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Proftest SYKE

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ABSTRACT

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Proftest SYKE carried out the proficiency test in cooperation with KVVY Tutkimus Oy for the laboratories conducting leaching tests for solid waste material in November-December 2018. The results of the one stage batch leaching test (EN 12457-2) for foundry sand samples were compared and evaluated. The tested measurands were metals (As, Ba, Cd, Cr, Cu, Hg, Mo, Ni, Pb, Sb, Se, V, Zn), Cl^-, SO_4^{2-}, F^-, DOC, pH, and conductivity. In total, 10 participants joined in the proficiency test.

In this PT for all the evaluated measurands the median of the results reported by the participants was used as the assigned value. The measurands Ba, conductivity, DOC, Ni, pH, SO_4, and Zn were evaluated with z scores and of those results 92 % were satisfactory, when deviation of 0.3 pH units and 20–30 % for other measurands was accepted from the assigned value. Further, measurands As, Cr, Cu, and V were evaluated with E_n scores and 76 % of the results were satisfactory.

Warm thanks to all participants in this proficiency test!

Keywords: leaching test, one stage batch leaching test, waste landfill acceptance criteria, environmental laboratories, proficiency test, interlaboratory comparisons

TIIVISTELMÄ

Laboratorioiden välinen pätevyyskoe 13/2018

Proftest SYKE järjesti yhteistyössä KVVY Tutkimus Oy:n kanssa pätevyyskokeen marras-joulukuussa 2018 laboratorioille, jotka tekevät liukoisuustestejä jätteiden kaatopaikkakelpoisuuden arvioimiseksi. Pätevyyskokeessa vertailun kohteena oli yksivaiheinen ravistelutesti (EN 12457-2) valimohiekalle. Pätevyyskokeessa oli yhteensä 10 osallistujaa.

Testisuureen vertailuarvona käytettiin osallistujatulosten mediaania. Tuloksia arvioitiin sekä z- että E_n-arvoilla. Testisuureet Ba, DOC, Ni, pH, SO_4, sähkönjohtavuus ja Zn arvioitiin z-arvoilla ja hyväksyttäviä tuloksia oli 92 % kun tavoitehajonnaksi 95 %:n luottamusvälillä asetettiin pH-määrityksille 0,3 pH-yksikköä ja muille määrityksille 20–30 %. Testisuureiden As, Cr, Cu ja V tulokset arvioitiin E_n-arvoilla, jolloin hyväksyttäviä tuloksia oli 76 %.

Kiitos pätevyyskokeen osallistujille!

Avainsanat: liukoisuustesti, yksivaiheinen ravistelutesti, kaatopaikkakelpoisuus, ympäristö-laboratoriot, pätevyyskoe, laboratorioiden välinen vertailumittaus

SAMMANDRAG

Provningsjämförelse 13/2018

Proftest SYKE genomförde i samarbete med föreningen KVVY Tutkimus Oy en provnings-jämförelse under november-december 2018 för laktester som används vid bedömningen av avfall som ska deponeras på deponi. Resultaten av enstegs skaktest (EN 12457-2) för gjuterisand jämförder och värderades. Sammanlagt 8 laboratorier deltog i proven.

Som referensvärde av analytens koncentration användes det median av deltagarnas resultat. I jämförelsen 92 % av resultaten som värderas med hjälp z värdet (Ba, DOC, ledningsförmåga, Ni, pH, SO_4, och Zn) var acceptabla, när 0.3 pH enhet eller 20–30 % totalavvikelsen från referensvärdet accepterades. Resultaten som värderades med hjälp E_n värdet (As, Cr, Cu och V) var 76 % acceptabla.

Ett varmt tack till alla deltagarna i testet!

Nyckelord: laktest, enstegs skaktest, klassificering av avfall för deponi, miljölaboratorier, provningsjämförelse, kompetensprövning

CONTENTS

1 Introduction

Proftest SYKE carried out the proficiency test (PT) in cooperation with KVVY Tutkimus Oy for the laboratories conducting leaching tests for solid waste material in November-December 2018 (LT 13/2018). In this PT, the results of the one stage batch leaching test (EN 12457-2 [1]) for foundry sand samples were compared and evaluated. The one stage batch leaching test is used as a compliance test in evaluation the waste landfill disposal. The tested measurands were metals (As, Ba, Cd, Cr, Cu, Hg, Mo, Ni, Pb, Sb, Se, V, Zn), Cl^-, SO_4^{2-}, F^-, DOC, pH, and conductivity.

Finnish Environment Institute (SYKE) is appointed National Reference Laboratory in the environmental sector in Finland. The duties of the reference laboratory include providing interlaboratory proficiency tests and other comparisons for analytical laboratories and other producers of environmental information. This proficiency test has been carried out under the scope of the SYKE reference laboratory and it provides an external quality evaluation between laboratory results, and mutual comparability of analytical reliability. The proficiency test was carried out in accordance with the international standard ISO/IEC 17043 [2] and applying ISO 13528 [3] and IUPAC Technical report [4]. The Proftest SYKE is accredited by the Finnish Accreditation Service as a proficiency testing provider (PT01, ISO/IEC 17043, www.finas.fi/sites/en). The organizing of this proficiency test is included in the accreditation scope of the Proftest SYKE.

2 Organizing the proficiency test

2.1 Responsibilities

Organizer

Proftest SYKE, Finnish Environment Institute (SYKE), Laboratory Centre
Ultramariinikuja 4, FI-00430 Helsinki, Finland
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The responsibilities in organizing the proficiency test

Riitta Koivikko	coordinator
Mirja Leivuori	substitute for coordinator
Keijo Tervonen	technical assistance
Markku Ilmakunnas	technical assistance
Sari Lanteri	technical assistance
Ritva Väisänen	technical assistance

Cooperation partner KVVY Tutkimus Oy (T064, www.finas.fi/sites/en)

	Analytical experts (KVVY Tutkimus Oy): Marika Kaasalainen: one stage batch leaching test Raija Ivalo: pH and conductivity Riikka Mattsson: anions (IC), DOC Suvi Pöyhönen: metals (ICP-OES and ICP-MS)
Subcontracting	KVVY Tutkimus Oy: Sample material preparation: homogenization and dividing into subsamples, leaching test (pretest, homogeneity) and the needed chemical and physico-chemical analysis

2.2 Participants

In total 10 laboratories participated in this proficiency test, 7 participants from Finland and 3 from abroad (Appendix 1). Altogether 90 % of the participants used accredited analytical methods at least for a part of the measurements. For this proficiency test, the expert laboratory (T064, www.finas.fi/sites/en) has the code 3 (KVVY Tutkimus Oy) in the results tables.

2.3 Samples and delivery

A foundry sand sample (RT1, about 200 g) was delivered to the participants. The test material was collected from Finland. This waste is included in the scopes of the Government Decree 591/2006 and the Government Decree 843/2017 [5, 6]. The sample material was homogenized prior to dividing into sub sample. Particle size was < 4 mm according to the leaching test standard EN 12457-2 [1].

The sample code on the result sheet was: **RT1LS10 = Sample RT1, L/S 10**

The samples were delivered on 12 November 2018 to the participants abroad and on 13 November 2018 to the national participants. The samples arrived to the participants mainly latest on 15 November 2018 and one participant received the samples on 20 November 2018.

The one stage batch leaching test was requested to be conducted latest on 28 December 2018.

Determinations from the leaching test eluate (L/S 10) were:

- metals (As, Ba, Cd, Cr, Cu, Hg, Mo, Ni, Pb, Sb, Se, V and Zn)
- Cl, SO_4, F, DOC, pH, conductivity

The results were requested to be reported latest on 11 January 2018 and all the participants reported the results accordingly. The preliminary results were delivered to the participants via ProftestWEB and email on 18 January 2019.

2.4 Sample pretesting and homogeneity

The material suitability for one stage batch leaching test was tested by conducting the test and analyzing all the measurands prior dividing the material into subsamples.

The homogeneity of the samples was tested by analyzing total metal concentration of As, Ba, and Pb. More detailed information of homogeneity studies is shown in Appendix 2. According to the homogeneity test results, the samples were considered homogeneous.

2.5 Feedback from the proficiency test

The feedback from the proficiency test is shown in Appendix 3. The comments from the participants dealt with e.g. sample delivery and the Webropol questionnaire. All feedback from the proficiency test is valuable and is exploited when improving the activities.

2.6 Processing the data

2.6.1 Pretesting the data

To test the normality of the data the Kolmogorov-Smirnov test was applied. The outliers were rejected according to the Grubbs test before calculating the mean. The results, which differed from the data more than $5 \times s_{rob}$ or 50 % from the robust mean, were rejected before the statistical results handling. If the result has been reported as below detection limit, it has not been included in the statistical calculations.

More information about the statistical handling of the data is available from the Guide for participant [7].

2.6.2 Assigned values

The detailed information of the assigned values, their uncertainties and reliability is shown in Appendix 6. Due to low concentration or leachability of some measurands, the variation of the results was very high or the number of reported results was very low and, thus, the assigned value was not set for those measurands and no performance evaluation is given (Cd, Cl, F, Hg, Mo, Pb, Sb, and Se).

For all the evaluated measurands the median of the results reported by the participants was used as the assigned value ($n_{stat} < 12$). The expanded uncertainty of the assigned value was calculated using the standard deviation of the reported results [2]. The assigned values based on the median of the results reported by the participants are not metrologically traceable values. As it was not possible to have metrologically traceable assigned values, the best available values were selected to be used as the assigned values. The reliability of the assigned values was statistically testes [3, 4].

The uncertainty of the assigned values varied between 2.3 % and 28 % (Appendix 4). For the measurands evaluated with z scores the uncertainties varied from 2.3 % to 12 % and for the ones evaluated with E_n scores the uncertainties varied between 12 % and 28 % (Chapter 2.6.3, Appendix 4).

After reporting the preliminary results no changes have been done for the assigned values.

2.6.3 Standard deviation for proficiency assessment and results' evaluation

The results of this proficiency test were evaluated both with z and E_n scores.

The standard deviation for proficiency assessment was estimated on the basis of the measurand concentration, the results of homogeneity test and the uncertainty of the assigned value. If the number of reported results was low ($n_{stat} < 6$) or the deviation of the results was very high, the standard deviation is not set, and the proficiency estimation as z scores is not given (As, Cr, Cu, and V).

The standard deviation for proficiency assessment ($2 \times s_{pt}$ at the 95 % confidence level) was set to 0.3 pH units and to 20–30 % for other measurands (Ba, conductivity, DOC, Ni, SO_4, and Zn). **After reporting the preliminary results no changes have been done for the standard deviations of the proficiency assessment values.**

In this proficiency test, the performance evaluation was done by means of E_n scores ('*Error, normalized*') for those measurands were the number of reported results was low ($n_{stat} < 6$) or the deviation of the results was very high, but the assigned value and its uncertainty were set (As, Cr, Cu, and V). These are used to evaluate the difference between the assigned value and participant's result within their claimed expanded uncertainty. E_n scores are calculated:

$$(E_n)_i = \frac{x_i - x_{pt}}{\sqrt{U_i^2 + U_{pt}^2}}, \text{ where}$$

x_i = participant's result, x_{pt} = assigned value, U_i = the expanded uncertainty of a participant's result and U_{pt} = the expanded uncertainty of the assigned value.

Scores of E_n $-1.0 < E_n < 1.0$ should be taken as an indicator of successful performance when the uncertainties are valid. Whereas scores $E_n \geq 1.0$ or $E_n \leq -1.0$ could indicate a need to review the uncertainty estimates, or to correct a measurement issue.

For the measurands where the standard deviation for proficiency assessment was set, the reliability of the assigned value was tested according to the criterion $u_{pt} / s_{pt} \leq 0.3$, where u_{pt} is the standard uncertainty of the assigned value (the expanded uncertainty of the assigned value (U_{pt}) divided by 2) and s_{pt} is the standard deviation for proficiency assessment [3]. The criterion was mainly fulfilled for the measurands evaluated with z scores.

The reliability of the standard deviation for proficiency assessment and the corresponding z score was estimated by comparing the deviation for proficiency assessment (s_{pt}) with the standard deviation of the reported results (s) [3]. The criterion $s / s_{pt} < 1.2$ was mainly fulfilled.

In the following case, the criterion for the reliability of the assigned value was not met and, therefore, the evaluation of the performance is weakened in this proficiency test:

Sample	Measurand
RT1LS10	Ba

3 Results and conclusions

3.1 Results

The terms used in the results table are explained in the Appendix 5. The results and the performance of each participant are presented in Appendix 6 and the summary of the results in Table 1. The reported results with their expanded uncertainties (k=2) are presented in Appendix 7. The summaries of the z and E_n scores are shown in Appendices 8 and 9 and z scores in the ascending order in Appendix 10.

Table 1. The summary of the results in the proficiency test LT 13/2018.

Measurand	Sample	Unit	Assigned value	Mean	Median	s	s %	Rob. mean	s_{rob}	s_{rob} %	2 x s_{pt} %	n_{all}	Acc. z %	Acc. E_n %
As	RT1LS10	mg/kg	0.017	0.016	0.017	0.002	15.5	-	-	-	-	10	-	75
Ba	RT1LS10	mg/kg	0.14	0.13	0.14	0.02	15.8	0.14	0.03	21.8	30	10	88	-
Cd	RT1LS10	mg/kg	-	0.002	0.002	0.001	72.3	-	-	-	-	10	-	-
Cl	RT1LS10	mg/kg	-	62.8	4.2	103.3	164.3	-	-	-	-	9	-	-
Conductivity	RT1LS10	mS/m	20.3	19.7	20.3	1.9	9.6	20.2	2.4	11.8	20	9	78	-
Cr	RT1LS10	mg/kg	0.030	0.032	0.030	0.010	31.2				-	10	-	80
Cu	RT1LS10	mg/kg	0.13	0.16	0.13	0.07	42.0	0.16	0.08	47.6	-	10	-	63
DOC	RT1LS10	mg/kg	304	309	304	19	6.3	307	18	5.9	20	10	100	-
F	RT1LS10	mg/kg	-	3.00	2.04	2.66	88.7	-	-	-	-	9	-	-
Ni	RT1LS10	mg/kg	0.14	0.14	0.14	0.02	14.2	0.14	0.02	14.1	30	10	100	-
Pb	RT1LS10	mg/kg	-	0.020	0.023	0.011	56.1	-	-	-	-	10	-	-
pH	RT1LS10		3.52	3.54	3.52	0.12	3.4	3.50	0.13	3.8	8.5	10	90	-
Sb	RT1LS10	mg/kg	-	0.002	0.002	< 0.001	< 0.01	-	-	-	-	10	-	-
Se	RT1LS10	mg/kg	-	0.002	0.002	< 0.001	< 0.01	-	-	-	-	10	-	-
SO_4	RT1LS10	mg/kg	203	204	203	15	7.3	209	23	11.2	20	9	86	-
V	RT1LS10	mg/kg	0.017	0.017	0.017	0.002	11.9	-	-	-	-	9	-	100
Zn	RT1LS10	mg/kg	1.75	1.76	1.75	0.22	12.4	1.76	0.25	14.0	25	10	100	-

Rob. mean: the robust mean, s: the standard deviation, s %: the standard deviation as percent, s_{rob}: the robust standard deviation, s_{rob} %: the robust standard deviation as percent, $2 \times s_{pt}$ %: the standard deviation for proficiency assessment at the 95 % confidence level, n_{all}: the total number of the participants, Acc z %: the results (%), where $|z| \leq 2$, Acc. E_n %: the results (%), where $|E_n| < 1$.

