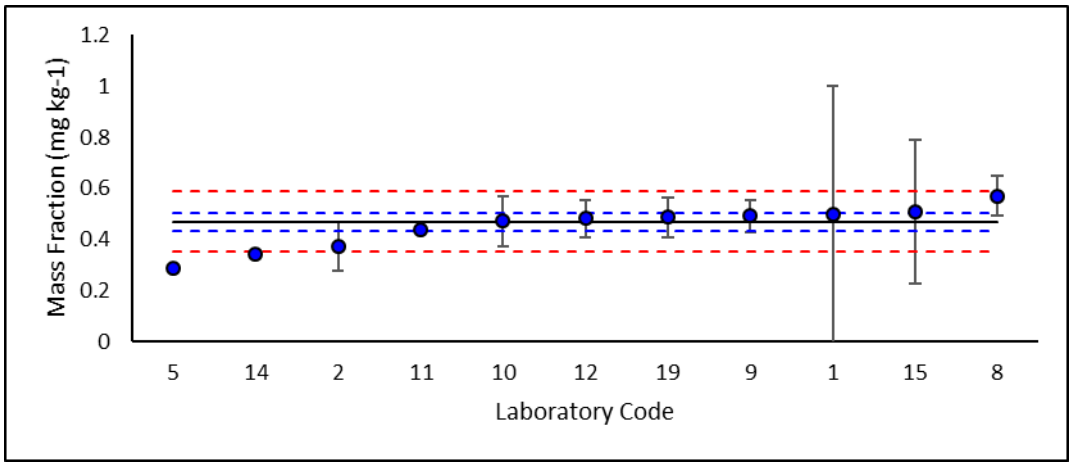
Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	82%	9%	9%
Zeta-score	88%	13%	0%

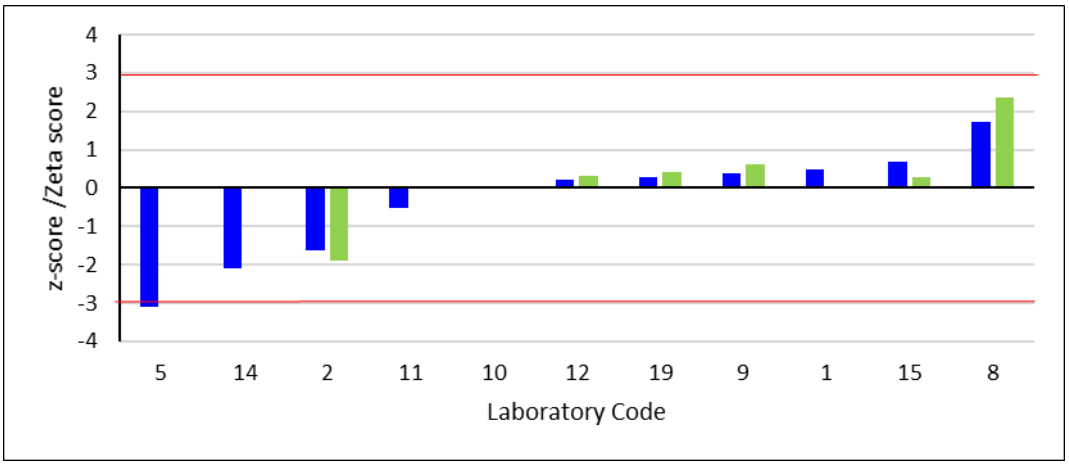
X_{Ass} mg kg^{-1}	0.470
U_{Ass} (k=2) mg kg^{-1}	0.034
$2\sigma_p$ mg kg^{-1}	0.120
Number of results:	11
Number of method:	4

Reported results and expanded uncertainties:

