Reports of the Finnish Environment Institute 1 | 2023

Proficiency Test 09/2022

Drinking water analyses

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Abstract

Proficiency Test 09/2022: Drinking water analyses
Proftest Syke carried out the proficiency test (PT) for analyses of synthetic samples and drinking water as well as raw water samples in September 2022. In total, there were 37 participants in the PT. Either the calculated concentration or the robust mean of the reported results was used as the assigned values for the measurands. The overall performance of the participants was evaluated by using z scores. In this PT 86 % of the results were satisfactory when total deviation of 0.2 pH units for pH values and 5–20 % for the other measurands was accepted from the assigned value. Warm thanks to all participants in this proficiency test!

Keywords: water analysis, Ca, Cl, COD_{Mn}, conductivity, F, Fe, K, hardness, Mg, Mn, Na, NH_4, NO_2, NO_3, pH, SO_4, water and environmental laboratories, proficiency test, interlaboratory comparison

Tiivistelmä

Pätevyyskoe 09/2022: Talousvesimääritykset
Proftest Syke järjesti syyskuussa 2022 pätevyyskokeen talousvesiä analysoiville laboratorioille synteettisestä vesinäytteestä sekä talous- ja raakavesinäytteistä. Pätevyyskokeeseen osallistui yhteensä 37 laboratoriota. Testisuureiden vertailuarvoina käytettiin joko laskennallista pitoisuutta tai osallistujien tulosten robustia keskiarvoa. Osallistujien pätevyyden arviointi tehtiin z-arvojen avulla. Koko tulosaineistossa oli z-arvoilla arvioituna 86 % hyväksyttäviä tuloksia, kun vertailuarvosta sallittiin pH-määrityksissä 0,2 pH-yksikön ja muissa määrityksissä 5–20 %:n poikkeama. Kiitos pätevyyskokeen osallistujille!

Asiasanat: vesianalyysi, Ca, Cl, COD_{Mn}, F, Fe, K, kovuus, Mg, Mn, Na, NH_4, NO_2, NO_3, pH, SO_4, sähkönjohtavuus, vesi- ja ympäristölaboratoriot, pätevyyskoe, laboratorioiden välinen vertailumittaus

Sammandrag

Kompetensprövning 09/2022: Hushållsvattenanalyser
Under september 2022 genomförde Proftest Syke en kompetensprövning för olika analyter i hushållsvatten och råvatten. Denna jämförsele hade totalt 37 deltagarna. Som referensvärde av analytens koncentration användes antingen det teoretiska värdet eller robust medelvärdet av deltagarnas resultat. Resultaten värderades med hjälp av z-värden. I denna kompetensprövning var 86 % av resultaten acceptabla. Resultatet var acceptabelt, om det devierade mindre än 0,2 pH enhet eller 5–20 % från referensvärdet. Ett varmt tack till alla deltagarna i testet!

Nyckelord: vattenanalyser, Ca, Cl, COD_{Mn}, F, Fe, K, hårdhet, ledningsförmåga, Mg, Mn, Na, NH_4, NO_2, NO_3, pH, SO_4, kompetensprövning, vatten- och miljölaboratorier, jämförelse mellan laboratorier

Contents

1 Introduction

Proftest Syke carried out the proficiency test (PT) for analysis of Ca, K, Mg, Na, hardness, Cl, SO_4, COD_{Mn}, F, Fe, Mn, NH_4, NO_2, NO_3, pH, and conductivity in synthetic samples and drinking water as well as raw water samples in September 2022 (DW 09/2022).

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 Finnish Environment Institute reference laboratory and it provides an external quality evaluation between laboratory results, and mutual comparability of analytical reliability. The proficiency test was carried out in accordance with the international standard ISO/IEC 17043 [1] and applying ISO 13528 [2] and IUPAC Technical report [3]. Proftest Syke is accredited by the Finnish Accreditation Service as a proficiency testing provider (PT01, ISO/IEC 17043, www.finas.fi/sites/en). The organizing of this proficiency test is included in the accreditation scope of Proftest Syke.

2 Organizing the proficiency test

2.1 Responsibilities

Organizer
Proftest Syke, Finnish Environment Institute (Syke)
Mustialankatu 3, FI-00790 Helsinki, Finland
Phone: +358 295 251 000, Email: *proftest@syke.fi*

The responsibilities in organizing the proficiency test

Päivi Grönroos	coordinator
Riitta Koivikko	substitute for coordinator
Keijo Tervonen	technical assistance
Markku Ilmakunnas	technical assistance
Sari Lanteri	technical assistance
Ritva Väisänen	technical assistance

Analytical expert

Teemu Näykki	Cl, SO_4, COD_{Mn}, F, NH_4, NO_2, NO_3, pH, conductivity
Jaana Kolehmainen	In expert orientation: Cl, SO_4, COD_{Mn}, F, NH_4, NO_2, NO_3, pH, conductivity
Timo Sara-Aho	Ca, K, Mg, Na, hardness, Fe, Mn,

Expert laboratory	Syke, Helsinki and Oulu (T003, www.finas.fi/sites/en)
Subcontracting	Analyses after the sample preparation (NO_3): KVVY Tutkimus Oy (T064, www.finas.fi/sites/en)

2.2 Participants

In total 37 laboratories participated in this PT (Appendix 1), 33 from Finland and 4 from abroad. 70 % of the participants have accredited quality management system based on ISO/IEC 17025 and 16 % have quality management system based on ISO 9000. Altogether 70 % of the participants used accredited analytical methods at least for a part of the measurements. For this PT, the expert laboratory has codes 27 (Syke, Oulu) and 37 (Syke, Helsinki) in the result tables.

2.3 Samples and delivery

Three types of samples were delivered to the participants: synthetic sample and drinking water as well as raw water samples for analysis of Ca, K, Mg, Na, hardness, Cl, SO_4, COD_{Mn}, F, Fe, Mn, NH_4, NO_2, NO_3, pH, and conductivity.

When preparing the samples, the cleanness of the used sample vessels was controlled. The randomly chosen sample vessels were filled with deionized water and the cleanness of the sample vessels was controlled after three days by analyzing TOC, Fe, NH_4, or conductivity. According to the test results all used vessels fulfilled the cleanness requirements.

The synthetic samples were mainly prepared by diluting from reagents produced by Supelco, Merck or by BDH Prolabo. The synthetic samples for NO_2, NO_3, NH_4, F, Fe, Mn, Na, K, Ca, Mg, Cl, and SO_4 analysis were prepared from the NIST traceable reference solutions. The drinking water sample was tap water from Helsinki, Southern Finland and the raw water sample was well water collected from Karkkila, Southern Finland. Additions of single element standard solutions were done to the samples when needed. The sample preparation is described in more detail in Appendix 2.

The samples were delivered at the latest on 12 September 2022 to the participants abroad and at the latest on 13 September 2022 to the national participants. The samples arrived to the participants mainly on 14 September 2022, one participant received the samples on 15 September 2022.

The samples were to be measured as follows:

COD_{Mn}, pH, conductivity	15 September 2022
N compounds	at the latest on 16 September 2022
Ca, K, Mg, Na, hardness	at the latest on 23 September 2022
Cl, F, SO_4	at the latest on 23 September 2022
Fe, Mn	at the latest on 23 September 2022

The results were requested to be reported at the latest on 26 September 2022 and the participants delivered the results mainly accordingly. The preliminary results report was delivered to the participants via ProftestWEB and email on 3 October 2022.

2.4 Homogeneity and stability studies

The homogeneity of the samples was tested by analyzing Cl, COD_{Mn}, F, Fe, Na, NH_4, and pH. More detailed information of homogeneity test is shown in Appendix 3. According to the homogeneity test results, all samples were considered homogenous.

The temperature control sample was placed into the sample package and the temperature was requested to be measured immediately after opening the package. The temperature of the control sample was mainly ≤ 14 °C and two participants reported higher arrival temperature. It is crucial to measure the

temperature of the control sample right after the sample package has arrived, especially when the package is not stored in refrigerator after the arrival.

The stability of the samples was tested by analyzing COD_{Mn}, N_{NH4}, and pH from the samples stored at the room temperature for one day. The measurement 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). Based on the stability test the possible increase of the sample temperature during the transportation did not affect the performance of the participants. Based on the literature and previous experience, other measurands are known to be stable over the given time period for the test.

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 delivered samples and participants' results reporting. The comments from the organizer mainly dealt with missing sample arrival documents and missing arrival temperature information. All the feedback from the proficiency test is valuable and is exploited when improving the activities.

2.6 Processing the data

2.6.1 Pretesting the data

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

More information about the statistical handling of the data is available from the Guide for participant [4].

2.6.2 Assigned values

The NIST traceable calculated values were used as the assigned values for the synthetic samples of Ca, Cl, F, Fe, K, Mg, Mn, Na, NH_4, and SO_4. For the other samples and measurands the robust mean of the results reported by the participants were used as the assigned value. Detailed information of the assigned values and their uncertainty as well as reliability is shown in Appendix 6.

The assigned values based on the robust mean are not metrologically traceable values. As it was not possible to have metrologically traceable assigned values, the best available values were selected to be used as the assigned values. The reliability of the assigned values was statistically tested [2, 3].

For the calculated assigned values, the expanded uncertainty (k=2) was evaluated by using standard uncertainties associated with individual operations involved in the preparation of the sample. The main individual source of the uncertainty was the uncertainty of the concentration of the stock solution. When the robust mean of the results reported by the participants was used as the assigned value, the uncertainty was calculated using the robust standard deviation [2, 4].

The uncertainty of the calculated assigned values was 0.3–1.8 % (at the 95 % confidence level). When using the robust mean of the participant results as the assigned value, the uncertainties of the assigned

values varied between 0.2 % and 5.7 %. **After reporting the preliminary results report no changes have been done for the assigned values.**

2.6.3 Proficiency assessment procedure

The results of this proficiency test were evaluated with the z scores.

The standard deviation for proficiency assessment was estimated based on the measurand concentration, the results of homogeneity and stability tests, the uncertainty of the assigned value, and the long-term variation in the former proficiency tests. The standard deviation for proficiency assessment ($2 \times s_{pt}$ at the 95 % confidence level) was set for pH measurements to 0.2 pH units and for the other measurements to 5–20 % depending on the measurands. **After reporting the preliminary results report no changes have been done for the standard deviations of the proficiency assessment values.**

When 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 and s_{pt} is the standard deviation for proficiency assessment [2, 3]. When testing the reliability of the assigned value the criterion was mainly fulfilled and the assigned values were considered reliable.

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

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

Sample	Measurement
G3K	Na

3 Results and conclusions

3.1 Results

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

The robust standard deviations of the results varied from 0.5 to 10 % (Table 1). The robust standard deviation was lower than 5 % for 60 % of the results (Table 1). The robust standard deviations were approximately in the same range as in the previous similar proficiency test DW 08/2020, where the deviations varied from 0.6 % to 9.5 % [5].

Table 1. The summary of the results in the proficiency test DW 09/2022.

