

Proficiency Test 01/2022

# Swimming pool water analyses

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Jaana Kolehmainen, Keijo Tervonen, Sari Lanteri,  
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Reports of the Finnish Environment Institute 21 | 2022  
Finnish Environment Institute  
Laboratory Centre

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Publisher and financier of publication: Finnish Environment Institute SYKE  
Latokartanonkaari 11, 00790 Helsinki, Finland, Phone +358 295 251 000, syke.fi

Layout: Markku Ilmakunnas

Cover photo: Adobe Stock

The publication is available in the internet (pdf): [syke.fi/publications](https://syke.fi/publications) | [helda.helsinki.fi/syke](https://helda.helsinki.fi/syke)

ISBN 978-952-11-5483-6 (PDF)

ISSN 1796-1726 (online)

Year of issue: 2022

## Abstract

### Proficiency Test 01/2022: Swimming pool water analyses

Profest SYKE carried out the proficiency test (PT) for analysis of chlorine,  $\text{KMnO}_4$ ,  $\text{NO}_3$ , pH, turbidity, and urea in swimming pool February 2022. In total, there were 26 participants in the PT. Either the calculated concentration or the robust mean, the mean, or the median of the reported results was used as the assigned values for the measurands. The performance of the participants was evaluated by using  $z$  and  $E_n$  scores. In this PT 95 % of the results evaluated based  $z$  score were satisfactory when deviation of 0.2 pH units for pH values and 10–25 % for the other measurands was accepted from the assigned value. From the results evaluated based on  $E_n$  scores 83 % were satisfactory. Warm thanks to all participants in this proficiency test!

**Keywords:** water analysis, chlorine, nitrate, pH,  $\text{KMnO}_4$ , turbidity, urea, swimming pool waters, water and environmental laboratories, proficiency test, interlaboratory comparisons

## Tiivistelmä

### Pätevyyskoe 01/2022: Uima-allasvesimääritykset

Profest SYKE järjesti helmikuussa 2022 pätevyyskokeen uima-allasvesien kloori-,  $\text{KMnO}_4$ -,  $\text{NO}_3$ -, pH-, sameus- ja ureamäärityksille. Pätevyyskokeeseen osallistui yhteensä 26 laboratoriota. Testisuureiden vertailuarvoina käytettiin joko laskennallista pitoisuutta tai osallistujien tulosten robustia keskiarvoa, keskiarvoa tai mediaania. Osallistujien pätevyuden arviointi tehtiin  $z$ - ja  $E_n$ -arvojen avulla. Koko tulosaineistossa oli  $z$ -arvoilla arvioituna 95 % hyväksyttävää tuloksia, kun vertailuarvosta sallittiin pH-määrityksissä 0,2 pH-yksikön ja muissa määrityksissä 10–25 %:n poikkeama.  $E_n$ -arvolla arvioiduista tuloksista näistä 83 % oli hyväksyttävää. Kiitos pätevyyskokeen osallistujille!

**Asiasanat:** vesianalyysi, vesi- ja ympäristölaboratoriot, uima-allasvedet, kloori, permanganaattiluku, nitraatti, pH, sameus, urea, pätevyyskoe, laboratorioden välinen vertailumittaus

## Sammandrag

### Kompetensprövning 01/2022: Simbassängvattenanalyser

Under februari 2022 genomförde Profest SYKE en kompetensprövning, som omfattade bestämningen av klor,  $\text{KMnO}_4$ , nitrat, pH, grumlighet och urea i simbassängvatten. Denna kompetensprövning hade totalt 26 deltagarna. Som referensvärde av analytens koncentration användes antingen det teoretiska värdet eller robust medelvärdet, medelvärdet eller median av deltagarnas resultat. Resultaten värderades med hjälp av  $z$ - och  $E_n$ -värden. I denna kompetensprövning var 95 % av resultaten värderades med  $z$ -värden tillfredsställande. Resultatet var tillfredsställande, om det devierade mindre än 0,2 pH enhet eller 10–25 % från referensvärdet. Av resultaten som bedömdes med  $E_n$ -värden var 83 % tillfredsställande. Ett varmt tack till alla deltagarna i testet!

**Nyckelord:** vattenanalyser, klor, nitrat, pH,  $\text{KMnO}_4$ , grumlighet, urea, simbassängvatten, kompetensprövning, vatten- och miljölaboratorier





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# 1 Introduction

Profest SYKE carried out the proficiency test (PT) for analysis of combined, free and total chlorine, permanganate index (KMnO<sub>4</sub>), nitrate, pH, turbidity, and urea from swimming pool waters in February 2022 (SPW 01/2022). 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]. Profest SYKE is accredited by the Finnish Accreditation Service as a proficiency testing provider (PT01, ISO/IEC 17043, [www.finas.fi/sites/en](http://www.finas.fi/sites/en)). The organizing of this proficiency test is included in the accreditation scope of Profest SYKE.

## 2 Organizing the proficiency test

### 2.1 Responsibilities

#### Organizer

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Mustialankatu 3, FI-00790 Helsinki, Finland  
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#### The responsibilities in organizing the proficiency test

Mirja Leivuori	coordinator
Riitta Koivikko	substitute for coordinator
Keijo Tervonen	technical assistance
Markku Ilmakunnas	technical assistance
Sari Lanteri	technical assistance
Ritva Väisänen	technical assistance
Teemu Näykki	analytical expert (SYKE: NO <sub>3</sub> , pH, turbidity, KMnO <sub>4</sub> )
Jaana Kolehmainen	in the expert orientation (SYKE: NO <sub>3</sub> , pH, turbidity, KMnO <sub>4</sub> )

<b>Cooperation partner</b>	Sami Tyrväinen, Eurofins Environment Testing Finland Oy (Lahti), analytical expert for chlorine and urea measurements.
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<b>Expert laboratory</b>	SYKE, Oulu (T003, <a href="http://www.finas.fi/sites/en">www.finas.fi/sites/en</a> )
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<b>Subcontracting</b>	Eurofins Environment Testing Finland Oy, Lahti (T039, <a href="http://www.finas.fi/sites/en">www.finas.fi/sites/en</a> ), chlorine and urea measurements
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## 2.2 Participants

In total 24 laboratories participated in this PT (Appendix 1), 21 from Finland and three from abroad. 95 % of the participants reported that they have accredited quality management system based on ISO/IEC 17025, while 3 participants did not report their accreditation status. One participant reported two sets of results. All of the 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 8 in the result tables. The other measurands were tested in the expert laboratory which has the code 15 in the result tables.

## 2.3 Samples and delivery

Two swimming pool water samples (U1 and U2) were delivered to the participants. Also, a synthetic sample (A1U) was delivered for the determination of urea. 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  $N_{NH_4}$  (for urea),  $N_{NO_3}$  (for nitrate), and conductivity (for pH). According to the test results all used vessels fulfilled the purity requirements.

The samples were delivered on 31 January 2022 to the participants abroad and mainly on 1 February 2022 to the national participants. The samples arrived to the participants on 2 February 2022.

To control the temperature during the transportation a temperature control sample was placed into the sample package and its temperature was to be measured when opening the package and to be reported to the provider. The reported temperatures of the control sample were lower than 11 °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 to be measured on 3 February 2022. The results were to be reported at the latest on 9 February 2022 and the participants delivered the results accordingly. One participant had analysed the urea samples on 7 February 2022. The preliminary results report was delivered to the participants via ProfTestWEB and email on 16 February 2022.

## 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 homogeneity test results, all samples were considered homogenous.

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 as stable (Appendix 4). No evident influence to the participants' performance was seen from the possible sample warming during the sample transportation (Chapter 2.3). According to the literature and

expertise, the other proficiency test items are known to be stable within the testing time of the proficiency test.

## 2.5 Feedback from the proficiency test

The feedback from the proficiency test is shown in Appendix 5. The comments from the participants focused mainly on reporting errors and difficulties. The comments from the provider are mainly related to the lacking conversancy to the given information with the samples and incorrect reporting. 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  $5 \times s_{\text{rob}}$  or 50 % from the robust mean, were rejected before the statistical results handling.

The participants were to report replicate results for the combined, free and total chlorine, turbidity, and urea measurements. The replicate results were tested using the Cochran's test, which compares the within-laboratory deviation of each participant to the standard deviation of the replicate results of all the participants. The replicate results which differ significantly from others are outliers. The Cochran's test rejects the results having significantly higher within-laboratory deviation than the results the average, regardless their z score evaluation. When two results were to be reported for the analysis and the participant reported only one, the result was not included in the statistical calculations, and it was not evaluated.

If the requested replicate results were not reported, the results were rejected from the statistical handling and no performance evaluation was given. If the participant informed, that they had not measured parallel samples, but they reported parallel results, the results were rejected from the statistical handling and no performance evaluation was given.

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 are shown in Appendix 6.

The calculated value was used as the assigned value for the urea measurements in the synthetic sample (A1U) and in the sample UE2 (enzymatic test). The robust mean was used as the assigned value for the other measurements, except for urea measurement with the Koroleff's method (sample UK2), where the median value was used ( $n_{\text{stat}} < 12$ ).

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 evaluated 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 0.6-0.7 % 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 0.7 % for pH measurements. For the other measurands the uncertainties of the assigned values varied between 1.8 % and 16 % (Appendix 6). **After reporting the preliminary results report no changes have been done for the assigned values.**

### 2.6.3 Proficiency assessment procedure

The results of this proficiency test were evaluated with the z scores. The standard deviation for proficiency assessment was estimated based on 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 report no changes have been done for the standard deviations of the proficiency assessment values.**

When the number of reported results was low ( $Urea_{Koroleff}$ ,  $n_{stat} < 6$ ), the assigned value was based on the participants' results and the uncertainty was set for the assigned value, the performance was evaluated by means of  $E_n$  scores ('Error, normalized', Appendix 7).

When using the robust mean or the median 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 and  $s_{pt}$  is the standard deviation for proficiency assessment [2, 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 for proficiency assessment ( $s_{pt}$ ) and the corresponding z score was estimated by comparing  $s_{pt}$  with the robust standard deviation ( $s_{rob}$ ) or standard deviation ( $s$ ) of the reported results [3]. The criterion  $s_{rob}$  (or  $s$ ) /  $s_{pt} < 1.2$  was fulfilled.

## 3 Results and conclusions

### 3.1 Results

The summary of the results is presented in Table 1. The terms in the results table are explained in Appendix 7. The results and the performance of each participant are presented in Appendix 8 and 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 0.6 to 12.3 % (Table 1). The robust standard deviations were somewhat lower than in the previous similar proficiency test SPW 01/2021, where the deviations varied from 1.0 % to 13.5 % [6].

Table 1. The summary of the results in the proficiency test SPW 01/2022.

Measurand	Sample	Unit	Assigned value	Mean	Rob. mean	Median	S <sub>rob</sub>	S <sub>rob</sub> %	2 x S <sub>pt</sub> %	n <sub>all</sub>	Acc z %
Cl <sub>2, comb</sub>	U1K	mg/l	0.48	0.48	0.48	0.49	0.05	10.5	20	21	100
	U2K	mg/l	0.77	0.77	0.77	0.74	0.08	10.1	20	20	100
Cl <sub>2, free</sub>	U1K	mg/l	0.52	0.52	0.52	0.53	0.04	7.0	15	21	100
	U2K	mg/l	0.59	0.59	0.59	0.60	0.03	5.7	15	20	94
Cl <sub>2, total</sub>	U1K	mg/l	1.00	1.00	1.00	0.99	0.05	5.0	10	22	95
	U2K	mg/l	1.35	1.36	1.35	1.35	0.06	4.2	10	21	100
KMnO <sub>4</sub>	U1P	mg/l	5.45	5.49	5.45	5.66	0.67	12.3	25	18	78
	U2P	mg/l	11.4	11.4	11.4	11.6	1.0	8.7	20	18	94
NO <sub>3</sub>	U1N	mg/l	18.0	18.0	18.0	17.9	0.5	2.8	10	14	100
	U2N	mg/l	8.78	8.78	8.78	8.79	0.31	3.5	10	14	100
pH	U1H		5.68	5.68	5.68	5.68	0.03	0.6	3.0	23	100
	U2H		7.35	7.34	7.35	7.36	0.08	1.1	2.6	22	95
Turbidity	U1S	FNU	0.72	0.71	0.72	0.73	0.07	9.2	25	22	95
	U2S	FNU	0.45	0.45	0.45	0.43	0.05	11.3	25	21	90
Urea	A1U	mg/l	0.77	0.78	0.78	0.78	0.06	7.8	10	13	92
Urea <sup>Enzymatic</sup>	UE2	mg/l	1.06	0.99	1.00	0.99	0.05	5.5	15	9	89
Urea <sup>Koroleff</sup>	UK2	mg/l	0.52	0.53	-	0.52	-	-	-	6	-

Rob. mean: the robust mean, S<sub>rob</sub>: the robust standard deviation, S<sub>rob</sub> %: the robust standard deviation as percent, 2 x S<sub>pt</sub> %: the standard deviation for proficiency assessment at the 95 % confidence level, n<sub>all</sub>: the number of the participants, Acc z %: the results (%), where  $|z| \leq 2$ .

In this PT the participants were to report replicate results for chlorine, turbidity and urea measurements. All the participants reported the replicate results with the exception of one participant (12) which did not report replicate results for chlorine measurements. Some of participants reported that they have not done replicate determinations. However, they had reported one measured result as replicate result (Appendix 5). Those results were not included in the statistical handling. The repeatability of the replicate determinations was tested using ANOVA statistical handling (Table 2). The estimation of the robustness of the methods could be done by the ratio  $s_b/s_w$ . For the robust methods the ratio  $s_b/s_w$  should not be exceeded 3. The criterion value varied between 0.9 and 6.1, in three cases the criterion was not fulfilled (Table 2).

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

Measurand	Sample	Unit	Assigned value	Mean	S <sub>w</sub>	S <sub>b</sub>	S <sub>t</sub>	S <sub>w</sub> %	S <sub>b</sub> %	S <sub>t</sub> %	S <sub>b</sub> /S <sub>w</sub>
Cl <sub>2, comb</sub>	U1K	mg/l	0.48	0.48	0.015	0.044	0.046	3.2	9.0	9.5	2.9
	U2K	mg/l	0.77	0.77	0.030	0.066	0.073	3.9	8.5	9.4	2.2
Cl <sub>2, free</sub>	U1K	mg/l	0.52	0.52	0.012	0.034	0.0356	2.3	6.5	6.9	2.8
	U2K	mg/l	0.59	0.59	0.029	0.023	0.037	4.9	3.9	6.2	0.79
Cl <sub>2, total</sub>	U1K	mg/l	1.00	1.00	0.008	0.046	0.047	0.79	4.6	4.7	5.8
	U2K	mg/l	1.35	1.36	0.017	0.055	0.058	1.2	4.1	4.3	3.3
Turbidity	U1S	FNU	0.72	0.71	0.021	0.063	0.066	2.9	8.8	9.2	3.1
	U2S	FNU	0.45	0.45	0.018	0.052	0.055	4.0	11	12	2.9
Urea	A1U	mg/l	0.77	0.78	0.015	0.054	0.056	1.9	7.0	7.2	3.7
Urea <sup>Enzymatic</sup>	UE2	mg/l	1.06	0.99	0.018	0.053	0.056	1.8	5.3	5.6	3.0
Urea <sup>Koroleff</sup>	UK2	mg/l	0.52	0.53	0.017	0.101	0.102	3.2	19	19	6.1

Ass.val.: assigned value; s<sub>w</sub>: repeatability standard error; s<sub>b</sub>: between participant's standard error; s<sub>t</sub>: reproducibility standard error.

## 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  $\geq 5$ .

### **Chlorine** ( $\text{Cl}_{2, \text{comb}}$ , $\text{Cl}_{2, \text{free}}$ , $\text{Cl}_{2, \text{total}}$ )

For the measurements of the total and free chlorine about 81 % 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). Three participants used other methods (e.g. Hach Lange tube method or different test kit methods). The combined chlorine was mainly 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 clear differences between the methods were observed (Appendix 12).

### **Permanganate index** ( $\text{KMnO}_4$ )

In the measurements of permanganate index mainly the automatic and manual titrimetric methods 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** ( $\text{NO}_3$ )

Eight of the participants used automatic CFA or FIA method based on the standard method EN ISO 13395 (Appendix 12). Two of the participants used IC method based on the standard method EN ISO 10304. One participant used the sulfanilamide spectrophotometric method after hydrazine reduction or after Cd/Cu reduction. Other reported methods were UV-screening and internal IC method. Based on the visual evaluation no differences between the methods were observed (Appendix 12).

### **pH**

About 51 % of the participants measured pH using the electrode for low ionic waters and 44 % of the participants used the universal electrode. One participant reported swan pool water electrode as the other method (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, whose used attenuation of radiant flux measurement or internal method as the other method (Appendix 12).

### **Urea**

For urea measurement enzymatic photometric method (urea is degraded into ammonium and  $\text{CO}_2$  using urease) was used by 8-9 participants depending on the sample. Six participants used 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 01/2020 [6]. The reported results obtained with the Koroleff's method (UK2) were about 50 % of the calculated concentration for the swimming pool water sample, while the reported results obtained with the enzymatic method (UE2) were 93 % of 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 with the enzymatic method (UE2).

### 3.3 Uncertainties of the results

Almost all the participants (96 %) reported the expanded uncertainties ( $k=2$ ) with their results for at least some of their results (Table 3, Appendix 9). The range of the reported uncertainties varied between the measurands and the sample types, and thus the harmonization of the uncertainty's estimation should be continued. It was evident, that for pH, chloride, and turbidity some uncertainties (very low values) had been reported erroneously, not as relative values (%) as the provider of this PT had requested (Table 3). The expanded uncertainties below 5 % could commonly be considered unrealistic uncertainty value for routine laboratories. In this proficiency test unrealistic high measurement uncertainty was reported, i.e. higher than 50 %, marked as bold in Table 3. Harmonization of the uncertainty's estimation should be continued.

Several approaches were used for estimating the measurement uncertainty (Appendix 13). The most used estimation approach was based on using the internal quality control data (Appendix 13). At maximum eight participants used MUKIT measurement uncertainty software for the estimation of their uncertainties [8]. The free software is available on the webpage: [www.syke.fi/envical/en](http://www.syke.fi/envical/en) [8, 9]. Generally, the used approach for estimating measurement uncertainty did not make definite impact on the uncertainty estimates.

Table 3. The ranges of the reported expanded uncertainties by participants as percent ( $k=2$ ,  $U_i\%$ ).

Measurement	Sample	The range of $U_i$ %
Cl <sub>2, comb</sub>	U1K	22
	U2K	10-40
Cl <sub>2, free</sub>	U1K	1.79-25
	U2K	1.79-25
Cl <sub>2, total</sub>	U1K	2.2-27
	U2K	2.2-27
KMnO <sub>4</sub>	U1P	10- <b>61</b>
	U2P	10-33
NO <sub>3</sub>	U1N	7-20
	U2N	7-20
pH	U1H	0.15-5
	U2H	0.15-5
Turbidity	U1S	0.1-25
	U2S	0.1-30
Urea	A1U	9.5-30
	UE2	9.5-25
	UK2	13-30

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  $E_n$  (Appendix 7), which were calculated using the assigned values and the standard deviation for proficiency assessment interpreted as follows:

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

In total, 95 % of the results evaluated with the  $z$  scores were satisfactory when total deviation of 0.2 pH units and for the other measurement 10–25 % from the assigned values were accepted. From the results evaluated based on  $E_n$  scores 83 % were satisfactory (Appendix 10). The summary of the performance evaluation and comparison to the previous performance is presented in Table 4. In the previous similar PT SPW 01/2021, the performance was satisfactory for 89 % of the results with the same deviations from the assigned values [6].

The recovery for urea in the swimming water sample was calculated from the mean concentrations of different methods (recovery% =  $100 \times \text{mean of results} / \text{calculated value}$ ). The recovery for the enzymatic method was 93 %, while for the Koroleff's method it was 50 %. The recovery percentage for the results obtained by Koroleff's method is in the same range as in the previous similar proficiency test SPW 01/2021 (51 %) [6]. In Finland, the national supervisory authority for welfare and health (Valvira) has considered 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.

Table 4. Summary of the performance evaluation in the proficiency test SPW 01/2022.

Measurand	2 x s <sub>pt</sub> %	Satisfactory results, %	Remarks
Cl <sub>2, comb</sub>	20	100	Very good performance. In the SPW 01/2021 the performance was satisfactory for 88 % of the results, when accepting the deviation of 20-25 % from the assigned value [6].
Cl <sub>2, free</sub>	15	97	Good performance. In the SPW 01/2021 the performance was satisfactory for 91 % of the results, with the same range of standard deviation for proficiency assessment [6].
Cl <sub>2, total</sub>	10	98	Good performance. In the SPW 01/2021 the performance was satisfactory for 87 % of the results, with the same range of standard deviation for proficiency assessment [6].
KMnO <sub>4</sub>	20-25	86	In the SPW 01/2021 the performance was satisfactory for 86 % of the results when accepting the deviation of 20 % from the assigned value [6].
NO <sub>3</sub>	10	100	Very good performance. In the SPW 01/2021 the performance was satisfactory for 88 % of the results, with the same range of standard deviation for proficiency assessment [6].
pH	3-2.6	98	Good performance. In the SPW 01/2021 the performance was satisfactory for 87 % of the results, when accepting the deviation of 2.6-3.1 % from the assigned value [6].
Turbidity	25	93	Good performance. In the SPW 01/2021 the performance was satisfactory for 93 % of the results, with the same range of standard deviation for proficiency assessment [6].
Urea A1U	10	92	Good performance. In the SPW 01/2021 the performance was satisfactory for 83 % of the results with the same range of standard deviation for proficiency assessment [6].
Urea <sup>Enzymatic</sup> UE2	15	89	<b>The recovery is in average 93 % of the calculated value.</b> Based on the PT the method is suitable for urea measurements of swimming pool waters. In the SPW 01/2021 the performance was satisfactory for 86 % of the results with the same range of standard deviation for proficiency assessment [6].
Urea <sup>Koroleff</sup> UK2	<i>E<sub>n</sub> score</i>	83	<b>The recovery is in average 50 % of the calculated value</b> and 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 01/2021 the performance was satisfactory based on E <sub>n</sub> scores for 83 % of the results [6].

## 5 Summary

Profest SYKE carried out the proficiency test (PT) for analysis of combined chlorine, free chlorine, total chlorine, permanganate index ( $\text{KMnO}_4$ ), nitrate, pH, turbidity, and urea from swimming pool waters in February 2022 (SPW 01/2022). In total, 24 participants joined in this proficiency test.

The evaluation of the performance was based on the  $z$  and  $E_n$  scores. In this PT 95 % 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. The results of Koroleff's method (sample UK2) were evaluated based on  $E_n$  scores and those 83 % 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, except for urea measurement with the Koroleff's method (sample UK2), where the median value was used ( $n_{\text{stat}} < 12$ ).

It should be noted 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 50 % of the calculated concentration, while the reported results obtained with the enzymatic method were in the 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

Profest SYKE järjesti helmikuussa 2022 pätevyyskokeen uima-allasvesiä analysoiville laboratorioille (SPW 01/2022). Pätevyyskokeessa testattiin allasvesien kloori-,  $\text{KMnO}_4$ -,  $\text{NO}_3$ -, pH-, sameus- ja ureamäärittäjä. Ureamäärittämistä varten toimitettiin myös synteettinen näyte. Pätevyyskokeeseen osallistui yhteensä 24 laboratoriota.

Pätevyyden arvioimisessa käytettiin  $z$ - ja  $E_n$ -arvoja. Hyväksyttäviä  $z$ -arvolla arvioituja tuloksia oli kokonaisuudessaan 95 %, kun sallittiin pH-määrittämissä 0,2 pH-yksikön ja muissa määrittämissä 10–25 %:n poikkeama vertailuarvosta. Koroleffin menetelmällä määritetyt ureatulokset arvioitiin  $E_n$ -arvoilla ja näistä 83 % oli hyväksytyjä. Laskennallista pitoisuutta käytettiin vertailuarvona synteettisen näytteen (A1U) sekä näytteen UE2 (entsyymaattinen menetelmä) ureamäärittämissä. Muissa määrittämissä vertailuarvona käytettiin osallistujien tulosten robustia keskiarvoa, poikkeuksena näytteen UK2 (Koroleffin menetelmä) ureamäärittämisessä, missä käytettiin tulosaineiston mediaania ( $n_{\text{stat}} < 12$ ).

