

Interlaboratory Proficiency Test 01/2016

Swimming pool water analysis

**Mirja Leivuori, Sami Tyrväinen, Teemu Näykki,
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REPORTS OF THE FINNISH ENVIRONMENT INSTITUTE 16|2016
Finnish Environment Institute SYKE
Profest SYKE

Layout: Markku Ilmakunnas

The publication is also available in the Internet: www.syke.fi/publication | helda.helsinki.fi/syke

ISBN 978-952-11-4566-7(PDF)
ISSN 1796-1726 (Online)

Author(s): Mirja Leivuori¹⁾, Sami Tyrväinen²⁾, Teemu Näykki¹⁾, Riitta Koivikko¹⁾, Keijo Tervonen¹⁾,
Sari Lanteri¹⁾ and Markku Ilmakunnas¹⁾

¹⁾ Finnish Environment Institute

²⁾ Ramboll Finland Oy

Publisher and financier of publication: Finnish Environment Institute (SYKE)
P.O. Box 140, FI-00251 Helsinki, Finland, Phone +358 295 251 000, syke.fi.

Year of issue: 2016



ABSTRACT

Profest SYKE carried out the proficiency test for the determination of chlorine, KMnO_4 , NO_3 , pH, turbidity, and urea in swimming pool waters in February 2016. In total, 23 participants joined in the proficiency test.

The robust mean of the results reported by the participants was chosen to be the assigned value for the concentration of most measurands. The performance of the participants was evaluated by using z scores. In this proficiency test 94 % of the results were satisfactory when in the pH determination 0.2 pH unit and in other determinations the deviation between 8–35 % from the assigned value was accepted.

Warm thanks to all the participants of this proficiency test!

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

TIIVISTELMÄ

Profest SYKE järjesti pätevyyskokeen helmikuussa 2016 uima-allasvesien kloori, KMnO_4 , NO_3 , pH, sameus ja urea määritysten testaamiseksi. Pätevyyskokeeseen osallistui yhteensä 23 osallistujaa.

Määrittelyn vertailuarvona käytettiin ureamäärittelyssä laskennallista pitoisuutta ja muulloin osallistujien tulosten robustia keskiarvoa. Tulosten arviointi tehtiin z-arvon perusteella, jolloin pH-määrittelyssä sallittiin 0,2 pH-yksikön ja muissa määrittelyissä 8–35 %:n poikkeama vertailuarvosta. Koko aineistossa hyväksyttävää tuloksia oli 94 %.

Kiitos pätevyyskokeen osallistujille!

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

SAMMANDRAG

Under februari 2016 genomförde Profest SYKE en provningsjämförelse, som omfattade bestämningen av klor, KMnO_4 , nitrat, pH, grumlighet och urea i simbassängvatten. Till proven ställde upp 23 deltagarna.

Som referensvärde av analytens koncentration användes det robust medelvärde av deltagarnas resultat. Resultaten värderades med hjälp av z-värden. I jämförelsen var 94 % av alla resultaten tillfredsställande, när 0.2 pH enhet eller 8–35 % totalavvikelsen från referensvärdet accepterades.

Ett varmt tack till alla deltagarna i testet!

Nyckelord: vattenanalyser, klor, nitrat, pH, KMnO_4 , grumlighet, urea, simbassängvatten, provningsjämförelse, 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, nitrate, pH, turbidity, and urea from swimming pool waters in February 2016 (SPW 01/2016). In the PT the results of Finnish laboratories providing environmental data for Finnish environmental authorities were evaluated. Additionally, other water and environmental laboratories were welcomed in the proficiency test.

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 guidelines ISO/IEC 17043 [1], ISO 13528 [2] and IUPAC Technical report [3]. The Profest SYKE has been accredited by the Finnish Accreditation Service as a proficiency testing provider (PT01, ISO/IEC 17043, www.finas.fi/Documents/PT01_M08_2016.pdf). The organizing of this proficiency test is included in the accreditation scope of the Profest SYKE.

2 Organizing the proficiency test

2.1 Responsibilities

Organizer:

Profest SYKE, Finnish Environment Institute (SYKE), Laboratory Centre
Hakuninmaantie 6, FI-00430 Helsinki, Finland
Phone: +358 295 251 000, Fax. +358 9 448 320
e-mail: profest@environment.fi

The responsibilities in organizing the proficiency test were as follows:

| | |
|-------------------|---|
| Mirja Leivuori | coordinator |
| Riitta Koivikko | substitute for coordinator |
| Keijo Tervonen | technical assistance |
| Markku Ilmakunnas | technical assistance |
| Sari Lanteri | technical assistance |
| Ritva Väisänen | technical assistance |
| Teemu Näykki | analytical expert (NO ₃ , pH, turbidity, KMnO ₄) |

Partner:

Sami Tyrväinen from Ramboll Finland Oy (Lahti) was participating in organizing the proficiency test as well as acting as the analytical expert for chlorine and urea measurements.

Subcontracting:

Ramboll Finland Oy / Ramboll Analytics (accredited testing laboratory T039 by the Finnish Accreditation Service, www.finas.fi/Documents/T039_M29_2016.pdf) chlorine and urea measurements.

2.2 Participants

In total 23 laboratories participated in this proficiency test (Appendix 1), 20 from Finland and 3 from other European countries. 87 % of the participants reported that they have accredited quality management system based on ISO/IEC 17025. All the participants used accredited analytical methods at least for a part of the measurements. About 70 % of the Finnish participants provide data for the Finnish environmental authorities. The samples were tested at the laboratory of Ramboll Finland in Lahti for chlorines and urea. Their participant code is 19 in the result tables. The other parameters were tested in the organizing laboratory (T003, www.finas.fi/Documents/T003_M34_2016.pdf) which has the code 15 (SYKE, Oulu) in the result tables.

2.3 Samples and delivery

Two swimming pool water samples (U1 and U2) were delivered to the participants. For the determination of urea also one synthetic sample (A1U) and third swimming pool water sample (U3) were delivered. The synthetic sample (A1U) was prepared from the commercial urea reagent (Merck). The sample preparation is described in details in the Appendix 2. The samples were prepared according to the usual concentration levels of swimming pool waters in Finland [4].

When preparing the samples, the purity of the used sample vessels was controlled. The randomly chosen sample vessels were filled with deionized water and the purity of the sample vessels was controlled after three days by analyzing N_{NH_4} (urea), N_{NO_3} (nitrate) and conductivity (pH). According to the test results all used vessels fulfilled the purity requirements.

The samples were delivered on 2 February 2016 and they arrived to the participants mainly on the next day. One participant received the samples on 4.2.2016 (participant 11) and another on 5.2.2016 (participant 6).

The sample for controlling the temperature during the transportation was placed into the sample package and the temperature was requested to be measured when opening the package. The temperature of the control sample was mainly ≤ 10 °C, while for the participants 3, 4, 5, 6, 7 and 9 it was higher, up to 17.1 °C. Additionally, for four participants a temperature logger was placed into the sample packages. The loggers were returned to the provider and data was evaluated. From **the temperature logger data** it was noticed that it is crucial to **measure the temperature of the control sample rather soon after the sample package has arrived**, especially when the package is not stored in refrigerator after the arrival. The warming up of the samples was taken into account when evaluating the results.

The samples were requested to be analysed on 5 February 2016. All results reported to the provider on 8 February 2016. The preliminary results were reported on 12 February 2016.

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). According to the literature and previous knowledge, the other proficiency test items are known to be stable within the testing time of the proficiency test. Based on the stability test the warming up of samples during the transportation did not affect the performance of the participants.

2.5 Feedback from the proficiency test

The feedback from the proficiency test is shown in Appendix 5. The comments from the participants mainly dealt with delivery delay and their reporting errors with the samples. 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

The normality of the data was tested by the Kolmogorov-Smirnov test. The outliers were rejected according to the Grubbs or Hampel test before calculating the mean. The results which differed more than 50 % or 5 times from the robust mean were rejected before the statistical results handling. The replicate results were tested using the Cochran-test.

More information about the statistical handling of the data is available from the Guide for participant [5].

2.6.2 Assigned values

The detailed information of the assigned values, their uncertainties and reliability is shown in Appendix 6. The calculated value was used as the assigned value for urea measurements and robust mean for the other measurements. 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 measurement uncertainty ($k=2$) was estimated by using standard uncertainties associated with individual operations involved in the

preparation of the sample. The main individual source of the uncertainty was the purity of the stock compound. For the assigned values based on the robust mean the uncertainty of the assigned value was calculated using the robust standard deviation of the reported results [2, 4].

The uncertainty of the calculated assigned values was 0.6 % at the 95 % confidence level. When using the robust mean of the participant results as the assigned value, the uncertainty of the assigned values was lower than 1 % for pH measurements. For the other measurands the uncertainties of the assigned values were lower than 10 % with the exception for the Cl₂_comb measurement of the sample U2K (13 %).

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

2.6.3 Standard deviation for proficiency assesment and z score

The standard deviation for proficiency assessment was estimated on the basis of the measurand concentration, the results of homogeneity and stability tests, the uncertainty of the assigned value, and the long-term variation in the former proficiency tests. The standard deviation for proficiency assessment ($2 \times s_{pt}$ at the 95 % confidence level) was set for pH measurement to 0.2 pH units and for the other measurements from 8 % to 35 % depending on the measurands. After reporting the preliminary results no changes have been done for the standard deviations of the proficiency assessment values.

When using the robust mean as the assigned value, the reliability was tested according to the criterion $u_{pt} / s_{pt} \leq 0.3$, where u_{pt} is the standard uncertainty of the assigned value (the expanded uncertainty of the assigned value (U_{pt}) divided by 2) and s_{pt} is the standard deviation for proficiency assessment [3]. When testing the reliability of the assigned value the criterion was mainly fulfilled and the assigned values were considered reliable.

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

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

| Sample | Measurand |
|--------|-----------------------|
| U2K | Cl ₂ _comb |
| U1K | Cl _{free} |

3 Results and conclusions

3.1 Results

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

In the evaluation the results of urea determination have been assessed only from the samples A1U. In the urea samples U2U and U3U a difference was observed between the results obtained with Koroleff method and enzymatic photometric method, and thus the performance evaluation of the results was not possible.

The robust standard deviations of the results varied from 1.1 to 21.9 % (Table 1). The robust standard deviations were approximately in the same range as in the previous similar proficiency test Profest SYKE SPW 01/2015 [6], where the deviations varied from 1.2 % to 20.3 %.

Table 1. The summary of the results in the proficiency test SPW 01/2016.

| Measurand | Sample | Unit | Assigned value | Mean | Rob. mean | Median | SD rob | SD rob % | 2 x s _{pt} % | n (all) | Acc z % |
|------------------------|--------|------|----------------|------|-----------|--------|--------|----------|-----------------------|---------|---------|
| Cl ₂ _comb | U1K | mg/l | 0.46 | 0.46 | 0.46 | 0.45 | 0.08 | 16.7 | 30.0 | 21 | 90 |
| | U2K | mg/l | 0.39 | 0.39 | 0.39 | 0.37 | 0.09 | 21.9 | 35.0 | 19 | 95 |
| Cl ₂ _free | U1K | mg/l | 0.67 | 0.67 | 0.67 | 0.67 | 0.09 | 13.4 | 20.0 | 22 | 86 |
| | U2K | mg/l | 0.87 | 0.88 | 0.87 | 0.87 | 0.07 | 7.7 | 15.0 | 20 | 95 |
| Cl ₂ _total | U1K | mg/l | 1.14 | 1.14 | 1.14 | 1.14 | 0.04 | 3.8 | 10.0 | 21 | 95 |
| | U2K | mg/l | 1.27 | 1.27 | 1.27 | 1.26 | 0.05 | 4.2 | 10.0 | 19 | 100 |
| KMnO ₄ | U1P | mg/l | 9.37 | 9.37 | 9.37 | 9.28 | 0.82 | 8.8 | 15.0 | 21 | 81 |
| | U2P | mg/l | 6.26 | 6.23 | 6.26 | 6.32 | 0.59 | 9.5 | 20.0 | 19 | 84 |
| NO ₃ | U1N | mg/l | 8.06 | 8.04 | 8.06 | 8.03 | 0.28 | 3.4 | 10.0 | 18 | 100 |
| | U2N | mg/l | 20.1 | 20.1 | 20.1 | 20.0 | 0.6 | 2.8 | 8.0 | 16 | 100 |
| pH | U1H | | 7.82 | 7.81 | 7.82 | 7.81 | 0.09 | 1.1 | 2.6 | 21 | 100 |
| | U2H | | 6.63 | 6.63 | 6.63 | 6.61 | 0.08 | 1.2 | 3.0 | 19 | 100 |
| Turbidity | U1S | FTU | 0.44 | 0.44 | 0.44 | 0.45 | 0.08 | 17.0 | 30.0 | 23 | 95 |
| | U2S | FTU | 0.68 | 0.68 | 0.68 | 0.68 | 0.09 | 12.5 | 25.0 | 21 | 90 |
| Urea | A1U | mg/l | 0.64 | 0.64 | 0.64 | 0.64 | 0.03 | 4.6 | 10.0 | 18 | 94 |
| | U2U | mg/l | 0.45 | 0.34 | 0.34 | 0.29 | 0.15 | 44.3 | - | 19 | - |
| | U3U | mg/l | 1.13 | 0.83 | 0.83 | 0.74 | 0.33 | 39.3 | - | 18 | - |

Rob. mean: the robust mean, SD rob: the robust standard deviation, SD rob %: the robust standard deviation as percent, 2 × s_{pt} %: the total standard deviation for proficiency assessment at the 95 % confidence interval, Acc z %: the results (%), where $|z| \leq 2$, n(all): the total number of the participants.

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

| Measurand | Sample | Unit | Assigned value | s_w | s_b | s_t | $s_w\%$ | $s_b\%$ | $s_t\%$ | s_b/s_w |
|------------------------|--------|------|----------------|-------|-------|-------|---------|---------|---------|-----------|
| Cl ₂ _comb | U1K | mg/l | 0.46 | 0.015 | 0.070 | 0.071 | 3.3 | 15 | 15 | 4.6 |
| | U2K | mg/l | 0.39 | 0.017 | 0.082 | 0.083 | 4.3 | 21 | 21 | 4.8 |
| Cl ₂ _free | U1K | mg/l | 0.67 | 0.015 | 0.088 | 0.089 | 2.2 | 13 | 13 | 5.9 |
| | U2K | mg/l | 0.87 | 0.022 | 0.061 | 0.065 | 2.5 | 6.9 | 7.4 | 2.7 |
| Cl ₂ _total | U1K | mg/l | 1.14 | 0.020 | 0.046 | 0.050 | 1.7 | 4.0 | 4.3 | 2.3 |
| | U2K | mg/l | 1.27 | 0.019 | 0.053 | 0.056 | 1.5 | 4.1 | 4.4 | 2.7 |
| Turbidity | U1S | FTU | 0.44 | 0.021 | 0.068 | 0.072 | 4.8 | 15 | 16 | 3.2 |
| | U2S | FTU | 0.68 | 0.031 | 0.089 | 0.094 | 4.6 | 13 | 14 | 2.8 |
| Urea | A1U | mg/l | 0.64 | 0.017 | 0.032 | 0.036 | 2.6 | 5.1 | 5.7 | 1.9 |
| | U2U | mg/l | 0.45 | 0.012 | 0.132 | 0.133 | 3.6 | 39 | 39 | 11 |
| | U3U | mg/l | 1.13 | 0.018 | 0.287 | 0.287 | 2.2 | 35 | 35 | 16 |

Ass.val.: assigned value; s_w : repeatability standard error; s_b : between participants standard error; s_t : reproducibility standard error.

In this PT the participants were requested to report duplicate results for chlorines, turbidity and urea measurements. The participants reported the replicates with the exception of one participant (15) for turbidity in the U1S sample. The results of the replicate determinations based on the ANOVA statistical handling are presented in Table 2. The estimation of the robustness of the methods could be done by the ratio s_b/s_w . The ratio s_b/s_w should not be exceeded 3 for robust methods. However, in many cases the robustness exceeded the value 3; varied between 1.9 and 16 (Table 2).

3.2 Analytical methods

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

Chlorine (Cl₂_comb, Cl₂_free, Cl₂_tot)

In the measurements of the total and free chlorine about 94 % of the participants used the colorimetric method based on the standard method EN ISO 7393-2 and three participants used the titrimetric method based on the standard method EN ISO 7393-1. 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 differences between the methods were observed (Appendix 12).

Permanganate index (KMnO₄)

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

Nitrate (NO₃)

Eight of the participants used automatic CFA- or FIA-method based on the standard method EN ISO 13395 (Appendix 12). Depending on the sample four to five participants used IC-method based on the standard method EN ISO 10304. The sulfanilamide spectrophotometric method after hydrazine or Cd/Cu reduction was used by 1-2 participants depending on the sample. One participant used the Hach Lange tube method and one used not specified other method. The statistical comparison between the methods was not carried out due to low number of results. Based on the visual evaluation no difference between the methods was observed (Appendix 12).

pH

About 58 % of the participants measured pH using an electrode for low ionic waters and 38 % of the participants used an universal electrode. One participant used some other electrode in the pH measurements (Appendix 12). In the statistical method comparison no statistically significant differences were observed between the used electrodes.

Turbidity

All participants measured turbidity with an apparatus based on diffused radiation measurement. (Appendix 12).

Urea

The most part of participant used the Koroleff's method, 11-12 participants depending on the sample, in the urea measurements [7]. Depending on the sample 6-7 participants used the enzymatic photometric method (Appendix 12). There was no statistically significant difference between the analytical methods in the measurements of the synthetic sample A1U. In the swimming pool water samples U2U and U3U a clear statistically significant difference between the used analytical methods was observed (Appendices 12 and 13). The mean value for the results of the sample U2U obtained by Koroleff's method was 0.25 mg/l (n=12), while for the enzymatic method it was 0.50 mg/l (n=7). Similarly, the mean value for the results of the sample U3U observed by Koroleff's method was 0.62 mg/l (n=11), while it was for the enzymatic method 1.16 mg/l (n=7). An average urea concentration in the samples U2U and U3U obtained by the Koroleff's method were about 56 % from the calculated values, while the results by the enzymatic photometric method were quite close to the calculated values. This was observed also in the same level as in the previous similar proficiency test SPW 01/2015 [6].

3.3 Uncertainties of the results

All participants reported the expanded uncertainties ($k=2$) with their results for at least some of their results (Table 3, Appendix 14). The lower value of uncertainty for pH and turbidity is probably reported as an absolute value and not as required a relative value (Table 3). The range of the reported uncertainties varied between the measurands and the sample types, and thus the harmonization of the uncertainties estimation should be continued.

Several approaches were used for estimating of measurement uncertainty (Appendix 14). The most used approach was based on using the internal quality control data in the estimation (Appendix 14). Four laboratories used MUKIT measurement uncertainty software for the estimation of their uncertainties [8]. The free software is available in the webpage: www.syke.fi/envical/en. Generally, the used approach for estimating measurement uncertainty did not make definite impact on the uncertainty estimates.

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

| Measurand | Sample | The range of U_i , % |
|------------------------|--------|------------------------|
| Cl ₂ _comb | U1K | 10-35 |
| | U2K | 10-40 |
| Cl ₂ _free | U1K | 10-23 |
| | U2K | 10-23 |
| Cl ₂ _total | U1K | 10-21 |
| | U2K | 10-21 |
| KMnO ₄ | U1P | 5-40 |
| | U2P | 5-54 |
| NO ₃ | U1N | 6-29 |
| | U2N | 6-29 |
| pH | U1H | 0.1-5 |
| | U2H | 0.1-5 |
| Turbidity | U1S | 1-40 |
| | U2S | 1-33 |
| Urea | A1U | 10-40 |
| | U2U | 10-40 |
| | U3U | 10-40 |

4 Evaluation of the results

The evaluation of the participants was based on the z scores, which were calculated using the assigned values and the standard deviation for the performance assessment (Appendix 7). The z scores were interpreted as follows:

| Criteria | Performance |
|---------------|----------------|
| $ z \leq 2$ | Satisfactory |
| $2 < z < 3$ | Questionable |
| $ z \geq 3$ | Unsatisfactory |

In total, 94 % of the results were satisfactory when total deviation of 8 – 35 % and 0.2 pH-units from the assigned values were accepted. All participants used accredited analytical methods at least for a part of the measurands. The summary of the performance evaluation and comparison to the previous performance is presented in Table 3. In the previous similar PT, SPW 01/2015 [6], the performance was satisfactory for 89 % of the all participants. All samples passed the stability test and, thus, no estimation was needed for the effect of increased temperature during the sample transportation.

Table 4. Summary of the performance evaluation in the proficiency test SPW 01/2016.

| Measurand | 2 x s _{pt} % | Satisfactory results, % | Remarks |
|------------------------|-----------------------|-------------------------|--|
| Cl ₂ _comb | 30-35 | 93 | Good performance. Somewhat approximate performance evaluation for the sample U2K. In the SPW 01/2015 the performance was satisfactory for 86 % of the results [6]. |
| Cl ₂ _free | 15-20 | 91 | Good performance. Somewhat approximate performance evaluation for the sample U1K. In the SPW 01/2015 the performance was satisfactory for 75 % of the results [6]. |
| Cl ₂ _total | 10 | 98 | Good performance. In the SPW 01/2015 the performance was satisfactory for 90 % of the results [6]. |
| KMnO ₄ | 15-20 | 83 | In the SPW 01/2015 the performance was satisfactory for 93 % of the results [6]. |
| NO ₃ | 8–10 | 100 | Good performance. In the SPW 01/2015 the performance was satisfactory for 86 % of the results [6]. |
| pH | 2.6–3.0 | 100 | Good performance. In the SPW 01/2015 the performance was satisfactory for 96 % of the results [6]. |
| Turbidity | 25-30 | 93 | Good performance. In the SPW 01/2015 the performance was satisfactory for 94 % of the results [6]. |
| Urea | 10 | 94 | Estimation only for the sample A1U. Good performance. In the SPW 01/2015 the performance was satisfactory for 83 % of the results [6]. |

Evaluation of the urea measurements

The evaluation of the results of urea determination has been performed only for the sample A1U. In the urea samples U2U and U3U a difference was observed between the results obtained with Koroleff's method and enzymatic photometric method. The participants are encouraged to report more results obtained by the enzymatic photometric method for the better method comparison. The evaluation of the urea results was done as in the previous proficiency test SPW 01/2015 [6].

The suitability of the used method for different sample types based on the recovery is shown in Table 5. The recovery was calculated from the mean concentration of different methods (recovery% = 100 × mean of results / calculated value). The recovery percentages are in the same level than in the previous similar proficiency test SPW 01/2015 [6].

The following criteria were used in the evaluation of used urea methods [6]:

| Recovery/sample, % | Assessment |
|---|---|
| 90-110 / A1U 80–120 / U2U, U3U | Suitable for urea measurement of swimming pool waters. |
| <90 tai > 110 / A1U < 80 tai >120 / U2U, U3U | Not suitable for urea measurement of swimming pool waters. There is need of method validation. |

Table 5. Assessment of the analytical methods used in urea determination.

| Method | Sample | Recovery, % | Assessment |
|------------------------------|--------|-------------|--|
| Koroleff's method | A1U | 100 | Use of the method in measurements of swimming pool waters requires method validation, in where the effect of matrix will be noticed. |
| | U2U | 56 | |
| | U3U | 55 | |
| Enzymatic photometric method | A1U | 102 | Based on the PT the method is suitable for urea measurements of swimming pool waters. |
| | U2U | 111 | |
| | U3U | 103 | |

5 Summary

Profest SYKE carried out the proficiency test for analysis of combined chlorine, free chlorine, total chlorine, permanganate index, nitrate, pH, turbidity and urea from swimming pool water in February 2016 (SPW 01/2016). In total, 23 participants joined in this proficiency test.

The evaluation of the performance was based on the z scores, which were calculated using the assigned value and standard deviation for proficiency assessment at 95 % confidence level. In this proficiency test 94 % of the data was regarded to be satisfactory when the results were accepted to deviate 8 to 35 % and 0.2 pH-unit from the assigned value. The calculated concentration was used as the assigned value for urea determination and the robust mean of the reported results for the other determinations.

Noticeable is that there is clear difference between the urea results of the swimming pool water samples (U2U and U3U) measured using the Koroleff's method and the enzymatic photometric method. An average urea concentration in the samples U2U and U3U obtained by the Koroleff's method was about 56 % from the calculated values, while the results by the enzymatic photometric method were quite close to the calculated values. Due this difference the urine results for the samples U2U and U3U were not evaluated. It is recommended to validate the Koroleff's method for the urea determination of the swimming pool waters.

6 Summary in Finnish

Proftest SYKE järjesti helmikuussa 2016 pätevyyskokeen uima-allasvesiä analysoiville laboratorioille (SPW 01/2016). Pätevyyskokeessa testattiin allasvesien kloori-, KMnO_4 -, NO_3 -, pH-, sameus- ja ureamäärityksiä. Ureamääritystä varten toimitettiin myös kaksi synteettistä näytettä. Pätevyyskokeeseen osallistui yhteensä 23 laboratoriota.

Pätevyyden arvioimisessa käytettiin z-arvoa ja sitä laskettaessa tulokselle sallittiin pH-määrityksessä 0,2 pH-yksikön ja muissa määrityksissä 8–35 %:n poikkeama vertailuarvosta. Määrityksen vertailuarvona käytettiin synteettisen näytteen ureamäärityksessä laskennallista arvoa ja muissa määrityksissä robustia keskiarvoa. Hyväksyttäviä tuloksia oli kokonaisuudessaan 94 %.

Ureatuloksista arvioitiin vain synteettisen näytteen A1U tulokset. Uima-allasvesinäytteiden U2U ja U3U ureatuloksia ei arvioitu, koska suurin osa osallistujista käytti Koroleffin menetelmään perustuvaa määritystä ja tällä menetelmällä saadut tulokset poikkesivat huomattavasti laskennallisista pitoisuuksista. Koroleffin menetelmällä saadut tulokset olivat keskimäärin ainoastaan 56 % laskennallisista ureapitoisuuksista. Käytettäessä uima-allasvesien ureapitoisuuden määrittämiseen Koroleffin menetelmää tulisi näytetyypin vaikutus tuloksiin selvittää paremmin.