Measurand	Sample	Unit	Assigned value	Mean	Rob. mean	Median	s_{rob}	s_{rob} %	2 x s_{pt} %	n_{all}	Acc z %
Ca	A1K	mg/l	4.54	4.50	4.49	4.51	0.31	6.9	10	17	82
	D2K	mg/l	19.7	19.9	19.7	19.8	1.1	5.5	10	16	88
	G3K	mg/l	7.33	7.29	7.33	7.32	0.32	4.3	10	15	81
Cl	A1S	mg/l	12.1	12.0	12.0	11.9	0.5	4.0	10	27	93
	D2S	mg/l	5.74	5.73	5.74	5.78	0.25	4.4	10	27	89
	G3S	mg/l	3.67	3.67	3.67	3.68	0.20	5.5	10	24	88
COD_{Mn}	A1C	mg/l	4.02	4.00	4.02	4.00	0.12	2.9	10	20	90
	D2C	mg/l	3.26	3.25	3.26	3.28	0.24	7.4	15	19	95
	G3C	mg/l	2.57	2.58	2.57	2.54	0.16	6.1	15	20	89
Conductivity	A1J	µS/cm	291	291	291	292	4	1.4	5	30	84
	D2PJ	µS/cm	162	162	162	163	3	1.7	5	29	81
	G3PJ	µS/cm	81.6	81.5	81.6	81.8	1.5	1.8	5	31	77
F	A1F	mg/l	1.35	1.38	1.38	1.38	0.08	6.0	10	20	90
	D2F	mg/l	0.32	0.32	0.32	0.31	0.03	10.0	20	19	100
	G3F	mg/l	0.46	0.45	0.46	0.46	0.04	8.5	15	20	90
Fe	A1Fe	µg/l	56.0	52.5	53.2	52.7	3.0	5.6	15	22	82
	D2Fe	µg/l	34.6	34.7	34.6	34.7	2.2	6.5	15	23	87
	G3Fe	µg/l	81.3	81.4	81.3	80.9	4.8	5.9	15	21	86
Hardness	A1K	mmol/l	0.14	0.14	0.14	0.14	0.01	4.8	10	20	80
	D2K	mmol/l	0.56	0.56	0.56	0.56	0.01	2.5	10	19	95
	G3K	mmol/l	0.23	0.23	0.23	0.24	0.01	4.2	10	19	89
K	A1K	mg/l	0.70	0.69	0.68	0.69	0.04	5.2	10	14	77
	D2K	mg/l	1.38	1.38	1.38	1.40	0.04	3.2	10	13	92
	G3K	mg/l	1.09	1.09	1.09	1.09	0.03	3.2	10	14	86
Mg	A1K	mg/l	0.84	0.82	0.82	0.82	0.03	4.0	10	16	81
	D2K	mg/l	1.68	1.68	1.68	1.69	0.05	3.0	10	15	87
	G3K	mg/l	1.33	1.33	1.33	1.33	0.05	3.6	10	16	88
Mn	A1Fe	µg/l	43.1	42.9	43.0	43.0	2.3	5.3	10	20	80
	D2Fe	µg/l	25.4	25.4	25.4	25.6	1.4	5.6	15	20	80
	G3Fe	µg/l	57.0	56.8	57.0	57.1	2.3	4.0	10	20	85
Na	A1K	mg/l	1.22	1.18	1.18	1.18	0.06	5.4	10	16	88
	D2K	mg/l	7.40	7.40	7.40	7.36	0.30	4.1	10	15	100
	G3K	mg/l	4.43	4.43	4.43	4.46	0.24	5.5	10	15	100
NH_4	A1N	mg/l	0.22	0.22	0.23	0.23	0.02	6.9	10	24	70
	D2N	mg/l	0.092	0.092	0.092	0.093	0.008	8.4	15	23	82
	G3N	mg/l	0.13	0.13	0.13	0.13	0.01	7.1	15	24	74
NO_2	A1N	mg/l	0.22	0.22	0.22	0.22	0.01	4.6	10	22	81
	D2N	mg/l	0.18	0.18	0.18	0.18	0.01	3.7	10	21	80
	G3N	mg/l	0.078	0.078	0.078	0.078	0.002	2.4	20	22	70
NO_3	A1N	mg/l	4.75	4.75	4.75	4.75	0.14	3.0	10	21	86
	D2N	mg/l	2.64	2.65	2.64	2.70	0.13	4.8	10	20	85
	G3N	mg/l	5.61	5.61	5.61	5.59	0.26	4.6	10	21	81
pH	A1P		7.28	7.28	7.28	7.28	0.03	0.5	2.7	33	94
	D2PJ		7.93	7.93	7.93	7.93	0.09	1.1	2.5	32	91
	G3PJ		7.22	7.22	7.22	7.20	0.09	1.2	2.8	31	87
SO_4	A1S	mg/l	6.17	6.13	6.14	6.13	0.19	3.0	10	23	91
	D2S	mg/l	26.7	26.8	26.7	26.8	0.8	3.1	10	22	95
	G3S	mg/l	9.37	9.34	9.37	9.29	0.36	3.8	10	22	95

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

3.2 Analytical methods

The participants could use different analytical methods for the measurements in the PT. The used analytical methods and 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. The statistical comparison of the analytical methods was not performed for the results measured with 'Other method', as these results are statistically treated as a group, which includes several methods. A case-specific visual method comparison was made for the 'Other method' results.

Ca, K, Mg, and Na

Most of the participants (7–8, depending on the sample) used ICP-OES techniques and 1–3 participants (depending on the sample) used FAAS techniques (Appendix 12) to determine Ca, K, Mg, and Na. The ICP-MS techniques were used by 3 participants. In addition, IC method was used by 1–2 participants (depending on the sample). Other used methods were the titrimetric method for the determination of calcium (2 participants), calculation of mass concentration of magnesium ions for the determination of magnesium (2 participants), and flame photometry for the determination of sodium (1 participant). Based on the visual evaluation, no clear differences between the used methods were noticed.

Chloride, Cl

16 participants determined chloride using the IC method based on standard EN ISO 10304 (Appendix 12). Depending on the sample, 4–5 participants used the potentiometric titration method. Other methods, such as photometric, IC, and ICP techniques, were used by 4–7 participants (depending on the sample). Based on the visual evaluation, no clear differences between the used methods were noticed.

COD_{Mn}

16 participants determined COD_{Mn} according to the standard method SFS 3036 (Appendix 12). 8–9 participants (depending on the sample) determined COD_{Mn} using manual method and 10 participants using automatic method. One participant determined COD_{Mn} based on national standard. No statistically significant differences were observed between the used methods.

Conductivity

Most of the participants (30–31, depending on the sample) determined conductivity according to the standard method EN 27888 (Appendix 12). Depending on the sample 1–2 participants used other electrometric methods.

Hardness

About half of the participants (7–8, depending on the sample) used EDTA titration of calcium and magnesium (SFS 3003) and 7 participants used ICP-OES or ICP-AES techniques, and 1 participant used AAS technique (Appendix 12) to determine hardness. In addition, 3 participants used ICP-MS technique and 1 participant used titrimetric method with Trilon B.

ICP-OES/AES gave statistically significantly higher results for samples A1K (1.455 ± 0.004 mmol/l, mean ± standard deviation) and G3K (0.239 ± 0.007 mmol/l) when compared to the results of EDTA titration (A1K: 0.138 ± 0.006 mmol/l and G3K: 0.226 ± 0.011 mmol/l, Appendix 13). No other statistically significant differences were observed between the used methods.

Fluoride, F

14 participants determined fluoride using the IC method based on standard EN ISO 10304 (Appendix 12). 3 participants used ion selective electrode. Depending on the sample, 2–3 participants used other methods, for example photometric method, IC method, and combustion IC. Based on the visual evaluation, no clear differences between the used methods were noticed.

Fe and Mn

Six participants used a spectrophotometric method according to national standard SFS 3028 for measurement of Fe and five participants used a spectrophotometric method according to the national standard SFS 3033 for measurement of Mn (Appendix 12). 7 participants used ICP-OES techniques for Fe measurement and ICP-OES or ICP-AES techniques for Mn measurements. One participant used FAAS and 7 participants used ICP-MS for both measurands. Depending on the sample, 1–2 participants used other methods (colorimetric analysis and spectrophotometer Hach Lange DR3900). The statistically significant difference between the results obtained with the ICP-OES technique and the national standard method SFS 3028 for measurement of Fe in raw water sample that has been observed in previous similar proficiency test was not observed in this PT [5]. With ICP techniques the acid matrix of the calibration solutions should be matched to the samples to ensure reliable results.

Ammonium, NH_4

Seven participants used manual indophenol blue spectrophotometric method according to the national standard SFS 3032 for measurement of ammonium in the samples (Appendix 12). Depending on the sample, 6–7 participants used automatic indophenol blue method according to EN ISO 11732. Depending on the sample, 9–10 participants used other methods such as method based on ISO 7150-1 (3 participants), methods based on fluorescence (3 participants) and Hach Lange tube method (2 participants). The results reported with other methods gave statistically significantly lower results for sample D2N when compared to the results with manual indophenol blue spectrophotometric method according to the national standard SFS 3032. The method specific results are not available from the group of other methods. Based on the visual evaluation, similar difference was observed. No other statistically significant or visual differences were observed between the used methods.

Nitrate, NO_3

Nine participants used the method based on standard ISO 13395 (Appendix 12). Five participants used method based on standard ISO 10304 or similar IC methods. Depending on the sample, 1–2 participants used tube method. Five participants used other methods such as HPLC, IC, and photometric method with Griess reagent. No statistically significant differences were observed between the used methods.

Nitrite, NO_2

Depending on the sample, 7–8 participants measured nitrite using the manual spectrophotometric sulfanilamide method based on standard SFS 3029 (Appendix 12). Seven participants used the ISO13395 based automatic (CFA, FIA) sulfanilamide method. Depending on the sample 5–7 participants used other methods, for example tube method, IC methods, or methods based on standard EN 26777. No statistically significant differences were observed between the used methods. The statistically significant difference between the results obtained with the manual spectrophotometric sulfanilamide method and the ISO 13395 based automatic (CFA, FIA) sulfanilamide method measurement of NO_2 in raw water sample that has been observed in previous similar proficiency tests was not observed in this PT [5, 6].

pH

17 participants measured pH using universal electrode and 12–14 participants (depending on the sample) used electrode for low ionic waters. Two participants used other method based on standard EN ISO 10523 (Appendix 12). Electrode for low ionic waters gave statistically significantly higher results for the sample G3PJ (7.26 ± 0.08, mean ± standard deviation) when compared to the results measured with the universal electrode (7.12 ± 0.08, Appendix 13). A similar difference was observed in previous similar PT [6]. No other statistically significant differences were observed between the used methods.

Sulphate, SO_4

Most of the participants (16) determined sulphate according to the standard method EN ISO 10304. Depending on the samples, 6–7 participants used other methods for example ICP-OES, IC, photometric method, tube method, or titrimetric method with lead nitrate. No statistically significant differences were observed between the used methods.

3.3 Uncertainties of the results

Together with their results, the participants were to report the expanded uncertainties (k=2) as percentage. Altogether 78 % of the participants reported the measurement uncertainty with at least some of their results (Table 2, Appendix 14). The number was somewhat lower than in the previous similar proficiency tests [5, 6]. To promote the enhancement of environmental measurements' quality standards and traceability, the national quality recommendations for the data entered in the water quality registers have been published in Finland [7]. The recommendations for measurement uncertainties for the tested measurands in natural waters vary from 5 % to 20 % (for pH measurement 0.2 pH units, see Table 2). The requirements of the drinking water regulation 1352/2015 amending regulation 683/2017 regarding the highest allowed measurement uncertainties of the methods for the analysis of drinking water are also summarized in Table 2 [8]. Within the optimal measuring range, the expanded measurement uncertainty (k=2) should typically be 20–40 %. Close to the limit of quantification the relative measurement uncertainty is higher. The expanded uncertainties below 5 % could commonly be considered unrealistic uncertainty values for routine laboratories. For many participants the reported measurement uncertainties were in the same scale with the recommendations. The share and scale of the reported measurement uncertainties were in the same scale than in the previous similar PT [5].

The most used approach to evaluate the measurement uncertainty was based on using the internal quality control data (synthetic sample and/or routine sample replicates, Appendix 14). Other approaches were using the internal quality control data and the results obtained from proficiency tests as well as evaluation using method validation data. Depending on the sample and measurand, up to 11 participants used MUkit measurement uncertainty software for the evaluation of their uncertainties, which is available on the webpage: www.syke.fi/envical/en [9, 10]. Generally, the used approach for evaluating the measurement uncertainty did not make definite impact on the uncertainty evaluations. Most of the participants reported the measurement uncertainty for all the results obtained with accredited methods.