Uima-allasvesinäytteiden ureatuloksissa havaittiin ero Koroleffin menetelmän ja entsyymaattisen spektrometrisen menetelmän välillä. Vastaava ero on havaittu myös aikaisemmissa pätevyyskokeissa. Koroleffin menetelmään perustuvalla määrittämisellä saadut tulokset poikkesivat huomattavasti laskennallisista pitoisuuksista. Koroleffin menetelmällä saadut ureapitoisuudet olivat noin 50 % laskennallisesta vertailuarvosta, kun entsyymaattisella testillä määritetyt tulokset ovat lähellä laskennallista arvoa. Onkin suositeltavaa käyttää entsyymaattista spektrometristä menetelmää uima-allasvesien ureapitoisuuksien määrittämisessä. Käytettäessä Koroleffin menetelmää uima-allasvesien ureapitoisuuden määrittämiseen tulisi näytetyypin vaikutus tuloksiin selvittää paremmin.

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**Appendix I. Participants in the proficiency test**

Country	Participant
<b>Finland</b>	Eurofins Ahma Oy Seinäjoki Eurofins Ahma Oy, Rovaniemi Eurofins Environment Testing Finland Oy, Lahti HSY Käyttölaboratorio Pitkälampi Helsinki KVVY Tutkimus Oy, Tampere KVVY-Botnialab, Vaasa Kymen Ympäristölaboratorio Oy Lounais-Suomen vesi- ja ympäristötutkimus Oy, Turku LUVVYLab Oy Ab 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
<b>Switzerland</b>	Amt für Lebensmittelsicherheit und Veterinärwesen Basel-Landschaft Amt für Verbraucherschutz (AVS), Labor AVS PCAM - Division Protection des eaux (PRE)

## Appendix 2. Sample preparation

Measurand/Sample		U1K	U2K
<b>Cl<sub>2</sub>, comb</b>	Initial concentration, mg/l	-	-
	Added compound (producer)	C <sub>7</sub> H <sub>7</sub> ClNaNO <sub>2</sub> S* 3H <sub>2</sub> O	C <sub>7</sub> H <sub>7</sub> ClNaNO <sub>2</sub> S* 3H <sub>2</sub> O
	Assigned value, mg/l	0.48	0.77
<b>Cl<sub>2</sub>, free</b>	Initial concentration, mg/l	0	0
	Added compound (producer)	NaClO (BHD)	NaClO (BHD)
	Assigned value, mg/l	0.52	0.59
<b>Cl<sub>2</sub>, total</b>	Initial concentration, mg/l	0.08	0.08
	Addition, mg/l	1.02	1.41
	Assigned value, mg/l	1.00	1.35
		<b>U1P</b>	<b>U2P</b>
<b>KMnO<sub>4</sub></b>	Initial concentration, mg/l	2.33	2.33
	Added compound (producer)	C <sub>7</sub> H <sub>6</sub> O <sub>3</sub> (Fluka)	C <sub>7</sub> H <sub>6</sub> O <sub>3</sub> (Fluka)
	Assigned value, mg/l	5.45	11.4
		<b>U1N</b>	<b>U2N</b>
<b>NO<sub>3</sub></b>	Initial concentration, mg/l	23.2	23.2
	Dilution	4.5 l sample + 1.5 l dilution	2.2 l sample + 3.8 l dilution
	Assigned value, mg/l	18.0	8.78
		<b>U1H</b>	<b>U2H</b>
<b>pH</b>	Initial concentration	7.16	7.16
	pH adjustment	C <sub>8</sub> H <sub>5</sub> KO <sub>4</sub>	-
	Assigned value	5.68	7.35
		<b>U1S</b>	<b>U2S</b>
<b>Turbidity</b>	Initial concentration, FNU	0.10	0.10
	Added compound (producer)	(HACH Formazin)	(HACH Formazin)
	Assigned value, FNU	0.72	0.45
		<b>A1U</b>	<b>UE2 / UK2</b>
<b>Urea</b>	Initial concentration, mg/l	-	0
	Added compound (producer)	CO(NH <sub>2</sub> ) <sub>2</sub>	CO(NH <sub>2</sub> ) <sub>2</sub>
	Assigned value, mg/l	0.77	1.06/0.52

First letter of the sample code indicates the sample matrix:

A = Synthetic sample

U = Swimming pool water

### Appendix 3. Homogeneity of the samples

Homogeneity was tested as replicate measurements of selected measurement from four to six of each sample types.

#### Criteria for homogeneity:

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

$s_{\text{pt}}$  = standard deviation for proficiency assessment

$s_{\text{anal}}$  = analytical deviation, standard deviation of the results in a sub sample

$s_{\text{sam}}$  = between-sample deviation, standard deviation of the results between sub samples

$$c = F1 \times s_{\text{all}}^2 + F2 \times s_{\text{anal}}^2, \text{ where}$$

$$s_{\text{all}}^2 = (0.3 \times s_{\text{pt}})^2$$

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, FNU or pH-unit	n	Spt%	Spt	Sanal	Sanal/Spt	Sanal/Spt<0.5?	Ssam	Ssam <sup>2</sup>	c	Ssam <sup>2</sup> <c?
KMnO <sub>4</sub> / U1P	5.83	4	12.5	0.73	0.15	0.21	Yes	0	0	0.19	Yes
KMnO <sub>4</sub> / U2P	11.9	4	10	0.18	0.17	0.15	Yes	0.04	0.002	0.41	Yes
NO <sub>3</sub> / U1N	18.0	4	5	0.90	0.04	0.04	Yes	0.14	0.02	0.19	Yes
NO <sub>3</sub> / U2N	8.71	4	5	0.44	0.04	0.08	Yes	0	0	0.05	Yes
pH / U1H	5.64	6	1.5	0.08	0.02	0.28	Yes	0	0	0.002	Yes
pH / U2H	7.36	6	1.3	0.10	0.01	0.11	Yes	0.008	<0.001	0.002	Yes
Turbidity / U1S	0.70	4	12.5	0.09	0.004	0.05	Yes	0.03	<0.001	0.002	Yes
Turbidity / U2S	0.46	4	12.5	0.06	0.02	0.43	Yes	0.03	0.001	0.003	Yes
Urea / U2U	1.01	4	7.5	0.08	0.008	0.10	Yes	0.002	0	0.002	Yes

**Conclusion:** All criteria for homogeneity were fulfilled and the samples could be considered homogeneous.



## Appendix 4. Stability of the samples

Stability of pH, Cl<sub>2</sub>\_free, Cl<sub>2</sub>\_comb, Cl<sub>2</sub>\_tot and urea were tested by analyzing the samples stored at the temperatures 4 and 20 °C.

**Criteria for stability:**  $D < 0.3 \times s_{pt}$ , where

$D = |\text{the difference of results measured from the samples stored at the temperatures 4 °C and 20 °C}|$

$s_{pt}$  = standard deviation for proficiency assessment

### Cl<sub>2</sub>, comb

Sample	Result, mg/l		Sample	Result, mg/l	
Date	3.2. (20 °C)	3.2. (4 °C)	Date	3.2. (20 °C)	3.2. (4 °C)
U1K	0.534	0.546	U2K	0.888	0.876
D	0.012		D	0.013	
0.3×s <sub>pt</sub>	0.014		0.3×s <sub>pt</sub>	0.023	
<b>D &lt; 0.3 × s<sub>pt</sub>? Yes</b>			<b>D &lt; 0.3 × s<sub>pt</sub>? Yes</b>		

### Cl<sub>2</sub>, free

Sample	Result, mg/l		Sample	Result, mg/l	
Date	3.2. (20 °C)	3.2. (4 °C)	Date	3.2. (20 °C)	3.2. (4 °C)
U1K	0.571	0.564	U2K	0.595	0.610
D	0.007		D	0.015	
0.3×s <sub>pt</sub>	0.012		0.3×s <sub>pt</sub>	0.013	
<b>D &lt; 0.3 × s<sub>pt</sub>? Yes</b>			<b>D &lt; 0.3 × s<sub>pt</sub>? No<sup>1)</sup></b>		

### Cl<sub>2</sub>, total

Sample	Result, mg/l		Sample	Result, mg/l	
Date	3.2. (20 °C)	3.2. (4 °C)	Date	3.2. (20 °C)	3.2. (4 °C)
U1K	1.080	1.109	U2K	1.483	1.486
D	0.029		D	0.003	
0.3×s <sub>pt</sub>	0.015		0.3×s <sub>pt</sub>	0.020	
<b>D &lt; 0.3 × s<sub>pt</sub>? No<sup>1)</sup></b>			<b>D &lt; 0.3 × s<sub>pt</sub>? Yes</b>		

### pH

Sample	Result		Sample	Result	
Date	3.2. (20 °C)	3.2. (4 °C)	Date	3.2. (20 °C)	3.2. (4 °C)
U1H	5.64	5.66	U2H	7.37	7.38
D	0.017		D	0.008	
0.3×s <sub>pt</sub>	0.026		0.3×s <sub>pt</sub>	0.029	
<b>D &lt; 0.3 × s<sub>pt</sub>? Yes</b>			<b>D &lt; 0.3 × s<sub>pt</sub>? Yes</b>		

### Urea

Sample	Result, mg/l		Sample	Result, mg/l	
Date	3.2. (20 °C)	3.2. (4 °C)	Date	3.2. (20 °C)	3.2. (4 °C)
A1U	0.802	0.805	U2U	1.013	1.058
D	0.003		D	0.045	
0.3×s <sub>pt</sub>	0.012		0.3×s <sub>pt</sub>	0.024	
<b>D &lt; 0.3 × s<sub>pt</sub>? Yes</b>			<b>D &lt; 0.3 × s<sub>pt</sub>? No<sup>1)</sup></b>		

<sup>1)</sup> The difference is within the analytical error.

**Conclusion:** All criteria for stability were fulfilled and the samples could be considered stable.

## Appendix 5. Feedback from the proficiency test

### Feedback from the participants

Participant	Comments to the results	Action / Profest SYKE
1	The participant had difficulties in reporting the results via ProfestWEB. The participant reported their results via email.	The organizer tried to help the participant with ProfestWEB reporting. However, the problem could not be solved, and the participant was allowed to report the results via email. The organizer transferred the results to ProfestWEB and the participant checked that their results were correctly transferred. It is recommended to contact the ICT's personnel of the participant's institute to solve out the communication problems with ProfestWEB.
15	The participant reported erroneously their $\text{KMnO}_4$ results as $\text{COD}_{\text{Mn}}$ in the samples U1P and U2P. Their corrected results were: U1P 6.004 mg/l U2P 12.262 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 questionable. The participant can re-calculate the z scores according to the Guide for participants [5].
10	The participant informed they analysed the samples for urea four days later than requested, on 7 February 2022.	The performance of the participant for urea measurements was satisfactory, thus the delay did not affect the participant's performance.

### Feedback to the participants

Participant	Comments
4, 7, 9, 11, 15, 19, 20, 23	The participants did not return the sample arrival document to the organizer. Thus, the information of the sample arrival temperature was missing for them. The participants should follow the instructions of the organizer.
12	The participant did not report the replicate result for Cl measurements thus these results were not included in the statistical calculations and no performance evaluation was given. The participant should follow the instructions of the organizer.
14	The participant informed, that they had not measured parallel samples, but they reported parallel results. The results were rejected from the statistical handling and no performance evaluation was given.
3, 10, 16, 17, 19, 20, 24	The deviation of replicate results was high in the following cases: $\text{Cl}_2, \text{comb}$ U1K: parts 3, 16; $\text{Cl}_2, \text{free}$ U2K: parts 3, 16, 20, 24; $\text{Cl}_2, \text{total}$ U1K: part 19, turbidity: U1S: part 10; U2 S: part 17. Thus, their results were Cochran outliers. The organizer recommends the participants to validate their accepted deviation for replicate measurements. Some of the participants' results were Cochran outliers. The participants are recommended to check the allowed difference for the parallel results.
7, 10, 18	The measurement uncertainty should be reported with the results obtained by accredited methods.
4, 11, 18	The participant reported absolute measurement uncertainty for their pH and/or turbidity results, but the request from the organizer was to report the relative measurement uncertainty. The participant should follow the instructions of the organizer.
11, 16, 18, 20	The participant did not inform the accreditation status of their method for some measurands. The participants should follow the instructions of the organizer.

## 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 <sub>2, comb</sub>	U1K	mg/l	0.48	0.03	6.0	Robust mean	0.30
	U2K	mg/l	0.77	0.05	6.0	Robust mean	0.30
Cl <sub>2, free</sub>	U1K	mg/l	0.52	0.02	4.0	Robust mean	0.27
	U2K	mg/l	0.59	0.02	3.5	Robust mean	0.23
Cl <sub>2, total</sub>	U1K	mg/l	1.00	0.03	2.8	Robust mean	0.28
	U2K	mg/l	1.35	0.03	2.4	Robust mean	0.24
KMnO <sub>4</sub>	U1P	mg/l	5.45	0.42	7.7	Robust mean	0.31
	U2P	mg/l	11.4	0.6	5.3	Robust mean	0.27
NO <sub>3</sub>	U1N	mg/l	18.0	0.3	1.8	Robust mean	0.18
	U2N	mg/l	8.78	0.21	2.4	Robust mean	0.24
pH	U1H		5.68	0.02	0.3	Robust mean	0.10
	U2H		7.35	0.04	0.6	Robust mean	0.23
Turbidity	U1S	FNU	0.72	0.04	5.2	Robust mean	0.21
	U2S	FNU	0.45	0.03	6.5	Robust mean	0.26
Urea	A1U	mg/l	0.77	0.01	0.7	Calculated value	0.07
Urea <sub>Enzymatic</sub>	UE2	mg/l	1.06	0.01	0.6	Calculated value	0.04
Urea <sub>Koroleff</sub>	UK2	mg/l	0.52	0.08	16.0	Median	-

$U_{pt}$  = 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.

## Appendix 7. Terms and definitions used in performance evaluation

The information could be applied according to the PT.

<b>Measurand</b>	The tested parameter
<b>Sample</b>	The code of the sample
<b>Assigned value</b>	The value attributed to a particular property of a proficiency test item
<b>Participant's result</b>	The result reported by the participant (when replicate results are reported, the mean value)
<b><math>2 \times s_{pt}</math> %</b>	The standard deviation for proficiency assessment ( $s_{pt}$ ) at the 95 % confidence level
<b>z score</b>	Used for the participant's performance evaluation in the PT. Calculated with formula:

$$z = (x_i - x_{pt})/s_{pt}, \text{ where}$$

$x_i$  = the result of the individual participant

$x_{pt}$  = the assigned value

$s_{pt}$  = the standard deviation for proficiency assessment

### Interpretation of the z scores

$ z  \leq 2$	Satisfactory
$2 <  z  < 3$	Questionable (warning signal), the result deviates more than $2 \times s_{pt}$ from the assigned value.
$ z  \geq 3$	Unsatisfactory (action signal), the result deviates more than $3 \times s_{pt}$ from the assigned value.

<b><math>E_n</math> score</b>	Error, normalized – Used to evaluate the difference between the assigned value and participant's result within their claimed expanded uncertainty. Calculated with formula:
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$$(E_n)_i = \frac{x_i - x_{pt}}{\sqrt{U_i^2 + U_{pt}^2}}, \text{ where}$$

$U_i$  = the expanded uncertainty of a participant's result

$U_{pt}$  = the expanded uncertainty of the assigned value

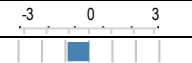
### Interpretation of the $E_n$ scores

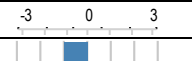
$ E_n  \leq 1.0$	Satisfactory, should be taken as an indicator of successful performance when the uncertainties are valid.
$ E_n  > 1.0$	Unsatisfactory (action signal), could indicate a need to review the uncertainty estimates, or to correct a measurement issue.

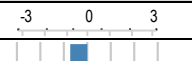
<b>Md</b>	Median
<b>s</b>	Standard deviation
<b>s %</b>	Standard deviation, %
<b>n<sub>stat</sub></b>	Number of results in statistical processing

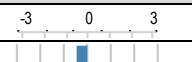
More information of the statistical calculations in international standards ISO/IEC 17043 and ISO 13528 as well as in Profest SYKE Guide for participants [1, 2, 5].

## Appendix 8. Results of each participant

Participant 1												
Measurand	Unit	Sample		z score	Assigned value	2*s <sub>pt</sub> %	Participant's result	Md	Mean	s	s %	n <sub>stat</sub>
Turbidity	FNU	U1S		-0.94	0.72	25	0.64	0.73	0.71	0.06	9.0	20
Urea <sup>Enzymatic</sup>	mg/l	UE2		-0.25	1.06	15	1.04	0.99	0.99	0.05	5.5	9

Participant 2												
Measurand	Unit	Sample		z score	Assigned value	2*s <sub>pt</sub> %	Participant's result	Md	Mean	s	s %	n <sub>stat</sub>
Cl <sub>2, comb</sub>	mg/l	U1K		-1.04	0.48	20	0.43	0.49	0.48	0.04	9.3	19
	mg/l	U2K		-0.47	0.77	20	0.73	0.74	0.77	0.07	9.0	18
Cl <sub>2, free</sub>	mg/l	U1K		1.00	0.52	15	0.56	0.53	0.52	0.03	6.7	19
	mg/l	U2K		0.23	0.59	15	0.60	0.60	0.59	0.03	5.2	17
Cl <sub>2, total</sub>	mg/l	U1K		-0.22	1.00	10	0.99	0.99	1.00	0.05	4.7	20
	mg/l	U2K		-0.22	1.35	10	1.34	1.35	1.36	0.06	4.2	19
KMnO <sub>4</sub>	mg/l	U1P		-0.47	5.45	25	5.13	5.66	5.49	0.80	14.5	16
	mg/l	U2P		0.18	11.4	20	11.6	11.6	11.4	0.9	7.7	17
NO <sub>3</sub>	mg/l	U1N		-0.56	18.0	10	17.5	17.9	18.0	0.4	2.4	14
	mg/l	U2N		-0.55	8.78	10	8.54	8.79	8.78	0.27	3.1	14
pH		U1H		0.35	5.68	3	5.71	5.68	5.68	0.04	0.7	22
		U2H		0.84	7.35	2,6	7.43	7.36	7.34	0.08	1.1	21
Turbidity	FNU	U1S		-0.19	0.72	25	0.70	0.73	0.71	0.06	9.0	20
	FNU	U2S		-0.03	0.45	25	0.45	0.43	0.45	0.05	11.8	19
Urea	mg/l	A1U		-1.65	0.77	10	0.71	0.78	0.78	0.06	7.1	13
Urea <sup>Enzymatic</sup>	mg/l	UE2		-2.18	1.06	15	0.89	0.99	0.99	0.05	5.5	9

Participant 3												
Measurand	Unit	Sample		z score	Assigned value	2*s <sub>pt</sub> %	Participant's result	Md	Mean	s	s %	n <sub>stat</sub>
Cl <sub>2, comb</sub>	mg/l	U1K		-0.75	0.48	20	0.44	0.49	0.48	0.04	9.3	19
	mg/l	U2K		-0.69	0.77	20	0.72	0.74	0.77	0.07	9.0	18
Cl <sub>2, free</sub>	mg/l	U1K		0.54	0.52	15	0.54	0.53	0.52	0.03	6.7	19
	mg/l	U2K		1.03	0.59	15	0.64	0.60	0.59	0.03	5.2	17
Cl <sub>2, total</sub>	mg/l	U1K		-0.30	1.00	10	0.99	0.99	1.00	0.05	4.7	20
	mg/l	U2K		0.04	1.35	10	1.35	1.35	1.36	0.06	4.2	19
KMnO <sub>4</sub>	mg/l	U1P		0.48	5.45	25	5.78	5.66	5.49	0.80	14.5	16
	mg/l	U2P		0.70	11.4	20	12.2	11.6	11.4	0.9	7.7	17
pH		U1H		0.23	5.68	3	5.70	5.68	5.68	0.04	0.7	22
		U2H		-0.63	7.35	2,6	7.29	7.36	7.34	0.08	1.1	21
Turbidity	FNU	U1S		0.87	0.72	25	0.80	0.73	0.71	0.06	9.0	20
	FNU	U2S		-0.85	0.45	25	0.40	0.43	0.45	0.05	11.8	19

Participant 4												
Measurand	Unit	Sample		z score	Assigned value	2*s <sub>pt</sub> %	Participant's result	Md	Mean	s	s %	n <sub>stat</sub>
Cl <sub>2, comb</sub>	mg/l	U1K		-0.43	0.48	20	0.46	0.49	0.48	0.04	9.3	19
	mg/l	U2K			0.77	20	0,775	0.74	0.77	0.07	9.0	18
Cl <sub>2, free</sub>	mg/l	U1K		-0.73	0.52	15	0.49	0.53	0.52	0.03	6.7	19
	mg/l	U2K			0.59	15	0,555	0.60	0.59	0.03	5.2	17
Cl <sub>2, total</sub>	mg/l	U1K		-0.98	1.00	10	0.95	0.99	1.00	0.05	4.7	20
	mg/l	U2K			1.35	10	1,33	1.35	1.36	0.06	4.2	19

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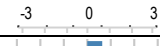










Participant 4												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2*s <sub>pt</sub> %	Participant's result	Md	Mean	s	s %	n <sub>stat</sub>
KMnO <sub>4</sub>	mg/l	U1P		0.46	5.45	25	5.76	5.66	5.49	0.80	14.5	16
	mg/l	U2P		0.53	11.4	20	12.0	11.6	11.4	0.9	7.7	17
pH		U1H		-0.35	5.68	3	5.65	5.68	5.68	0.04	0.7	22
		U2H		0.21	7.35	2,6	7.37	7.36	7.34	0.08	1.1	21
Turbidity	FNU	U1S		0.00	0.72	25	0.72	0.73	0.71	0.06	9.0	20
	FNU	U2S		-0.61	0.45	25	0.42	0.43	0.45	0.05	11.8	19
Urea	mg/l	A1U		1.95	0.77	10	0.85	0.78	0.78	0.06	7.1	13
Urea <sub>Koroleff</sub>	mg/l	UK2			0.52		0.56	0.52	0.53	0.10	19.4	6

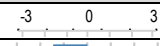

















Participant 5												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2*s <sub>pt</sub> %	Participant's result	Md	Mean	s	s %	n <sub>stat</sub>
Cl <sub>2</sub> , comb	mg/l	U1K		-0.69	0.48	20	0.45	0.49	0.48	0.04	9.3	19
	mg/l	U2K		-0.45	0.77	20	0.74	0.74	0.77	0.07	9.0	18
Cl <sub>2</sub> , free	mg/l	U1K		-0.14	0.52	15	0.51	0.53	0.52	0.03	6.7	19
	mg/l	U2K		0.34	0.59	15	0.61	0.60	0.59	0.03	5.2	17
Cl <sub>2</sub> , total	mg/l	U1K		-0.77	1.00	10	0.96	0.99	1.00	0.05	4.7	20
	mg/l	U2K		-0.15	1.35	10	1.34	1.35	1.36	0.06	4.2	19
pH		U1H		-0.94	5.68	3	5.60	5.68	5.68	0.04	0.7	22
		U2H		-4.92	7.35	2,6	6.88	7.36	7.34	0.08	1.1	21
Turbidity	FNU	U1S		0.28	0.72	25	0.75	0.73	0.71	0.06	9.0	20
	FNU	U2S		-0.09	0.45	25	0.45	0.43	0.45	0.05	11.8	19


















Participant 6												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2*s <sub>pt</sub> %	Participant's result	Md	Mean	s	s %	n <sub>stat</sub>
Cl <sub>2</sub> , total	mg/l	U1K		0.10	1.00	10	1.01	0.99	1.00	0.05	4.7	20
	mg/l	U2K		-0.52	1.35	10	1.32	1.35	1.36	0.06	4.2	19
KMnO <sub>4</sub>	mg/l	U1P		-0.95	5.45	25	4.80	5.66	5.49	0.80	14.5	16
	mg/l	U2P		-0.79	11.4	20	10.5	11.6	11.4	0.9	7.7	17
pH		U1H		0.00	5.68	3	5.68	5.68	5.68	0.04	0.7	22
		U2H		0.52	7.35	2,6	7.40	7.36	7.34	0.08	1.1	21
Turbidity	FNU	U1S		-1.64	0.72	25	0.57	0.73	0.71	0.06	9.0	20
	FNU	U2S		-0.86	0.45	25	0.40	0.43	0.45	0.05	11.8	19