REFERENCES

1. SFS-EN ISO 17043, 2010. Conformity assessment – General requirements for Proficiency Testing.
2. ISO 13528, 2015. Statistical methods for use in proficiency testing by interlaboratory comparisons.
3. Thompson, M., Ellison, S. L. R., Wood, R., 2006. The International Harmonized Protocol for the Proficiency Testing of Analytical Chemistry laboratories (IUPAC Technical report). Pure Appl. Chem. 78: 145-196, www.iupac.org.
4. STM asetus 315/2002 Uimahallien ja kylpylöiden allasvesien laatuvaatimuksia ja valvontatutkimuksia (in Finnish).
5. Profitest SYKE Guide for laboratories: www.syke.fi/proftest/en → Current proficiency tests www.syke.fi/download/noname/%7B3FFB2F05-9363-4208-9265-1E2CE936D48C%7D/39886.
6. Leivuori, M., Tyrväinen, S., Näykki, T., Björklöf, K., Koivikko, R., Tervonen, K., Lanteri, S. ja Ilmakunnas, M., 2015. Laboratorioiden välinen pätevyyskoe 1/2015, Uimaallasvesivertailu. Suomen ympäristökeskuksen raportteja 12/2015, 62 s, Helsinki. <http://hdl.handle.net/10138/154078>.
7. Koroleff, F. 1983. Determination of urea. In Methods of Seawater Analysis (Grasshoff, K., Erhardt, M. & Kremling K., eds.). Verlag Chemie, Weinheim, pp. 158-162.
8. Näykki, T., Virtanen, A. and Leito, I., 2012. Software support for the Nordtest method of measurement uncertainty evaluation. Accred. Qual. Assur. 17: 603-612. *MUKit website: www.syke.fi/envical*.
9. Magnusson, B. Näykki, T., Hovind, H. and Krysell, M., 2012. Handbook for Calculation of Measurement Uncertainty in Environmental Laboratories. NT Technical Report 537. Nordtest.
10. Ellison, S., L., R. and Williams, A. (Eds). (2012) Eurachem/CITAC guide: Quantifying Uncertainty in Analytical Measurement, Third edition, ISBN 978-0-948926-30-3.
11. ISO/IEC Guide 98-3:2008. Uncertainty of measurement -- Part 3: Guide to the expression of uncertainty in measurement (GUM: 1995).

APPENDIX 1: Participants in the proficiency test

| Country | Participants |
|-------------|---|
| Finland | Ahma Ympäristö Oy, Rovaniemi Ahma ympäristö, Seinäjoki BotniaLab Oy, Vaasa Eurofins Scientific Finland Oy Kokkolan yksikkö HaKaLab Oy, Haapavesi KCL Kymen Laboratorio Oy, Kuusankoski Kokemäenjoen vesistön vesiensuojeluyhdistys ry, Tampere Lounais-Suomen vesi- ja ympäristötutkimus Oy, Turku Metropolilab Oy, Helsinki Nab Labs Oy / Ambiotica, Jyväskylä Oulun kaupungin elintarvike- ja ympäristölaboratorio Oy Ramboll Finland Oy, Ramboll Analytics, Lahti Saimaan Vesi- ja Ympäristötutkimus Oy, Lappeenranta Savo-Karjalan Ympäristötutkimus Oy, Joensuu Savo-Karjalan Ympäristötutkimus Oy, Kajaani Savo-Karjalan Ympäristötutkimus Oy, Kuopio SeiLab Oy, Seinäjoki SYKE Oulun toimipaikka VITA-Terveyspalvelut Oy, VITA Laboratorio, Helsinki ÅMHH laboratoriet, Jomala, Åland |
| Portugal | Aguas do Algarve, S.A. |
| Sweden | Eurofins Environment testing Sweden AB, Lidköping |
| Switzerland | Service de la securite alimentaire et des affaires veterinaires |

APPENDIX 2: Preparation of the samples

| Measurand/Sample | | U1K | U2K | |
|-----------------------|----------------------------------|--|--------|--------|
| Cl ₂ _comb | Initial concentration, mg/l | 0.22 | 0.22 | |
| | Addition, mg/l | C ₇ H ₇ ClNaNO ₂ S* 3H ₂ O 0.41 | 0.29 | |
| | Assigned value, mg/l | 0.46 | 0.39 | |
| Cl ₂ _free | Initial concentration, mg/l | < 0.10 | < 0.10 | |
| | Addition, mg/l | NaClO 0.79 | 1.06 | |
| | Assigned value, mg/l | 0.67 | 0.87 | |
| Cl ₂ _tot | Initial concentration, mg/l | 0.22 | 0.22 | |
| | Addition, mg/l | 1.20 | 1.35 | |
| | Assigned value, mg/l | 1.14 | 1.27 | |
| | | U1H | U2H | |
| pH | Initial concentration pH-unit | Na ₂ HPO ₄ /KH ₂ PO ₄ 7.32 | 6.4 | |
| | Assigned value pH-yksikkö | 7.82 | 6.63 | |
| | | U1S | U2S | |
| Turbidity | Initial concentration, FTU | 0.17 | 0.17 | |
| | Addition, FTU | HACH Formazin 0.4 | 0.64 | |
| | Assigned value, FTU | 0.44 | 0.68 | |
| | | U1N | U2N | |
| NO ₃ | Initial concentration, mg/l | 20.4 | 20.4 | |
| | Dilution | 1:4 | - | |
| | Assigned value, mg/l | 8.06 | 20.1 | |
| | | U1P | U2P | |
| KMnO ₄ | Initial concentration, mg/l | 4.56 | 4.56 | |
| | Addition, mg/l | C ₇ H ₆ O ₃ 6.42 | 2.97 | |
| | Assigned value, mg/l | 9.37 | 6.26 | |
| | | A1U | U2U | U3U |
| Urea | Initial concentration, mg/l | - | < 0.10 | < 0.10 |
| | Addition, mg/l | CO(NH ₂) ₂ 0.61 | 0.43 | 1.09 |
| | Assigned value, mg/l | 0.64 | 0.45 | 1.13 |

APPENDIX 3: Homogeneity of the samples

Homogeneity was tested from duplicate measurements from six samples of each sample types.

Criteria for homogeneity:

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

- s_{pt} = standard deviation for testing of homogeneity
 s_a = analytical deviation, standard deviation of the results within sub samples
 s_{sam} = between-sample deviation, standard deviation of the results between sub samples

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

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

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

| Measurand/Sample | Concentration mg/l or FTU | S _{pt} % | S _{pt} | S _a | S _a /S _{pt} | S _a /S _{pt} <0,5? | S _{sam} | S _{sam} ² | c | S _{sam} ² <c? |
|------------------------|------------------------------|-------------------|-----------------|----------------|---------------------------------|---------------------------------------|------------------|-------------------------------|--------|-----------------------------------|
| KMnO ₄ /U1P | 9.91 | 7.5 | 0.74 | 0.23 | 0.31 | Yes | 0.00 | 0.00 | 0.20 | Yes |
| KMnO ₄ /U2P | 7.04 | 10 | 0.70 | 0.17 | 0.25 | Yes | 0.00 | 0.00 | 0.15 | Yes |
| Turbidity/U1S | 0.49 | 15 | 0.07 | 0.02 | 0.28 | Yes | 0.007 | 0.00005 | 0.002 | Yes |
| Turbidity/U2S | 0.78 | 12.5 | 0.10 | 0.03 | 0.30 | Yes | 0.00 | 0.00 | 0.003 | Yes |
| NO ₃ /U1N | 7.51 | 5 | 0.38 | 0.03 | 0.07 | Yes | 0.04 | 0.001 | 0.03 | Yes |
| NO ₃ /U2N | 18.6 | 4 | 0.74 | 0.03 | 0.04 | Yes | 0.09 | 0.008 | 0.11 | Yes |
| Urea/U2U | 0.48 | 5 | 0.02 | 0.004 | 0.18 | Yes | 0.004 | 0.00002 | 0.0002 | Yes |
| Urea/U3U | 1.12 | 5 | 0.06 | 0.02 | 0.28 | Yes | 0.00 | 0.00 | 0.001 | Yes |

pH:

Homogeneity was tested from measurement from ten samples of each sample types.

Criterion for homogeneity

$$s_{sam} < 0.5 \times s_{pt}$$

| Measurand/Sample | Concentration pH-unit | S _{pt} | 0,5 · S _{pt} | Standard deviation between samples, S _{sam} | S _{sam} < 0.5 · S _{pt} ? |
|------------------|--------------------------|-----------------|-----------------------|---|--|
| pH/ U1H | 7.87 | 0.10 | 0.05 | 0.02 | Yes |
| pH/ U2H | 6.64 | 0.10 | 0.05 | 0.02 | Yes |

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

APPENDIX 4: Stability of the samples

The samples were delivered 2 February 2016 and they arrived to the participants mainly on the following day. The samples were requested to be measured on 5 February 2016. Stability of pH, Cl₂_free, Cl₂_comb, Cl₂_tot and urea was tested by analyzing the samples stored at the temperatures 4 and 20 °C.

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

D = |the difference of results measured from the samples stored at the temperatures 4 °C and 20 °C|

s_{pt} = standard deviation for proficiency assessment

pH

| Sample | Result | | | Sample | Result | | |
|---------------|---------------------------------------|-----------------|----------------|--------------------------|--------|-----------------|----------------|
| Date | 2.2. | 4.2. (20 °C) | 4.2. (4 °C) | Date | 2.2. | 4.2. (20 °C) | 4.2. (4 °C) |
| U1H | 7.854 | 7.752 | 7.814 | U2H | 6.584 | 6.650 | 6.641 |
| D | 0.062 | | | 0.009 | | | |
| 0.3× s_{pt} | 0.03 | | | 0.03 | | | |
| | D < 0.3 × s_{pt} ? No ¹⁾ | | | D < 0.3 × s_{pt} ? Yes | | | |

Cl₂_free

| Sample | Result, mg/l | | | Sample | Result, mg/l | | |
|---------------|--------------------------|-----------------|----------------|---------------------------------------|--------------|-----------------|----------------|
| Date | 2.2. | 4.2. (20 °C) | 4.2. (4 °C) | Date | 2.2. | 4.2. (20 °C) | 4.2. (4 °C) |
| U1K | 0.694 | 0.668 | 0.680 | U2K | 0.876 | 0.886 | 0.924 |
| D | 0.012 | | | 0.038 | | | |
| 0.3× s_{pt} | 0.020 | | | 0.020 | | | |
| | D < 0.3 × s_{pt} ? Yes | | | D < 0.3 × s_{pt} ? No ¹⁾ | | | |

Cl₂_comb

| Sample | Result, mg/l | | | Sample | Result, mg/l | | |
|---------------|--------------------------|-----------------|----------------|--------------------------|--------------|-----------------|----------------|
| Date | 2.2. | 4.2. (20 °C) | 4.2. (4 °C) | Date | 2.2. | 4.2. (20 °C) | 4.2. (4 °C) |
| U1K | 0.476 | 0.480 | 0.473 | U2K | 0.387 | 0.370 | 0.368 |
| D | 0.007 | | | 0.002 | | | |
| 0.3× s_{pt} | 0.021 | | | 0.020 | | | |
| | D < 0.3 × s_{pt} ? Yes | | | D < 0.3 × s_{pt} ? Yes | | | |

Cl₂_tot

| Sample | Result, mg/l | | | Sample | Result, mg/l | | |
|---------------|--------------------------|-----------------|----------------|---------------------------------------|--------------|-----------------|----------------|
| Date | 2.2. | 4.2. (20 °C) | 4.2. (4 °C) | Date | 2.2. | 4.2. (20 °C) | 4.2. (4 °C) |
| U1K | 1.17 | 1.15 | 1.15 | U2K | 1.26 | 1.26 | 1.30 |
| D | 0.002 | | | 0.04 | | | |
| 0.3× s_{pt} | 0.02 | | | 0.02 | | | |
| | D < 0.3 × s_{pt} ? Yes | | | D < 0.3 × s_{pt} ? No ¹⁾ | | | |

Urea

| Sample | Result, mg/l | | | Sample | Result, mg/l | | | Sample | Result, mg/l | | |
|---------------|--------------------------|-----------------|----------------|--------------------------|--------------|-----------------|--|--------|--------------|-----------------|----------------|
| Date | 2.2. | 4.2. (20 °C) | 4.2. (4 °C) | Date | 2.2. | 4.2. (20 °C) | 4.2. (4 °C) | Date | 2.2. | 4.2. (20 °C) | 4.2. (4 °C) |
| A1U | 0.635 | 0.562 | 0.556 | U2U | 0.510 | 0.459 | 0.456 | U3U | 1.20 | 1.11 | 1.09 |
| D | 0.006 | | | 0.003 | | | 0.02 | | | | |
| 0.3× s_{pt} | 0.010 | | | 0.007 | | | 0.02 | | | | |
| | D < 0.3 × s_{pt} ? Yes | | | D < 0.3 × s_{pt} ? Yes | | | D < 0.3 × s_{pt} ? Yes ¹⁾ | | | | |

¹⁾ The difference is within the analytic error

Conclusion: The criteria for stability mainly fulfilled. For pH, Cl₂_free, Cl₂_tot and urea the noticed variation of results are within the analytical error. Thus the samples could be regarded as homogenous.

APPENDIX 5: Feedback from the proficiency test

FEEDBACK FROM THE PARTICIPANTS

| Participant | Comments on technical execution | Action / Proftest |
|-------------|--|---|
| 6,11 | Participants received the samples within two days after the target delivery day. | The used distributor (Posti) did not deliver the samples on time. In future other distributor will be used. |
| 19 | The bottle of addition solution for chlorine sample was not enough tightly closed. | In future, the provider will be more careful when tightening the sample bottles |

| Participant | Comments to the results | Action / Proftest |
|-------------|---|--|
| 19 | Analytical problems in the measurement of urea from the sample A1U (on date 4.2.-16). | All comments to the results are warmly welcomed. |

FEEDBACK TO THE PARTICIPANTS

| Participant | Comments |
|--------------------------------------|--|
| 15 | The participant reported only one result for turbidity in the sample U1S, though replicate results were requested. These results were not included in the calculation of assigned values. The provider recommends the participants to follow the given guidelines. |
| Participants using Koroleff's method | It is encouraged to validate the Koroleff's method for the urea determination of the swimming pool waters. |
| All | The participants are encouraged to report more results obtained by the enzymatic photometric method for the better method comparison with the Koroleff's method. |

APPENDIX 6: Evaluation of the assigned values and their uncertainties

| Measurand | Sample | Unit | Assigned value | U_{pt} | $U_{pt}, \%$ | Evaluation method of assigned value | u_{pt}/s_{pt} |
|------------------------|--------|------|----------------|----------|--------------|-------------------------------------|-----------------|
| Cl ₂ _comb | U1K | mg/l | 0.46 | 0.04 | 9.6 | Robust mean | 0.32 |
| | U2K | mg/l | 0.39 | 0.05 | 13.0 | Robust mean | 0.37 |
| Cl ₂ _free | U1K | mg/l | 0.67 | 0.05 | 7.1 | Robust mean | 0.36 |
| | U2K | mg/l | 0.87 | 0.04 | 4.3 | Robust mean | 0.29 |
| Cl ₂ _total | U1K | mg/l | 1.14 | 0.02 | 2.1 | Robust mean | 0.21 |
| | U2K | mg/l | 1.27 | 0.03 | 2.4 | Robust mean | 0.24 |
| KMnO ₄ | U1P | mg/l | 9.37 | 0.47 | 5.0 | Robust mean | 0.33 |
| | U2P | mg/l | 6.26 | 0.36 | 5.7 | Robust mean | 0.29 |
| NO ₃ | U1N | mg/l | 8.06 | 0.16 | 2.0 | Robust mean | 0.20 |
| | U2N | mg/l | 20.1 | 0.4 | 1.8 | Robust mean | 0.23 |
| pH | U1H | | 7.82 | 0.05 | 0.6 | Robust mean | 0.23 |
| | U2H | | 6.63 | 0.05 | 0.7 | Robust mean | 0.23 |
| Turbidity | U1S | FTU | 0.44 | 0.04 | 9.1 | Robust mean | 0.30 |
| | U2S | FTU | 0.68 | 0.05 | 6.8 | Robust mean | 0.27 |
| Urea | A1U | mg/l | 0.64 | 0.00 | 0.6 | Calculated value | 0.06 |
| | U2U | mg/l | 0.45 | 0.00 | 0.6 | Calculated value | |
| | U3U | mg/l | 1.13 | 0.01 | 0.6 | Calculated value | |

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} = target value of the standard deviation for proficiency assessment

u_{pt} = standard uncertainty of the assigned value

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

APPENDIX 7: Terms in the results tables

Results of each participant

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

Summary on the z scores

S – satisfactory ($-2 \leq z \leq 2$)

Q – questionable ($2 < z < 3$), positive error, the result deviates more than $2 \times s_{pt}$ from the assigned value

q – questionable ($-3 < z < -2$), negative error, the result deviates more than $2 \times s_{pt}$ from the assigned value

U – unsatisfactory ($z \geq 3$), positive error, the result deviates more than $3 \times s_{pt}$ from the assigned value

u – unsatisfactory ($z \leq -3$), negative error, the result deviates more than $3 \times s_{pt}$ from the assigned value

Robust analysis

The items of data are sorted into increasing order, $x_1, x_2, x_i, \dots, x_p$.

Initial values for x^* and s^* are calculated as:

$$x^* = \text{median of } x_i \text{ (} i = 1, 2, \dots, p \text{)}$$

$$s^* = 1,483 \times \text{median of } |x_i - x^*| \text{ (} i = 1, 2, \dots, p \text{)}$$

The mean x^* and s^* are updated as follows:

Calculate $\varphi = 1.5 \times s^*$. A new value is then calculated for each result x_i ($i = 1, 2 \dots p$):

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

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

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

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















The robust estimates x^* and s^* can be derived by an iterative calculation, i.e. by updating the values of x^* and s^* several times, until the process convergences [2].






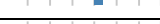







APPENDIX 8: Results of each participant
















| Participant 1 | | | | | | | | | | | | |
|------------------------|------|--------|--|---------|----------------|---------------------|----------------------|------|------|------|------|----------|
| Measurand | Unit | Sample | | z score | Assigned value | 2*s _{pt} % | Participant's result | Md | Mean | SD | SD% | n (stat) |
| Cl ₂ _comb | mg/l | U1K | | -0.64 | 0.46 | 30 | 0.42 | 0.45 | 0.46 | 0.07 | 15.2 | 19 |
| | mg/l | U2K | | -0.72 | 0.39 | 35 | 0.34 | 0.37 | 0.39 | 0.08 | 21.0 | 19 |
| Cl ₂ _free | mg/l | U1K | | 0.66 | 0.67 | 20 | 0.71 | 0.67 | 0.67 | 0.09 | 13.2 | 22 |
| | mg/l | U2K | | 0.31 | 0.87 | 15 | 0.89 | 0.87 | 0.88 | 0.06 | 7.2 | 20 |
| Cl ₂ _total | mg/l | U1K | | -0.18 | 1.14 | 10 | 1.13 | 1.14 | 1.14 | 0.04 | 3.3 | 21 |
| | mg/l | U2K | | -0.63 | 1.27 | 10 | 1.23 | 1.26 | 1.27 | 0.05 | 4.3 | 19 |
| KMnO ₄ | mg/l | U1P | | 2.60 | 9.37 | 15 | 11.20 | 9.28 | 9.37 | 0.85 | 9.1 | 19 |
| | mg/l | U2P | | 3.93 | 6.26 | 20 | 8.72 | 6.32 | 6.23 | 0.57 | 9.1 | 17 |
| NO ₃ | mg/l | U1N | | 0.30 | 8.06 | 10 | 8.18 | 8.03 | 8.04 | 0.31 | 3.9 | 18 |
| | mg/l | U2N | | 0.62 | 20.1 | 8 | 20.6 | 20.0 | 20.1 | 0.5 | 2.7 | 16 |
| pH | | U1H | | 1.18 | 7.82 | 2,6 | 7.94 | 7.81 | 7.81 | 0.08 | 1.1 | 21 |
| | | U2H | | 0.70 | 6.63 | 3 | 6.70 | 6.61 | 6.63 | 0.08 | 1.2 | 19 |
| Turbidity | FTU | U1S | | 1.31 | 0.44 | 30 | 0.53 | 0.45 | 0.44 | 0.07 | 15.8 | 22 |
| | FTU | U2S | | 1.05 | 0.68 | 25 | 0.77 | 0.68 | 0.68 | 0.09 | 13.5 | 21 |
| Urea | mg/l | A1U | | -0.52 | 0.64 | 10 | 0.62 | 0.64 | 0.64 | 0.02 | 3.7 | 17 |
| | mg/l | U2U | | | 0.45 | | 0.17 | 0.29 | 0.34 | 0.13 | 39.3 | 19 |
| | mg/l | U3U | | | 1.13 | | 0.46 | 0.74 | 0.83 | 0.29 | 34.7 | 18 |

| Participant 2 | | | | | | | | | | | | |
|------------------------|------|--------|--|---------|----------------|---------------------|----------------------|------|------|------|------|----------|
| Measurand | Unit | Sample | | z score | Assigned value | 2*s _{pt} % | Participant's result | Md | Mean | SD | SD% | n (stat) |
| Cl ₂ _comb | mg/l | U1K | | -0.17 | 0.46 | 30 | 0.45 | 0.45 | 0.46 | 0.07 | 15.2 | 19 |
| | mg/l | U2K | | -0.34 | 0.39 | 35 | 0.37 | 0.37 | 0.39 | 0.08 | 21.0 | 19 |
| Cl ₂ _free | mg/l | U1K | | 0.55 | 0.67 | 20 | 0.71 | 0.67 | 0.67 | 0.09 | 13.2 | 22 |
| | mg/l | U2K | | 0.82 | 0.87 | 15 | 0.92 | 0.87 | 0.88 | 0.06 | 7.2 | 20 |
| Cl ₂ _total | mg/l | U1K | | 0.26 | 1.14 | 10 | 1.16 | 1.14 | 1.14 | 0.04 | 3.3 | 21 |
| | mg/l | U2K | | 0.31 | 1.27 | 10 | 1.29 | 1.26 | 1.27 | 0.05 | 4.3 | 19 |
| KMnO ₄ | mg/l | U1P | | -0.27 | 9.37 | 15 | 9.18 | 9.28 | 9.37 | 0.85 | 9.1 | 19 |
| | mg/l | U2P | | -0.64 | 6.26 | 20 | 5.86 | 6.32 | 6.23 | 0.57 | 9.1 | 17 |
| NO ₃ | mg/l | U1N | | -1.41 | 8.06 | 10 | 7.49 | 8.03 | 8.04 | 0.31 | 3.9 | 18 |
| | mg/l | U2N | | -0.25 | 20.1 | 8 | 19.9 | 20.0 | 20.1 | 0.5 | 2.7 | 16 |
| pH | | U1H | | -0.20 | 7.82 | 2,6 | 7.80 | 7.81 | 7.81 | 0.08 | 1.1 | 21 |
| | | U2H | | -0.30 | 6.63 | 3 | 6.60 | 6.61 | 6.63 | 0.08 | 1.2 | 19 |
| Turbidity | FTU | U1S | | 0.76 | 0.44 | 30 | 0.49 | 0.45 | 0.44 | 0.07 | 15.8 | 22 |
| | FTU | U2S | | 0.71 | 0.68 | 25 | 0.74 | 0.68 | 0.68 | 0.09 | 13.5 | 21 |
| Urea | mg/l | A1U | | 1.25 | 0.64 | 10 | 0.68 | 0.64 | 0.64 | 0.02 | 3.7 | 17 |
| | mg/l | U2U | | | 0.45 | | 0.16 | 0.29 | 0.34 | 0.13 | 39.3 | 19 |
| | mg/l | U3U | | | 1.13 | | 0.38 | 0.74 | 0.83 | 0.29 | 34.7 | 18 |

| Participant 3 | | | | | | | | | | | | |
|-----------------------|------|--------|--|---------|----------------|---------------------|----------------------|------|------|------|------|----------|
| Measurand | Unit | Sample | | z score | Assigned value | 2*s _{pt} % | Participant's result | Md | Mean | SD | SD% | n (stat) |
| Cl ₂ _comb | mg/l | U1K | | -0.14 | 0.46 | 30 | 0.45 | 0.45 | 0.46 | 0.07 | 15.2 | 19 |
| | mg/l | U2K | | 0.66 | 0.39 | 35 | 0.44 | 0.37 | 0.39 | 0.08 | 21.0 | 19 |
| Cl ₂ _free | mg/l | U1K | | 0.97 | 0.67 | 20 | 0.74 | 0.67 | 0.67 | 0.09 | 13.2 | 22 |
| | mg/l | U2K | | -0.77 | 0.87 | 15 | 0.82 | 0.87 | 0.88 | 0.06 | 7.2 | 20 |

| Participant 3 | | | | | | | | | | | | |
|------------------------|------|--------|---|---------|----------------|---------------------|----------------------|------|------|------|------|----------|
| Measurand | Unit | Sample |  | z score | Assigned value | 2*s _{pt} % | Participant's result | Md | Mean | SD | SD% | n (stat) |
| Cl ₂ _total | mg/l | U1K |  | 0.79 | 1.14 | 10 | 1.19 | 1.14 | 1.14 | 0.04 | 3.3 | 21 |
| | mg/l | U2K |  | -0.24 | 1.27 | 10 | 1.26 | 1.26 | 1.27 | 0.05 | 4.3 | 19 |
| KMnO ₄ | mg/l | U1P |  | -0.17 | 9.37 | 15 | 9.25 | 9.28 | 9.37 | 0.85 | 9.1 | 19 |
| | mg/l | U2P |  | 0.44 | 6.26 | 20 | 6.54 | 6.32 | 6.23 | 0.57 | 9.1 | 17 |
| NO ₃ | mg/l | U1N |  | -0.65 | 8.06 | 10 | 7.80 | 8.03 | 8.04 | 0.31 | 3.9 | 18 |
| | mg/l | U2N |  | 0.97 | 20.1 | 8 | 20.9 | 20.0 | 20.1 | 0.5 | 2.7 | 16 |
| pH | | U1H |  | 1.18 | 7.82 | 2,6 | 7.94 | 7.81 | 7.81 | 0.08 | 1.1 | 21 |
| | | U2H |  | -0.50 | 6.63 | 3 | 6.58 | 6.61 | 6.63 | 0.08 | 1.2 | 19 |
| Turbidity | FTU | U1S |  | 0.61 | 0.44 | 30 | 0.48 | 0.45 | 0.44 | 0.07 | 15.8 | 22 |
| | FTU | U2S |  | 1.35 | 0.68 | 25 | 0.80 | 0.68 | 0.68 | 0.09 | 13.5 | 21 |
| Urea | mg/l | A1U |  | 0.23 | 0.64 | 10 | 0.65 | 0.64 | 0.64 | 0.02 | 3.7 | 17 |
| | mg/l | U2U |  | 0.45 | 0.45 | | 0.50 | 0.29 | 0.34 | 0.13 | 39.3 | 19 |
| | mg/l | U3U |  | 1.13 | 1.13 | | 1.18 | 0.74 | 0.83 | 0.29 | 34.7 | 18 |

| Participant 4 | | | | | | | | | | | | |
|------------------------|------|--------|---|---------|----------------|---------------------|----------------------|------|------|------|------|----------|
| Measurand | Unit | Sample |  | z score | Assigned value | 2*s _{pt} % | Participant's result | Md | Mean | SD | SD% | n (stat) |
| Cl ₂ _comb | mg/l | U1K |  | -0.51 | 0.46 | 30 | 0.43 | 0.45 | 0.46 | 0.07 | 15.2 | 19 |
| | mg/l | U2K |  | -0.97 | 0.39 | 35 | 0.32 | 0.37 | 0.39 | 0.08 | 21.0 | 19 |
| Cl ₂ _free | mg/l | U1K |  | 0.00 | 0.67 | 20 | 0.67 | 0.67 | 0.67 | 0.09 | 13.2 | 22 |
| | mg/l | U2K |  | 0.41 | 0.87 | 15 | 0.90 | 0.87 | 0.88 | 0.06 | 7.2 | 20 |
| Cl ₂ _total | mg/l | U1K |  | -0.79 | 1.14 | 10 | 1.10 | 1.14 | 1.14 | 0.04 | 3.3 | 21 |
| | mg/l | U2K |  | -0.79 | 1.27 | 10 | 1.22 | 1.26 | 1.27 | 0.05 | 4.3 | 19 |
| KMnO ₄ | mg/l | U1P |  | -0.30 | 9.37 | 15 | 9.16 | 9.28 | 9.37 | 0.85 | 9.1 | 19 |
| | mg/l | U2P |  | 0.10 | 6.26 | 20 | 6.32 | 6.32 | 6.23 | 0.57 | 9.1 | 17 |
| pH | | U1H |  | -0.98 | 7.82 | 2,6 | 7.72 | 7.81 | 7.81 | 0.08 | 1.1 | 21 |
| | | U2H |  | 0.10 | 6.63 | 3 | 6.64 | 6.61 | 6.63 | 0.08 | 1.2 | 19 |
| Turbidity | FTU | U1S |  | -0.83 | 0.44 | 30 | 0.39 | 0.45 | 0.44 | 0.07 | 15.8 | 22 |
| | FTU | U2S |  | 0.47 | 0.68 | 25 | 0.72 | 0.68 | 0.68 | 0.09 | 13.5 | 21 |

| Participant 5 | | | | | | | | | | | | |
|------------------------|------|--------|---|---------|----------------|---------------------|----------------------|------|------|------|------|----------|
| Measurand | Unit | Sample |  | z score | Assigned value | 2*s _{pt} % | Participant's result | Md | Mean | SD | SD% | n (stat) |
| Cl ₂ _comb | mg/l | U1K |  | -1.59 | 0.46 | 30 | 0.35 | 0.45 | 0.46 | 0.07 | 15.2 | 19 |
| | mg/l | U2K |  | -1.76 | 0.39 | 35 | 0.27 | 0.37 | 0.39 | 0.08 | 21.0 | 19 |
| Cl ₂ _free | mg/l | U1K |  | 1.79 | 0.67 | 20 | 0.79 | 0.67 | 0.67 | 0.09 | 13.2 | 22 |
| | mg/l | U2K |  | 2.15 | 0.87 | 15 | 1.01 | 0.87 | 0.88 | 0.06 | 7.2 | 20 |
| Cl ₂ _total | mg/l | U1K |  | 0.00 | 1.14 | 10 | 1.14 | 1.14 | 1.14 | 0.04 | 3.3 | 21 |
| | mg/l | U2K |  | 0.16 | 1.27 | 10 | 1.28 | 1.26 | 1.27 | 0.05 | 4.3 | 19 |
| KMnO ₄ | mg/l | U1P |  | -1.52 | 9.37 | 15 | 8.30 | 9.28 | 9.37 | 0.85 | 9.1 | 19 |
| | mg/l | U2P |  | 1.34 | 6.26 | 20 | 7.10 | 6.32 | 6.23 | 0.57 | 9.1 | 17 |
| NO ₃ | mg/l | U1N |  | -0.15 | 8.06 | 10 | 8.00 | 8.03 | 8.04 | 0.31 | 3.9 | 18 |
| | mg/l | U2N |  | -1.37 | 20.1 | 8 | 19.0 | 20.0 | 20.1 | 0.5 | 2.7 | 16 |
| pH | | U1H |  | -1.08 | 7.82 | 2,6 | 7.71 | 7.81 | 7.81 | 0.08 | 1.1 | 21 |
| | | U2H |  | 1.11 | 6.63 | 3 | 6.74 | 6.61 | 6.63 | 0.08 | 1.2 | 19 |
| Turbidity | FTU | U1S |  | 1.14 | 0.44 | 30 | 0.52 | 0.45 | 0.44 | 0.07 | 15.8 | 22 |
| | FTU | U2S |  | -0.47 | 0.68 | 25 | 0.64 | 0.68 | 0.68 | 0.09 | 13.5 | 21 |