Table 2. The ranges of the reported expanded uncertainties by participants as percent and recommendation for measurement uncertainties in natural waters and highest allowed measurement uncertainty of the methods for the analysis of drinking waters [7, 8].

Measurand	U_i, Drinking water	U_i, Raw water	Recommendation U_i, [7]	Highest allowed U_i, [8]
Ca	5 – 25 %	6 – 25 %	± 10 %	-
Cl	5 – **60** [1] %	5 – **66** %	± 10 %	± 15 %
COD_{Mn}	10 – 32 %	10 – 35 %	± 10 %	± 50 %
Conductivity	2 – 10 %	2 – 10 %	± 5 %	± 20 %
F	6 – **85** %	6 – **57** %	± 15 %	± 20 %
Fe	2 – **50** %	2 – 40 %	± 10 %	± 30 %
Hardness	3 – 34 %	3 – 42 %	± 10 %	-
K	10 – **50** %	10 – **51** %	± 10 %	-
Mg	10 – 49 %	10 – **50** %	± 10 %	-
Mn	2 – 40 %	2 – 40 %	± 10 %	± 30 %
Na	10 – 20 %	10 – 30 %	± 10 %	± 15 %
NH_4	6 – 32 %	6 – 32 %	± 15 % [2]	± 40 %
NO_2	6 – 30 %	6 – 30 %	± 15 % [2]	± 20 %
NO_3	6 – 35 %	6 – 35 %	± 15 % [2]	± 15 %
pH	0.2 – 5 %	0.2 – 5 %	± 0.2 pH-units (3 %)	± 0.2 pH-units (3 %)
SO_4^2	5 – 25 %	6 – 44 %	± 10 %	± 15 %

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

[2] Recommendation given per nitrogen.

4 Evaluation of the results

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

Criteria	Performance
$\lvert z \rvert \leq 2$	Satisfactory
$2 < \lvert z \rvert < 3$	Questionable
$\lvert z \rvert \geq 3$	Unsatisfactory

In total, 86 % of the results were satisfactory when deviation of 5–20 % and 0.2 pH units from the assigned values were accepted. Altogether 70 % of participants used accredited analytical methods at least for a part of the measurands, and 92 % of those results were satisfactory. The summary of the performance evaluation and comparison to the previous performance is presented in Table 3. In the previous similar PT, DW 08/2020, the performance was satisfactory for 91 % of the participant results [5]. Further, the measurands here were partly same than in PT DW 08/2021, and thus the performance is partly compared also against those results. In DW 08/2021, the performance was satisfactory for 89 % of the participant results when deviation of 5–40 % and 0.2 pH units from the assigned values were accepted [6].

Table 3. Summary of the performance evaluation in the proficiency test DW 09/2022.

Measurand	2 x s_{pt}%	Satisfactory results, %	Remarks
Anions (Cl^-, F^-, SO_4^{2-})	10 – 20	92	Good overall performance. Excellent performance for F^- for drinking water sample D2F and for SO_4^{2-} for drinking water sample D2S and raw water sample G3S. In the PT DW 08/21 the performance was satisfactory for 96 % of the results when deviation of 8–20 % from the assigned value was accepted [6].
COD_{Mn}	10 – 15	91	Good overall performance and excellent performance for drinking water sample D2S. In the PT DW 08/20 the performance was satisfactory for 94 % of the results [5].
Ca, K, Mg, Na	10	88	The performance evaluation for Na for the sample G3K only approximate. Excellent performance for Na for drinking water sample D2K and raw water sample G3K. In the PT DW 08/21 the performance was satisfactory for 89 % of the results when deviation of 10–15 % from the assigned value was accepted [6].
Hardness	10	88	In the PT DW 08/20 the performance was satisfactory for 90 % of the results [5].
pH	2.5 – 2.7 (0.2 pH units)	91	Good overall performance. In the PT DW 08/21 the performance was satisfactory for 95 % of the results [6].
Conductivity	5	81	In the PT DW 08/21 the performance was satisfactory for 97 % of the results [6].
Fe, Mn	10 – 15	83	In the PT DW 08/21 the performance was satisfactory for 76 % of the results when deviation of 15–25 % from the assigned value was accepted [6].
NH_4, NO_2, NO_3	10 – 20	79	In the PT DW 08/21 the performance was satisfactory for 84 % of the results [6].

5 Summary

Proftest Syke carried out the proficiency test (PT) for analysis of Ca, K, Mg, Na, hardness, Cl, SO_4, COD_{Mn}, F, Fe, Mn, NH_4, NO_2, NO_3, pH, and conductivity in synthetic samples and drinking water as well as raw water in September 2022 (DW 09/2022). In total, 37 laboratories participated in this proficiency test. The homogeneity and the stability of the samples were tested and the samples were regarded to be sufficiently homogenous and stable. Significant differences in the results reported using different methods were observed for ICP-OES/AES and EDTA titration when analyzing hardness in synthetic and raw water samples, and for electrode for low ionic waters and universal electrode when analyzing pH in raw water samples.

The performance of the participants was evaluated by using z scores. In this proficiency test 86 % of the results were satisfactory when deviation of 0.2 units for pH and 5–20 % for the other measurands was accepted from the assigned value at the 95 % confidence level. The performance was similar as in the previous similar proficiency tests.

6 Summary in Finnish

Proftest Syke järjesti pätevyyskokeen talousvesiä analysoiville laboratorioille syyskuussa 2022 (DW 09/2022). Pätevyyskokeessa testattiin Ca, Cl, COD_{Mn}, F, Fe, K, kovuus, Mg, Mn, Na, NH_4, NO_2, NO_3, pH, SO_4 ja sähkönjohtavuus raaka- ja talousvedestä sekä synteettisestä vesinäytteestä. Pätevyyskokeessa oli yhteensä 37 osallistujaa (Liite 1).

Näytteiden valmistus on esitetty liitteessä 2. Näytteiden homogeenisuus ja stabiilisuus testattiin ja näytteiden todettiin täyttävän sekä homogeenisuudelle että säilyvyydelle asetetut kriteerit (Liitteet 3 ja 4). Pätevyyskokeesta saatu palaute koski muun muassa vuotaneita näytepulloja ja puutteellisesti raportoituja tuloksia (Liite 5).

Testisuureen vertailuarvona käytettiin laskennallista pitoisuutta tai osallistujien tulosten robustia keskiarvoa. Vertailuarvojen laajennettu epävarmuus oli 0.3–1.8 % laskennallisille vertailuarvoille ja 0.2–5.7 % kun vertailuarvon epävarmuus arvioitiin robustin keskihajonnan tai keskihajonnan avulla (Liite 6).

Yhteenveto tuloksista on esitetty taulukossa 1. Raportin tulostaulukoissa esiintyviä lyhenteitä ja käsitteitä on selitetty liitteessä 7. Osallistujakohtaiset tulokset on esitetty liitteessä 8. Osallistujatulokset ja niiden mittausepävarmuudet on esitetty graafisesti liitteessä 9 ja yhteenvedot z-arvoista liitteessä 10. Liitteessä 11 z-arvot on esitetty suuruusjärjestyksessä. Asiantuntijalaboratorion (T003, www.finas.fi) tunnukset tässä pätevyyskokeessa olivat 27 (Syke, Oulu) ja 37 (Syke, Helsinki)

Määritysmenetelmien mukaan ryhmitellyt tulokset on esitetty liitteessä 12. Menetelmävertailuissa todettiin tilastollisesti merkitsevä ero ICP-OES/AES ja EDTA titrauksen tulosten välillä kovuuden määrityksessä synteettisestä ja raakavesinäytteestä sekä matalaionisille vesille tarkoitetun elektrodin ja yleiselektrodin välillä pH:n määrityksessä raakavesinäytteestä (Liite 13).

Tuloksia arvioitiin z-arvojen avulla ja tavoitehajonnan arvoksi 95 % luottamusvälillä asetettiin pH-määrityksissä 0,2 pH-yksikköä ja muissa määrityksissä 5–20 %. Koko tulosaineistossa hyväksyttäviä tuloksia oli 86 %, mikä oli lähes samalla tasolla kuin edellisissä vastaavissa pätevyyskokeessa. Vuoden 2020 vastaavassa pätevyyskokeessa (DW 08/2020) hyväksyttäviä tuloksia oli 91 % ja vuoden 2021 pätevyyskokeessa (DW 08/2021), jossa testattiin osittain samoja testisuureita, hyväksyttäviä tuloksia oli 89 %, kun tulosten sallittiin vaihdella pH-määrityksissä 0,2-yksikköä ja muissa määrityksissä 5–40 % vertailuarvosta [5, 6].

Osallistujista 78 % ilmoitti mittausepävarmuuden ainakin osalle tuloksistaan. Määrä oli hieman matalampi kuin edellisissä vastaavassa pätevyyskokeissa. Raportoitujen mittausepävarmuuksien välillä oli eroja, mutta visuaalisen arvioinnin perusteella käytetyllä mittausepävarmuuden arviointimenettelyllä ei ollut vaikutusta epävarmuuden suuruuteen (Taulukko 2, Liite 14).

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. Proftest Syke Guide for laboratories: www.syke.fi/proftest/en → Current proficiency tests www.syke.fi/download/noname/%7B3FFB2F05-9363-4208-9265-1E2CE936D48C%7D/39886.

5. Koivikko, R., Grönroos, P., Leivuori, M., Sarkkinen, M., Sara-Aho, T., Näykki, T., Tervonen, K., Lanteri, S, Väisänen, R. and Ilmakunnas, M. 2021. Laboratorioiden välinen pätevyyskoe 08/2020. Talousvesimääritykset. Suomen ympäristökeskuksen raportteja 2/2021. http://hdl.handle.net/10138/325211.

6. Grönroos, P., Koivikko, R., Näykki, T., Sara-Aho, T., Tervonen, K., Lanteri, S, Väisänen, R. and Ilmakunnas, M. 2021. Laboratorioiden välinen pätevyyskoe 08/2021. Talousvesimääritykset. Suomen ympäristökeskuksen raportteja 49/2021. http://hdl.handle.net/10138/337576.

7. Näykki, T., and Väisänen, T. (Eds.) 2016. Laatusuositukset ympäristöhallinnon vedenlaaturekistereihin vietävälle tiedolle: Vesistä tehtävien analyyttien määritysrajat, mittausepävarmuudet sekä säilytysajat ja –tavat. 2. uudistettu painos. (Quality recommendations for data entered into the environmental administration's water quality registers: Quantification limits, measurement uncertainties, storage times and methods associated with analytes determined from waters. 2nd edition). Suomen ympäristökeskuksen raportteja 22/2016. 57 pp., http://hdl.handle.net/10138/163532.

8. Sosiaali- ja terveysministeriön asetus talousveden laatuvaatimuksista ja valvontatutkimuksista annetun sosiaali- ja terveysministeriön asetuksen muuttamisesta 683/2017 https://www.finlex.fi/fi/laki/alkup/2017/20170683#Pidp446679152

9. 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.