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

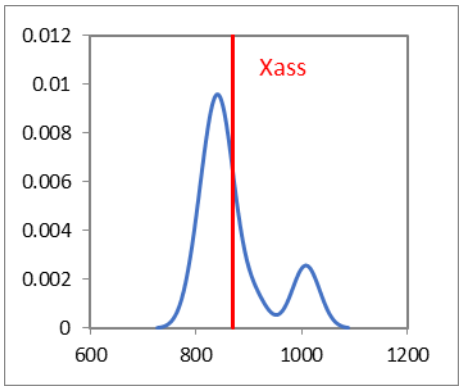


Performance evaluation: *z*-score Zeta-score



Reported data for Mn in the IAEA-MESL-2019-02-TE

Kernel density Plot



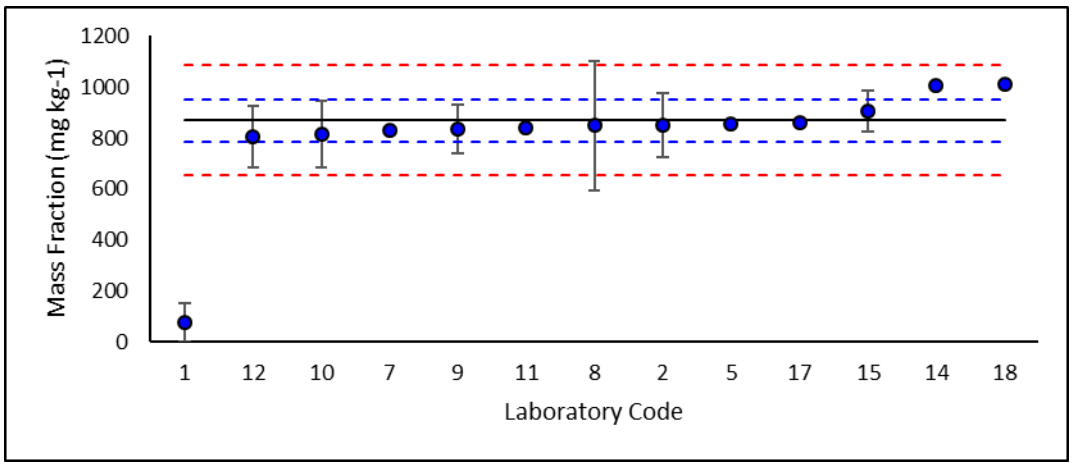
Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	92%	0%	8%
Zeta-score	88%	0%	13%

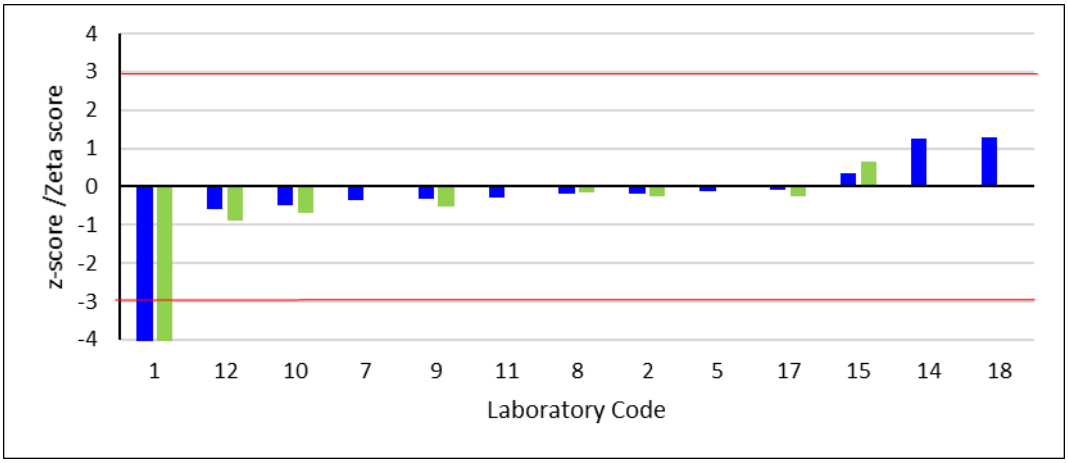
X_{Ass} mg kg^{-1}	870
U_{Ass} (k=2) mg kg^{-1}	83
$2\sigma_p$ mg kg^{-1}	217
Number of results:	13
Number of method:	4