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| Participant 6 | | | | | | | | | | | | |
|------------------------|------|--------|--|---------|----------------|----------------------|----------------------|------|------|------|------|----------|
| Measurand | Unit | Sample | | z score | Assigned value | 2* _{Sp} t % | Participant's result | Md | Mean | SD | SD% | n (stat) |
| Cl ₂ _comb | mg/l | U1K | | 1.23 | 0.46 | 30 | 0.55 | 0.45 | 0.46 | 0.07 | 15.2 | 19 |
| Cl ₂ _free | mg/l | U1K | | -1.87 | 0.67 | 20 | 0.55 | 0.67 | 0.67 | 0.09 | 13.2 | 22 |
| Cl ₂ _total | mg/l | U1K | | -0.88 | 1.14 | 10 | 1.09 | 1.14 | 1.14 | 0.04 | 3.3 | 21 |
| KMnO ₄ | mg/l | U1P | | -11.14 | 9.37 | 15 | 1.54 | 9.28 | 9.37 | 0.85 | 9.1 | 19 |
| NO ₃ | mg/l | U1N | | 1.29 | 8.06 | 10 | 8.58 | 8.03 | 8.04 | 0.31 | 3.9 | 18 |
| pH | | U1H | | 0.49 | 7.82 | 2,6 | 7.87 | 7.81 | 7.81 | 0.08 | 1.1 | 21 |
| Turbidity | FTU | U1S | | -1.59 | 0.44 | 30 | 0.34 | 0.45 | 0.44 | 0.07 | 15.8 | 22 |

| Participant 7 | | | | | | | | | | | | |
|------------------------|------|--------|--|---------|----------------|----------------------|----------------------|------|------|------|------|----------|
| Measurand | Unit | Sample | | z score | Assigned value | 2* _{Sp} t % | Participant's result | Md | Mean | SD | SD% | n (stat) |
| Cl ₂ _comb | mg/l | U1K | | 1.96 | 0.46 | 30 | 0.60 | 0.45 | 0.46 | 0.07 | 15.2 | 19 |
| | mg/l | U2K | | 0.29 | 0.39 | 35 | 0.41 | 0.37 | 0.39 | 0.08 | 21.0 | 19 |
| Cl ₂ _free | mg/l | U1K | | -1.72 | 0.67 | 20 | 0.56 | 0.67 | 0.67 | 0.09 | 13.2 | 22 |
| | mg/l | U2K | | -1.15 | 0.87 | 15 | 0.80 | 0.87 | 0.88 | 0.06 | 7.2 | 20 |
| Cl ₂ _total | mg/l | U1K | | 0.18 | 1.14 | 10 | 1.15 | 1.14 | 1.14 | 0.04 | 3.3 | 21 |
| | mg/l | U2K | | -1.02 | 1.27 | 10 | 1.21 | 1.26 | 1.27 | 0.05 | 4.3 | 19 |
| KMnO ₄ | mg/l | U1P | | -1.17 | 9.37 | 15 | 8.55 | 9.28 | 9.37 | 0.85 | 9.1 | 19 |
| | mg/l | U2P | | -0.85 | 6.26 | 20 | 5.73 | 6.32 | 6.23 | 0.57 | 9.1 | 17 |
| NO ₃ | mg/l | U1N | | 0.27 | 8.06 | 10 | 8.17 | 8.03 | 8.04 | 0.31 | 3.9 | 18 |
| | mg/l | U2N | | 0.35 | 20.1 | 8 | 20.4 | 20.0 | 20.1 | 0.5 | 2.7 | 16 |
| pH | | U1H | | -0.59 | 7.82 | 2,6 | 7.76 | 7.81 | 7.81 | 0.08 | 1.1 | 21 |
| | | U2H | | 1.31 | 6.63 | 3 | 6.76 | 6.61 | 6.63 | 0.08 | 1.2 | 19 |
| Turbidity | FTU | U1S | | 0.45 | 0.44 | 30 | 0.47 | 0.45 | 0.44 | 0.07 | 15.8 | 22 |
| | FTU | U2S | | -0.72 | 0.68 | 25 | 0.62 | 0.68 | 0.68 | 0.09 | 13.5 | 21 |
| Urea | mg/l | A1U | | -0.52 | 0.64 | 10 | 0.62 | 0.64 | 0.64 | 0.02 | 3.7 | 17 |
| | mg/l | U2U | | | 0.45 | | 0.27 | 0.29 | 0.34 | 0.13 | 39.3 | 19 |
| | mg/l | U3U | | | 1.13 | | 0.73 | 0.74 | 0.83 | 0.29 | 34.7 | 18 |

| Participant 8 | | | | | | | | | | | | |
|------------------------|------|--------|--|---------|----------------|----------------------|----------------------|------|------|------|------|----------|
| Measurand | Unit | Sample | | z score | Assigned value | 2* _{Sp} t % | Participant's result | Md | Mean | SD | SD% | n (stat) |
| Cl ₂ _comb | mg/l | U1K | | 1.40 | 0.46 | 30 | 0.56 | 0.45 | 0.46 | 0.07 | 15.2 | 19 |
| | mg/l | U2K | | 0.69 | 0.39 | 35 | 0.44 | 0.37 | 0.39 | 0.08 | 21.0 | 19 |
| Cl ₂ _free | mg/l | U1K | | -0.92 | 0.67 | 20 | 0.61 | 0.67 | 0.67 | 0.09 | 13.2 | 22 |
| | mg/l | U2K | | -0.19 | 0.87 | 15 | 0.86 | 0.87 | 0.88 | 0.06 | 7.2 | 20 |
| Cl ₂ _total | mg/l | U1K | | 0.44 | 1.14 | 10 | 1.17 | 1.14 | 1.14 | 0.04 | 3.3 | 21 |
| | mg/l | U2K | | 0.39 | 1.27 | 10 | 1.29 | 1.26 | 1.27 | 0.05 | 4.3 | 19 |
| KMnO ₄ | mg/l | U1P | | -0.53 | 9.37 | 15 | 9.00 | 9.28 | 9.37 | 0.85 | 9.1 | 19 |
| | mg/l | U2P | | -0.78 | 6.26 | 20 | 5.77 | 6.32 | 6.23 | 0.57 | 9.1 | 17 |
| NO ₃ | mg/l | U1N | | -0.15 | 8.06 | 10 | 8.00 | 8.03 | 8.04 | 0.31 | 3.9 | 18 |
| | mg/l | U2N | | -0.06 | 20.1 | 8 | 20.1 | 20.0 | 20.1 | 0.5 | 2.7 | 16 |
| pH | | U1H | | 0.94 | 7.82 | 2,6 | 7.92 | 7.81 | 7.81 | 0.08 | 1.1 | 21 |
| | | U2H | | -0.68 | 6.63 | 3 | 6.56 | 6.61 | 6.63 | 0.08 | 1.2 | 19 |
| Turbidity | FTU | U1S | | 0.95 | 0.44 | 30 | 0.50 | 0.45 | 0.44 | 0.07 | 15.8 | 22 |
| | FTU | U2S | | -1.41 | 0.68 | 25 | 0.56 | 0.68 | 0.68 | 0.09 | 13.5 | 21 |
| Urea | mg/l | A1U | | -0.28 | 0.64 | 10 | 0.63 | 0.64 | 0.64 | 0.02 | 3.7 | 17 |
| | mg/l | U2U | | | 0.45 | | 0.29 | 0.29 | 0.34 | 0.13 | 39.3 | 19 |
| | mg/l | U3U | | | 1.13 | | 0.67 | 0.74 | 0.83 | 0.29 | 34.7 | 18 |

| Participant 9 | | | | | | | | | | | | |
|------------------------|------|--------|--|---------|----------------|---------------------|----------------------|------|------|------|------|----------|
| Measurand | Unit | Sample | | z score | Assigned value | 2*s _{pt} % | Participant's result | Md | Mean | SD | SD% | n (stat) |
| Cl ₂ _comb | mg/l | U1K | | 0.29 | 0.46 | 30 | 0.48 | 0.45 | 0.46 | 0.07 | 15.2 | 19 |
| | mg/l | U2K | | -1.01 | 0.39 | 35 | 0.32 | 0.37 | 0.39 | 0.08 | 21.0 | 19 |
| Cl ₂ _free | mg/l | U1K | | -0.97 | 0.67 | 20 | 0.61 | 0.67 | 0.67 | 0.09 | 13.2 | 22 |
| | mg/l | U2K | | 0.37 | 0.87 | 15 | 0.89 | 0.87 | 0.88 | 0.06 | 7.2 | 20 |
| Cl ₂ _total | mg/l | U1K | | -0.96 | 1.14 | 10 | 1.09 | 1.14 | 1.14 | 0.04 | 3.3 | 21 |
| | mg/l | U2K | | -0.87 | 1.27 | 10 | 1.22 | 1.26 | 1.27 | 0.05 | 4.3 | 19 |
| KMnO ₄ | mg/l | U1P | | -0.13 | 9.37 | 15 | 9.28 | 9.28 | 9.37 | 0.85 | 9.1 | 19 |
| | mg/l | U2P | | -0.22 | 6.26 | 20 | 6.12 | 6.32 | 6.23 | 0.57 | 9.1 | 17 |
| NO ₃ | mg/l | U1N | | 0.00 | 8.06 | 10 | 8.06 | 8.03 | 8.04 | 0.31 | 3.9 | 18 |
| | mg/l | U2N | | -0.20 | 20.1 | 8 | 19.9 | 20.0 | 20.1 | 0.5 | 2.7 | 16 |
| pH | | U1H | | 0.10 | 7.82 | 2,6 | 7.83 | 7.81 | 7.81 | 0.08 | 1.1 | 21 |
| | | U2H | | 0.30 | 6.63 | 3 | 6.66 | 6.61 | 6.63 | 0.08 | 1.2 | 19 |
| Turbidity | FTU | U1S | | 0.14 | 0.44 | 30 | 0.45 | 0.45 | 0.44 | 0.07 | 15.8 | 22 |
| | FTU | U2S | | 0.10 | 0.68 | 25 | 0.69 | 0.68 | 0.68 | 0.09 | 13.5 | 21 |
| Urea | mg/l | A1U | | -0.19 | 0.64 | 10 | 0.63 | 0.64 | 0.64 | 0.02 | 3.7 | 17 |
| | mg/l | U2U | | 0.45 | 0.45 | | 0.49 | 0.29 | 0.34 | 0.13 | 39.3 | 19 |
| | mg/l | U3U | | 1.13 | 1.13 | | 1.17 | 0.74 | 0.83 | 0.29 | 34.7 | 18 |

| Participant 10 | | | | | | | | | | | | |
|------------------------|------|--------|--|---------|----------------|---------------------|----------------------|------|------|------|------|----------|
| Measurand | Unit | Sample | | z score | Assigned value | 2*s _{pt} % | Participant's result | Md | Mean | SD | SD% | n (stat) |
| Cl ₂ _comb | mg/l | U1K | | -1.72 | 0.46 | 30 | 0.34 | 0.45 | 0.46 | 0.07 | 15.2 | 19 |
| | mg/l | U2K | | -1.27 | 0.39 | 35 | 0.30 | 0.37 | 0.39 | 0.08 | 21.0 | 19 |
| Cl ₂ _free | mg/l | U1K | | 2.37 | 0.67 | 20 | 0.83 | 0.67 | 0.67 | 0.09 | 13.2 | 22 |
| | mg/l | U2K | | 1.49 | 0.87 | 15 | 0.97 | 0.87 | 0.88 | 0.06 | 7.2 | 20 |
| Cl ₂ _total | mg/l | U1K | | 0.53 | 1.14 | 10 | 1.17 | 1.14 | 1.14 | 0.04 | 3.3 | 21 |
| | mg/l | U2K | | 0.00 | 1.27 | 10 | 1.27 | 1.26 | 1.27 | 0.05 | 4.3 | 19 |
| Turbidity | FTU | U1S | | -0.38 | 0.44 | 30 | 0.42 | 0.45 | 0.44 | 0.07 | 15.8 | 22 |
| | FTU | U2S | | 0.00 | 0.68 | 25 | 0.68 | 0.68 | 0.68 | 0.09 | 13.5 | 21 |
| Urea | mg/l | A1U | | -1.09 | 0.64 | 10 | 0.61 | 0.64 | 0.64 | 0.02 | 3.7 | 17 |
| | mg/l | U2U | | 0.45 | 0.45 | | 0.25 | 0.29 | 0.34 | 0.13 | 39.3 | 19 |
| | mg/l | U3U | | 1.13 | 1.13 | | 0.58 | 0.74 | 0.83 | 0.29 | 34.7 | 18 |

| Participant 11 | | | | | | | | | | | | |
|-----------------------|------|--------|--|---------|----------------|---------------------|----------------------|------|------|------|------|----------|
| Measurand | Unit | Sample | | z score | Assigned value | 2*s _{pt} % | Participant's result | Md | Mean | SD | SD% | n (stat) |
| Cl ₂ _free | mg/l | U1K | | -1.57 | 0.67 | 20 | 0.57 | 0.67 | 0.67 | 0.09 | 13.2 | 22 |
| | mg/l | U2K | | -0.46 | 0.87 | 15 | 0.84 | 0.87 | 0.88 | 0.06 | 7.2 | 20 |
| KMnO ₄ | mg/l | U1P | | 4.88 | 9.37 | 15 | 12.80 | 9.28 | 9.37 | 0.85 | 9.1 | 19 |
| | mg/l | U2P | | 4.22 | 6.26 | 20 | 8.90 | 6.32 | 6.23 | 0.57 | 9.1 | 17 |
| Turbidity | FTU | U1S | | 0.91 | 0.44 | 30 | 0.50 | 0.45 | 0.44 | 0.07 | 15.8 | 22 |
| | FTU | U2S | | -0.24 | 0.68 | 25 | 0.66 | 0.68 | 0.68 | 0.09 | 13.5 | 21 |
| Urea | mg/l | A1U | | 0.63 | 0.64 | 10 | 0.66 | 0.64 | 0.64 | 0.02 | 3.7 | 17 |
| | mg/l | U2U | | 0.45 | 0.45 | | 0.49 | 0.29 | 0.34 | 0.13 | 39.3 | 19 |
| | mg/l | U3U | | 1.13 | 1.13 | | 1.21 | 0.74 | 0.83 | 0.29 | 34.7 | 18 |

| Participant 12 | | | | | | | | | | | | |
|-----------------------|------|--------|--|---------|----------------|---------------------|----------------------|------|------|------|------|----------|
| Measurand | Unit | Sample | | z score | Assigned value | 2*s _{pt} % | Participant's result | Md | Mean | SD | SD% | n (stat) |
| Cl ₂ _comb | mg/l | U1K | | 1.51 | 0.46 | 30 | 0.56 | 0.45 | 0.46 | 0.07 | 15.2 | 19 |
| | mg/l | U2K | | 1.10 | 0.39 | 35 | 0.47 | 0.37 | 0.39 | 0.08 | 21.0 | 19 |








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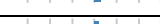

| Participant 12 | | | | | | | | | | | | |
|------------------------|------|--------|--|---------|----------------|---------------------|----------------------|------|------|------|------|----------|
| Measurand | Unit | Sample | | z score | Assigned value | 2*s _{pt} % | Participant's result | Md | Mean | SD | SD% | n (stat) |
| Cl ₂ _free | mg/l | U1K | | -0.18 | 0.67 | 20 | 0.66 | 0.67 | 0.67 | 0.09 | 13.2 | 22 |
| | mg/l | U2K | | -1.29 | 0.87 | 15 | 0.79 | 0.87 | 0.88 | 0.06 | 7.2 | 20 |
| Cl ₂ _total | mg/l | U1K | | 1.44 | 1.14 | 10 | 1.22 | 1.14 | 1.14 | 0.04 | 3.3 | 21 |
| | mg/l | U2K | | -0.30 | 1.27 | 10 | 1.25 | 1.26 | 1.27 | 0.05 | 4.3 | 19 |
| KMnO ₄ | mg/l | U1P | | 1.84 | 9.37 | 15 | 10.66 | 9.28 | 9.37 | 0.85 | 9.1 | 19 |
| | mg/l | U2P | | 0.96 | 6.26 | 20 | 6.86 | 6.32 | 6.23 | 0.57 | 9.1 | 17 |
| NO ₃ | mg/l | U1N | | 0.00 | 8.06 | 10 | 8.06 | 8.03 | 8.04 | 0.31 | 3.9 | 18 |
| | mg/l | U2N | | -0.29 | 20.1 | 8 | 19.9 | 20.0 | 20.1 | 0.5 | 2.7 | 16 |
| pH | | U1H | | 0.98 | 7.82 | 2,6 | 7.92 | 7.81 | 7.81 | 0.08 | 1.1 | 21 |
| | | U2H | | -0.70 | 6.63 | 3 | 6.56 | 6.61 | 6.63 | 0.08 | 1.2 | 19 |
| Turbidity | FTU | U1S | | -0.28 | 0.44 | 30 | 0.42 | 0.45 | 0.44 | 0.07 | 15.8 | 22 |
| | FTU | U2S | | -0.56 | 0.68 | 25 | 0.63 | 0.68 | 0.68 | 0.09 | 13.5 | 21 |
| Urea | mg/l | A1U | | -0.25 | 0.64 | 10 | 0.63 | 0.64 | 0.64 | 0.02 | 3.7 | 17 |
| | mg/l | U2U | | | 0.45 | | 0.25 | 0.29 | 0.34 | 0.13 | 39.3 | 19 |
| | mg/l | U3U | | | 1.13 | | 0.59 | 0.74 | 0.83 | 0.29 | 34.7 | 18 |


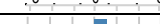














| Participant 13 | | | | | | | | | | | | |
|------------------------|------|--------|--|---------|----------------|---------------------|----------------------|------|------|------|------|----------|
| Measurand | Unit | Sample | | z score | Assigned value | 2*s _{pt} % | Participant's result | Md | Mean | SD | SD% | n (stat) |
| Cl ₂ _comb | mg/l | U1K | | 4.18 | 0.46 | 30 | 0.75 | 0.45 | 0.46 | 0.07 | 15.2 | 19 |
| | mg/l | U2K | | 2.82 | 0.39 | 35 | 0.58 | 0.37 | 0.39 | 0.08 | 21.0 | 19 |
| Cl ₂ _free | mg/l | U1K | | -2.07 | 0.67 | 20 | 0.53 | 0.67 | 0.67 | 0.09 | 13.2 | 22 |
| | mg/l | U2K | | -1.11 | 0.87 | 15 | 0.80 | 0.87 | 0.88 | 0.06 | 7.2 | 20 |
| Cl ₂ _total | mg/l | U1K | | 2.46 | 1.14 | 10 | 1.28 | 1.14 | 1.14 | 0.04 | 3.3 | 21 |
| | mg/l | U2K | | 1.73 | 1.27 | 10 | 1.38 | 1.26 | 1.27 | 0.05 | 4.3 | 19 |
| KMnO ₄ | mg/l | U1P | | 0.98 | 9.37 | 15 | 10.06 | 9.28 | 9.37 | 0.85 | 9.1 | 19 |
| | mg/l | U2P | | 0.67 | 6.26 | 20 | 6.68 | 6.32 | 6.23 | 0.57 | 9.1 | 17 |
| NO ₃ | mg/l | U1N | | 0.50 | 8.06 | 10 | 8.26 | 8.03 | 8.04 | 0.31 | 3.9 | 18 |
| | mg/l | U2N | | 0.62 | 20.1 | 8 | 20.6 | 20.0 | 20.1 | 0.5 | 2.7 | 16 |
| pH | | U1H | | -0.49 | 7.82 | 2,6 | 7.77 | 7.81 | 7.81 | 0.08 | 1.1 | 21 |
| | | U2H | | 1.91 | 6.63 | 3 | 6.82 | 6.61 | 6.63 | 0.08 | 1.2 | 19 |
| Turbidity | FTU | U1S | | -1.82 | 0.44 | 30 | 0.32 | 0.45 | 0.44 | 0.07 | 15.8 | 22 |
| | FTU | U2S | | -0.82 | 0.68 | 25 | 0.61 | 0.68 | 0.68 | 0.09 | 13.5 | 21 |

| Participant 14 | | | | | | | | | | | | |
|------------------------|------|--------|--|---------|----------------|---------------------|----------------------|------|------|------|------|----------|
| Measurand | Unit | Sample | | z score | Assigned value | 2*s _{pt} % | Participant's result | Md | Mean | SD | SD% | n (stat) |
| Cl ₂ _comb | mg/l | U1K | | -3.27 | 0.46 | 30 | 0.23 | 0.45 | 0.46 | 0.07 | 15.2 | 19 |
| Cl ₂ _free | mg/l | U1K | | 3.14 | 0.67 | 20 | 0.88 | 0.67 | 0.67 | 0.09 | 13.2 | 22 |
| Cl ₂ _total | mg/l | U1K | | -0.44 | 1.14 | 10 | 1.12 | 1.14 | 1.14 | 0.04 | 3.3 | 21 |
| KMnO ₄ | mg/l | U1P | | -0.54 | 9.37 | 15 | 8.99 | 9.28 | 9.37 | 0.85 | 9.1 | 19 |
| NO ₃ | mg/l | U1N | | 0.89 | 8.06 | 10 | 8.42 | 8.03 | 8.04 | 0.31 | 3.9 | 18 |
| pH | | U1H | | 0.39 | 7.82 | 2,6 | 7.86 | 7.81 | 7.81 | 0.08 | 1.1 | 21 |
| Turbidity | FTU | U1S | | -1.36 | 0.44 | 30 | 0.35 | 0.45 | 0.44 | 0.07 | 15.8 | 22 |
| Urea | mg/l | U2U | | | 0.45 | | 0.21 | 0.29 | 0.34 | 0.13 | 39.3 | 19 |



















| Participant 15 | | | | | | | | | | | | |
|-------------------|------|--------|--|---------|----------------|---------------------|----------------------|------|------|------|-----|----------|
| Measurand | Unit | Sample | | z score | Assigned value | 2*s _{pt} % | Participant's result | Md | Mean | SD | SD% | n (stat) |
| KMnO ₄ | mg/l | U1P | | 0.46 | 9.37 | 15 | 9.69 | 9.28 | 9.37 | 0.85 | 9.1 | 19 |
| | mg/l | U2P | | 0.61 | 6.26 | 20 | 6.64 | 6.32 | 6.23 | 0.57 | 9.1 | 17 |