3.2 Analytical methods

The standard method EN 12457-2 (one stage batch leaching test) [1] was used to determine the leaching properties of studied measurands from the foundry sand sample. The concentration of the measurands was analyzed from the eluate (L/S 10) and they are expressed as the leached amounts (mg/kg dry weight) relative to the total mass of the sample. The reported results of the participants grouped by methods with their expanded uncertainties (k=2) are presented in Appendix 11. The statistical comparison of the analytical methods was not possible due to low number of results.

The details of the procedures the participants followed were requested via Webropol questionnaire. Only four participants (40 %) replied to the questionnaire and therefore the replies are not combined with the participation codes (Appendix 12).

The participants were allowed to use different analytical methods for the measurements of the measurands' concentrations in the PT. The standard EN 16192 summarizes the analytical test methods for the waste eluates [8]. The statistical comparison of the analytical methods was not possible for the data due to low number of results. The applied standard methods are listed in Appendix 13.

3.3 Uncertainties of the results

Altogether 90 % of the participants reported the expanded uncertainties (k=2) with their results for at least some of their results (Table 2, Appendix 11 and 14). The range of the reported uncertainties varied between the measurands and the sample types, and thus the harmonization of the uncertainties estimation should be continued.

Several approaches were used for estimating the measurement uncertainty (Appendix 14). The most used approach was based on data from method validation. Also the approach based on the data from internal quality control was used (Appendix 14). Two participants used MUkit measurement uncertainty software for the estimation of their uncertainties [9]. The free software is available on the webpage: www.syke.fi/envical/en. Generally, the used approach for estimating measurement uncertainty did not make definite impact on the uncertainty estimates.

Table 2. The range of the expanded measurement uncertainties (k=2, U_i%) reported by the participants.

Measurand	As	Ba	Conductivity	Cr	Cu	DOC
U_i%	12.2 – 60 [1)]	11.9 – 58	3.3 – 33	13.6 – 62	12.27 – 60	8.64 – 62

Measurand	Ni	pH	SO_4^{2-}	V	Zn
U_i%	13.98 – 59	2.82 – 10	6 – 62	16.3 – 58	12.4 – 61

[1)] In table with bold the values of expanded measurement uncertainty over 50 %.

4 Evaluation of the results

The performance evaluation of the participants was based on the z and E_n scores. The z scores were calculated using the assigned values and the standard deviation for the performance assessment (Appendix 8). The E_n scores were calculated using the assigned values and their uncertainties (Appendix 9).

The z and E_n scores were interpreted as follows:

Criteria	Performance
$\lvert z \rvert \leq 2$	Satisfactory
$2 < \lvert z \rvert < 3$	Questionable
$\lvert z \rvert \geq 3$	Unsatisfactory
$-1.0 < E_n < 1.0$	Satisfactory
$E_n \leq -1.0$ or $E_n \geq 1.0$	Unsatisfactory

In total, 92 % of the results evaluated with z scores (Ba, conductivity, DOC, Ni, pH, SO_4, and Zn) were satisfactory when total deviation of 20–30 % and 0.3 pH units from the assigned values was accepted. Further, the results of As, Cr, Cu, and V were evaluated with E_n scores and 76 % of those results were satisfactory. 90 % of participants used accredited analytical methods at least for a part of the measurands, and 90 % of those results were satisfactory. The summary of the performance evaluation and comparison to the previous performance is presented in Table 3. In the previous similar PT, Proftest SYKE 10/2012, 91 % of the results were satisfactory when evaluated with z scores and accepting total deviation of 10 – 50 % and 0.4 pH units from the assigned value [10].

Table 3. Summary of the performance evaluation in the proficiency test LT 13/2018.

Measurand	2 x s_{pt}%	Satisfactory results, %		Remarks
		z	E_n	
Metals	25 – 30	96	80	The results for Ba, Ni, and Zn were evaluated with z scores and the performance was excellent. The criterion for the reliability of the assigned value was not met for Ba. The results for As, Cr, Cu, and V were evaluated with E_n scores. In the previous similar PT the performance evaluation was based on z scores and it satisfactory for 85 % of the results when accepting deviation of 20 – 50 % [10].
Anions	20	86	–	Only the results of SO_4 were evaluated, as concentration or leachability of the sample was low for Cl and F. In the previous similar PT the performance was satisfactory for 85 % of the results when accepting deviation of 10 – 25 % [10].
Conductivity	20	78	–	In the previous similar PT the performance was satisfactory for 94 % of the results when accepting deviation of 10 % [10].
DOC	20	100	–	Excellent performance. In the previous similar PT the concentration or leachability was low and performance evaluation was not done [10].
pH	0.3 (pH units)	90	–	Good performance. In the previous similar PT the performance was satisfactory for 94 % of the results when accepting deviation of 0.4 pH units [10].

5 Summary

Proftest SYKE carried out the proficiency test (PT) in cooperation with KVVY Tutkimus Oy for laboratories conducting leaching tests for solid waste material in November-December 2018. The results of the one stage batch leaching test (EN 12457-2) for foundry sand samples were compared and evaluated. The tested measurands were metals (As, Ba, Cd, Cr, Cu, Hg, Mo, Ni, Pb, Sb, Se, V, Zn), Cl^-, SO_4^{2-}, F^-, DOC, pH, and conductivity. In total, 10 participants joined in the proficiency test.

The median of the results reported by the participants was used as the assigned value for all the evaluated measurands. The measurands Ba, conductivity, DOC, Ni, pH, SO_4, and Zn were evaluated with z scores and of those results 92 % were satisfactory, when deviation of 0.3 pH units and 20–30 % for other measurands was accepted from the assigned value. Further, measurands As, Cr, Cu, and V were evaluated with E_n scores and 76 % of the results were satisfactory.

6 Summary in Finnish

Proftest SYKE järjesti yhteistyössä KVVY Tutkimus Oy:n kanssa pätevyyskokeen marras-joulukuussa 2018 laboratorioille, jotka tekevät liukoisuustestejä jätteiden kaatopaikka-kelpoisuuden arvioimiseksi. Pätevyyskokeessa vertailun kohteena oli yksivaiheinen ravistelu-testi (EN 12457-2) valimohiekalle. Pätevyyskokeessa oli yhteensä 10 osallistujaa.

Testisuureen vertailuarvona käytettiin osallistujatulosten mediaania. Tuloksia arvioitiin sekä z- että E_n-arvoilla. Testisuureet Ba, DOC, Ni, pH, SO_4, sähkönjohtavuus ja Zn arvioitiin z-arvoilla ja hyväksyttäviä tuloksia oli 92 %, kun tavoitehajonnaksi 95 %:n luottamusvälillä asetettiin pH-määrityksille 0,3 pH-yksikköä ja muille määrityksille 20–30 %. Testisuureiden As, Cr, Cu ja V tulokset arvioitiin E_n-arvoilla, jolloin hyväksyttäviä tuloksia oli 76 %.

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APPENDIX 1: Participants in the proficiency test

Country	Participant
Finland	Eurofins Ahma Oy, Oulu
	Eurofins Labtium Oy, Kuopio
	Fortum Waste Solutions Oy, Riihimäki
	KVVY Tutkimus Oy, Tampere
	MetropoliLab Oy
	SGS Finland Oy, Kotka
	SYNLAB Analytics & Services Finland Oy
Germany	Eurofins Umwelt Ost GmbH, Niederlassung Freiberg
Greece	Laboratory of Metallurgy, National Technical University of Athens
Sweden	Eurofins Water Testing Sweden AB

APPENDIX 2: Homogeneity of the samples

Homogeneity of the samples was tested by analyzing the total metal concentrations from 4 subsamples with replicate analyses.

Criteria for homogeneity:

$\mathbf{s_{anal}/s_h<0.5}$ and $\mathbf{s_{sam}^2<c}$, where

s_h = standard deviation for testing the homogeneity
s_{anal} = analytical deviation, standard deviation of the results in a sub samples
s_{sam} = between-sample deviation, standard deviation of the results between sub samples

$c = F1 \times s_{all}^2 + F2 \times s_{anal}^2$, where
$s_{all}^2 = (0.3 \times s_h)^2$

F1 and F2 are constants of F distribution derived from the standard statistical tables for the tested number of samples [3, 4].

Measurand	Concentration [mg/kg]	n	s_h %	s_h	s_{anal}	s_{anal}/s_h	$s_{anal}/s_h < 0.5$?	s_{sam}^2	c	$s_{sam}^2<c$?
As	0.39	4	20	0.077	0.032	0.41	Yes	0.0002	0.0056	Yes
Ba	14.3	4	20	2.85	1.32	0.46	Yes	0	6.80	Yes
Pb	1.24	4	20	0.25	0.12	0.47	Yes	0	0.053	Yes

Conclusion: Total metal concentrations were used for homogeneity testing. Those do not completely correlate with the test results of the one stage batch leaching test. Foundry sand is coarse-grained material which causes increased deviation for the replicate results. The results were evaluated with separately set standard deviation values (s_h). Further, the results were compared to the participant results.

The criteria for homogeneity were fulfilled and the samples could be considered homogeneous.

APPENDIX 3: Feedback from the proficiency test

FEEDBACK FROM THE PARTICIPANTS

Participant	Comments on technical excecution	Action / Proftest SYKE
4, 5	The participants received the samples one day after the estimated delivery day.	The used distributor did not deliver the samples according to the agreed schedule.
6	The participant received the samples six days after the estimated delivery day.	
5	Webropol survey gave unclear error messages, thus sending the form was not possible. The participant sent the electronic questionnaire by e-mail.	The provider apologized the unclear error messages (due to the program) and informed the participant that their replies were received.
8	The participant informed that they received the samples on 15 November.	According to the distributor's tracking system the samples arrived to the participant on 14 November.
9	Webropol survey accepted only integers.	Settings were corrected in the questionnaire and this was informed to the participant.

FEEDBACK TO THE PARTICIPANTS

Participant	Comments
2	The participant reported zero results for some measurands. The provider recommends participant to update the reporting procedure for low concentration results as low values should be reported as lower or equal to detection limit.

APPENDIX 4: Evaluation of the assigned values and their uncertainties

Measurand	Sample	Unit	Assigned value	U_{pt}	U_{pt}, %	Evaluation method of assigned value	u_{pt}/s_{pt} [1)]
As	RT1LS10	mg/kg	0.017	0.003	15.5	Median	
Ba	RT1LS10	mg/kg	0.14	0.02	12.0	Median	0.40
Conductivity 25	RT1LS10	mS/m	20.3	1.4	6.8	Median	0.34
Cr	RT1LS10	mg/kg	0.030	0.008	27.9	Median	
Cu	RT1LS10	mg/kg	0.13	0.04	28.0	Median	
DOC	RT1LS10	mg/kg	304	12	4.0	Median	0.20
Ni	RT1LS10	mg/kg	0.14	0.01	9.0	Median	0.30
pH	RT1LS10		3.52	0.08	2.3	Median	0.27
SO_4	RT1LS10	mg/kg	203	12	6.0	Median	0.30
V	RT1LS10	mg/kg	0.017	0.002	11.9	Median	
Zn	RT1LS10	mg/kg	1.75	0.14	7.8	Median	0.31

[1)] Value calculated only for the measurands where the standard deviation for proficiency assessment was set.

U_{pt} = Expanded uncertainty of the assigned value
Criterion for reliability of the assigned value $u_{pt}/s_{pt} \leq 0.3$, where
s_{pt}= the standard deviation for proficiency assessment
u_{pt}= the standard uncertainty of the assigned value

If $u_{pt}/s_{pt} \leq 0.3$, the assigned value is reliable and the z scores are qualified.

APPENDIX 5: Terms in the results tables

Results of each participant

Measurand	The tested parameter
Sample	The code of the sample
z score	Calculated as follows: $z = (x_i - x_{pt})/s_{pt}$, where x_i = the result of the individual participant x_{pt} = the assigned value s_{pt} = the standard deviation for proficiency assessment
Assigned value	The value attributed to a particular property of a proficiency test item
2 × s_{pt} %	The standard deviation for proficiency assessment (s_{pt}) at the 95 % confidence level
Participant's result	The result reported by the participant (the mean value of the replicates)
Md	Median
s	Standard deviation
s %	Standard deviation, %
n_{stat}	Number of results in statistical processing

Summary on the z scores

S – satisfactory ($-2 \leq z \leq 2$)
Q – questionable ($2 < z < 3$), positive error, the result deviates more than 2 × s_{pt} from the assigned value
q – questionable ($-3 < z < -2$), negative error, the result deviates more than 2 × s_{pt} from the assigned value
U – unsatisfactory ($z \geq 3$), positive error, the result deviates more than 3 × s_{pt} from the assigned value
u – unsatisfactory ($z \leq -3$), negative error, the result deviates more than 3 × s_{pt} from the assigned value

Robust analysis

The items of data are sorted into increasing order, $x_1, x_2, x_i, \ldots, x_p$.
Initial values for x^* and s^* are calculated as:
x^* = median of x_i (i = 1, 2, ...,p)
s^* = 1.483 × median of $|x_i - x^*|$ (i = 1, 2, ...,p)

The mean x^* and s^* are updated as follows:
Calculate $\varphi = 1.5 \times s^*$. A new value is then calculated for each result x_i $(i = 1, 2 \ldots p)$:

$$x_i^* = \begin{cases} x^* - \varphi, & \text{if } x_i < x^* - \varphi \\ x^* + \varphi, & \text{if } x_i > x^* + \varphi, \\ x_i & \text{otherwise} \end{cases}$$

The new values of x^* and s^* are calculated from:

$$x^* = \sum x_i^* / p$$

$$s^* = 1.134\sqrt{\sum (x_i^* - x^*)^2 / (p-1)}$$

The robust estimates x^* and s^* can be derived by an iterative calculation, i.e. by updating the values of x^* and s^* several times, until the process convergences [3].