Reported results and expanded uncertainties:

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

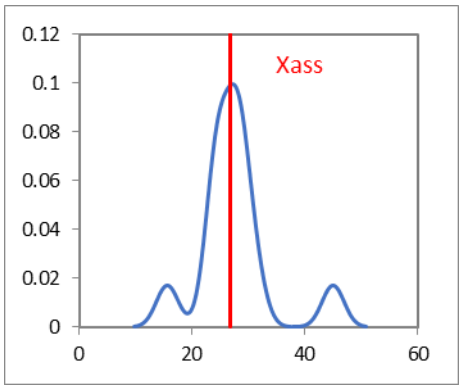


Performance evaluation: *z*-score Zeta-score



Reported data for Pb in the IAEA-MESL-2019-02-TE

Kernel density Plot



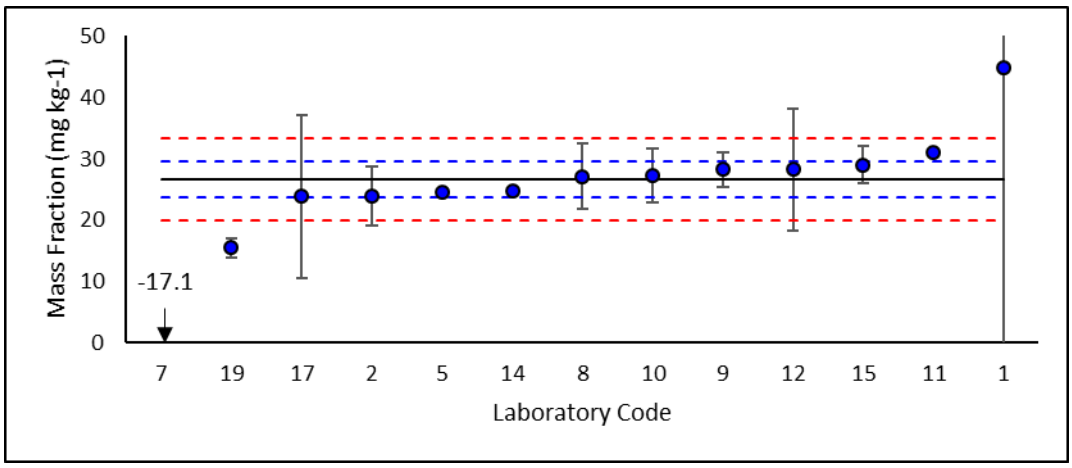
Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	77%	0%	23%
Zeta-score	89%	0%	11%

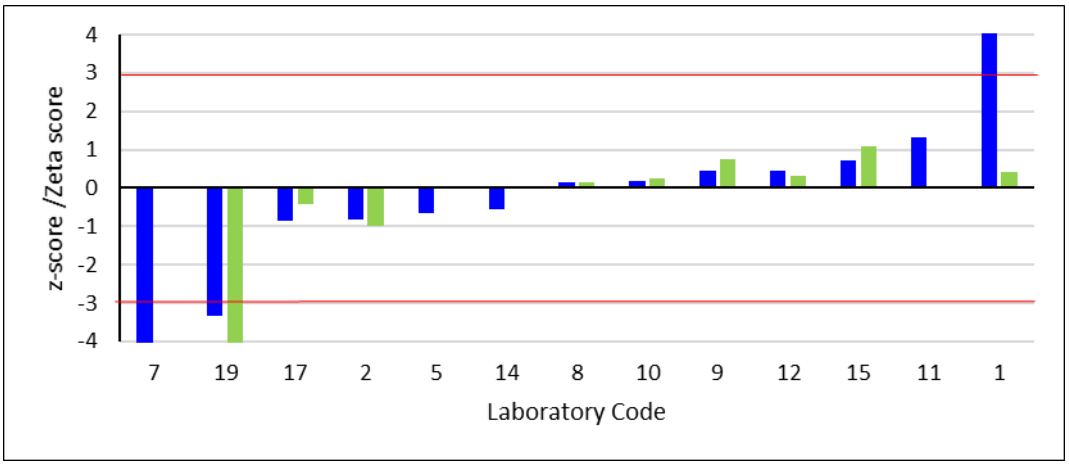
X_{Ass} mg kg^{-1}	26.7
U_{Ass} (k=2) mg kg^{-1}	2.9
$2\sigma_p$ mg kg^{-1}	6.7
Number of results:	13
Number of method:	5