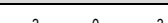

















| Participant 15 | | | | | | | | | | | | |
|-----------------|------|--------|---|---------|----------------|---------------------|----------------------|------|------|------|------|----------|
| Measurand | Unit | Sample |  | z score | Assigned value | 2*s _{pt} % | Participant's result | Md | Mean | SD | SD% | n (stat) |
| NO ₃ | mg/l | U1N |  | -0.20 | 8.06 | 10 | 7.98 | 8.03 | 8.04 | 0.31 | 3.9 | 18 |
| | mg/l | U2N |  | -0.12 | 20.1 | 8 | 20.0 | 20.0 | 20.1 | 0.5 | 2.7 | 16 |
| pH | | U1H |  | 0.20 | 7.82 | 2,6 | 7.84 | 7.81 | 7.81 | 0.08 | 1.1 | 21 |
| | | U2H |  | -0.10 | 6.63 | 3 | 6.62 | 6.61 | 6.63 | 0.08 | 1.2 | 19 |
| Turbidity | FTU | U1S |  | 1.15 | 0.44 | 30 | 0,483 | 0.45 | 0.44 | 0.07 | 15.8 | 22 |
| | FTU | U2S |  | 1.15 | 0.68 | 25 | 0.78 | 0.68 | 0.68 | 0.09 | 13.5 | 21 |










| Participant 16 | | | | | | | | | | | | |
|------------------------|------|--------|---|---------|----------------|---------------------|----------------------|------|------|------|------|----------|
| Measurand | Unit | Sample |  | z score | Assigned value | 2*s _{pt} % | Participant's result | Md | Mean | SD | SD% | n (stat) |
| Cl ₂ _comb | mg/l | U1K |  | -0.54 | 0.46 | 30 | 0.42 | 0.45 | 0.46 | 0.07 | 15.2 | 19 |
| | mg/l | U2K |  | -0.77 | 0.39 | 35 | 0.34 | 0.37 | 0.39 | 0.08 | 21.0 | 19 |
| Cl ₂ _free | mg/l | U1K |  | 0.33 | 0.67 | 20 | 0.69 | 0.67 | 0.67 | 0.09 | 13.2 | 22 |
| | mg/l | U2K |  | -0.11 | 0.87 | 15 | 0.86 | 0.87 | 0.88 | 0.06 | 7.2 | 20 |
| Cl ₂ _total | mg/l | U1K |  | -0.44 | 1.14 | 10 | 1.12 | 1.14 | 1.14 | 0.04 | 3.3 | 21 |
| | mg/l | U2K |  | -1.10 | 1.27 | 10 | 1.20 | 1.26 | 1.27 | 0.05 | 4.3 | 19 |
| KMnO ₄ | mg/l | U1P |  | -1.37 | 9.37 | 15 | 8.41 | 9.28 | 9.37 | 0.85 | 9.1 | 19 |
| | mg/l | U2P |  | -1.18 | 6.26 | 20 | 5.52 | 6.32 | 6.23 | 0.57 | 9.1 | 17 |
| NO ₃ | mg/l | U1N |  | 0.27 | 8.06 | 10 | 8.17 | 8.03 | 8.04 | 0.31 | 3.9 | 18 |
| | mg/l | U2N |  | 1.00 | 20.1 | 8 | 20.9 | 20.0 | 20.1 | 0.5 | 2.7 | 16 |
| pH | | U1H |  | -0.30 | 7.82 | 2,6 | 7.79 | 7.81 | 7.81 | 0.08 | 1.1 | 21 |
| | | U2H |  | 0.00 | 6.63 | 3 | 6.63 | 6.61 | 6.63 | 0.08 | 1.2 | 19 |
| Turbidity | FTU | U1S |  | 0.08 | 0.44 | 30 | 0.45 | 0.45 | 0.44 | 0.07 | 15.8 | 22 |
| | FTU | U2S |  | 0.32 | 0.68 | 25 | 0.71 | 0.68 | 0.68 | 0.09 | 13.5 | 21 |
| Urea | mg/l | A1U |  | 0.14 | 0.64 | 10 | 0.64 | 0.64 | 0.64 | 0.02 | 3.7 | 17 |
| | mg/l | U2U |  | 0.14 | 0.45 | | 0.24 | 0.29 | 0.34 | 0.13 | 39.3 | 19 |
| | mg/l | U3U |  | 0.14 | 1.13 | | 0.62 | 0.74 | 0.83 | 0.29 | 34.7 | 18 |

| Participant 17 | | | | | | | | | | | | |
|------------------------|------|--------|---|---------|----------------|---------------------|----------------------|------|------|------|------|----------|
| Measurand | Unit | Sample |  | z score | Assigned value | 2*s _{pt} % | Participant's result | Md | Mean | SD | SD% | n (stat) |
| Cl ₂ _comb | mg/l | U1K |  | 0.51 | 0.46 | 30 | 0.50 | 0.45 | 0.46 | 0.07 | 15.2 | 19 |
| | mg/l | U2K |  | 1.73 | 0.39 | 35 | 0.51 | 0.37 | 0.39 | 0.08 | 21.0 | 19 |
| Cl ₂ _free | mg/l | U1K |  | -0.54 | 0.67 | 20 | 0.63 | 0.67 | 0.67 | 0.09 | 13.2 | 22 |
| | mg/l | U2K |  | 0.03 | 0.87 | 15 | 0.87 | 0.87 | 0.88 | 0.06 | 7.2 | 20 |
| Cl ₂ _total | mg/l | U1K |  | -0.18 | 1.14 | 10 | 1.13 | 1.14 | 1.14 | 0.04 | 3.3 | 21 |
| | mg/l | U2K |  | 1.73 | 1.27 | 10 | 1.38 | 1.26 | 1.27 | 0.05 | 4.3 | 19 |
| KMnO ₄ | mg/l | U1P |  | 0.28 | 9.37 | 15 | 9.57 | 9.28 | 9.37 | 0.85 | 9.1 | 19 |
| | mg/l | U2P |  | -0.65 | 6.26 | 20 | 5.85 | 6.32 | 6.23 | 0.57 | 9.1 | 17 |
| pH | | U1H |  | -0.98 | 7.82 | 2,6 | 7.72 | 7.81 | 7.81 | 0.08 | 1.1 | 21 |
| | | U2H |  | 0.70 | 6.63 | 3 | 6.70 | 6.61 | 6.63 | 0.08 | 1.2 | 19 |
| Turbidity | FTU | U1S |  | -0.24 | 0.44 | 30 | 0.42 | 0.45 | 0.44 | 0.07 | 15.8 | 22 |
| | FTU | U2S |  | -0.47 | 0.68 | 25 | 0.64 | 0.68 | 0.68 | 0.09 | 13.5 | 21 |
| Urea | mg/l | A1U |  | 1.23 | 0.64 | 10 | 0.68 | 0.64 | 0.64 | 0.02 | 3.7 | 17 |
| | mg/l | U2U |  | 1.23 | 0.45 | | 0.33 | 0.29 | 0.34 | 0.13 | 39.3 | 19 |
| | mg/l | U3U |  | 1.23 | 1.13 | | 0.74 | 0.74 | 0.83 | 0.29 | 34.7 | 18 |

APPENDIX 8 (7/9)

| Participant 18 | | | | | | | | | | | | |
|------------------------|------|--------|---|---------|----------------|---------------------|----------------------|------|------|------|------|----------|
| Measurand | Unit | Sample |  | z score | Assigned value | 2*s _{pt} % | Participant's result | Md | Mean | SD | SD% | n (stat) |
| Cl ₂ _comb | mg/l | U1K |  | -1.01 | 0.46 | 30 | 0.39 | 0.45 | 0.46 | 0.07 | 15.2 | 19 |
| | mg/l | U2K |  | -0.51 | 0.39 | 35 | 0.36 | 0.37 | 0.39 | 0.08 | 21.0 | 19 |
| Cl ₂ _free | mg/l | U1K |  | 0.75 | 0.67 | 20 | 0.72 | 0.67 | 0.67 | 0.09 | 13.2 | 22 |
| | mg/l | U2K |  | 0.38 | 0.87 | 15 | 0.90 | 0.87 | 0.88 | 0.06 | 7.2 | 20 |
| Cl ₂ _total | mg/l | U1K |  | -0.53 | 1.14 | 10 | 1.11 | 1.14 | 1.14 | 0.04 | 3.3 | 21 |
| | mg/l | U2K |  | -0.31 | 1.27 | 10 | 1.25 | 1.26 | 1.27 | 0.05 | 4.3 | 19 |
| KMnO ₄ | mg/l | U1P |  | 1.18 | 9.37 | 15 | 10.20 | 9.28 | 9.37 | 0.85 | 9.1 | 19 |
| | mg/l | U2P |  | 0.81 | 6.26 | 20 | 6.77 | 6.32 | 6.23 | 0.57 | 9.1 | 17 |
| NO ₃ | mg/l | U1N |  | -0.57 | 8.06 | 10 | 7.83 | 8.03 | 8.04 | 0.31 | 3.9 | 18 |
| | mg/l | U2N |  | -0.66 | 20.1 | 8 | 19.6 | 20.0 | 20.1 | 0.5 | 2.7 | 16 |
| pH | | U1H |  | -1.77 | 7.82 | 2,6 | 7.64 | 7.81 | 7.81 | 0.08 | 1.1 | 21 |
| | | U2H |  | -0.20 | 6.63 | 3 | 6.61 | 6.61 | 6.63 | 0.08 | 1.2 | 19 |
| Turbidity | FTU | U1S |  | 2.20 | 0.44 | 30 | 0.59 | 0.45 | 0.44 | 0.07 | 15.8 | 22 |
| | FTU | U2S |  | 2.18 | 0.68 | 25 | 0.87 | 0.68 | 0.68 | 0.09 | 13.5 | 21 |
| Urea | mg/l | A1U |  | -0.47 | 0.64 | 10 | 0.63 | 0.64 | 0.64 | 0.02 | 3.7 | 17 |
| | mg/l | U2U |  | | 0.45 | | 0.28 | 0.29 | 0.34 | 0.13 | 39.3 | 19 |
| | mg/l | U3U |  | | 1.13 | | 0.77 | 0.74 | 0.83 | 0.29 | 34.7 | 18 |

| Participant 19 | | | | | | | | | | | | |
|------------------------|------|--------|---|---------|----------------|---------------------|----------------------|------|------|------|------|----------|
| Measurand | Unit | Sample |  | z score | Assigned value | 2*s _{pt} % | Participant's result | Md | Mean | SD | SD% | n (stat) |
| Cl ₂ _comb | mg/l | U1K |  | 0.67 | 0.46 | 30 | 0.51 | 0.45 | 0.46 | 0.07 | 15.2 | 19 |
| | mg/l | U2K |  | -0.24 | 0.39 | 35 | 0.37 | 0.37 | 0.39 | 0.08 | 21.0 | 19 |
| Cl ₂ _free | mg/l | U1K |  | -0.18 | 0.67 | 20 | 0.66 | 0.67 | 0.67 | 0.09 | 13.2 | 22 |
| | mg/l | U2K |  | 1.46 | 0.87 | 15 | 0.97 | 0.87 | 0.88 | 0.06 | 7.2 | 20 |
| Cl ₂ _total | mg/l | U1K |  | 0.44 | 1.14 | 10 | 1.17 | 1.14 | 1.14 | 0.04 | 3.3 | 21 |
| | mg/l | U2K |  | 0.87 | 1.27 | 10 | 1.33 | 1.26 | 1.27 | 0.05 | 4.3 | 19 |
| KMnO ₄ | mg/l | U1P |  | 0.34 | 9.37 | 15 | 9.61 | 9.28 | 9.37 | 0.85 | 9.1 | 19 |
| | mg/l | U2P |  | 0.19 | 6.26 | 20 | 6.38 | 6.32 | 6.23 | 0.57 | 9.1 | 17 |
| NO ₃ | mg/l | U1N |  | -0.25 | 8.06 | 10 | 7.96 | 8.03 | 8.04 | 0.31 | 3.9 | 18 |
| | mg/l | U2N |  | -0.09 | 20.1 | 8 | 20.0 | 20.0 | 20.1 | 0.5 | 2.7 | 16 |
| pH | | U1H |  | 0.10 | 7.82 | 2,6 | 7.83 | 7.81 | 7.81 | 0.08 | 1.1 | 21 |
| | | U2H |  | -0.20 | 6.63 | 3 | 6.61 | 6.61 | 6.63 | 0.08 | 1.2 | 19 |
| Turbidity | FTU | U1S |  | 0.45 | 0.44 | 30 | 0.47 | 0.45 | 0.44 | 0.07 | 15.8 | 22 |
| | FTU | U2S |  | -0.41 | 0.68 | 25 | 0.65 | 0.68 | 0.68 | 0.09 | 13.5 | 21 |
| Urea | mg/l | A1U |  | -3.23 | 0.64 | 10 | 0.54 | 0.64 | 0.64 | 0.02 | 3.7 | 17 |
| | mg/l | U2U |  | | 0.45 | | 0.45 | 0.29 | 0.34 | 0.13 | 39.3 | 19 |
| | mg/l | U3U |  | | 1.13 | | 1.10 | 0.74 | 0.83 | 0.29 | 34.7 | 18 |

| Participant 20 | | | | | | | | | | | | |
|------------------------|------|--------|---|---------|----------------|---------------------|----------------------|------|------|------|------|----------|
| Measurand | Unit | Sample |  | z score | Assigned value | 2*s _{pt} % | Participant's result | Md | Mean | SD | SD% | n (stat) |
| Cl ₂ _comb | mg/l | U1K |  | -0.34 | 0.46 | 30 | 0.44 | 0.45 | 0.46 | 0.07 | 15.2 | 19 |
| | mg/l | U2K |  | -0.38 | 0.39 | 35 | 0.36 | 0.37 | 0.39 | 0.08 | 21.0 | 19 |
| Cl ₂ _free | mg/l | U1K |  | 0.05 | 0.67 | 20 | 0.67 | 0.67 | 0.67 | 0.09 | 13.2 | 22 |
| | mg/l | U2K |  | -0.37 | 0.87 | 15 | 0.85 | 0.87 | 0.88 | 0.06 | 7.2 | 20 |
| Cl ₂ _total | mg/l | U1K |  | -0.53 | 1.14 | 10 | 1.11 | 1.14 | 1.14 | 0.04 | 3.3 | 21 |
| | mg/l | U2K |  | -0.94 | 1.27 | 10 | 1.21 | 1.26 | 1.27 | 0.05 | 4.3 | 19 |
| pH | | U1H |  | -0.10 | 7.82 | 2,6 | 7.81 | 7.81 | 7.81 | 0.08 | 1.1 | 21 |
| | | U2H |  | -0.70 | 6.63 | 3 | 6.56 | 6.61 | 6.63 | 0.08 | 1.2 | 19 |

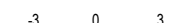















| Participant 20 | | | | | | | | | | | | |
|----------------|------|--------|--|---------|----------------|---------------------|----------------------|------|------|------|------|----------|
| Measurand | Unit | Sample | | z score | Assigned value | 2*s _{pt} % | Participant's result | Md | Mean | SD | SD% | n (stat) |
| Turbidity | FTU | U1S | | 0.89 | 0.44 | 30 | 0.50 | 0.45 | 0.44 | 0.07 | 15.8 | 22 |
| | FTU | U2S | | 0.41 | 0.68 | 25 | 0.71 | 0.68 | 0.68 | 0.09 | 13.5 | 21 |





| Participant 21 | | | | | | | | | | | | |
|------------------------|------|--------|--|---------|----------------|---------------------|----------------------|------|------|------|------|----------|
| Measurand | Unit | Sample | | z score | Assigned value | 2*s _{pt} % | Participant's result | Md | Mean | SD | SD% | n (stat) |
| Cl ₂ _comb | mg/l | U1K | | 0.14 | 0.46 | 30 | 0.47 | 0.45 | 0.46 | 0.07 | 15.2 | 19 |
| | mg/l | U2K | | 1.47 | 0.39 | 35 | 0.49 | 0.37 | 0.39 | 0.08 | 21.0 | 19 |
| Cl ₂ _free | mg/l | U1K | | 0.67 | 0.67 | 20 | 0.72 | 0.67 | 0.67 | 0.09 | 13.2 | 22 |
| | mg/l | U2K | | -1.07 | 0.87 | 15 | 0.80 | 0.87 | 0.88 | 0.06 | 7.2 | 20 |
| Cl ₂ _total | mg/l | U1K | | 0.96 | 1.14 | 10 | 1.20 | 1.14 | 1.14 | 0.04 | 3.3 | 21 |
| | mg/l | U2K | | 0.39 | 1.27 | 10 | 1.30 | 1.26 | 1.27 | 0.05 | 4.3 | 19 |
| KMnO ₄ | mg/l | U1P | | 0.90 | 9.37 | 15 | 10.00 | 9.28 | 9.37 | 0.85 | 9.1 | 19 |
| | mg/l | U2P | | -0.42 | 6.26 | 20 | 6.00 | 6.32 | 6.23 | 0.57 | 9.1 | 17 |
| NO ₃ | mg/l | U1N | | -0.15 | 8.06 | 10 | 8.00 | 8.03 | 8.04 | 0.31 | 3.9 | 18 |
| | mg/l | U2N | | -0.12 | 20.1 | 8 | 20.0 | 20.0 | 20.1 | 0.5 | 2.7 | 16 |
| pH | | U1H | | -0.20 | 7.82 | 2,6 | 7.80 | 7.81 | 7.81 | 0.08 | 1.1 | 21 |
| | | U2H | | -0.30 | 6.63 | 3 | 6.60 | 6.61 | 6.63 | 0.08 | 1.2 | 19 |
| Turbidity | FTU | U1S | | -1.06 | 0.44 | 30 | 0.37 | 0.45 | 0.44 | 0.07 | 15.8 | 22 |
| | FTU | U2S | | -2.71 | 0.68 | 25 | 0.45 | 0.68 | 0.68 | 0.09 | 13.5 | 21 |
| Urea | mg/l | A1U | | 0.31 | 0.64 | 10 | 0.65 | 0.64 | 0.64 | 0.02 | 3.7 | 17 |
| | mg/l | U2U | | | 0.45 | | 0.51 | 0.29 | 0.34 | 0.13 | 39.3 | 19 |
| | mg/l | U3U | | | 1.13 | | 1.20 | 0.74 | 0.83 | 0.29 | 34.7 | 18 |

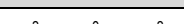



| Participant 22 | | | | | | | | | | | | |
|------------------------|------|--------|--|---------|----------------|---------------------|----------------------|------|------|------|------|----------|
| Measurand | Unit | Sample | | z score | Assigned value | 2*s _{pt} % | Participant's result | Md | Mean | SD | SD% | n (stat) |
| Cl ₂ _comb | mg/l | U1K | | -0.65 | 0.46 | 30 | 0.42 | 0.45 | 0.46 | 0.07 | 15.2 | 19 |
| | mg/l | U2K | | -1.25 | 0.39 | 35 | 0.31 | 0.37 | 0.39 | 0.08 | 21.0 | 19 |
| Cl ₂ _free | mg/l | U1K | | 0.30 | 0.67 | 20 | 0.69 | 0.67 | 0.67 | 0.09 | 13.2 | 22 |
| | mg/l | U2K | | 1.07 | 0.87 | 15 | 0.94 | 0.87 | 0.88 | 0.06 | 7.2 | 20 |
| Cl ₂ _total | mg/l | U1K | | -0.61 | 1.14 | 10 | 1.11 | 1.14 | 1.14 | 0.04 | 3.3 | 21 |
| | mg/l | U2K | | -0.39 | 1.27 | 10 | 1.25 | 1.26 | 1.27 | 0.05 | 4.3 | 19 |
| KMnO ₄ | mg/l | U1P | | -2.55 | 9.37 | 15 | 7.58 | 9.28 | 9.37 | 0.85 | 9.1 | 19 |
| | mg/l | U2P | | -2.04 | 6.26 | 20 | 4.98 | 6.32 | 6.23 | 0.57 | 9.1 | 17 |
| NO ₃ | mg/l | U1N | | 0.94 | 8.06 | 10 | 8.44 | 8.03 | 8.04 | 0.31 | 3.9 | 18 |
| | mg/l | U2N | | -0.75 | 20.1 | 8 | 19.5 | 20.0 | 20.1 | 0.5 | 2.7 | 16 |
| pH | | U1H | | -0.89 | 7.82 | 2,6 | 7.73 | 7.81 | 7.81 | 0.08 | 1.1 | 21 |
| | | U2H | | -0.70 | 6.63 | 3 | 6.56 | 6.61 | 6.63 | 0.08 | 1.2 | 19 |
| Turbidity | FTU | U1S | | 0.05 | 0.44 | 30 | 0.44 | 0.45 | 0.44 | 0.07 | 15.8 | 22 |
| | FTU | U2S | | 0.45 | 0.68 | 25 | 0.72 | 0.68 | 0.68 | 0.09 | 13.5 | 21 |
| Urea | mg/l | A1U | | 0.94 | 0.64 | 10 | 0.67 | 0.64 | 0.64 | 0.02 | 3.7 | 17 |
| | mg/l | U2U | | | 0.45 | | 0.32 | 0.29 | 0.34 | 0.13 | 39.3 | 19 |
| | mg/l | U3U | | | 1.13 | | 0.71 | 0.74 | 0.83 | 0.29 | 34.7 | 18 |

| Participant 23 | | | | | | | | | | | | |
|-----------------------|------|--------|--|---------|----------------|---------------------|----------------------|------|------|------|------|----------|
| Measurand | Unit | Sample | | z score | Assigned value | 2*s _{pt} % | Participant's result | Md | Mean | SD | SD% | n (stat) |
| Cl ₂ _comb | mg/l | U1K | | 0.57 | 0.46 | 30 | 0.50 | 0.45 | 0.46 | 0.07 | 15.2 | 19 |
| | mg/l | U2K | | 1.03 | 0.39 | 35 | 0.46 | 0.37 | 0.39 | 0.08 | 21.0 | 19 |

APPENDIX 8 (9/9)

| Participant 23 | | | | | | | | | | | | |
|------------------------|------|--------|---|---------|----------------|---------------------|----------------------|------|------|------|------|----------|
| Measurand | Unit | Sample |  | z score | Assigned value | 2*s _{pt} % | Participant's result | Md | Mean | SD | SD% | n (stat) |
| Cl ₂ _free | mg/l | U1K |  | -0.13 | 0.67 | 20 | 0.66 | 0.67 | 0.67 | 0.09 | 13.2 | 22 |
| | mg/l | U2K |  | -0.16 | 0.87 | 15 | 0.86 | 0.87 | 0.88 | 0.06 | 7.2 | 20 |
| Cl ₂ _total | mg/l | U1K |  | 0.35 | 1.14 | 10 | 1.16 | 1.14 | 1.14 | 0.04 | 3.3 | 21 |
| | mg/l | U2K |  | 0.79 | 1.27 | 10 | 1.32 | 1.26 | 1.27 | 0.05 | 4.3 | 19 |
| KMnO ₄ | mg/l | U1P |  | 0.01 | 9.37 | 15 | 9.38 | 9.28 | 9.37 | 0.85 | 9.1 | 19 |
| | mg/l | U2P |  | 0.94 | 6.26 | 20 | 6.85 | 6.32 | 6.23 | 0.57 | 9.1 | 17 |
| NO ₃ | mg/l | U1N |  | -1.86 | 8.06 | 10 | 7.31 | 8.03 | 8.04 | 0.31 | 3.9 | 18 |
| | mg/l | U2N |  | 0.88 | 20.1 | 8 | 20.8 | 20.0 | 20.1 | 0.5 | 2.7 | 16 |
| pH | | U1H |  | 0.69 | 7.82 | 2,6 | 7.89 | 7.81 | 7.81 | 0.08 | 1.1 | 21 |
| | | U2H |  | -1.41 | 6.63 | 3 | 6.49 | 6.61 | 6.63 | 0.08 | 1.2 | 19 |
| Turbidity | FTU | U1S |  | -1.42 | 0.44 | 30 | 0.35 | 0.45 | 0.44 | 0.07 | 15.8 | 22 |
| | FTU | U2S |  | -1.21 | 0.68 | 25 | 0.58 | 0.68 | 0.68 | 0.09 | 13.5 | 21 |
| Urea | mg/l | A1U |  | 0.33 | 0.64 | 10 | 0.65 | 0.64 | 0.64 | 0.02 | 3.7 | 17 |
| | mg/l | U2U |  | | 0.45 | | 0.20 | 0.29 | 0.34 | 0.13 | 39.3 | 19 |
| | mg/l | U3U |  | | 1.13 | | 0.54 | 0.74 | 0.83 | 0.29 | 34.7 | 18 |

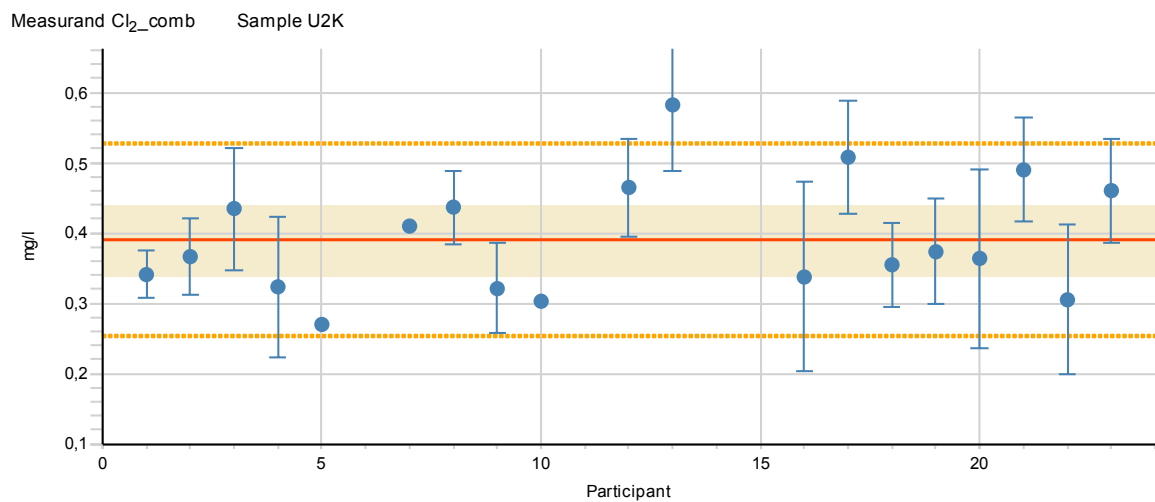
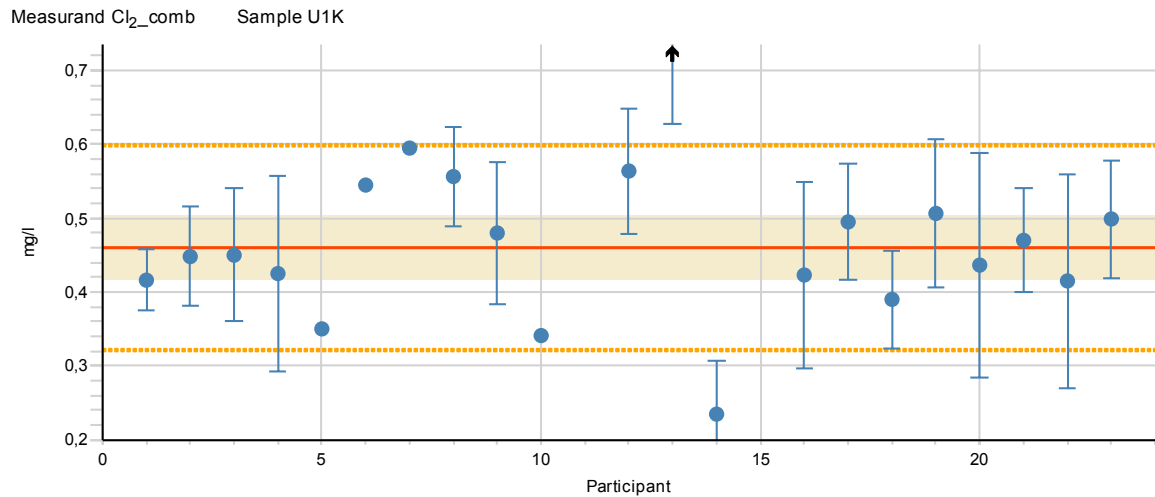
| Participant 24 | | | | | | | | | | | | |
|----------------|------|--------|--|---------|----------------|---------------------|----------------------|------|------|------|------|----------|
| Measurand | Unit | Sample |  | z score | Assigned value | 2*s _{pt} % | Participant's result | Md | Mean | SD | SD% | n (stat) |
| Urea | mg/l | A1U |  | -1.09 | 0.64 | 10 | 0.61 | 0.64 | 0.64 | 0.02 | 3.7 | 17 |
| | mg/l | U2U |  | | 0.45 | | 0.47 | 0.29 | 0.34 | 0.13 | 39.3 | 19 |
| | mg/l | U3U |  | | 1.13 | | 1.15 | 0.74 | 0.83 | 0.29 | 34.7 | 18 |

| Participant 25 | | | | | | | | | | | | |
|----------------|------|--------|---|---------|----------------|---------------------|----------------------|------|------|------|------|----------|
| Measurand | Unit | Sample |  | z score | Assigned value | 2*s _{pt} % | Participant's result | Md | Mean | SD | SD% | n (stat) |
| Urea | mg/l | A1U |  | 1.14 | 0.64 | 10 | 0.68 | 0.64 | 0.64 | 0.02 | 3.7 | 17 |
| | mg/l | U2U |  | | 0.45 | | 0.57 | 0.29 | 0.34 | 0.13 | 39.3 | 19 |
| | mg/l | U3U |  | | 1.13 | | 1.11 | 0.74 | 0.83 | 0.29 | 34.7 | 18 |