Participant 7												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2*s <sub>pt</sub> %	Participant's result	Md	Mean	s	s %	n <sub>stat</sub>
Cl <sub>2</sub> , comb	mg/l	U1K		1.46	0.48	20	0.55	0.49	0.48	0.04	9.3	19
Cl <sub>2</sub> , free	mg/l	U1K		-1.79	0.52	15	0.45	0.53	0.52	0.03	6.7	19
Cl <sub>2</sub> , total	mg/l	U1K		0.00	1.00	10	1.00	0.99	1.00	0.05	4.7	20
pH		U1H		0.23	5.68	3	5.70	5.68	5.68	0.04	0.7	22

Participant 8												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2*s <sub>pt</sub> %	Participant's result	Md	Mean	s	s %	n <sub>stat</sub>
Cl <sub>2</sub> , comb	mg/l	U1K		1.07	0.48	20	0.53	0.49	0.48	0.04	9.3	19
	mg/l	U2K		1.46	0.77	20	0.88	0.74	0.77	0.07	9.0	18
Cl <sub>2</sub> , free	mg/l	U1K		1.24	0.52	15	0.57	0.53	0.52	0.03	6.7	19
	mg/l	U2K		0.27	0.59	15	0.60	0.60	0.59	0.03	5.2	17
Cl <sub>2</sub> , total	mg/l	U1K		2.00	1.00	10	1.10	0.99	1.00	0.05	4.7	20
	mg/l	U2K		2.00	1.35	10	1.49	1.35	1.36	0.06	4.2	19

Participant 8												
Measurand	Unit	Sample		z score	Assigned value	2×s <sub>pt</sub> %	Participant's result	Md	Mean	s	s %	n <sub>stat</sub>
KMnO <sub>4</sub>	mg/l	U1P		0.63	5.45	25	5.88	5.66	5.49	0.80	14.5	16
	mg/l	U2P		1.05	11.4	20	12.6	11.6	11.4	0.9	7.7	17
NO <sub>3</sub>	mg/l	U1N		0.22	18.0	10	18.2	17.9	18.0	0.4	2.4	14
	mg/l	U2N		0.36	8.78	10	8.94	8.79	8.78	0.27	3.1	14
pH		U1H		0.23	5.68	3	5.70	5.68	5.68	0.04	0.7	22
		U2H		0.52	7.35	2,6	7.40	7.36	7.34	0.08	1.1	21
Turbidity	FNU	U1S		0.22	0.72	25	0.74	0.73	0.71	0.06	9.0	20
	FNU	U2S		0.62	0.45	25	0.49	0.43	0.45	0.05	11.8	19
Urea	mg/l	A1U		1.26	0.77	10	0.82	0.78	0.78	0.06	7.1	13
Urea <sub>Enzymatic</sub>	mg/l	UE2		-0.31	1.06	15	1.04	0.99	0.99	0.05	5.5	9

Participant 9												
Measurand	Unit	Sample		z score	Assigned value	2×s <sub>pt</sub> %	Participant's result	Md	Mean	s	s %	n <sub>stat</sub>
Cl <sub>2, comb</sub>	mg/l	U1K		-1.48	0.48	20	0.41	0.49	0.48	0.04	9.3	19
	mg/l	U2K		-0.78	0.77	20	0.71	0.74	0.77	0.07	9.0	18
Cl <sub>2, free</sub>	mg/l	U1K		0.47	0.52	15	0.54	0.53	0.52	0.03	6.7	19
	mg/l	U2K		0.03	0.59	15	0.59	0.60	0.59	0.03	5.2	17
Cl <sub>2, total</sub>	mg/l	U1K		-1.00	1.00	10	0.95	0.99	1.00	0.05	4.7	20
	mg/l	U2K		-0.74	1.35	10	1.30	1.35	1.36	0.06	4.2	19
KMnO <sub>4</sub>	mg/l	U1P		0.50	5.45	25	5.79	5.66	5.49	0.80	14.5	16
	mg/l	U2P		0.18	11.4	20	11.6	11.6	11.4	0.9	7.7	17
NO <sub>3</sub>	mg/l	U1N		0.56	18.0	10	18.5	17.9	18.0	0.4	2.4	14
	mg/l	U2N		0.59	8.78	10	9.04	8.79	8.78	0.27	3.1	14
pH		U1H		-0.35	5.68	3	5.65	5.68	5.68	0.04	0.7	22
		U2H		-1.57	7.35	2,6	7.20	7.36	7.34	0.08	1.1	21
Turbidity	FNU	U1S		-0.81	0.72	25	0.65	0.73	0.71	0.06	9.0	20
	FNU	U2S		-0.28	0.45	25	0.43	0.43	0.45	0.05	11.8	19
Urea	mg/l	A1U		0.23	0.77	10	0.78	0.78	0.78	0.06	7.1	13
Urea <sub>Enzymatic</sub>	mg/l	UE2		-1.03	1.06	15	0.98	0.99	0.99	0.05	5.5	9
Urea <sub>Koroleff</sub>	mg/l	UK2		0.52			0.40	0.52	0.53	0.10	19.4	6

Participant 10												
Measurand	Unit	Sample		z score	Assigned value	2×s <sub>pt</sub> %	Participant's result	Md	Mean	s	s %	n <sub>stat</sub>
Cl <sub>2, comb</sub>	mg/l	U1K		1.15	0.48	20	0.54	0.49	0.48	0.04	9.3	19
	mg/l	U2K		1.23	0.77	20	0.87	0.74	0.77	0.07	9.0	18
Cl <sub>2, free</sub>	mg/l	U1K		-0.13	0.52	15	0.52	0.53	0.52	0.03	6.7	19
	mg/l	U2K		-0.79	0.59	15	0.56	0.60	0.59	0.03	5.2	17
Cl <sub>2, total</sub>	mg/l	U1K		1.00	1.00	10	1.05	0.99	1.00	0.05	4.7	20
	mg/l	U2K		1.04	1.35	10	1.42	1.35	1.36	0.06	4.2	19
KMnO <sub>4</sub>	mg/l	U1P		0.19	5.45	25	5.58	5.66	5.49	0.80	14.5	16
	mg/l	U2P		0.53	11.4	20	12.0	11.6	11.4	0.9	7.7	17
NO <sub>3</sub>	mg/l	U1N		-0.22	18.0	10	17.8	17.9	18.0	0.4	2.4	14
	mg/l	U2N		-0.05	8.78	10	8.76	8.79	8.78	0.27	3.1	14
pH		U1H		1.53	5.68	3	5.81	5.68	5.68	0.04	0.7	22
		U2H		1.47	7.35	2,6	7.49	7.36	7.34	0.08	1.1	21
Turbidity	FNU	U1S		-0.92	0.72	25	0.64	0.73	0.71	0.06	9.0	20
	FNU	U2S		-1.26	0.45	25	0.38	0.43	0.45	0.05	11.8	19
Urea	mg/l	A1U		-1.25	0.77	10	0.72	0.78	0.78	0.06	7.1	13
Urea <sub>Koroleff</sub>	mg/l	UK2		0.52			0.56	0.52	0.53	0.10	19.4	6

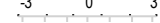






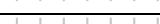











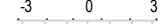








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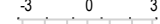










Participant 11												
Measurand	Unit	Sample		z score	Assigned value	2*s <sub>pt</sub> %	Participant's result	Md	Mean	s	s %	n <sub>stat</sub>
Cl <sub>2, comb</sub>	mg/l	U1K		0.73	0.48	20	0.52	0.49	0.48	0.04	9.3	19
	mg/l	U2K		0.45	0.77	20	0.81	0.74	0.77	0.07	9.0	18
Cl <sub>2, free</sub>	mg/l	U1K		-1.28	0.52	15	0.47	0.53	0.52	0.03	6.7	19
	mg/l	U2K		-2.60	0.59	15	0.48	0.60	0.59	0.03	5.2	17
Cl <sub>2, total</sub>	mg/l	U1K		-0.40	1.00	10	0.98	0.99	1.00	0.05	4.7	20
	mg/l	U2K		-0.96	1.35	10	1.29	1.35	1.36	0.06	4.2	19
pH		U1H		0.94	5.68	3	5.76	5.68	5.68	0.04	0.7	22
		U2H		-1.78	7.35	2,6	7.18	7.36	7.34	0.08	1.1	21
Urea	mg/l	A1U		2.95	0.77	10	0.88	0.78	0.78	0.06	7.1	13
Urea <sub>Enzymatic</sub>	mg/l	UE2		-0.42	1.06	15	1.03	0.99	0.99	0.05	5.5	9

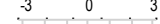




Participant 12												
Measurand	Unit	Sample		z score	Assigned value	2*s <sub>pt</sub> %	Participant's result	Md	Mean	s	s %	n <sub>stat</sub>
Cl <sub>2, comb</sub>	mg/l	U1K		0.39	0.48	20	0.39	0.49	0.48	0.04	9.3	19
	mg/l	U2K		-0.97	0.77	20	0.70	0.74	0.77	0.07	9.0	18
Cl <sub>2, free</sub>	mg/l	U1K		0.57	0.52	15	0.57	0.53	0.52	0.03	6.7	19
	mg/l	U2K		0.59	0.59	15	0.59	0.60	0.59	0.03	5.2	17
Cl <sub>2, total</sub>	mg/l	U1K		0.96	1.00	10	0.96	0.99	1.00	0.05	4.7	20
	mg/l	U2K		-0.96	1.35	10	1.29	1.35	1.36	0.06	4.2	19
KMnO <sub>4</sub>	mg/l	U1P		0.06	5.45	25	5.49	5.66	5.49	0.80	14.5	16
	mg/l	U2P		-0.26	11.4	20	11.1	11.6	11.4	0.9	7.7	17
NO <sub>3</sub>	mg/l	U1N		0.78	18.0	10	18.7	17.9	18.0	0.4	2.4	14
	mg/l	U2N		1.05	8.78	10	9.24	8.79	8.78	0.27	3.1	14
pH		U1H		-0.35	5.68	3	5.65	5.68	5.68	0.04	0.7	22
		U2H		-1.05	7.35	2,6	7.25	7.36	7.34	0.08	1.1	21
Turbidity	FNU	U1S		-0.59	0.72	25	0.67	0.73	0.71	0.06	9.0	20
	FNU	U2S		-0.47	0.45	25	0.42	0.43	0.45	0.05	11.8	19
Urea	mg/l	A1U		1.04	0.77	10	0.81	0.78	0.78	0.06	7.1	13
Urea <sub>Koroleff</sub>	mg/l	UK2		0.52	0.52		0.47	0.52	0.53	0.10	19.4	6

Participant 13												
Measurand	Unit	Sample		z score	Assigned value	2*s <sub>pt</sub> %	Participant's result	Md	Mean	s	s %	n <sub>stat</sub>
Cl <sub>2, comb</sub>	mg/l	U1K		0.10	0.48	20	0.49	0.49	0.48	0.04	9.3	19
	mg/l	U2K		0.19	0.77	20	0.79	0.74	0.77	0.07	9.0	18
Cl <sub>2, free</sub>	mg/l	U1K		0.26	0.52	15	0.53	0.53	0.52	0.03	6.7	19
	mg/l	U2K		-0.11	0.59	15	0.59	0.60	0.59	0.03	5.2	17
Cl <sub>2, total</sub>	mg/l	U1K		0.30	1.00	10	1.02	0.99	1.00	0.05	4.7	20
	mg/l	U2K		0.30	1.35	10	1.37	1.35	1.36	0.06	4.2	19
KMnO <sub>4</sub>	mg/l	U1P		-1.23	5.45	25	4.61	5.66	5.49	0.80	14.5	16
	mg/l	U2P		-1.05	11.4	20	10.2	11.6	11.4	0.9	7.7	17
NO <sub>3</sub>	mg/l	U1N		-0.22	18.0	10	17.8	17.9	18.0	0.4	2.4	14
	mg/l	U2N		-0.02	8.78	10	8.77	8.79	8.78	0.27	3.1	14
pH		U1H		0.47	5.68	3	5.72	5.68	5.68	0.04	0.7	22
		U2H		0.21	7.35	2,6	7.37	7.36	7.34	0.08	1.1	21
Turbidity	FNU	U1S		0.34	0.72	25	0.75	0.73	0.71	0.06	9.0	20
	FNU	U2S		0.50	0.45	25	0.48	0.43	0.45	0.05	11.8	19
Urea	mg/l	A1U		0.78	0.77	10	0.80	0.78	0.78	0.06	7.1	13
Urea <sub>Enzymatic</sub>	mg/l	UE2		0.00	1.06	15	1.06	0.99	0.99	0.05	5.5	9

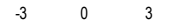












Participant 14												
Measurand	Unit	Sample		z score	Assigned value	2*s <sub>pt</sub> %	Participant's result	Md	Mean	s	s %	n <sub>stat</sub>
Cl <sub>2, comb</sub>	mg/l	U1K			0.48	20	0,45	0.49	0.48	0.04	9.3	19
	mg/l	U2K			0.77	20	0,74	0.74	0.77	0.07	9.0	18
Cl <sub>2, free</sub>	mg/l	U1K			0.52	15	0,516	0.53	0.52	0.03	6.7	19
	mg/l	U2K			0.59	15	0,578	0.60	0.59	0.03	5.2	17
Cl <sub>2, total</sub>	mg/l	U1K			1.00	10	0,967	0.99	1.00	0.05	4.7	20
	mg/l	U2K			1.35	10	1,32	1.35	1.36	0.06	4.2	19
KMnO <sub>4</sub>	mg/l	U1P		3.02	5.45	25	7.51	5.66	5.49	0.80	14.5	16
	mg/l	U2P		-0.96	11.4	20	10.3	11.6	11.4	0.9	7.7	17
NO <sub>3</sub>	mg/l	U1N		0.00	18.0	10	18.0	17.9	18.0	0.4	2.4	14
	mg/l	U2N		0.27	8.78	10	8.90	8.79	8.78	0.27	3.1	14
pH		U1H		0.00	5.68	3	5.68	5.68	5.68	0.04	0.7	22
		U2H		-0.21	7.35	2,6	7.33	7.36	7.34	0.08	1.1	21
Turbidity	FNU	U1S			0.72	25	0,59	0.73	0.71	0.06	9.0	20
	FNU	U2S			0.45	25	0,38	0.43	0.45	0.05	11.8	19
Urea	mg/l	A1U		-0.39	0.77	10	0.76	0.78	0.78	0.06	7.1	13
Urea <sup>Enzymatic</sup>	mg/l	UE2		-1.01	1.06	15	0.98	0.99	0.99	0.05	5.5	9

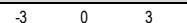














Participant 15												
Measurand	Unit	Sample		z score	Assigned value	2*s <sub>pt</sub> %	Participant's result	Md	Mean	s	s %	n <sub>stat</sub>
KMnO <sub>4</sub>	mg/l	U1P		-5.77	5.45	25	1.52	5.66	5.49	0.80	14.5	16
	mg/l	U2P		-7.30	11.4	20	3.1	11.6	11.4	0.9	7.7	17
NO <sub>3</sub>	mg/l	U1N		-0.15	18.0	10	17.9	17.9	18.0	0.4	2.4	14
	mg/l	U2N		-0.13	8.78	10	8.72	8.79	8.78	0.27	3.1	14
pH		U1H		-0.23	5.68	3	5.66	5.68	5.68	0.04	0.7	22
		U2H		0.10	7.35	2,6	7.36	7.36	7.34	0.08	1.1	21
Turbidity	FNU	U1S		-0.47	0.72	25	0.68	0.73	0.71	0.06	9.0	20
	FNU	U2S		-0.49	0.45	25	0.42	0.43	0.45	0.05	11.8	19

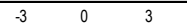
















Participant 16												
Measurand	Unit	Sample		z score	Assigned value	2*s <sub>pt</sub> %	Participant's result	Md	Mean	s	s %	n <sub>stat</sub>
Cl <sub>2, comb</sub>	mg/l	U1K		-0.95	0.48	20	0.43	0.49	0.48	0.04	9.3	19
	mg/l	U2K		-0.40	0.77	20	0.74	0.74	0.77	0.07	9.0	18
Cl <sub>2, free</sub>	mg/l	U1K		0.65	0.52	15	0.55	0.53	0.52	0.03	6.7	19
	mg/l	U2K		0.28	0.59	15	0.60	0.60	0.59	0.03	5.2	17
Cl <sub>2, total</sub>	mg/l	U1K		-0.40	1.00	10	0.98	0.99	1.00	0.05	4.7	20
	mg/l	U2K		-0.07	1.35	10	1.35	1.35	1.36	0.06	4.2	19
pH		U1H		0.23	5.68	3	5.70	5.68	5.68	0.04	0.7	22
		U2H		-0.52	7.35	2,6	7.30	7.36	7.34	0.08	1.1	21
Turbidity	FNU	U1S		-0.42	0.72	25	0.68	0.73	0.71	0.06	9.0	20
	FNU	U2S		-0.49	0.45	25	0.42	0.43	0.45	0.05	11.8	19

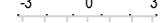
















Participant 17												
Measurand	Unit	Sample		z score	Assigned value	2*s <sub>pt</sub> %	Participant's result	Md	Mean	s	s %	n <sub>stat</sub>
Cl <sub>2, comb</sub>	mg/l	U1K		1.23	0.48	20	0.54	0.49	0.48	0.04	9.3	19
	mg/l	U2K		1.51	0.77	20	0.89	0.74	0.77	0.07	9.0	18
Cl <sub>2, free</sub>	mg/l	U1K		0.28	0.52	15	0.53	0.53	0.52	0.03	6.7	19
	mg/l	U2K		-0.59	0.59	15	0.56	0.60	0.59	0.03	5.2	17

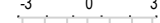














Appendix 8 (6/8)

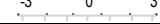












Participant 17												
Measurand	Unit	Sample		z score	Assigned value	2×s <sub>pt</sub> %	Participant's result	Md	Mean	s	s %	n <sub>stat</sub>
Cl <sub>2, total</sub>	mg/l	U1K		1.40	1.00	10	1.07	0.99	1.00	0.05	4.7	20
	mg/l	U2K		1.54	1.35	10	1.45	1.35	1.36	0.06	4.2	19
KMnO <sub>4</sub>	mg/l	U1P		0.41	5.45	25	5.73	5.66	5.49	0.80	14.5	16
	mg/l	U2P		0.72	11.4	20	12.2	11.6	11.4	0.9	7.7	17
NO <sub>3</sub>	mg/l	U1N		-0.79	18.0	10	17.3	17.9	18.0	0.4	2.4	14
	mg/l	U2N		-0.82	8.78	10	8.42	8.79	8.78	0.27	3.1	14
pH		U1H		-0.47	5.68	3	5.64	5.68	5.68	0.04	0.7	22
		U2H		0.10	7.35	2,6	7.36	7.36	7.34	0.08	1.1	21
Turbidity	FNU	U1S		1.21	0.72	25	0.83	0.73	0.71	0.06	9.0	20
	FNU	U2S		2.04	0.45	25	0.57	0.43	0.45	0.05	11.8	19
Urea	mg/l	A1U		-1.00	0.77	10	0.73	0.78	0.78	0.06	7.1	13
Urea <sub>Koroleff</sub>	mg/l	UK2			0.52		0.48	0.52	0.53	0.10	19.4	6

Participant 18												
Measurand	Unit	Sample		z score	Assigned value	2×s <sub>pt</sub> %	Participant's result	Md	Mean	s	s %	n <sub>stat</sub>
Cl <sub>2, comb</sub>	mg/l	U1K		-0.98	0.48	20	0.43	0.49	0.48	0.04	9.3	19
	mg/l	U2K		-0.45	0.77	20	0.74	0.74	0.77	0.07	9.0	18
Cl <sub>2, free</sub>	mg/l	U1K		0.85	0.52	15	0.55	0.53	0.52	0.03	6.7	19
	mg/l	U2K		0.55	0.59	15	0.61	0.60	0.59	0.03	5.2	17
Cl <sub>2, total</sub>	mg/l	U1K		-0.28	1.00	10	0.99	0.99	1.00	0.05	4.7	20
	mg/l	U2K		0.00	1.35	10	1.35	1.35	1.36	0.06	4.2	19
KMnO <sub>4</sub>	mg/l	U1P		-0.63	5.45	25	5.02	5.66	5.49	0.80	14.5	16
	mg/l	U2P		0.09	11.4	20	11.5	11.6	11.4	0.9	7.7	17
NO <sub>3</sub>	mg/l	U1N		0.11	18.0	10	18.1	17.9	18.0	0.4	2.4	14
	mg/l	U2N		0.05	8.78	10	8.80	8.79	8.78	0.27	3.1	14
pH		U1H		-0.47	5.68	3	5.64	5.68	5.68	0.04	0.7	22
		U2H		-0.10	7.35	2,6	7.34	7.36	7.34	0.08	1.1	21
Turbidity	FNU	U1S		-3.14	0.72	25	0.44	0.73	0.71	0.06	9.0	20
	FNU	U2S		-2.88	0.45	25	0.29	0.43	0.45	0.05	11.8	19

Participant 19												
Measurand	Unit	Sample		z score	Assigned value	2×s <sub>pt</sub> %	Participant's result	Md	Mean	s	s %	n <sub>stat</sub>
Cl <sub>2, comb</sub>	mg/l	U1K		-0.46	0.48	20	0.46	0.49	0.48	0.04	9.3	19
	mg/l	U2K		-0.43	0.77	20	0.74	0.74	0.77	0.07	9.0	18
Cl <sub>2, free</sub>	mg/l	U1K		-0.56	0.52	15	0.50	0.53	0.52	0.03	6.7	19
	mg/l	U2K		0.29	0.59	15	0.60	0.60	0.59	0.03	5.2	17
Cl <sub>2, total</sub>	mg/l	U1K		-0.88	1.00	10	0.96	0.99	1.00	0.05	4.7	20
	mg/l	U2K		-0.15	1.35	10	1.34	1.35	1.36	0.06	4.2	19
KMnO <sub>4</sub>	mg/l	U1P		-0.98	5.45	25	4.78	5.66	5.49	0.80	14.5	16
	mg/l	U2P		-1.23	11.4	20	10.0	11.6	11.4	0.9	7.7	17
NO <sub>3</sub>	mg/l	U1N		0.67	18.0	10	18.6	17.9	18.0	0.4	2.4	14
	mg/l	U2N		0.43	8.78	10	8.97	8.79	8.78	0.27	3.1	14
pH		U1H		0.04	5.68	3	5.68	5.68	5.68	0.04	0.7	22
		U2H		-1.49	7.35	2,6	7.21	7.36	7.34	0.08	1.1	21
Turbidity	FNU	U1S		0.67	0.72	25	0.78	0.73	0.71	0.06	9.0	20
	FNU	U2S		1.96	0.45	25	0.56	0.43	0.45	0.05	11.8	19
Urea	mg/l	A1U		1.56	0.77	10	0.83	0.78	0.78	0.06	7.1	13
Urea <sub>Koroleff</sub>	mg/l	UK2			0.52		0.69	0.52	0.53	0.10	19.4	6

Participant 20												
Measurand	Unit	Sample		z score	Assigned value	2x <sub>s<sub>pt</sub></sub> %	Participant's result	Md	Mean	s	s %	n <sub>stat</sub>
Cl <sub>2, comb</sub>	mg/l	U1K		0.31	0.48	20	0.50	0.49	0.48	0.04	9.3	19
	mg/l	U2K		-0.13	0.77	20	0.76	0.74	0.77	0.07	9.0	18
Cl <sub>2, free</sub>	mg/l	U1K		-1.67	0.52	15	0.46	0.53	0.52	0.03	6.7	19
	mg/l	U2K		-1.02	0.59	15	0.55	0.60	0.59	0.03	5.2	17
Cl <sub>2, total</sub>	mg/l	U1K		-0.80	1.00	10	0.96	0.99	1.00	0.05	4.7	20
	mg/l	U2K		-0.67	1.35	10	1.31	1.35	1.36	0.06	4.2	19
KMnO <sub>4</sub>	mg/l	U1P		1.18	5.45	25	6.26	5.66	5.49	0.80	14.5	16
	mg/l	U2P		0.79	11.4	20	12.3	11.6	11.4	0.9	7.7	17
NO <sub>3</sub>	mg/l	U1N		-0.23	18.0	10	17.8	17.9	18.0	0.4	2.4	14
	mg/l	U2N		0.73	8.78	10	9.10	8.79	8.78	0.27	3.1	14
pH		U1H		0.12	5.68	3	5.69	5.68	5.68	0.04	0.7	22
		U2H		0.84	7.35	2,6	7.43	7.36	7.34	0.08	1.1	21
Turbidity	FNU	U1S		0.89	0.72	25	0.80	0.73	0.71	0.06	9.0	20
	FNU	U2S		1.16	0.45	25	0.52	0.43	0.45	0.05	11.8	19
Urea	mg/l	A1U		-1.56	0.77	10	0.71	0.78	0.78	0.06	7.1	13
Urea <sup>Enzymatic</sup>	mg/l	UE2		-1.45	1.06	15	0.95	0.99	0.99	0.05	5.5	9