10. Magnusson B., Näykki T., Hovind H., Krysell M., Sahlin E., 2017. Handbook for Calculation of Measurement Uncertainty in Environmental Laboratories. Nordtest Report TR 537 (ed. 4). (http://www.nordtest.info)

Appendix 1. Participants in the proficiency test

Country	Participant
Finland	Eurofins Ahma Oy, Oulu
	Eurofins Ahma Oy, Rovaniemi
	Eurofins Environment Testing Finland Oy, Lahti
	Finnsementti Oy
	Fortum Waste Solutions Oy, Riihimäki
	Hortilab Ab Oy
	HSY Käyttölaboratorio Pitkäkoski Helsinki
	KVVY Tutkimus Oy, Tampere
	Kymen Ympäristölaboratorio Oy
	Lounais-Suomen vesi- ja ympäristötutkimus Oy, Turku
	LUVYLab Oy Ab
	Neste Corporation, Technology Center, Kilpilahti
	Neste Oyj, Tutkimus ja kehitys/Vesilaboratorio, Kulloo
	Norilsk Nickel Harjavalta Oy
	Oulun Vesi Liikelaitos
	Saimaan Vesi- ja Ympäristötutkimus Oy, Lappeenranta
	Savo-Karjalan Ympäristötutkimus Oy, Joensuu
	Savo-Karjalan Ympäristötutkimus Oy, Kajaani
	Savo-Karjalan Ympäristötutkimus Oy, Kuopio
	ScanLab Oy
	SeiLab Oy Haapaveden toimipiste
	SeiLab Oy Seinäjoen toimipiste
	SGS Finland Oy, Kotka
	Stora Enso Oulu Oy, Oulun tehdas
	Syke, Oulun toimipaikka
	Syke, Helsingin toimipaikka
	Tampereen Vesi/Viemärilaitoksen laboratorio
	UPM Oyj, Kymi
	UPM Specialty Papers, Tervasaari
	UPM Tutkimuskeskus, Lappeenranta
	Vita Laboratoriot Oy
	Yara Suomi Oy, Uusikaupunki
	ÅMHM laboratoriet, Jomala, Åland
Kyrgyz Republic	Surface water pollution control Unit (Lab), Hydrometeorological Service of the Ministry of Emergency Situations of the Kyrgyz Republic
Norway	NIVA, Oslo, Norway
Sweden	SakLab, Luossavaara-Kirunavaara AB
	Stockholm University, ACES

Appendix 2. Sample preparation

Measurand	Sample	Initial concentration	Addition	Assigned value
Ca [mg/l]	A1K	-	$Ca(NO_3)_2$ 4.54	4.54
	D2K	20.1	-	19.7
	G3K	7.35	-	7.33
Cl [mg/l]	A1S	-	NaCl 12.1	12.1
	D2S	5.92	-	5.74
	G3S	3.65	-	3.67
COD_{Mn} [mg/l]	A1C	-	$C_7H_6O_3$ 4.00	4.02
	D2C	1.26	2.14	3.26
	G3C	0.60	2.00	2.57
γ_{25} [µS/cm]	A1J	-	KCl 268	291
	D2PJ	160	-	162
	G3PJ	80	-	81.6
F [mg/l]	A1F	-	NaF 1.35	1.35
	D2F	0.10	0.22	0.32
	G3F	0.17	0.30	0.46
Fe [µg/l]	A1Fe	-	$Fe(NO_3)_3$ 56.0	56.0
	D2Fe	11.5	24.6	34.6
	G3Fe	5.70	80.0	81.3
Hardness [mmol/l]	A1K	-	0.15	0.14
	D2K	0.57	-	0.56
	G3K	0.24	-	0.23
K [mg/l]	A1K	-	KNO_3 0.70	0.70
	D2K	1.45	-	1.38
	G3K	1.13	-	1.09
Mg [mg/l]	A1K	-	$Mg(NO_3)_2$ 0.84	0.84
	D2K	1.75	-	1.68
	G3K	1.40	-	1.33
Mn [µg/l]	A1Fe	-	$Mn(NO_3)_2$ 43.1	43.1
	D2Fe	0.90	25.1	25.4
	G3Fe	6.80	54.1	57.0

Measurand	Sample	Initial concentration	Addition	Assigned value
Na [mg/l]	A1K	-	$NaNO_3$ 1.22	1.22
	D2K	7.56	-	7.40
	G3K	4.44	-	4.43
NH_4 [mg/l]	A1N	-	NH_4Cl 0.22	0.22
	D2N	0.095	0.03	0.092
	G3N	0	0.18	0.13
NO_2 [mg/l]	A1N	-	$NaNO_2$ 0.21	0.22
	D2N	0.03	0.14	0.18
	G3N	0	0.07	0.078
NO_3 [mg/l]	A1N	-	$NaNO_3$ 4.51	4.75
	D2N	1.12	1.44	2.64
	G3N	5.36	-	5.61
pH pH-unit	A1P	-	KH_2PO_4 + Na_2HPO_4 ~7.30	7.28
	D2PJ	7.88	-	7.93
	G3PJ	6.41	-	7.22
SO_4 [mg/l]	A1S	-	Na_2SO_4 6.17	6.17
	D2S	25.5	-	26.7
	G3S	9.10	-	9.37

Appendix 3. Homogeneity of the samples

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

Criteria for homogeneity:

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

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

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

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, µg/l, pH unit	n	s_{pt}%	s_{pt}	s_{anal}	s_{anal}/s_{pt}	$s_{anal}/s_{pt}<0.5$?	s_{sam}^2	c	$s_{sam}^2<c$?
Cl / D2CS	5.87	6	5	0.29	0.02	0.08	Yes	0.003	0.02	Yes
Cl / G3CS	3.69	6	5	0.18	0.01	0.07	Yes	0	0.007	Yes
COD_{Mn} / D2C	3.30	6	7.5	0.25	0.02	0.09	Yes	0.001	0.01	Yes
COD_{Mn} / G3C	2.49	6	7.5	0.19	0.05	0.26	Yes	0.002	0.01	Yes
F / D2F	0.31	4	10	0.03	0.003	0.11	Yes	0	<0.001	Yes
F / G3F	0.46	4	7.5	0.03	0.002	0.07	Yes	0	<0.001	Yes
Fe / D2Fe	36.6	4	7.5	2.75	0.30	0.11	Yes	0	2.02	Yes
Fe / G3Fe	83.1	4	7.5	6.23	0.45	0.07	Yes	0.59	9.68	Yes
Na / D2K	7.57	6	5	0.38	0.06	0.15	Yes	0	0.03	Yes
Na / G3K	4.64	6	5	0.23	0.03	0.11	Yes	0	0.01	Yes
NH_4 / D2N	0.09	6	7.5	0.007	0.002	0.32	Yes	0	<0.001	Yes
NH_4 / G3N	0.14	6	7.5	0.01	0.002	0.15	Yes	0	<0.001	Yes
pH / D2PJ	7.96	8	1.25	0.10	0.009	0.09	Yes	<0.001	0.002	Yes
pH / G3PJ	7.27	8	1.4	0.10	0.02	0.15	Yes	<0.001	0.002	Yes

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

Appendix 4. Stability of the samples

The samples were delivered on 12 or 13 September 2022 and they arrived to the participants mainly on 14 September 2022. The samples were to be analysed as follows:

COD_{Mn}, pH, conductivity	15 September 2022
N compounds	at the latest on 16 September 2022
Ca, K, Mg, Na, hardness	at the latest on 23 September 2022
Cl, F, SO_4	at the latest on 23 September 2022
Fe, Mn	at the latest on 23 September 2022

Stability of COD_{Mn}, NH_4, and pH samples were tested by analyzing the samples stored at the temperatures 4 and 20 ºC.

Criterion 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

COD_{Mn}

Sample	**Result** [mg/l]		**Sample**	**Result** [mg/l]		**Sample**	**Result** [mg/l]	
Date	15.9. (20 ºC)	15.9. (4 ºC)	Date	15.9. (20 ºC)	15.9. (4 ºC)	Date	15.9. (20 ºC)	15.9. (4 ºC)
A1C	3.986	3.917	**D2C**	3,383	3,421	**G3C**	2.608	2.597
D	0.069		D	0.038		D	0.011	
$0.3 \times s_{pt}$	0.06		$0.3 \times s_{pt}$	0.07		$0.3 \times s_{pt}$	0.06	
D <0.3 × s_{pt}? No [1)]			**D < 0.3 × s_{pt}? Yes**			**D < 0.3 × s_{pt}? Yes**		

NH_4

Sample	**Result** [mg/l]		**Sample**	**Result** [mg/l]		**Sample**	**Result** [mg/l]	
Date	15.9. (20 ºC)	15.9. (4 ºC)	Date	15.9. (20 ºC)	15.9. (4 ºC)	Date	15.9. (20 ºC)	15.9. (4 ºC)
A1N	0.230	0.228	**D2N**	0.088	0.087	**G3N**	0.138	0.140
D	0.002		D	0.001		D	0.002	
$0.3 \times s_{pt}$	0.003		$0.3 \times s_{pt}$	0.002		$0.3 \times s_{pt}$	0.003	
D <0.3 × s_{pt}? Yes			**D < 0.3 × s_{pt}? Yes**			**D < 0.3 × s_{pt}? Yes**		

pH

Sample	**Result** [pH unit]		**Sample**	**Result** [pH unit]		**Sample**	**Result** [pH unit]	
Date	15.9. (20 ºC)	15.9. (4 ºC)	Date	15.9. (20 ºC)	15.9. (4 ºC)	Date	15.9. (20 ºC)	15.9. (4 ºC)
A1P	7.248	7.260	**D2PJ**	7.923	7.953	**G3PJ**	7.198	7.208
D	0.013		D	0.030		D	0.010	
$0.3 \times s_{pt}$	0.03		$0.3 \times s_{pt}$	0.030		$0.3 \times s_{pt}$	0.03	
D <0.3 × s_{pt}? Yes			**D < 0.3 × s_{pt}? No** [1)]			**D < 0.3 × s_{pt}? Yes**		

[1)] The difference is within the analytical error

Conclusion: According to the test results, the concentration of COD_{Mn} in the sample A1C and pH in the sample D2PJ might have changed slightly if the sample temperature increased during the sample distribution. For these samples the observed differences in the concentrations are within the analytical error. Thus, all samples were regarded stable under the sample distribution conditions.

Appendix 5. Feedback from the proficiency test

Feedback from the participants

Participant	Comments on technical excecution	Action / Proftest SYKE
6, 10, 12, 25	The bottles of N compounds had leaked.	The provider will pay more attention to careful closing of the bottles. The participants did not request the new samples.
31	The samples A1N and G3N had leaked.	The new samples were sent to the participant.

Participant	Comments to the results	Action / Proftest SYKE
23	The participant reported the results for conductivity in wrong unit. The corrected results were: A1J: 292 µS/cm D2PJ: 162 µS/cm G3PJ: 81 µS/cm	The results were outliers in the statistical treatment, and thus did not affect the performance evaluation. If the results had been reported correctly, the evaluation of the results would have been, based on z scores: Satisfactory. The participant can re-calculate the z scores according to the Guide of participants [4].
27	The participant reported the results for conductivity, NO_2 and NH_4 in wrong unit. The corrected results were: Conductivity: A1J 283.4 µs/cm, D2PJ 158.9 µs/cm, G3PJ 79,4 µs/cm NO_2: A1N 0.225 mg/l, D2N 0.186 mg/l ja G3N 0.078 mg/l NH_4: A1N 0.229 mg/l, D2N 0.088 mg/l ja G3N 0.141 mg/l	The results were outliers in the statistical treatment, and thus did not affect the performance evaluation. If the results had been reported correctly, the evaluation of the results would have been, based on z scores: Satisfactory. The participant can re-calculate the z scores according to the Guide of participants [4].
28	The participant could not find their results in Summary of the z and zeta scores (Appendix 5) of the preliminary results report.	The participant has not reported the measurement uncertainty. Because of this, calculating the zeta value was not possible.

Feedback to the participants

Participant	Comments
2, 19, 21, 22, 23, 24, 27, 28, 29, 32, 37	The participant did not return the sample arrival document to the organizer. Thus, the information of the sample arrival temperature was missing for them. The participant should follow the instructions.
9, 34	The participant returned the sample arrival document without temperature. The participant should follow the instructions.
1, 22, 23, 29, 36	The measurement uncertainty should be reported with the results obtained by accredited methods.