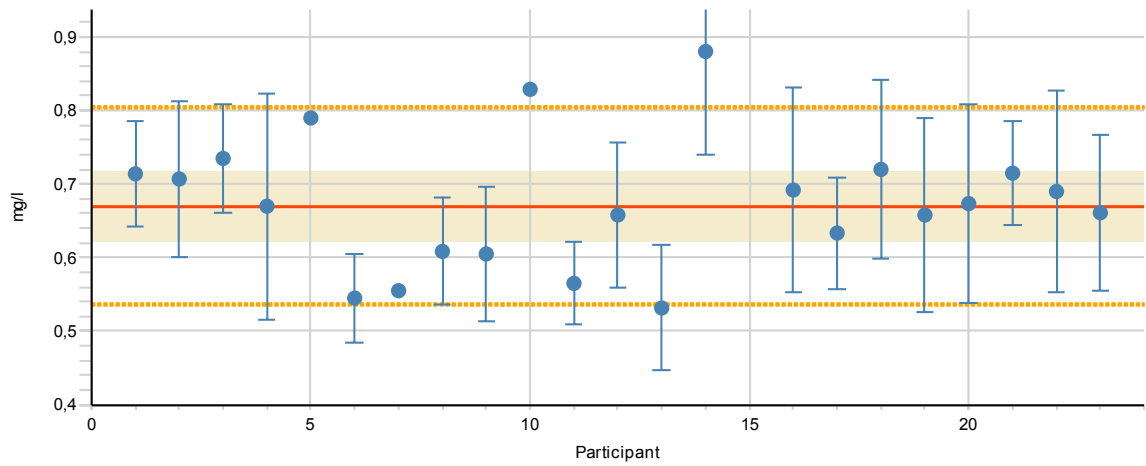
APPENDIX 9: Results of participants and their uncertainties

In figures:

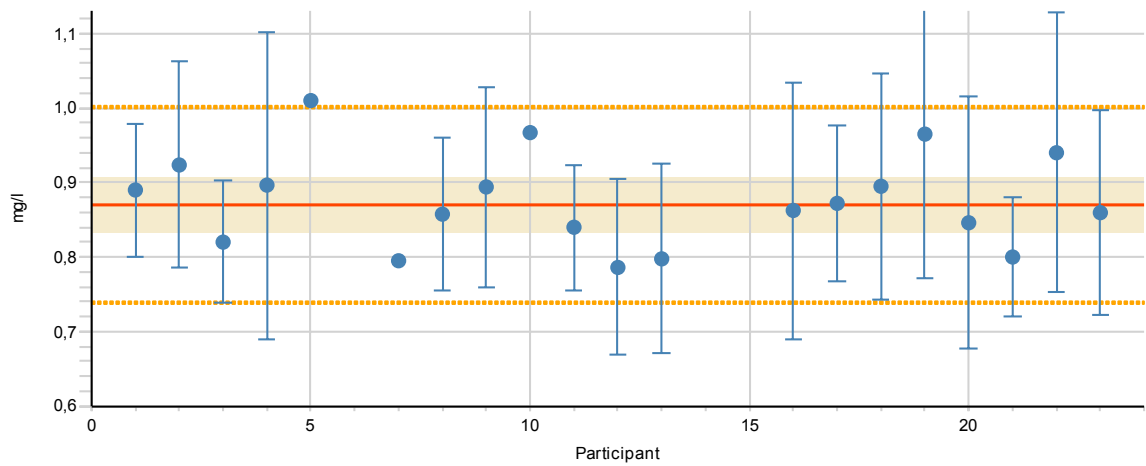
- The dashed lines describe the standard deviation for the proficiency assessment, the red solid line shows the assigned value, the shaded area describes the expanded measurement uncertainty of the assigned value, and the arrow describes the value outside the scale.



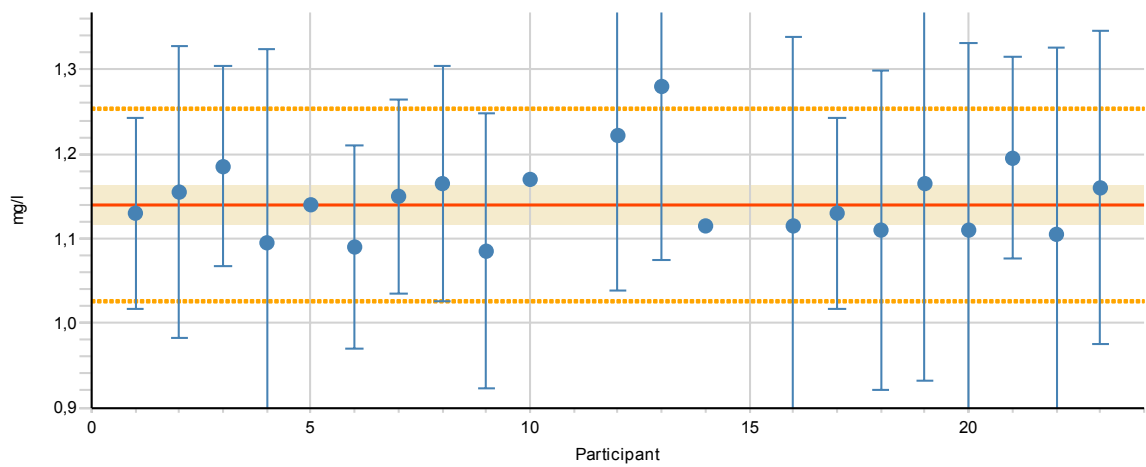
Measurand Cl₂_free Sample U1K



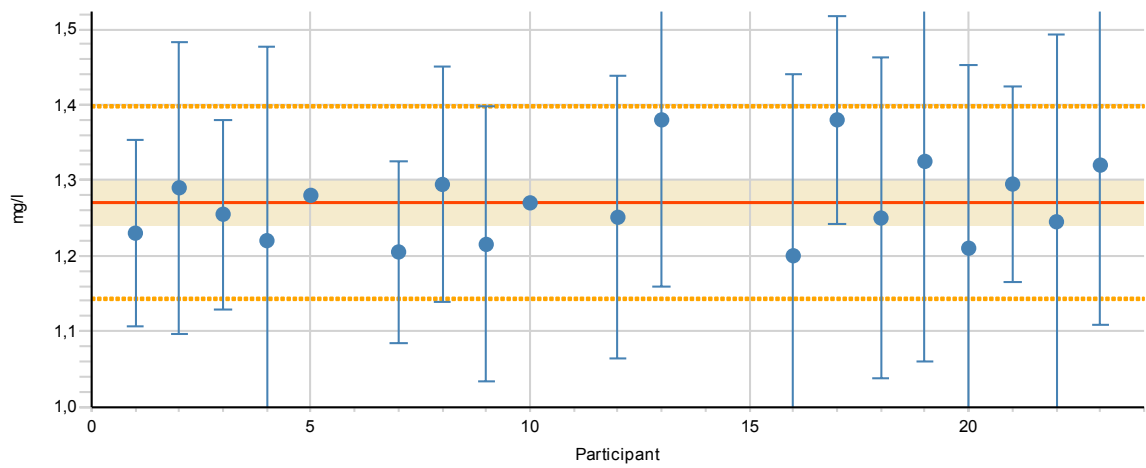
Measurand Cl₂_free Sample U2K



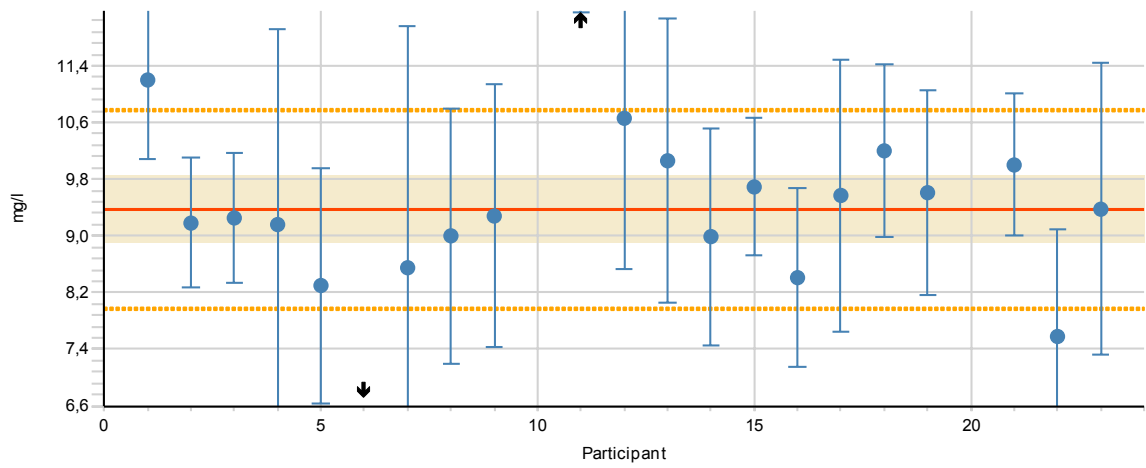
Measurand Cl₂_total Sample U1K



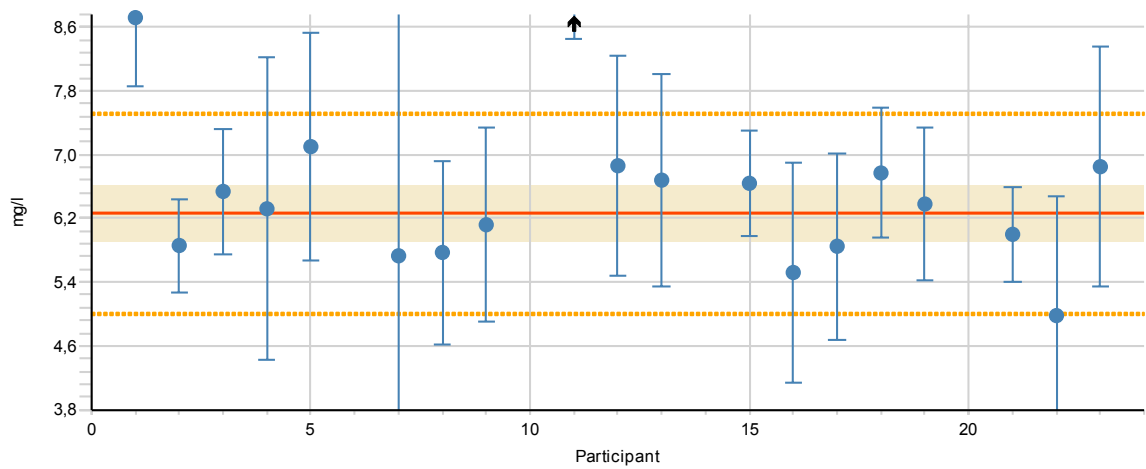
Measurand Cl₂_total Sample U2K



Measurand KMnO₄ Sample U1P

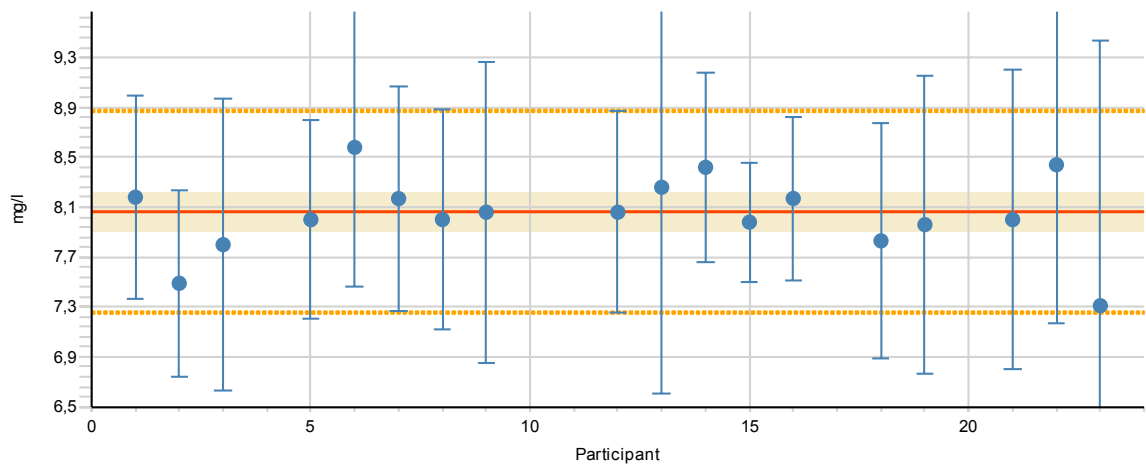


Measurand KMnO₄ Sample U2P

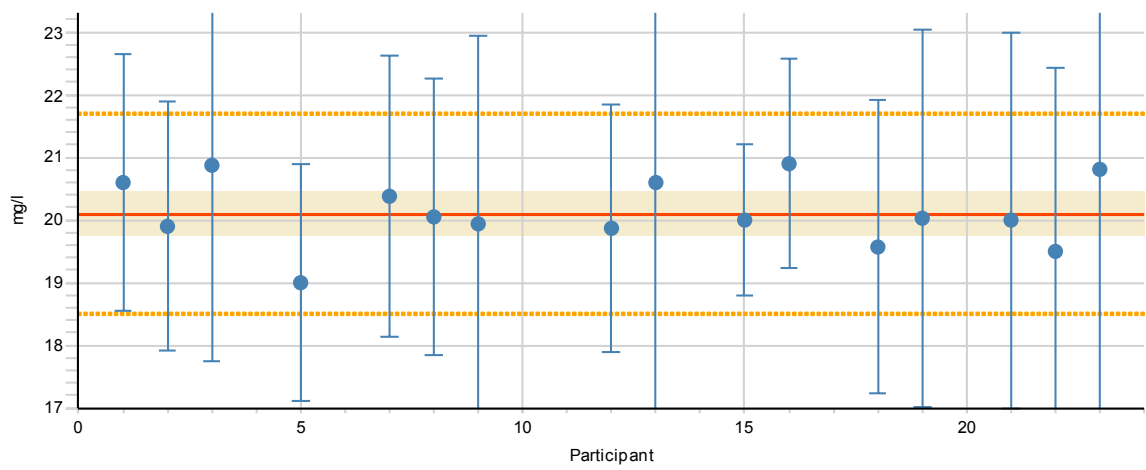


APPENDIX 9 (4/6)

