REPORTS OF THE FINNISH ENVIRONMENT INSTITUTE 14 | 2019

Interlaboratory Proficiency Test 01/2019

Swimming pool water analysis

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Mirja Leivuori[1], Sami Tyrväinen[2], Mika Sarkkinen[1], Riitta Koivikko[1], Keijo Tervonen[1], Sari Lanteri[1], Ritva Väisänen[1] and Markku Ilmakunnas[1]

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ABSTRACT

Interlaboratory Proficiency Test 01/2019

Proftest SYKE carried out the proficiency test for the determination of chlorine, $KMnO_4$, NO_3, pH, turbidity, and urea in swimming pool waters in January-February 2019. In total, 22 participants joined in the proficiency test.

In this proficiency test 93 % of the results evaluated with z score were satisfactory when deviation of 0.2 pH units for pH determination and 10–25 % for the other determinations was accepted from the assigned value. Of the results evaluated with E_n scores, 71 % were satisfactory. The calculated value, the robust mean or the median of the results reported by the participants was chosen as the assigned value for the concentration of measurands.

Warm thanks to all participants in this proficiency test!

Keywords: water analysis, chlorine, nitrate, pH, $KMnO_4$, turbidity, urea, swimming pool waters, water and environmental laboratories, proficiency test, interlaboratory comparison

TIIVISTELMÄ

Laboratorioiden välinen pätevyyskoe 01/2019

Proftest SYKE järjesti tammi-helmikuussa 2019 pätevyyskokeen uima-allasvesien kloori-, $KMnO_4$-, NO_3-, pH-, sameus- ja ureamääritysten testaamiseksi. Pätevyyskokeessa oli yhteensä 22 osallistujaa.

Tulosten arviointi tehtiin z- arvojen perusteella, jolloin pH-määrityksessä sallittiin 0,2 pH-yksikön ja muissa määrityksissä 10–25 %:n poikkeama vertailuarvosta. Koko aineistossa hyväksyttäviä tuloksia oli 93 %. Tuloksia arvioitiin lisäksi E_n-arvoilla, jolloin hyväksyttäviä tuloksia oli 71 %. Testisuureen vertailuarvona käytettiin laskennallista pitoisuutta, osallistujien tulosten robustia keskiarvoa tai mediaania.

Kiitos pätevyyskokeen osallistujille!

Avainsanat: vesianalyysi, vesi- ja ympäristölaboratoriot, uima-allasvedet, kloori, permanganaattiluku, nitraatti, pH, sameus, urea, pätevyyskoe, laboratorioiden välinen vertailumittaus

SAMMANDRAG

Provningsjämförelse 01/2019

Under januari-februari 2019 genomförde Proftest SYKE en provningsjämförelse, som omfattade bestämningen av klor, $KMnO_4$, nitrat, pH, grumlighet och urea i simbassängvatten. Till proven ställde upp 22 deltagarna.

I jämförelsen 93 % av resultaten som värderas med hjälp av z-värdet var acceptabla, när 0.2 pH enhet eller 10–25 % totalavvikelsen från referensvärdet accepterades. Resultaten som värderades med hjälp av E_n-värdet var 71 % acceptabla. Som referensvärde av analytens koncentration användes det teoriska värdet, robust medelvärdet eller median av deltagarnas resultat.

Ett varmt tack till alla deltagarna i testet!

Nyckelord: vattenanalyser, klor, nitrat, pH, $KMnO_4$, grumlighet, urea, simbassängvatten, provningsjämförelse, vatten- och miljölaboratorier

CONTENTS

1 Introduction

Proftest SYKE carried out the proficiency test (PT) for analysis of combined, free and total chlorine, permanganate index ($KMnO_4$), nitrate, pH, turbidity, and urea from swimming pool waters in January-February 2019 (SPW 01/2019). In the PT the results of laboratories providing measurements of the swimming pool waters were evaluated.

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 [1] and applying ISO 13528 [2] and IUPAC Technical report [3]. 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.

2 Organizing the proficiency test

2.1 Responsibilities

Organizer:
Proftest SYKE, Finnish Environment Institute (SYKE), Laboratory Centre
Ultramariinikuja 4, FI-00430 Helsinki, Finland
Phone: +358 295 251 000, E-mail: proftest@environment.fi

The responsibilities in organizing the proficiency test were as follows:

Mirja Leivuori	coordinator
Riitta Koivikko	substitute for coordinator
Keijo Tervonen	technical assistance
Markku Ilmakunnas	technical assistance
Sari Lanteri	technical assistance
Ritva Väisänen	technical assistance
Mika Sarkkinen	analytical expert (SYKE, NO_3, pH, turbidity, $KMnO_4$)

Cooperation partner:
Sami Tyrväinen, Eurofins Environment Testing Finland Oy (Lahti), chlorine and urea measurements.

Subcontracting:
Eurofins Environment Testing Finland Oy (formerly Ramboll Finland Oy, T039, www.finas.fi/sites/en), chlorine and urea measurements.

2.2 Participants

In total 22 laboratories participated in this proficiency test (Appendix 1), 20 from Finland and 2 from other European countries. 91 % of the participants reported that they have accredited quality management system based on ISO/IEC 17025, while two participants did not report their accreditation status. All participants used accredited analytical methods at least for a part of the measurements.

The samples were tested at the laboratory of Eurofins Environment Testing Finland Oy in Lahti for chlorines and urea. Their participant code is 11 in the result tables. The other measurands were tested in the organizing laboratory (T003, www.finas.fi/sites/en) which has the code 13 (SYKE, Oulu) in the result tables.

2.3 Samples and delivery

Two swimming pool water samples (U1 and U2) were delivered to the participants. For the determination of urea also a synthetic sample (A1U) was delivered. The synthetic sample (A1U) was prepared from the commercial urea reagent (Merck). The sample preparation is described in details in the Appendix 2. The samples were prepared according to the usual concentration levels of swimming pool waters in Finland [4].

When preparing the samples, the purity of the used sample vessels was controlled. The randomly chosen sample vessels were filled with deionized water and the purity of the sample vessels was controlled after three days by analyzing N_{NH4} (for urea), N_{NO3} (for nitrate) and conductivity (for pH). According to the test results all used vessels fulfilled the purity requirements.

The samples were delivered to the participants on 28 January 2019 (participants abroad) or on 29 January 2019 (domestic participants) and basically they arrived to the participants on 30 January 2019.

To control the temperature during the transportation a control sample was placed into the sample package and the temperature was requested to be measured when opening the package and to be reported to the provider. The reported temperatures of the control sample were below 10 °C. It is recommended to measure the temperature of the control sample shortly after the sample package arrival, especially when the package is not stored in refrigerator after the arrival.

The samples were requested to be analyzed on 31 January 2019. The results were reported latest on 4 February 2019 as requested. The preliminary results were delivered to the participants on 7 February 2019.

2.4 Homogeneity and stability studies

The homogeneity of the samples was tested by analyzing permanganate index, nitrate, pH, turbidity, and urea. More detailed information of homogeneity studies is shown in Appendix 3. According to the test results, all samples were considered homogeneous.

The stability of the samples was tested by analysing combined, free and total chlorine, pH and urea from the samples stored at the room temperature for one day. The measurand values were checked against the results of the samples stored at 4 °C. According to the test all samples were considered stable (Appendix 4). According to the literature and expertise, the other proficiency test items are known to be stable over the duration of the proficiency test. Based on the stability test the possible increase of the sample temperature during the transportation did not affect the performance of the participants.

2.5 Feedback from the proficiency test

The feedback from the proficiency test is shown in Appendix 5. The comments from the participants mainly focused on the sample delivery and errors in the results reporting. The comments from the provider are mainly focused on the lacking information of the sample arrival document and on the deviation of the replicate measurements. All the 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.

The participants reported replicate results for the chloride, turbidity and urea measurements. The replicate results were tested using the Cochran test.

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 [5].

2.6.2 Assigned values

The detailed information of the assigned values, their uncertainties and reliability is shown in Appendix 6.

The calculated value was used as the assigned value for the urea measurements of the synthetic sample (A1U) and of the sample UE2 (enzymatic test). The robust mean of the results reported by the participants was used as the assigned value for the other measurements, with the exception of urea measurement with the Koroleff test (sample UK2), where the median value was used (n_{stat}<6).

The used assigned values 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 tested [2, 3].

For the calculated assigned values the expanded uncertainty (k=2) was estimated by using standard uncertainties associated with individual operations involved in the preparation of the sample. The main individual source of the uncertainty was the purity of the stock compound. When the robust mean or the median was used as the assigned value, the uncertainty was calculated using the robust standard deviation or the standard deviation [2, 5].

The uncertainty of the calculated assigned values was 0.6 % at the 95 % confidence level. When using the robust mean or the median of the participant results as the assigned value, the uncertainty of the assigned values was lower than 1 % for pH measurements. For the other measurands the uncertainties of the assigned values were mainly lower than 10 % (Appendix 6).

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 standard deviation for proficiency assessment was estimated on the basis of the measurand concentration, the results of homogeneity and stability tests, the uncertainty of the assigned value, and the long-term variation in the former proficiency tests. The standard deviation for proficiency assessment ($2 \times s_{pt}$ at the 95 % confidence level) was set for pH measurements to 0.2 pH units and for the other measurements from 10 % to 25 % depending on the measurands. **After reporting the preliminary results no changes have been done for the standard deviations of the proficiency assessment values.**

When the number of reported results was low (n_{stat}<6), the assigned value based on the participants' results as well as the uncertainty for the assigned value were set, the performance was evaluated by means of E_n scores ('*Error, normalized*'). These are used to evaluate the difference between the assigned value and participant's result within their reported 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.

When using the robust mean as the assigned value, the reliability 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]. When testing the reliability of the assigned value the criterion was mainly fulfilled and the assigned values were considered reliable.

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

3 Results and conclusions

3.1 Results

The terms in the results table are explained in the Appendix 7. The results and the performance of each participant are presented in Appendix 8 and the summary of the results in Table 1. The reported results with their expanded uncertainties (k=2) are presented in Appendix 9. The summaries of the z and E_n scores are shown in Appendix 10 and z scores in the ascending order in Appendix 11.

The robust standard deviations of the results varied from 1.0 to 25.6 % (Table 1). The robust standard deviations were approximately in the same range as in the previous similar proficiency test SPW 01/2018, where the deviations varied from 1.1 % to 19.2 % [6].

Table 1. The summary of the results in the proficiency test SPW 01/2019.

Measurand	Sample	Unit	Assigned value	Mean	Rob. mean	Median	s_{rob}	s_{rob} %	2 x s_{pt} %	n_{all}	Acc z %
$Cl_{2, comb}$	U1K	mg/l	0.40	0.40	0.40	0.41	0.04	10.0	25.0	21	95
	U2K	mg/l	0.74	0.75	0.74	0.74	0.06	7.8	20.0	20	89
$Cl_{2, free}$	U1K	mg/l	0.51	0.51	0.51	0.52	0.05	10.6	20.0	21	100
	U2K	mg/l	0.38	0.38	0.38	0.38	0.04	10.2	20.0	20	95
$Cl_{2, total}$	U1K	mg/l	0.92	0.92	0.92	0.92	0.03	3.3	10.0	21	100
	U2K	mg/l	1.12	1.13	1.12	1.13	0.03	3.0	10.0	20	100
$KMnO_4$	U1P	mg/l	6.77	6.75	6.77	6.68	0.56	8.2	20.0	20	90
	U2P	mg/l	13.0	13.0	13.0	13.1	0.7	5.1	15.0	20	95
NO_3	U1N	mg/l	33.4	33.4	33.4	33.6	1.4	4.3	10.0	17	94
	U2N	mg/l	6.62	6.60	6.62	6.60	0.34	5.2	10.0	17	82
pH	U1H		7.39	7.40	7.39	7.40	0.09	1.2	2.7	22	95
	U2H		5.97	5.98	5.97	5.96	0.06	1.0	3.4	21	100
Turbidity	U1S	FNU	0.59	0.60	0.59	0.61	0.06	10.5	25.0	21	90
	U2S	FNU	0.29	0.29	0.29	0.30	0.03	12.2	25.0	21	90
Urea	A1U	mg/l	0.41	0.42	0.42	0.42	0.03	6.6	15.0	14	93
Urea	UE2	mg/l	0.86	0.91	0.84	0.90	0.13	14.9	15.0	7	71
Urea	UK2	mg/l	0.47	0.48	0.55	0.47	0.14	25.6	20.0	7	71

Rob. mean: the robust mean, 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, Acc z %: the results (%), where $|z| \leq 2$, n_{all}: the number of the participants.

Table 2. The summary of repeatability on the basis of replicate determinations (ANOVA statistics).

Measurand	Sample	Unit	Assigned value	Mean	s_w	s_b	s_t	s_w%	s_b%	s_t%	s_b/s_w
$Cl_{2, comb}$	U1K	mg/l	0.40	0.40	0.0105	0.0348	0.0364	2.6	8.7	9.1	3.3
	U2K	mg/l	0.74	0.75	0.0156	0.0884	0.0898	2.2	12	12	5.7
$Cl_{2, free}$	U1K	mg/l	0.51	0.51	0.0147	0.0466	0.0489	2.9	9.1	9.6	3.2
	U2K	mg/l	0.38	0.38	0.0463	0.0136	0.0482	12	3.6	13	0.29
$Cl_{2, total}$	U1K	mg/l	0.92	0.92	0.0106	0.0282	0.0302	1.2	3.1	3.3	2.7
	U2K	mg/l	1.12	1.13	0.0174	0.0352	0.0392	1.6	3.1	3.5	2.0
Turbidity	U1S	FNU	0.59	0.60	0.0284	0.0790	0.0840	4.9	14	14	2.8
	U2S	FNU	0.29	0.29	0.0199	0.0304	0.0363	6.9	11	13	1.5
Urea	A1U	mg/l	0.41	0.42	0.0428	0	0.0428	10	0	10	0
Urea	UE2	mg/l	0.86	0.91	0.0167	0.191	0.192	2.1	24	24	11
Urea	UK2	mg/l	0.47	0.48	0.0194	0.143	0.145	3.5	26	26	7.4

s_w**:** repeatability standard error; s_b**:** between participants standard error; s_t: reproducibility standard error.

In this PT the participants were requested to report duplicate results for chlorine, turbidity and urea measurements. The participants reported the replicates with the exception of two participants for some measurands (Appendix 5). The results of the replicate determinations based on the ANOVA statistical handling are presented in Table 2. The estimation of the robustness of the methods could be done by the ratio s_b/s_w. The ratio s_b/s_w should not be exceeded 3 for robust methods. However, in some cases the robustness exceeded the value 3 and varied between 0 and 11 (Table 2).

3.2 Analytical methods

The participants were allowed to use different analytical methods for the measurands in the PT. The results of the participants grouped by methods are shown in more detail in Appendix 12. The statistical comparison of the analytical methods was possible for the data where the number of the results was ≥ 5.

Chlorine ($Cl_{2,\ comb}$, $Cl_{2,\ free}$, $Cl_{2,\ total}$)
In the measurements of the total and free chlorine over 80 % of the participants used the colorimetric method based on the standard method EN ISO 7393-2 and one participant used the titrimetric method based on the standard method EN ISO 7393-1 (Appendix 12). Two participants used other methods (both were photometric methods). The combined chlorine was calculated as the difference of the total and free chlorine concentrations based on the EN ISO 7393 (Appendix 12). Based on the visual evaluation no differences between the methods were observed (Appendix 12).

Permangate index ($KMnO_4$)
In the measurements of permanganate index mainly the automatic titrimetric method and the manual titrimetric method based on the standard method SFS 3036 were used (Appendix 12). In the statistical comparison of the analytical methods no statistically significant differences were noticed.

Nitrate (NO_3)
Nine participants used automatic CFA or FIA method based on the standard method EN ISO 13395 (Appendix 12). Three participants used IC method based on the standard method EN ISO 10304. The sulfanilamide spectrophotometric method after hydrazine reduction was used by three participants and after Cd/Cu reduction by one participant. One participant used the Hach Lange tube method. Based on the visual evaluation no differences between the used methods were observed (Appendix 12).

pH
About 60 % of the participants measured pH using the electrode for low ionic waters and 40 % of the participants used the universal electrode. One participant used some other electrode in the pH measurements (Appendix 12). In the statistical method comparison no statistically significant differences were observed between the used electrodes.

Turbidity
Participants measured turbidity mainly with an apparatus based on diffused radiation measurement with exception of two participants, who used attenuation of radiant flux measurement (Appendix 12).

Urea
For urea measurement enzymatic photometric method was used as often as Koroleff's method (Appendix 12) [7]. For the synthetic sample A1U no statistically significant difference between the used analytical methods was observed. For the swimming pool water sample U2U a clear difference between the used analytical methods was observed (Appendix 12). The similar

difference has been observed also in the previous similar proficiency tests, e.g. SPW 01/2018 [6]. The reported results obtained with the Koroleff's method (UK2) were about 55 % of the calculated concentration for the swimming pool water sample, while the reported results obtained with the enzymatic method (UE2) were close to the calculated value (Table 1, Appendix 12). Due to this difference, the calculated value was used as the assigned value only for the results obtained by the enzymatic method.

3.3 Uncertainties of the results

Almost all participants (ca. 95 %) reported the expanded uncertainties (k=2) with their results for at least some of their results (Table 3, Appendix 13). 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 13). The most commonly used approach was based on using the internal quality control data in the estimation (Appendix 13). At maximum seven participants used MUkit measurement uncertainty software for the estimation of their uncertainties [8]. The free software is available in 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 3. The range of the expanded measurement uncertainties (k=2, U_i%) reported by the participants.

Measurement	Sample	The range of U_i %
$Cl_{2,\ comb}$	U1K	10-42
	U2K	10-40
$Cl_{2,\ free}$	U1K	10-25
	U2K	10-42
$Cl_{2,\ total}$	U1K	6-27
	U2K	6-27
$KMnO_4$	U1P	6-46
	U2P	6-31
NO_3	U1N	4-22
	U2N	4-22
pH	U1H	1-17
	U2H	1-14
Turbidity	U1S	5-50
	U2S	5-50
Urea	A1U	12-40
	UE2	15-25
	UK2	12-40

4 Evaluation of the results

The performance evaluation of the participants was based mainly on the z scores. The assessment of urea results based on the Koroleff's method (UK2) using z score is given as indicative due to the low number of results (n_{stat}<6). Those results were also evaluated with E_n scores. 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

The summary of the performance evaluation and comparison to the previous similar proficiency test is presented in Table 4. In total, 93 % of the results evaluated with z scores were satisfactory when total deviation of 10–25 % and 0.2 pH units from the assigned values was accepted. 91 % of participants used accredited analytical methods at least for a part of the measurands and 93 % of their results were satisfactory (Appendix 10). Of the results evaluated with E_n scores, 71 % were satisfactory. In the previous similar PT, SPW 01/2018, the performance was satisfactory for 92 % of the results, when accepting the deviation of 8–30 % and 0.2 pH units from the assigned value [6].

Evaluation of the urea measurements

The results of urea determination have been evaluated, both those obtained with Koroleff's method and those obtained with enzymatic photometric method for the synthetic sample A1U. As observed in the previous similar proficiency tests, a clear difference between the urea results obtained with Koroleff's method (UK2) and enzymatic photometric method (urea degraded using urease, UE2) in the swimming pool water was evident also here. The mean value of the reported results obtained by Koroleff's method was in average 53 % of the value obtained by the enzymatic method (Table 1). The reported results obtained with the Koroleff's method were about 55 % of the calculated concentration for the swimming pool water sample U2U, while the reported results obtained with the enzymatic method were in vicinity of the calculated value. Due to this difference, it was possible to use the calculated value as the assigned value only for the results obtained by the enzymatic method for the swimming water sample (Appendix 6).