Participant 21												
Measurand	Unit	Sample		z score	Assigned value	2x <sub>s<sub>pt</sub></sub> %	Participant's result	Md	Mean	s	s %	n <sub>stat</sub>
Cl <sub>2, comb</sub>	mg/l	U1K		1.08	0.48	20	0.53	0.49	0.48	0.04	9.3	19
	mg/l	U2K		0.64	0.77	20	0.82	0.74	0.77	0.07	9.0	18
Cl <sub>2, free</sub>	mg/l	U1K		0.74	0.52	15	0.55	0.53	0.52	0.03	6.7	19
	mg/l	U2K		-0.34	0.59	15	0.58	0.60	0.59	0.03	5.2	17
Cl <sub>2, total</sub>	mg/l	U1K		1.62	1.00	10	1.08	0.99	1.00	0.05	4.7	20
	mg/l	U2K		0.64	1.35	10	1.39	1.35	1.36	0.06	4.2	19
KMnO <sub>4</sub>	mg/l	U1P		0.43	5.45	25	5.74	5.66	5.49	0.80	14.5	16
	mg/l	U2P		0.09	11.4	20	11.5	11.6	11.4	0.9	7.7	17
NO <sub>3</sub>	mg/l	U1N		-0.67	18.0	10	17.4	17.9	18.0	0.4	2.4	14
	mg/l	U2N		-0.96	8.78	10	8.36	8.79	8.78	0.27	3.1	14
pH		U1H		0.12	5.68	3	5.69	5.68	5.68	0.04	0.7	22
		U2H		-0.21	7.35	2,6	7.33	7.36	7.34	0.08	1.1	21
Turbidity	FNU	U1S		0.14	0.72	25	0.73	0.73	0.71	0.06	9.0	20
	FNU	U2S		-0.53	0.45	25	0.42	0.43	0.45	0.05	11.8	19

Participant 22												
Measurand	Unit	Sample		z score	Assigned value	2x <sub>s<sub>pt</sub></sub> %	Participant's result	Md	Mean	s	s %	n <sub>stat</sub>
Cl <sub>2, comb</sub>	mg/l	U1K		-0.47	0.48	20	0.46	0.49	0.48	0.04	9.3	19
	mg/l	U2K		-1.21	0.77	20	0.68	0.74	0.77	0.07	9.0	18
Cl <sub>2, free</sub>	mg/l	U1K		-0.29	0.52	15	0.51	0.53	0.52	0.03	6.7	19
	mg/l	U2K		1.21	0.59	15	0.64	0.60	0.59	0.03	5.2	17
Cl <sub>2, total</sub>	mg/l	U1K		-0.68	1.00	10	0.97	0.99	1.00	0.05	4.7	20
	mg/l	U2K		-0.44	1.35	10	1.32	1.35	1.36	0.06	4.2	19
KMnO <sub>4</sub>	mg/l	U1P		-2.42	5.45	25	3.80	5.66	5.49	0.80	14.5	16
	mg/l	U2P		-1.23	11.4	20	10.0	11.6	11.4	0.9	7.7	17
pH		U1H		-0.23	5.68	3	5.66	5.68	5.68	0.04	0.7	22
		U2H		0.42	7.35	2,6	7.39	7.36	7.34	0.08	1.1	21
Turbidity	FNU	U1S		0.28	0.72	25	0.75	0.73	0.71	0.06	9.0	20
	FNU	U2S		0.18	0.45	25	0.46	0.43	0.45	0.05	11.8	19

Appendix 8 (8/8)

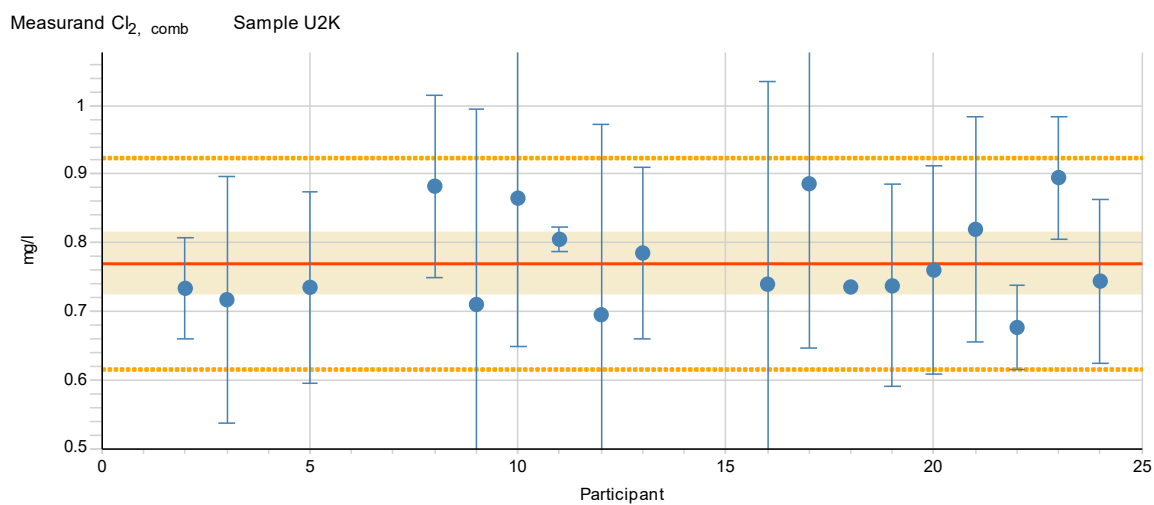
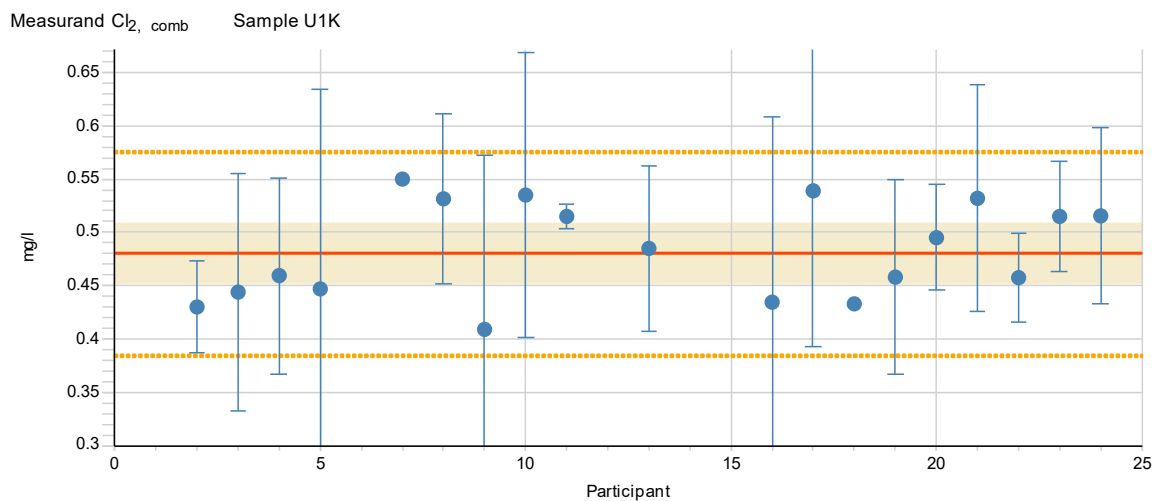
Participant 23												
Measurand	Unit	Sample		z score	Assigned value	2*s <sub>pt</sub> %	Participant's result	Md	Mean	s	s %	n <sub>stat</sub>
Cl <sub>2, comb</sub>	mg/l	U1K		0.73	0.48	20	0.52	0.49	0.48	0.04	9.3	19
	mg/l	U2K		1.62	0.77	20	0.90	0.74	0.77	0.07	9.0	18
Cl <sub>2, free</sub>	mg/l	U1K		-0.64	0.52	15	0.50	0.53	0.52	0.03	6.7	19
	mg/l	U2K		-1.24	0.59	15	0.54	0.60	0.59	0.03	5.2	17
Cl <sub>2, total</sub>	mg/l	U1K		1.00	1.00	10	1.05	0.99	1.00	0.05	4.7	20
	mg/l	U2K		1.19	1.35	10	1.43	1.35	1.36	0.06	4.2	19
NO <sub>3</sub>	mg/l	U1N		0.33	18.0	10	18.3	17.9	18.0	0.4	2.4	14
	mg/l	U2N		-0.87	8.78	10	8.40	8.79	8.78	0.27	3.1	14
pH		U1H		0.23	5.68	3	5.70	5.68	5.68	0.04	0.7	22
		U2H		0.52	7.35	2,6	7.40	7.36	7.34	0.08	1.1	21
Turbidity	FNU	U1S		-0.22	0.72	25	0.70	0.73	0.71	0.06	9.0	20
	FNU	U2S		-0.89	0.45	25	0.40	0.43	0.45	0.05	11.8	19
Urea	mg/l	A1U		0.22	0.77	10	0.78	0.78	0.78	0.06	7.1	13
Urea <sup>Enzymatic</sup>	mg/l	UE2		-0.94	1.06	15	0.99	0.99	0.99	0.05	5.5	9

Participant 24												
Measurand	Unit	Sample		z score	Assigned value	2*s <sub>pt</sub> %	Participant's result	Md	Mean	s	s %	n <sub>stat</sub>
Cl <sub>2, comb</sub>	mg/l	U1K		0.74	0.48	20	0.52	0.49	0.48	0.04	9.3	19
	mg/l	U2K		-0.34	0.77	20	0.74	0.74	0.77	0.07	9.0	18
Cl <sub>2, free</sub>	mg/l	U1K		0.46	0.52	15	0.54	0.53	0.52	0.03	6.7	19
	mg/l	U2K		0.93	0.59	15	0.63	0.60	0.59	0.03	5.2	17
Cl <sub>2, total</sub>	mg/l	U1K		1.07	1.00	10	1.05	0.99	1.00	0.05	4.7	20
	mg/l	U2K		0.37	1.35	10	1.38	1.35	1.36	0.06	4.2	19
KMnO <sub>4</sub>	mg/l	U1P		-2.13	5.45	25	4.00	5.66	5.49	0.80	14.5	16
	mg/l	U2P		0.53	11.4	20	12.0	11.6	11.4	0.9	7.7	17
pH		U1H		-0.82	5.68	3	5.61	5.68	5.68	0.04	0.7	22
		U2H		0.10	7.35	2,6	7.36	7.36	7.34	0.08	1.1	21
Turbidity	FNU	U1S		0.18	0.72	25	0.74	0.73	0.71	0.06	9.0	20
	FNU	U2S		0.84	0.45	25	0.50	0.43	0.45	0.05	11.8	19

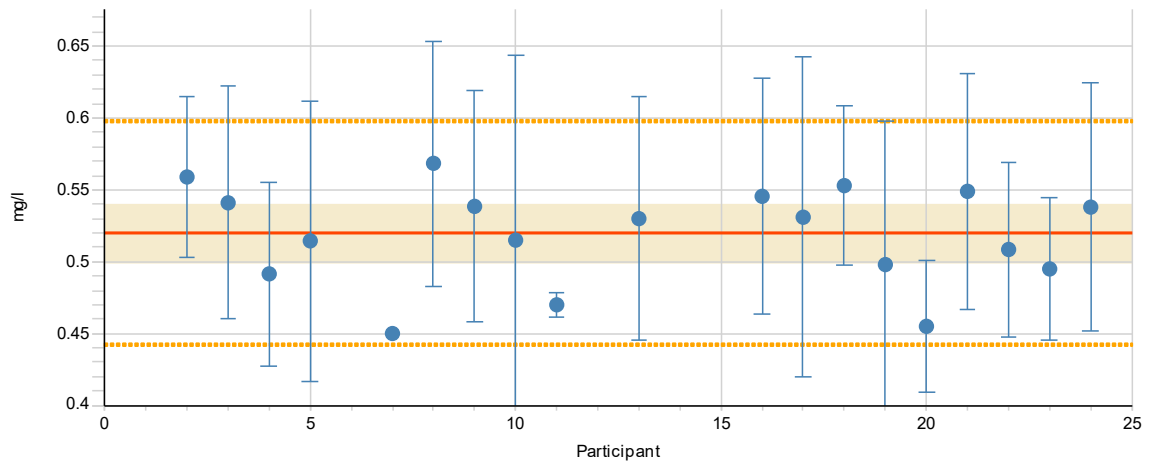
## Appendix 9. Results of participants and their uncertainties

In figures:

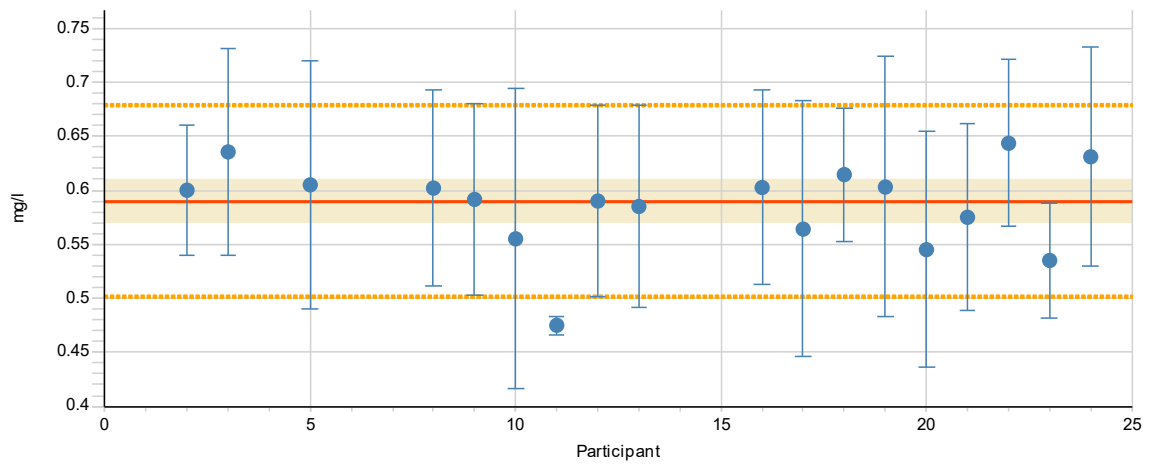
- The dashed lines describe the standard deviation for the proficiency assessment, the red solid line shows the assigned value, the shaded area describes the expanded uncertainty of the assigned value, and the arrow describes the value outside the scale.



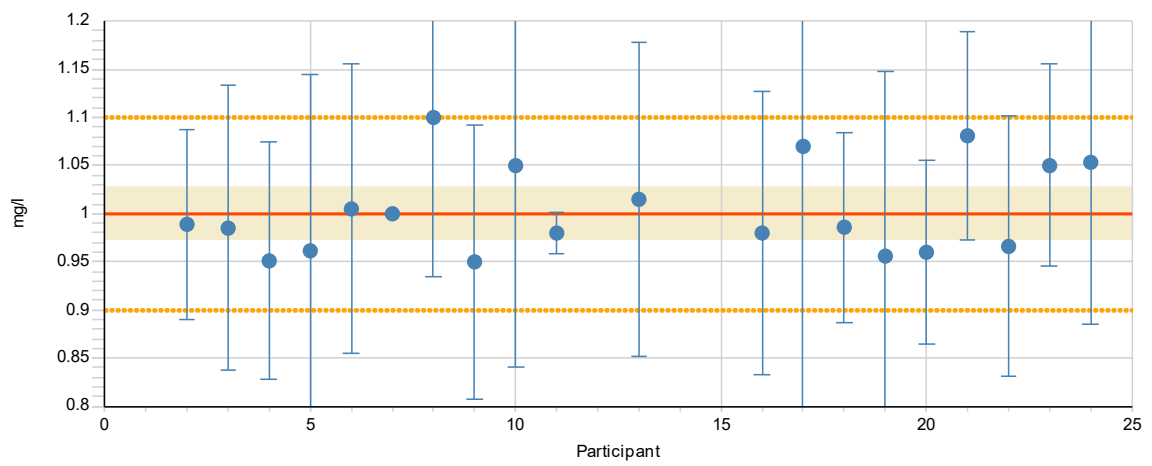
Measurand Cl<sub>2, free</sub> Sample U1K



Measurand Cl<sub>2, free</sub> Sample U2K

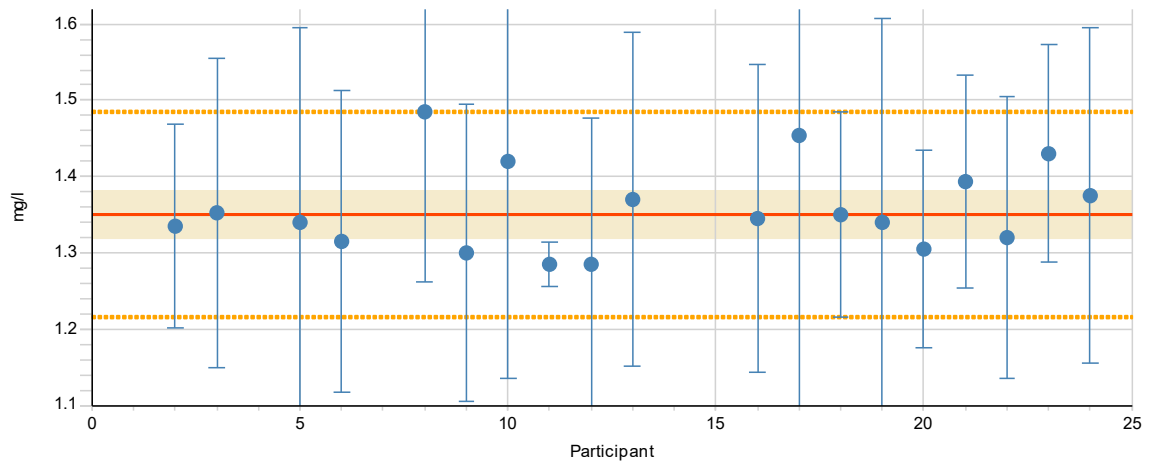


Measurand Cl<sub>2, total</sub> Sample U1K

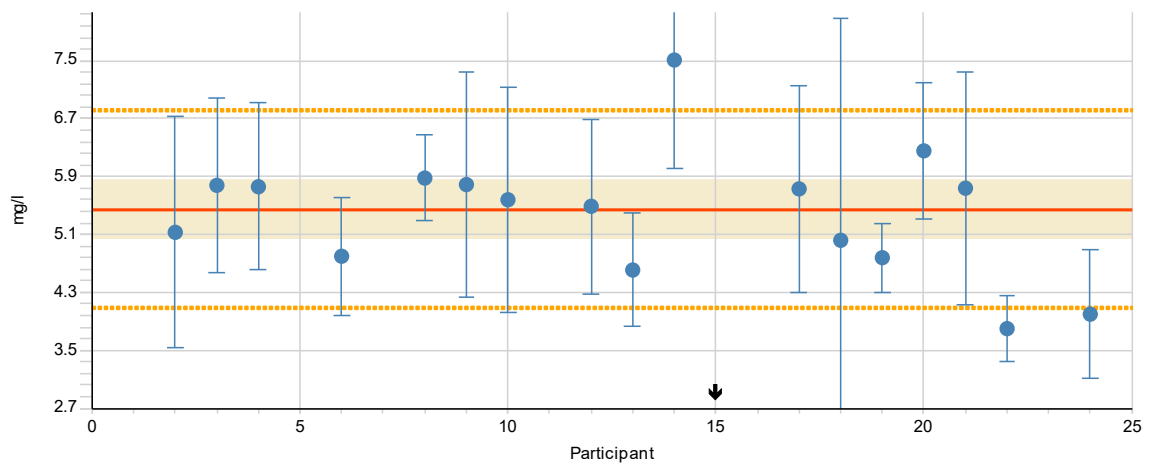




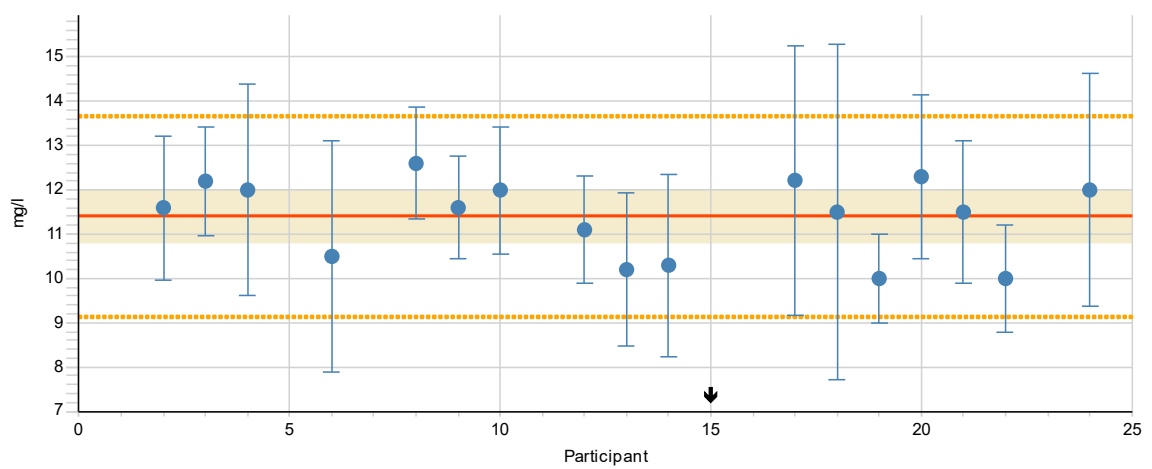
Measurand  $\text{Cl}_2$ , total Sample U2K