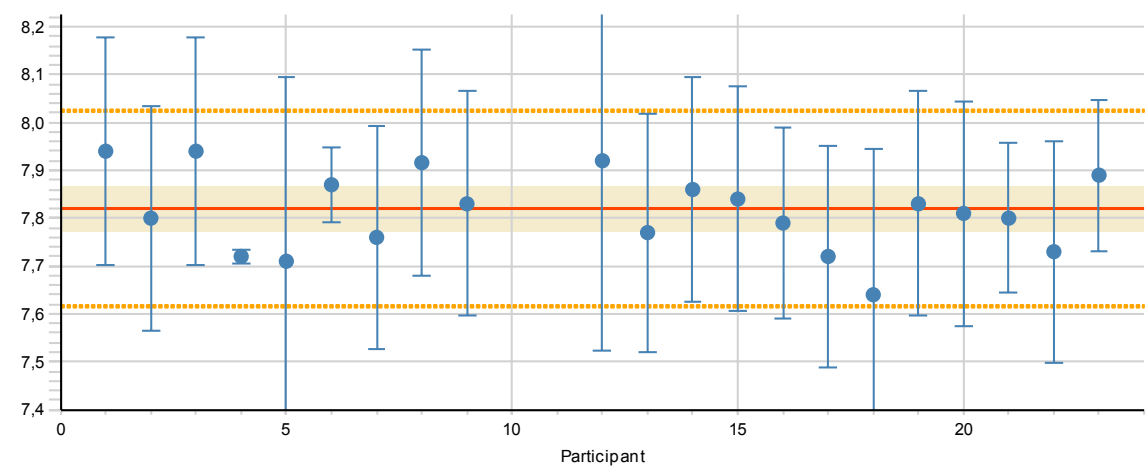
Measurand NO₃ Sample U1N



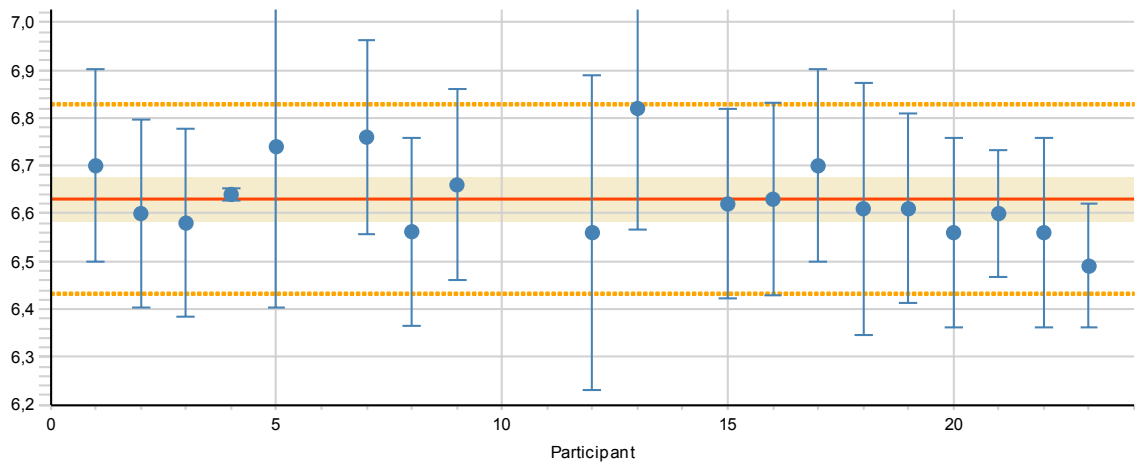
Measurand NO₃ Sample U2N



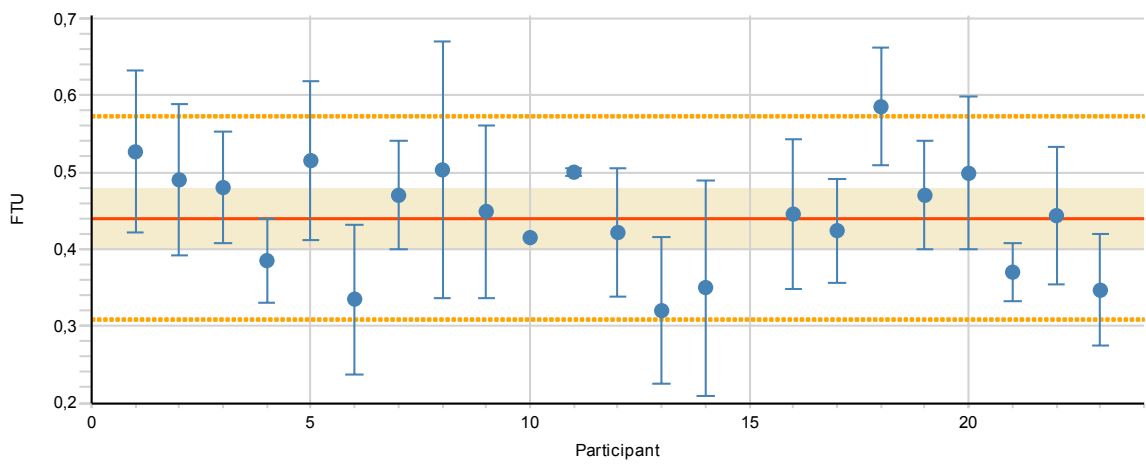
Measurand pH Sample U1H



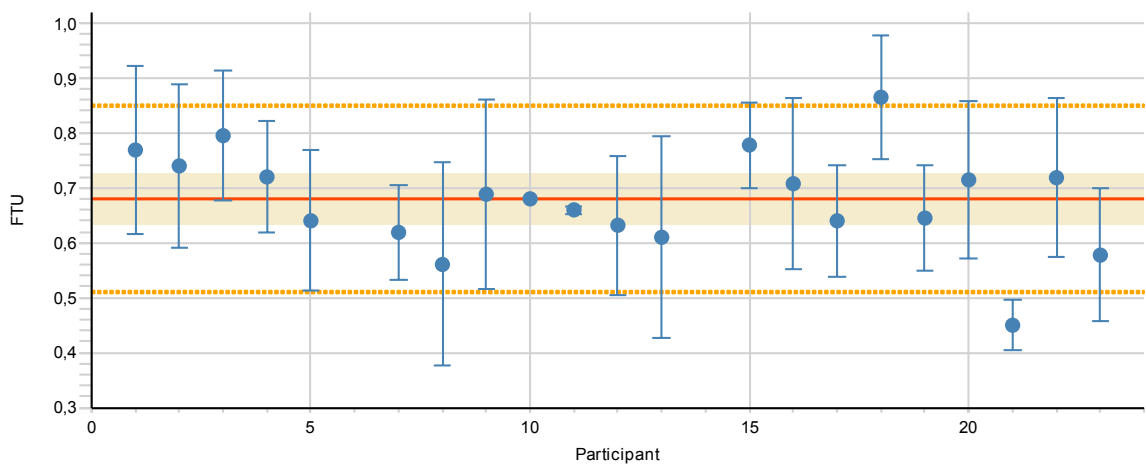
Measurand pH Sample U2H



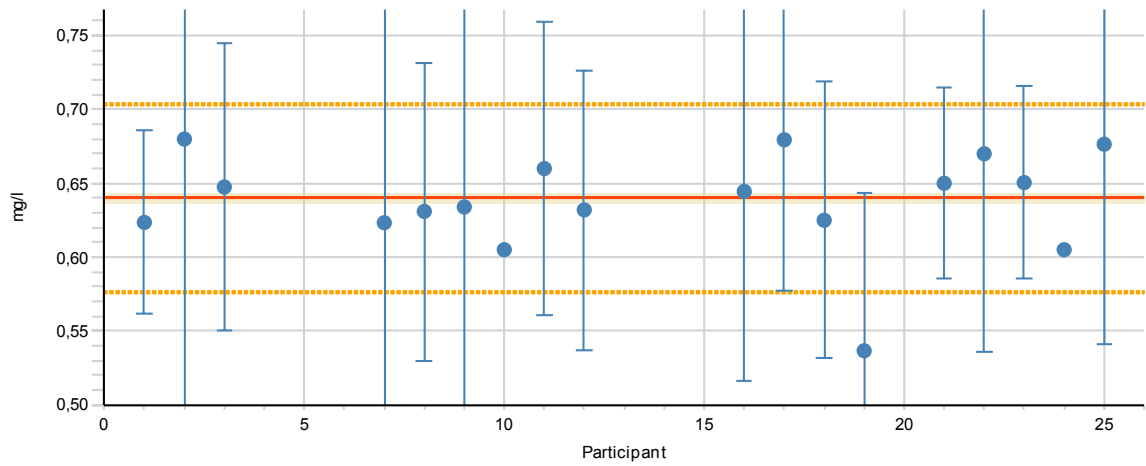
Measurand Turbidity Sample U1S



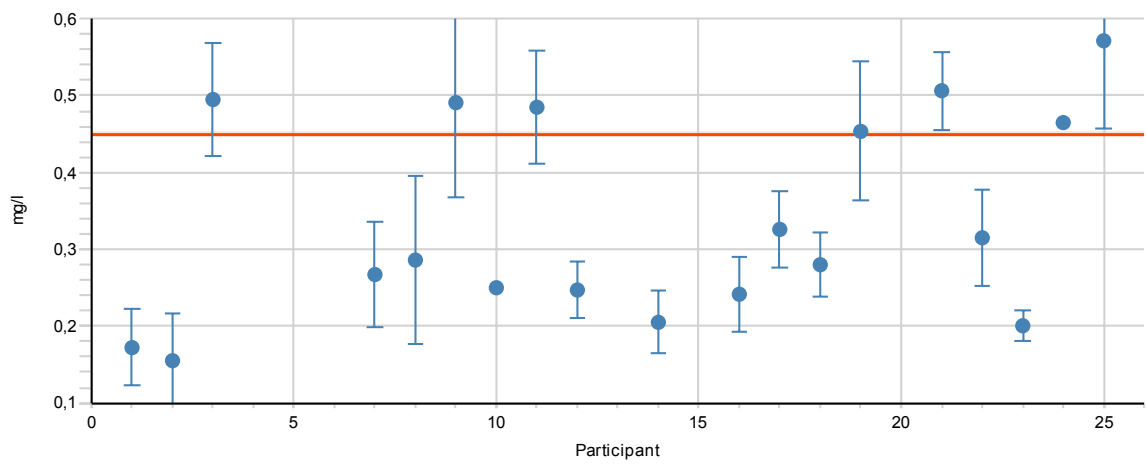
Measurand Turbidity Sample U2S



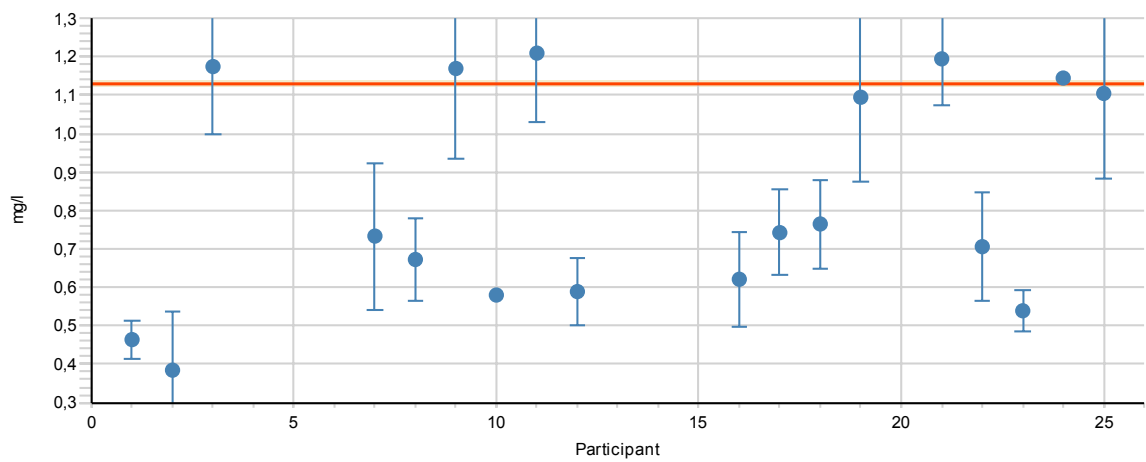
Measurand Urea Sample A1U



Measurand Urea Sample U2U



Measurand Urea Sample U3U



APPENDIX 10: Summary of the z scores

| Measurand | Sample | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | 21 | 22 | 23 | % | |
|------------------------|--------|-----|-----|-----|-----|----|----|-----|-----|-----|----|----|-----|----|----|-----|-----|-----|----|----|-----|----|----|-----|------|------|
| Cl ₂ _comb | U1K | S | S | S | S | S | S | S | S | S | S | S | S | S | U | u | S | S | S | S | S | S | S | S | S | 90,5 |
| | U2K | S | S | S | S | S | S | S | S | S | S | S | S | S | Q | S | S | S | S | S | S | S | S | S | S | 94,7 |
| Cl ₂ _free | U1K | S | S | S | S | S | S | S | S | S | Q | S | S | q | U | S | S | S | S | S | S | S | S | S | S | 86,4 |
| | U2K | S | S | S | S | Q | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | 95,0 |
| Cl ₂ _total | U1K | S | S | S | S | S | S | S | S | S | S | S | S | S | Q | S | S | S | S | S | S | S | S | S | S | 95,2 |
| | U2K | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | 100 |
| KMnO ₄ | U1P | Q | S | S | S | S | u | S | S | S | S | U | S | S | S | S | S | S | S | S | S | S | S | S | q | 81,0 |
| | U2P | U | S | S | S | S | S | S | S | S | S | U | S | S | S | S | S | S | S | S | S | S | S | S | q | 84,2 |
| NO ₃ | U1N | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | 100 |
| | U2N | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | 100 |
| pH | U1H | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | 100 |
| | U2H | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | 100 |
| Turbidity | U1S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | Q | S | S | S | S | S | S | 95,5 |
| | U2S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | Q | S | S | q | S | S | S | 90,5 |
| Urea | A1U | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | u | S | S | S | S | S | S | 94,4 |
| | U2U | | | | | | | | | | | | | | | | | | | | | | | | | |
| | U3U | | | | | | | | | | | | | | | | | | | | | | | | | |
| % | | 87 | 100 | 100 | 100 | 93 | 86 | 100 | 100 | 100 | 89 | 71 | 100 | 71 | 71 | 100 | 100 | 100 | 87 | 93 | 100 | 93 | 87 | 100 | | |
| accredited | | 15 | 15 | 15 | 8 | 8 | 6 | 15 | 15 | 15 | 9 | 7 | 15 | 14 | 7 | 7 | 15 | 13 | 15 | 15 | 10 | 8 | 15 | 15 | | |
| Measurand | Sample | 24 | 25 | 26 | 27 | 28 | 29 | 30 | 31 | 32 | 33 | 34 | 35 | 36 | 37 | 38 | 39 | 40 | 41 | 42 | 43 | 44 | 45 | 46 | % | |
| Cl ₂ _comb | U1K | | | | | | | | | | | | | | | | | | | | | | | | 90,5 | |
| | U2K | | | | | | | | | | | | | | | | | | | | | | | | | 94,7 |
| Cl ₂ _free | U1K | | | | | | | | | | | | | | | | | | | | | | | | | 86,4 |
| | U2K | | | | | | | | | | | | | | | | | | | | | | | | | 95,0 |
| Cl ₂ _total | U1K | | | | | | | | | | | | | | | | | | | | | | | | | 95,2 |
| | U2K | | | | | | | | | | | | | | | | | | | | | | | | | 100 |
| KMnO ₄ | U1P | | | | | | | | | | | | | | | | | | | | | | | | | 81,0 |
| | U2P | | | | | | | | | | | | | | | | | | | | | | | | | 84,2 |
| NO ₃ | U1N | | | | | | | | | | | | | | | | | | | | | | | | | 100 |
| | U2N | | | | | | | | | | | | | | | | | | | | | | | | | 100 |
| pH | U1H | | | | | | | | | | | | | | | | | | | | | | | | | 100 |
| | U2H | | | | | | | | | | | | | | | | | | | | | | | | | 100 |
| Turbidity | U1S | | | | | | | | | | | | | | | | | | | | | | | | | 95,5 |
| | U2S | | | | | | | | | | | | | | | | | | | | | | | | | 90,5 |
| Urea | A1U | S | S | | | | | | | | | | | | | | | | | | | | | | | 94,4 |
| | U2U | | | | | | | | | | | | | | | | | | | | | | | | | |
| | U3U | | | | | | | | | | | | | | | | | | | | | | | | | |
| % | | 100 | 100 | | | | | | | | | | | | | | | | | | | | | | | |
| accredited | | | | | | | | | | | | | | | | | | | | | | | | | | |

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

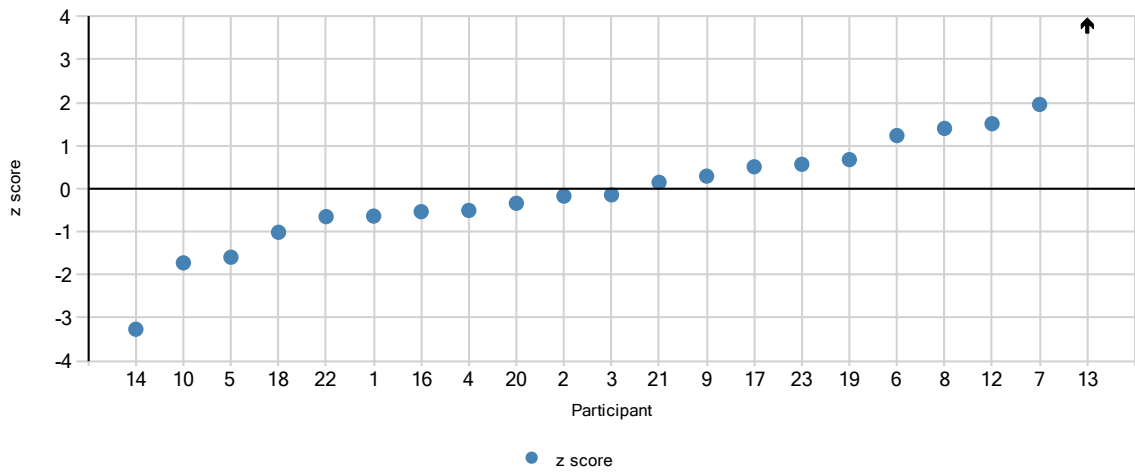
U - unsatisfactory ($z \geq 3$), and **u** - unsatisfactory ($z \leq -3$), respectively

bold - accredited, **italics** - non-accredited, **normal** - other, **%** - percentage of satisfactory results

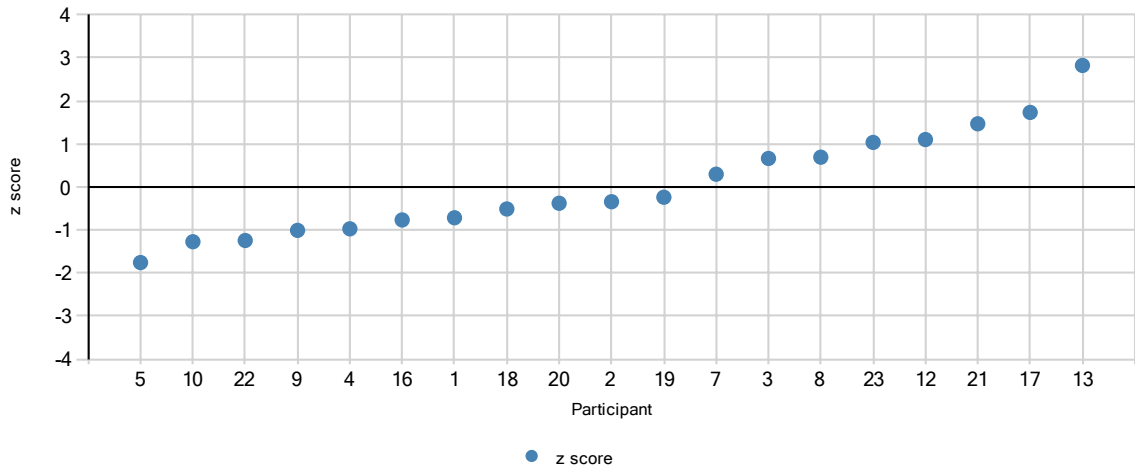
Totally satisfactory, % in all: 94 % in accredited: 94 % in non-accredited: 95

APPENDIX 11: z scores in ascending order

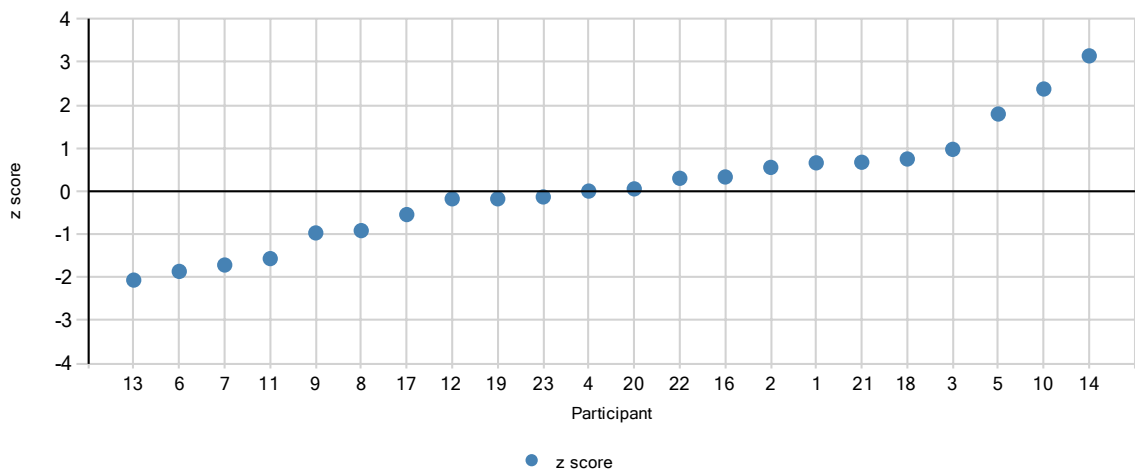
Measurand Cl₂_comb Sample U1K



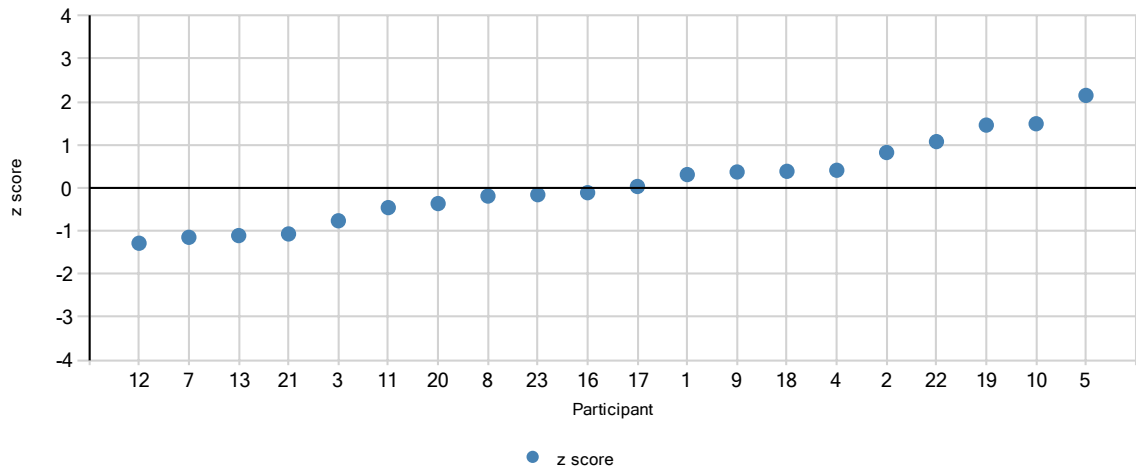
Measurand Cl₂_comb Sample U2K



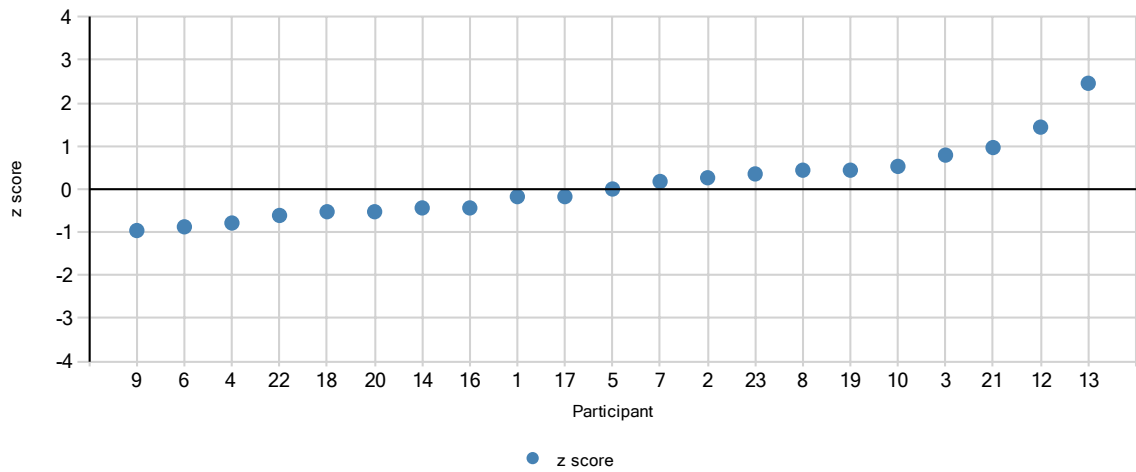
Measurand Cl₂_free Sample U1K



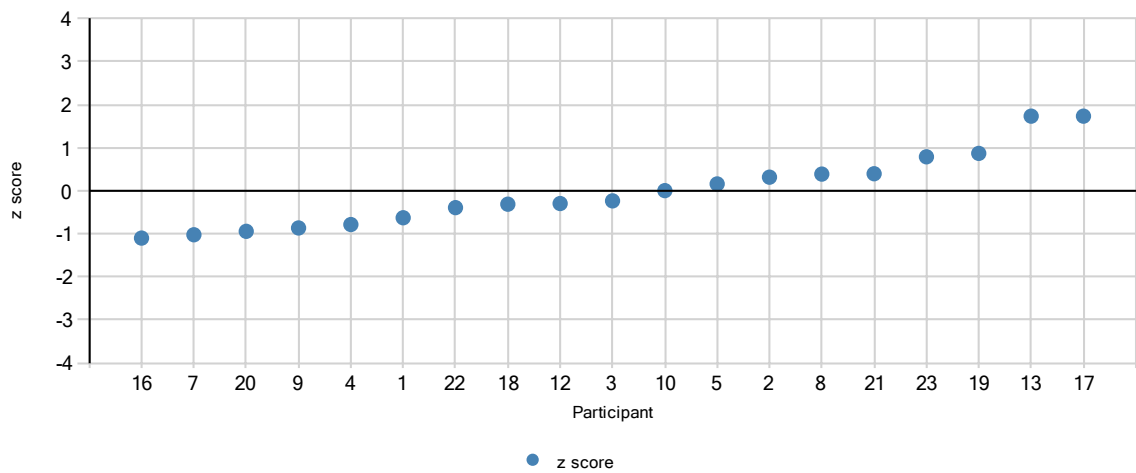
Measurand Cl₂_free Sample U2K



Measurand Cl₂_total Sample U1K

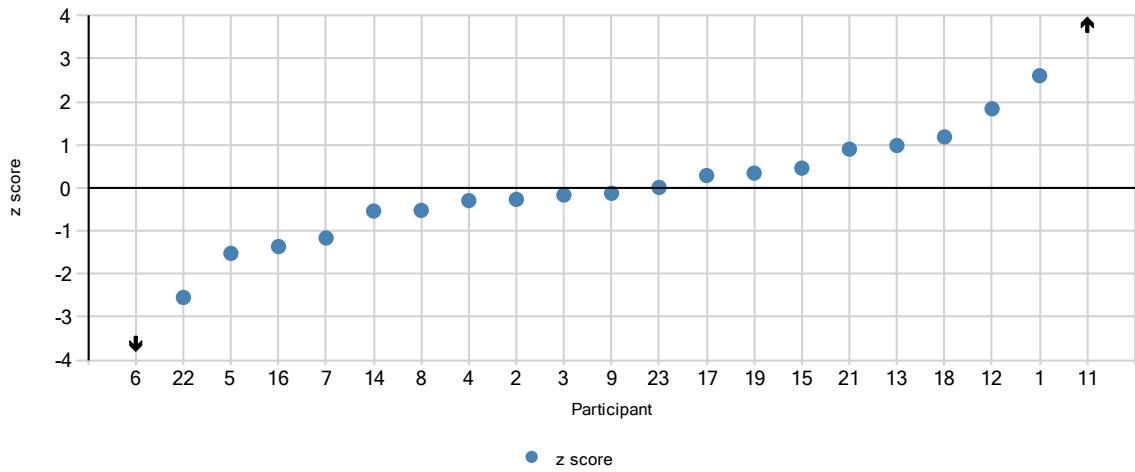


Measurand Cl₂_total Sample U2K

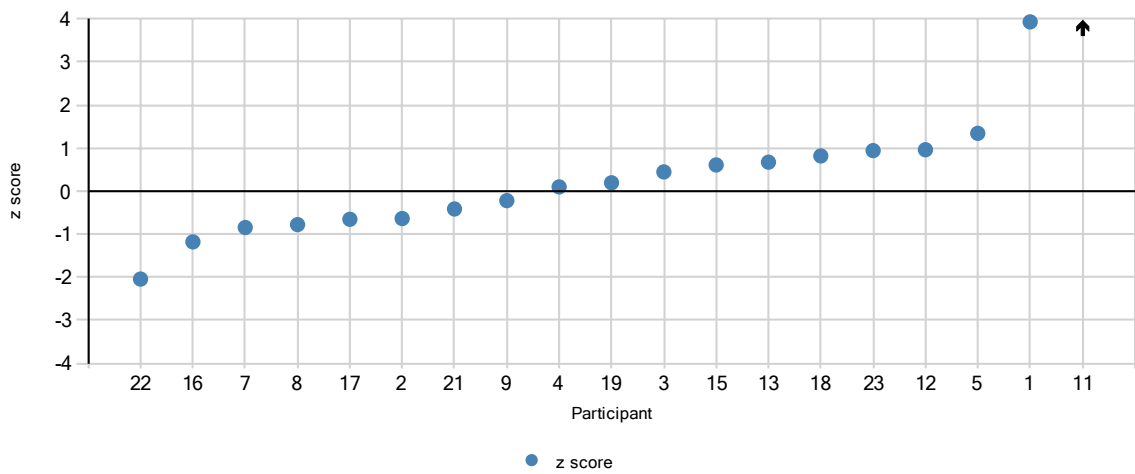


APPENDIX 11 (3/5)

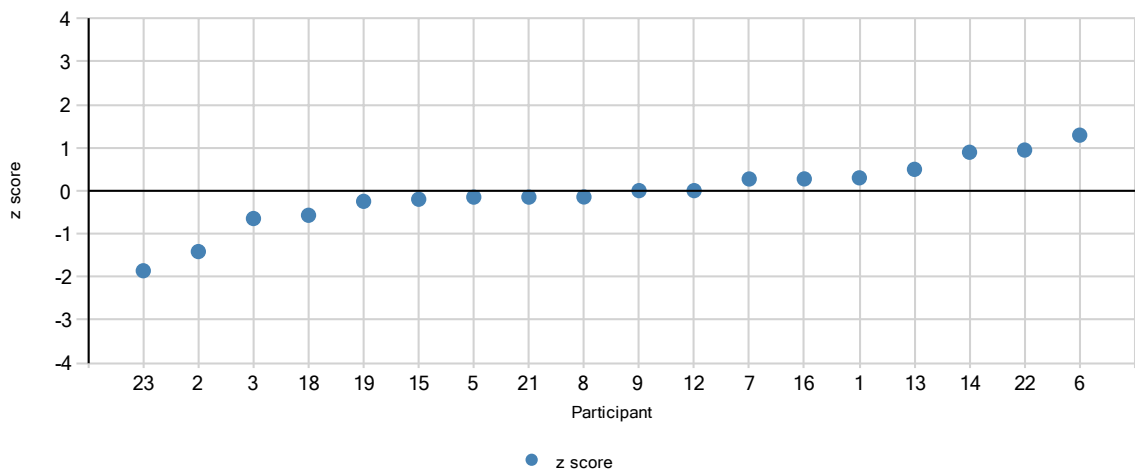
Measurand KMnO_4 Sample U1P



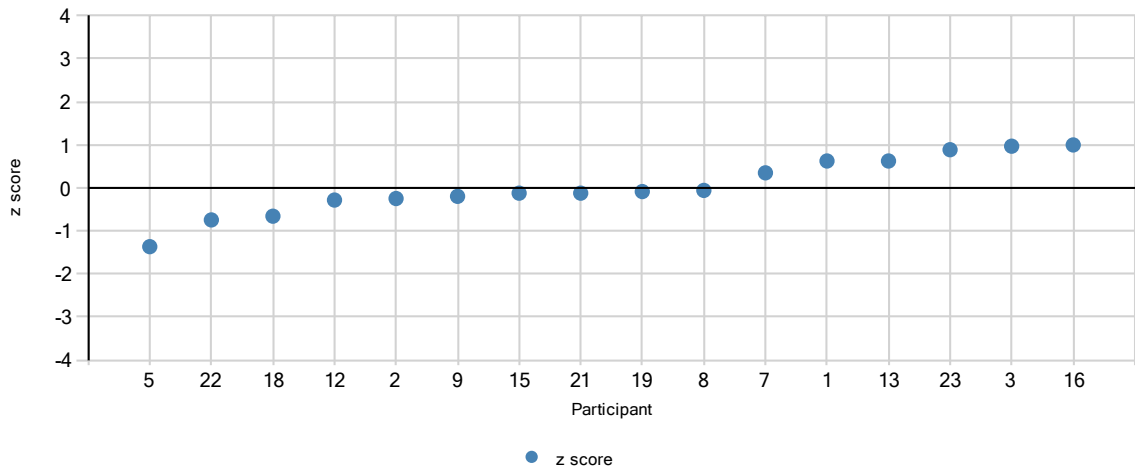
Measurand KMnO_4 Sample U2P



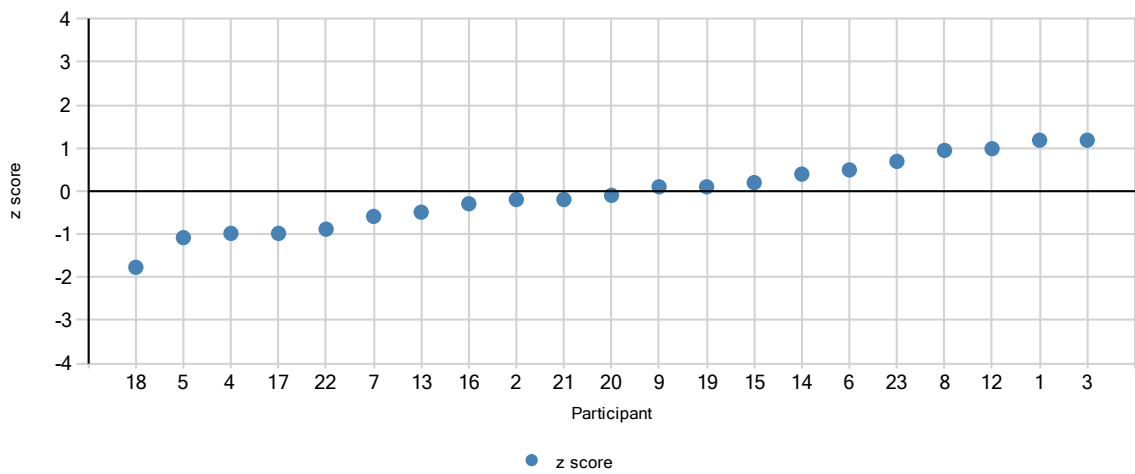
Measurand NO_3 Sample U1N



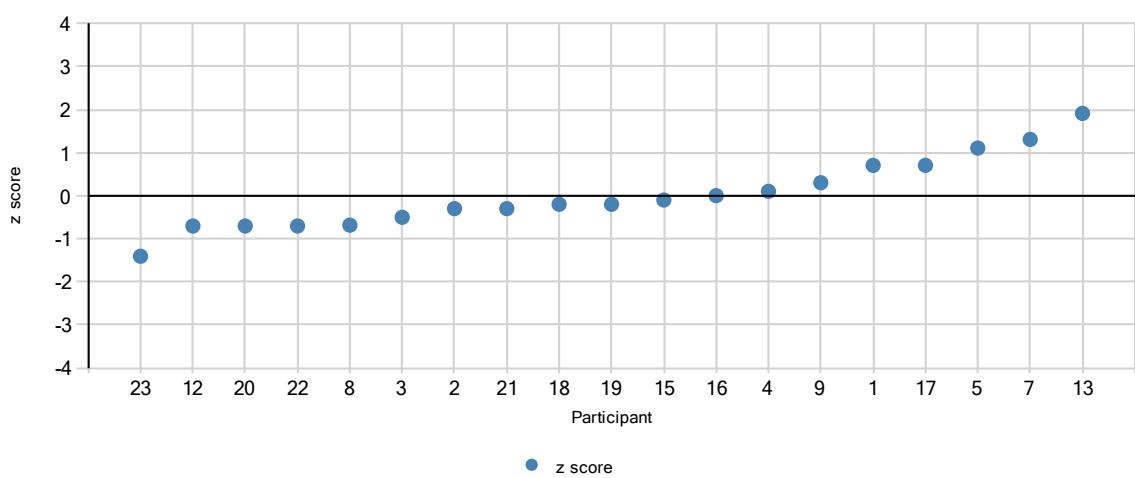
Measurand NO₃ Sample U2N



Measurand pH Sample U1H

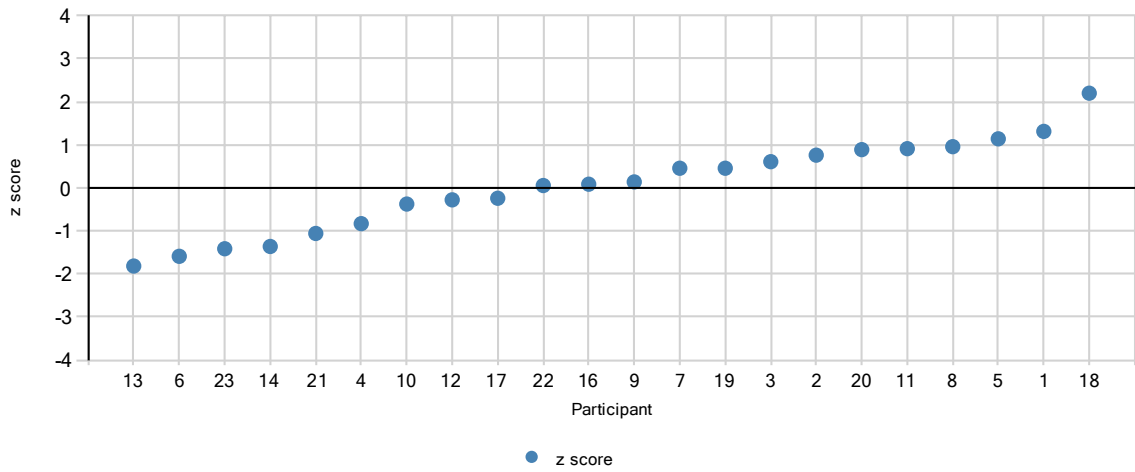


Measurand pH Sample U2H

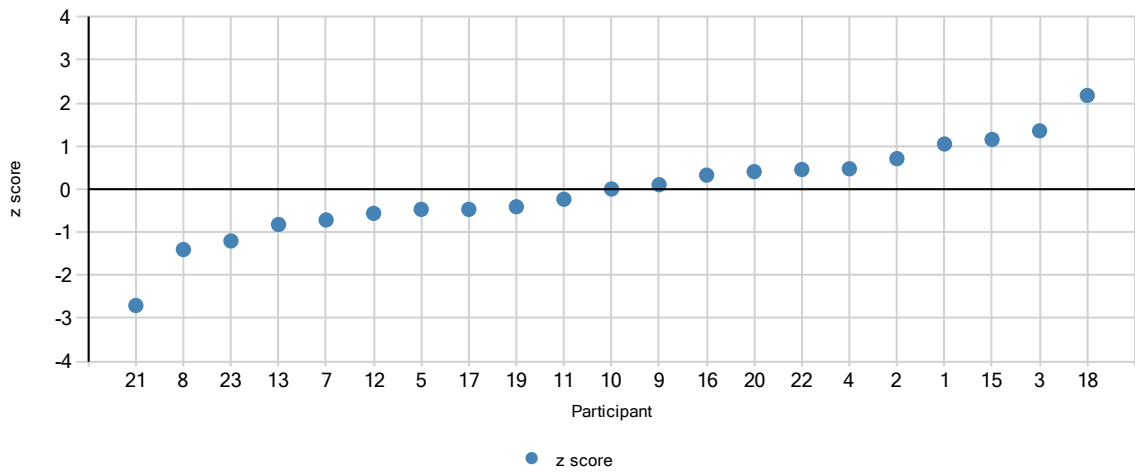


APPENDIX 11 (5/5)