Table 4. Summary of the performance evaluation in the proficiency test SPW 01/2019.

Measurand	2 x s_{pt}%	Satisfactory results, %	Remarks
$Cl_{2, comb}$	20-25	92	Good performance. In the SPW 01/2018 the performance was satisfactory for 95 % of the results, when accepting the deviation of 20-30 % from the assigned value [6].
$Cl_{2, free}$	20	97	Excellent performance. In the SPW 01/2018 the performance was satisfactory for 85 % of the results, with the same range of standard deviation for performance assessment [6].
$Cl_{2, total}$	10	100	Excellent performance. In the SPW 01/2018 the performance was satisfactory for 97 % of the results, when accepting the deviation of 10-15 % from the assigned value [6].
$KMnO_4$	15–20	93	Good performance. In the SPW 01/2018 the performance was satisfactory for 98 % of the results, with the same range of standard deviation for performance assessment [6].
NO_3	10	88	In the SPW 01/2018 the performance was satisfactory for 97 % of the results, when accepting the deviation of 8-10 % from the assigned value [6].
pH	2.7-3.4	98	Excellent performance. In the SPW 01/2018 the performance was satisfactory for 93 % of the results, when accepting the deviation of 2.7-3.3 % from the assigned value [6].
Turbidity	25	90	Good performance. In the SPW 01/2018 the performance was satisfactory for 90 % of the results, when accepting the deviation of 30 % from the assigned value [6].
Urea A1U	15	93	Good performance. In the SPW 01/2018 the performance was satisfactory for 85 % of the results with the same range of standard deviation for performance assessment [6].
Enzymatic, UE2	15	71	Difficulties in measurements of the sample, <80 % satisfactory results. The recovery is in average 106 % of the calculated value. Based on the PT the method is suitable for urea measurements of swimming pool waters. In the SPW 01/2018 the performance was satisfactory for 71 % of the results with the same range of standard deviation for performance assessment [6].
Koroleff, UK2	20	z score 71 E_n score 71	Approximate performance evaluation based on z score (low number of results). Difficulties in measurements of the sample, <80 % satisfactory results. The recovery is in average 56 % of the calculated value and 53 % of the results obtained by enzymatic method. Usage of the method for swimming pool waters requires method validation where the matrix effect needs to be taken into consideration. In the SPW 01/2018 the performance was satisfactory for 67 % of the results with the same range of standard deviation for performance assessment [6].

The recovery for urea in the swimming water sample was calculated from the mean concentrations of different methods (recovery% = 100 × mean of results / calculated value). The recovery for the enzymatic method was 106 %, while for the Koroleff's method it was 56 %. The recovery percentage for the results obtained by Koroleff's method is in the same range as in the previous similar proficiency test SPW 01/2018 (55 %) [6]. In Finland, the national supervisory authority for welfare and health (Valvira) has taken into account the differences between urea concentrations obtained by Koroleff's method and enzymatic photometric method in the national guide for quality and monitoring of swimming pool waters [10]. The participants are encouraged to continue reporting more results obtained by the enzymatic photometric method for better method comparison.

5 Summary

Proftest SYKE carried out the proficiency test (PT) for analysis of combined chlorine, free chlorine, total chlorine, permanganate index ($KMnO_4$), nitrate, pH, turbidity, and urea from swimming pool waters in January-February 2019 (SPW 01/2019). In total, 22 participants joined in this proficiency test.

The evaluation of the performance was based on the z scores, which were calculated using the assigned value and standard deviation for proficiency assessment at 95 % confidence level. In this PT 93 % of the data evaluated based on the z scores was regarded satisfactory when the results were accepted to deviate 10 to 25 % or 0.2 pH units from the assigned value. E_n scores were used in the evaluation of urea results obtained by Koroleff's method of the swimming pool water sample (UK2), and 71 % of those results were satisfactory. The calculated value was used as the assigned value for the urea measurements of the synthetic sample (A1U) and of the sample UE2 (enzymatic method). The robust mean of the results reported by participants was used as the assigned value for the other measurements, with the exception of urea measurement with the Koroleff's method (sample UK2), where the median value was used (n_{stat}<6).

Notice should be taken that there is a clear difference between the urea results of the swimming pool water sample (U2U) measured with the Koroleff's method and with the enzymatic photometric method. The reported results obtained with the Koroleff's method were about 55 % of the calculated concentration, while the reported results obtained with the enzymatic method were in vicinity of the calculated value. It is recommended to use the enzymatic photometric method for the urea measurements of the swimming pool waters or to validate the Koroleff's method for the urea determination of the swimming pool waters.

6 Summary in Finnish

Proftest SYKE järjesti tammi-helmikuussa 2019 pätevyyskokeen uima-allasvesiä analysoiville laboratorioille (SPW 01/2019). Pätevyyskokeessa testattiin allasvesien kloori-, $KMnO_4$-, NO_3-, pH-, sameus- ja ureamäärityksiä. Ureamääritystä varten toimitettiin myös synteettinen näyte. Pätevyyskokeeseen osallistui yhteensä 22 laboratoriota.

Pätevyyden arvioimisessa käytettiin pääsääntöisesti z-arvoa ja sitä laskettaessa tuloksille sallittiin pH-määrityksessä 0,2 pH-yksikön ja muissa määrityksissä 10–25 %:n poikkeama vertailuarvosta. Laskennallista pitoisuutta käytettiin vertailuarvona synteettisen näytteen (A1U) sekä näytteen UE2 (entsymaattinen menetelmä) ureamäärityksissä. Muissa määrityksissä vertailuarvona käytettiin osallistujien tulosten robustia keskiarvoa, poikkeuksena näytteen UK2 (Koroleffin menetelmä) ureamääritys, missä käytettiin tulosaineiston mediaania (n_{stat}<6). Hyväksyttäviä tuloksia oli kokonaisuudessaan 93 %. Koroleffin menetelmällä määritetyn uima-allasveden, UK2, tulokset arvioitiin lisäksi E_n-arvoilla ja näistä tuloksista hyväksyttäviä oli 71 %.

Uima-allasvesinäytteiden ureatuloksissa havaittiin ero Koroleffin menetelmän ja entsymaattisen spektrometrisen menetelmän välillä. Vastaava ero on havaittu myös aikaisemmissa pätevyyskokeissa. Koroleffin menetelmään perustuvalla määrityksellä saadut tulokset poikkesivat huomattavasti laskennallisista pitoisuuksista. Koroleffin menetelmällä saadut ureapitoisuudet olivat noin 55 % laskennallisesta vertailuarvosta, kun entsymaattisella testillä määritetyt tulokset ovat lähellä laskennallista arvoa. Onkin suositeltavaa käyttää entsymaattista spektrometristä menetelmää uima-allasvesien ureapitoisuuksien määrittämisessä. Käytettäessä Koroleffin menetelmää uima-allasvesien ureapitoisuuden määrittämiseen tulisi näytetyypin vaikutus tuloksiin selvittää paremmin.

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APPENDIX 1: Participants in the proficiency test

Country	Participant
Finland	Eurofins Ahma Oy Seinäjoki
	Eurofins Ahma Oy, Rovaniemi
	Eurofins Environment Testing Finland Oy, Lahti
	Eurofins Nab Labs Oy Jyväskylä
	KVVY Tutkimus Oy, Tampere
	KVVY-Botnialab, Vaasa
	Kymen Ympäristölaboratorio Oy
	Lounais-Suomen vesi- ja ympäristötutkimus Oy, Turku
	MetropoliLab Oy
	Saimaan Vesi- ja Ympäristötutkimus Oy, Lappeenranta
	Savo-Karjalan Ympäristötutkimus Oy, Joensuu
	Savo-Karjalan Ympäristötutkimus Oy, Kajaani
	Savo-Karjalan Ympäristötutkimus Oy, Kuopio
	ScanLab Oy
	SeiLab Oy Haapaveden toimipiste
	SeiLab Oy Seinäjoen toimipiste
	Snellmans Köttförädling, Laboratorium
	SYKE Oulun toimipaikka
	Vita Laboratoriot Oy
	ÅMHM laboratoriet, Jomala, Åland
Germany	Eigenbetrieb Stadtentwässerung Stuttgart (SES)
Sweden	Eurofins Water Testing Sweden AB

APPENDIX 2: Preparation of the samples

Measurand/Sample		U1K	U2K
$Cl_{2, comb}$	Initial concentration, mg/l	< 0.1	< 0.1
	Added compound (producer) Addition, mg/l	$C_7H_7ClNaNO_2S^*$ $3H_2O$ (Merck) 0.38	$C_7H_7ClNaNO_2S^*$ $3H_2O$ 0.75
	Assigned value, mg/l	0.40	0.74
$Cl_{2, free}$	Initial concentration, mg/l	< 0.1	< 0.1
	Added compound (producer) Addition, mg/l	NaClO (BHD) 0.60	NaClO (BHD) 0.45
	Assigned value, mg/l	0.51	0.38
$Cl_{2, total}$	Initial concentration, mg/l	0.17	0.17
	Addition, mg/l	0.98	1.21
	Assigned value, mg/l	0.92	1.12
		U1P	U2P
$KMnO_4$	Initial concentration, mg/l	0.5	0.5
	Added compound (producer) Addition, mg/l	$C_7H_6O_3$ (Fluka) 5.21	$C_7H_6O_3$ (Fluka) 11.6
	Assigned value, mg/l	6.77	13.0
		U1N	U2N
NO_3	Initial concentration, mg/l	13.1	13.1
	Added compound (producer) Addition, mg/l	$NaNO_3$ (Merck) 20.9	- -
	Dilution	-	1 : 1
	Assigned value, mg/l	33.4	6.62
		U1H	U2H
pH	Initial concentration	7.11	7.11
	pH adjustment	-	$C_8H_5KO_4$ (Radiometer, pH 4.0)
	Assigned value	7.39	5.97
		U1S	U2S
Turbidity	Initial concentration, FNU	0.09	0.09
	Added compound (producer) Addition, FNU	Formazin (Hach) 0.60	Formazin (Hach) 0.26
	Assigned value, FNU	0.59	0.29
		A1U	UE2 / UK2
Urea	Initial concentration, mg/l	-	< 0.1
	Added compound (producer) Addition, mg/l	$CO(NH_2)_2$ (Merck) 0.43	$CO(NH_2)_2$ (Merck) 0.89
	Assigned value, mg/l	0.41	0.86 / 0.47

APPENDIX 3: Homogeneity of the samples

Homogeneity was tested from duplicate measurements of selected measurement from four to eight samples of each sample types.

Criteria for homogeneity:

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

s_{pt} = standard deviation for proficiency assessment
s_{anal} = analytical deviation, standard deviation of the results within sub samples
s_{sam} = between-sample deviation, standard deviation of the results between sub samples

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

F1 and F2 are constants of F distribution derived from the standard statistical tables for the tested number of samples [2, 3].

Measurand/Sample	Concentration mg/l or FNU	n	s_{pt}%	s_{pt}	s_{anal}	s_{anal}/s_{pt}	$s_{anal}/s_{pt}<0.5$?	s_{sam}	s_{sam}^2	c	$s_{sam}^2<c$?
$KMnO_4$ / U1P	6.65	4	10	0.66	0.12	0.18	Yes	0.24	0.06	0.14	Yes
$KMnO_4$ / U2P	12.9	4	7.5	0.97	0.19	0.20	Yes	0.06	0.004	0.32	Yes
NO_3 / U1N	33.1	4	5	1.65	0.12	0.07	Yes	0.14	0.02	0.68	Yes
NO_3 / U2N	6.36	4	5	0.32	0.09	0.27	Yes	0	0	0.05	Yes
pH / U1H	7.42	8	1.35	0.10	0.01	0.14	Yes	0.03	0.0009	0.002	Yes
pH / U2H	6.00	8	1.7	0.10	0.02	0.15	Yes	0.02	0.0003	0.002	Yes
Turbidity / U1S	0.67	4	12.5	0.08	0.01	0.14	Yes	0	0	0.002	Yes
Turbidity / U2S	0.33	4	12.5	0.04	0.01	0.25	Yes	0	0	0.0007	Yes
Urea / U2U	0.91	4	7.5	0.07	0.008	0.11	Yes	0	0	0.001	Yes

Conclusion: The criteria of homogeneity fulfilled for all tested parameters and the samples could be regarded homogeneous.

APPENDIX 4: Stability of the samples

The samples were delivered 29 January 2019 and they arrived to the participants mainly on the following day. The samples were requested to be measured on 31 January 2019. Stability of pH, $Cl_{2,\ free}$, $Cl_{2,\ comb}$, $Cl_{2,\ total}$, and urea was tested by analyzing the samples stored at the temperatures 4 and 20 ºC.

Criteria for stability: $D < 0.3 \times s_{pt}$, where
D = |the difference of results measured from the samples stored at the temperatures 4 °C and 20 °C|
s_{pt} = standard deviation for proficiency assessment

$Cl_{2,\ comb}$

Sample	Result, mg/l		Sample	Result, mg/l	
Date	31.1. (20 ºC)	31.1. (4 ºC)	Date	31.1. (20 ºC)	31.1. (4 ºC)
U1K	0.430	0.439	U2K	0.809	0.811
D	0.009		D	0.002	
$0.3 \times s_{pt}$	0.02		$0.3 \times s_{pt}$	0.02	
$D < 0.3 \times s_{pt}$? Yes			$D < 0.3 \times s_{pt}$? Yes		

$Cl_{2,\ free}$

Sample	Result, mg/l		Sample	Result, mg/l	
Date	31.1. (20 ºC)	31.1. (4 ºC)	Date	31.1. (20 ºC)	31.1. (4 ºC)
U1K	0.511	0.510	U2K	0.356	0.352
D	0.001		D	0.004	
$0.3 \times s_{pt}$	0.02		$0.3 \times s_{pt}$	0.01	
$D < 0.3 \times s_{pt}$? Yes			$D < 0.3 \times s_{pt}$? Yes		

$Cl_{2,\ total}$

Sample	Result, mg/l		Sample	Result, mg/l	
Date	31.1. (20 ºC)	31.1. (4 ºC)	Date	31.1. (20 ºC)	31.1. (4 ºC)
U1K	0.941	0.949	U2K	1.168	1.165
D	0.008		D	0.003	
$0.3 \times s_{pt}$	0.01		$0.3 \times s_{pt}$	0.02	
$D < 0.3 \times s_{pt}$? Yes			$D < 0.3 \times s_{pt}$? Yes		

pH

Sample	Result		Sample	Result	
Date	31.1. (20 ºC)	31.1. (4 ºC)	Date	31.1. (20 ºC)	31.1. (4 ºC)
U1H	7.26	7.33	U2H	5.93	5.94
D	0.07		D	0.01	
$0.3 \times s_{pt}$	0.03		$0.3 \times s_{pt}$	0.03	
$D < 0.3 \times s_{pt}$? No[1)]			$D < 0.3 \times s_{pt}$? Yes		

[1)]The difference is within the analytic error

Urea

Sample	Result, mg/l		Sample	Result, mg/l	
Date	31.1. (20 ºC)	31.1. (4 ºC)	Date	31.1. (20 ºC)	31.1. (4 ºC)
A1U	0.424	0.424	U2U	0.932	0.931
D	0		D	0.001	
$0.3 \times s_{pt}$	0.009		$0.3 \times s_{pt}$	0.02	
$D < 0.3 \times s_{pt}$? Yes			$D < 0.3 \times s_{pt}$? Yes		

Conclusion: The criteria for stability mainly fulfilled. For pH in the sample U1H, the noticed variation of results is within the analytical error. Thus the samples could be regarded stable.

APPENDIX 5: Feedback from the proficiency test

FEEDBACK FROM THE PARTICIPANTS

Participant	Comments on technical excecution	Action / Proftest SYKE
4	Participant received the samples one day after the estimated delivery day.	The distributor informed they had difficulties in delivering of the samples due to bad weather.
5	The bottle for the temperature control was missing.	The provider will pay more attention for the delivery in the future.
8	The participant did not receive the addition solution L2K.	The missing bottle was delivered to the participant. The provider will pay more attention for the delivery in the future.
11	The cool box was broken during the delivery.	The samples were not damaged and no further action was required.
18	Participant received the samples one day after the estimated delivery day.	According to the distributor's tracking system the samples arrived to the participant on time.

Participant	Comments to the results	Action / Proftest SYKE
10	The participant reported their urea result as Koroleff's method result (UK2) but gave further information about the method: urea was degraded into ammonium and CO_2 using urease and ammonium was analyzed by the standardized photometric method.	As the participant degraded urea into ammonium and CO_2 using urease, their method responded to the enzymatic method (UE2) not to the Koroleff's method (UK2) as reported. The reported result was outlier in the statistical treatment, and thus did not affect the performance evaluation. If the results had been reported correctly (as sample UE2), the result would have been satisfactory, as the z score would have been –0.47. The provider will consider how to collect the data for urea results, use of terminology and describe the differences of these two methods more in detail for the next similar proficiency test.
20	The results for $KMnO_4$ and NO_3 were reported in the wrong unit. The corrected results were: $KMnO_4$ U1P: 6.52 mg/l U2P: 13.04 mg/l NO_3 U1N: 32.78 mg/l U2N: 6.62 mg/l	The results were outliers in the statistical treatment, and thus did not affect the performance evaluation. If the results had been reported correctly, the results would have been satisfactory. The participant can re-calculate the z scores according to the Guide for participants [5].

FEEDBACK TO THE PARTICIPANTS

Participant	Comments
3, 19, 20	The participants did not return the sample arrival document to the provider. Thus their information of the sample arrival temperature missed as well. The participants should follow the instructions of the provider.
4, 19	The participant reported only one result for chlorine measurements (4) and for turbidity measurement (19), though replicate results were requested. These results were not included in the statistical calculations. The provider recommends the participants to follow the given instructions.
1, 2, 10, 17, 18	For these participants the deviation of replicate measurements for some measurands (i.e. $Cl_{2,\ comb}$, $Cl_{2,\ free}$ (1, 10, 18), urea (2, 17, 18)) in the samples U1K, U2K, and A1U was high and those results were Cochran outliers. The provider recommends the participants to validate their accepted deviation of replicate measurements.
1, 9	The participants did not report the expanded measurement uncertainties for some measurands. Participants are accredited laboratories, whom should report uncertainties with their results.
Participants using Koroleff's method	It is recommended to validate the Koroleff's method for the urea measurements from the swimming pool waters.
All	The participants are encouraged to report more results obtained by the enzymatic photometric method for the better method comparison with the Koroleff's method.

APPENDIX 6: 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}
$Cl_{2,\ comb}$	U1K	mg/l	0.40	0.02	5.7	Robust mean	0.23
	U2K	mg/l	0.74	0.03	4.5	Robust mean	0.23
$Cl_{2,\ free}$	U1K	mg/l	0.51	0.03	5.9	Robust mean	0.30
	U2K	mg/l	0.38	0.02	6.0	Robust mean	0.30
$Cl_{2,\ total}$	U1K	mg/l	0.92	0.02	1.8	Robust mean	0.18
	U2K	mg/l	1.12	0.02	1.7	Robust mean	0.17
$KMnO_4$	U1P	mg/l	6.77	0.33	4.8	Robust mean	0.24
	U2P	mg/l	13.0	0.4	2.9	Robust mean	0.19
NO_3	U1N	mg/l	33.4	0.9	2.7	Robust mean	0.27
	U2N	mg/l	6.62	0.23	3.4	Robust mean	0.34
pH	U1H		7.39	0.04	0.6	Robust mean	0.22
	U2H		5.97	0.03	0.5	Robust mean	0.15
Turbidity	U1S	FNU	0.59	0.03	5.7	Robust mean	0.23
	U2S	FNU	0.29	0.02	7.2	Robust mean	0.29
Urea	A1U	mg/l	0.41	0.00	0.6	Calculated value	0.04
Urea	UE2	mg/l	0.86	0.01	0.6	Calculated value	0.04
Urea	UK2	mg/l	0.47	0.02	4.2	Median	0.21

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 7: 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 [2].