APPENDIX 6: Results of each participant

Participant 1												
Measurand	Unit	Sample	-3 . 0 . 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
As	mg/kg	RT1LS10			0.017		*< 0.1*	0.017	0.016	0.002	15.5	4
Ba	mg/kg	RT1LS10			0.14	30	*< 4.0*	0.14	0.13	0.02	15.8	7
Cd	mg/kg	RT1LS10					*< 0.01*	0.002	0.002	0.001	72.3	2
Cl	mg/kg	RT1LS10					*< 160*	4.2	62.8	103.3	164.3	3
Conductivity 25	mS/m	RT1LS10		0.10	20.3	20	20.5	20.3	19.7	1.9	9.6	8
Cr	mg/kg	RT1LS10			0.030		*< 0.1*	0.030	0.032	0.010	31.2	5
Cu	mg/kg	RT1LS10			0.13		*< 0.4*	0.13	0.16	0.07	42.0	9
DOC	mg/kg	RT1LS10		-0.13	304	20	300	304	309	19	6.3	10
F	mg/kg	RT1LS10					*< 2*	2.04	3.00	2.66	88.7	4
Hg	mg/kg	RT1LS10					*< 0.002*	0	0	0		1
Mo	mg/kg	RT1LS10					*< 0.1*	0	0	0		1
Ni	mg/kg	RT1LS10		0.48	0.14	30	0.15	0.14	0.14	0.02	14.2	10
Pb	mg/kg	RT1LS10					*< 0.1*	0.023	0.020	0.011	56.1	4
pH		RT1LS10		-0.60	3.52	8.5	3.43	3.52	3.54	0.12	3.4	9
Sb	mg/kg	RT1LS10					*< 0.05*	0.002	0.002	0.000	0.0	1
Se	mg/kg	RT1LS10					*< 0.03*	0.002	0.002	0.000	0.0	1
SO_4	mg/kg	RT1LS10			203	20	*< 200*	203	204	15	7.3	6
V	mg/kg	RT1LS10			0.017		*< 0.4*	0.017	0.017	0.002	11.9	4
Zn	mg/kg	RT1LS10		0.05	1.75	25	1.76	1.75	1.76	0.22	12.4	10

Participant 2												
Measurand	Unit	Sample	-3 . 0 . 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
As	mg/kg	RT1LS10			0.017		0.017	0.017	0.016	0.002	15.5	4
Ba	mg/kg	RT1LS10		0.12	0.14	30	0.14	0.14	0.13	0.02	15.8	7
Cd	mg/kg	RT1LS10					0.001	0.002	0.002	0.001	72.3	2
Cl	mg/kg	RT1LS10					*< 10*	4.2	62.8	103.3	164.3	3
Conductivity 25	mS/m	RT1LS10		-2.12	20.3	20	16.0	20.3	19.7	1.9	9.6	8
Cr	mg/kg	RT1LS10			0.030		0.031	0.030	0.032	0.010	31.2	5
Cu	mg/kg	RT1LS10			0.13		0.12	0.13	0.16	0.07	42.0	9
DOC	mg/kg	RT1LS10		0.63	304	20	323	304	309	19	6.3	10
F	mg/kg	RT1LS10					1.24	2.04	3.00	2.66	88.7	4
Hg	mg/kg	RT1LS10					0	0	0	0		1
Mo	mg/kg	RT1LS10					0	0	0	0		1
Ni	mg/kg	RT1LS10		0.37	0.14	30	0.15	0.14	0.14	0.02	14.2	10
Pb	mg/kg	RT1LS10					0.005	0.023	0.020	0.011	56.1	4
pH		RT1LS10		1.80	3.52	8.5	3.79	3.52	3.54	0.12	3.4	9
Sb	mg/kg	RT1LS10					0.002	0.002	0.002	0.000	0.0	1
Se	mg/kg	RT1LS10					0.002	0.002	0.002	0.000	0.0	1
SO_4	mg/kg	RT1LS10		-0.14	203	20	200	203	204	15	7.3	6
V	mg/kg	RT1LS10			0.017		0.018	0.017	0.017	0.002	11.9	4
Zn	mg/kg	RT1LS10		-0.19	1.75	25	1.71	1.75	1.76	0.22	12.4	10

Participant 3													
Measurand	Unit	Sample	-3 . . 0 . . 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
As	mg/kg	RT1LS10			0.017		0.017	0.017	0.016	0.002	15.5	4
Ba	mg/kg	RT1LS10		-0.95	0.14	30	0.12	0.14	0.13	0.02	15.8	7
Cd	mg/kg	RT1LS10					*<0.02*	0.002	0.002	0.001	72.3	2
Cl	mg/kg	RT1LS10					*<1*	4.2	62.8	103.3	164.3	3
Conductivity 25	mS/m	RT1LS10		0.32	20.3	20	21.0	20.3	19.7	1.9	9.6	8
Cr	mg/kg	RT1LS10			0.030		0.030	0.030	0.032	0.010	31.2	5
Cu	mg/kg	RT1LS10			0.13		0.16	0.13	0.16	0.07	42.0	9
DOC	mg/kg	RT1LS10		-0.66	304	20	284	304	309	19	6.3	10
F	mg/kg	RT1LS10					*<0.1*	2.04	3.00	2.66	88.7	4
Hg	mg/kg	RT1LS10					*<0.01*	0	0	0		1
Mo	mg/kg	RT1LS10					*<0.05*	0	0	0		1
Ni	mg/kg	RT1LS10		0.00	0.14	30	0.14	0.14	0.14	0.02	14.2	10
Pb	mg/kg	RT1LS10					*<0.05*	0.023	0.020	0.011	56.1	4
pH		RT1LS10		0.00	3.52	8.5	3.52	3.52	3.54	0.12	3.4	9
Sb	mg/kg	RT1LS10					*<0.05*	0.002	0.002	0.000	0.0	1
Se	mg/kg	RT1LS10					*<0.05*	0.002	0.002	0.000	0.0	1
SO_4	mg/kg	RT1LS10		5.71	203	20	319	203	204	15	7.3	6
V	mg/kg	RT1LS10			0.017		0.020	0.017	0.017	0.002	11.9	4
Zn	mg/kg	RT1LS10		-1.60	1.75	25	1.40	1.75	1.76	0.22	12.4	10

Participant 4												
Measurand	Unit	Sample	-3 . . 0 . . 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
As	mg/kg	RT1LS10			0.017		*<0.1*	0.017	0.016	0.002	15.5	4
Ba	mg/kg	RT1LS10		0.95	0.14	30	0.16	0.14	0.13	0.02	15.8	7
Cd	mg/kg	RT1LS10					*<0.02*	0.002	0.002	0.001	72.3	2
Cl	mg/kg	RT1LS10					4.2	4.2	62.8	103.3	164.3	3
Conductivity 25	mS/m	RT1LS10		-1.13	20.3	20	18.0	20.3	19.7	1.9	9.6	8
Cr	mg/kg	RT1LS10			0.030		*<0.1*	0.030	0.032	0.010	31.2	5
Cu	mg/kg	RT1LS10			0.13		0.25	0.13	0.16	0.07	42.0	9
DOC	mg/kg	RT1LS10		1.51	304	20	350	304	309	19	6.3	10
F	mg/kg	RT1LS10					1.10	2.04	3.00	2.66	88.7	4
Hg	mg/kg	RT1LS10					*<0.01*	0	0	0		1
Mo	mg/kg	RT1LS10					*<0.1*	0	0	0		1
Ni	mg/kg	RT1LS10		0.00	0.14	30	0.14	0.14	0.14	0.02	14.2	10
Pb	mg/kg	RT1LS10					*<0.1*	0.023	0.020	0.011	56.1	4
pH		RT1LS10		0.53	3.52	8.5	3.60	3.52	3.54	0.12	3.4	9
Sb	mg/kg	RT1LS10					*<0.06*	0.002	0.002	0.000	0.0	1
Se	mg/kg	RT1LS10					*<0.1*	0.002	0.002	0.000	0.0	1
SO_4	mg/kg	RT1LS10		0.10	203	20	205	203	204	15	7.3	6
V	mg/kg	RT1LS10			0.017		*<0.1*	0.017	0.017	0.002	11.9	4
Zn	mg/kg	RT1LS10		1.60	1.75	25	2.10	1.75	1.76	0.22	12.4	10

Participant 5												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
As	mg/kg	RT1LS10			0.017		0.018	0.017	0.016	0.002	15.5	4
Ba	mg/kg	RT1LS10		0.81	0.14	30	0.16	0.14	0.13	0.02	15.8	7
Cd	mg/kg	RT1LS10					*< 0.002*	0.002	0.002	0.001	72.3	2
Cl	mg/kg	RT1LS10					182.1	4.2	62.8	103.3	164.3	3
Conductivity 25	mS/m	RT1LS10		22.76	20.3	20	66.5	20.3	19.7	1.9	9.6	8
Cr	mg/kg	RT1LS10			0.030		0.049	0.030	0.032	0.010	31.2	5
Cu	mg/kg	RT1LS10			0.13		0.27	0.13	0.16	0.07	42.0	9
DOC	mg/kg	RT1LS10		0.00	304	20	304	304	309	19	6.3	10
F	mg/kg	RT1LS10					2.84	2.04	3.00	2.66	88.7	4
Hg	mg/kg	RT1LS10					*< 0.002*	0	0	0		1
Mo	mg/kg	RT1LS10					*< 0.01*	0	0	0		1
Ni	mg/kg	RT1LS10		1.38	0.14	30	0.17	0.14	0.14	0.02	14.2	10
Pb	mg/kg	RT1LS10					0.018	0.023	0.020	0.011	56.1	4
pH		RT1LS10		-4.47	3.52	8.5	2.85	3.52	3.54	0.12	3.4	9
Sb	mg/kg	RT1LS10					*< 0.01*	0.002	0.002	0.000	0.0	1
Se	mg/kg	RT1LS10					*< 0.01*	0.002	0.002	0.000	0.0	1
SO_4	mg/kg	RT1LS10		1.36	203	20	231	203	204	15	7.3	6
V	mg/kg	RT1LS10			0.017		*< 0.1*	0.017	0.017	0.002	11.9	4
Zn	mg/kg	RT1LS10		-0.09	1.75	25	1.73	1.75	1.76	0.22	12.4	10

Participant 6												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
As	mg/kg	RT1LS10			0.017		*<0.06*	0.017	0.016	0.002	15.5	4
Ba	mg/kg	RT1LS10			0.14	30	*<0.13*	0.14	0.13	0.02	15.8	7
Cd	mg/kg	RT1LS10					*<0.002*	0.002	0.002	0.001	72.3	2
Conductivity 25	mS/m	RT1LS10		0.15	20.3	20	20.6	20.3	19.7	1.9	9.6	8
Cr	mg/kg	RT1LS10			0.030		*<0.06*	0.030	0.032	0.010	31.2	5
Cu	mg/kg	RT1LS10			0.13		0.11	0.13	0.16	0.07	42.0	9
DOC	mg/kg	RT1LS10		0.59	304	20	322	304	309	19	6.3	10
Mo	mg/kg	RT1LS10					*<0.02*	0	0	0		1
Ni	mg/kg	RT1LS10		-0.95	0.14	30	0.12	0.14	0.14	0.02	14.2	10
Pb	mg/kg	RT1LS10					*<0.10*	0.023	0.020	0.011	56.1	4
pH		RT1LS10		-0.27	3.52	8.5	3.48	3.52	3.54	0.12	3.4	9
Sb	mg/kg	RT1LS10					*<0.02*	0.002	0.002	0.000	0.0	1
Se	mg/kg	RT1LS10					*<0.03*	0.002	0.002	0.000	0.0	1
Zn	mg/kg	RT1LS10		1.01	1.75	25	1.97	1.75	1.76	0.22	12.4	10

Participant 7												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
As	mg/kg	RT1LS10			0.017		*<0.006*	0.017	0.016	0.002	15.5	4
Ba	mg/kg	RT1LS10		-0.14	0.14	30	0.14	0.14	0.13	0.02	15.8	7
Cd	mg/kg	RT1LS10					0.003	0.002	0.002	0.001	72.3	2
Cl	mg/kg	RT1LS10					*<10*	4.2	62.8	103.3	164.3	3
Cr	mg/kg	RT1LS10			0.030		0.030	0.030	0.032	0.010	31.2	5
Cu	mg/kg	RT1LS10			0.13		0.24	0.13	0.16	0.07	42.0	9
DOC	mg/kg	RT1LS10		0.03	304	20	305	304	309	19	6.3	10
F	mg/kg	RT1LS10					*<1.0*	2.04	3.00	2.66	88.7	4
Hg	mg/kg	RT1LS10					*<0.002*	0	0	0		1
Mo	mg/kg	RT1LS10					*<0.006*	0	0	0		1
Ni	mg/kg	RT1LS10		-0.52	0.14	30	0.13	0.14	0.14	0.02	14.2	10
Pb	mg/kg	RT1LS10					0.030	0.023	0.020	0.011	56.1	4
pH		RT1LS10		-1.07	3.52	8.5	3.36	3.52	3.54	0.12	3.4	9
Sb	mg/kg	RT1LS10					*<0.06*	0.002	0.002	0.000	0.0	1
Se	mg/kg	RT1LS10					*<0.030*	0.002	0.002	0.000	0.0	1
SO_4	mg/kg	RT1LS10			203	20	*<10*	203	204	15	7.3	6
V	mg/kg	RT1LS10			0.017		0.016	0.017	0.017	0.002	11.9	4
Zn	mg/kg	RT1LS10		-1.05	1.75	25	1.52	1.75	1.76	0.22	12.4	10

Participant 8												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
As	mg/kg	RT1LS10			0.017		*<0.10*	0.017	0.016	0.002	15.5	4
Ba	mg/kg	RT1LS10		35.24	0.14	30	0.88	0.14	0.13	0.02	15.8	7
Cd	mg/kg	RT1LS10					*<0.010*	0.002	0.002	0.001	72.3	2
Cl	mg/kg	RT1LS10					*<10*	4.2	62.8	103.3	164.3	3
Conductivity 25	mS/m	RT1LS10		-0.49	20.3	20	19.3	20.3	19.7	1.9	9.6	8
Cr	mg/kg	RT1LS10			0.030		*<0.050*	0.030	0.032	0.010	31.2	5
Cu	mg/kg	RT1LS10			0.13		0.10	0.13	0.16	0.07	42.0	9
DOC	mg/kg	RT1LS10		-0.46	304	20	290	304	309	19	6.3	10
F	mg/kg	RT1LS10					*<10*	2.04	3.00	2.66	88.7	4
Hg	mg/kg	RT1LS10					*<0.0010*	0	0	0		1
Mo	mg/kg	RT1LS10					*<0.10*	0	0	0		1
Ni	mg/kg	RT1LS10		0.95	0.14	30	0.16	0.14	0.14	0.02	14.2	10
Pb	mg/kg	RT1LS10					*<0.10*	0.023	0.020	0.011	56.1	4
pH		RT1LS10		-0.13	3.52	8.5	3.50	3.52	3.54	0.12	3.4	9
Sb	mg/kg	RT1LS10					*<0.10*	0.002	0.002	0.000	0.0	1
Se	mg/kg	RT1LS10					*<0.10*	0.002	0.002	0.000	0.0	1
SO_4	mg/kg	RT1LS10		-0.64	203	20	190	203	204	15	7.3	6
V	mg/kg	RT1LS10			0.017		*<0.10*	0.017	0.017	0.002	11.9	4
Zn	mg/kg	RT1LS10		0.69	1.75	25	1.90	1.75	1.76	0.22	12.4	10