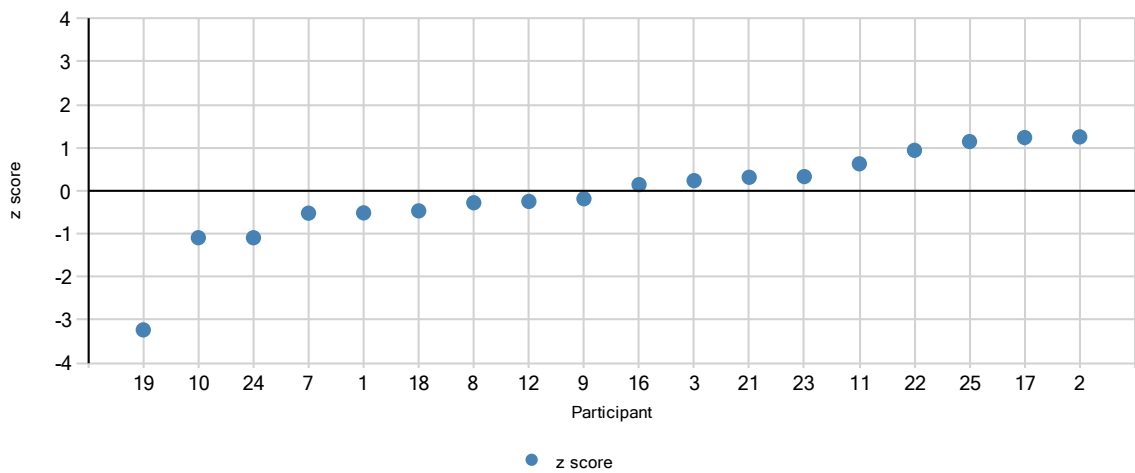
Measurand Turbidity Sample U1S



Measurand Turbidity Sample U2S

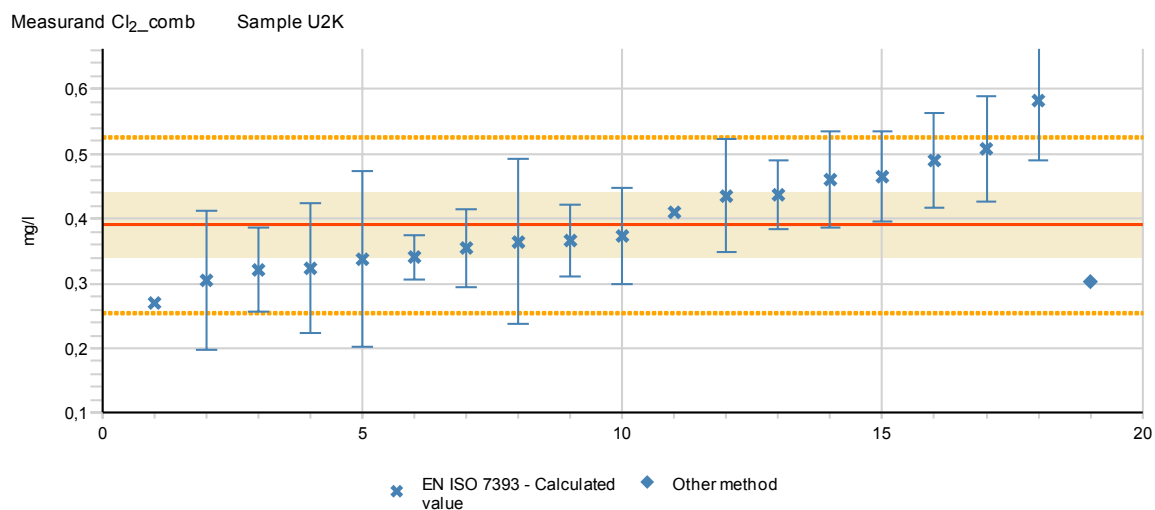
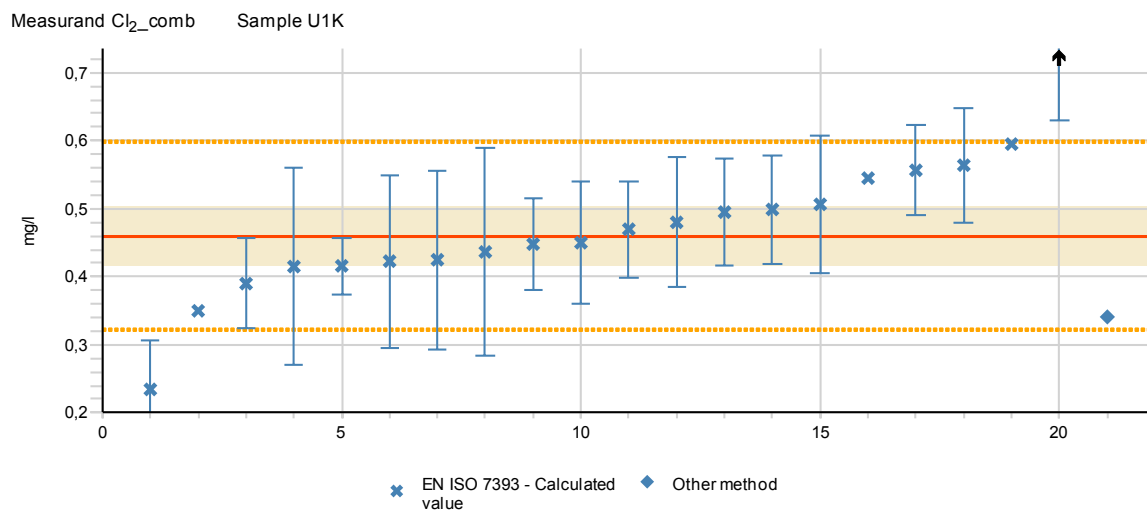


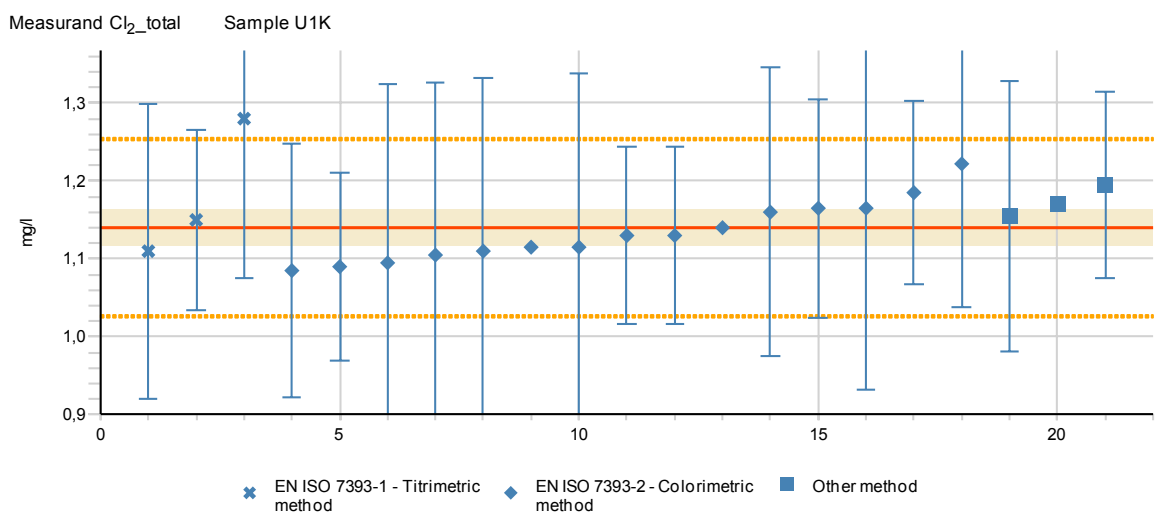
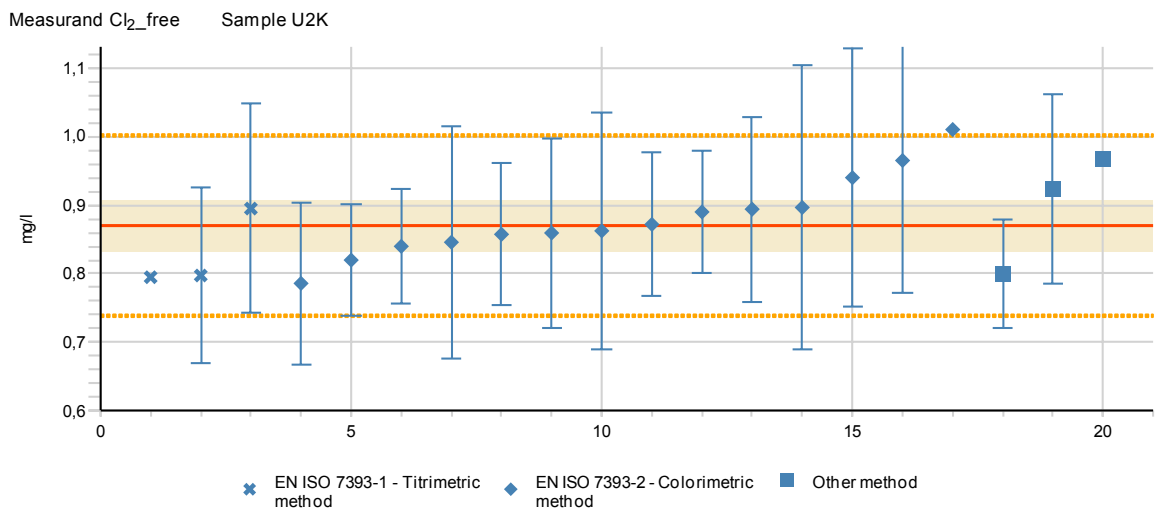
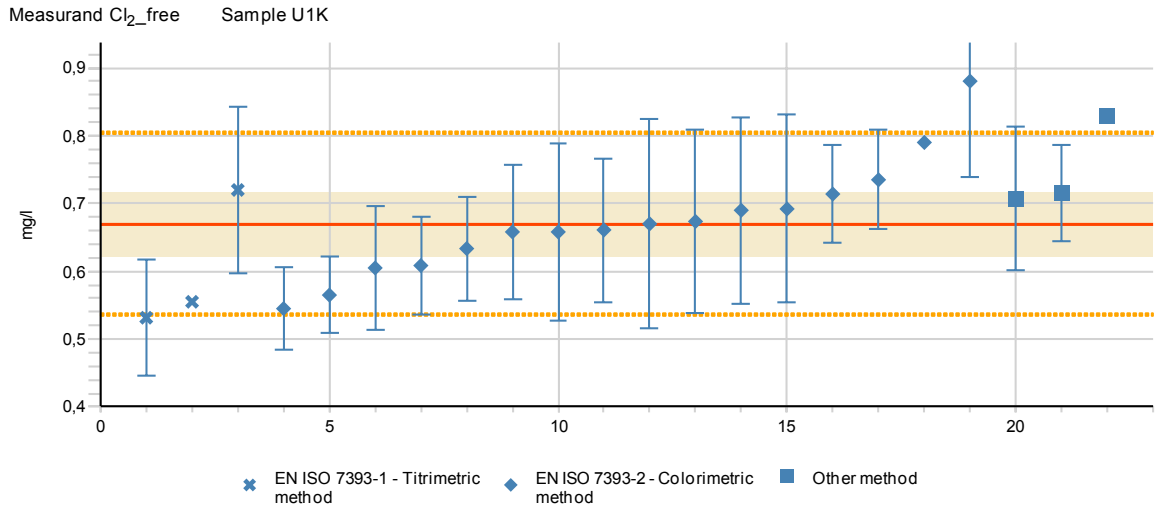
Measurand Urea Sample A1U



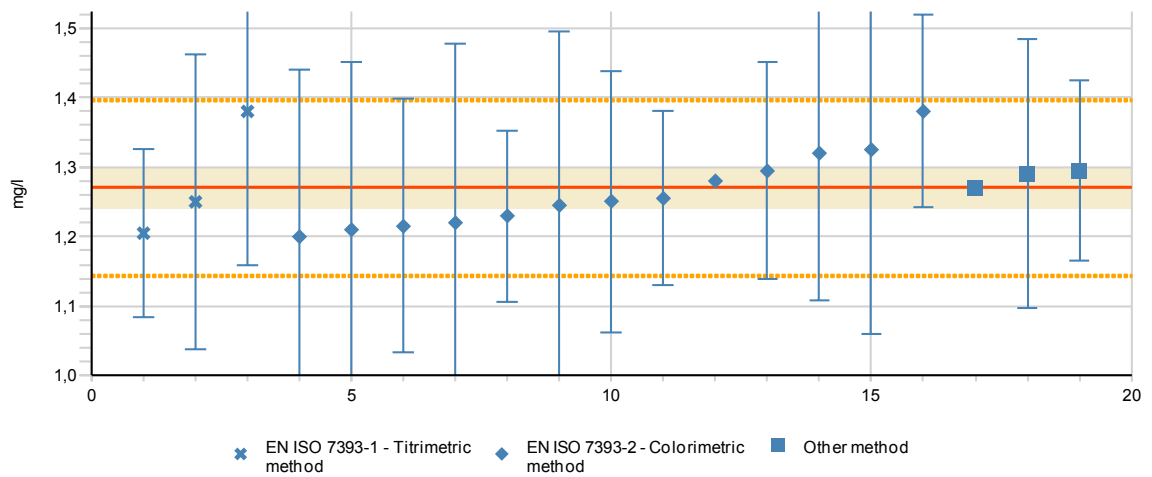
APPENDIX 12: Results grouped according to the methods

The explanations for the figures are described in the Appendix 9.

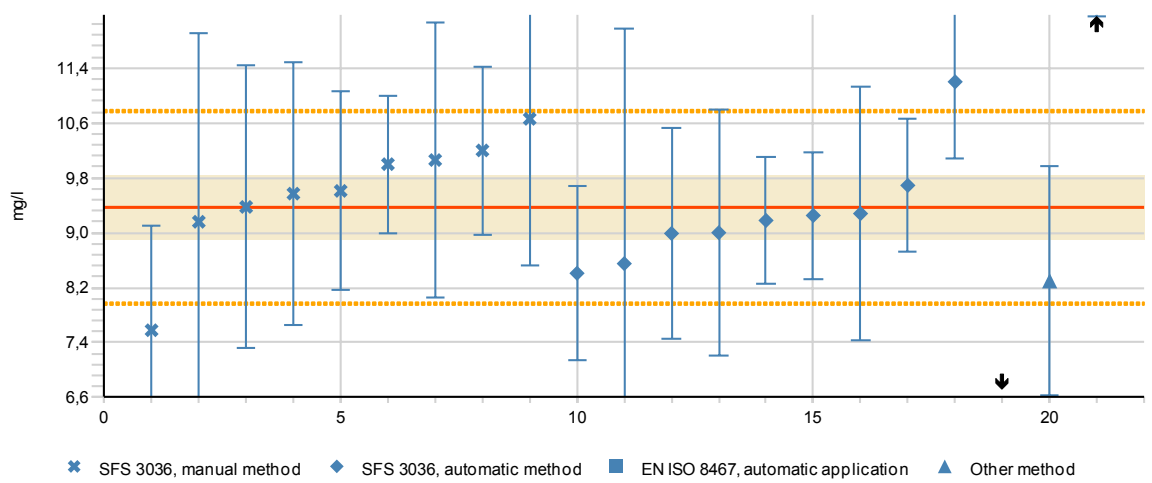




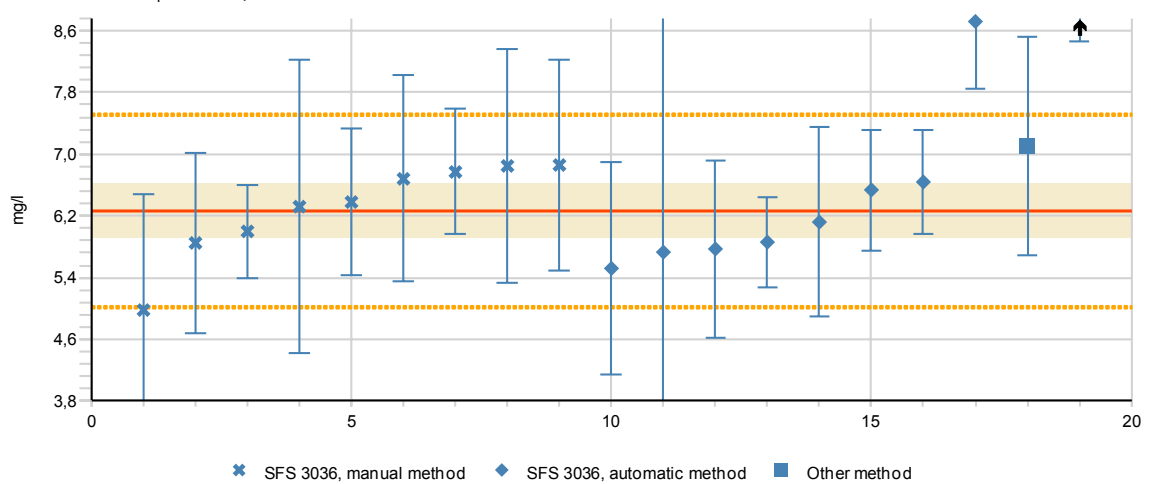
Measurand Cl₂_total Sample U2K

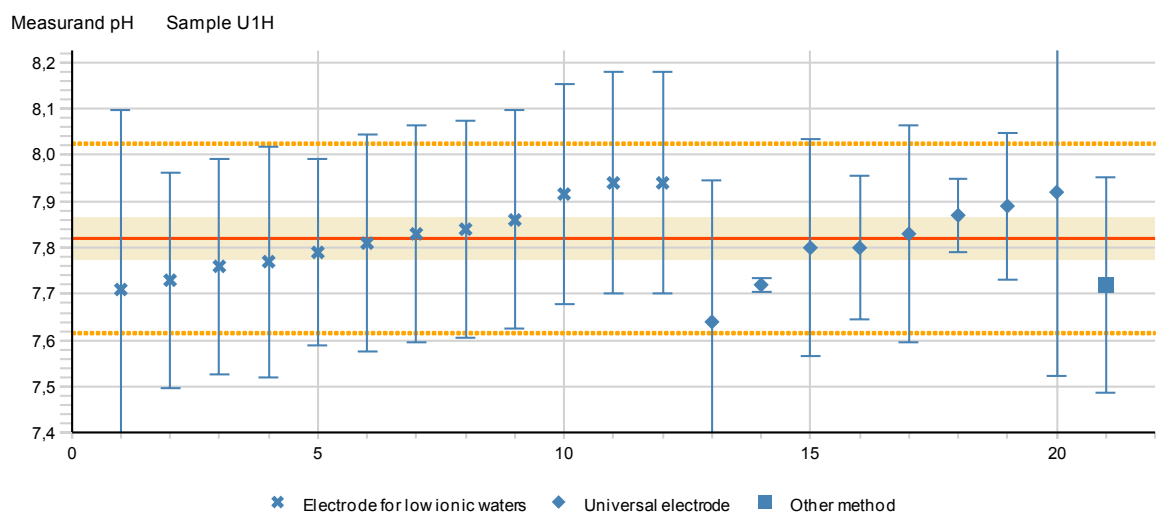
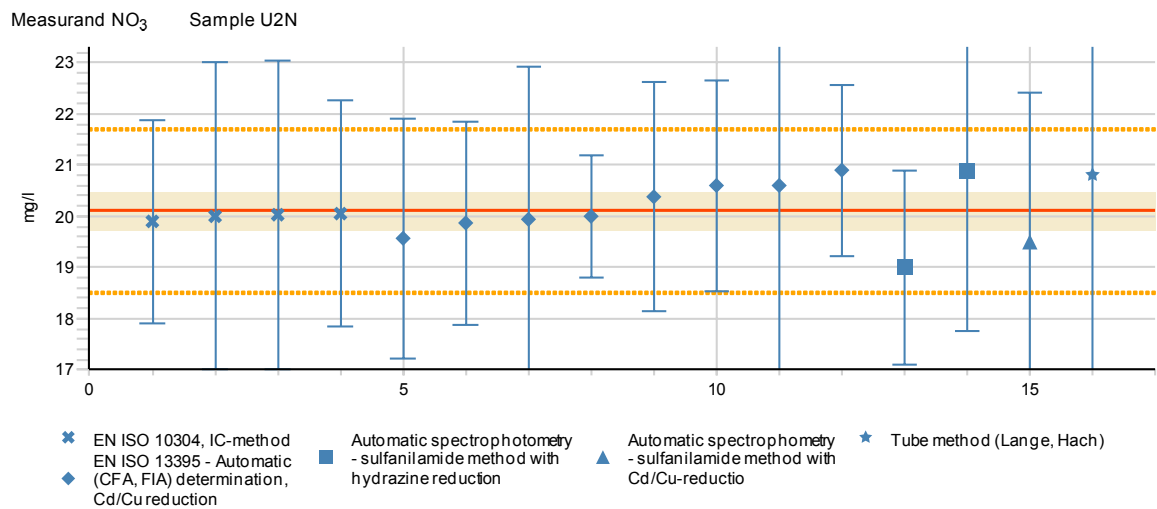
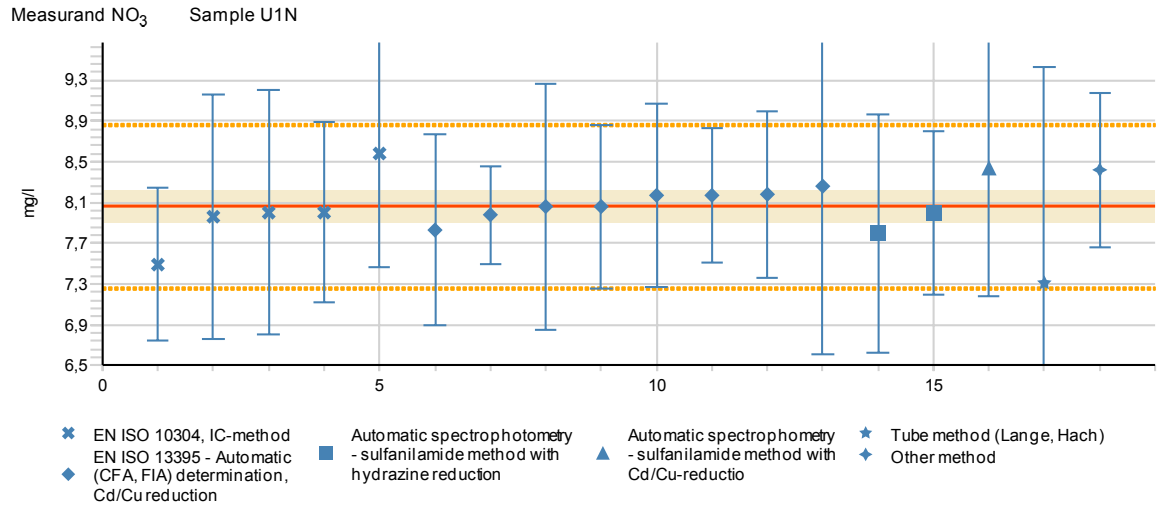