Reported results and expanded uncertainties:

— X_{Cert} ; $\overset{\top}{\bullet}$ $X_{lab} \pm U_{lab}$; ---- $X_{Cert} \pm 2\sigma_p$; ---- $X_{Cert} \pm U_{Cert}(k=2)$

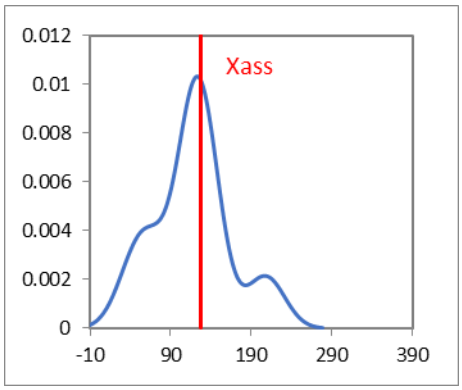


Performance evaluation: *z*-score Zeta-score



Reported data for V in the IAEA-MESL-2019-02-TE

Kernel density Plot



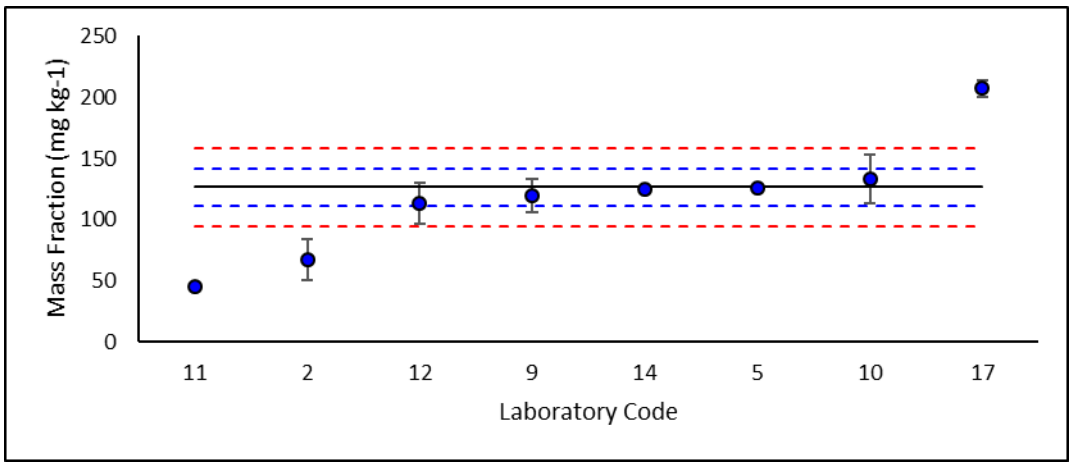
Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	63%	0%	38%
Zeta-score	60%	0%	40%