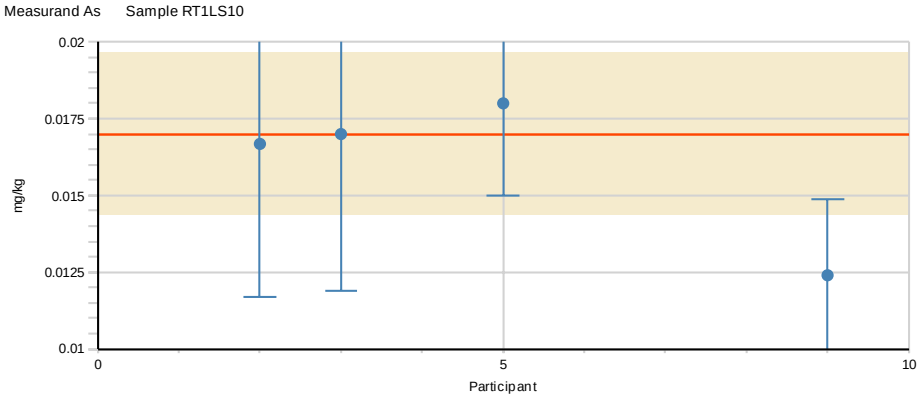
Participant 9													
Measurand	Unit	Sample	-3 . . 0 . . 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
As	mg/kg	RT1LS10			0.017		0.012	0.017	0.016	0.002	15.5	4
Ba	mg/kg	RT1LS10		-0.71	0.14	30	0.13	0.14	0.13	0.02	15.8	7
Cd	mg/kg	RT1LS10					*<0.005*	0.002	0.002	0.001	72.3	2
Cl	mg/kg	RT1LS10					*<50*	4.2	62.8	103.3	164.3	3
Conductivity 25	mS/m	RT1LS10		-0.10	20.3	20	20.1	20.3	19.7	1.9	9.6	8
Cr	mg/kg	RT1LS10			0.030		0.021	0.030	0.032	0.010	31.2	5
Cu	mg/kg	RT1LS10			0.13		0.13	0.13	0.16	0.07	42.0	9
DOC	mg/kg	RT1LS10		0.30	304	20	313	304	309	19	6.3	10
F	mg/kg	RT1LS10					*<5*	2.04	3.00	2.66	88.7	4
Hg	mg/kg	RT1LS10					*<0.004*	0	0	0		1
Mo	mg/kg	RT1LS10					*<0.01*	0	0	0		1
Ni	mg/kg	RT1LS10		0.00	0.14	30	0.14	0.14	0.14	0.02	14.2	10
Pb	mg/kg	RT1LS10					0.027	0.023	0.020	0.011	56.1	4
pH		RT1LS10		0.40	3.52	8.5	3.58	3.52	3.54	0.12	3.4	9
Sb	mg/kg	RT1LS10					*<0.01*	0.002	0.002	0.000	0.0	1
Se	mg/kg	RT1LS10					*<0.04*	0.002	0.002	0.000	0.0	1
SO_4	mg/kg	RT1LS10		-0.64	203	20	190	203	204	15	7.3	6
V	mg/kg	RT1LS10			0.017		0.015	0.017	0.017	0.002	11.9	4
Zn	mg/kg	RT1LS10		-0.82	1.75	25	1.57	1.75	1.76	0.22	12.4	10

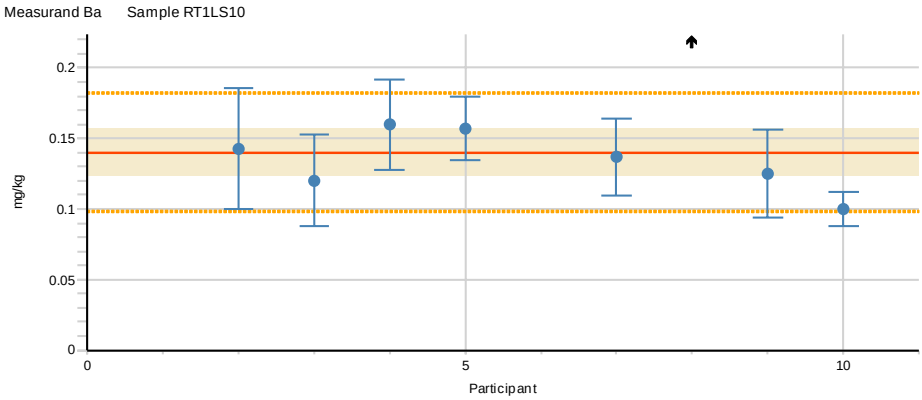
Participant 10												
Measurand	Unit	Sample	-3 . . 0 . . 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
As	mg/kg	RT1LS10			0.017		*< 0.05*	0.017	0.016	0.002	15.5	4
Ba	mg/kg	RT1LS10		-1.90	0.14	30	0.10	0.14	0.13	0.02	15.8	7
Cd	mg/kg	RT1LS10					*< 0.02*	0.002	0.002	0.001	72.3	2
Cl	mg/kg	RT1LS10					2.2	4.2	62.8	103.3	164.3	3
Conductivity 25	mS/m	RT1LS10		0.84	20.3	20	22.0	20.3	19.7	1.9	9.6	8
Cr	mg/kg	RT1LS10			0.030		*< 0.05*	0.030	0.032	0.010	31.2	5
Cu	mg/kg	RT1LS10			0.13		0.10	0.13	0.16	0.07	42.0	9
DOC	mg/kg	RT1LS10		-0.30	304	20	295	304	309	19	6.3	10
F	mg/kg	RT1LS10					6.80	2.04	3.00	2.66	88.7	4
Hg	mg/kg	RT1LS10					*< 0.01*	0	0	0		1
Mo	mg/kg	RT1LS10					*< 0.05*	0	0	0		1
Ni	mg/kg	RT1LS10		-1.90	0.14	30	0.10	0.14	0.14	0.02	14.2	10
Pb	mg/kg	RT1LS10					*< 0.05*	0.023	0.020	0.011	56.1	4
pH		RT1LS10		0.27	3.52	8.5	3.56	3.52	3.54	0.12	3.4	9
Sb	mg/kg	RT1LS10					*<0.10*	0.002	0.002	0.000	0.0	1
Se	mg/kg	RT1LS10					*< 0.05*	0.002	0.002	0.000	0.0	1
SO_4	mg/kg	RT1LS10		0.15	203	20	206	203	204	15	7.3	6
V	mg/kg	RT1LS10			0.017		*< 0.05*	0.017	0.017	0.002	11.9	4
Zn	mg/kg	RT1LS10		0.69	1.75	25	1.90	1.75	1.76	0.22	12.4	10

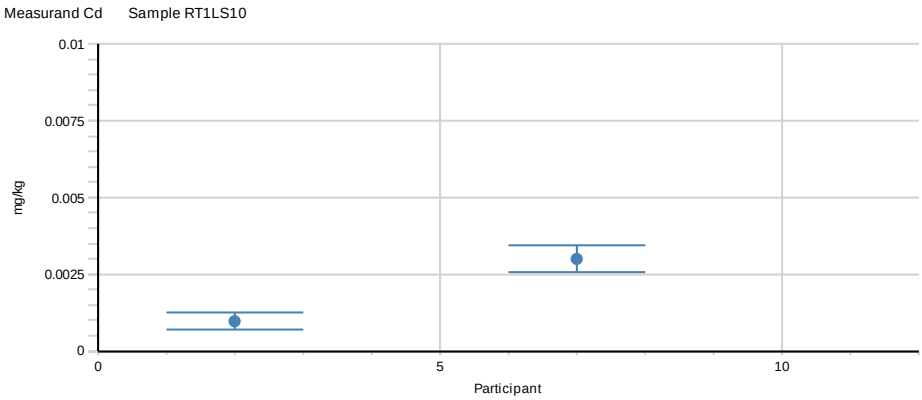
APPENDIX 7: Results of participants and their uncertainties

In figures:

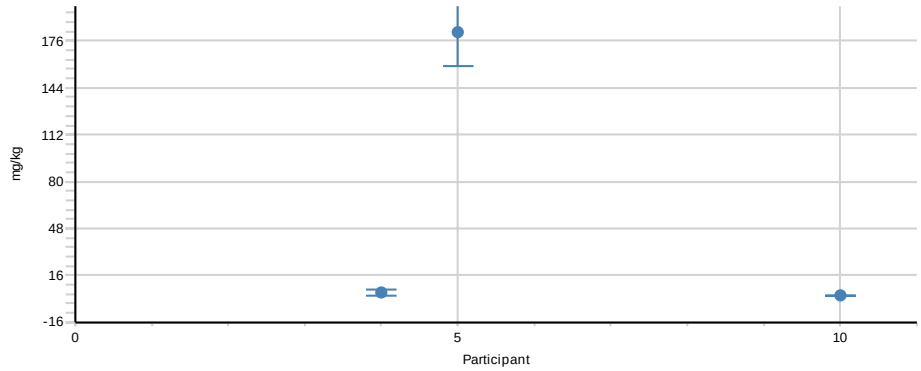
- The dashed lines describe the standard deviation for the proficiency assessment, the red solid line shows the assigned value, the shaded area describes the expanded uncertainty of the assigned value, and the arrow describes the value outside the scale.



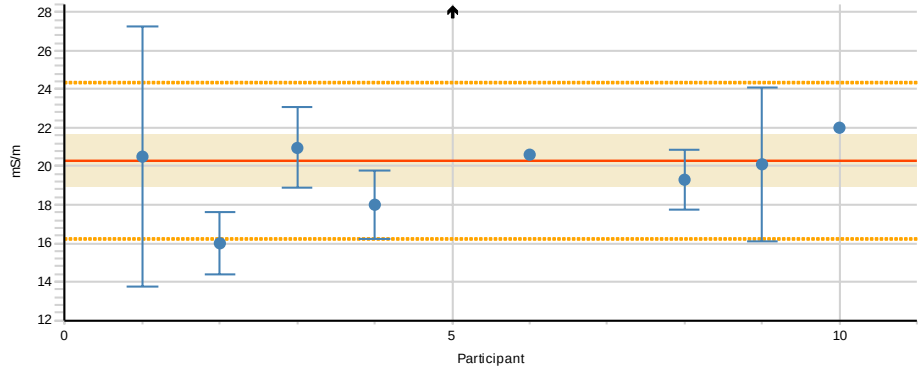




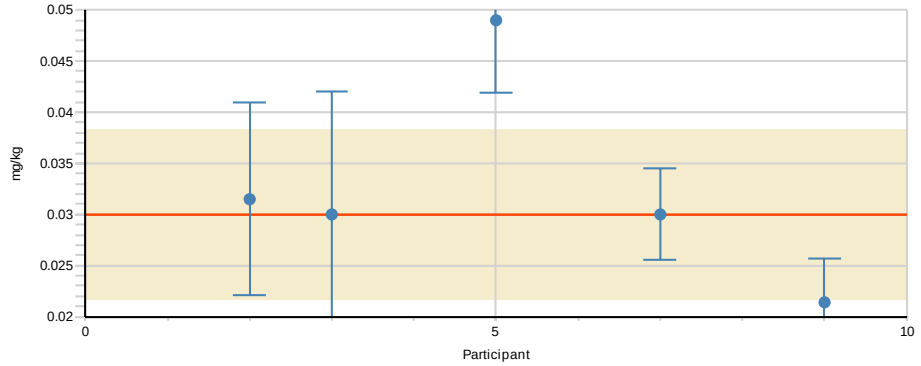
Measurand Cl Sample RT1LS10



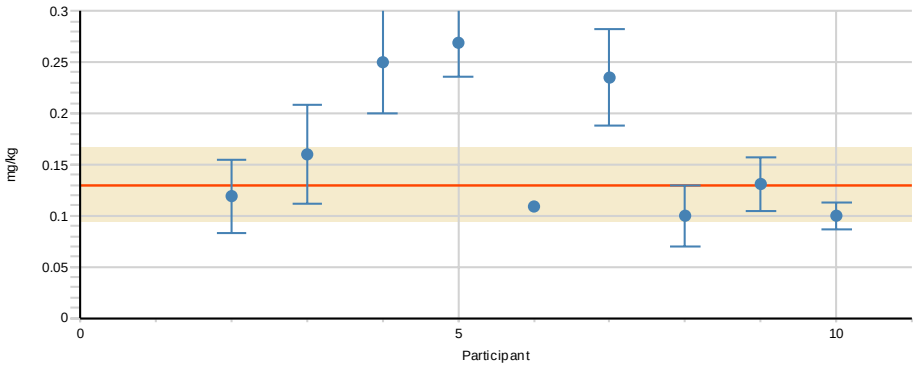
Measurand Conductivity 25 Sample RT1LS10