APPENDIX 8: Results of each participant

Participant 1												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	$2\times s_{pt}$ %	Participant's result	Md	Mean	s	s %	n_{stat}
$Cl_{2,\ comb}$	mg/l	U1K		2.80	0.40	25	0.54	0.41	0.40	0.04	8.9	19
$Cl_{2,\ free}$	mg/l	U1K		-1.57	0.51	20	0.43	0.52	0.51	0.05	9.3	20
$Cl_{2,\ total}$	mg/l	U1K		1.09	0.92	10	0.97	0.92	0.92	0.03	3.2	20
pH		U1H		0.10	7.39	2,7	7.40	7.40	7.40	0.08	1.0	22

Participant 2												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	$2\times s_{pt}$ %	Participant's result	Md	Mean	s	s %	n_{stat}
$Cl_{2,\ comb}$	mg/l	U1K		-0.28	0.40	25	0.39	0.41	0.40	0.04	8.9	19
	mg/l	U2K		0.01	0.74	20	0.74	0.74	0.75	0.04	5.8	19
$Cl_{2,\ free}$	mg/l	U1K		0.71	0.51	20	0.55	0.52	0.51	0.05	9.3	20
	mg/l	U2K		0.91	0.38	20	0.41	0.38	0.38	0.04	9.4	18
$Cl_{2,\ total}$	mg/l	U1K		0.26	0.92	10	0.93	0.92	0.92	0.03	3.2	20
	mg/l	U2K		0.62	1.12	10	1.16	1.13	1.13	0.03	2.2	19
$KMnO_4$	mg/l	U1P		0.74	6.77	20	7.27	6.68	6.75	0.53	7.8	18
	mg/l	U2P		0.31	13.0	15	13.3	13.1	13.0	0.7	5.1	19
pH		U1H		-0.10	7.39	2,7	7.38	7.40	7.40	0.08	1.0	22
		U2H		0.20	5.97	3,4	5.99	5.96	5.98	0.06	1.0	21
Turbidity	FNU	U1S		-0.47	0.59	25	0.56	0.61	0.60	0.05	7.9	21
	FNU	U2S		-0.97	0.29	25	0.26	0.30	0.29	0.03	11.7	18
Urea	mg/l	A1U		0.83	0.41	15	0.44	0.42	0.42	0.03	6.7	13
Urea	mg/l	UE2		1.22	0.86	15	0.94	0.90	0.91	0.02	2.6	5

Participant 3												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	$2\times s_{pt}$ %	Participant's result	Md	Mean	s	s %	n_{stat}
$Cl_{2,\ comb}$	mg/l	U1K		0.80	0.40	25	0.44	0.41	0.40	0.04	8.9	19
	mg/l	U2K		0.95	0.74	20	0.81	0.74	0.75	0.04	5.8	19
$Cl_{2,\ free}$	mg/l	U1K		0.00	0.51	20	0.51	0.52	0.51	0.05	9.3	20
	mg/l	U2K		-1.05	0.38	20	0.34	0.38	0.38	0.04	9.4	18
$Cl_{2,\ total}$	mg/l	U1K		0.65	0.92	10	0.95	0.92	0.92	0.03	3.2	20
	mg/l	U2K		0.54	1.12	10	1.15	1.13	1.13	0.03	2.2	19
$KMnO_4$	mg/l	U1P		-0.69	6.77	20	6.30	6.68	6.75	0.53	7.8	18
	mg/l	U2P		-0.21	13.0	15	12.8	13.1	13.0	0.7	5.1	19
NO_3	mg/l	U1N		0.12	33.4	10	33.6	33.6	33.4	1.3	3.8	16
	mg/l	U2N		4.17	6.62	10	8.00	6.60	6.60	0.36	5.4	15
pH		U1H		0.10	7.39	2,7	7.40	7.40	7.40	0.08	1.0	22
		U2H		-0.69	5.97	3,4	5.90	5.96	5.98	0.06	1.0	21
Turbidity	FNU	U1S		-2.24	0.59	25	0.43	0.61	0.60	0.05	7.9	21
	FNU	U2S		-0.28	0.29	25	0.28	0.30	0.29	0.03	11.7	18

Participant 4												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
$Cl_{2, comb}$	mg/l	U1K			0.40	25	*0,050**	0.41	0.40	0.04	8.9	19
	mg/l	U2K			0.74	20	*0,070**	0.74	0.75	0.04	5.8	19
$Cl_{2, free}$	mg/l	U1K			0.51	20	*0,89**	0.52	0.51	0.05	9.3	20
	mg/l	U2K			0.38	20	*1,11**	0.38	0.38	0.04	9.4	18
$Cl_{2, total}$	mg/l	U1K			0.92	10	*0,94**	0.92	0.92	0.03	3.2	20
	mg/l	U2K			1.12	10	*1,18**	1.13	1.13	0.03	2.2	19
$KMnO_4$	mg/l	U1P		0.68	6.77	20	7.23	6.68	6.75	0.53	7.8	18
	mg/l	U2P		-0.82	13.0	15	12.2	13.1	13.0	0.7	5.1	19
NO_3	mg/l	U1N		0.18	33.4	10	33.7	33.6	33.4	1.3	3.8	16
	mg/l	U2N		-0.60	6.62	10	6.42	6.60	6.60	0.36	5.4	15
pH		U1H		-0.40	7.39	2,7	7.35	7.40	7.40	0.08	1.0	22
		U2H		0.59	5.97	3,4	6.03	5.96	5.98	0.06	1.0	21
Turbidity	FNU	U1S		-3.46	0.59	25	0.34	0.61	0.60	0.05	7.9	21
	FNU	U2S		9.93	0.29	25	0.65	0.30	0.29	0.03	11.7	18

* Participant did not report requested replicate results.

Participant 5												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
$Cl_{2, comb}$	mg/l	U1K		-1.03	0.40	25	0.35	0.41	0.40	0.04	8.9	19
	mg/l	U2K		-0.59	0.74	20	0.70	0.74	0.75	0.04	5.8	19
$Cl_{2, free}$	mg/l	U1K		1.14	0.51	20	0.57	0.52	0.51	0.05	9.3	20
	mg/l	U2K		0.66	0.38	20	0.41	0.38	0.38	0.04	9.4	18
$Cl_{2, total}$	mg/l	U1K		-0.08	0.92	10	0.92	0.92	0.92	0.03	3.2	20
	mg/l	U2K		-0.36	1.12	10	1.10	1.13	1.13	0.03	2.2	19
pH		U1H		0.30	7.39	2,7	7.42	7.40	7.40	0.08	1.0	22
		U2H		0.10	5.97	3,4	5.98	5.96	5.98	0.06	1.0	21
Turbidity	FNU	U1S		1.12	0.59	25	0.67	0.61	0.60	0.05	7.9	21
	FNU	U2S		0.41	0.29	25	0.31	0.30	0.29	0.03	11.7	18

Participant 6												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
$Cl_{2, comb}$	mg/l	U1K		0.90	0.40	25	0.45	0.41	0.40	0.04	8.9	19
	mg/l	U2K		0.81	0.74	20	0.80	0.74	0.75	0.04	5.8	19
$Cl_{2, free}$	mg/l	U1K		0.20	0.51	20	0.52	0.52	0.51	0.05	9.3	20
	mg/l	U2K		-0.53	0.38	20	0.36	0.38	0.38	0.04	9.4	18
$Cl_{2, total}$	mg/l	U1K		0.65	0.92	10	0.95	0.92	0.92	0.03	3.2	20
	mg/l	U2K		0.89	1.12	10	1.17	1.13	1.13	0.03	2.2	19
$KMnO_4$	mg/l	U1P		-0.43	6.77	20	6.48	6.68	6.75	0.53	7.8	18
	mg/l	U2P		-0.41	13.0	15	12.6	13.1	13.0	0.7	5.1	19
NO_3	mg/l	U1N		-1.26	33.4	10	31.3	33.6	33.4	1.3	3.8	16
	mg/l	U2N		-1.15	6.62	10	6.24	6.60	6.60	0.36	5.4	15
pH		U1H		-0.10	7.39	2,7	7.38	7.40	7.40	0.08	1.0	22
		U2H		0.30	5.97	3,4	6.00	5.96	5.98	0.06	1.0	21
Turbidity	FNU	U1S		0.41	0.59	25	0.62	0.61	0.60	0.05	7.9	21
	FNU	U2S		-1.93	0.29	25	0.22	0.30	0.29	0.03	11.7	18
Urea	mg/l	A1U		0.00	0.41	15	0.41	0.42	0.42	0.03	6.7	13
Urea	mg/l	UK2		4.79	0.47	20	0.70	0.47	0.48	0.02	4.7	5

Participant 7												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
$Cl_{2, comb}$	mg/l	U1K		0.28	0.40	25	0.41	0.41	0.40	0.04	8.9	19
	mg/l	U2K		0.00	0.74	20	0.74	0.74	0.75	0.04	5.8	19
$Cl_{2, free}$	mg/l	U1K		0.04	0.51	20	0.51	0.52	0.51	0.05	9.3	20
	mg/l	U2K		0.64	0.38	20	0.40	0.38	0.38	0.04	9.4	18
$Cl_{2, total}$	mg/l	U1K		0.13	0.92	10	0.93	0.92	0.92	0.03	3.2	20
	mg/l	U2K		0.44	1.12	10	1.14	1.13	1.13	0.03	2.2	19
$KMnO_4$	mg/l	U1P		-0.25	6.77	20	6.60	6.68	6.75	0.53	7.8	18
	mg/l	U2P		-0.31	13.0	15	12.7	13.1	13.0	0.7	5.1	19
NO_3	mg/l	U1N		0.72	33.4	10	34.6	33.6	33.4	1.3	3.8	16
	mg/l	U2N		1.09	6.62	10	6.98	6.60	6.60	0.36	5.4	15
pH		U1H		-0.80	7.39	2,7	7.31	7.40	7.40	0.08	1.0	22
		U2H		-0.49	5.97	3,4	5.92	5.96	5.98	0.06	1.0	21
Turbidity	FNU	U1S		0.34	0.59	25	0.62	0.61	0.60	0.05	7.9	21
	FNU	U2S		0.55	0.29	25	0.31	0.30	0.29	0.03	11.7	18

Participant 8												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
$Cl_{2, comb}$	mg/l	U1K		-0.78	0.40	25	0.36	0.41	0.40	0.04	8.9	19
	mg/l	U2K		-0.41	0.74	20	0.71	0.74	0.75	0.04	5.8	19
$Cl_{2, free}$	mg/l	U1K		0.30	0.51	20	0.53	0.52	0.51	0.05	9.3	20
	mg/l	U2K		0.46	0.38	20	0.40	0.38	0.38	0.04	9.4	18
$Cl_{2, total}$	mg/l	U1K		-0.73	0.92	10	0.89	0.92	0.92	0.03	3.2	20
	mg/l	U2K		-0.27	1.12	10	1.11	1.13	1.13	0.03	2.2	19
$KMnO_4$	mg/l	U1P		0.28	6.77	20	6.96	6.68	6.75	0.53	7.8	18
	mg/l	U2P		0.51	13.0	15	13.5	13.1	13.0	0.7	5.1	19
NO_3	mg/l	U1N		1.14	33.4	10	35.3	33.6	33.4	1.3	3.8	16
	mg/l	U2N		1.06	6.62	10	6.97	6.60	6.60	0.36	5.4	15
pH		U1H		1.30	7.39	2,7	7.52	7.40	7.40	0.08	1.0	22
		U2H		0.69	5.97	3,4	6.04	5.96	5.98	0.06	1.0	21
Turbidity	FNU	U1S		0.60	0.59	25	0.63	0.61	0.60	0.05	7.9	21
	FNU	U2S		0.29	0.29	25	0.30	0.30	0.29	0.03	11.7	18
Urea	mg/l	A1U		-1.82	0.41	15	0.35	0.42	0.42	0.03	6.7	13
Urea	mg/l	UE2		-2.22	0.86	15	0.72	0.90	0.91	0.02	2.6	5

Participant 9												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
$Cl_{2, comb}$	mg/l	U1K		-0.35	0.40	25	0.38	0.41	0.40	0.04	8.9	19
	mg/l	U2K		0.17	0.74	20	0.75	0.74	0.75	0.04	5.8	19
$Cl_{2, free}$	mg/l	U1K		0.64	0.51	20	0.54	0.52	0.51	0.05	9.3	20
	mg/l	U2K		-0.33	0.38	20	0.37	0.38	0.38	0.04	9.4	18
$Cl_{2, total}$	mg/l	U1K		0.11	0.92	10	0.93	0.92	0.92	0.03	3.2	20
	mg/l	U2K		0.00	1.12	10	1.12	1.13	1.13	0.03	2.2	19
$KMnO_4$	mg/l	U1P		0.52	6.77	20	7.12	6.68	6.75	0.53	7.8	18
	mg/l	U2P		0.92	13.0	15	13.9	13.1	13.0	0.7	5.1	19
NO_3	mg/l	U1N		1.20	33.4	10	35.4	33.6	33.4	1.3	3.8	16
	mg/l	U2N		1.18	6.62	10	7.01	6.60	6.60	0.36	5.4	15
pH		U1H		-0.80	7.39	2,7	7.31	7.40	7.40	0.08	1.0	22
		U2H		0.79	5.97	3,4	6.05	5.96	5.98	0.06	1.0	21

Participant 9												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Turbidity	FNU	U1S		-0.96	0.59	25	0.52	0.61	0.60	0.05	7.9	21
	FNU	U2S		-1.48	0.29	25	0.24	0.30	0.29	0.03	11.7	18

Participant 10												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
$Cl_{2,\ comb}$	mg/l	U1K		-1.30	0.40	25	0.34	0.41	0.40	0.04	8.9	19
	mg/l	U2K		-0.95	0.74	20	0.67	0.74	0.75	0.04	5.8	19
$Cl_{2,\ free}$	mg/l	U1K		1.18	0.51	20	0.57	0.52	0.51	0.05	9.3	20
	mg/l	U2K		-0.26	0.38	20	0.37	0.38	0.38	0.04	9.4	18
$Cl_{2,\ total}$	mg/l	U1K		-0.33	0.92	10	0.91	0.92	0.92	0.03	3.2	20
	mg/l	U2K		-1.43	1.12	10	1.04	1.13	1.13	0.03	2.2	19
$KMnO_4$	mg/l	U1P		17.62	6.77	20	18.70	6.68	6.75	0.53	7.8	18
	mg/l	U2P		1.13	13.0	15	14.1	13.1	13.0	0.7	5.1	19
NO_3	mg/l	U1N		-0.12	33.4	10	33.2	33.6	33.4	1.3	3.8	16
	mg/l	U2N		0.60	6.62	10	6.82	6.60	6.60	0.36	5.4	15
pH		U1H		-2.81	7.39	2,7	7.11	7.40	7.40	0.08	1.0	22
		U2H		0.10	5.97	3,4	5.98	5.96	5.98	0.06	1.0	21
Turbidity	FNU	U1S		-0.68	0.59	25	0.54	0.61	0.60	0.05	7.9	21
	FNU	U2S		-0.97	0.29	25	0.26	0.30	0.29	0.03	11.7	18
Urea	mg/l	A1U		-1.06	0.41	15	0.38	0.42	0.42	0.03	6.7	13
Urea	mg/l	UK2		7.63	0.47	20	0.83	0.47	0.48	0.02	4.7	5

Participant 11												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
$Cl_{2,\ comb}$	mg/l	U1K		0.54	0.40	25	0.43	0.41	0.40	0.04	8.9	19
	mg/l	U2K		0.94	0.74	20	0.81	0.74	0.75	0.04	5.8	19
$Cl_{2,\ free}$	mg/l	U1K		0.22	0.51	20	0.52	0.52	0.51	0.05	9.3	20
	mg/l	U2K		-0.76	0.38	20	0.35	0.38	0.38	0.04	9.4	18
$Cl_{2,\ total}$	mg/l	U1K		0.61	0.92	10	0.95	0.92	0.92	0.03	3.2	20
	mg/l	U2K		0.71	1.12	10	1.16	1.13	1.13	0.03	2.2	19
$KMnO_4$	mg/l	U1P		-0.30	6.77	20	6.57	6.68	6.75	0.53	7.8	18
	mg/l	U2P		0.10	13.0	15	13.1	13.1	13.0	0.7	5.1	19
NO_3	mg/l	U1N		0.88	33.4	10	34.9	33.6	33.4	1.3	3.8	16
	mg/l	U2N		1.18	6.62	10	7.01	6.60	6.60	0.36	5.4	15
pH		U1H		-0.30	7.39	2,7	7.36	7.40	7.40	0.08	1.0	22
		U2H		-0.59	5.97	3,4	5.91	5.96	5.98	0.06	1.0	21
Turbidity	FNU	U1S		-0.76	0.59	25	0.53	0.61	0.60	0.05	7.9	21
	FNU	U2S		0.22	0.29	25	0.30	0.30	0.29	0.03	11.7	18
Urea	mg/l	A1U		0.60	0.41	15	0.43	0.42	0.42	0.03	6.7	13
Urea	mg/l	UE2		0.94	0.86	15	0.92	0.90	0.91	0.02	2.6	5

Participant 12												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
$Cl_{2, comb}$	mg/l	U1K		0.60	0.40	25	0.43	0.41	0.40	0.04	8.9	19
	mg/l	U2K		0.81	0.74	20	0.80	0.74	0.75	0.04	5.8	19
$Cl_{2, free}$	mg/l	U1K		-0.78	0.51	20	0.47	0.52	0.51	0.05	9.3	20
	mg/l	U2K		-1.84	0.38	20	0.31	0.38	0.38	0.04	9.4	18
$Cl_{2, total}$	mg/l	U1K		-0.43	0.92	10	0.90	0.92	0.92	0.03	3.2	20
	mg/l	U2K		-0.18	1.12	10	1.11	1.13	1.13	0.03	2.2	19
$KMnO_4$	mg/l	U1P		-0.25	6.77	20	6.60	6.68	6.75	0.53	7.8	18
	mg/l	U2P		-0.51	13.0	15	12.5	13.1	13.0	0.7	5.1	19
NO_3	mg/l	U1N		-0.24	33.4	10	33.0	33.6	33.4	1.3	3.8	16
	mg/l	U2N		-0.06	6.62	10	6.60	6.60	6.60	0.36	5.4	15
pH		U1H		1.10	7.39	2,7	7.50	7.40	7.40	0.08	1.0	22
		U2H		1.28	5.97	3,4	6.10	5.96	5.98	0.06	1.0	21
Turbidity	FNU	U1S		-0.20	0.59	25	0.58	0.61	0.60	0.05	7.9	21
	FNU	U2S		0.14	0.29	25	0.30	0.30	0.29	0.03	11.7	18
Urea	mg/l	A1U		17.24	0.41	15	0.94	0.42	0.42	0.03	6.7	13
Urea	mg/l	UE2		-7.05	0.86	15	0.41	0.90	0.91	0.02	2.6	5