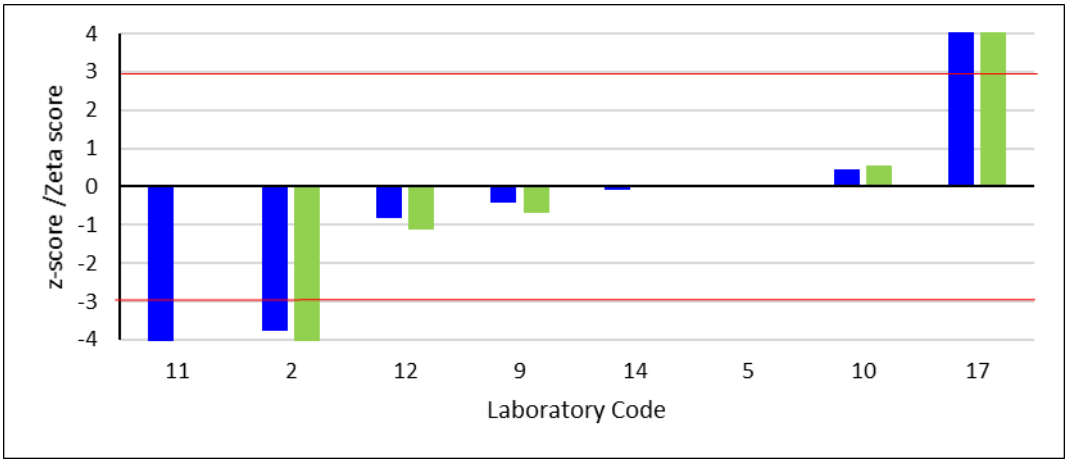
X_{Ass} mg kg^{-1}	127
U_{Ass} (k=2) mg kg^{-1}	15
$2\sigma_p$ mg kg^{-1}	32
Number of results:	8
Number of method:	4

Reported results and expanded uncertainties:

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

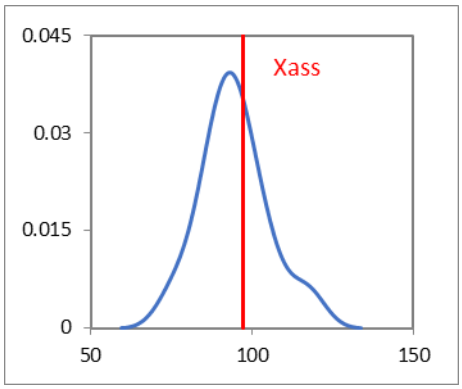


Performance evaluation: *z*-score Zeta-score



Reported data for Zn in the IAEA-MESL-2019-02-TE

Kernel density Plot



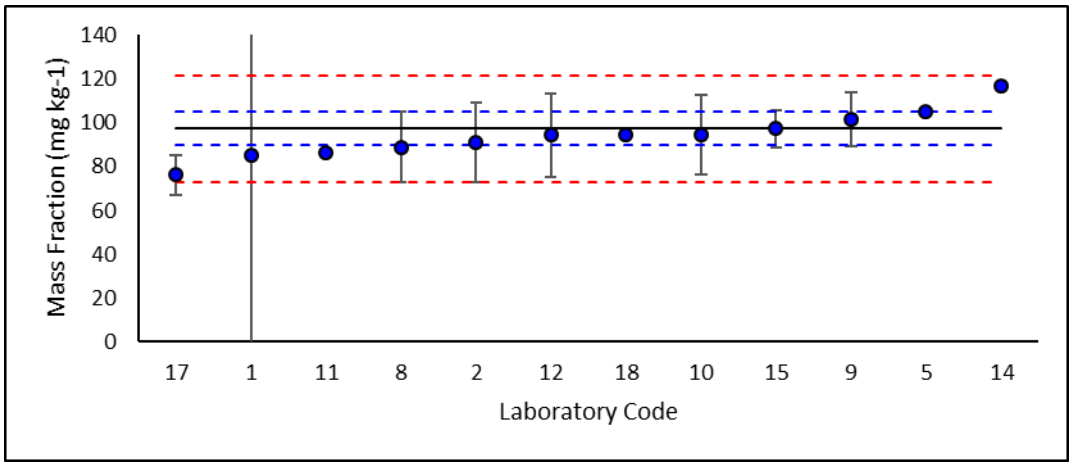
Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	100%	0%	0%
Zeta-score	88%	0%	13%

X_{Ass} mg kg^{-1}	97.4
U_{Ass} (k=2) mg kg^{-1}	7.8
$2\sigma_p$ mg kg^{-1}	24.3
Number of results:	12
Number of method:	4

Reported results and expanded uncertainties:

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



Performance evaluation: *z*-score Zeta-score