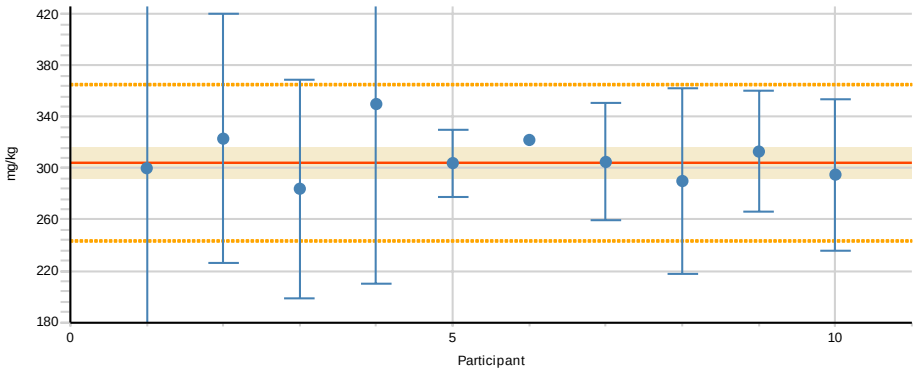
Measurand Cr Sample RT1LS10



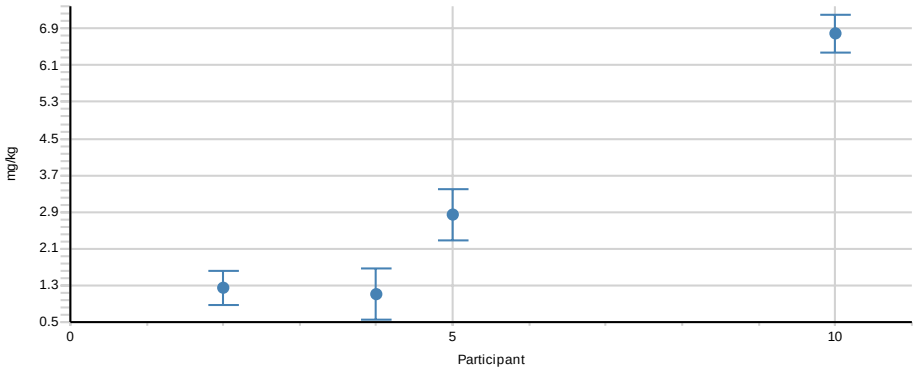
Measurand Cu Sample RT1LS10



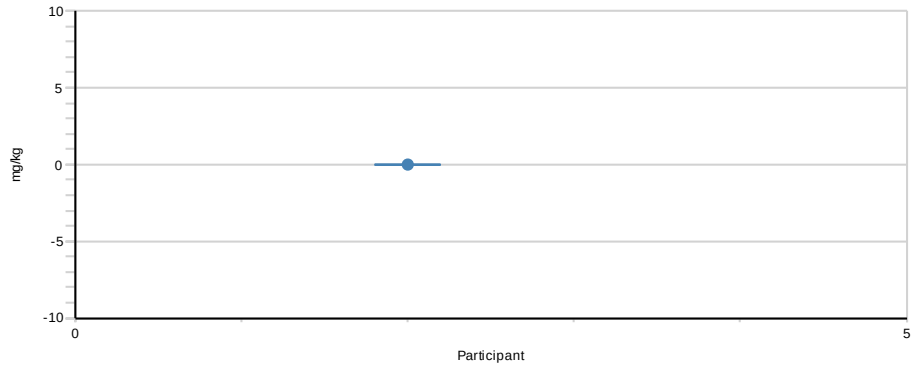
Measurand DOC Sample RT1LS10



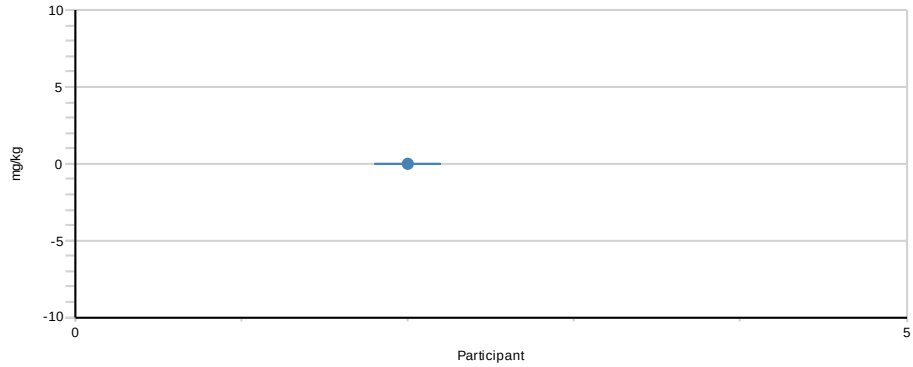
Measurand F Sample RT1LS10



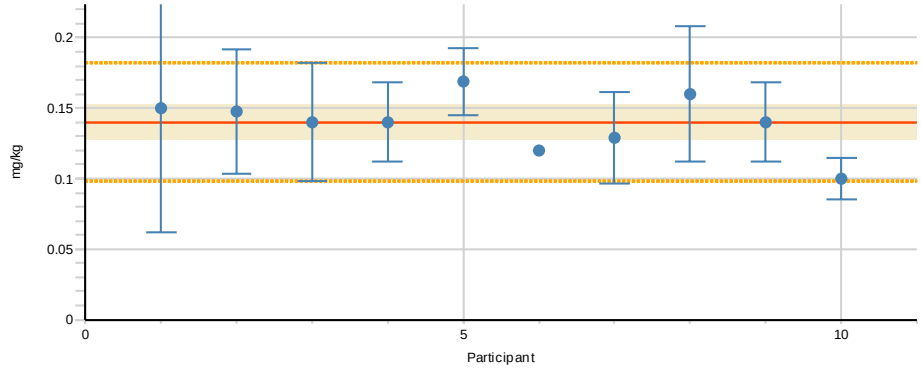
Measurand Hg Sample RT1LS10



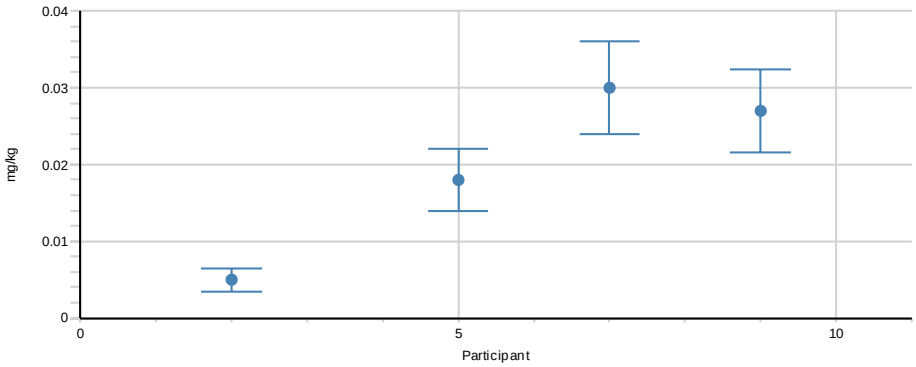
Measurand Mo Sample RT1LS10



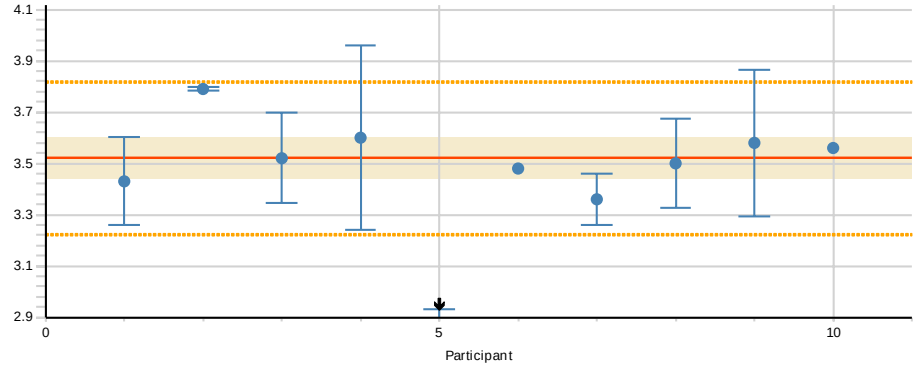
Measurand Ni Sample RT1LS10



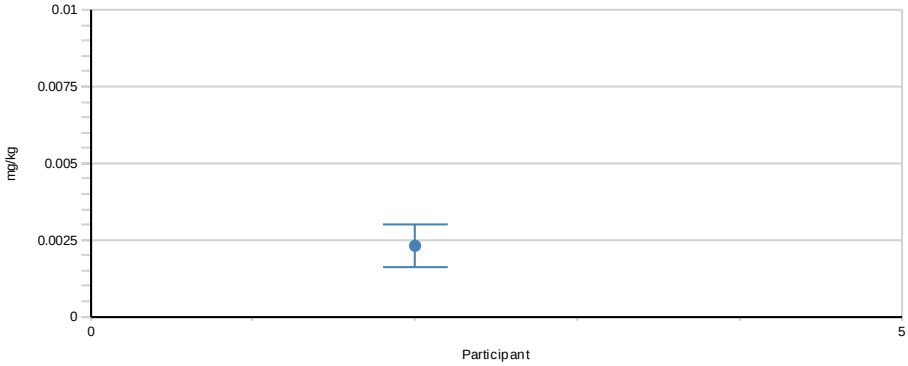
Measurand Pb Sample RT1LS10



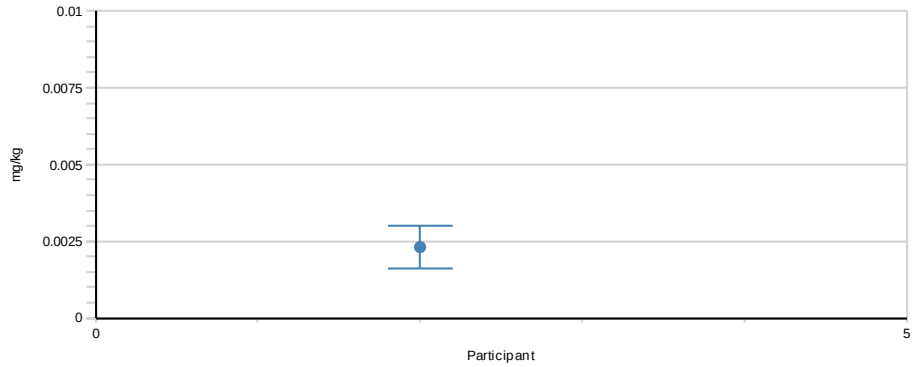
Measurand pH Sample RT1LS10



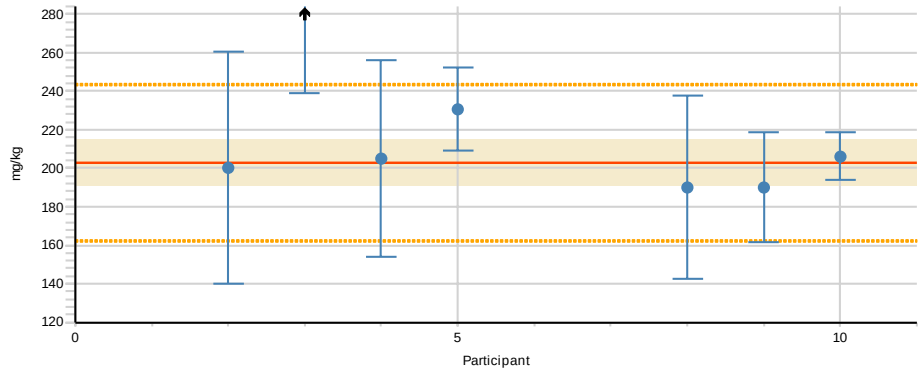
Measurand Sb Sample RT1LS10



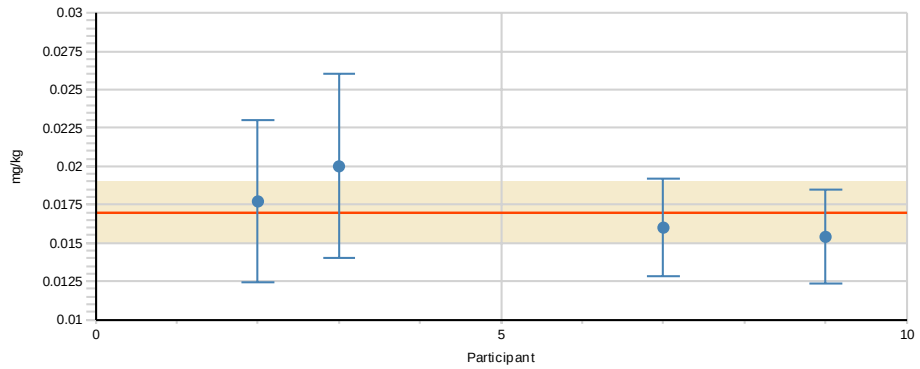
Measurand Se Sample RT1LS10

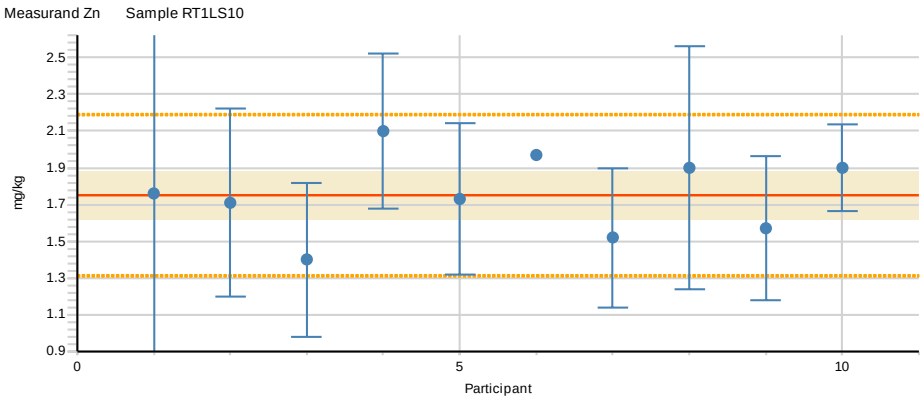


Measurand SO_4 Sample RT1LS10



Measurand V Sample RT1LS10




Measurand Zn
Sample RT1LS10
mg/kg
2.5
2.3
2.1
1.9
1.7
1.5
1.3
1.1
0.9
0
5
10
Participant

APPENDIX 8: Summary of the z scores

Measurand	Sample	1	2	3	4	5	6	7	8	9	10		%
Ba	RT1LS10	.	S	S	*S*	S	.	S	U	S	S	. . . . .	87.5
Conductivity 25	RT1LS10	S	q	S	*S*	U	*S*	.	S	S	S	. . . . .	77.8
DOC	RT1LS10	S	S	S	S	S	*S*	S	S	S	*S*	. . . . .	100
Ni	RT1LS10	S	S	S	S	S	*S*	S	S	S	S	. . . . .	100
pH	RT1LS10	S	S	S	*S*	u	*S*	S	S	S	S	. . . . .	90.0
SO_4	RT1LS10	.	S	U	S	S	.	.	S	S	S	. . . . .	85.7
Zn	RT1LS10	S	S	S	S	S	*S*	S	S	S	S	. . . . .	100
%		100	86	86	100	71	100	100	86	100	100		
accredited		5	7	7	2	7		5	7	7	4		

S - satisfactory (-2 ≤ z ≤ 2), Q - questionable (2 < z < 3), q - questionable (-3 < z < -2),
U - unsatisfactory (z ≥ 3), and u - unsatisfactory (z ≤ -3), respectively
bold - accredited, italics - non-accredited
% - percentage of satisfactory results

Totally satisfactory, % in all: 92 % in accredited: 90 % in non-accredited: 100

APPENDIX 9: Summary of the E_n scores

Measurand	Sample	1	2	3	4	5	6	7	8	9	10		%
As	RT1LS10	.	-0.1	0.0	.	0.2	.	.	.	-1.3	.	. . . . .	75.0
Cr	RT1LS10	.	0.1	0.0	.	1.7	.	0.0	.	-0.9	.	. . . . .	80.0
Cu	RT1LS10	.	-0.2	0.5	1.9	2.8	.	1.8	-0.6	0.0	-0.8	. . . . .	62.5
V	RT1LS10	.	0.1	0.5	.	.	.	-0.3	.	-0.4	.	. . . . .	100
%		100	82	91	75	40		75	88	91	67		

***E_n* scores enable to estimate the proximity of participant results to the assigned value taking into consideration their reported expanded uncertainty**

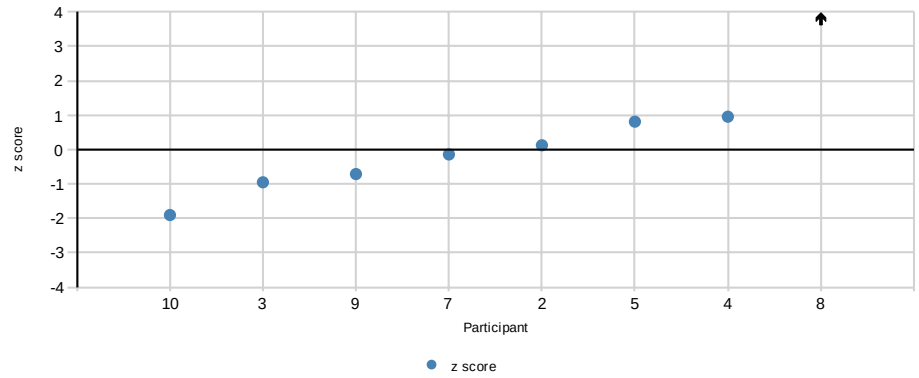
Scores of $-1.0 < E_n < 1.0$ indicate successful performance

Scores of $E_n \geq 1.0$ or $E_n \leq -1.0$ indicate a need to review the uncertainty estimated or to correct a measurement issue

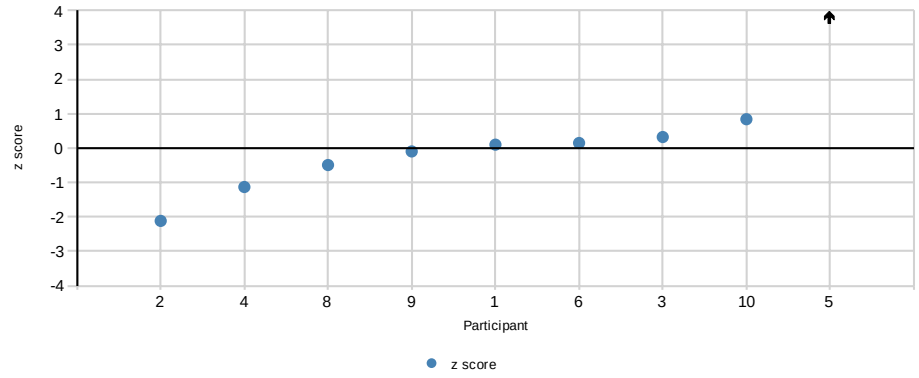
Totally satisfactory, % in all: 76

APPENDIX 10: z scores in ascending order

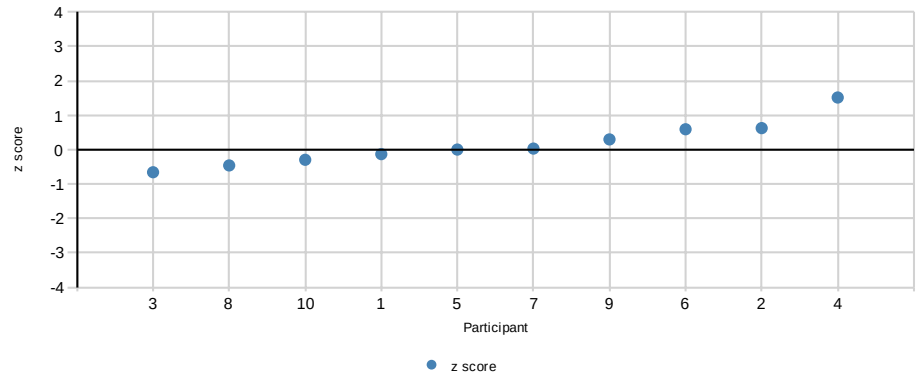
Measurand Ba Sample RT1LS10



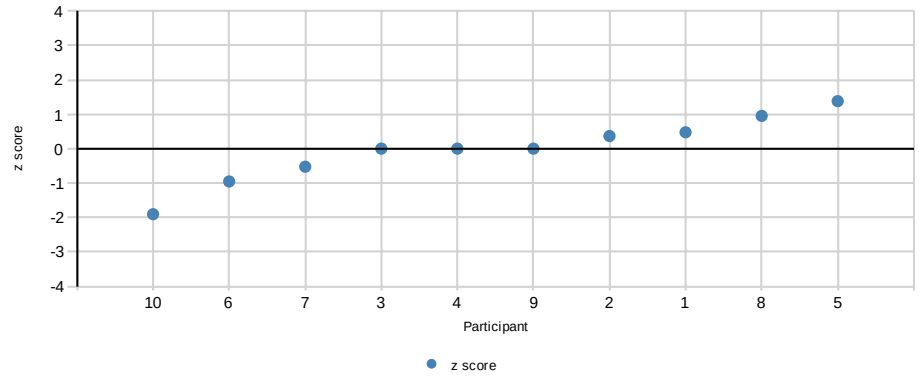
Measurand Conductivity 25 Sample RT1LS10