Participant 13												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
$KMnO_4$	mg/l	U1P		0.34	6.77	20	7.00	6.68	6.75	0.53	7.8	18
	mg/l	U2P		0.41	13.0	15	13.4	13.1	13.0	0.7	5.1	19
NO_3	mg/l	U1N		-0.30	33.4	10	32.9	33.6	33.4	1.3	3.8	16
	mg/l	U2N		-0.42	6.62	10	6.48	6.60	6.60	0.36	5.4	15
pH		U1H		-1.00	7.39	2,7	7.29	7.40	7.40	0.08	1.0	22
		U2H		-0.30	5.97	3,4	5.94	5.96	5.98	0.06	1.0	21
Turbidity	FNU	U1S		0.36	0.59	25	0.62	0.61	0.60	0.05	7.9	21
	FNU	U2S		0.33	0.29	25	0.30	0.30	0.29	0.03	11.7	18

Participant 14												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
$Cl_{2, comb}$	mg/l	U1K		-0.38	0.40	25	0.38	0.41	0.40	0.04	8.9	19
	mg/l	U2K		-0.28	0.74	20	0.72	0.74	0.75	0.04	5.8	19
$Cl_{2, free}$	mg/l	U1K		1.13	0.51	20	0.57	0.52	0.51	0.05	9.3	20
	mg/l	U2K		1.07	0.38	20	0.42	0.38	0.38	0.04	9.4	18
$Cl_{2, total}$	mg/l	U1K		0.62	0.92	10	0.95	0.92	0.92	0.03	3.2	20
	mg/l	U2K		0.36	1.12	10	1.14	1.13	1.13	0.03	2.2	19
$KMnO_4$	mg/l	U1P		-1.68	6.77	20	5.63	6.68	6.75	0.53	7.8	18
	mg/l	U2P		-1.59	13.0	15	11.5	13.1	13.0	0.7	5.1	19
NO_3	mg/l	U1N		0.09	33.4	10	33.6	33.6	33.4	1.3	3.8	16
	mg/l	U2N		0.18	6.62	10	6.68	6.60	6.60	0.36	5.4	15
pH		U1H		0.80	7.39	2,7	7.47	7.40	7.40	0.08	1.0	22
		U2H		-0.30	5.97	3,4	5.94	5.96	5.98	0.06	1.0	21
Turbidity	FNU	U1S		-0.47	0.59	25	0.56	0.61	0.60	0.05	7.9	21
	FNU	U2S		0.34	0.29	25	0.30	0.30	0.29	0.03	11.7	18

Participant 15												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
$Cl_{2, comb}$	mg/l	U1K		0.20	0.40	25	0.41	0.41	0.40	0.04	8.9	19
	mg/l	U2K		-0.14	0.74	20	0.73	0.74	0.75	0.04	5.8	19
$Cl_{2, free}$	mg/l	U1K		-0.10	0.51	20	0.51	0.52	0.51	0.05	9.3	20
	mg/l	U2K		0.13	0.38	20	0.39	0.38	0.38	0.04	9.4	18
$Cl_{2, total}$	mg/l	U1K		0.00	0.92	10	0.92	0.92	0.92	0.03	3.2	20
	mg/l	U2K		0.00	1.12	10	1.12	1.13	1.13	0.03	2.2	19
$KMnO_4$	mg/l	U1P		-0.03	6.77	20	6.75	6.68	6.75	0.53	7.8	18
	mg/l	U2P		-0.41	13.0	15	12.6	13.1	13.0	0.7	5.1	19
NO_3	mg/l	U1N		0.42	33.4	10	34.1	33.6	33.4	1.3	3.8	16
	mg/l	U2N		-0.06	6.62	10	6.60	6.60	6.60	0.36	5.4	15
pH		U1H		-1.60	7.39	2,7	7.23	7.40	7.40	0.08	1.0	22
		U2H		-0.49	5.97	3,4	5.92	5.96	5.98	0.06	1.0	21
Turbidity	FNU	U1S		0.65	0.59	25	0.64	0.61	0.60	0.05	7.9	21
	FNU	U2S		0.19	0.29	25	0.30	0.30	0.29	0.03	11.7	18
Urea	mg/l	A1U		1.32	0.41	15	0.45	0.42	0.42	0.03	6.7	13
Urea	mg/l	UK2		0.62	0.47	20	0.50	0.47	0.48	0.02	4.7	5

Participant 16												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
$Cl_{2, comb}$	mg/l	U1K		-1.20	0.40	25	0.34	0.41	0.40	0.04	8.9	19
	mg/l	U2K		-0.24	0.74	20	0.72	0.74	0.75	0.04	5.8	19
$Cl_{2, free}$	mg/l	U1K		1.47	0.51	20	0.59	0.52	0.51	0.05	9.3	20
	mg/l	U2K		0.80	0.38	20	0.41	0.38	0.38	0.04	9.4	18
$Cl_{2, total}$	mg/l	U1K		0.11	0.92	10	0.93	0.92	0.92	0.03	3.2	20
	mg/l	U2K		0.18	1.12	10	1.13	1.13	1.13	0.03	2.2	19
$KMnO_4$	mg/l	U1P		-1.08	6.77	20	6.04	6.68	6.75	0.53	7.8	18
	mg/l	U2P		-0.82	13.0	15	12.2	13.1	13.0	0.7	5.1	19
NO_3	mg/l	U1N		-1.02	33.4	10	31.7	33.6	33.4	1.3	3.8	16
	mg/l	U2N		-2.63	6.62	10	5.75	6.60	6.60	0.36	5.4	15
pH		U1H		0.10	7.39	2,7	7.40	7.40	7.40	0.08	1.0	22
		U2H		-0.10	5.97	3,4	5.96	5.96	5.98	0.06	1.0	21
Turbidity	FNU	U1S		0.81	0.59	25	0.65	0.61	0.60	0.05	7.9	21
	FNU	U2S		1.39	0.29	25	0.34	0.30	0.29	0.03	11.7	18
Urea	mg/l	A1U		1.25	0.41	15	0.45	0.42	0.42	0.03	6.7	13
Urea	mg/l	UK2		0.79	0.47	20	0.51	0.47	0.48	0.02	4.7	5

Participant 17												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
$Cl_{2, comb}$	mg/l	U1K		-0.24	0.40	25	0.39	0.41	0.40	0.04	8.9	19
	mg/l	U2K		0.99	0.74	20	0.81	0.74	0.75	0.04	5.8	19
$Cl_{2, free}$	mg/l	U1K		-0.27	0.51	20	0.50	0.52	0.51	0.05	9.3	20
	mg/l	U2K		-1.45	0.38	20	0.33	0.38	0.38	0.04	9.4	18
$Cl_{2, total}$	mg/l	U1K		-0.78	0.92	10	0.88	0.92	0.92	0.03	3.2	20
	mg/l	U2K		0.32	1.12	10	1.14	1.13	1.13	0.03	2.2	19
$KMnO_4$	mg/l	U1P		-0.49	6.77	20	6.44	6.68	6.75	0.53	7.8	18
	mg/l	U2P		0.43	13.0	15	13.4	13.1	13.0	0.7	5.1	19
NO_3	mg/l	U1N		-1.06	33.4	10	31.6	33.6	33.4	1.3	3.8	16
	mg/l	U2N		-1.03	6.62	10	6.28	6.60	6.60	0.36	5.4	15

Participant 17												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
pH		U1H		-0.30	7.39	2,7	7.36	7.40	7.40	0.08	1.0	22
		U2H		-0.49	5.97	3,4	5.92	5.96	5.98	0.06	1.0	21
Turbidity	FNU	U1S		0.14	0.59	25	0.60	0.61	0.60	0.05	7.9	21
	FNU	U2S		-1.10	0.29	25	0.25	0.30	0.29	0.03	11.7	18
Urea	mg/l	A1U		1.06	0.41	15	0.44	0.42	0.42	0.03	6.7	13
Urea	mg/l	UK2		0.06	0.47	20	0.47	0.47	0.48	0.02	4.7	5

Participant 18												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
$Cl_{2, comb}$	mg/l	U1K		0.50	0.40	25	0.43	0.41	0.40	0.04	8.9	19
	mg/l	U2K		-2.43	0.74	20	0.56	0.74	0.75	0.04	5.8	19
$Cl_{2, free}$	mg/l	U1K		-1.47	0.51	20	0.44	0.52	0.51	0.05	9.3	20
	mg/l	U2K		1.58	0.38	20	0.44	0.38	0.38	0.04	9.4	18
$Cl_{2, total}$	mg/l	U1K		-1.30	0.92	10	0.86	0.92	0.92	0.03	3.2	20
	mg/l	U2K		-1.61	1.12	10	1.03	1.13	1.13	0.03	2.2	19
$KMnO_4$	mg/l	U1P		0.97	6.77	20	7.43	6.68	6.75	0.53	7.8	18
	mg/l	U2P		0.29	13.0	15	13.3	13.1	13.0	0.7	5.1	19
pH		U1H		0.60	7.39	2,7	7.45	7.40	7.40	0.08	1.0	22
		U2H		0.30	5.97	3,4	6.00	5.96	5.98	0.06	1.0	21
Turbidity	FNU	U1S		0.22	0.59	25	0.61	0.61	0.60	0.05	7.9	21
	FNU	U2S		-0.33	0.29	25	0.28	0.30	0.29	0.03	11.7	18
Urea	mg/l	A1U		0.23	0.41	15	0.42	0.42	0.42	0.03	6.7	13
Urea	mg/l	UE2		0.42	0.86	15	0.89	0.90	0.91	0.02	2.6	5

Participant 19												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
$Cl_{2, comb}$	mg/l	U1K		-0.27	0.40	25	0.39	0.41	0.40	0.04	8.9	19
	mg/l	U2K		0.06	0.74	20	0.74	0.74	0.75	0.04	5.8	19
$Cl_{2, free}$	mg/l	U1K		0.65	0.51	20	0.54	0.52	0.51	0.05	9.3	20
	mg/l	U2K		0.01	0.38	20	0.38	0.38	0.38	0.04	9.4	18
$Cl_{2, total}$	mg/l	U1K		0.21	0.92	10	0.93	0.92	0.92	0.03	3.2	20
	mg/l	U2K		0.09	1.12	10	1.13	1.13	1.13	0.03	2.2	19
$KMnO_4$	mg/l	U1P		1.24	6.77	20	7.61	6.68	6.75	0.53	7.8	18
	mg/l	U2P		0.10	13.0	15	13.1	13.1	13.0	0.7	5.1	19
NO_3	mg/l	U1N		-0.78	33.4	10	32.1	33.6	33.4	1.3	3.8	16
	mg/l	U2N		-0.82	6.62	10	6.35	6.60	6.60	0.36	5.4	15
pH		U1H		-0.24	7.39	2,7	7.37	7.40	7.40	0.08	1.0	22
		U2H		-0.14	5.97	3,4	5.96	5.96	5.98	0.06	1.0	21
Turbidity	FNU	U1S		0.95	0.59	25	0.66	0.61	0.60	0.05	7.9	21
	FNU	U2S			0.29	25	*0,33*	0.30	0.29	0.03	11.7	18
Urea	mg/l	A1U		0.24	0.41	15	0.42	0.42	0.42	0.03	6.7	13
Urea	mg/l	UK2		-0.05	0.47	20	0.47	0.47	0.48	0.02	4.7	5

Participant 20												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
$Cl_{2,\ comb}$	mg/l	U1K		0.94	0.40	25	0.45	0.41	0.40	0.04	8.9	19
	mg/l	U2K		0.22	0.74	20	0.76	0.74	0.75	0.04	5.8	19
$Cl_{2,\ free}$	mg/l	U1K		-1.13	0.51	20	0.45	0.52	0.51	0.05	9.3	20
	mg/l	U2K		-0.95	0.38	20	0.34	0.38	0.38	0.04	9.4	18
$Cl_{2,\ total}$	mg/l	U1K		-0.41	0.92	10	0.90	0.92	0.92	0.03	3.2	20
	mg/l	U2K		-0.36	1.12	10	1.10	1.13	1.13	0.03	2.2	19
$KMnO_4$	mg/l	U1P		-7.56	6.77	20	1.65	6.68	6.75	0.53	7.8	18
	mg/l	U2P		-10.00	13.0	15	3.3	13.1	13.0	0.7	5.1	19
NO_3	mg/l	U1N		-15.55	33.4	10	7.4	33.6	33.4	1.3	3.8	16
	mg/l	U2N		-15.56	6.62	10	1.47	6.60	6.60	0.36	5.4	15
pH		U1H		0.50	7.39	2,7	7.44	7.40	7.40	0.08	1.0	22
		U2H		1.58	5.97	3,4	6.13	5.96	5.98	0.06	1.0	21
Turbidity	FNU	U1S		-0.47	0.59	25	0.56	0.61	0.60	0.05	7.9	21
	FNU	U2S		-0.28	0.29	25	0.28	0.30	0.29	0.03	11.7	18
Urea	mg/l	A1U		0.03	0.41	15	0.41	0.42	0.42	0.03	6.7	13
Urea	mg/l	UE2		0.58	0.86	15	0.90	0.90	0.91	0.02	2.6	5

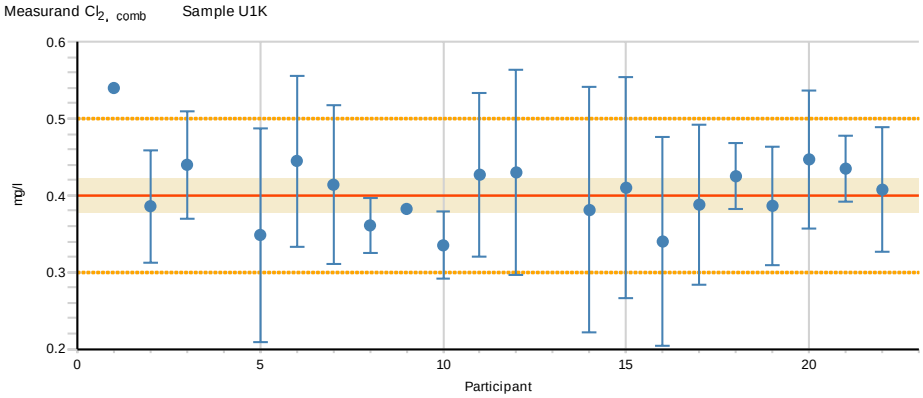
Participant 21												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
$Cl_{2,\ comb}$	mg/l	U1K		0.70	0.40	25	0.44	0.41	0.40	0.04	8.9	19
	mg/l	U2K		-3.92	0.74	20	0.45	0.74	0.75	0.04	5.8	19
$Cl_{2,\ free}$	mg/l	U1K		-1.57	0.51	20	0.43	0.52	0.51	0.05	9.3	20
	mg/l	U2K		6.84	0.38	20	0.64	0.38	0.38	0.04	9.4	18
$Cl_{2,\ total}$	mg/l	U1K		-1.20	0.92	10	0.87	0.92	0.92	0.03	3.2	20
	mg/l	U2K		-0.54	1.12	10	1.09	1.13	1.13	0.03	2.2	19
$KMnO_4$	mg/l	U1P		0.71	6.77	20	7.25	6.68	6.75	0.53	7.8	18
	mg/l	U2P		0.70	13.0	15	13.7	13.1	13.0	0.7	5.1	19
NO_3	mg/l	U1N		0.14	33.4	10	33.6	33.6	33.4	1.3	3.8	16
	mg/l	U2N		0.54	6.62	10	6.80	6.60	6.60	0.36	5.4	15
pH		U1H		0.85	7.39	2,7	7.48	7.40	7.40	0.08	1.0	22
		U2H		-0.15	5.97	3,4	5.96	5.96	5.98	0.06	1.0	21
Turbidity	FNU	U1S		0.07	0.59	25	0.60	0.61	0.60	0.05	7.9	21
	FNU	U2S		6.76	0.29	25	0.54	0.30	0.29	0.03	11.7	18
Urea	mg/l	A1U		-0.49	0.41	15	0.40	0.42	0.42	0.03	6.7	13
Urea	mg/l	UE2		0.39	0.86	15	0.89	0.90	0.91	0.02	2.6	5

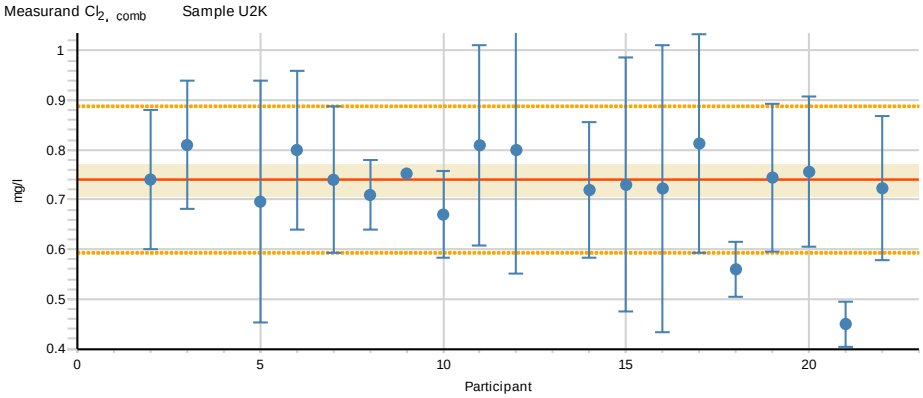
Participant 22												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	$2\times s_{pt}$ %	Participant's result	Md	Mean	s	s %	n_{stat}
$Cl_{2,\ comb}$	mg/l	U1K		0.15	0.40	25	0.41	0.41	0.40	0.04	8.9	19
	mg/l	U2K		-0.23	0.74	20	0.72	0.74	0.75	0.04	5.8	19
$Cl_{2,\ free}$	mg/l	U1K		-0.11	0.51	20	0.50	0.52	0.51	0.05	9.3	20
	mg/l	U2K		-0.38	0.38	20	0.37	0.38	0.38	0.04	9.4	18
$Cl_{2,\ total}$	mg/l	U1K		-0.17	0.92	10	0.91	0.92	0.92	0.03	3.2	20
	mg/l	U2K		-0.56	1.12	10	1.09	1.13	1.13	0.03	2.2	19
$KMnO_4$	mg/l	U1P		-0.83	6.77	20	6.21	6.68	6.75	0.53	7.8	18
	mg/l	U2P		-0.41	13.0	15	12.6	13.1	13.0	0.7	5.1	19
pH		U1H		1.10	7.39	2,7	7.50	7.40	7.40	0.08	1.0	22
		U2H		-0.39	5.97	3,4	5.93	5.96	5.98	0.06	1.0	21
Turbidity	FNU	U1S		1.07	0.59	25	0.67	0.61	0.60	0.05	7.9	21
	FNU	U2S		1.61	0.29	25	0.35	0.30	0.29	0.03	11.7	18
Urea	mg/l	A1U		0.13	0.41	15	0.41	0.42	0.42	0.03	6.7	13
Urea	mg/l	UK2		-0.36	0.47	20	0.45	0.47	0.48	0.02	4.7	5

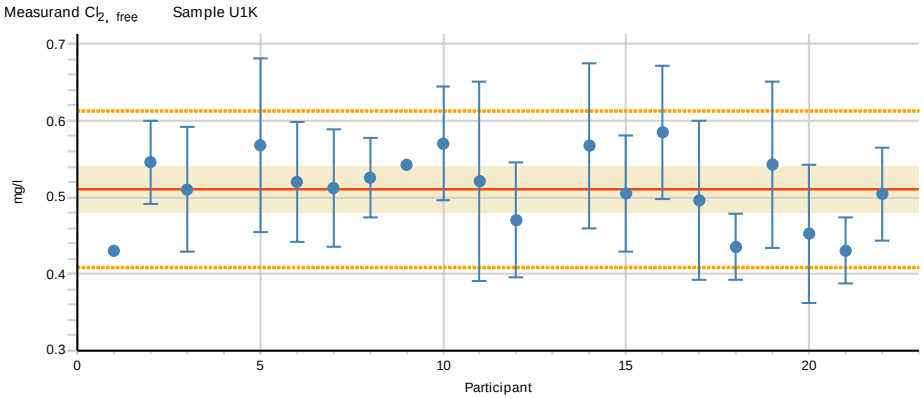
APPENDIX 9: Results of participants and their uncertainties

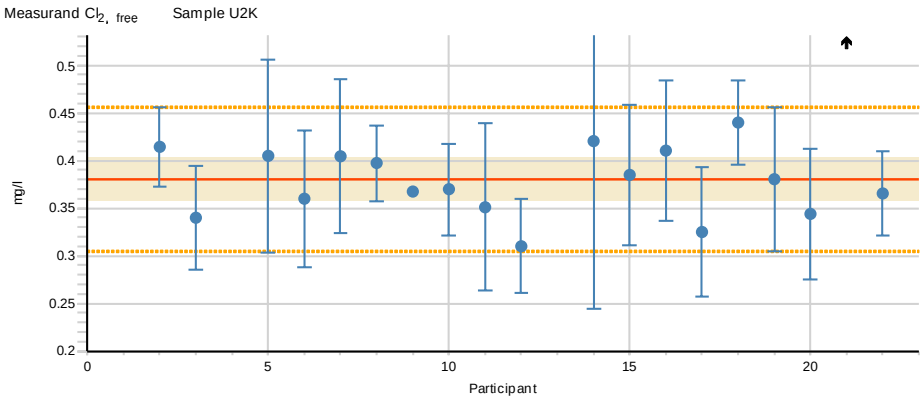
In figures:

- 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 measurement uncertainty of the assigned value, and the arrow describes the value outside the scale.