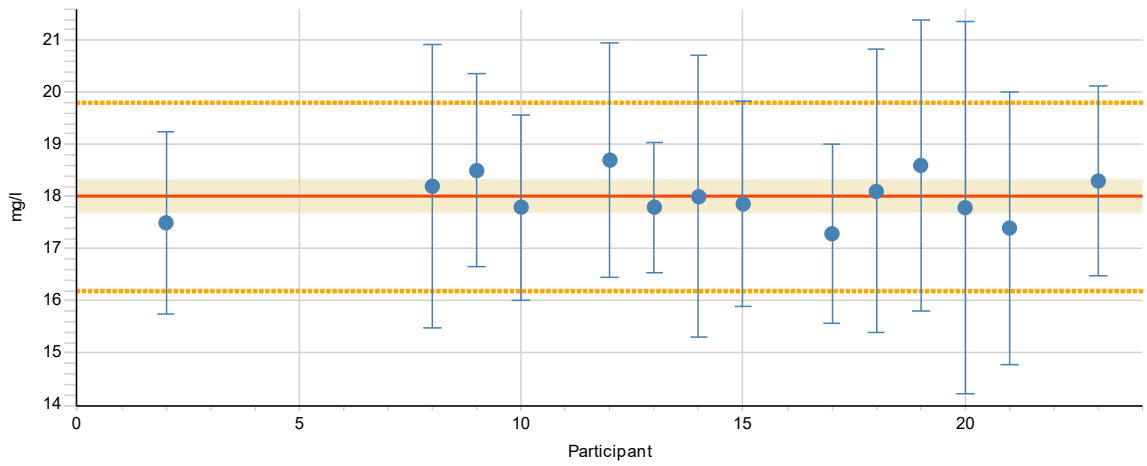
Measurand  $\text{KMnO}_4$  Sample U1P



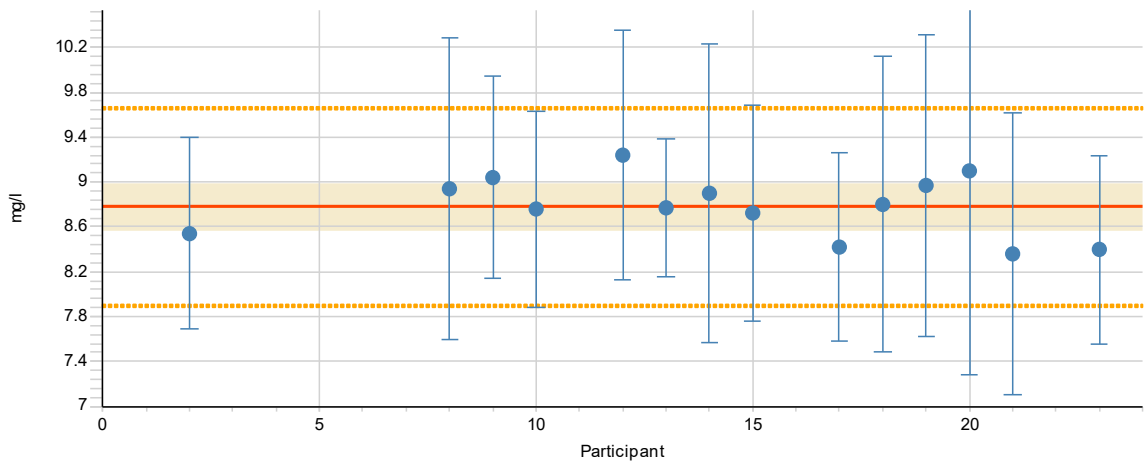
Measurand  $\text{KMnO}_4$  Sample U2P



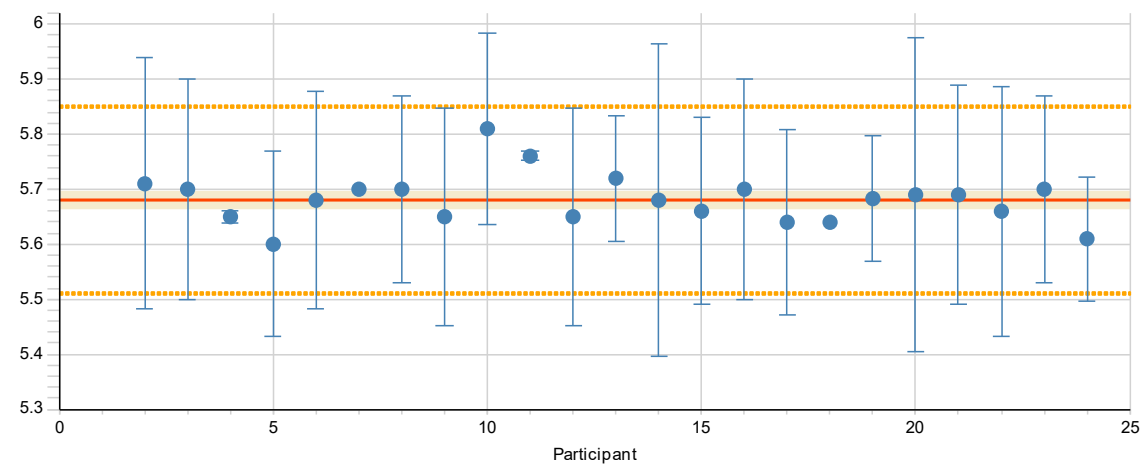
Measurand NO<sub>3</sub> Sample U1N



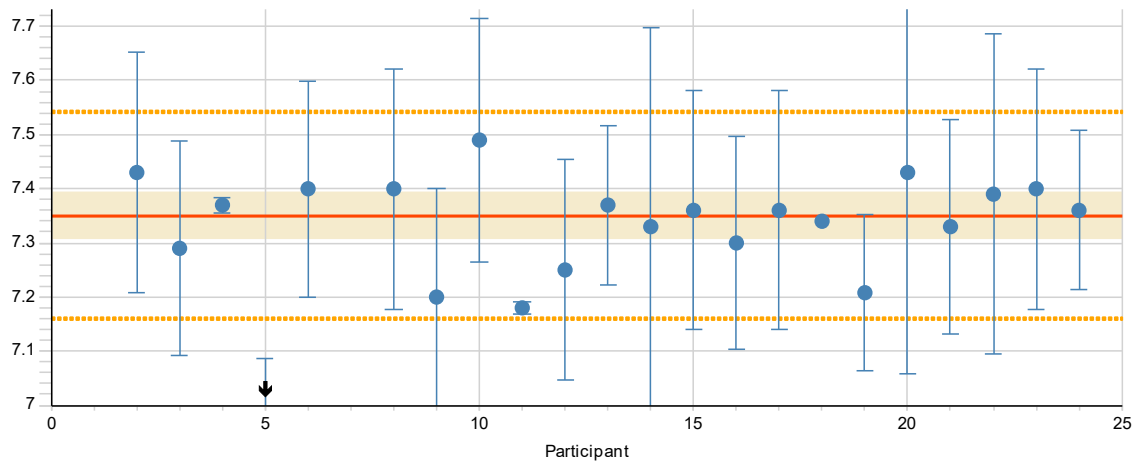
Measurand NO<sub>3</sub> Sample U2N



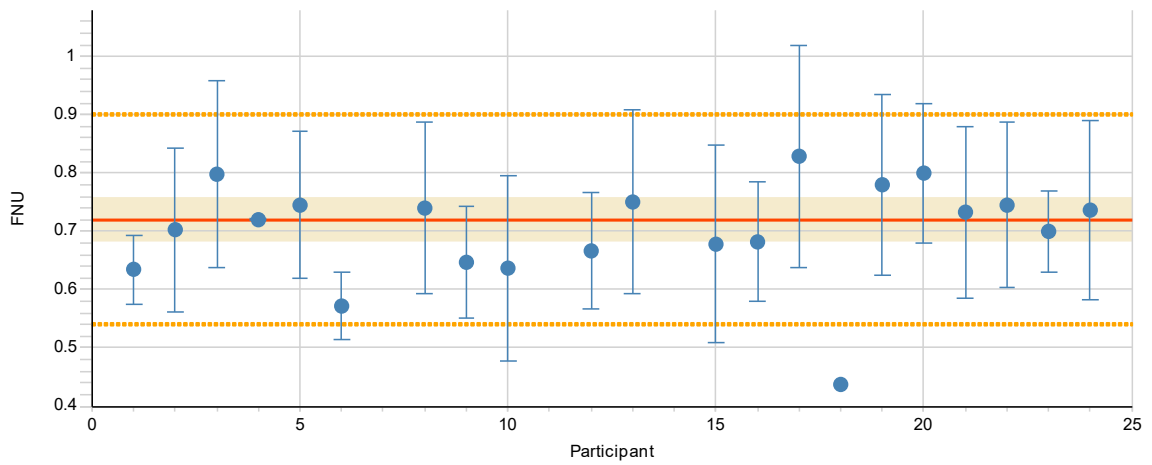
Measurand pH Sample U1H



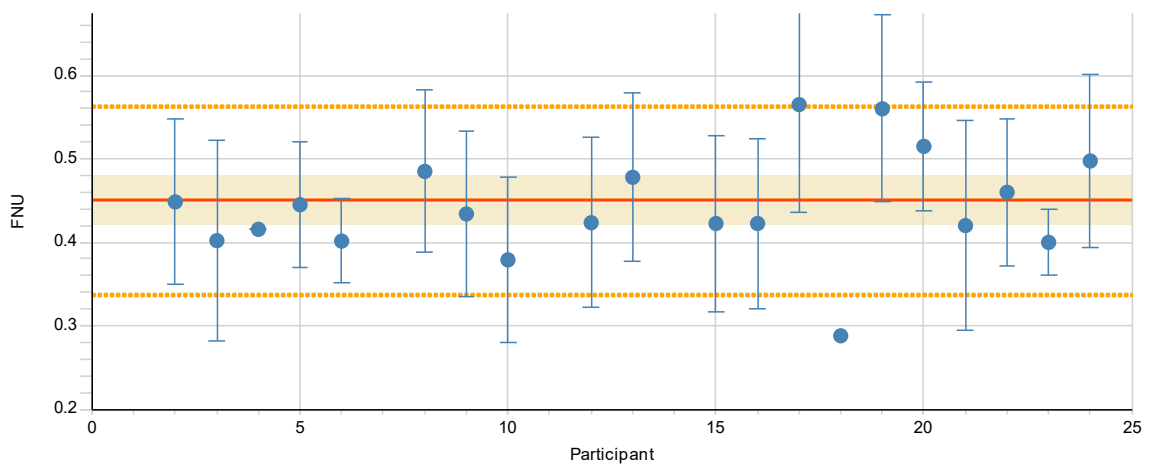
Measurand pH Sample U2H



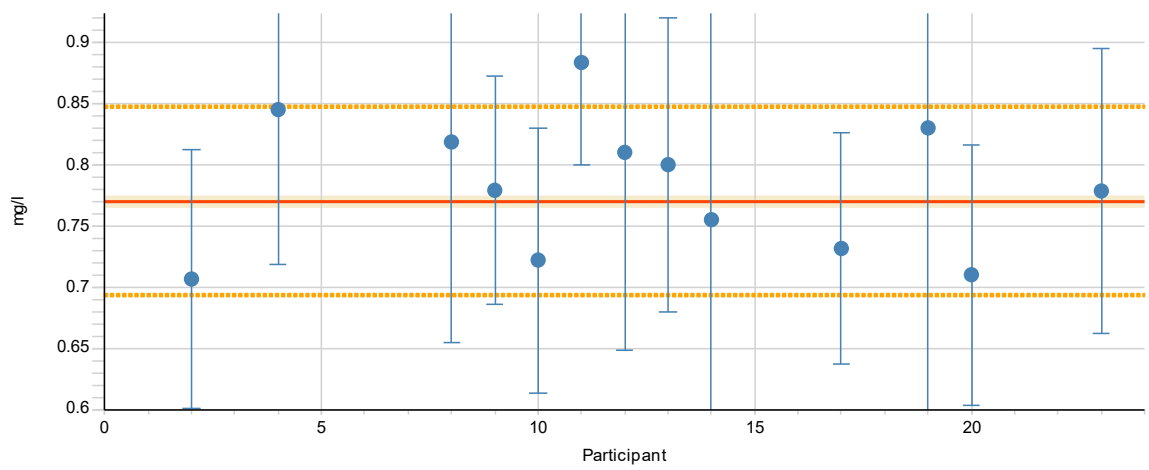
Measurand Turbidity Sample U1S



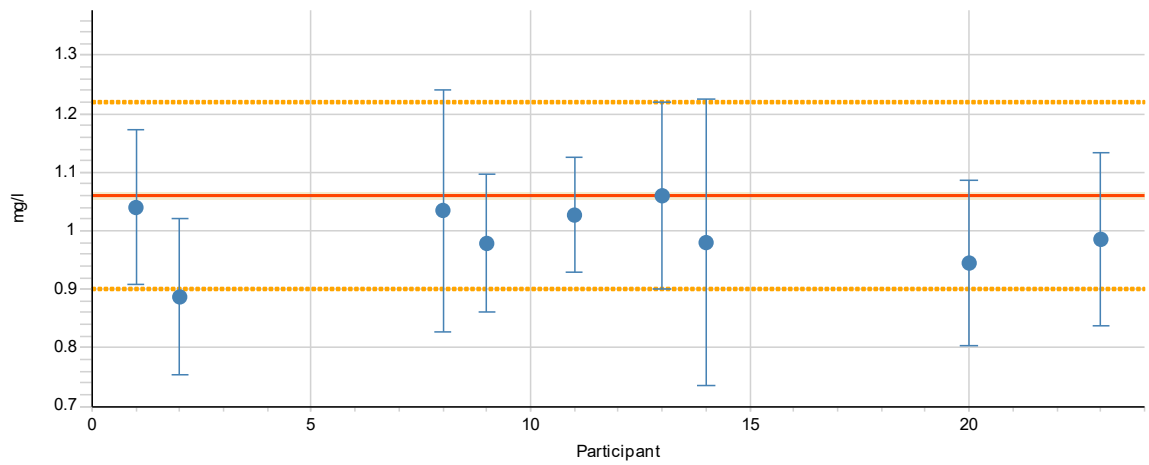
Measurand Turbidity Sample U2S



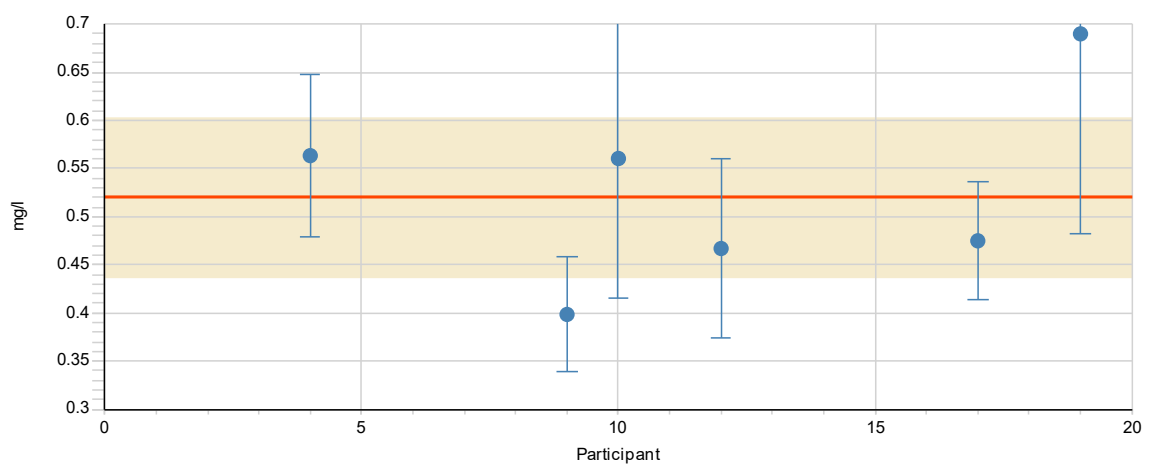
Measurand Urea Sample A1U



Measurand Urea<sub>Enzymatic</sub> Sample UE2



Measurand Urea<sub>Koroleff</sub> Sample UK2



## Appendix 10. Summaries of the z and E<sub>n</sub> 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	24	%		
Cl <sub>2</sub> , comb	U1K	.	<b>S</b>	<b>S</b>	<b>S</b>	<i>S</i>	.	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	.	.	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	100	
	U2K	.	<b>S</b>	<b>S</b>	.	<i>S</i>	.	.	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	.	.	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	100	
Cl <sub>2</sub> , free	U1K	.	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	.	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	.	<b>S</b>	.	.	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	100	
	U2K	.	<b>S</b>	<b>S</b>	.	<i>S</i>	.	.	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>q</b>	<b>S</b>	<b>S</b>	.	.	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	94.4	
Cl <sub>2</sub> , total	U1K	.	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>Q</b>	<b>S</b>	<b>S</b>	<b>S</b>	.	<b>S</b>	.	.	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	95.0	
	U2K	.	<b>S</b>	<b>S</b>	.	<i>S</i>	<i>S</i>	.	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	.	.	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	100	
KMnO <sub>4</sub>	U1P	.	<b>S</b>	<b>S</b>	<b>S</b>	.	<b>S</b>	.	<b>S</b>	<b>S</b>	<b>S</b>	.	<b>S</b>	<b>S</b>	<b>U</b>	<b>u</b>	.	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>q</b>	.	<b>q</b>	77.8	
	U2P	.	<b>S</b>	<b>S</b>	<b>S</b>	.	<b>S</b>	.	<b>S</b>	<b>S</b>	<b>S</b>	.	<b>S</b>	<b>S</b>	<b>S</b>	<b>u</b>	.	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	94.4	
NO <sub>3</sub>	U1N	.	<b>S</b>	.	.	.	.	.	<b>S</b>	<b>S</b>	<b>S</b>	.	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	.	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	100	
	U2N	.	<b>S</b>	.	.	.	.	.	<b>S</b>	<b>S</b>	<b>S</b>	.	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	.	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	100	
pH	U1H	.	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	100	
	U2H	.	<b>S</b>	<b>S</b>	<b>S</b>	<b>u</b>	<b>S</b>	.	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	95.5	
Turbidity	U1S	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	.	<b>S</b>	<b>S</b>	<b>S</b>	.	<b>S</b>	<b>S</b>	.	<b>S</b>	<b>S</b>	<b>S</b>	<b>u</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	95.2	
	U2S	.	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	.	<b>S</b>	<b>S</b>	<b>S</b>	.	<b>S</b>	<b>S</b>	.	<b>S</b>	<b>S</b>	<b>Q</b>	<b>q</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	<b>S</b>	90.0	
Urea	A1U	.	<b>S</b>	.	<b>S</b>	.	.	.	<b>S</b>	<b>S</b>	<b>S</b>	<b>Q</b>	<b>S</b>	<b>S</b>	<b>S</b>	.	.	<b>S</b>	.	<b>S</b>	<b>S</b>	.	.	<b>S</b>	.	<b>S</b>	92.3	
Urea <sub>Enzymatic</sub>	UE2	<b>S</b>	<b>q</b>	.	.	.	.	.	<b>S</b>	<b>S</b>	.	<b>S</b>	.	<b>S</b>	<b>S</b>	.	.	.	.	.	.	.	.	.	<b>S</b>	.	<b>S</b>	88.9
Urea <sub>Koroleff</sub>	UK2	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
%		100	94	100	100	90	100	100	94	100	100	80	100	100	88	75	100	93	86	100	100	100	92	100	92			
accredited		2	16	12	10	8	6	4	16	16	15	9	12	16	8	8	8	8	15	14	15	15	14	12	8	12		

S - satisfactory ( $-2 \leq z \leq 2$ ), Q - questionable ( $2 < z < 3$ ), q - questionable ( $-3 < z < -2$ ),

U - unsatisfactory ( $z \geq 3$ ), and u - unsatisfactory ( $z \leq -3$ ), respectively

bold - accredited, italics - non-accredited, normal - unknown

% - percentage of satisfactory results

Satisfactory results, in total %: 95      in accredited %: 95      in non-accredited %: 100

### E<sub>n</sub> scores

Measurand	Sample	4	9	10	12	17	19	%
Urea <sub>Koroleff</sub>	UK2	0.4	-1.2	0.2	-0.4	-0.4	0.8	83.3

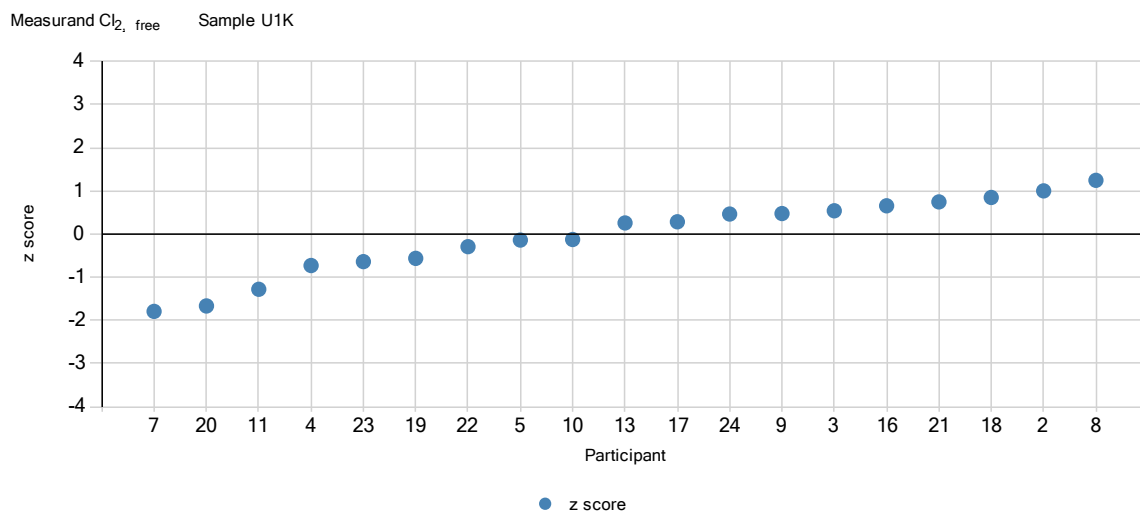
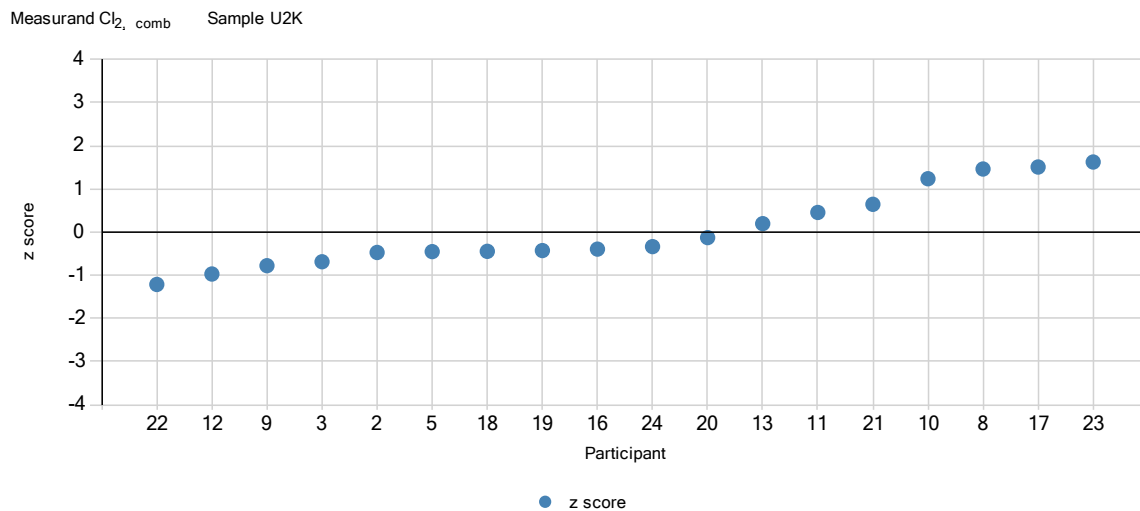
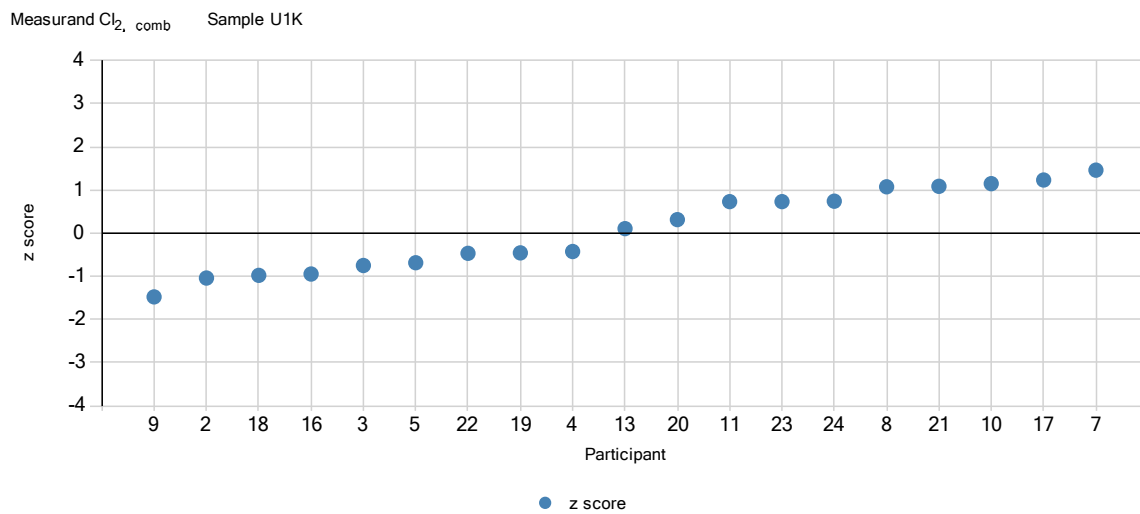
$-1.0 \leq E_n \leq 1.0$  - satisfactory