Measurand KMnO₄ Sample U1P

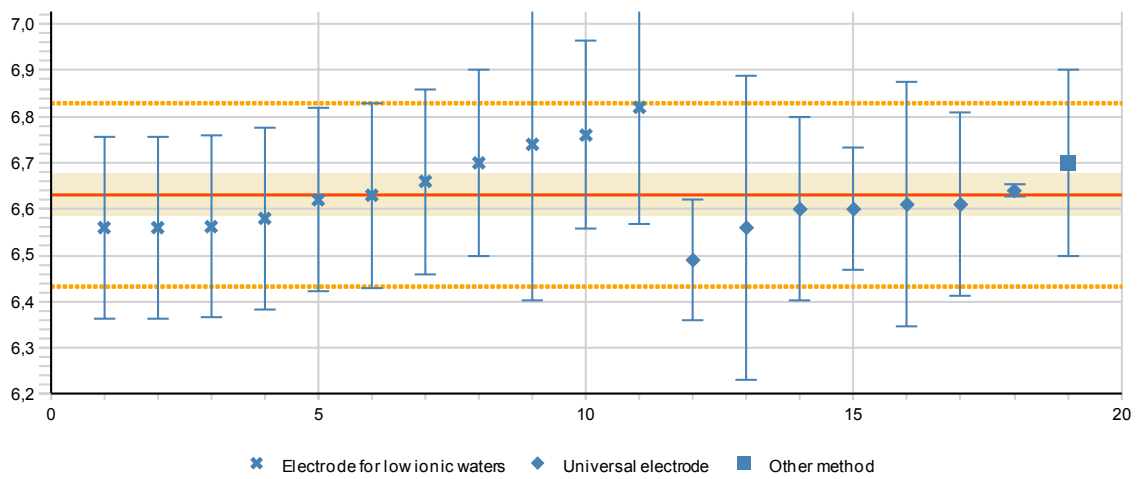


Measurand KMnO₄ Sample U2P

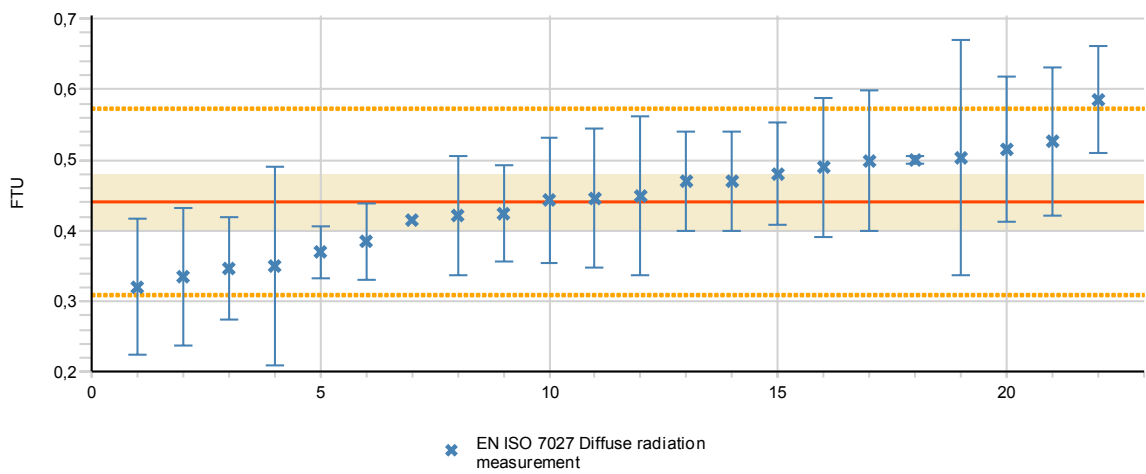




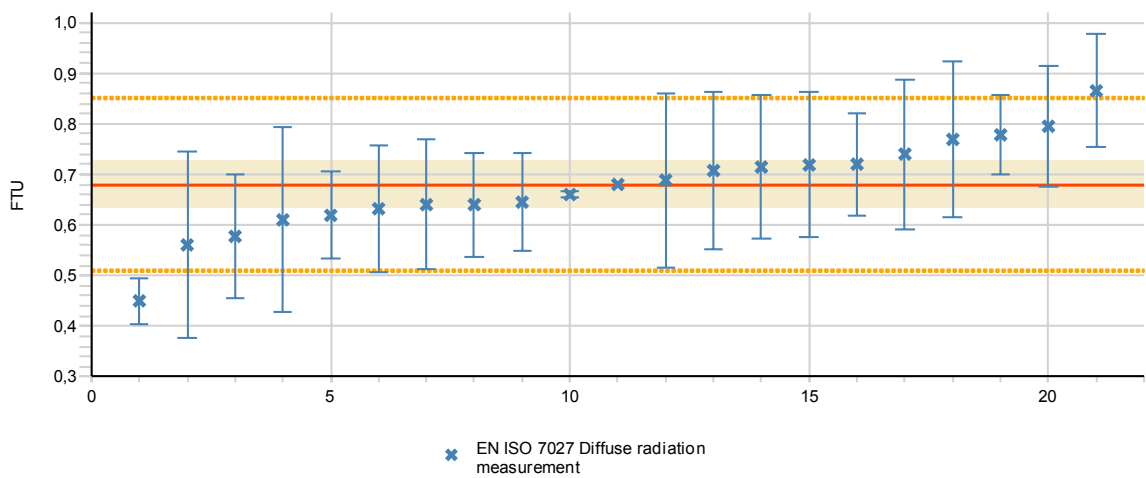
Measurand pH Sample U2H



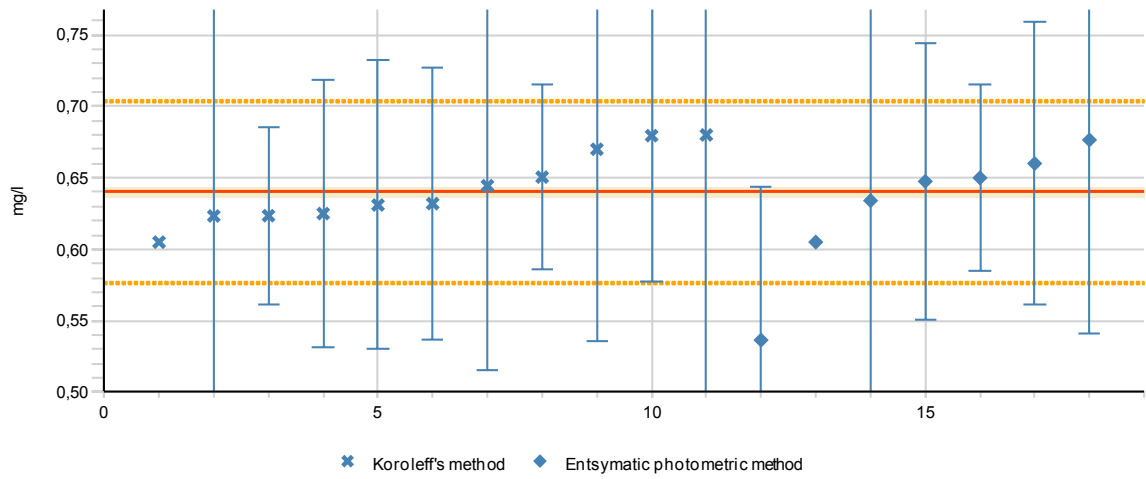
Measurand Turbidity Sample U1S



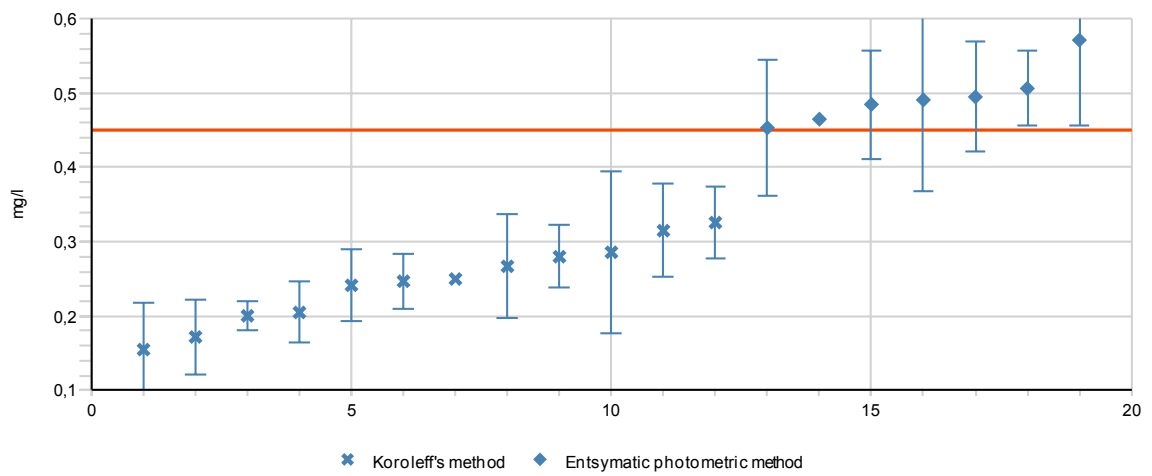
Measurand Turbidity Sample U2S



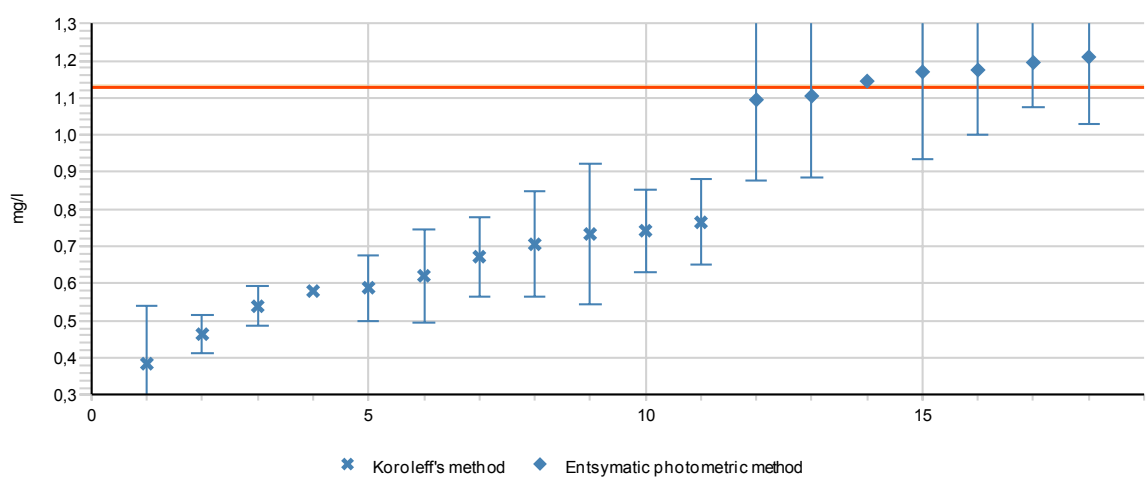
Measurand Urea Sample A1U



Measurand Urea Sample U2U

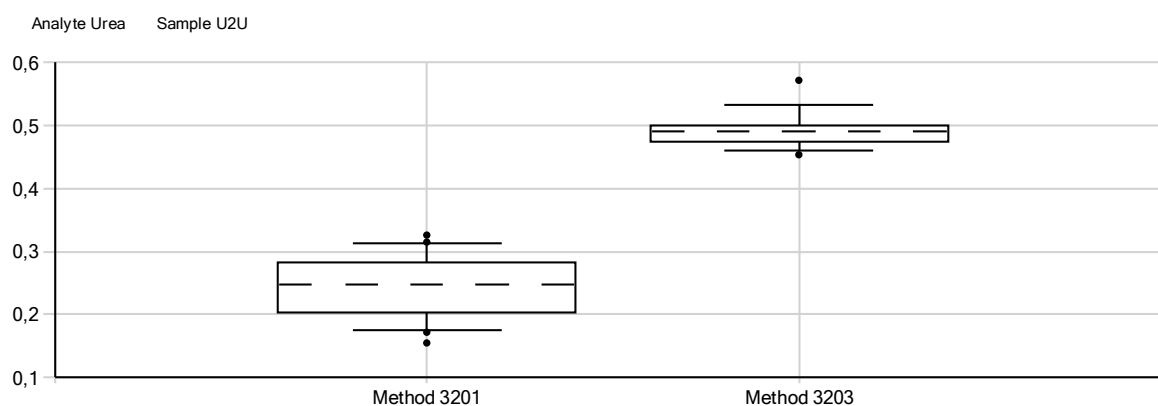


Measurand Urea Sample U3U



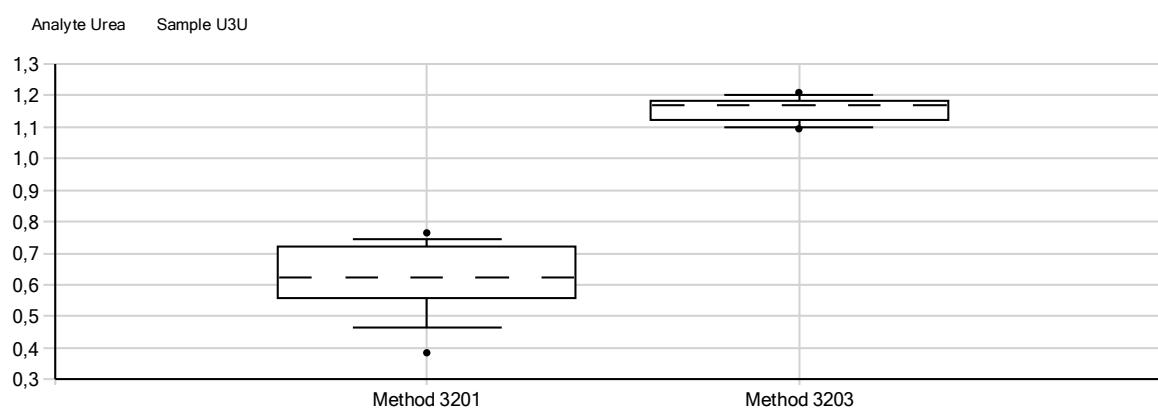
APPENDIX 13: Significant differences in the results reported using different methods

Boxplot figures: In the box the upper and lower limit included 50 % of the results. The dashed vertical line in the middle of the box is the median of the results. The vertical lines above and under the box describe the limits of 80 % of the results. The black dots describe the highest and smallest results within the center 90 % of the results.



| Method | n | Mean (mg/l) | SD (mg/l) |
|---|----|-------------|-----------|
| Method 3201:the Koroleff method | 12 | 0.25 | 0.05 |
| Method 3203: the enzymatic photometric method | 7 | 0.50 | 0.04 |

n = number of results; SD = standard deviation

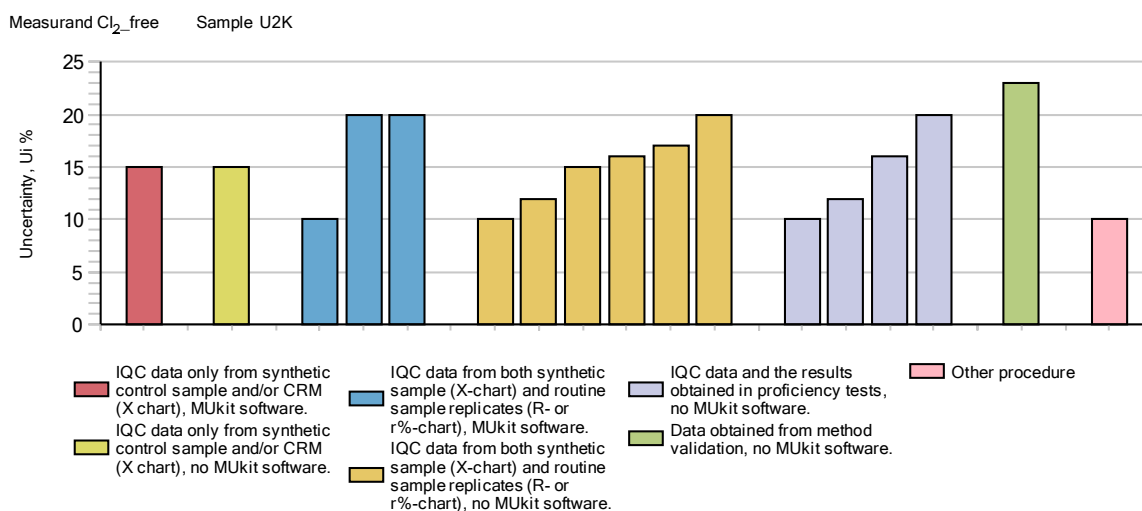
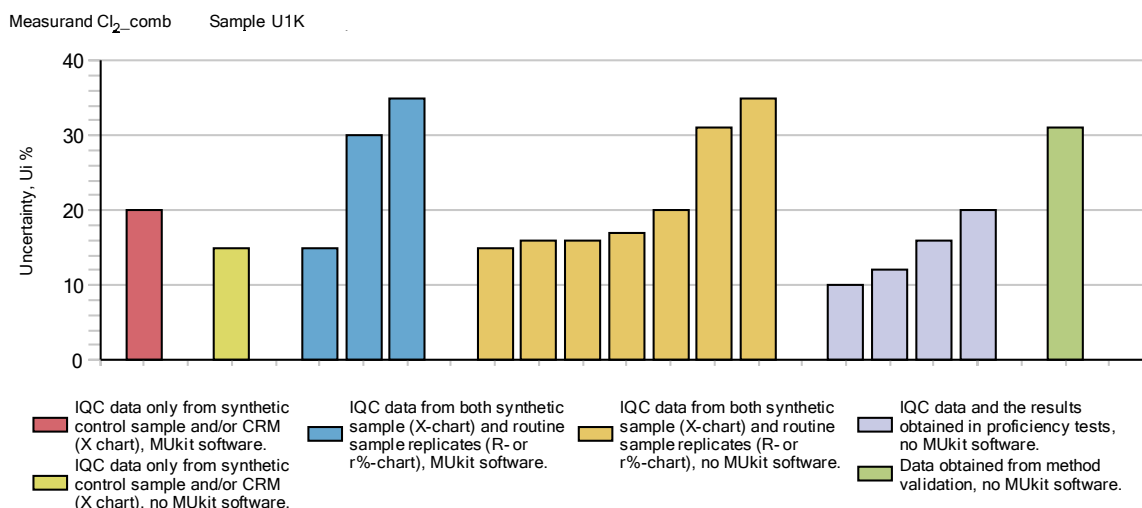


| Method | n | Mean (mg/l) | SD (mg/l) |
|---|----|-------------|-----------|
| Method 3201:the Koroleff method | 11 | 0.62 | 0.12 |
| Method 3203: the enzymatic photometric method | 7 | 1.16 | 0.04 |

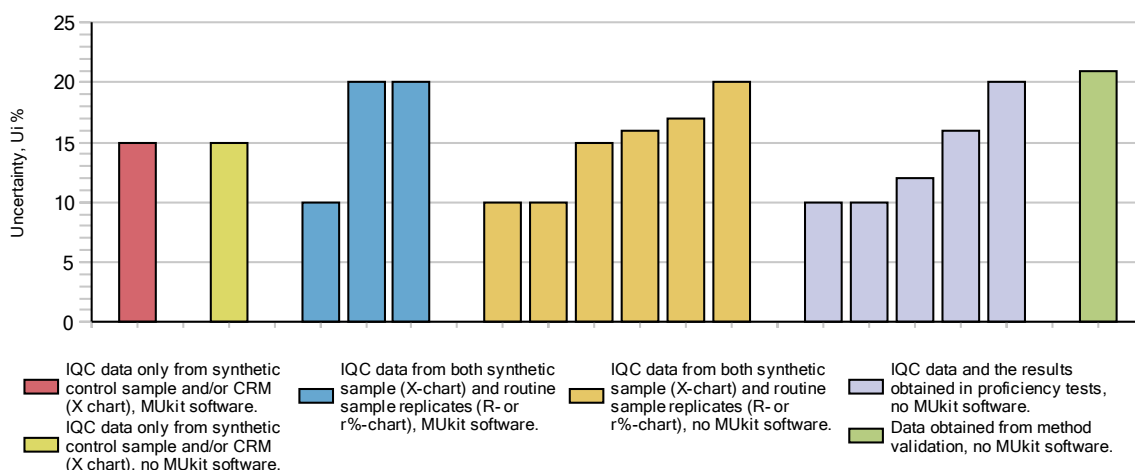
n = number of results; SD = standard deviation

APPENDIX 14: Examples of measurement uncertainties reported by the participants

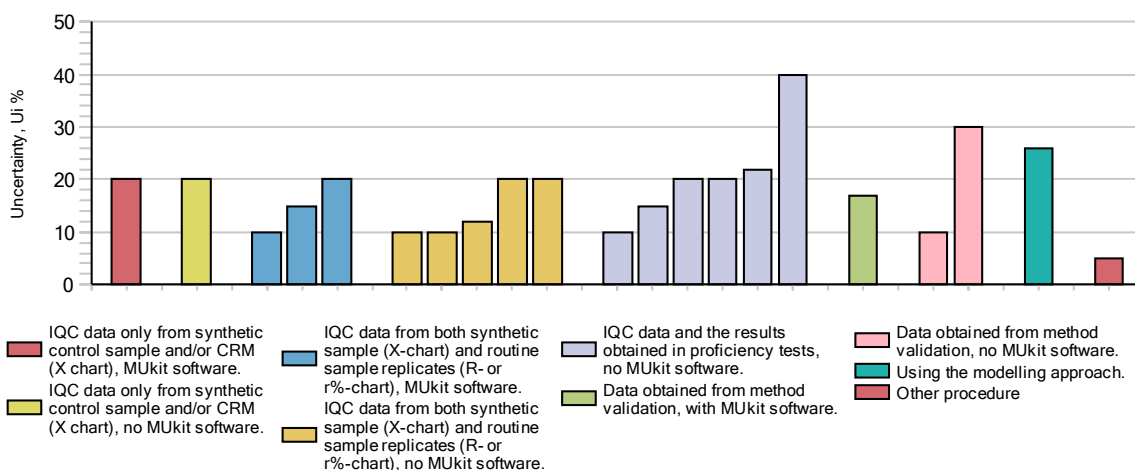
In figures, the presented expanded measurement uncertainties are grouped according to the method of estimation at 95 % confidence level ($k=2$). The expanded uncertainties were estimated mainly by using the internal quality control (IQC) data. The used procedures in figures below are distinguished e.g. between using or not using the MUKIT software for uncertainty estimation [8, 9] or using a modelling approach based [10, 11].



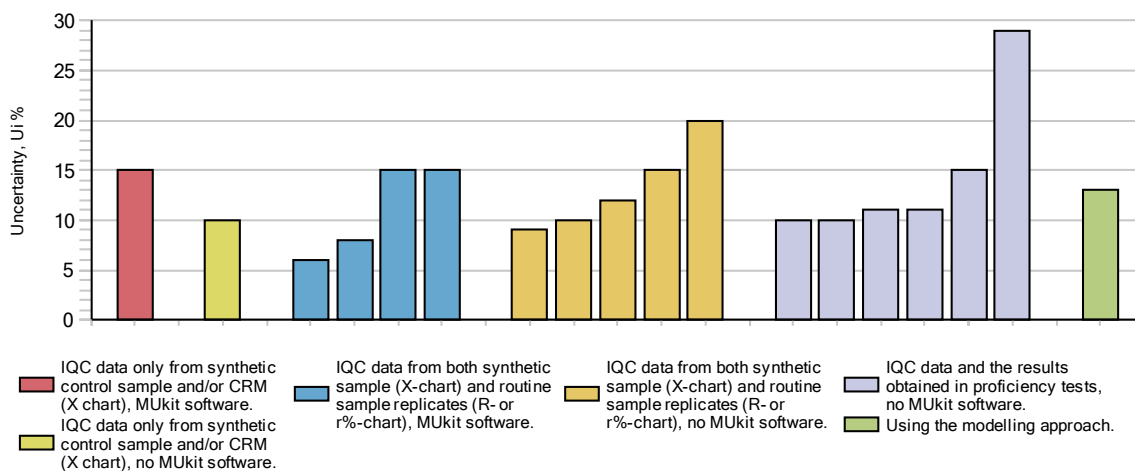
Measurand Cl₂_total Sample U2K



Measurand KMnO₄ Sample U1P

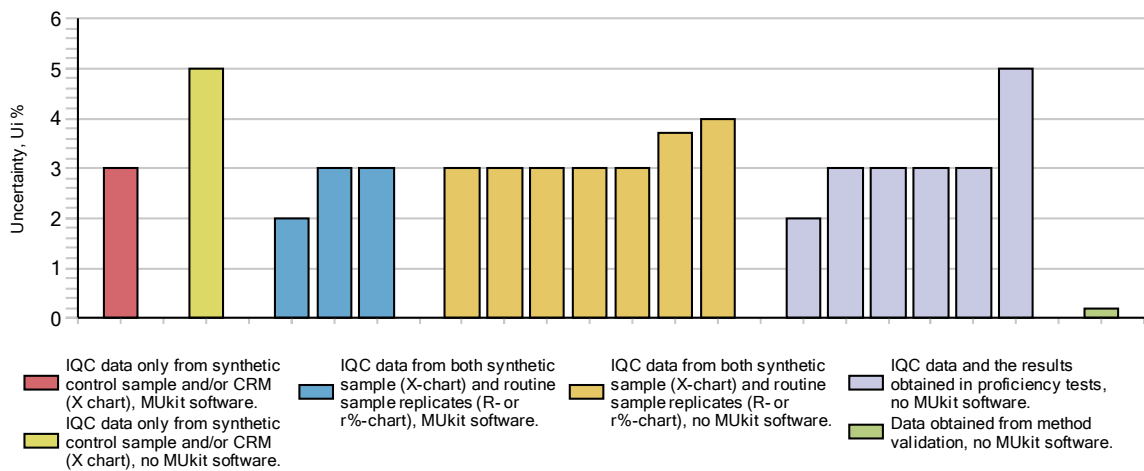


Measurand NO₃ Sample U1N

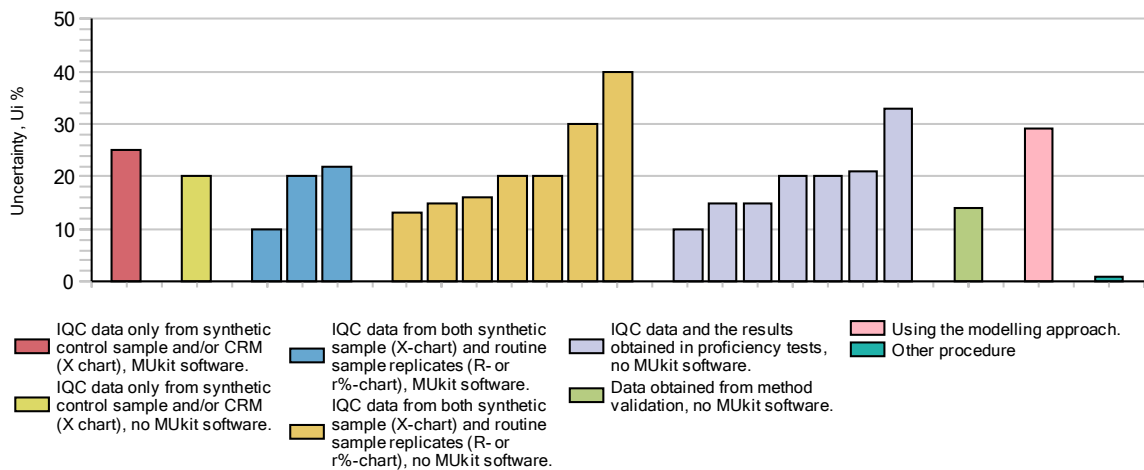


APPENDIX 14 (3/3)

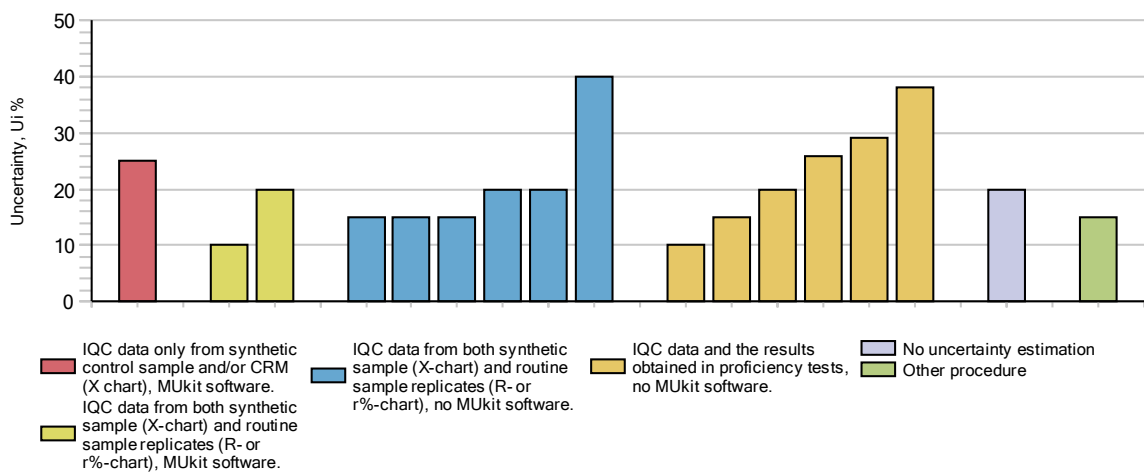
Measurand pH Sample U2H



Measurand Turbidity Sample U1S



Measurand Urea Sample U2U





ISBN 978-952-11-4566-7 (PDF)

ISSN 1796-1726 (online)