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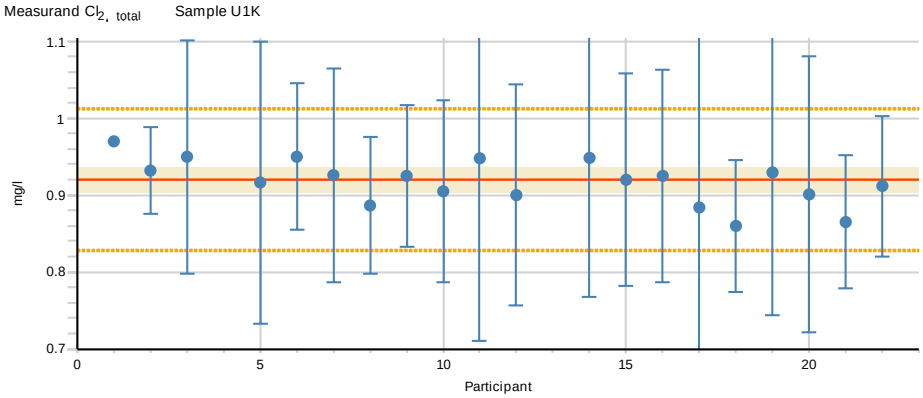
0.3
0.25
0.2
0
5
10
15
20
Participant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mg/l
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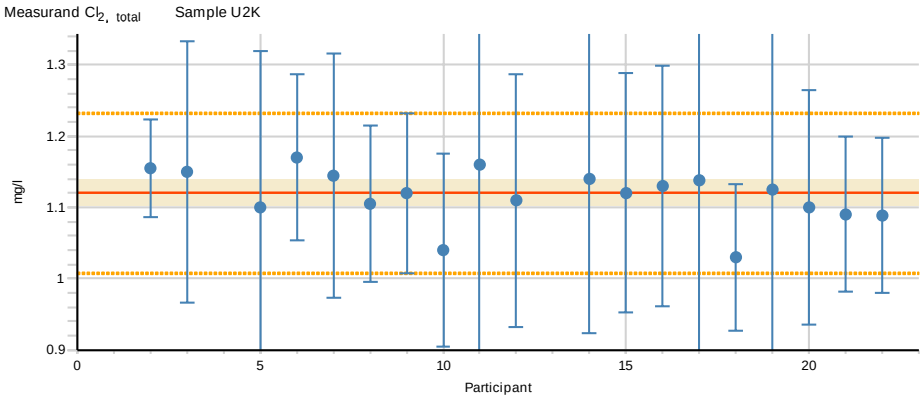
0.9
0.8
0.7
0
5
10
15
20
Participant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Sample U2K
mg/l
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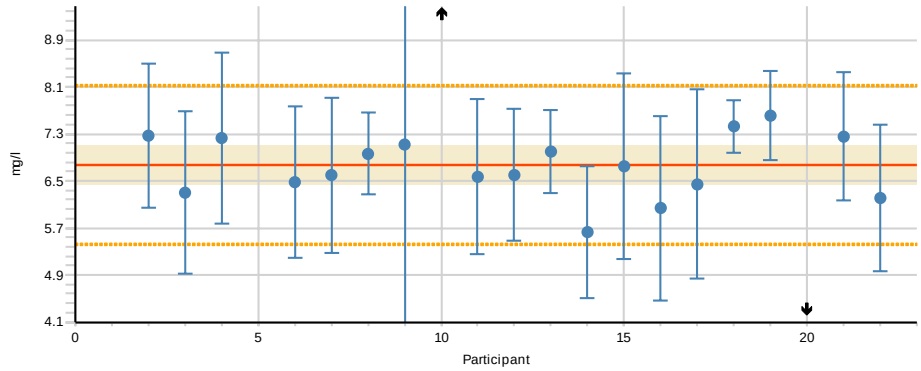
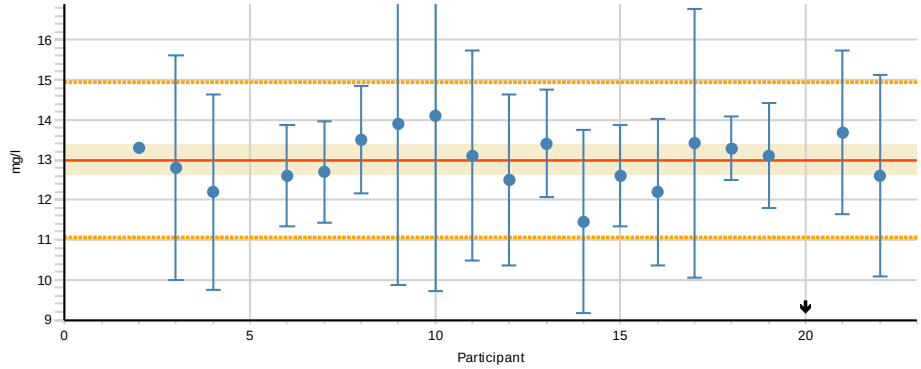
1.2
1.1
1
0.9
0
5
10
15
20
Participant

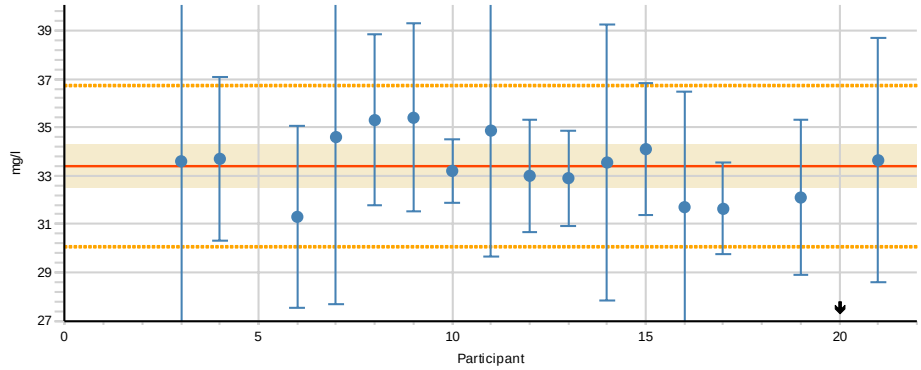
Measurand $KMnO_4$ Sample U1P

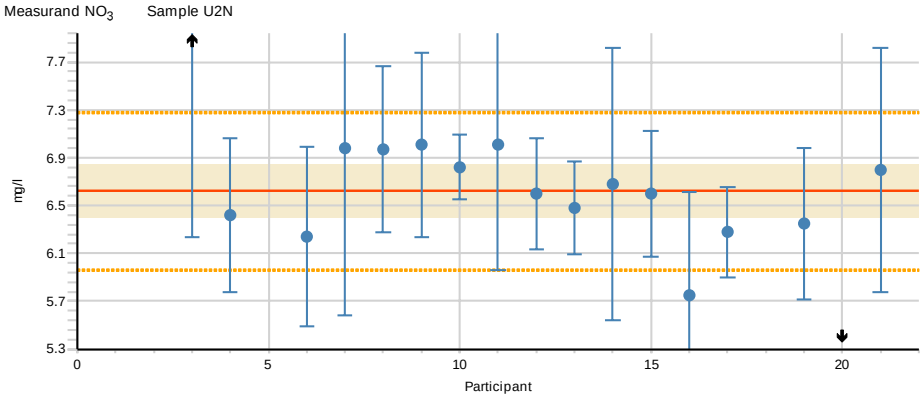


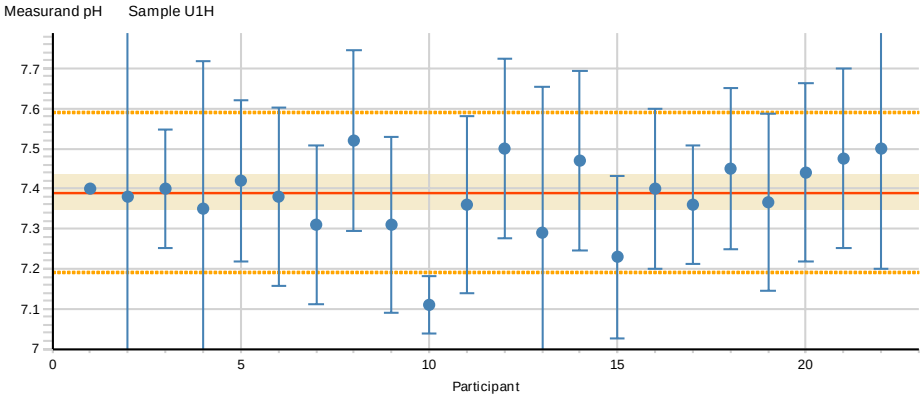
Measurand $KMnO_4$ Sample U2P

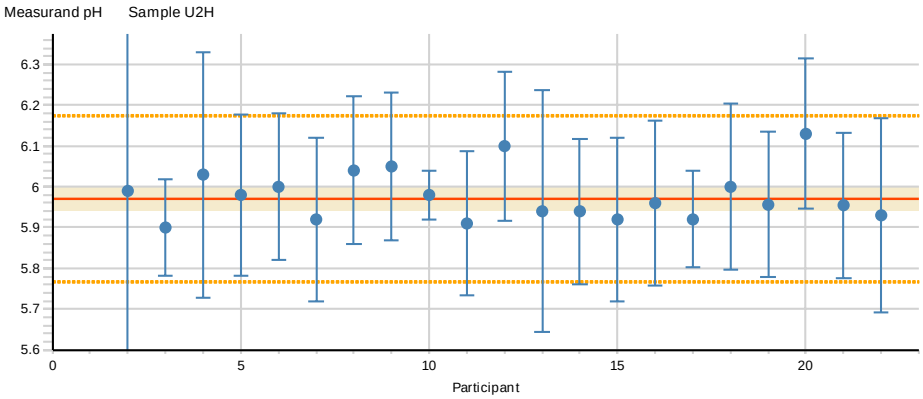


Measurand NO_3 Sample U1N

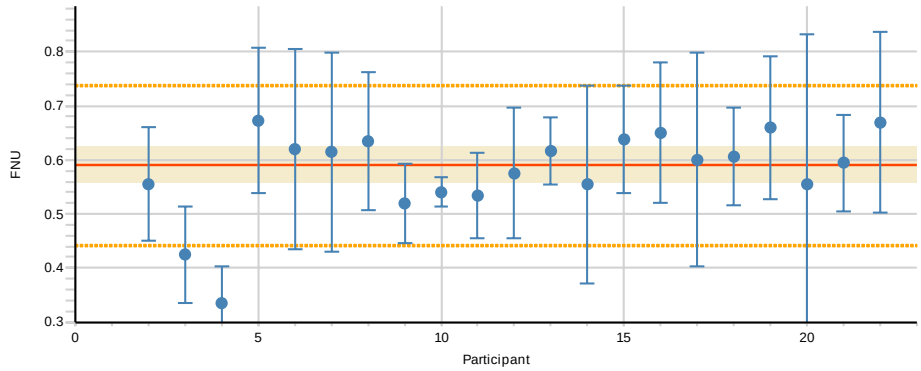



Measurand NO_3 Sample U2N
mg/l
7.7
7.3
6.9
6.5
6.1
5.7
5.3
0
5
10
15
20
Participant

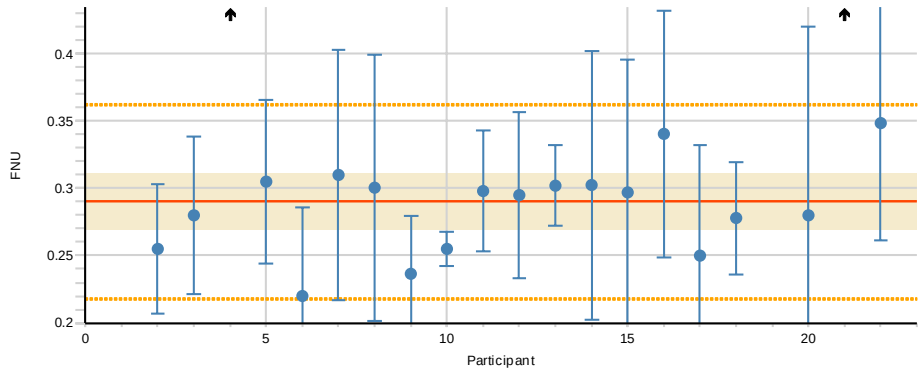

Measurand pH Sample U1H
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7
0
5
10
15
20
Participant


Measurand pH Sample U2H
6.3
6.2
6.1
6
5.9
5.8
5.7
5.6
0
5
10
15
20
Participant

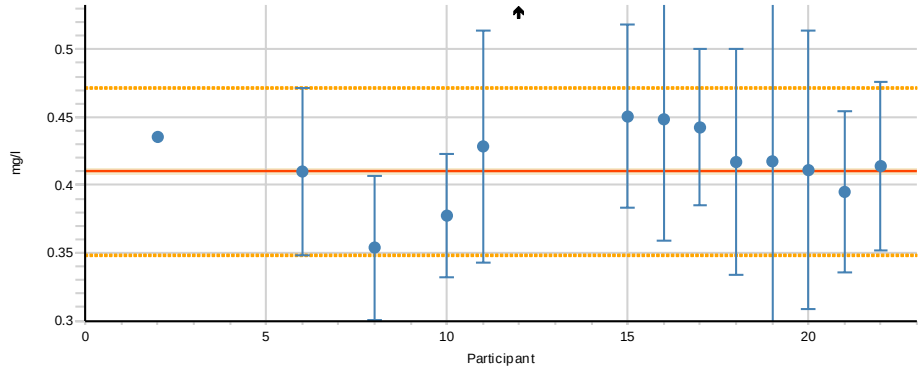
Measurand Turbidity Sample U1S

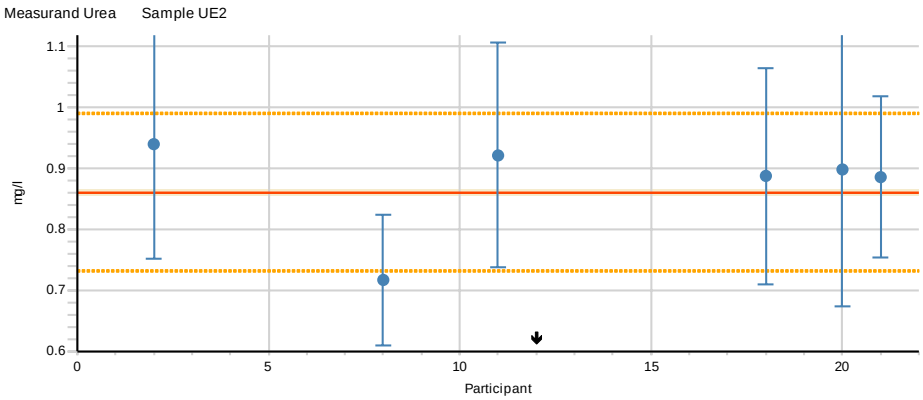


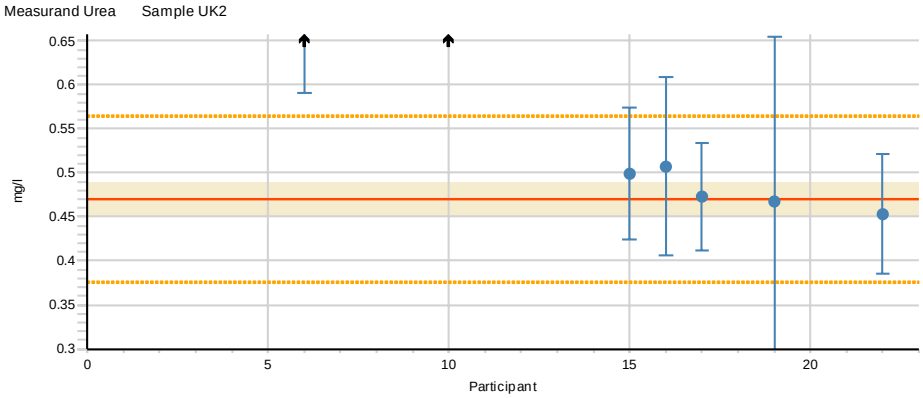
Measurand Turbidity Sample U2S



Measurand Urea Sample A1U




Measurand Urea
Sample UE2
mg/l
1.1
1
0.9
0.8
0.7
0.6
0
5
10
15
20
Participant


Measurand Urea
Sample UK2
mg/l
0.65
0.6
0.55
0.5
0.45
0.4
0.35
0.3
0
5
10
15
20
Participant

APPENDIX 10: Summary of the z and E_n scores

z scores

Measurand	Sample	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	%
$Cl_{2,\ comb}$	U1K	Q	S	S	.	S	S	S	S	S	S	S	S	.	S	S	S	S	S	S	S	S	S	.	95.0
	U2K	.	S	S	.	S	S	S	S	S	S	S	S	.	*S*	S	S	S	q	*S*	S	u	S	.	89.5
$Cl_{2,\ free}$	U1K	S	S	S	.	S	S	S	S	S	S	S	S	.	S	S	S	S	S	S	S	S	S	.	100
	U2K	.	S	S	.	S	S	S	S	S	S	S	S	.	S	S	S	S	S	S	S	U	S	.	94.7
$Cl_{2,\ total}$	U1K	S	S	S	.	S	S	S	S	S	S	S	*S*	.	S	S	S	S	S	S	S	S	S	.	100
	U2K	.	S	S	.	S	S	S	S	S	S	S	S	.	S	S	S	S	S	S	S	S	S	.	100
$KMnO_4$	U1P	.	S	S	S	.	S	S	S	S	U	S	S	S	S	S	S	S	S	S	u	S	S	.	90.0
	U2P	.	S	S	S	.	S	S	S	S	S	S	S	S	S	S	S	S	S	S	u	S	S	.	95.0
NO_3	U1N	.	.	S	S	.	S	S	S	S	S	S	S	S	S	S	S	S	.	S	u	S	.	.	94.1
	U2N	.	.	U	S	.	S	S	S	S	S	S	S	S	S	S	q	S	.	S	u	S	.	.	82.4
pH	U1H	S	S	S	S	S	S	S	S	S	q	S	S	S	S	S	S	S	S	S	S	S	S	.	95.5
	U2H	.	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	.	100
Turbidity	U1S	.	S	q	u	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	.	90.5
	U2S	.	S	S	U	S	S	S	S	S	S	S	S	S	S	S	S	S	S	.	S	U	S	.	90.0
Urea	A1U	.	*S*	.	.	.	S	.	S	.	S	S	U	.	.	S	S	S	S	S	S	S	S	.	92.9
Urea	UE2	.	*S*	.	.	.	.	.	q	.	.	S	u	.	.	.	.	.	S	.	S	S	.	.	71.4
Urea	UK2	.	.	.	.	.	U	.	.	.	U	.	.	.	.	S	S	S	.	S	.	.	S	.	71.4
%		75	100	86	75	100	94	100	94	100	81	100	88	100	100	100	94	100	93	100	75	81	100		
accredited		4	12	14	8	10	16	14	16	14	16	16	14	8	12	16	16	16	14	13	16	16	14		