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}
Ca	A1K	mg/l	4.54	0.03	0.6	Calculated value	0.06
	D2K	mg/l	19.7	0.7	3.4	Robust mean	0.34
	G3K	mg/l	7.33	0.22	3.0	Robust mean	0.30
Cl	A1S	mg/l	12.1	0.1	0.5	Calculated value	0.05
	D2S	mg/l	5.74	0.13	2.2	Robust mean	0.22
	G3S	mg/l	3.67	0.11	2.9	Robust mean	0.29
COD_{Mn}	A1C	mg/l	4.02	0.07	1.7	Robust mean	0.17
	D2C	mg/l	3.26	0.13	4.1	Robust mean	0.27
	G3C	mg/l	2.57	0.10	3.7	Robust mean	0.25
Conductivity	A1J	µS/cm	291	2	0.7	Robust mean	0.14
	D2PJ	µS/cm	162	1	0.8	Robust mean	0.16
	G3PJ	µS/cm	81.6	0.7	0.9	Robust mean	0.18
F	A1F	mg/l	1.35	<0.01	0.3	Calculated value	0.03
	D2F	mg/l	0.32	0.02	5.7	Robust mean	0.29
	G3F	mg/l	0.46	0.02	4.9	Robust mean	0.33
Fe	A1Fe	µg/l	56.0	0.5	0.9	Calculated value	0.06
	D2Fe	µg/l	34.6	1.2	3.6	Robust mean	0.24
	G3Fe	µg/l	81.3	2.7	3.3	Robust mean	0.22
Hardness	A1K	mmol/l	0.14	<0.01	3.0	Robust mean	0.30
	D2K	mmol/l	0.56	0.01	1.5	Robust mean	0.15
	G3K	mmol/l	0.23	0.01	2.5	Robust mean	0.25
K	A1K	mg/l	0.70	<0.01	0.7	Calculated value	0.07
	D2K	mg/l	1.38	0.03	2.2	Robust mean	0.22
	G3K	mg/l	1.09	0.02	2.2	Robust mean	0.22
Mg	A1K	mg/l	0.84	0.01	0.6	Calculated value	0.06
	D2K	mg/l	1.68	0.04	2.1	Robust mean	0.21
	G3K	mg/l	1.33	0.03	2.4	Robust mean	0.24
Mn	A1Fe	µg/l	43.1	0.4	0.9	Calculated value	0.09
	D2Fe	µg/l	25.4	0.8	3.3	Robust mean	0.22
	G3Fe	µg/l	57.0	1.3	2.3	Robust mean	0.23
Na	A1K	mg/l	1.22	<0.01	0.3	Calculated value	0.03
	D2K	mg/l	7.40	0.19	2.6	Robust mean	0.26
	G3K	mg/l	4.43	0.16	3.5	Robust mean	0.35
NH_4	A1N	mg/l	0.22	<0.01	1.8	Calculated value	0.18
	D2N	mg/l	0.092	<0.01	4.8	Robust mean	0.32
	G3N	mg/l	0.13	0.01	4.1	Robust mean	0.27
NO_2	A1N	mg/l	0.22	0.01	2.8	Robust mean	0.28
	D2N	mg/l	0.18	<0.01	2.3	Robust mean	0.23
	G3N	mg/l	0.078	<0.01	1.5	Robust mean	0.08
NO_3	A1N	mg/l	4.75	0.08	1.7	Robust mean	0.17
	D2N	mg/l	2.64	0.08	2.9	Robust mean	0.29
	G3N	mg/l	5.61	0.16	2.8	Robust mean	0.28
pH	A1P		7.28	0.01	0.2	Robust mean	0.07
	D2PJ		7.93	0.04	0.5	Robust mean	0.20
	G3PJ		7.22	0.04	0.6	Robust mean	0.21

Measurand	Sample	Unit	Assigned value	U_{pt}	U_{pt}, %	Evaluation method of assigned value	u_{pt}/s_{pt}
SO_4	A1S	mg/l	6.17	0.03	0.5	Calculated value	0.05
	D2S	mg/l	26.7	0.4	1.6	Robust mean	0.16
	G3S	mg/l	9.37	0.20	2.1	Robust mean	0.21

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

If $u_{pt}/s_{pt} \leq 0.3$, the assigned value is reliable.

Appendix 7. Terms in the results tables

The information could be applied according to the PT.

Measurand The tested parameter

Sample The code of the sample

Assigned value The value attributed to a particular property of a proficiency test item

Participant's result The result reported by the participant (when replicate results are reported, the mean value)

2 × s_{pt} % The standard deviation for proficiency assessment (s_{pt}) at the 95 % confidence level

z score Used for the participant's performance evaluation in the PT.
Calculated with formula:

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

x_i = the result of the individual participant
x_{pt} = the assigned value
s_{pt} = the standard deviation for proficiency assessment

Interpretation of the z scores

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

E_n score Error, normalized – Used to evaluate the difference between the assigned value and participant's result within their claimed expanded uncertainty. Calculated with formula:

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

U_i = the expanded uncertainty of a participant's result
U_{pt} = the expanded uncertainty of the assigned value

Interpretation of the E_n scores

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

Md Median

s Standard deviation

s % Standard deviation, %

n_{stat} Number of results in statistical processing

More information of the statistical calculations in international standards ISO/IEC 17043 and ISO 13528 as well as in Proftest Syke Guide for participants [1, 2, 4].

Appendix 8. Results of each participant

Participant 1												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Conductivity	µS/cm	D2PJ		-19.88	162	5	82	163	162	3	1.7	26
	µS/cm	G3PJ		39.90	81.6	5	163.0	81.8	81.5	1.3	1.6	25
Fe	µg/l	A1Fe		-0.78	56.0	15	52.7	52.7	52.5	4.6	8.8	19
	µg/l	D2Fe		-0.73	34.6	15	32.7	34.7	34.7	2.2	6.3	20
	µg/l	G3Fe		1.12	81.3	15	88.1	80.9	81.4	4.0	4.9	20
Mn	µg/l	A1Fe		0.97	43.1	10	45.2	43.0	42.9	1.9	4.5	17
	µg/l	D2Fe		0.02	25.4	15	25.4	25.6	25.4	1.1	4.3	18
	µg/l	G3Fe		0.03	57.0	10	57.1	57.1	56.8	2.0	3.6	18
pH		D2PJ		-1.11	7.93	2,5	7.82	7.93	7.93	0.08	1.0	29
		G3PJ		-1.58	7.22	2,8	7.06	7.20	7.22	0.08	1.1	27

Participant 2												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Cl	mg/l	A1S		0.00	12.1	10	12.1	11.9	12.0	0.4	3.1	22
	mg/l	D2S		-0.03	5.74	10	5.73	5.78	5.73	0.25	4.3	24
	mg/l	G3S		0.33	3.67	10	3.73	3.68	3.67	0.21	5.6	23
Conductivity	µS/cm	A1J		-0.69	291	5	286	292	291	4	1.4	27
	µS/cm	D2PJ		-0.49	162	5	160	163	162	3	1.7	26
	µS/cm	G3PJ		-0.49	81.6	5	80.6	81.8	81.5	1.3	1.6	25
NH_4	mg/l	A1N		0.91	0.22	10	0.23	0.23	0.22	0.03	12.1	21
	mg/l	D2N		-0.29	0.092	15	0.090	0.093	0.092	0.008	8.2	19
	mg/l	G3N		0.00	0.13	15	0.13	0.13	0.13	0.01	5.5	19
NO_2	mg/l	A1N		-1.82	0.22	10	0.20	0.22	0.22	0.01	4.8	17
	mg/l	D2N		-6.67	0.18	10	0.12	0.18	0.18	0.01	3.7	16
	mg/l	G3N			0.078	20	*<0,1*	0.078	0.078	0.001	1.5	16
NO_3	mg/l	A1N		0.00	4.75	10	4.75	4.75	4.75	0.14	3.0	18
	mg/l	D2N		-1.97	2.64	10	2.38	2.70	2.65	0.12	4.5	18
	mg/l	G3N		-1.35	5.61	10	5.23	5.59	5.61	0.24	4.2	17
pH		A1P		0.00	7.28	2,7	7.28	7.28	7.28	0.04	0.6	31
		D2PJ		-4.64	7.93	2,5	7.47	7.93	7.93	0.08	1.0	29
		G3PJ		2.37	7.22	2,8	7.46	7.20	7.22	0.08	1.1	27
SO_4	mg/l	A1S		-0.26	6.17	10	6.09	6.13	6.13	0.20	3.3	21
	mg/l	D2S		0.00	26.7	10	26.7	26.8	26.8	0.7	2.7	22
	mg/l	G3S		-0.09	9.37	10	9.33	9.29	9.34	0.33	3.5	21

Participant 3												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Cl	mg/l	A1S		-0.31	12.1	10	11.9	11.9	12.0	0.4	3.1	22
	mg/l	D2S		0.70	5.74	10	5.94	5.78	5.73	0.25	4.3	24
	mg/l	G3S		1.58	3.67	10	3.96	3.68	3.67	0.21	5.6	23
Conductivity	µS/cm	A1J		0.41	291	5	294	292	291	4	1.4	27
	µS/cm	D2PJ		0.64	162	5	165	163	162	3	1.7	26
	µS/cm	G3PJ		0.49	81.6	5	82.6	81.8	81.5	1.3	1.6	25
F	mg/l	A1F		-0.80	1.35	10	1.30	1.38	1.38	0.07	5.3	19
	mg/l	D2F		0.06	0.32	20	0.32	0.31	0.32	0.03	9.4	19
	mg/l	G3F		0.06	0.46	15	0.46	0.46	0.45	0.04	8.6	19

Participant 3												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
pH		A1P		1.02	7.28	2,7	7.38	7.28	7.28	0.04	0.6	31
		D2PJ		1.31	7.93	2,5	8.06	7.93	7.93	0.08	1.0	29
		G3PJ		1.09	7.22	2,8	7.33	7.20	7.22	0.08	1.1	27
SO_4	mg/l	A1S		0.34	6.17	10	6.27	6.13	6.13	0.20	3.3	21
	mg/l	D2S		0.50	26.7	10	27.4	26.8	26.8	0.7	2.7	22
	mg/l	G3S		1.11	9.37	10	9.89	9.29	9.34	0.33	3.5	21