$E_n > 1.0$  or  $E_n < -1.0$  - unsatisfactory

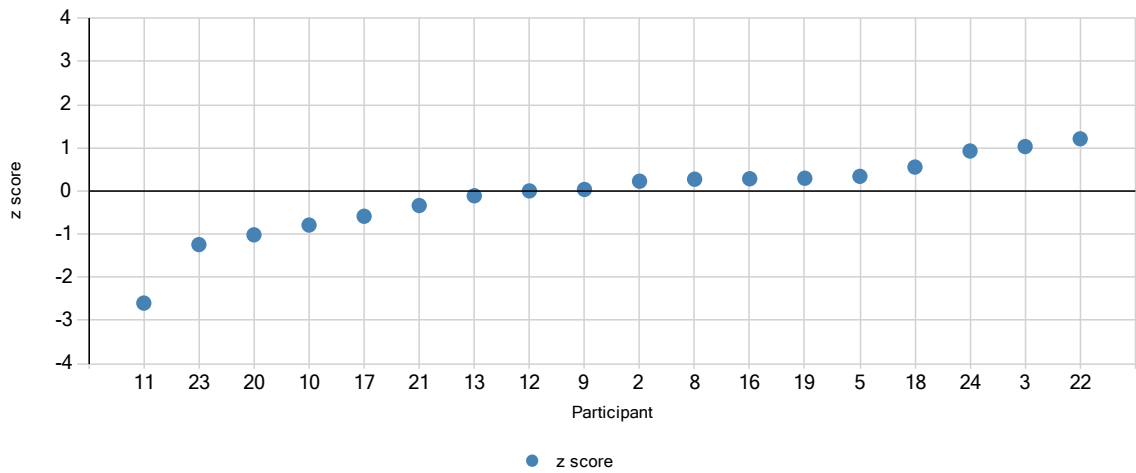
% - percentage of satisfactory results

Satisfactory results, in total %: 83

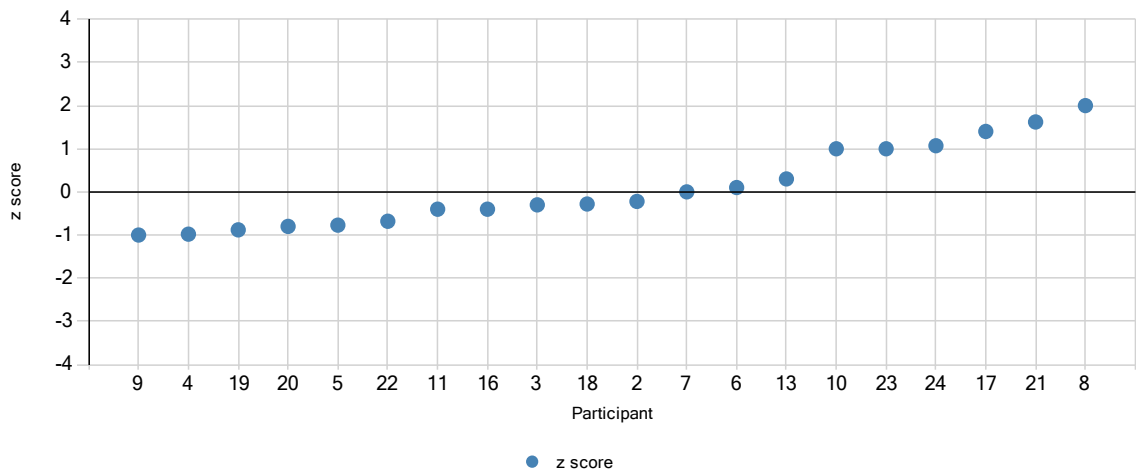
## Appendix I I. z scores in ascending order



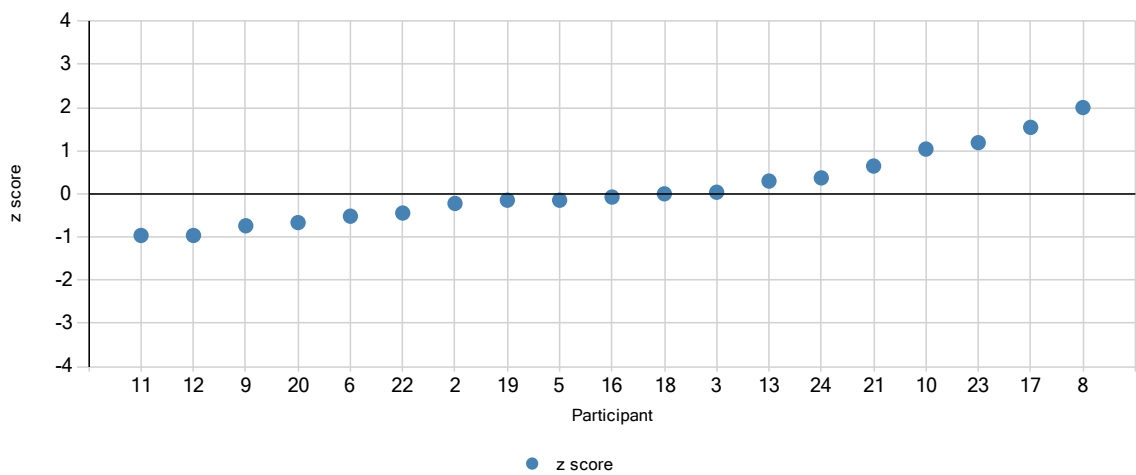
Measurand  $Cl_{2, \text{ free}}$  Sample U2K



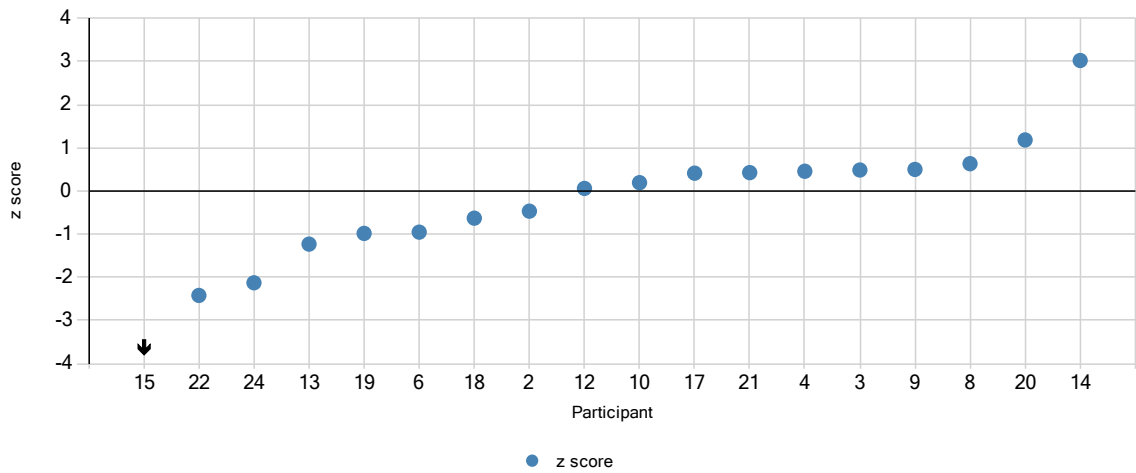
Measurand  $Cl_{2, \text{ total}}$  Sample U1K



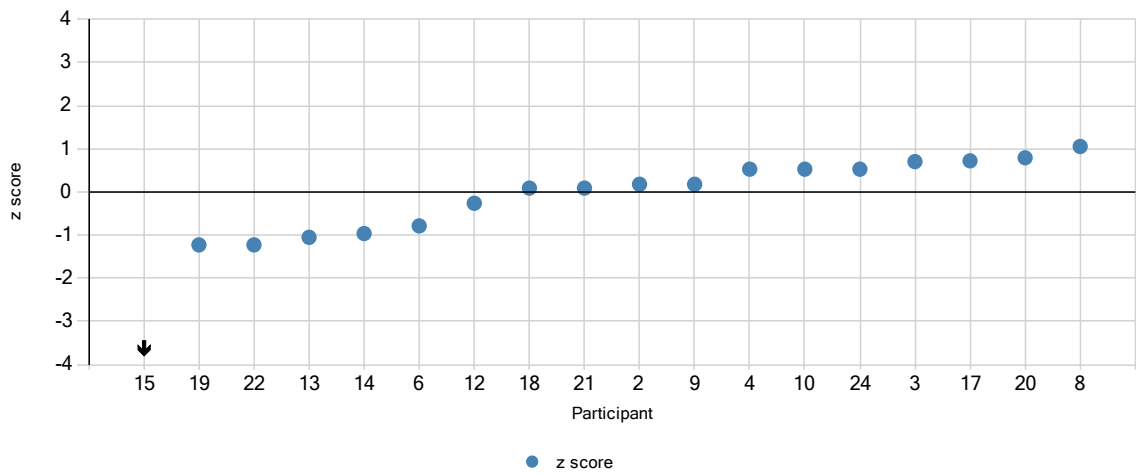
Measurand  $Cl_{2, \text{ total}}$  Sample U2K



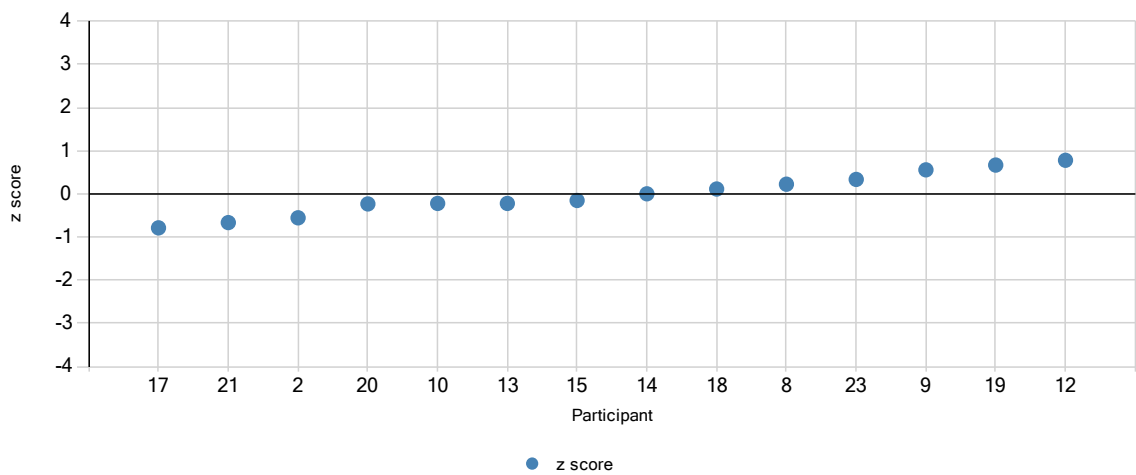
Measurand  $\text{KMnO}_4$  Sample U1P



Measurand  $\text{KMnO}_4$  Sample U2P

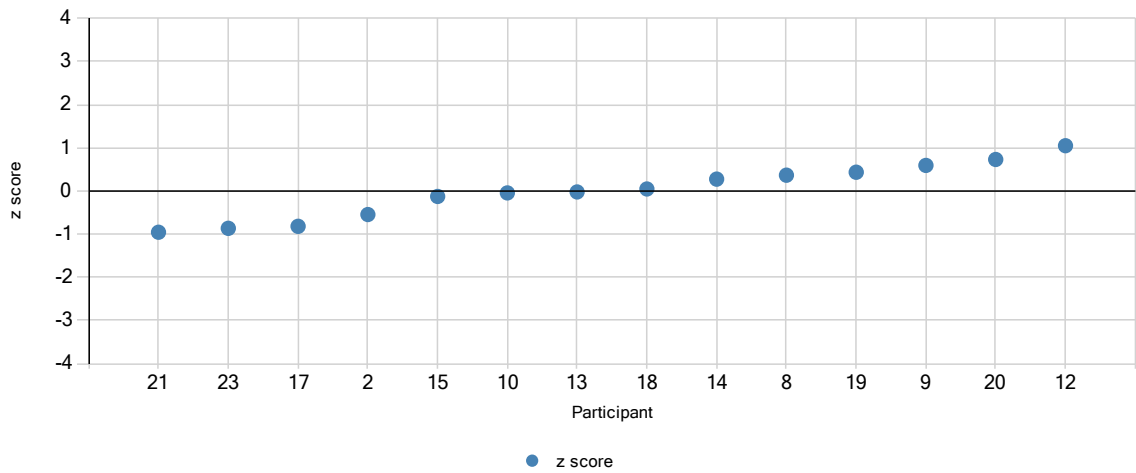


Measurand  $\text{NO}_3$  Sample U1N

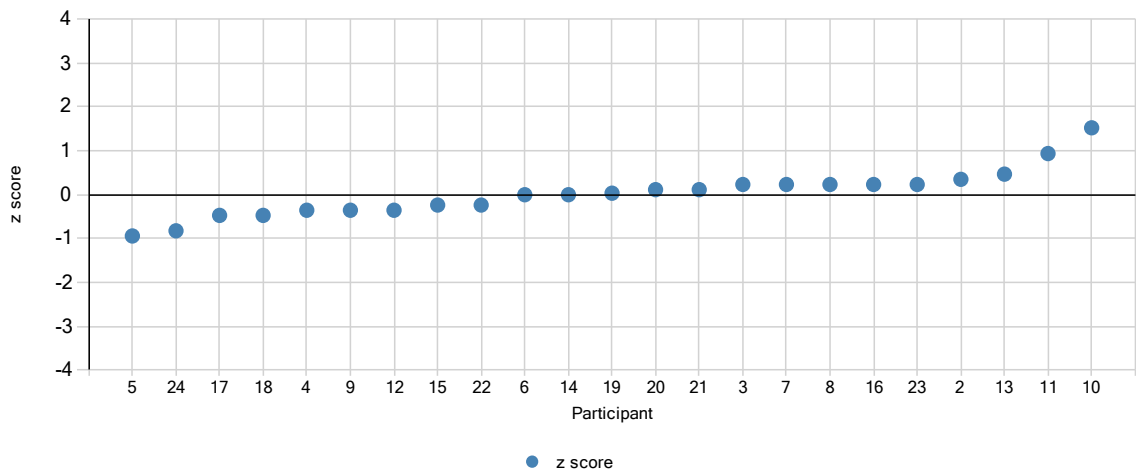




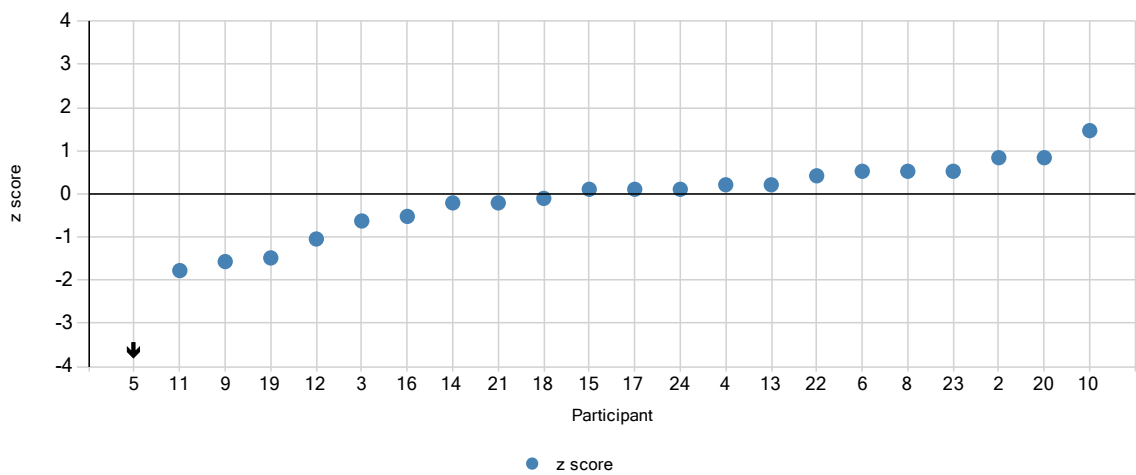
Measurand NO<sub>3</sub> Sample U2N



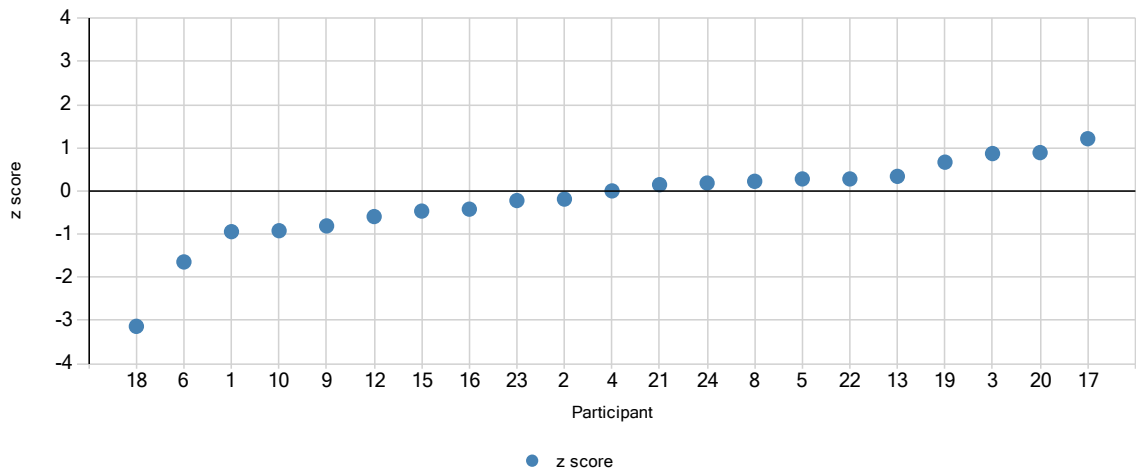
Measurand pH Sample U1H



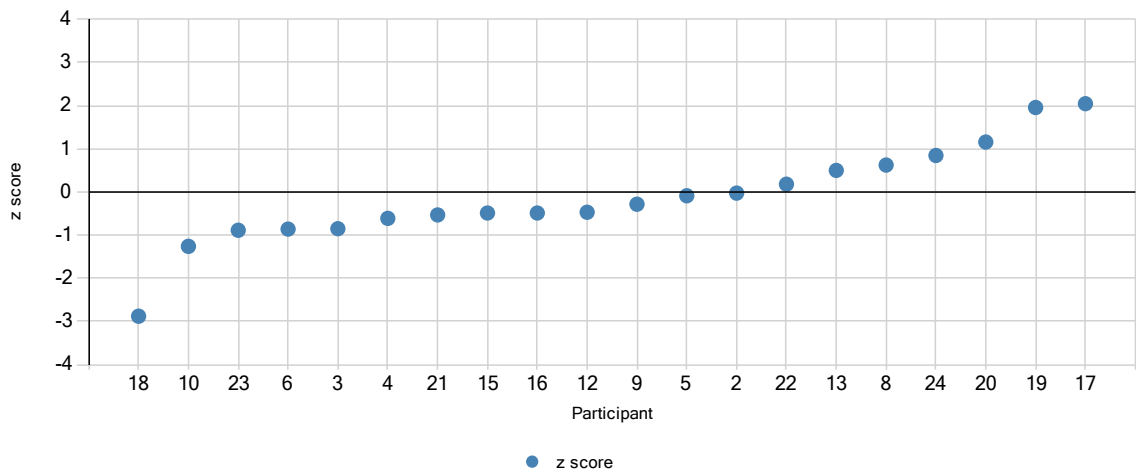
Measurand pH Sample U2H



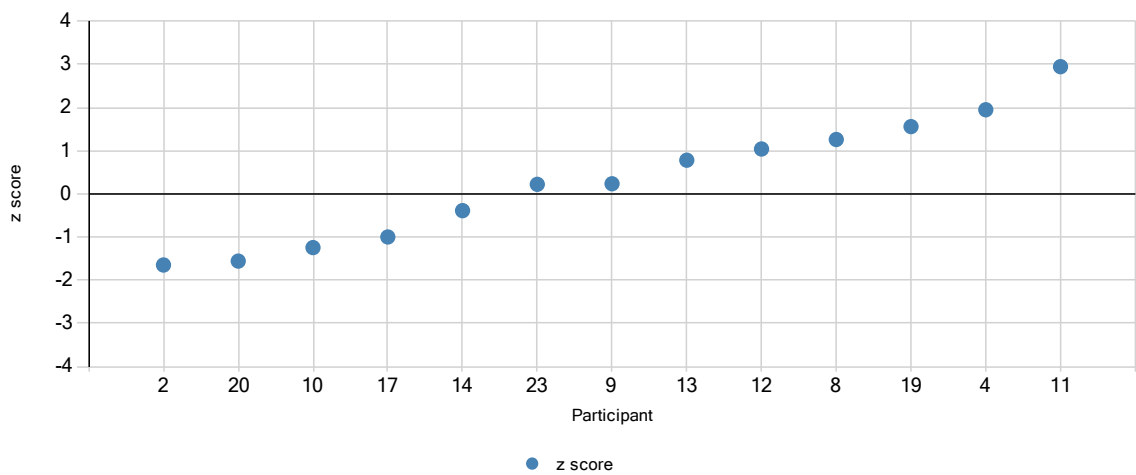
Measurand Turbidity Sample U1S

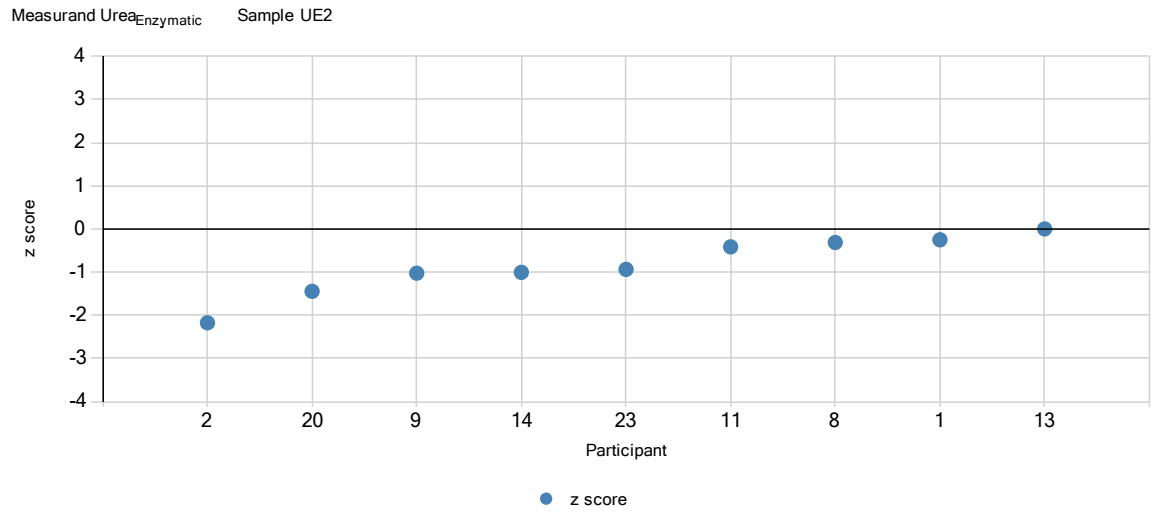


Measurand Turbidity Sample U2S



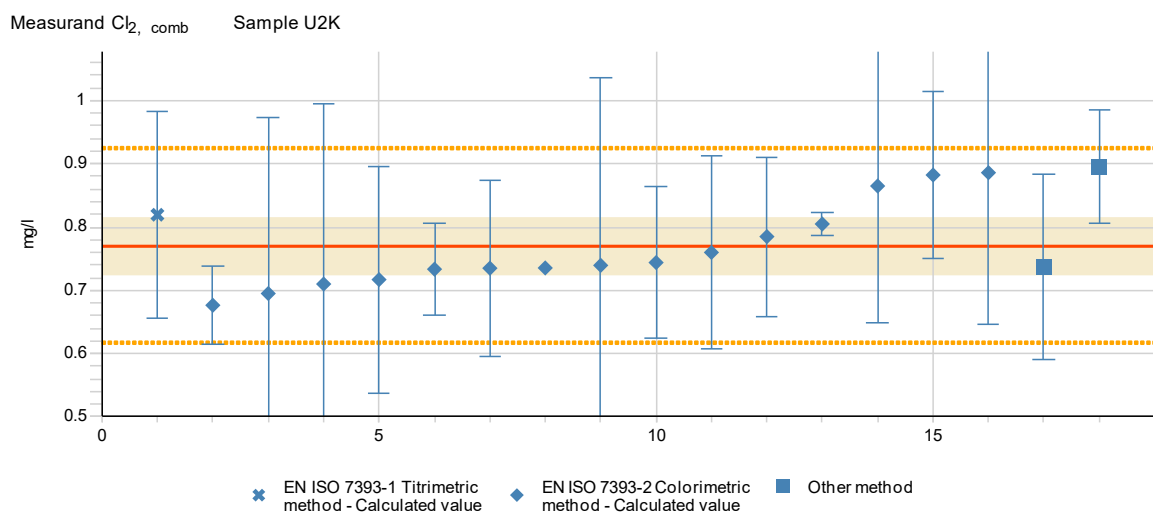
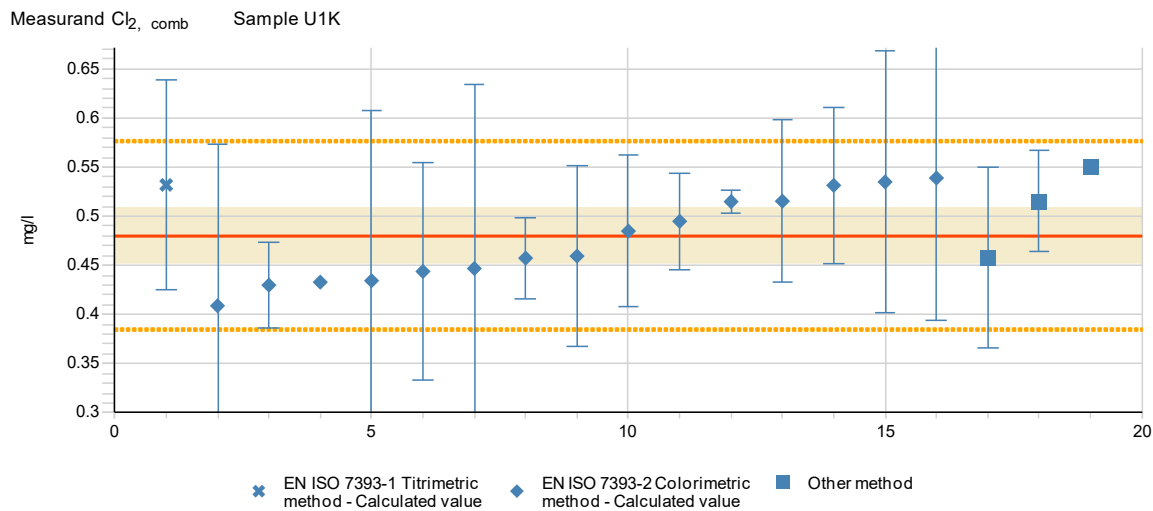
Measurand Urea Sample A1U