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: 93 % in accredited: 93 % in non-accredited: 100

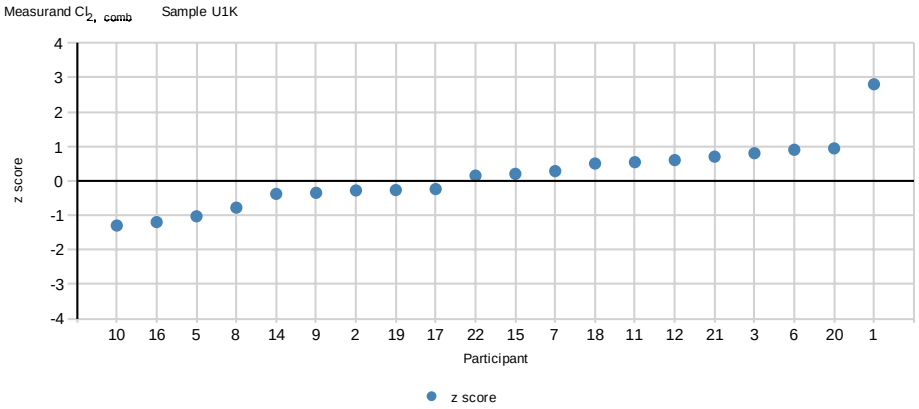
E_n scores

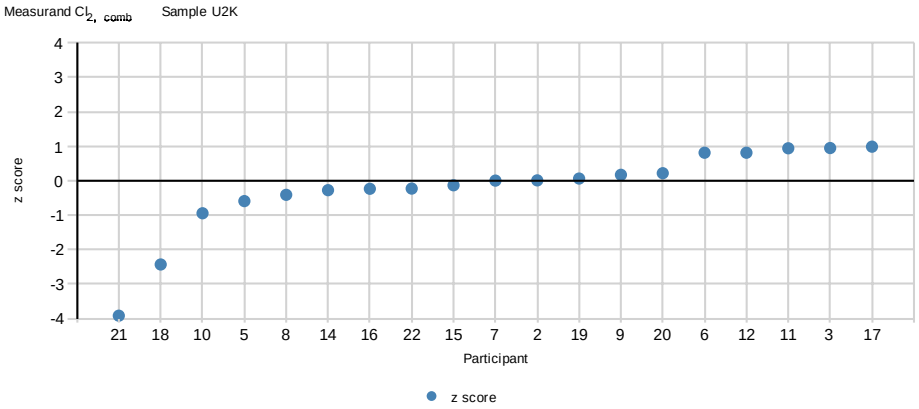
Measurand	Sample	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	%
Urea	UK2	.	.	.	.	.	2.1	.	.	.	3.5	.	.	.	.	0.4	0.4	0.0	.	0.0	.	.	-0.2	.	71.4

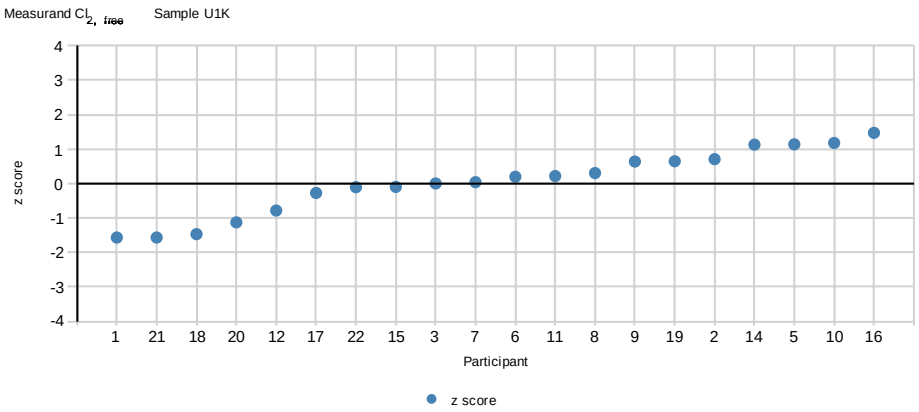
E_n scores enable to estimate the proximity of participant results to the assigned value taking into consideration their reported expanded uncertainty
Scores of $-1.0 < E_n < 1.0$ indicate successful performance
Scores of $E_n \geq 1.0$ or $E_n \leq -1.0$ indicate a need to review the uncertainty estimated or to correct a measurement issue

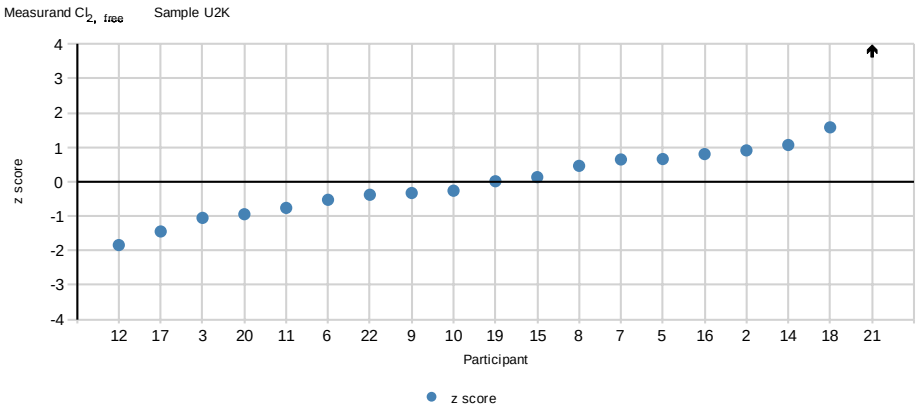
Totally satisfactory, % in all: 71

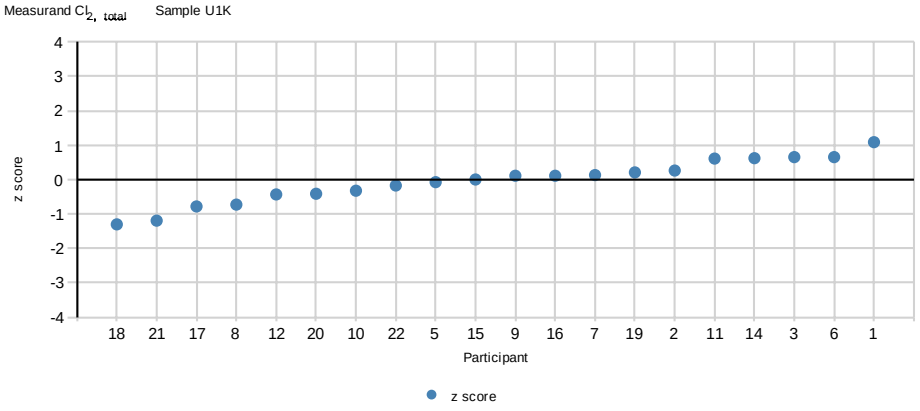
APPENDIX 11: z scores in ascending order

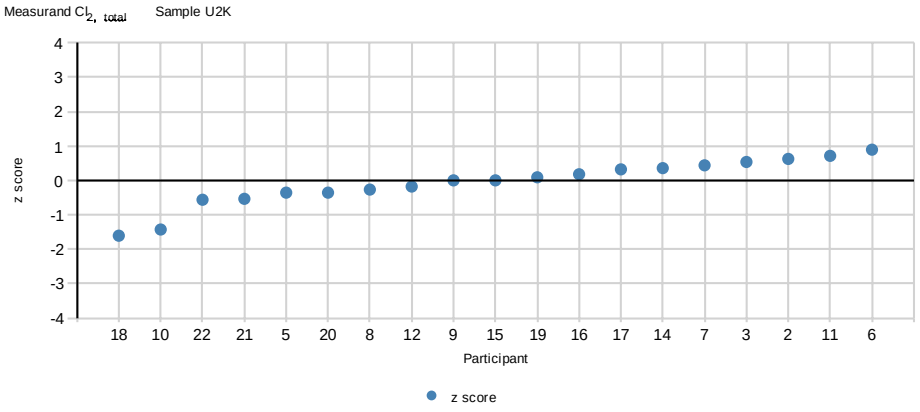


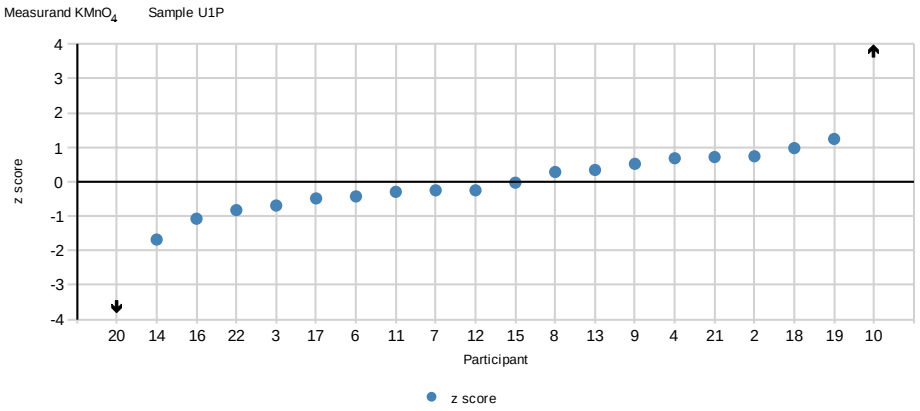


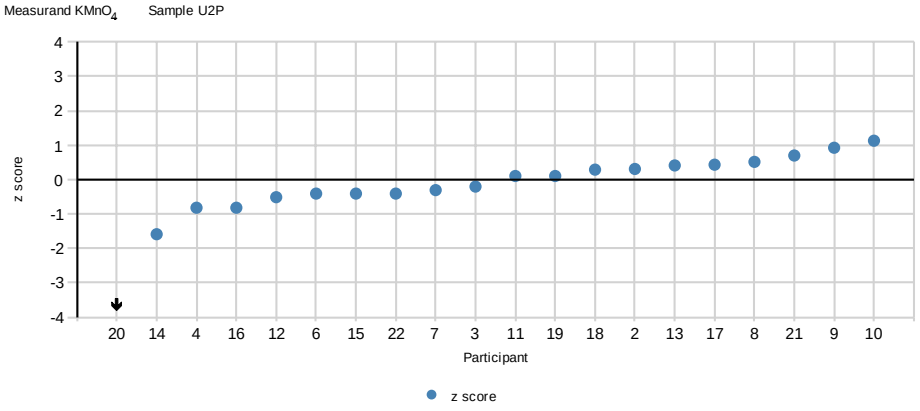


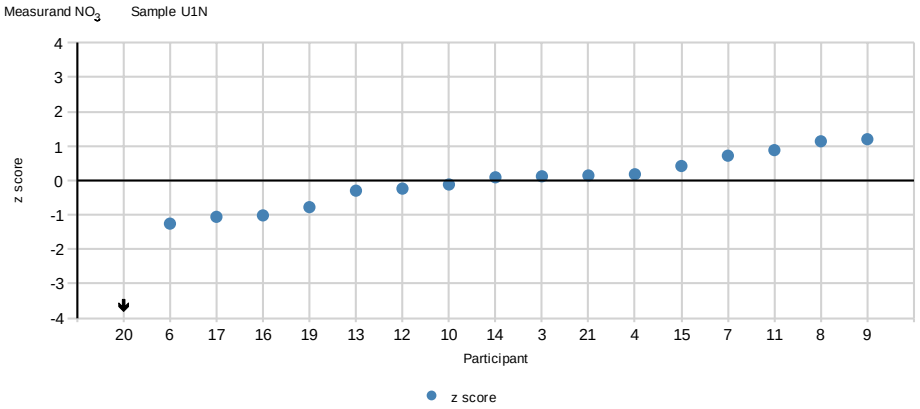

Measurand $Cl_{2,\ free}$
Sample U2K
z score
4
3
2
1
0
-1
-2
-3
-4
12 17 3 20 11 6 22 9 10 19 15 8 7 5 16 2 14 18 21
Participant
z score


Measurand $Cl_{2,\ total}$
Sample U1K
z score
4
3
2
1
0
-1
-2
-3
-4
18 21 17 8 12 20 10 22 5 15 9 16 7 19 2 11 14 3 6 1
Participant
z score

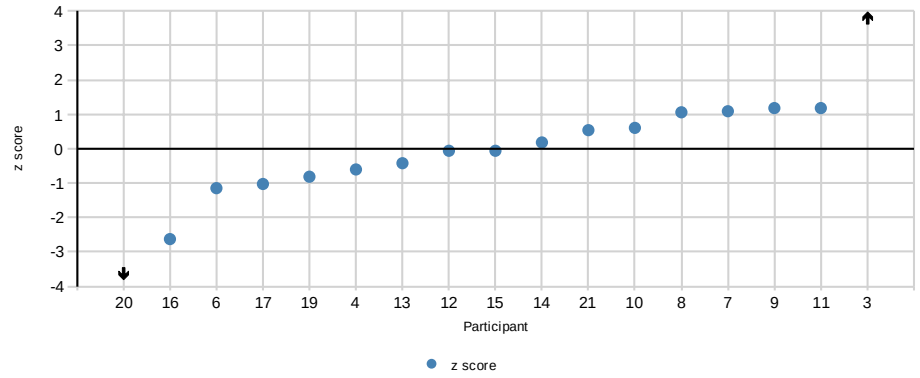

Measurand $Cl_{2,\ total}$
Sample U2K
z score
4
3
2
1
0
-1
-2
-3
-4
18 10 22 21 5 20 8 12 9 15 19 16 17 14 7 3 2 11 6
Participant
z score


Measurand $KMnO_4$ Sample U1P
z score
4
3
2
1
0
-1
-2
-3
-4
20 14 16 22 3 17 6 11 7 12 15 8 13 9 4 21 2 18 19 10
Participant
z score

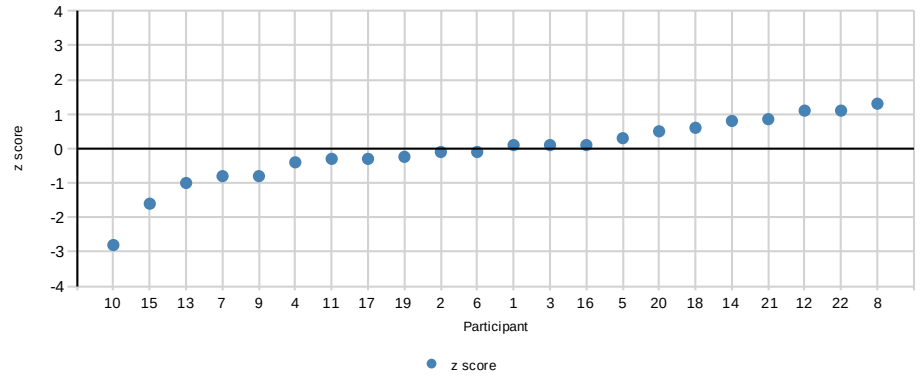

Measurand $KMnO_4$ Sample U2P
z score
4
3
2
1
0
-1
-2
-3
-4
20 14 4 16 12 6 15 22 7 3 11 19 18 2 13 17 8 21 9 10
Participant
z score


Measurand NO_3 Sample U1N
z score
4
3
2
1
0
-1
-2
-3
-4
20 6 17 16 19 13 12 10 14 3 21 4 15 7 11 8 9
Participant
z score