Participant 4												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Cl	mg/l	A1S		-0.17	12.1	10	12.0	11.9	12.0	0.4	3.1	22
	mg/l	D2S		0.59	5.74	10	5.91	5.78	5.73	0.25	4.3	24
	mg/l	G3S		-0.76	3.67	10	3.53	3.68	3.67	0.21	5.6	23
Conductivity	µS/cm	A1J		-17.70	291	5	162	292	291	4	1.4	27
	µS/cm	D2PJ		-19.88	162	5	82	163	162	3	1.7	26
	µS/cm	G3PJ		104.12	81.6	5	294.0	81.8	81.5	1.3	1.6	25
F	mg/l	A1F		0.44	1.35	10	1.38	1.38	1.38	0.07	5.3	19
	mg/l	D2F		0.31	0.32	20	0.33	0.31	0.32	0.03	9.4	19
	mg/l	G3F		0.70	0.46	15	0.48	0.46	0.45	0.04	8.6	19
Fe	µg/l	A1Fe		-0.17	56.0	15	55.3	52.7	52.5	4.6	8.8	19
	µg/l	D2Fe		0.08	34.6	15	34.8	34.7	34.7	2.2	6.3	20
	µg/l	G3Fe		0.43	81.3	15	83.9	80.9	81.4	4.0	4.9	20
Hardness	mmol/l	A1K		-1.57	0.14	10	0.13	0.14	0.14	0.01	4.5	16
	mmol/l	D2K		-0.50	0.56	10	0.55	0.56	0.56	0.01	2.3	18
	mmol/l	G3K		-0.78	0.23	10	0.22	0.24	0.23	0.01	4.5	17
Mn	µg/l	A1Fe		0.88	43.1	10	45.0	43.0	42.9	1.9	4.5	17
	µg/l	D2Fe		1.15	25.4	15	27.6	25.6	25.4	1.1	4.3	18
	µg/l	G3Fe		0.53	57.0	10	58.5	57.1	56.8	2.0	3.6	18
NH_4	mg/l	A1N		4.36	0.22	10	0.27	0.23	0.22	0.03	12.1	21
	mg/l	D2N		0.87	0.092	15	0.098	0.093	0.092	0.008	8.2	19
	mg/l	G3N		1.85	0.13	15	0.15	0.13	0.13	0.01	5.5	19
NO_2	mg/l	A1N		0.91	0.22	10	0.23	0.22	0.22	0.01	4.8	17
	mg/l	D2N		1.11	0.18	10	0.19	0.18	0.18	0.01	3.7	16
	mg/l	G3N		0.26	0.078	20	0.080	0.078	0.078	0.001	1.5	16
NO_3	mg/l	A1N		-0.29	4.75	10	4.68	4.75	4.75	0.14	3.0	18
	mg/l	D2N		0.45	2.64	10	2.70	2.70	2.65	0.12	4.5	18
	mg/l	G3N		-0.25	5.61	10	5.54	5.59	5.61	0.24	4.2	17
pH		A1P		-1.02	7.28	2,7	7.18	7.28	7.28	0.04	0.6	31
		D2PJ		-1.31	7.93	2,5	7.80	7.93	7.93	0.08	1.0	29
		G3PJ		-0.20	7.22	2,8	7.20	7.20	7.22	0.08	1.1	27
SO_4	mg/l	A1S		-0.32	6.17	10	6.07	6.13	6.13	0.20	3.3	21
	mg/l	D2S		-0.52	26.7	10	26.0	26.8	26.8	0.7	2.7	22
	mg/l	G3S		-0.26	9.37	10	9.25	9.29	9.34	0.33	3.5	21

Participant 5												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Cl	mg/l	A1S		1.02	12.1	10	12.7	11.9	12.0	0.4	3.1	22
	mg/l	D2S		0.80	5.74	10	5.97	5.78	5.73	0.25	4.3	24
	mg/l	G3S		1.85	3.67	10	4.01	3.68	3.67	0.21	5.6	23
Conductivity	µS/cm	A1J		-1.83	291	5	278	292	291	4	1.4	27
	µS/cm	D2PJ		-1.14	162	5	157	163	162	3	1.7	26
	µS/cm	G3PJ		-1.19	81.6	5	79.2	81.8	81.5	1.3	1.6	25
Fe	µg/l	A1Fe		-0.20	56.0	15	55.2	52.7	52.5	4.6	8.8	19
	µg/l	D2Fe		0.16	34.6	15	35.0	34.7	34.7	2.2	6.3	20
	µg/l	G3Fe		6.35	81.3	15	120.0	80.9	81.4	4.0	4.9	20
Hardness	mmol/l	A1K		-2.43	0.14	10	0.12	0.14	0.14	0.01	4.5	16
	mmol/l	D2K		-1.14	0.56	10	0.53	0.56	0.56	0.01	2.3	18
	mmol/l	G3K		-1.91	0.23	10	0.21	0.24	0.23	0.01	4.5	17
Mn	µg/l	A1Fe		0.16	43.1	10	43.5	43.0	42.9	1.9	4.5	17
	µg/l	D2Fe		0.08	25.4	15	25.6	25.6	25.4	1.1	4.3	18
	µg/l	G3Fe		0.31	57.0	10	57.9	57.1	56.8	2.0	3.6	18
pH		A1P		1.12	7.28	2,7	7.39	7.28	7.28	0.04	0.6	31
		D2PJ		1.21	7.93	2,5	8.05	7.93	7.93	0.08	1.0	29
		G3PJ		-0.10	7.22	2,8	7.21	7.20	7.22	0.08	1.1	27

Participant 6												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
COD_{Mn}	mg/l	A1C		-0.10	4.02	10	4.00	4.00	4.00	0.08	2.0	19
	mg/l	D2C		0.04	3.26	15	3.27	3.28	3.25	0.25	7.8	20
	mg/l	G3C		-0.16	2.57	15	2.54	2.54	2.58	0.15	6.0	17
Conductivity	µS/cm	A1J		-0.14	291	5	290	292	291	4	1.4	27
	µS/cm	D2PJ		0.42	162	5	164	163	162	3	1.7	26
	µS/cm	G3PJ		0.44	81.6	5	82.5	81.8	81.5	1.3	1.6	25
Fe	µg/l	A1Fe		-1.00	56.0	15	51.8	52.7	52.5	4.6	8.8	19
	µg/l	D2Fe		-0.77	34.6	15	32.6	34.7	34.7	2.2	6.3	20
	µg/l	G3Fe		-0.21	81.3	15	80.0	80.9	81.4	4.0	4.9	20
Hardness	mmol/l	A1K		-1.14	0.14	10	0.13	0.14	0.14	0.01	4.5	16
	mmol/l	D2K		-0.29	0.56	10	0.55	0.56	0.56	0.01	2.3	18
	mmol/l	G3K		-0.26	0.23	10	0.23	0.24	0.23	0.01	4.5	17
NH_4	mg/l	A1N		-6.73	0.22	10	0.15	0.23	0.22	0.03	12.1	21
	mg/l	D2N		0.87	0.092	15	0.098	0.093	0.092	0.008	8.2	19
	mg/l	G3N		1.03	0.13	15	0.14	0.13	0.13	0.01	5.5	19
pH		A1P		0.41	7.28	2,7	7.32	7.28	7.28	0.04	0.6	31
		D2PJ		0.81	7.93	2,5	8.01	7.93	7.93	0.08	1.0	29
		G3PJ		-0.59	7.22	2,8	7.16	7.20	7.22	0.08	1.1	27

Participant 7												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
COD_{Mn}	mg/l	A1C		0.00	4.02	10	4.02	4.00	4.00	0.08	2.0	19
	mg/l	D2C		1.02	3.26	15	3.51	3.28	3.25	0.25	7.8	20
	mg/l	G3C		-0.67	2.57	15	2.44	2.54	2.58	0.15	6.0	17
Conductivity	µS/cm	A1J		0.00	291	5	291	292	291	4	1.4	27
	µS/cm	D2PJ		0.25	162	5	163	163	162	3	1.7	26
	µS/cm	G3PJ		0.10	81.6	5	81.8	81.8	81.5	1.3	1.6	25

Participant 7												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
NH_4	mg/l	A1N		1.00	0.22	10	0.23	0.23	0.22	0.03	12.1	21
	mg/l	D2N		0.14	0.092	15	0.093	0.093	0.092	0.008	8.2	19
	mg/l	G3N		0.92	0.13	15	0.14	0.13	0.13	0.01	5.5	19
NO_2	mg/l	A1N		-0.91	0.22	10	0.21	0.22	0.22	0.01	4.8	17
	mg/l	D2N		-1.11	0.18	10	0.17	0.18	0.18	0.01	3.7	16
	mg/l	G3N		-2.44	0.078	20	0.059	0.078	0.078	0.001	1.5	16
NO_3	mg/l	A1N		-0.55	4.75	10	4.62	4.75	4.75	0.14	3.0	18
	mg/l	D2N		-0.98	2.64	10	2.51	2.70	2.65	0.12	4.5	18
	mg/l	G3N		-19.79	5.61	10	0.06	5.59	5.61	0.24	4.2	17
pH		A1P		-0.20	7.28	2,7	7.26	7.28	7.28	0.04	0.6	31
		D2PJ		0.00	7.93	2,5	7.93	7.93	7.93	0.08	1.0	29
		G3PJ		-0.40	7.22	2,8	7.18	7.20	7.22	0.08	1.1	27

Participant 8												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
COD_{Mn}	mg/l	A1C		-1.49	4.02	10	3.72	4.00	4.00	0.08	2.0	19
	mg/l	D2C		-0.90	3.26	15	3.04	3.28	3.25	0.25	7.8	20
	mg/l	G3C		-0.05	2.57	15	2.56	2.54	2.58	0.15	6.0	17
Conductivity	µS/cm	A1J		0.69	291	5	296	292	291	4	1.4	27
	µS/cm	D2PJ		0.49	162	5	164	163	162	3	1.7	26
	µS/cm	G3PJ		0.20	81.6	5	82.0	81.8	81.5	1.3	1.6	25
NH_4	mg/l	A1N		2.73	0.22	10	0.25	0.23	0.22	0.03	12.1	21
	mg/l	D2N		2.61	0.092	15	0.110	0.093	0.092	0.008	8.2	19
	mg/l	G3N		3.08	0.13	15	0.16	0.13	0.13	0.01	5.5	19
NO_2	mg/l	A1N		0.00	0.22	10	0.22	0.22	0.22	0.01	4.8	17
	mg/l	D2N		0.00	0.18	10	0.18	0.18	0.18	0.01	3.7	16
	mg/l	G3N		0.00	0.078	20	0.078	0.078	0.078	0.001	1.5	16
pH		A1P		0.00	7.28	2,7	7.28	7.28	7.28	0.04	0.6	31
		D2PJ		0.00	7.93	2,5	7.93	7.93	7.93	0.08	1.0	29
		G3PJ		-0.89	7.22	2,8	7.13	7.20	7.22	0.08	1.1	27

Participant 9												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Cl	mg/l	D2S		2.65	5.74	10	6.50	5.78	5.73	0.25	4.3	24
Conductivity	µS/cm	A1J		0.14	291	5	292	292	291	4	1.4	27
	µS/cm	D2PJ		0.00	162	5	162	163	162	3	1.7	26
Fe	µg/l	D2Fe		0.15	34.6	15	35.0	34.7	34.7	2.2	6.3	20
Hardness	mmol/l	A1K		0.54	0.14	10	0.14	0.14	0.14	0.01	4.5	16
	mmol/l	D2K		-0.16	0.56	10	0.56	0.56	0.56	0.01	2.3	18
pH		A1P		-0.20	7.28	2,7	7.26	7.28	7.28	0.04	0.6	31
		D2PJ		-0.10	7.93	2,5	7.92	7.93	7.93	0.08	1.0	29