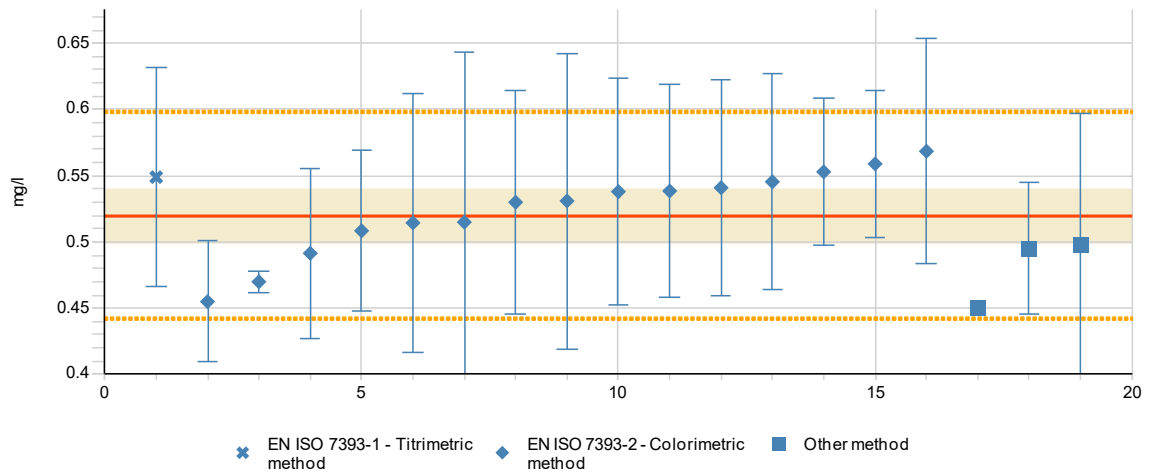


## Appendix 12. Results grouped according to the methods

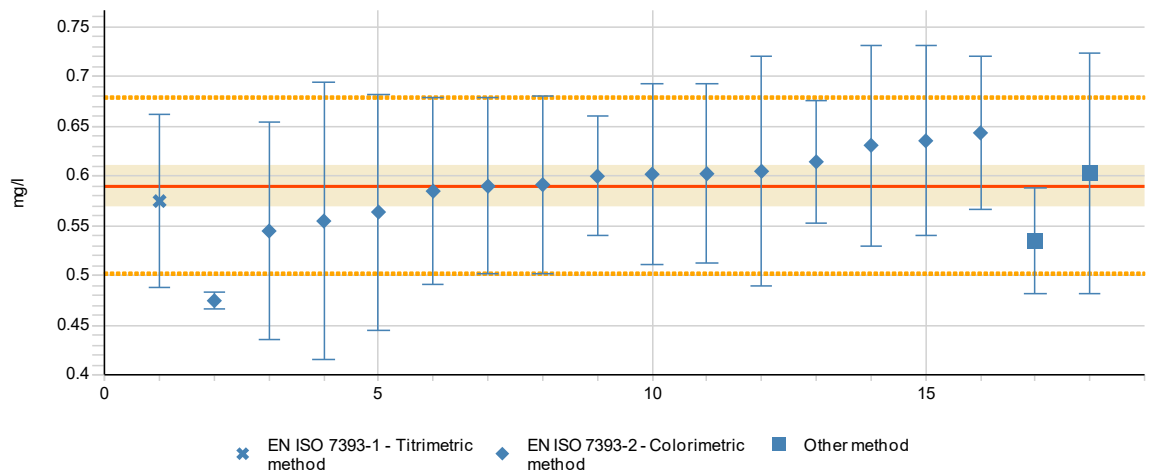
The explanations for the figures are described in the Appendix 9. The results are shown in ascending order.



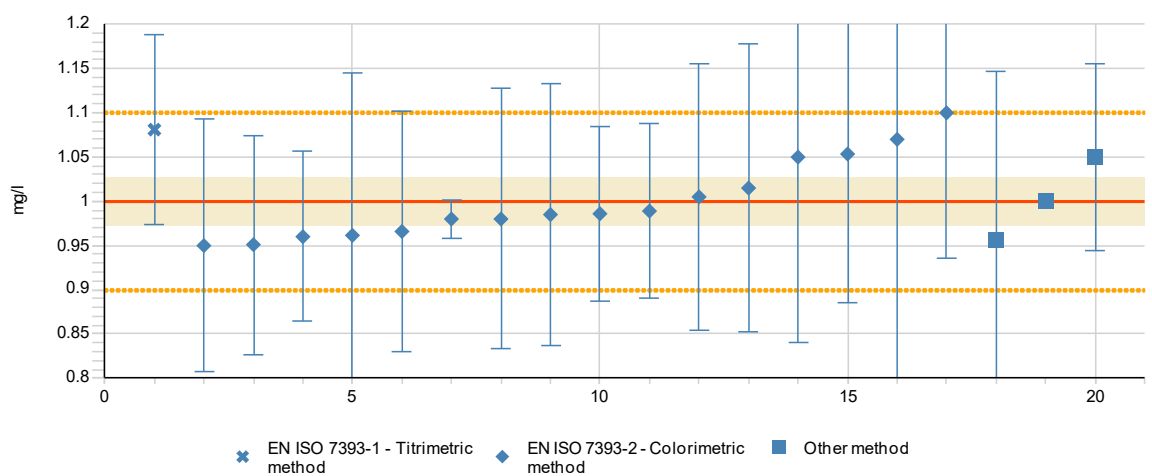
Measurand Cl<sub>2, free</sub> Sample U1K

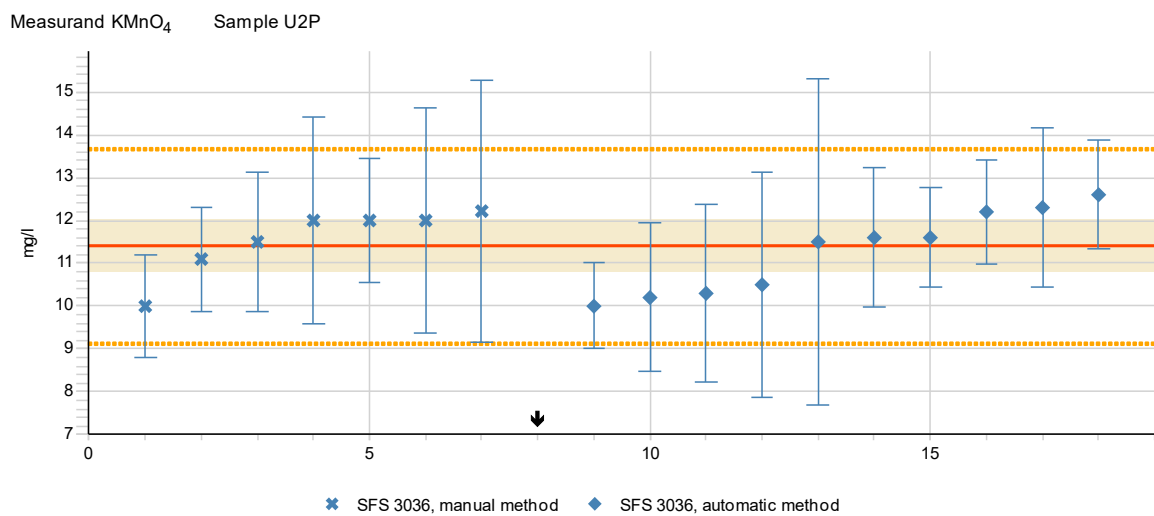
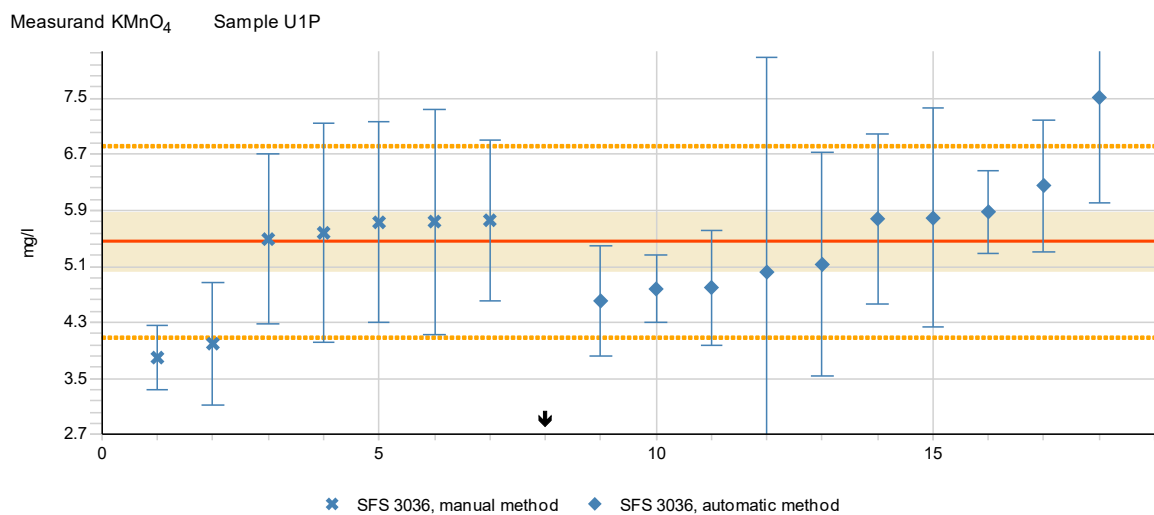
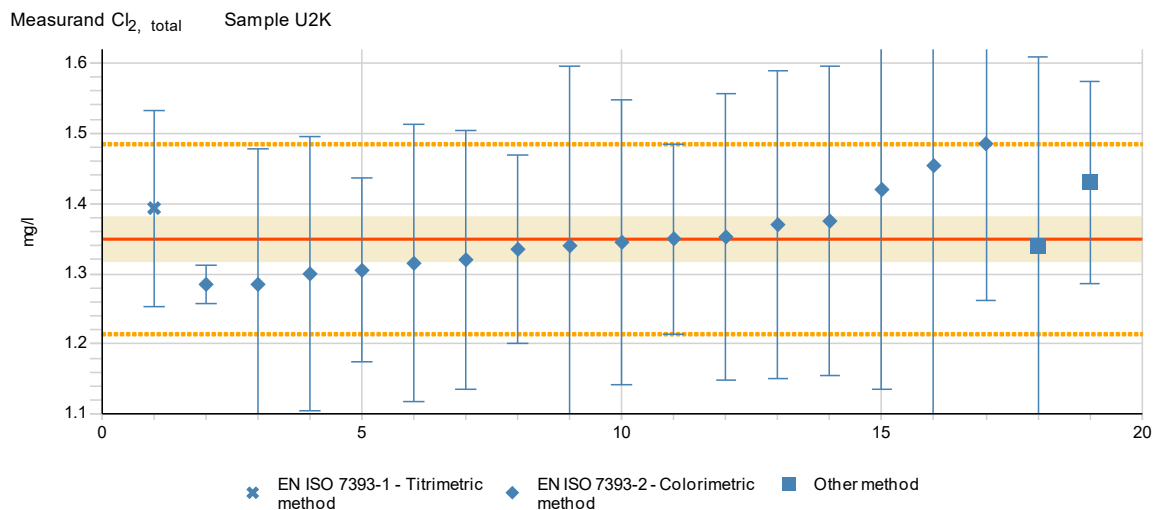