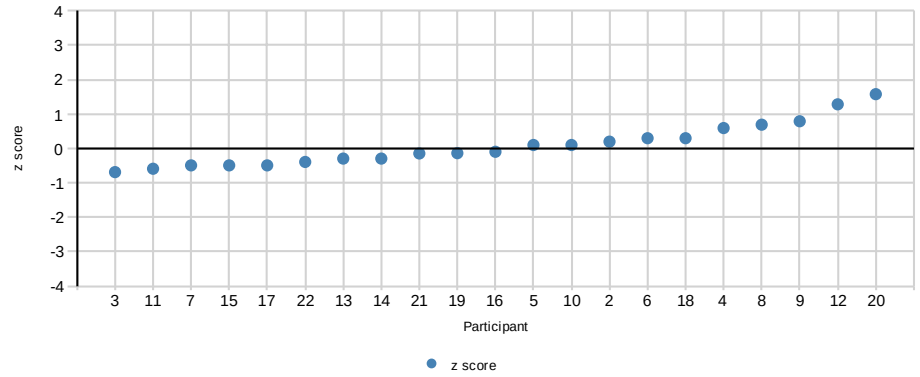
Measurand NO_3 Sample U2N

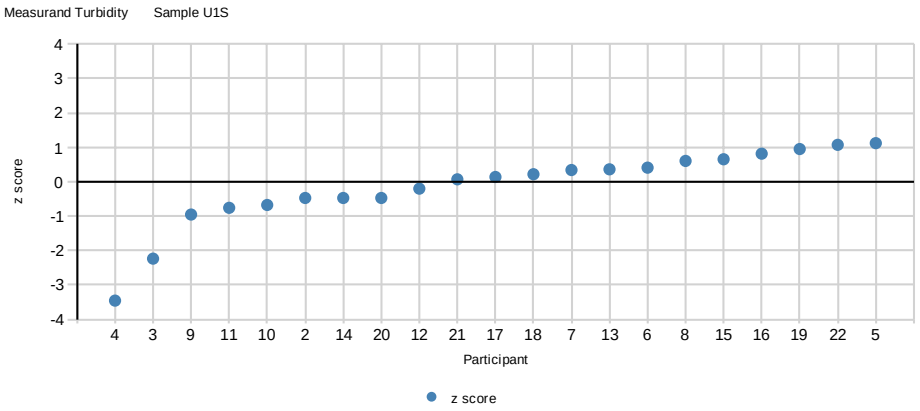


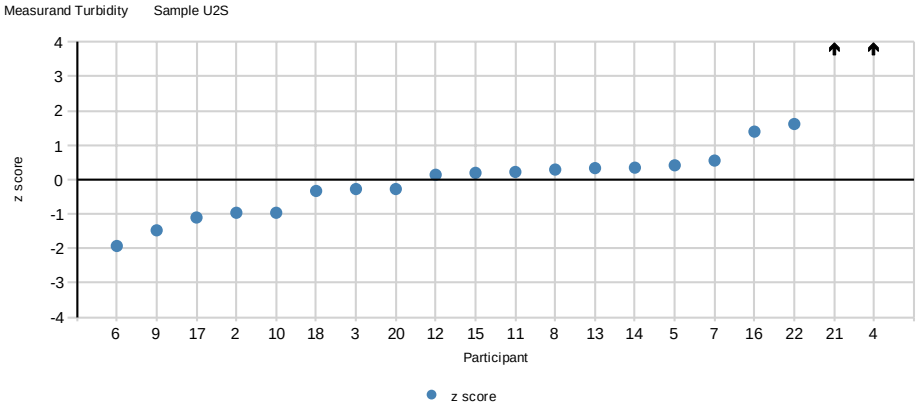
Measurand pH Sample U1H

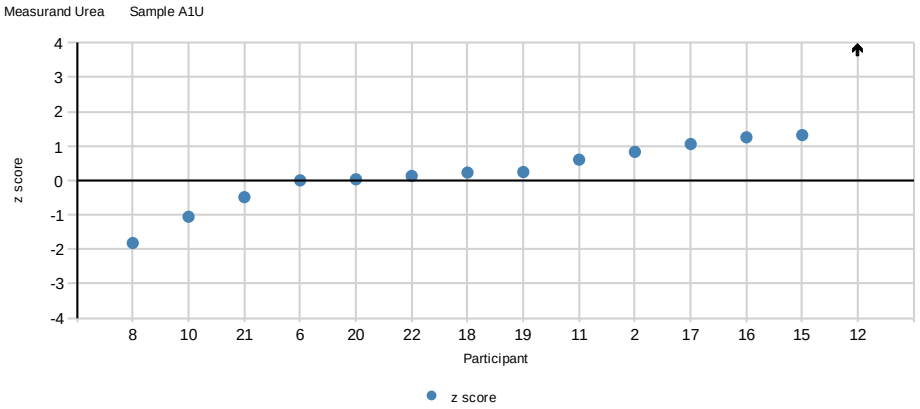


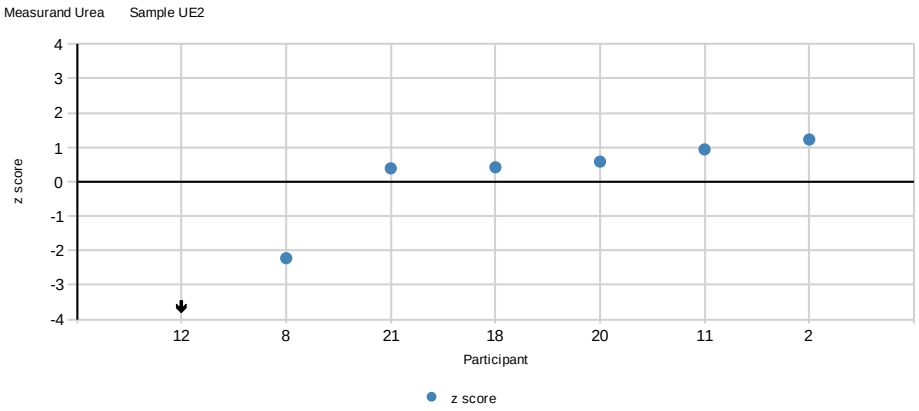
Measurand pH Sample U2H

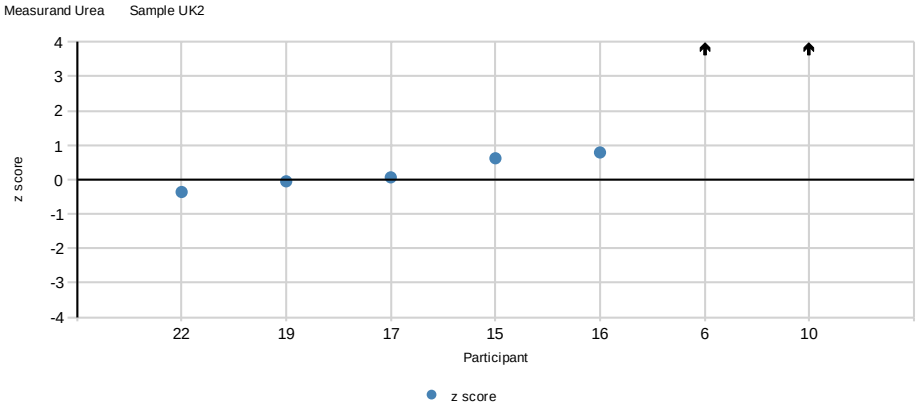



Measurand Turbidity Sample U1S
z score
4
3
2
1
0
-1
-2
-3
-4
4 3 9 11 10 2 14 20 12 21 17 18 7 13 6 8 15 16 19 22 5
Participant
z score


Measurand Turbidity Sample U2S
z score
4
3
2
1
0
-1
-2
-3
-4
6 9 17 2 10 18 3 20 12 15 11 8 13 14 5 7 16 22 21 4
Participant
z score

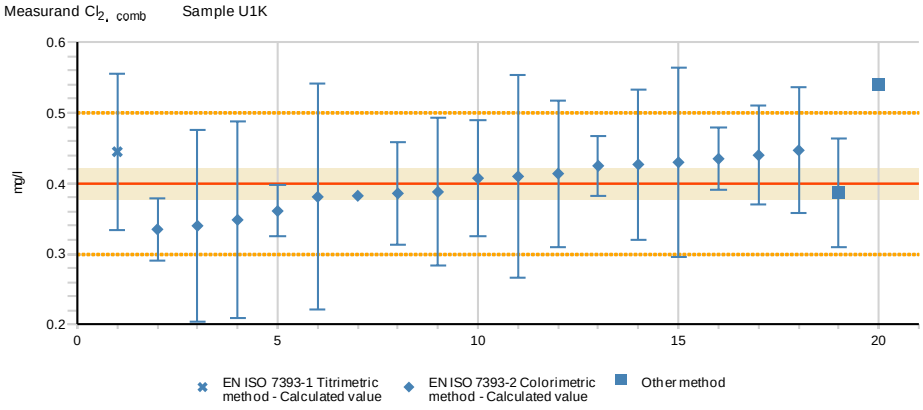

Measurand Urea Sample A1U
z score
4
3
2
1
0
-1
-2
-3
-4
8 10 21 6 20 22 18 19 11 2 17 16 15 12
Participant
z score

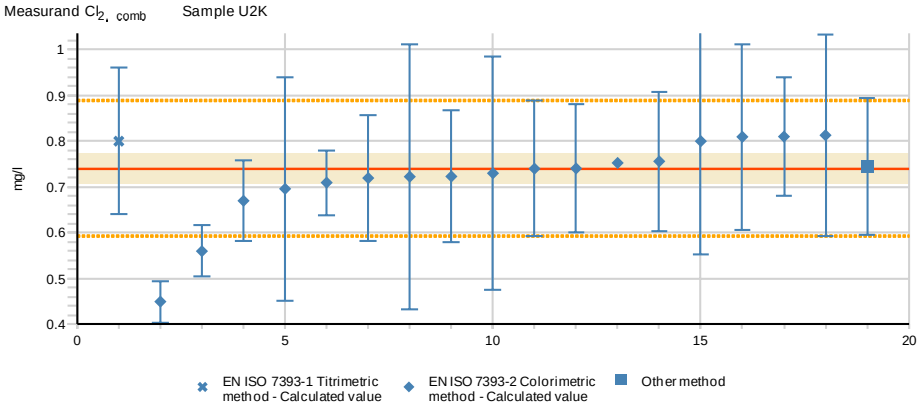

Measurand Urea
Sample UE2
z score
4
3
2
1
0
-1
-2
-3
-4
12
8
21
18
20
11
2
Participant
z score

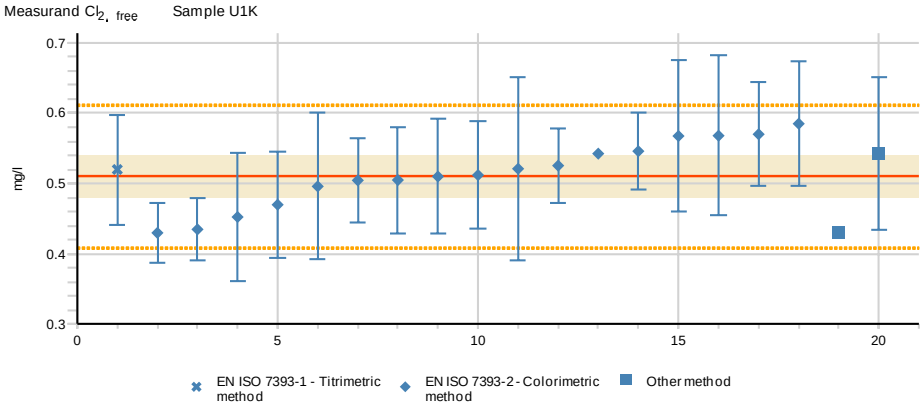

Measurand Urea
Sample UK2
z score
4
3
2
1
0
-1
-2
-3
-4
22
19
17
15
16
6
10
Participant
z score

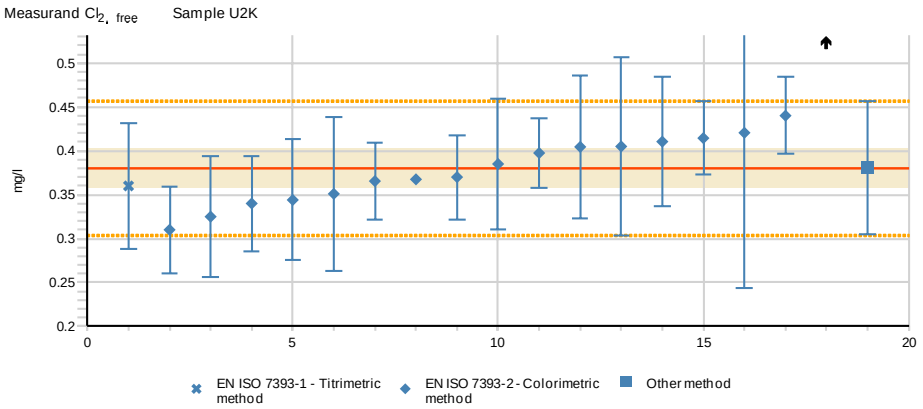
APPENDIX 12: Results grouped according to the methods

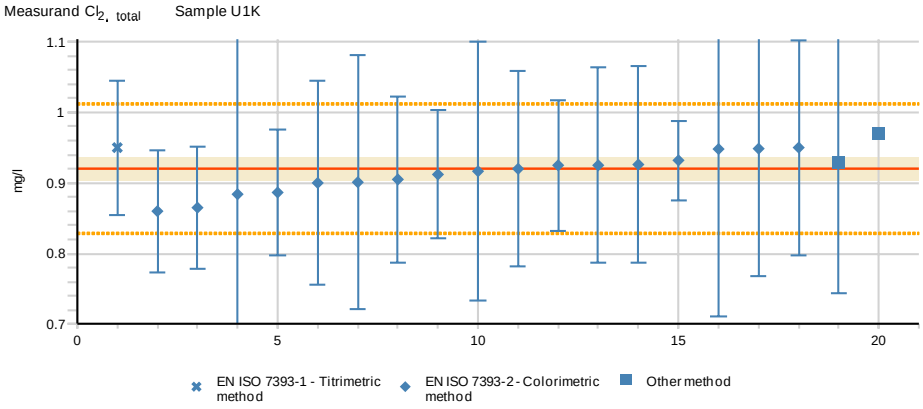
The explanations for the figures are described in the Appendix 9. The results are shown in ascending order.

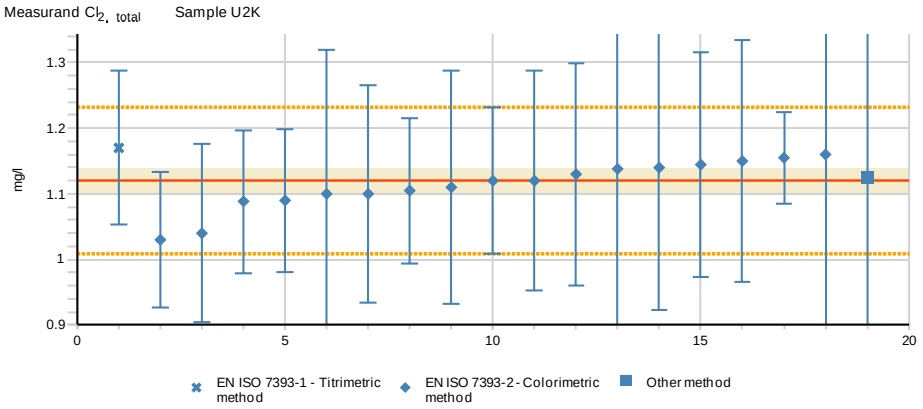


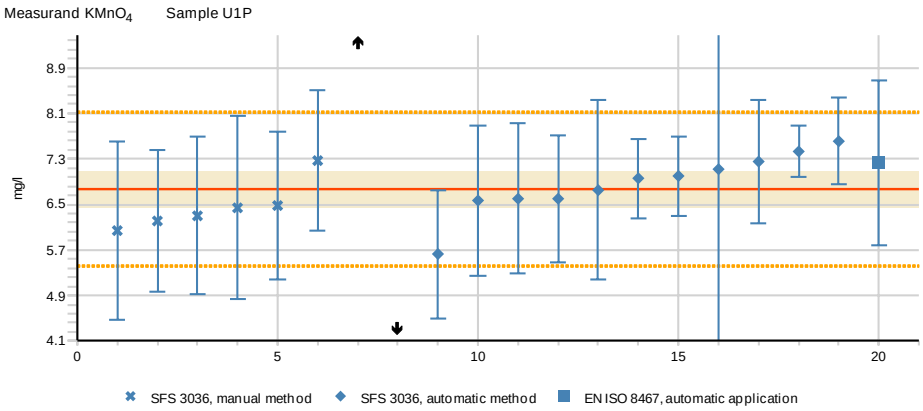


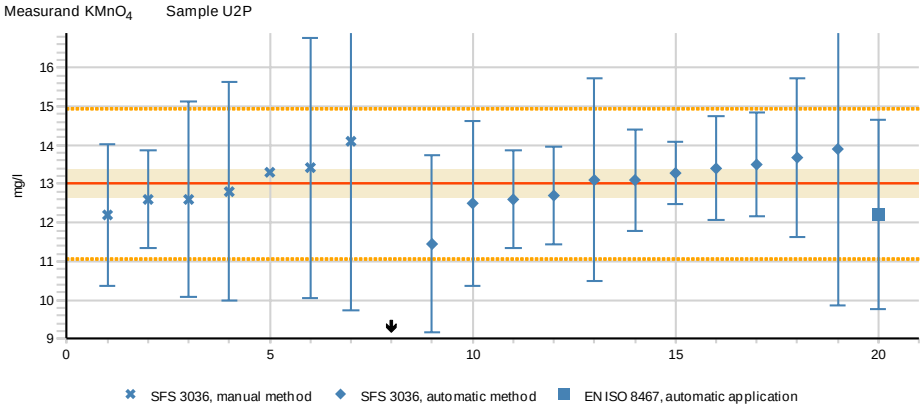


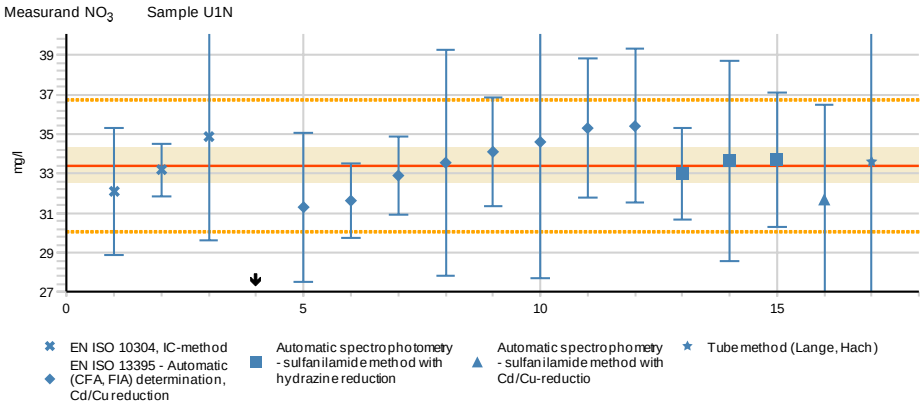

Measurand Cl2, free
Sample U2K
mg/l
0.5
0.45
0.4
0.35
0.3
0.25
0.2
0
5
10
15
20
EN ISO 7393-1 - Titrimetric method
EN ISO 7393-2 - Colorimetric method
Other method


Measurand Cl2, total
Sample U1K
mg/l
1.1
1
0.9
0.8
0.7
0
5
10
15
20
EN ISO 7393-1 - Titrimetric method
EN ISO 7393-2 - Colorimetric method
Other method

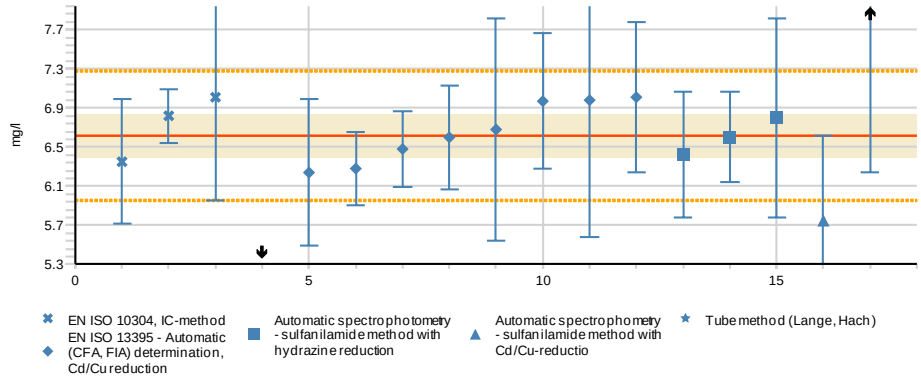

Measurand Cl2, total
Sample U2K
mg/l
1.3
1.2
1.1
1
0.9
0
5
10
15
20
EN ISO 7393-1 - Titrimetric method
EN ISO 7393-2 - Colorimetric method
Other method


Measurand KMnO4 Sample U1P
mg/l
8.9
8.1
7.3
6.5
5.7
4.9
4.1
0
5
10
15
20
SFS 3036, manual method
SFS 3036, automatic method
EN ISO 8467, automatic application

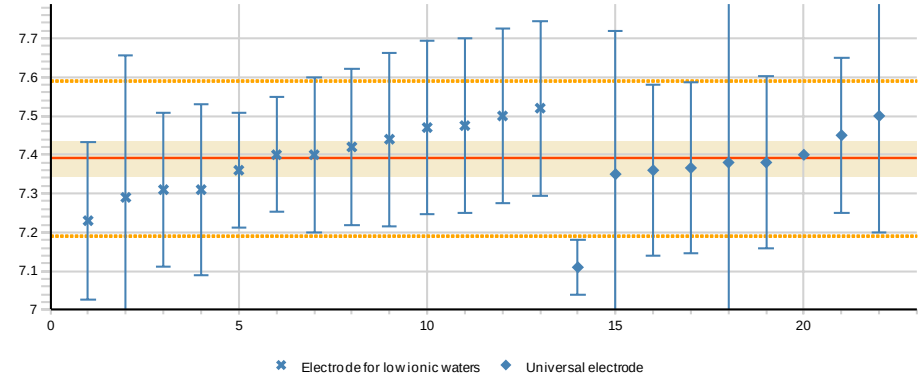

Measurand KMnO4 Sample U2P
mg/l
16
15
14
13
12
11
10
9
0
5
10
15
20
SFS 3036, manual method
SFS 3036, automatic method
EN ISO 8467, automatic application