Participant 10												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Cl	mg/l	A1S		-0.33	12.1	10	11.9	11.9	12.0	0.4	3.1	22
	mg/l	D2S		0.91	5.74	10	6.00	5.78	5.73	0.25	4.3	24
	mg/l	G3S		1.25	3.67	10	3.90	3.68	3.67	0.21	5.6	23
COD_{Mn}	mg/l	A1C		0.80	4.02	10	4.18	4.00	4.00	0.08	2.0	19
	mg/l	D2C		1.76	3.26	15	3.69	3.28	3.25	0.25	7.8	20
	mg/l	G3C		1.25	2.57	15	2.81	2.54	2.58	0.15	6.0	17
Conductivity	µS/cm	A1J		-0.14	291	5	290	292	291	4	1.4	27
	µS/cm	D2PJ		0.27	162	5	163	163	162	3	1.7	26
	µS/cm	G3PJ		0.29	81.6	5	82.2	81.8	81.5	1.3	1.6	25
F	mg/l	A1F		0.59	1.35	10	1.39	1.38	1.38	0.07	5.3	19
	mg/l	D2F		0.31	0.32	20	0.33	0.31	0.32	0.03	9.4	19
	mg/l	G3F		0.58	0.46	15	0.48	0.46	0.45	0.04	8.6	19
Fe	µg/l	A1Fe		-1.90	56.0	15	48.0	52.7	52.5	4.6	8.8	19
	µg/l	D2Fe		-4.08	34.6	15	24.0	34.7	34.7	2.2	6.3	20
	µg/l	G3Fe		-0.87	81.3	15	76.0	80.9	81.4	4.0	4.9	20
Hardness	mmol/l	A1K		0.00	0.14	10	0.14	0.14	0.14	0.01	4.5	16
	mmol/l	D2K		0.29	0.56	10	0.57	0.56	0.56	0.01	2.3	18
	mmol/l	G3K		0.35	0.23	10	0.23	0.24	0.23	0.01	4.5	17
Mn	µg/l	A1Fe		-4.22	43.1	10	34.0	43.0	42.9	1.9	4.5	17
	µg/l	D2Fe		-3.88	25.4	15	18.0	25.6	25.4	1.1	4.3	18
	µg/l	G3Fe		-5.96	57.0	10	40.0	57.1	56.8	2.0	3.6	18
NH_4	mg/l	A1N		1.09	0.22	10	0.23	0.23	0.22	0.03	12.1	21
	mg/l	D2N		0.43	0.092	15	0.095	0.093	0.092	0.008	8.2	19
	mg/l	G3N		0.72	0.13	15	0.14	0.13	0.13	0.01	5.5	19
NO_2	mg/l	A1N		0.18	0.22	10	0.22	0.22	0.22	0.01	4.8	17
	mg/l	D2N		0.22	0.18	10	0.18	0.18	0.18	0.01	3.7	16
	mg/l	G3N		-0.13	0.078	20	0.077	0.078	0.078	0.001	1.5	16
NO_3	mg/l	A1N		-0.01	4.75	10	4.75	4.75	4.75	0.14	3.0	18
	mg/l	D2N		-0.12	2.64	10	2.62	2.70	2.65	0.12	4.5	18
	mg/l	G3N		-0.46	5.61	10	5.48	5.59	5.61	0.24	4.2	17
pH		A1P		-0.20	7.28	2,7	7.26	7.28	7.28	0.04	0.6	31
		D2PJ		0.30	7.93	2,5	7.96	7.93	7.93	0.08	1.0	29
		G3PJ		1.39	7.22	2,8	7.36	7.20	7.22	0.08	1.1	27

Participant 11												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
COD_{Mn}	mg/l	A1C		1.39	4.02	10	4.30	4.00	4.00	0.08	2.0	19
	mg/l	D2C		0.20	3.26	15	3.31	3.28	3.25	0.25	7.8	20
	mg/l	G3C		1.87	2.57	15	2.93	2.54	2.58	0.15	6.0	17
Conductivity	µS/cm	A1J		0.00	291	5	291	292	291	4	1.4	27
	µS/cm	D2PJ		0.47	162	5	164	163	162	3	1.7	26
	µS/cm	G3PJ		0.25	81.6	5	82.1	81.8	81.5	1.3	1.6	25
pH		A1P		0.00	7.28	2,7	7.28	7.28	7.28	0.04	0.6	31
		D2PJ		0.30	7.93	2,5	7.96	7.93	7.93	0.08	1.0	29
		G3PJ		0.20	7.22	2,8	7.24	7.20	7.22	0.08	1.1	27

Participant 12												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Ca	mg/l	A1K		0.93	4.54	10	4.75	4.51	4.50	0.28	6.3	16
	mg/l	D2K		0.30	19.7	10	20.0	19.8	19.9	1.0	5.1	16
	mg/l	G3K		11.11	7.33	10	11.40	7.32	7.29	0.25	3.4	13
Cl	mg/l	A1S		-0.99	12.1	10	11.5	11.9	12.0	0.4	3.1	22
	mg/l	D2S		0.56	5.74	10	5.90	5.78	5.73	0.25	4.3	24
	mg/l	G3S		0.33	3.67	10	3.73	3.68	3.67	0.21	5.6	23
COD_{Mn}	mg/l	A1C		0.05	4.02	10	4.03	4.00	4.00	0.08	2.0	19
	mg/l	D2C		-0.65	3.26	15	3.10	3.28	3.25	0.25	7.8	20
	mg/l	G3C		-0.93	2.57	15	2.39	2.54	2.58	0.15	6.0	17
Conductivity	µS/cm	A1J		0.41	291	5	294	292	291	4	1.4	27
	µS/cm	D2PJ		0.77	162	5	165	163	162	3	1.7	26
	µS/cm	G3PJ		1.03	81.6	5	83.7	81.8	81.5	1.3	1.6	25
F	mg/l	A1F		-0.44	1.35	10	1.32	1.38	1.38	0.07	5.3	19
	mg/l	D2F		-0.50	0.32	20	0.30	0.31	0.32	0.03	9.4	19
	mg/l	G3F		-0.17	0.46	15	0.45	0.46	0.45	0.04	8.6	19
Fe	µg/l	A1Fe		-1.19	56.0	15	51.0	52.7	52.5	4.6	8.8	19
	µg/l	D2Fe		-1.16	34.6	15	31.6	34.7	34.7	2.2	6.3	20
	µg/l	G3Fe		-0.23	81.3	15	79.9	80.9	81.4	4.0	4.9	20
Hardness	mmol/l	A1K		230.00	0.14	10	1.75	0.14	0.14	0.01	4.5	16
	mmol/l	D2K		0.71	0.56	10	0.58	0.56	0.56	0.01	2.3	18
	mmol/l	G3K		10.43	0.23	10	0.35	0.24	0.23	0.01	4.5	17
Mg	mg/l	A1K		922.86	0.84	10	39.60	0.82	0.82	0.03	3.5	13
	mg/l	D2K		3.69	1.68	10	1.99	1.69	1.68	0.04	2.6	13
	mg/l	G3K		4.06	1.33	10	1.60	1.33	1.33	0.04	3.2	14
Mn	µg/l	A1Fe		0.70	43.1	10	44.6	43.0	42.9	1.9	4.5	17
	µg/l	D2Fe		-1.00	25.4	15	23.5	25.6	25.4	1.1	4.3	18
	µg/l	G3Fe		-0.88	57.0	10	54.5	57.1	56.8	2.0	3.6	18
NH_4	mg/l	A1N		-0.27	0.22	10	0.22	0.23	0.22	0.03	12.1	21
	mg/l	D2N		-0.17	0.092	15	0.091	0.093	0.092	0.008	8.2	19
	mg/l	G3N		-0.21	0.13	15	0.13	0.13	0.13	0.01	5.5	19
NO_2	mg/l	A1N		-0.45	0.22	10	0.22	0.22	0.22	0.01	4.8	17
	mg/l	D2N		-0.22	0.18	10	0.18	0.18	0.18	0.01	3.7	16
	mg/l	G3N		-0.15	0.078	20	0.077	0.078	0.078	0.001	1.5	16
NO_3	mg/l	A1N		-0.17	4.75	10	4.71	4.75	4.75	0.14	3.0	18
	mg/l	D2N		0.76	2.64	10	2.74	2.70	2.65	0.12	4.5	18
	mg/l	G3N		-0.43	5.61	10	5.49	5.59	5.61	0.24	4.2	17
pH		A1P		0.10	7.28	2,7	7.29	7.28	7.28	0.04	0.6	31
		D2PJ		0.50	7.93	2,5	7.98	7.93	7.93	0.08	1.0	29
		G3PJ		0.99	7.22	2,8	7.32	7.20	7.22	0.08	1.1	27
SO_4	mg/l	A1S		-0.13	6.17	10	6.13	6.13	6.13	0.20	3.3	21
	mg/l	D2S		-0.30	26.7	10	26.3	26.8	26.8	0.7	2.7	22
	mg/l	G3S		0.11	9.37	10	9.42	9.29	9.34	0.33	3.5	21

Participant 13												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Cl	mg/l	A1S		-0.33	12.1	10	11.9	11.9	12.0	0.4	3.1	22
	mg/l	D2S		-1.15	5.74	10	5.41	5.78	5.73	0.25	4.3	24
Conductivity	µS/cm	A1J		0.08	291	5	292	292	291	4	1.4	27
	µS/cm	D2PJ		0.17	162	5	163	163	162	3	1.7	26
Fe	µg/l	A1Fe		4.76	56.0	15	76.0	52.7	52.5	4.6	8.8	19
	µg/l	D2Fe		25.59	34.6	15	101.0	34.7	34.7	2.2	6.3	20
pH		A1P		0.00	7.28	2,7	7.28	7.28	7.28	0.04	0.6	31
		D2PJ		-0.30	7.93	2,5	7.90	7.93	7.93	0.08	1.0	29

Participant 14												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
COD_{Mn}	mg/l	A1C		-0.10	4.02	10	4.00	4.00	4.00	0.08	2.0	19
	mg/l	D2C		0.08	3.26	15	3.28	3.28	3.25	0.25	7.8	20
	mg/l	G3C		-0.88	2.57	15	2.40	2.54	2.58	0.15	6.0	17
Conductivity	µS/cm	A1J		-0.55	291	5	287	292	291	4	1.4	27
	µS/cm	D2PJ		-0.74	162	5	159	163	162	3	1.7	26
	µS/cm	G3PJ		-1.62	81.6	5	78.3	81.8	81.5	1.3	1.6	25
NH_4	mg/l	A1N		0.27	0.22	10	0.22	0.23	0.22	0.03	12.1	21
	mg/l	D2N		0.14	0.092	15	0.093	0.093	0.092	0.008	8.2	19
	mg/l	G3N		0.00	0.13	15	0.13	0.13	0.13	0.01	5.5	19
NO_2	mg/l	A1N		-0.09	0.22	10	0.22	0.22	0.22	0.01	4.8	17
	mg/l	D2N		0.11	0.18	10	0.18	0.18	0.18	0.01	3.7	16
	mg/l	G3N		-0.13	0.078	20	0.077	0.078	0.078	0.001	1.5	16
pH		A1P		0.00	7.28	2,7	7.28	7.28	7.28	0.04	0.6	31
		D2PJ		-1.41	7.93	2,5	7.79	7.93	7.93	0.08	1.0	29
		G3PJ		-0.40	7.22	2,8	7.18	7.20	7.22	0.08	1.1	27

Participant 15												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Ca	mg/l	A1K		2.29	4.54	10	5.06	4.51	4.50	0.28	6.3	16
	mg/l	D2K		2.13	19.7	10	21.8	19.8	19.9	1.0	5.1	16
	mg/l	G3K		1.80	7.33	10	7.99	7.32	7.29	0.25	3.4	13
Cl	mg/l	A1S		-1.32	12.1	10	11.3	11.9	12.0	0.4	3.1	22
	mg/l	D2S		-1.50	5.74	10	5.31	5.78	5.73	0.25	4.3	24
	mg/l	G3S		-2.62	3.67	10	3.19	3.68	3.67	0.21	5.6	23
Conductivity	µS/cm	A1J		0.69	291	5	296	292	291	4	1.4	27
	µS/cm	D2PJ		0.49	162	5	164	163	162	3	1.7	26
	µS/cm	G3PJ		0.25	81.6	5	82.1	81.8	81.5	1.3	1.6	25
Fe	µg/l	A1Fe		-4.67	56.0	15	36.4	52.7	52.5	4.6	8.8	19
	µg/l	D2Fe		0.00	34.6	15	34.6	34.7	34.7	2.2	6.3	20
	µg/l	G3Fe		-3.43	81.3	15	60.4	80.9	81.4	4.0	4.9	20
Hardness	mmol/l	A1K		2.71	0.14	10	0.16	0.14	0.14	0.01	4.5	16
	mmol/l	D2K		1.79	0.56	10	0.61	0.56	0.56	0.01	2.3	18
	mmol/l	G3K		1.91	0.23	10	0.25	0.24	0.23	0.01	4.5	17
K	mg/l	A1K		0.86	0.70	10	0.73	0.69	0.69	0.04	5.5	11
	mg/l	D2K		-0.87	1.38	10	1.32	1.40	1.38	0.04	2.9	13
	mg/l	G3K		-2.02	1.09	10	0.98	1.09	1.09	0.02	2.2	13