Measurand Cl<sub>2, free</sub> Sample U2K

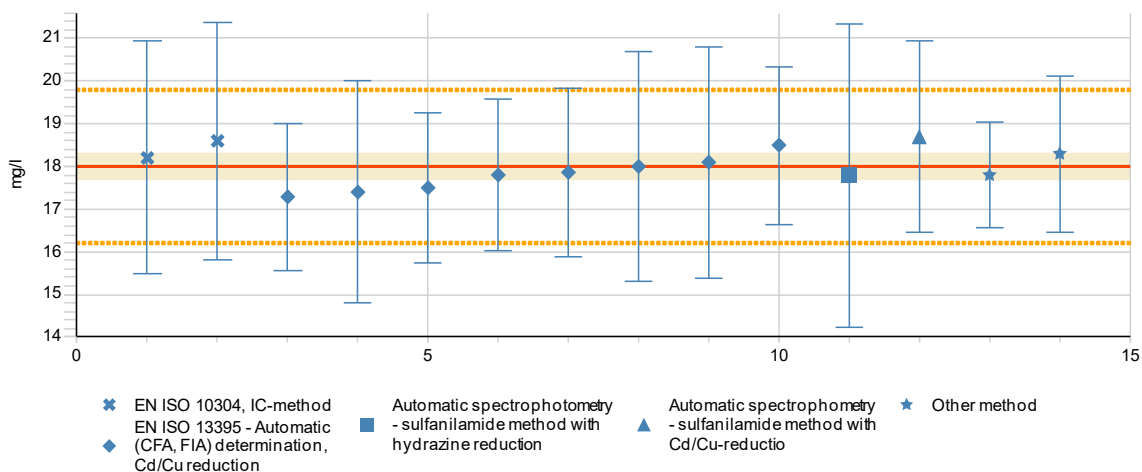


Measurand Cl<sub>2, total</sub> Sample U1K

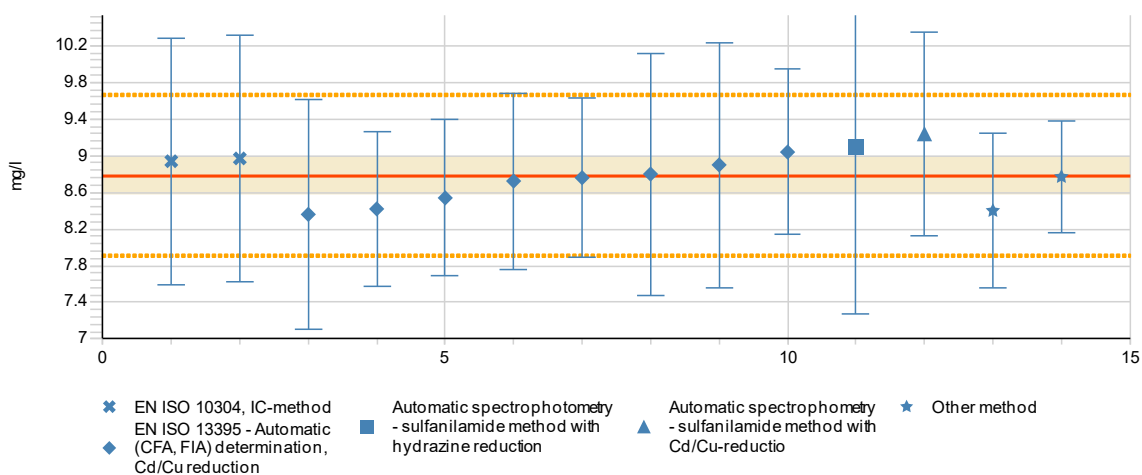




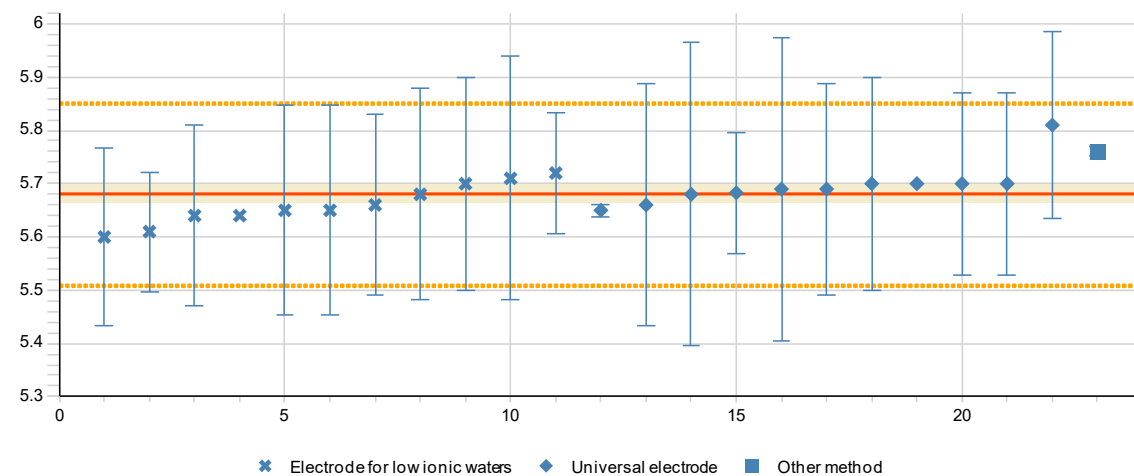
Measurand NO<sub>3</sub> Sample U1N



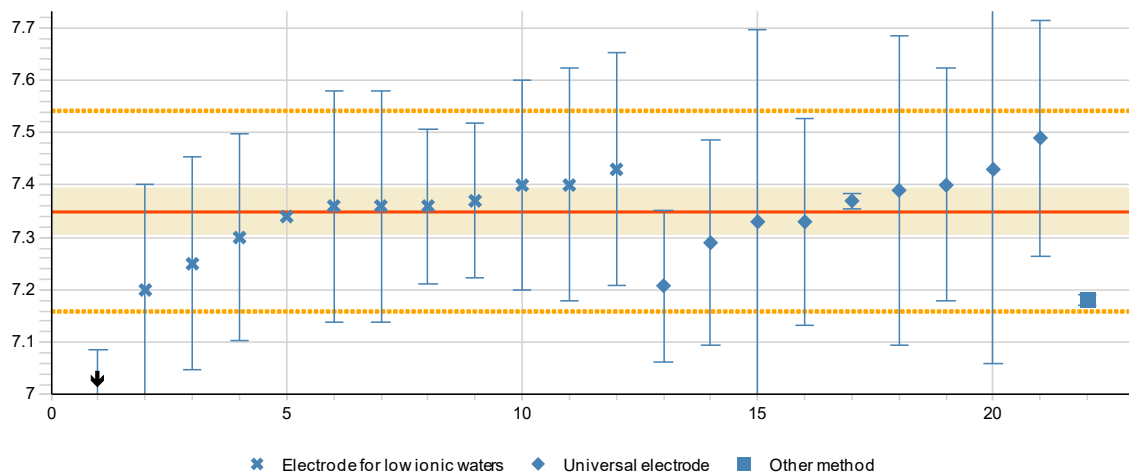
Measurand NO<sub>3</sub> Sample U2N



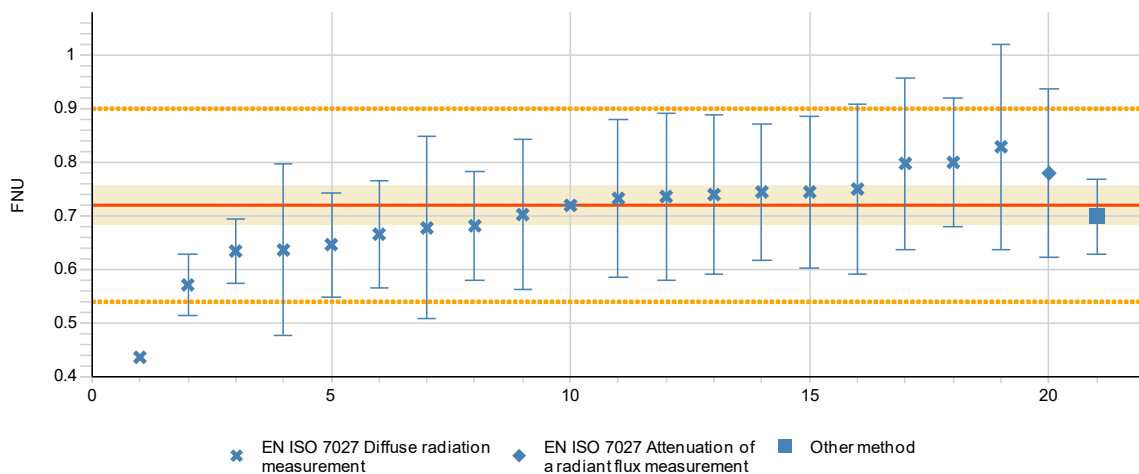
Measurand pH Sample U1H



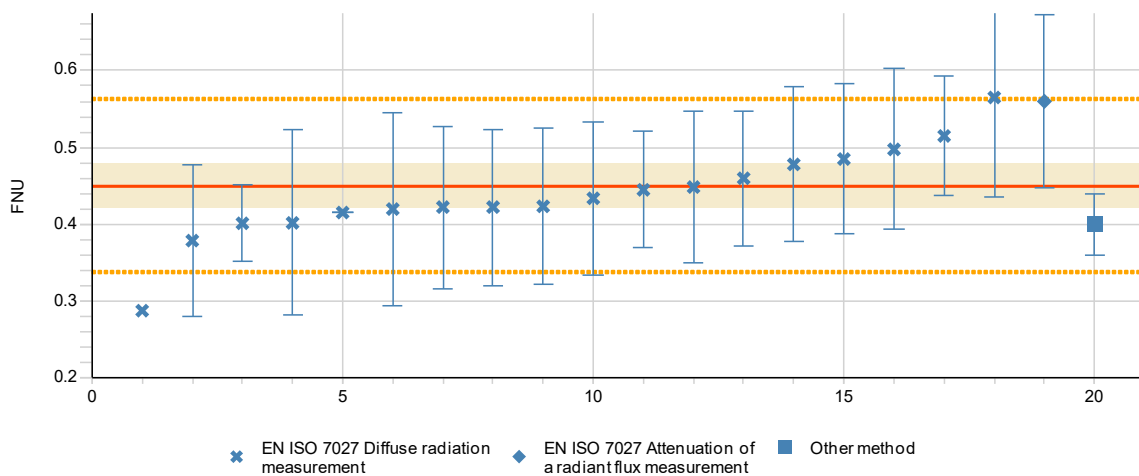
Measurand pH Sample U2H



Measurand Turbidity Sample U1S

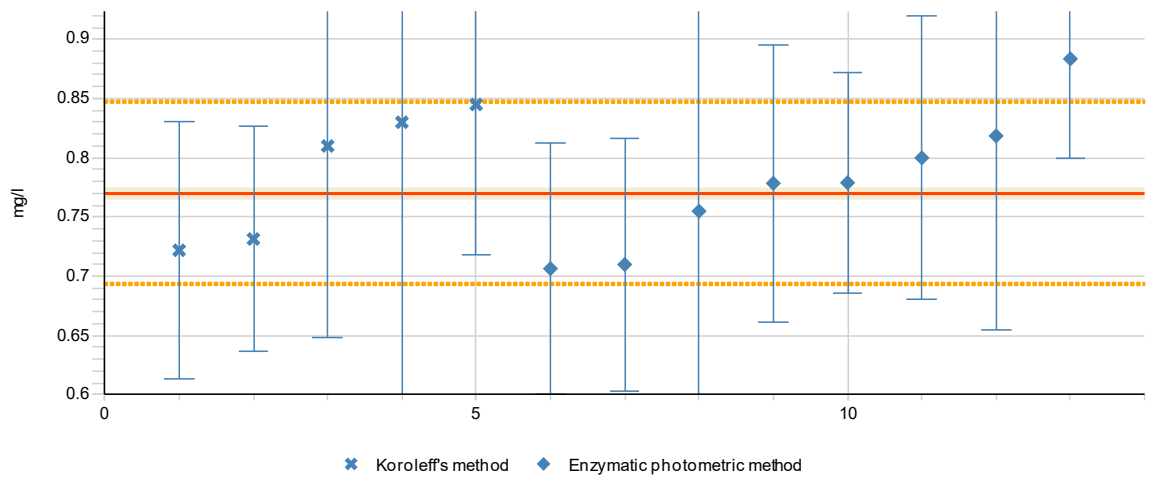


Measurand Turbidity Sample U2S

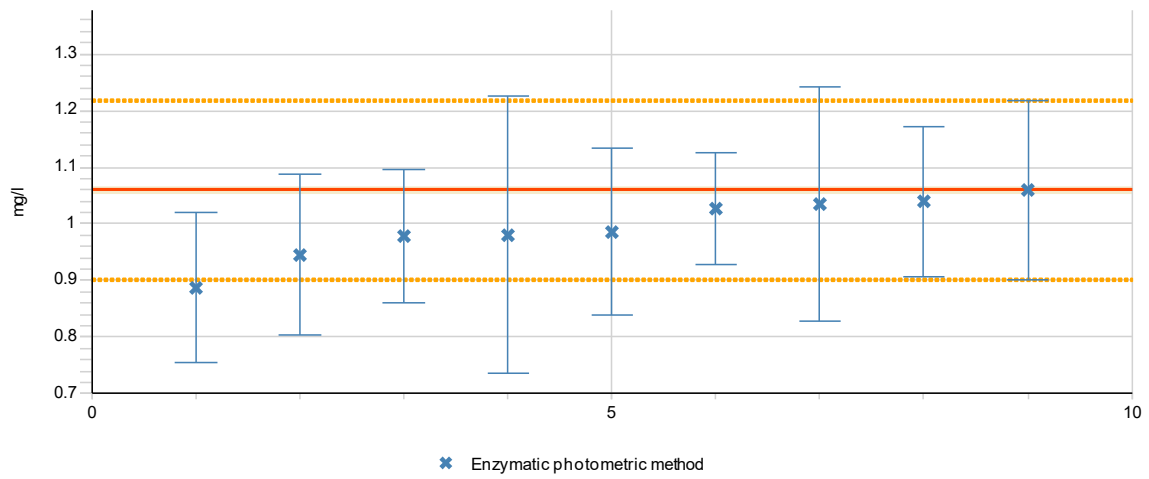




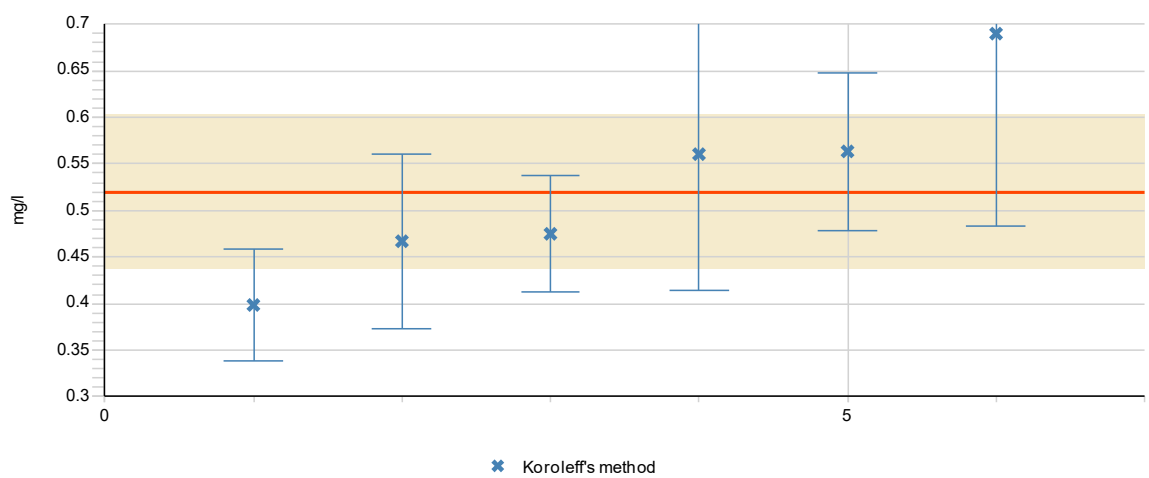
Measurand Urea Sample A1U



Measurand Urea<sub>Enzymatic</sub> Sample UE2

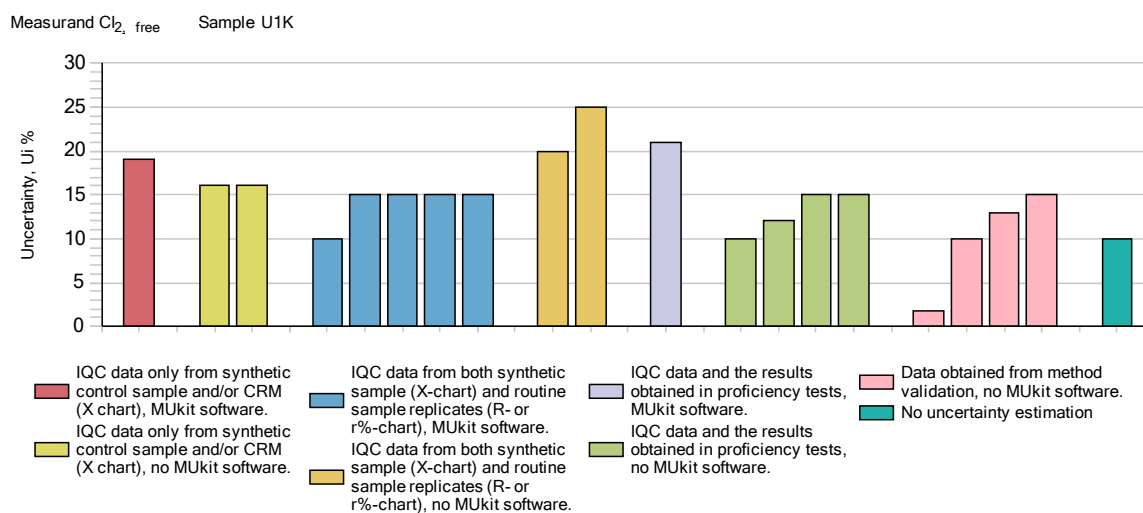
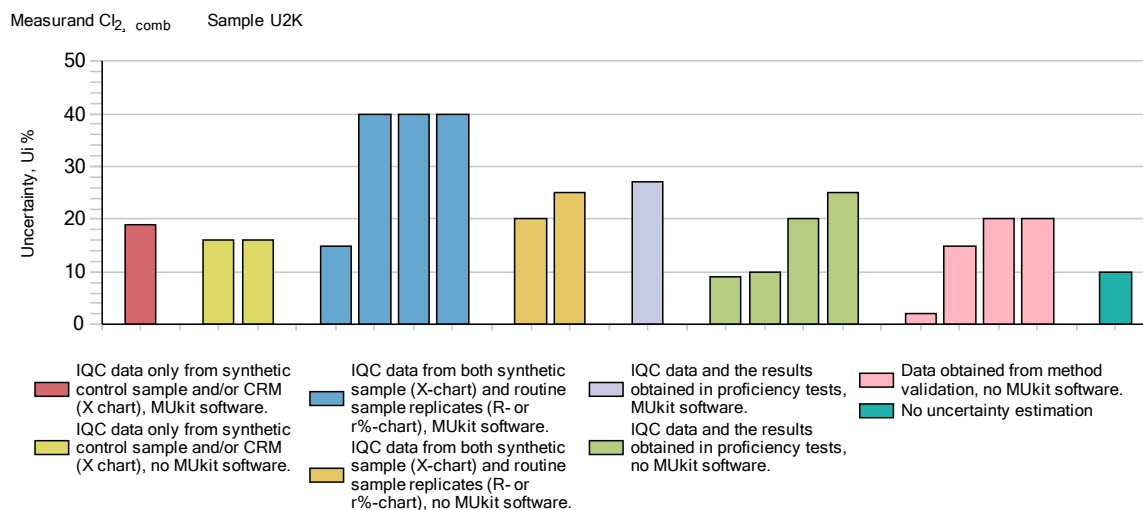


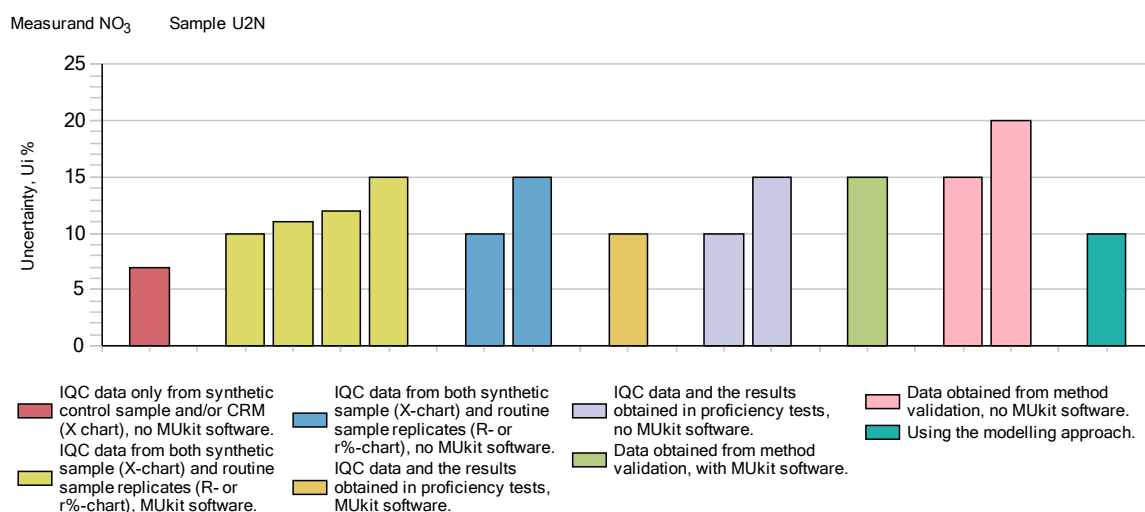
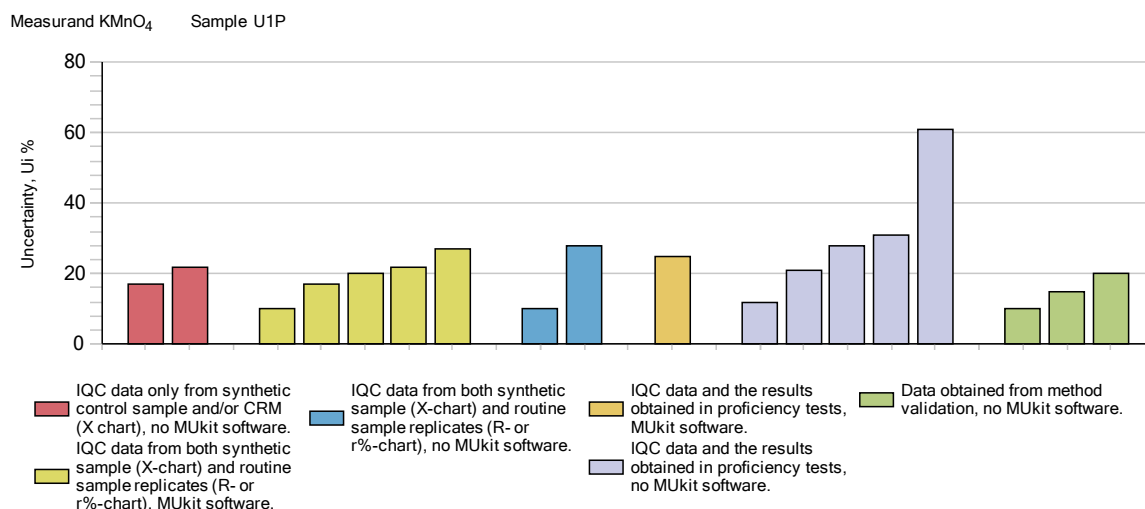
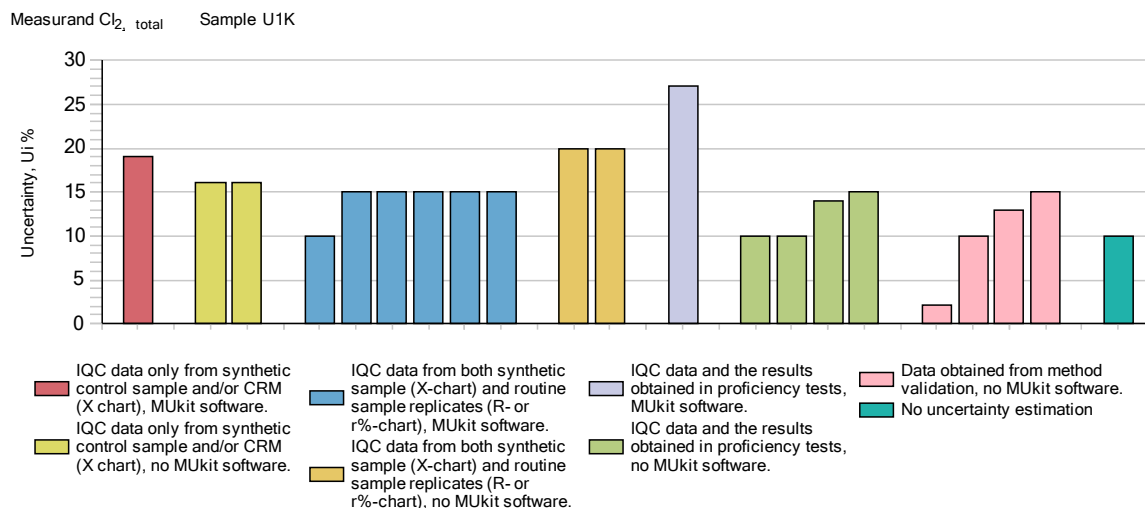
Measurand Urea<sub>Koroleff</sub> Sample UK2

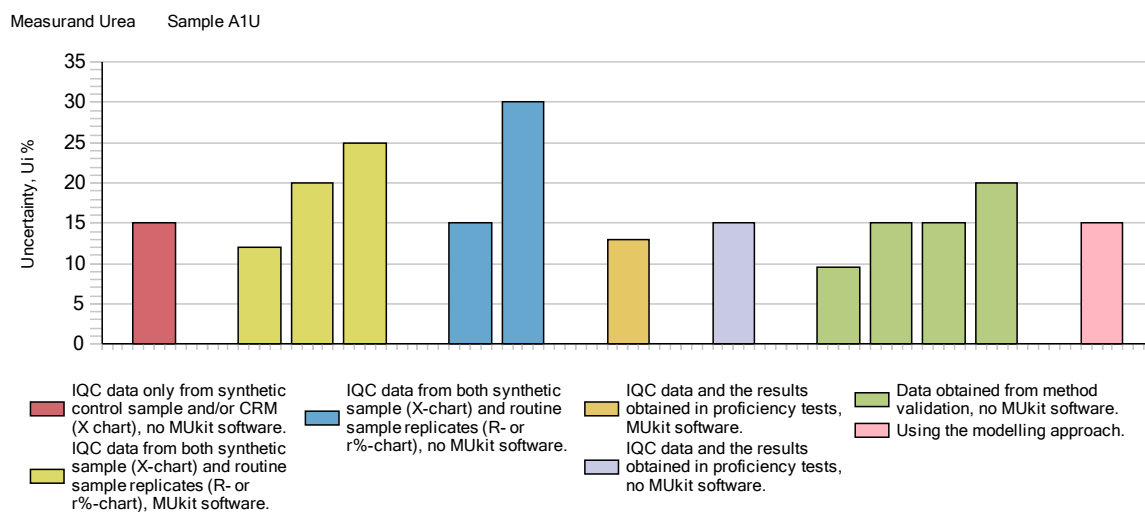
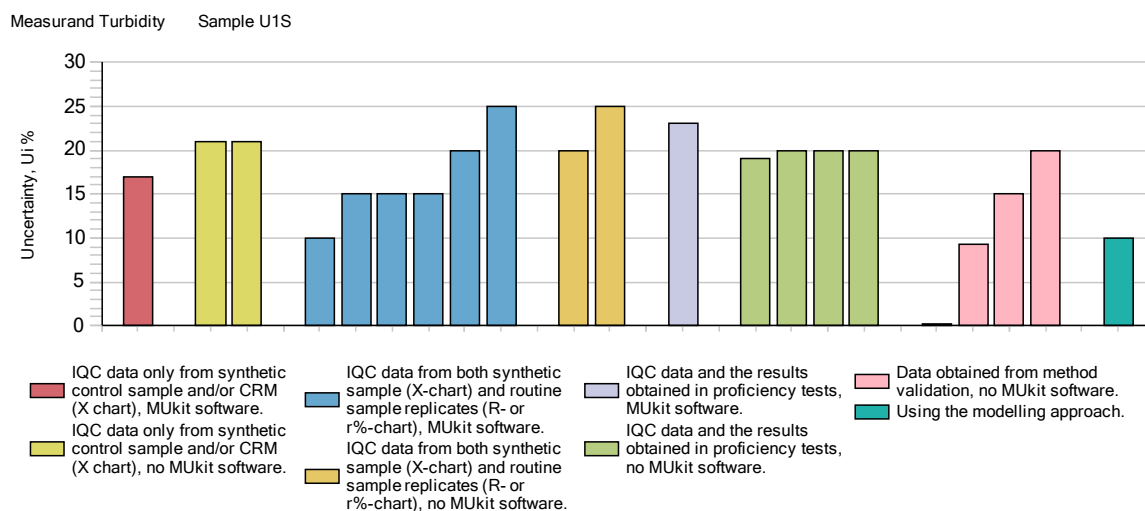
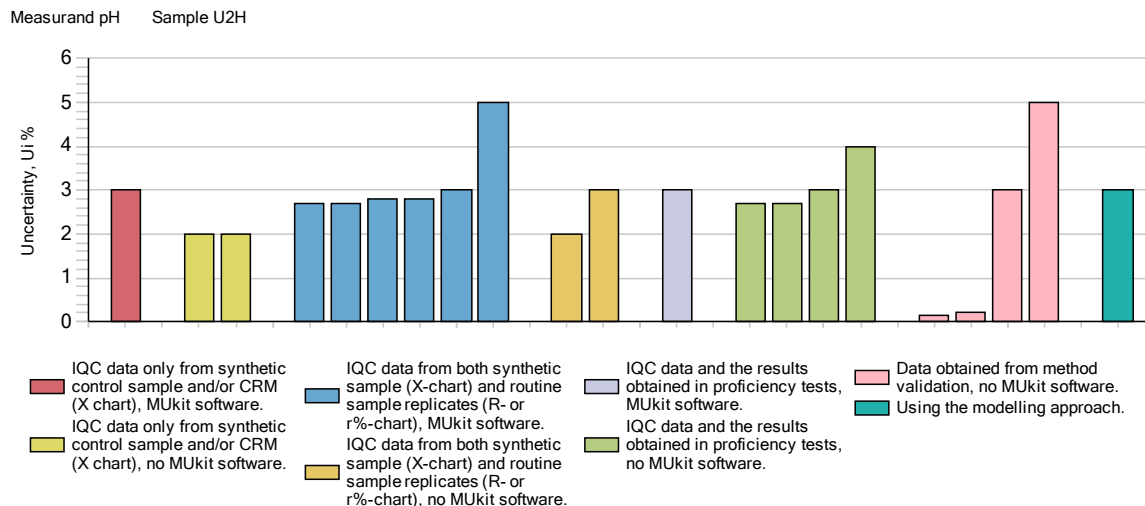


## Appendix 13. Examples of measurement uncertainties reported by the participants

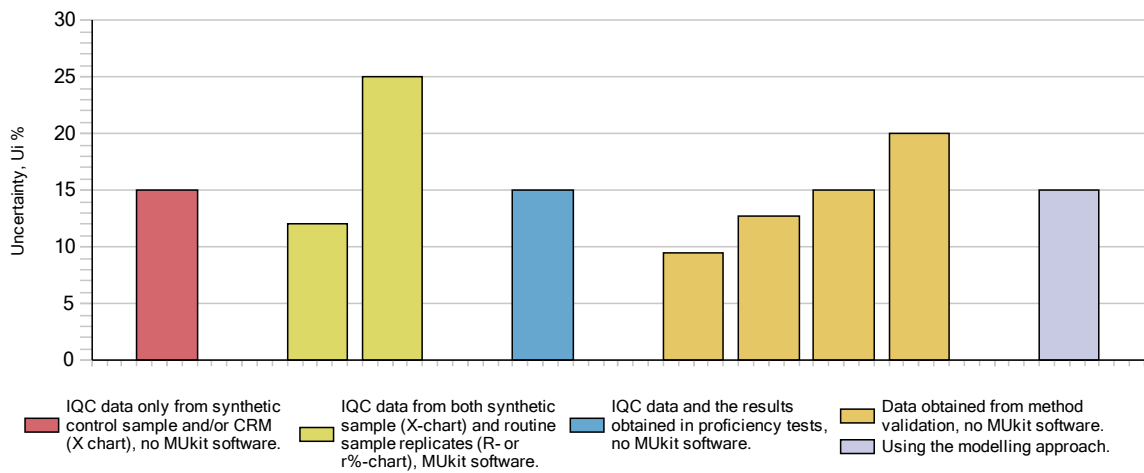
In figures, the presented expanded measurement uncertainties are grouped according to the method of estimation at 95 % confidence level ( $k=2$ ). The expanded uncertainties were estimated mainly by using the internal quality control (IQC) data. The used procedures in figures below are distinguished e.g. between using or not using the MUKIT software for uncertainty estimation [8, 9] or using a modelling approach based [11, 12].



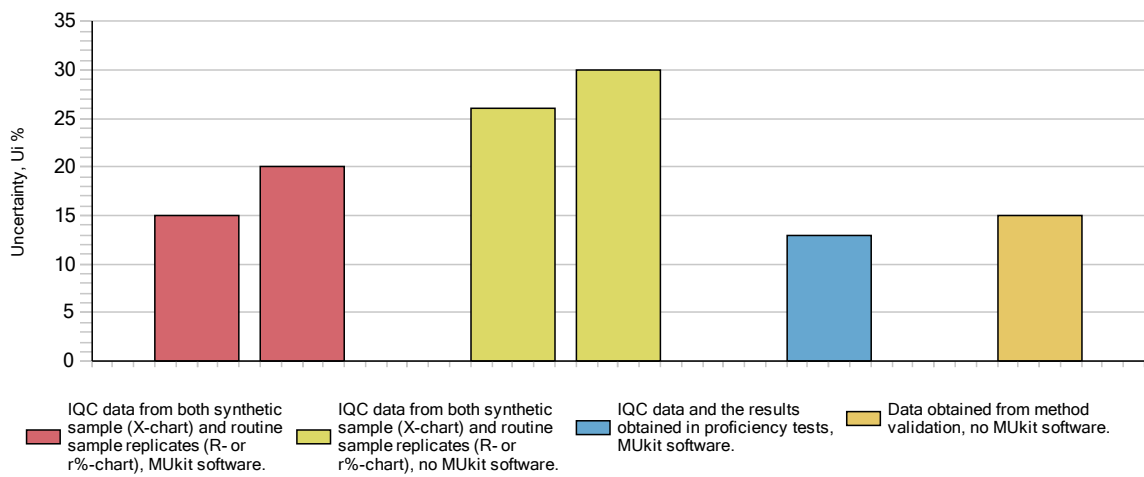




Measurand Urea<sub>Enzymatic</sub> Sample UE2



Measurand Urea<sub>Koroleff</sub> Sample UK2





ISBN 978-952-11-5483-6 (PDF)

ISSN 1796-1726 (online)