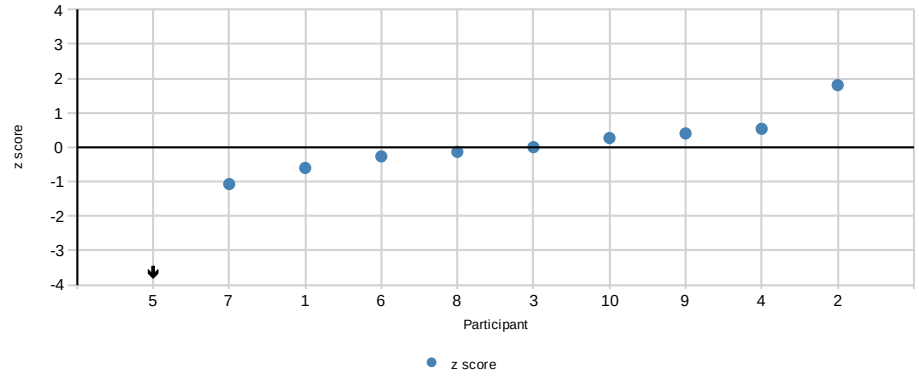
Measurand DOC Sample RT1LS10



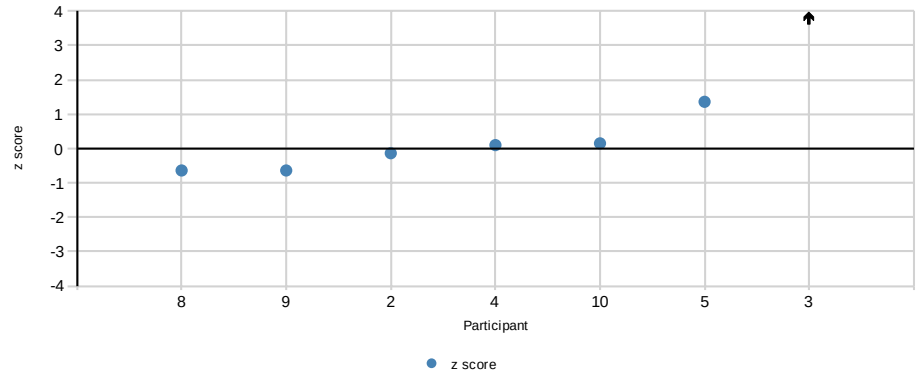
Measurand Ni Sample RT1LS10

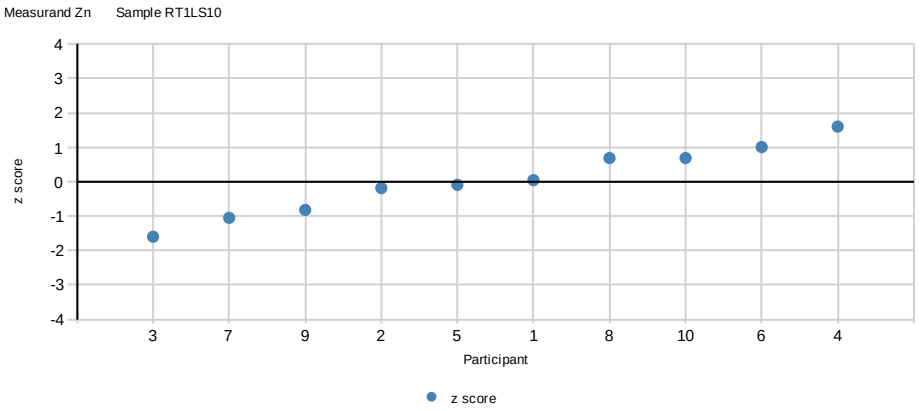


Measurand pH Sample RT1LS10



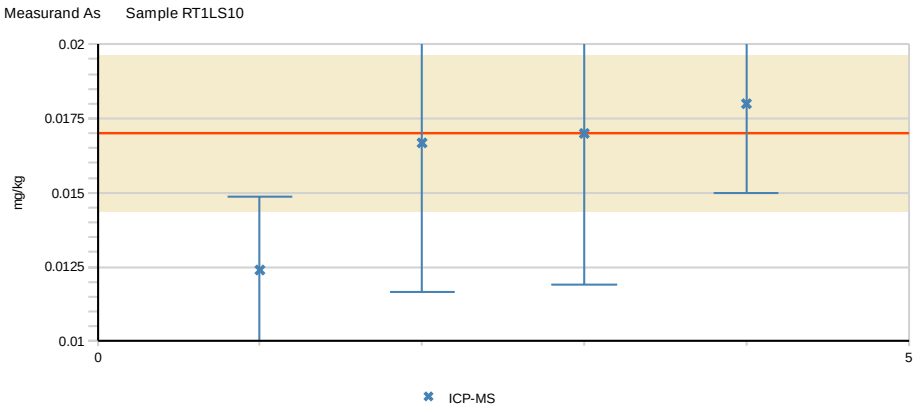
Measurand SO_4 Sample RT1LS10

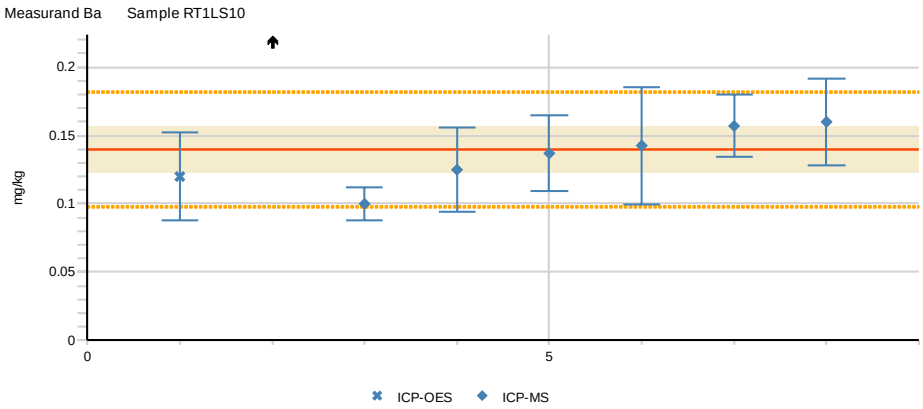


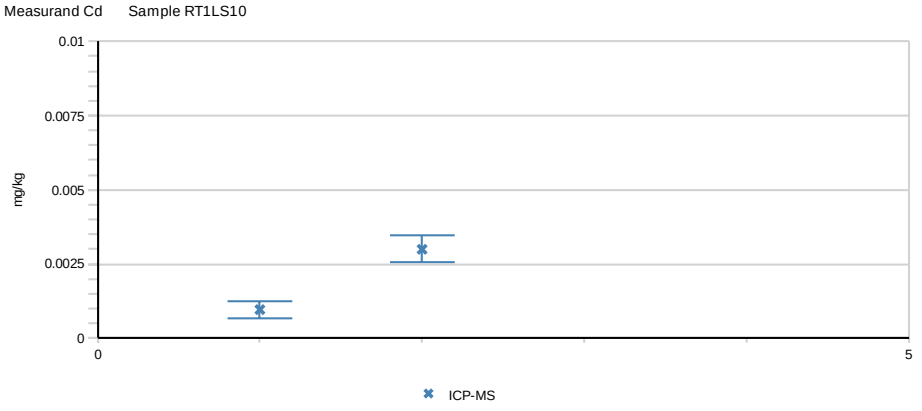

Measurand Zn
Sample RT1LS10
z score
4
3
2
1
0
-1
-2
-3
-4
3
7
9
2
5
1
8
10
6
4
Participant
z score

APPENDIX 11: Results grouped according to the methods

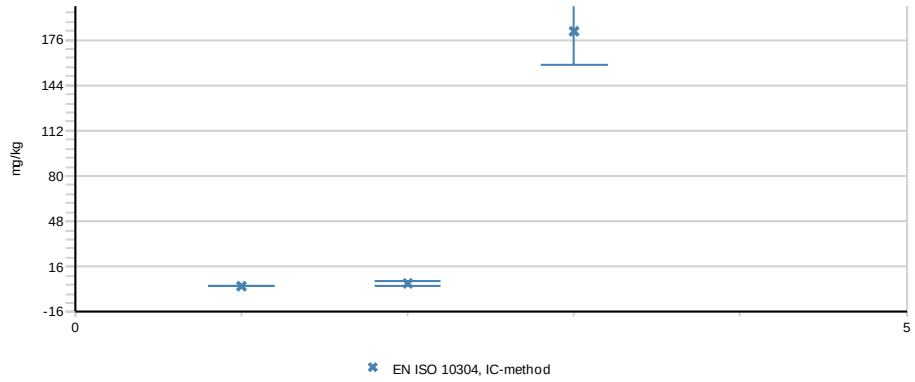
The explanations for the figures are described in the Appendix 7. The results are shown in ascending order.



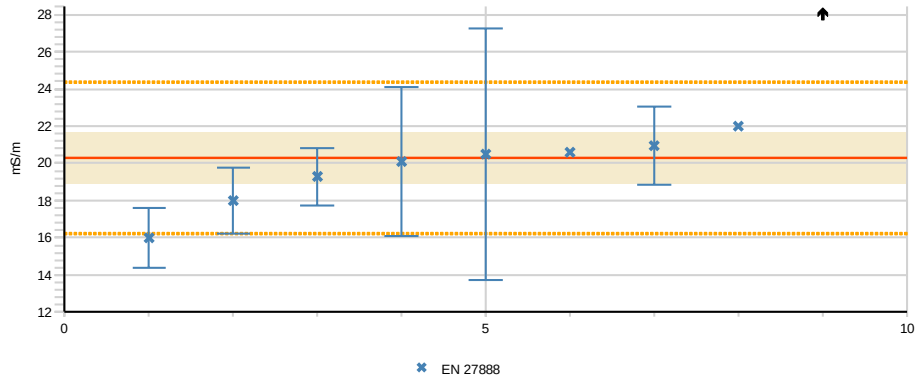




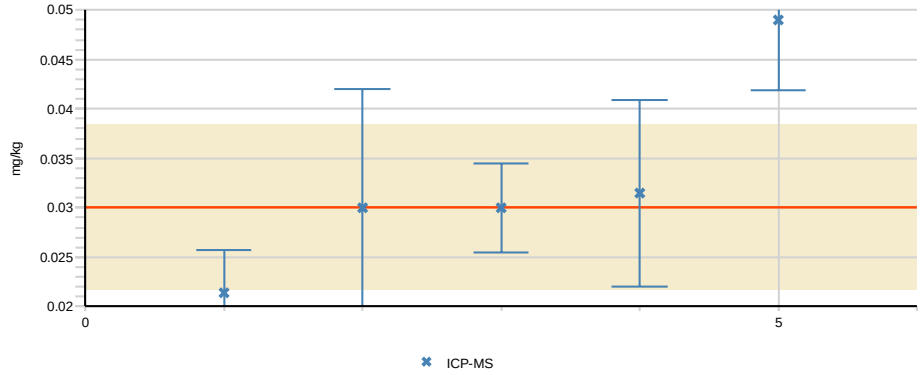
Measurand Cl Sample RT1LS10



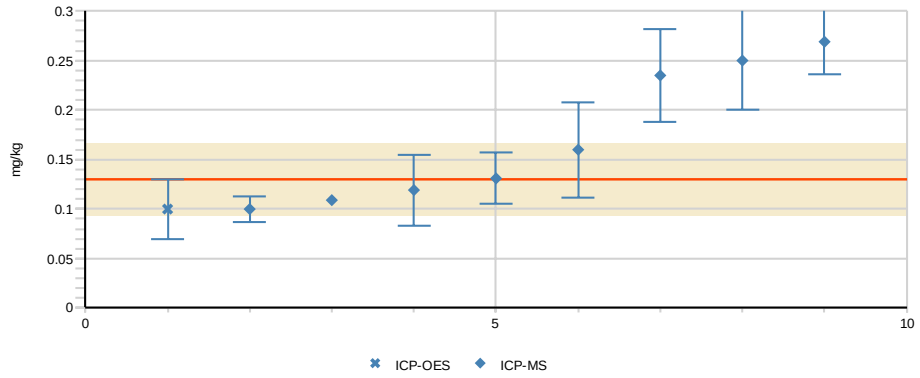
Measurand Conductivity 25 Sample RT1LS10