Measurand NO3 Sample U1N
mg/l
39
37
35
33
31
29
27
0
5
10
15
EN ISO 10304, IC-method
EN ISO 13395 - Automatic (CFA, FIA) determination, Cd/Cu reduction
Automatic spectrophotometry - sulfanilamide method with hydrazine reduction
Automatic spectrophotometry - sulfanilamide method with Cd/Cu-reductio
Tube method (Lange, Hach)

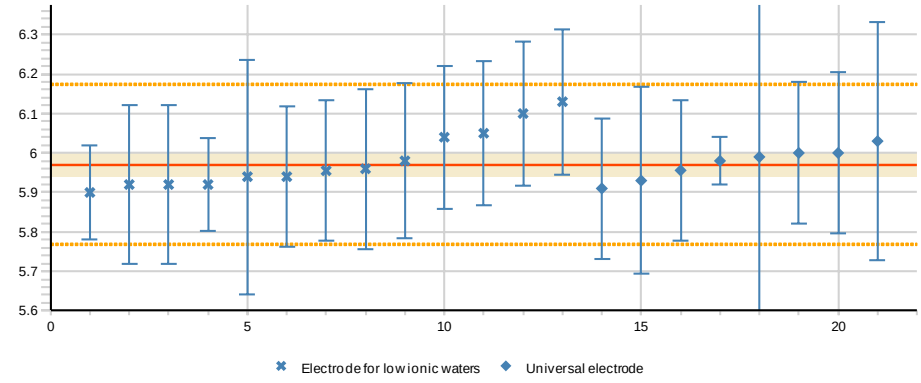
Measurand NO_3 Sample U2N



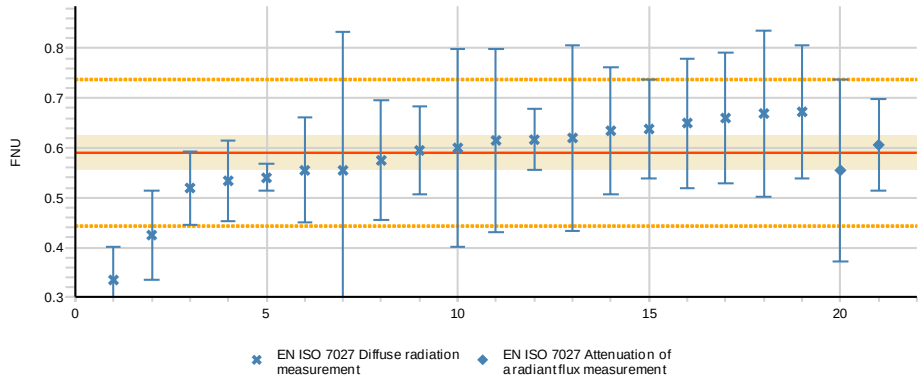
Measurand pH Sample U1H



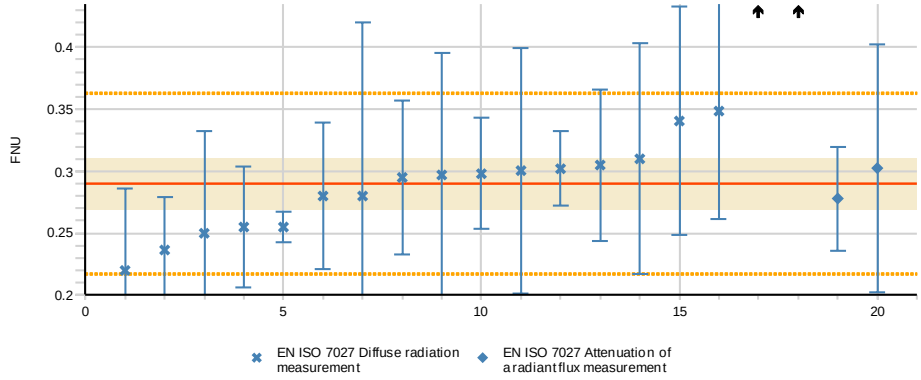
Measurand pH Sample U2H



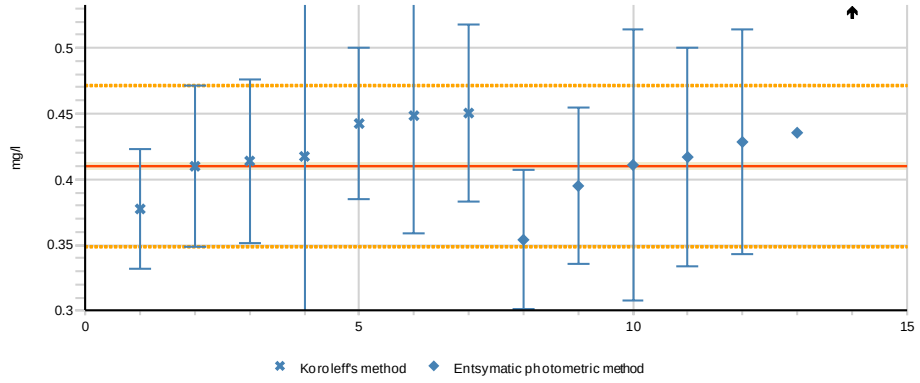
Measurand Turbidity Sample U1S

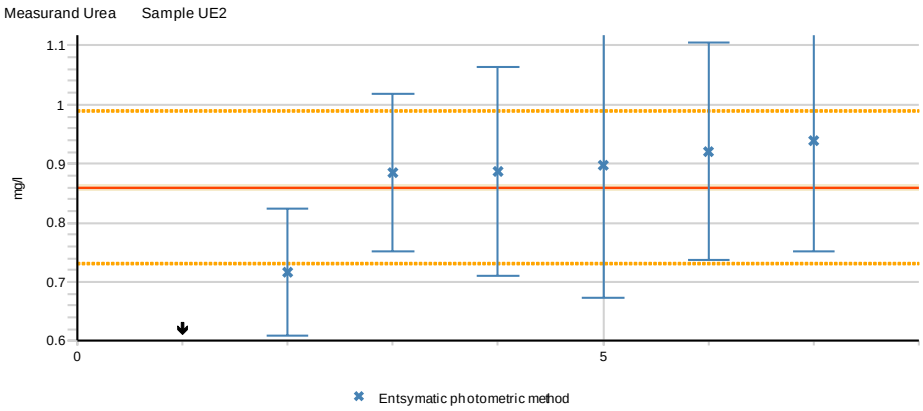


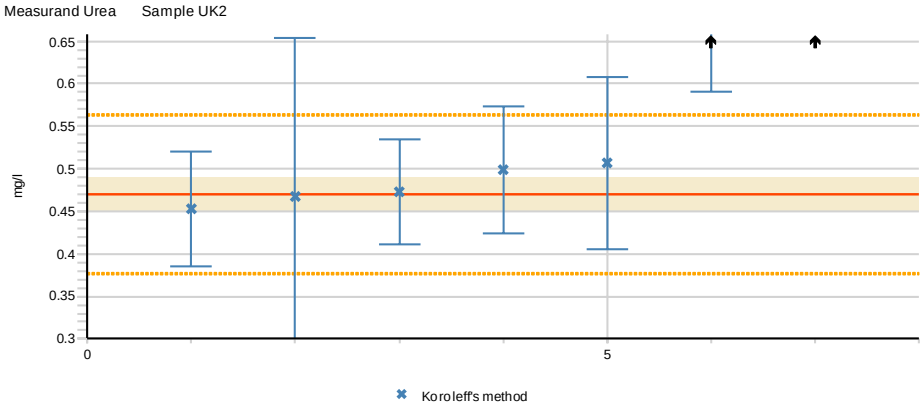
Measurand Turbidity Sample U2S



Measurand Urea Sample A1U

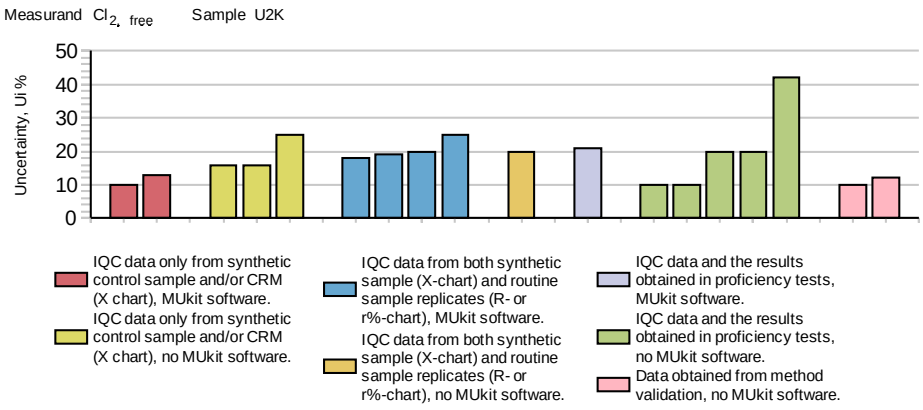


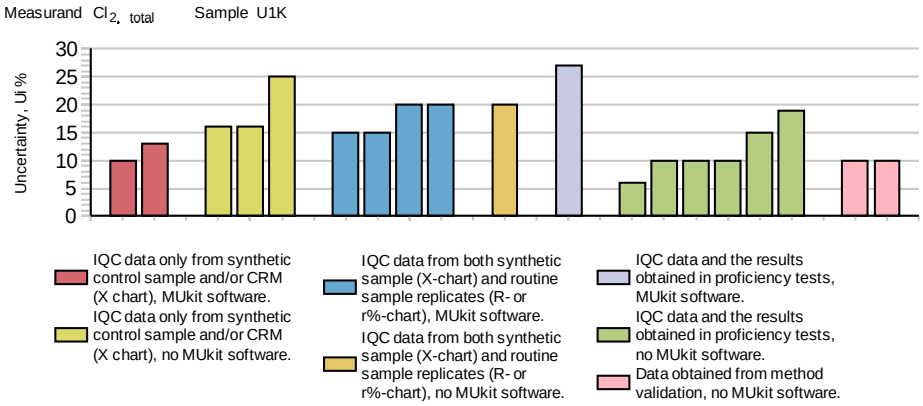

Measurand Urea Sample UE2
1.1
1
0.9
0.8
0.7
0.6
mg/l
0
5
Entsymatic photometric method

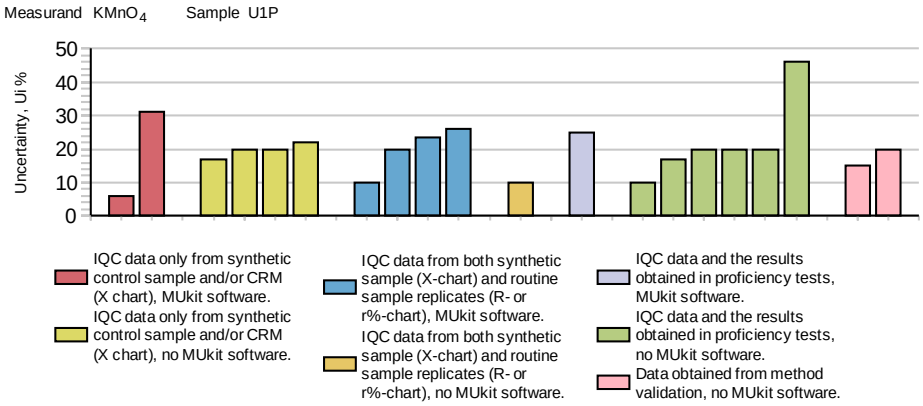

Measurand Urea Sample UK2
0.65
0.6
0.55
0.5
0.45
0.4
0.35
0.3
mg/l
0
5
Koroleff's method

APPENDIX 13: Examples of measurement uncertainties reported by the participants

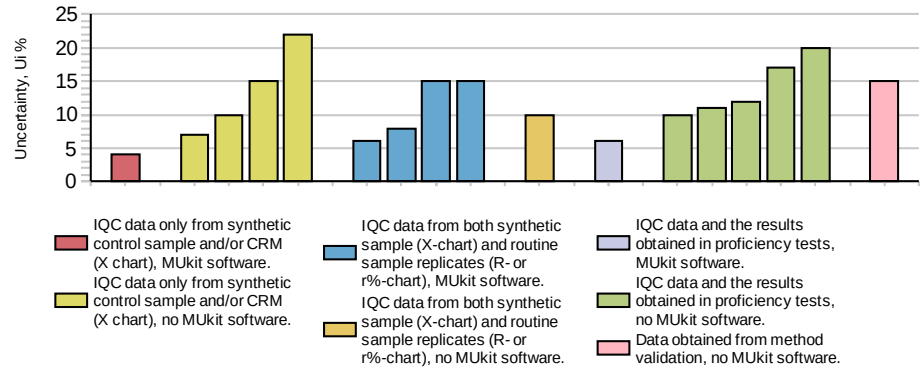
In figures, the presented expanded measurement uncertainties are grouped according to the method of estimation at 95 % confidence level (k=2). The expanded uncertainties were estimated mainly by using the internal quality control (IQC) data. The used procedures in figures below are distinguished e.g. between using or not using the MUkit software for uncertainty estimation [8, 10].





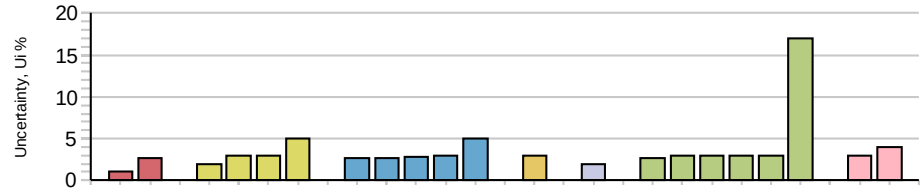


Measurand NO_3 Sample U2N



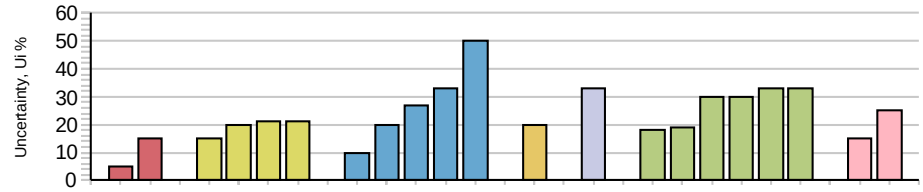
IQC data only from synthetic control sample and/or CRM (X chart), MUkit software.
IQC data only from synthetic control sample and/or CRM (X chart), no MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), no MUkit software.
IQC data and the results obtained in proficiency tests, MUkit software.
IQC data and the results obtained in proficiency tests, no MUkit software.
Data obtained from method validation, no MUkit software.

Measurand pH Sample U1H



IQC data only from synthetic control sample and/or CRM (X chart), MUkit software.
IQC data only from synthetic control sample and/or CRM (X chart), no MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), no MUkit software.
IQC data and the results obtained in proficiency tests, MUkit software.
IQC data and the results obtained in proficiency tests, no MUkit software.
Data obtained from method validation, no MUkit software.

Measurand Turbidity Sample U2S



IQC data only from synthetic control sample and/or CRM (X chart), MUkit software.
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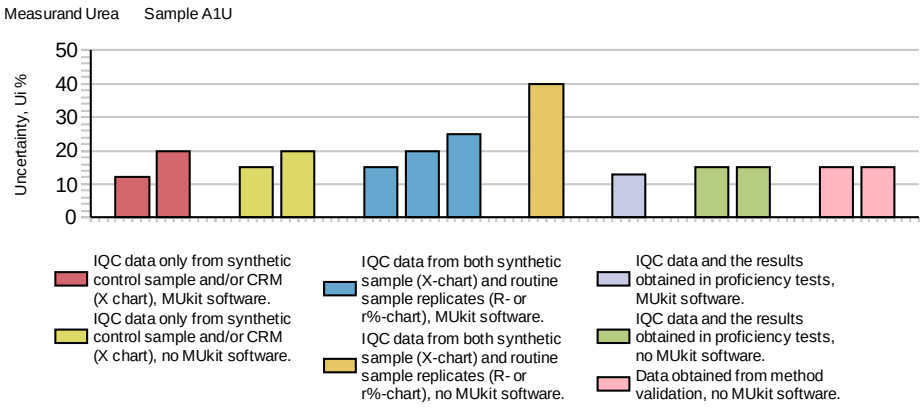
Data obtained from method validation, no MUkit software.


Measurand Urea Sample A1U
Uncertainty, Ui %
50
40
30
20
10
0
IQC data only from synthetic control sample and/or CRM (X chart), MUkit software.
IQC data only from synthetic control sample and/or CRM (X chart), no MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), no MUkit software.
IQC data and the results obtained in proficiency tests, MUkit software.
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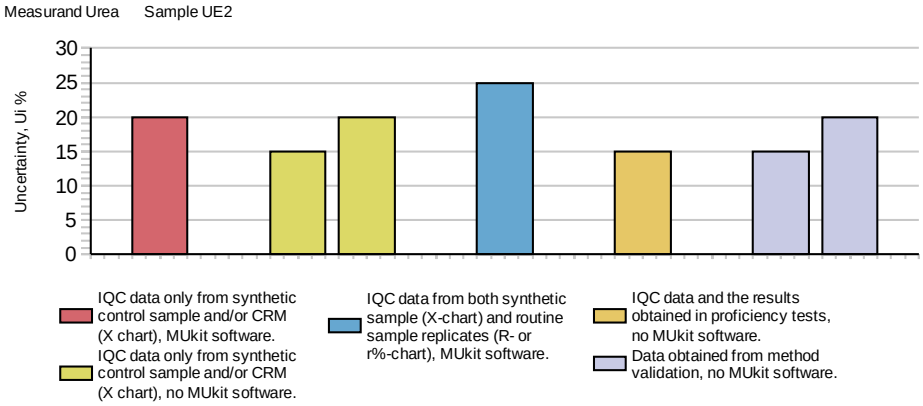
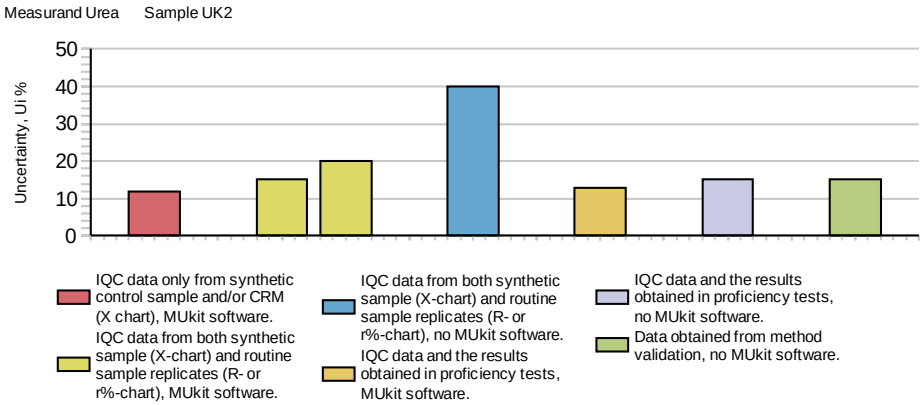
Data obtained from method validation, no MUkit software.


Measurand Urea Sample UE2
Uncertainty, Ui %
30
25
20
15
10
5
0
IQC data only from synthetic control sample and/or CRM (X chart), MUkit software.
IQC data only from synthetic control sample and/or CRM (X chart), no MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.
IQC data and the results obtained in proficiency tests, no MUkit software.
Data obtained from method validation, no MUkit software.


Measurand Urea Sample UK2
Uncertainty, Ui %
50
40
30
20
10
0
IQC data only from synthetic control sample and/or CRM (X chart), MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), no MUkit software.
IQC data and the results obtained in proficiency tests, MUkit software.
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