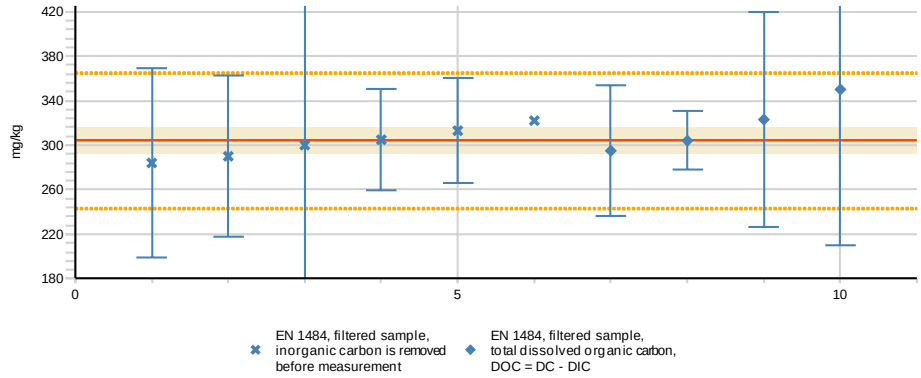
Measurand Cr Sample RT1LS10



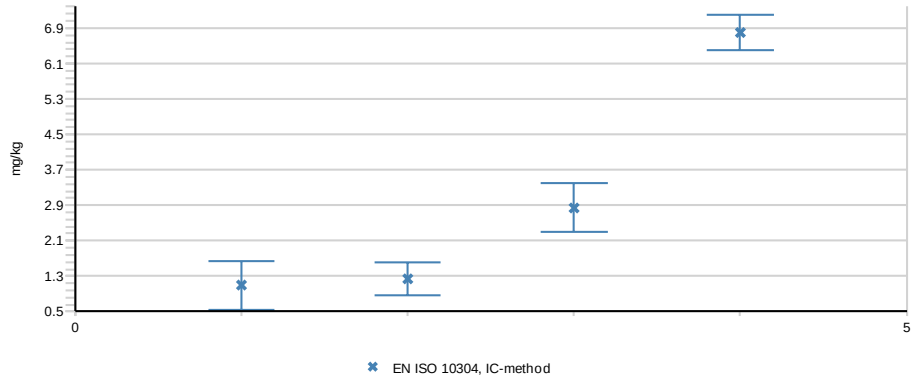
Measurand Cu Sample RT1LS10



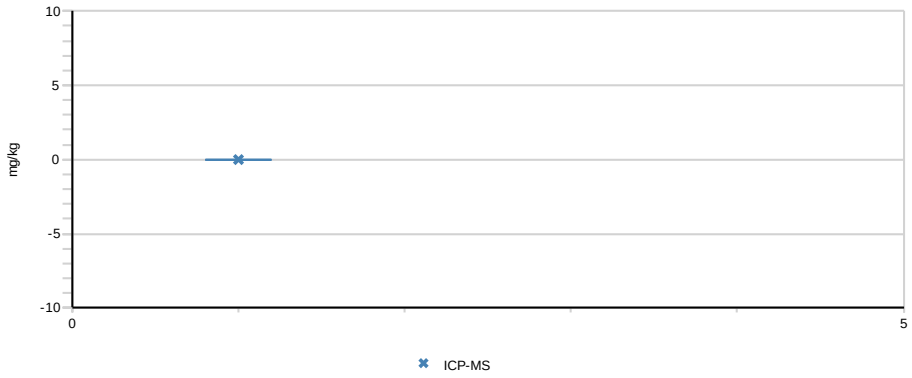
Measurand DOC Sample RT1LS10



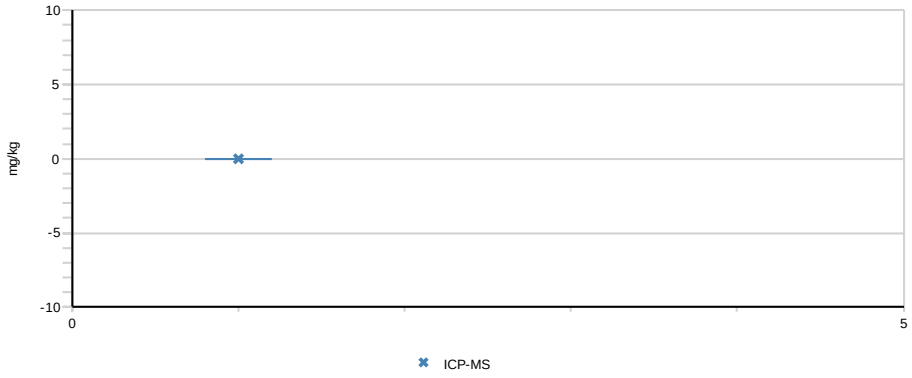
Measurand F Sample RT1LS10



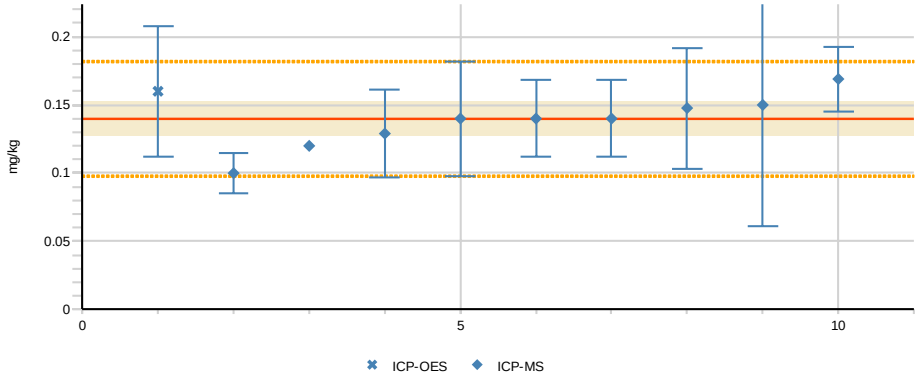
Measurand Hg Sample RT1LS10

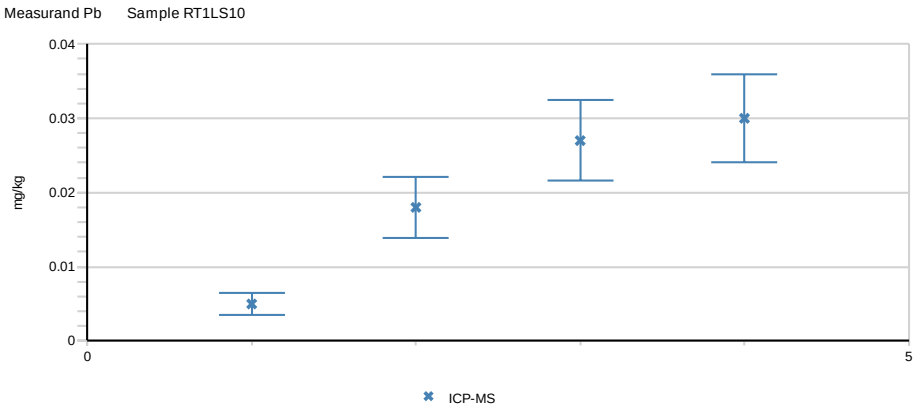


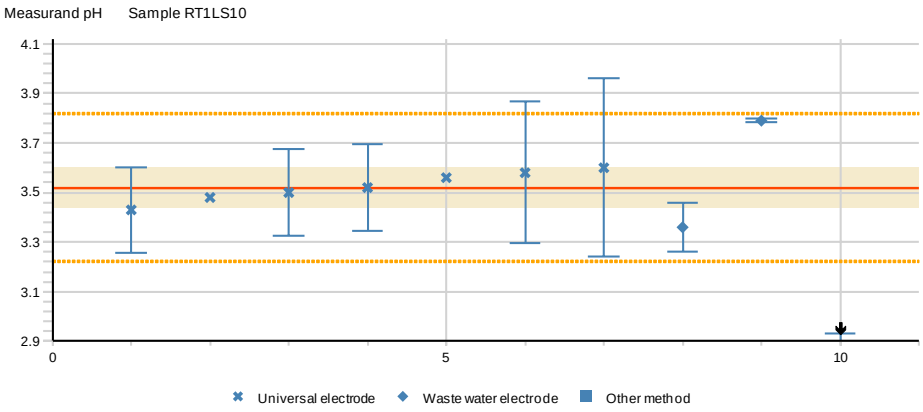
Measurand Mo Sample RT1LS10

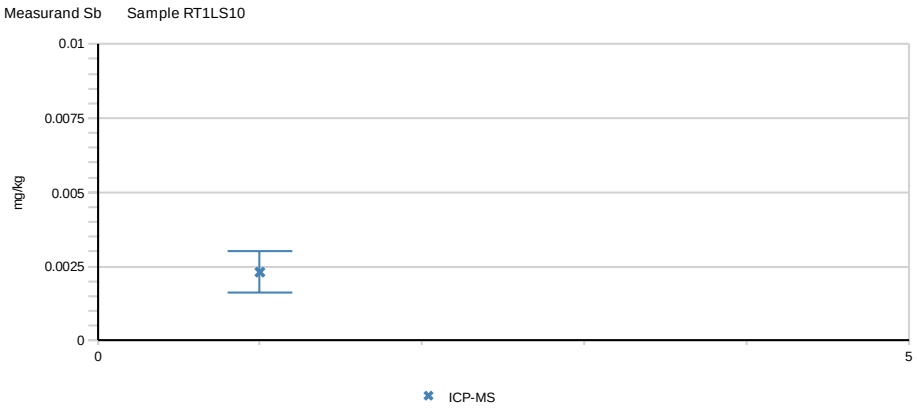


Measurand Ni Sample RT1LS10

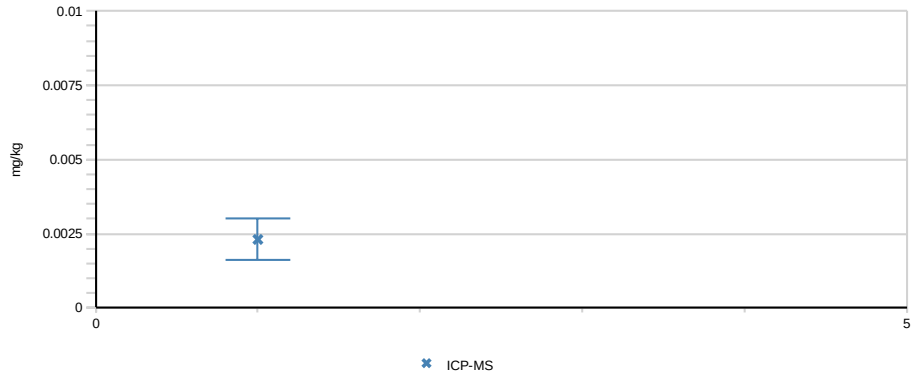



Measurand Pb Sample RT1LS10
0.04
0.03
0.02
0.01
0
mg/kg
0
5
ICP-MS

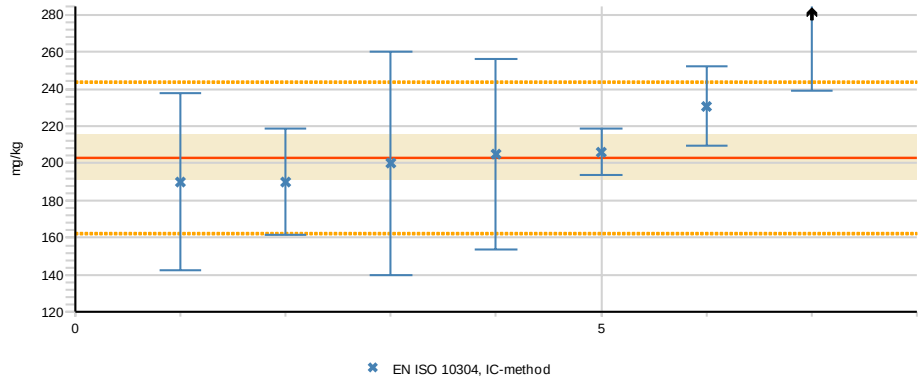

Measurand pH Sample RT1LS10
4.1
3.9
3.7
3.5
3.3
3.1
2.9
0
5
10
Universal electrode
Waste water electrode
Other method


Measurand Sb Sample RT1LS10
0.01
0.0075
0.005
0.0025
0
mg/kg
0
5
ICP-MS

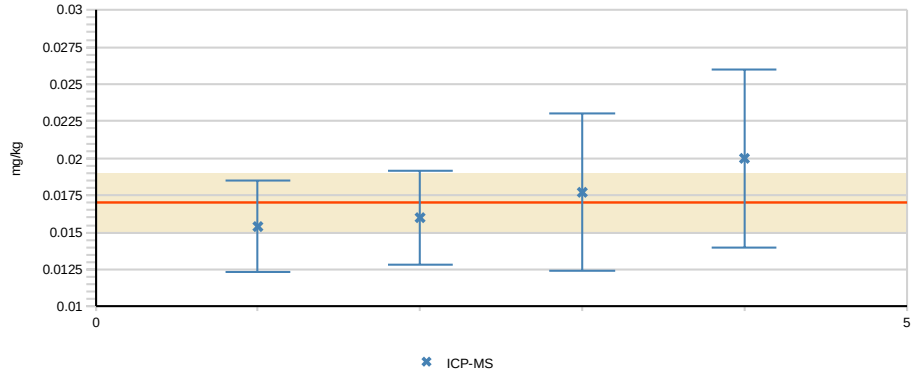
Measurand Se Sample RT1LS10

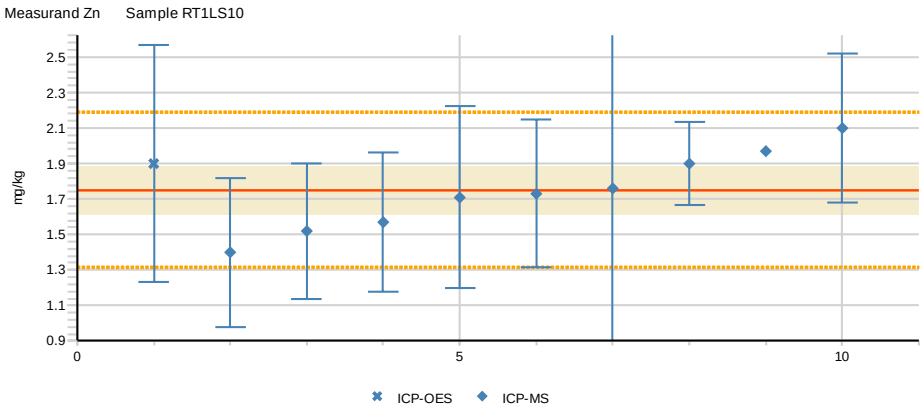


Measurand SO_4 Sample RT1LS10



Measurand V Sample RT1LS10




Measurand Zn
Sample RT1LS10
mg/kg
2.5
2.3
2.1
1.9
1.7
1.5
1.3
1.1
0.9
0
5
10
ICP-OES
ICP-MS

APPENDIX 12: One stage batch leaching test, background information

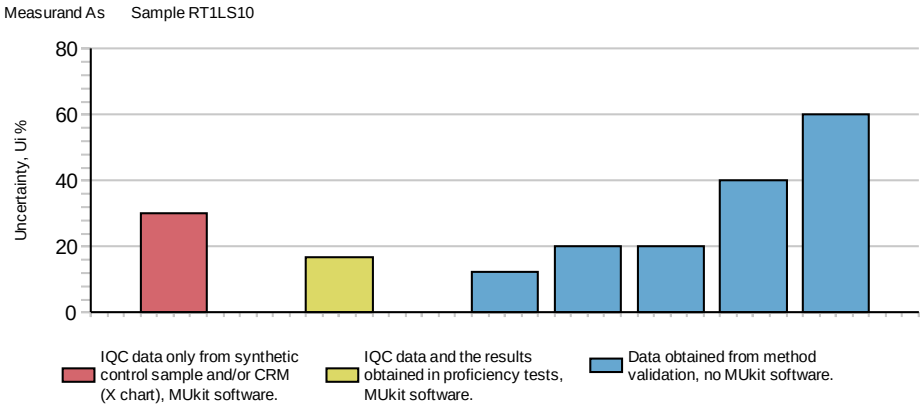
Start date of the one stage batch leaching test	Sample amount, Mw (kg)	Shaking/mixing equipment (with rpm)	Volume of leachant, L (l)	Settling time between agitation and separation, T1 (min)	Description of the liquid-solid separation procedure (Separation method, type and material of the filter, pore size)	Centrifugation (duration, rpm)	Volume of the filtered eluate, VE (l)	Duration of the filtration, T2 (min)
22.11.2018	0.09	End-over-end, 10 rpm		10	Vacuum filtering Membrane filter Gelman 0.45 µm	-	-	15
26.11.2018	0.18	Horizontal shaker Edmund Bühler VKS-75 Control	1.8	1440	-	Centrifuge (Speed), 8 rpm, 30 min	1.76	0.75
4.12.2018	0.1	Heidolph REAX20 5-10 rpm	1	15	High pressure filtration (5 bar) Filter paper: 0.45 µm Membrane filter Whatman NC45 diameter 142 mm, cellulose-nitrate membrane filter	-	1	-
17.12.2018	0.0901	Turn-over head shaker, 10 rpm	0.900	15	Suction filtration, membrane 0.45 µm, Cellulose-acetate	-	0.880	20

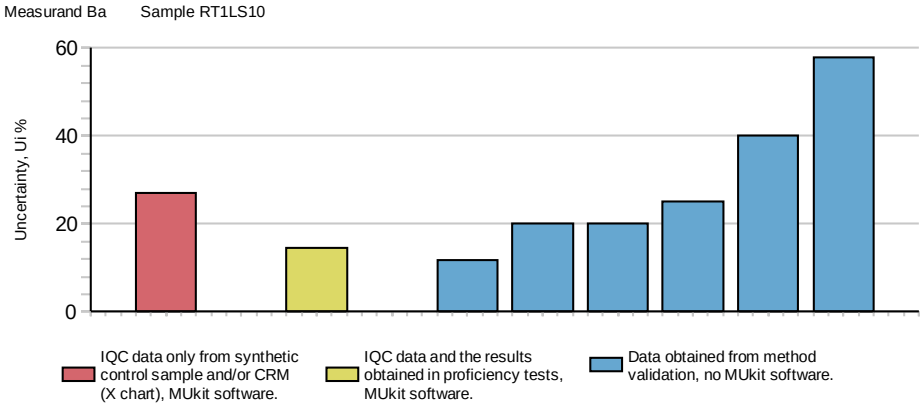
APPENDIX 13: Standard method of analysis by measurand

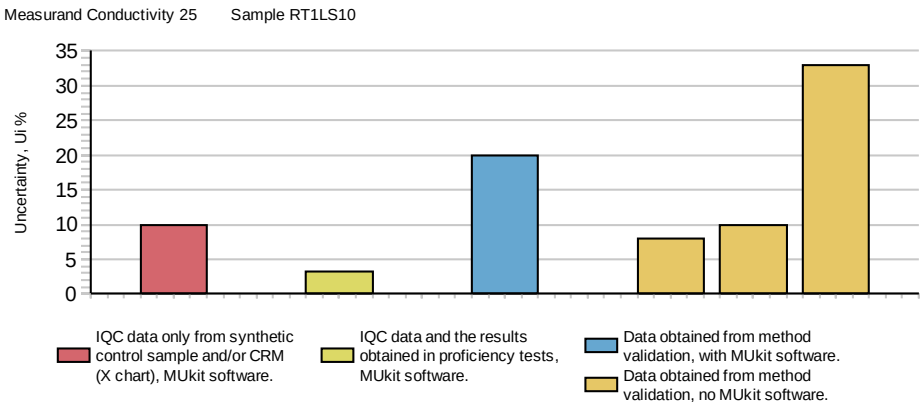
Measurand	Standard options	Applied / modified / more information	No. of participants
As (n=4, the number of participants who answered)	EN ISO 17294-1:2006	Applied standard	1
	EN ISO 17294-2:2004	Applied standard	3
	Other method	Applied standard: EN ISO 17294-2:2016	1
Ba n=4	EN ISO 17294-1:2006	Applied standard	1
	EN ISO 17294-2:2004	Applied standard	3
	Other method	Applied standard: EN ISO 17294-2:2016	1
Cd n=4	EN ISO 17294-1:2006	Applied standard	1
	EN ISO 17294-2:2004	Applied standard	3
	Other method	Applied standard: EN ISO 17294-2:2016	1
Cl^-, n=4	EN ISO 10304-1:2009	Applied standard	4
Conductivity, n=4	EN 27888	Applied standard	4
Cr n=4	EN ISO 17294-1:2006	Applied standard	1
	EN ISO 17294-2:2004	Applied standard	3
	Other method	Applied standard: EN ISO 17294-2:2016	1
Cu n=4	EN ISO 17294-1:2006	Applied standard	1
	EN ISO 17294-2:2004	Applied standard	3
	Other method	Applied standard: EN ISO 17294-2:2016	1
DOC, n=4	EN 1484	Applied standard	4
F^-, n=4	EN ISO 10304-1:2009	Applied standard	4
Mo n=4	EN ISO 17294-1:2006	Applied standard	1
	EN ISO 17294-2:2004	Applied standard	3
	Other method	Applied standard: EN ISO 17294-2:2016	1
Ni n=4	EN ISO 17294-1:2006	Applied standard	1
	EN ISO 17294-2:2004	Applied standard	3
	Other method	Applied standard: EN ISO 17294-2:2016	1
Pb n=4	EN ISO 17294-1:2006	Applied standard	1
	EN ISO 17294-2:2004	Applied standard	3
	Other method	Applied standard: EN ISO 17294-2:2016	1
pH n=4	ISO 10523:2008	Applied standard	3
	Other		
Sb n=4	EN ISO 17294-1:2006	Applied standard	1
	EN ISO 17294-2:2004	Applied standard	3
	Other method	Applied standard: EN ISO 17294-2:2016	1
Se n=4	EN ISO 17294-1:2004	Applied standard	3
	ISO 9965:1993	Applied standard	1
	Other method	Applied standard: EN ISO 17294-2:2016	1
SO_4^{2-}, n=4	EN ISO 10304-1:2009	Applied standard	4
TDS, n=2	EN 15216:2007	Applied standard	2
V n=4	EN ISO 17294-1:2006	Applied standard	1
	EN ISO 17294-2:2004	Applied standard	3
	Other method	Applied standard: EN ISO 17294-2:2016	1
Zn n=4	EN ISO 17294-1:2006	Applied standard	1
	EN ISO 17294-2:2004	Applied standard	3
	Other method	Applied standard: EN ISO 17294-2:2016	1

APPENDIX 14: Examples of measurement uncertainties reported by the participants

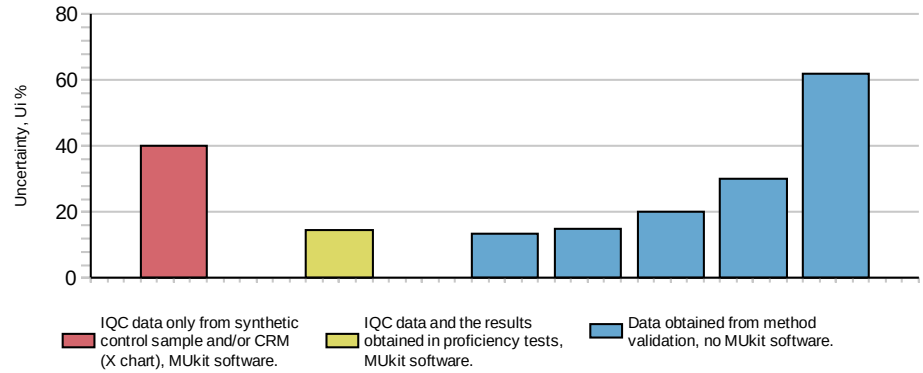
In figures, the presented expanded measurement uncertainties are grouped according to the method of estimation at 95 % confidence level (k=2). The expanded uncertainties were estimated mainly by using the internal quality control (IQC) data. The used procedures in figures below are distinguished e.g. between using or not using the MUkit software for uncertainty estimation or using data from method validation [10, 11].



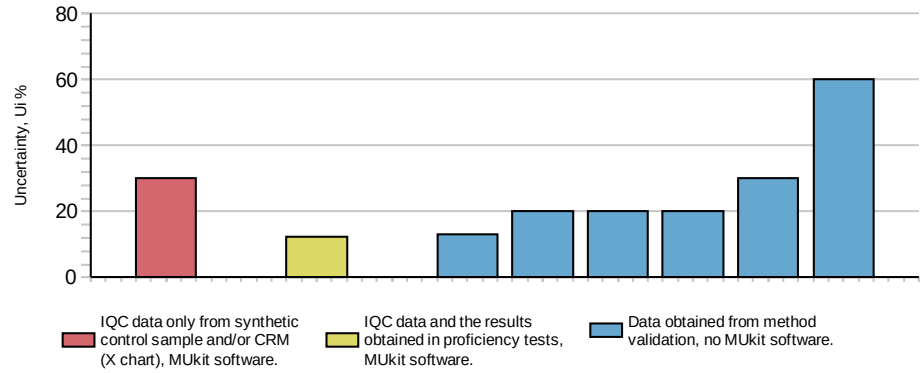




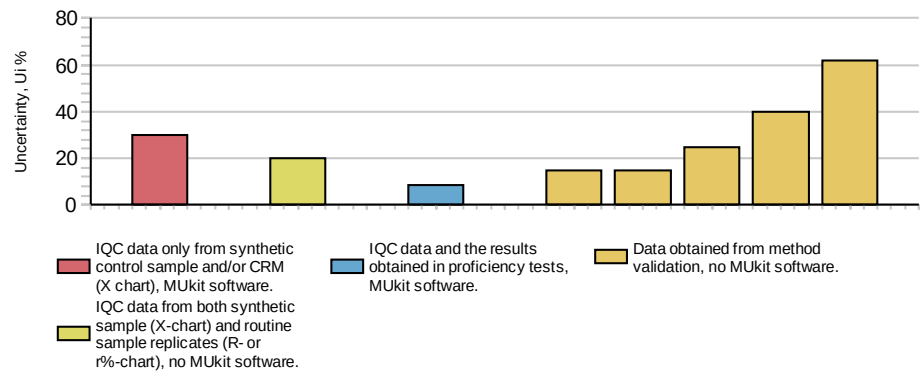
Measurand Cr Sample RT1LS10



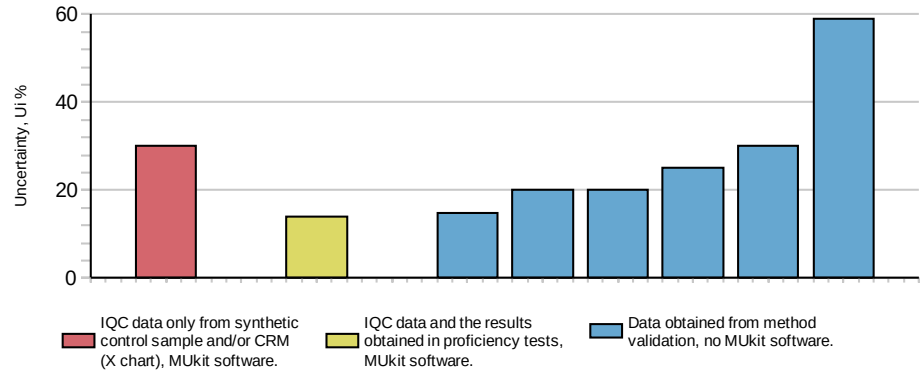
Measurand Cu Sample RT1LS10



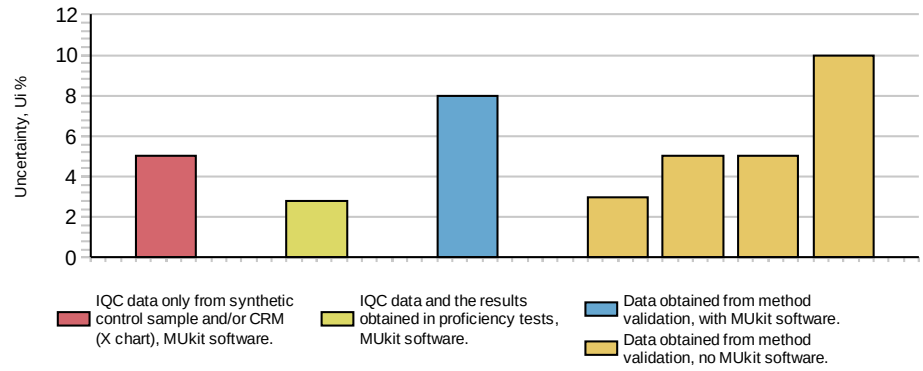
Measurand DOC Sample RT1LS10



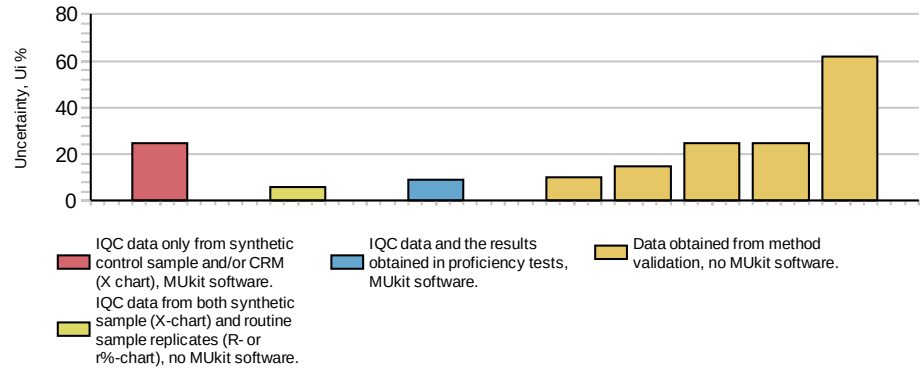
Measurand Ni Sample RT1LS10



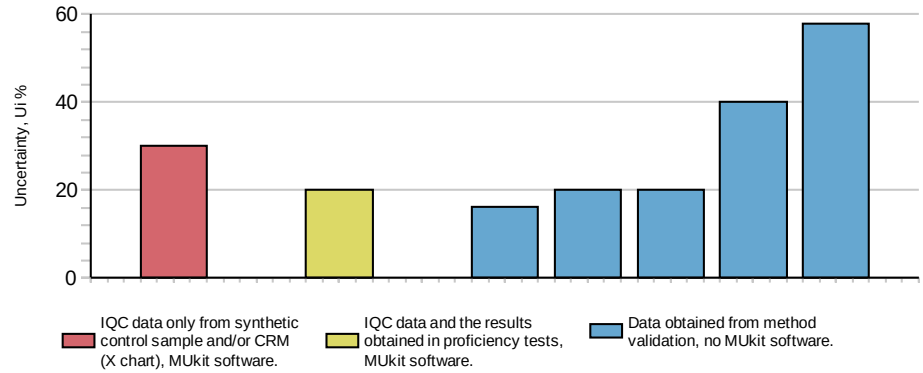
Measurand pH Sample RT1LS10



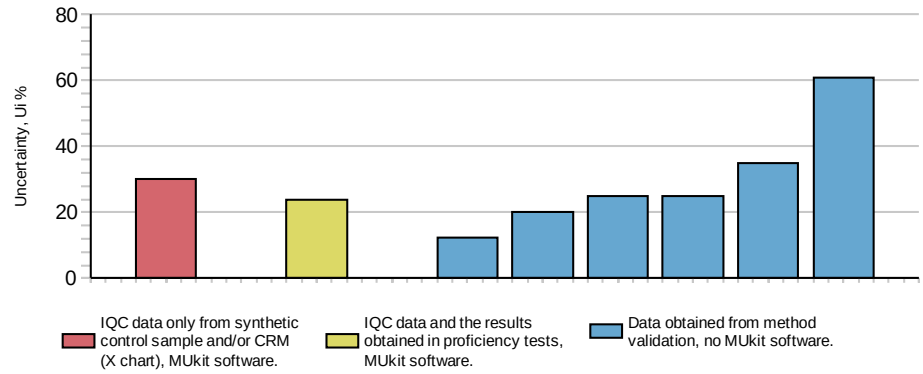
Measurand SO_4 Sample RT1LS10



Measurand V Sample RT1LS10



Measurand Zn Sample RT1LS10



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