Participant 15												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Mg	mg/l	A1K		-0.95	0.84	10	0.80	0.82	0.82	0.03	3.5	13
	mg/l	D2K		-0.71	1.68	10	1.62	1.69	1.68	0.04	2.6	13
	mg/l	G3K		-0.60	1.33	10	1.29	1.33	1.33	0.04	3.2	14
Mn	µg/l	A1Fe		0.05	43.1	10	43.2	43.0	42.9	1.9	4.5	17
	µg/l	D2Fe		0.58	25.4	15	26.5	25.6	25.4	1.1	4.3	18
	µg/l	G3Fe		0.49	57.0	10	58.4	57.1	56.8	2.0	3.6	18
Na	mg/l	A1K		0.00	1.22	10	1.22	1.18	1.18	0.06	4.7	15
	mg/l	D2K		0.08	7.40	10	7.43	7.36	7.40	0.27	3.6	15
	mg/l	G3K		0.41	4.43	10	4.52	4.46	4.43	0.21	4.8	15
NH_4	mg/l	A1N		3.64	0.22	10	0.26	0.23	0.22	0.03	12.1	21
	mg/l	D2N		8.41	0.092	15	0.150	0.093	0.092	0.008	8.2	19
	mg/l	G3N		4.10	0.13	15	0.17	0.13	0.13	0.01	5.5	19
NO_3	mg/l	A1N		-0.72	4.75	10	4.58	4.75	4.75	0.14	3.0	18
	mg/l	D2N		-0.98	2.64	10	2.51	2.70	2.65	0.12	4.5	18
	mg/l	G3N		-0.57	5.61	10	5.45	5.59	5.61	0.24	4.2	17
pH		A1P		-0.10	7.28	2,7	7.27	7.28	7.28	0.04	0.6	31
		D2PJ		0.20	7.93	2,5	7.95	7.93	7.93	0.08	1.0	29
		G3PJ		0.49	7.22	2,8	7.27	7.20	7.22	0.08	1.1	27
SO_4	mg/l	A1S		-1.65	6.17	10	5.66	6.13	6.13	0.20	3.3	21
	mg/l	D2S		-0.90	26.7	10	25.5	26.8	26.8	0.7	2.7	22
	mg/l	G3S		-0.88	9.37	10	8.96	9.29	9.34	0.33	3.5	21

Participant 16												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Ca	mg/l	A1K		-1.94	4.54	10	4.10	4.51	4.50	0.28	6.3	16
	mg/l	D2K		-2.84	19.7	10	16.9	19.8	19.9	1.0	5.1	16
Cl	mg/l	A1S		-1.62	12.1	10	11.1	11.9	12.0	0.4	3.1	22
	mg/l	D2S		-1.60	5.74	10	5.28	5.78	5.73	0.25	4.3	24
COD_{Mn}	mg/l	A1C		0.95	4.02	10	4.21	4.00	4.00	0.08	2.0	19
	mg/l	D2C		0.61	3.26	15	3.41	3.28	3.25	0.25	7.8	20
Conductivity	µS/cm	A1J		-0.55	291	5	287	292	291	4	1.4	27
	µS/cm	D2PJ		-0.25	162	5	161	163	162	3	1.7	26
Na	mg/l	A1K		-0.82	1.22	10	1.17	1.18	1.18	0.06	4.7	15
	mg/l	D2K		0.76	7.40	10	7.68	7.36	7.40	0.27	3.6	15
pH		A1P		-0.31	7.28	2,7	7.25	7.28	7.28	0.04	0.6	31
		D2PJ		0.20	7.93	2,5	7.95	7.93	7.93	0.08	1.0	29

Participant 17												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Ca	mg/l	A1K		-1.23	4.54	10	4.26	4.51	4.50	0.28	6.3	16
	mg/l	D2K		-1.93	19.7	10	17.8	19.8	19.9	1.0	5.1	16
	mg/l	G3K		-0.98	7.33	10	6.97	7.32	7.29	0.25	3.4	13
Cl	mg/l	A1S		-0.15	12.1	10	12.0	11.9	12.0	0.4	3.1	22
	mg/l	D2S		0.35	5.74	10	5.84	5.78	5.73	0.25	4.3	24
	mg/l	G3S		0.05	3.67	10	3.68	3.68	3.67	0.21	5.6	23
COD_{Mn}	mg/l	A1C		-3.83	4.02	10	3.25	4.00	4.00	0.08	2.0	19
	mg/l	D2C		-2.74	3.26	15	2.59	3.28	3.25	0.25	7.8	20
	mg/l	G3C		-3.06	2.57	15	1.98	2.54	2.58	0.15	6.0	17

Participant 17												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Conductivity	µS/cm	A1J		0.82	291	5	297	292	291	4	1.4	27
	µS/cm	D2PJ		-0.49	162	5	160	163	162	3	1.7	26
	µS/cm	G3PJ		-0.29	81.6	5	81.0	81.8	81.5	1.3	1.6	25
F	mg/l	A1F		-1.48	1.35	10	1.25	1.38	1.38	0.07	5.3	19
	mg/l	D2F		-0.69	0.32	20	0.30	0.31	0.32	0.03	9.4	19
	mg/l	G3F		-0.99	0.46	15	0.43	0.46	0.45	0.04	8.6	19
Fe	µg/l	A1Fe		0.24	56.0	15	57.0	52.7	52.5	4.6	8.8	19
	µg/l	D2Fe		1.46	34.6	15	38.4	34.7	34.7	2.2	6.3	20
	µg/l	G3Fe		0.49	81.3	15	84.3	80.9	81.4	4.0	4.9	20
Hardness	mmol/l	A1K		1.29	0.14	10	0.15	0.14	0.14	0.01	4.5	16
	mmol/l	D2K		-0.07	0.56	10	0.56	0.56	0.56	0.01	2.3	18
	mmol/l	G3K		0.96	0.23	10	0.24	0.24	0.23	0.01	4.5	17
K	mg/l	A1K			0.70	10	*<1,0*	0.69	0.69	0.04	5.5	11
	mg/l	D2K		0.43	1.38	10	1.41	1.40	1.38	0.04	2.9	13
	mg/l	G3K		-0.37	1.09	10	1.07	1.09	1.09	0.02	2.2	13
Mg	mg/l	A1K		0.57	0.84	10	0.86	0.82	0.82	0.03	3.5	13
	mg/l	D2K		0.71	1.68	10	1.74	1.69	1.68	0.04	2.6	13
	mg/l	G3K		0.75	1.33	10	1.38	1.33	1.33	0.04	3.2	14
Mn	µg/l	A1Fe		1.21	43.1	10	45.7	43.0	42.9	1.9	4.5	17
	µg/l	D2Fe		0.42	25.4	15	26.2	25.6	25.4	1.1	4.3	18
	µg/l	G3Fe		0.42	57.0	10	58.2	57.1	56.8	2.0	3.6	18
Na	mg/l	A1K		0.82	1.22	10	1.27	1.18	1.18	0.06	4.7	15
	mg/l	D2K		1.11	7.40	10	7.81	7.36	7.40	0.27	3.6	15
	mg/l	G3K		1.40	4.43	10	4.74	4.46	4.43	0.21	4.8	15
NH_4	mg/l	A1N			0.22	10	*<0,64*	0.23	0.22	0.03	12.1	21
	mg/l	D2N			0.092	15	*<0,64*	0.093	0.092	0.008	8.2	19
	mg/l	G3N			0.13	15	*<0,64*	0.13	0.13	0.01	5.5	19
NO_2	mg/l	A1N			0.22	10	*<0,50*	0.22	0.22	0.01	4.8	17
	mg/l	D2N			0.18	10	*<0,50*	0.18	0.18	0.01	3.7	16
	mg/l	G3N			0.078	20	*<0,50*	0.078	0.078	0.001	1.5	16
NO_3	mg/l	A1N		0.88	4.75	10	4.96	4.75	4.75	0.14	3.0	18
	mg/l	D2N		0.91	2.64	10	2.76	2.70	2.65	0.12	4.5	18
	mg/l	G3N		0.96	5.61	10	5.88	5.59	5.61	0.24	4.2	17
pH		A1P		0.71	7.28	2,7	7.35	7.28	7.28	0.04	0.6	31
		D2PJ		-0.10	7.93	2,5	7.92	7.93	7.93	0.08	1.0	29
		G3PJ		-1.29	7.22	2,8	7.09	7.20	7.22	0.08	1.1	27
SO_4	mg/l	A1S		0.03	6.17	10	6.18	6.13	6.13	0.20	3.3	21
	mg/l	D2S		0.30	26.7	10	27.1	26.8	26.8	0.7	2.7	22
	mg/l	G3S		0.21	9.37	10	9.47	9.29	9.34	0.33	3.5	21

Participant 18												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Ca	mg/l	A1K		-2.11	4.54	10	4.06	4.51	4.50	0.28	6.3	16
	mg/l	D2K		-0.71	19.7	10	19.0	19.8	19.9	1.0	5.1	16
	mg/l	G3K		-1.12	7.33	10	6.92	7.32	7.29	0.25	3.4	13
Cl	mg/l	A1S		-0.33	12.1	10	11.9	11.9	12.0	0.4	3.1	22
	mg/l	D2S		-0.10	5.74	10	5.71	5.78	5.73	0.25	4.3	24
	mg/l	G3S		0.11	3.67	10	3.69	3.68	3.67	0.21	5.6	23

Participant 18												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
COD_{Mn}	mg/l	A1C		-0.85	4.02	10	3.85	4.00	4.00	0.08	2.0	19
	mg/l	D2C		-1.15	3.26	15	2.98	3.28	3.25	0.25	7.8	20
	mg/l	G3C		0.99	2.57	15	2.76	2.54	2.58	0.15	6.0	17
Conductivity	µS/cm	A1J		-0.36	291	5	288	292	291	4	1.4	27
	µS/cm	D2PJ		-0.37	162	5	161	163	162	3	1.7	26
	µS/cm	G3PJ		0.49	81.6	5	82.6	81.8	81.5	1.3	1.6	25
F	mg/l	A1F		0.59	1.35	10	1.39	1.38	1.38	0.07	5.3	19
	mg/l	D2F		1.28	0.32	20	0.36	0.31	0.32	0.03	9.4	19
	mg/l	G3F		0.99	0.46	15	0.49	0.46	0.45	0.04	8.6	19
Fe	µg/l	A1Fe		0.34	56.0	15	57.4	52.7	52.5	4.6	8.8	19
	µg/l	D2Fe		0.48	34.6	15	35.8	34.7	34.7	2.2	6.3	20
	µg/l	G3Fe		0.47	81.3	15	84.2	80.9	81.4	4.0	4.9	20
Hardness	mmol/l	A1K		-0.86	0.14	10	0.13	0.14	0.14	0.01	4.5	16
	mmol/l	D2K		-0.68	0.56	10	0.54	0.56	0.56	0.01	2.3	18
	mmol/l	G3K		-0.43	0.23	10	0.23	0.24	0.23	0.01	4.5	17
K	mg/l	A1K		0.00	0.70	10	0.70	0.69	0.69	0.04	5.5	11
	mg/l	D2K		0.14	1.38	10	1.39	1.40	1.38	0.04	2.9	13
	mg/l	G3K		0.37	1.09	10	1.11	1.09	1.09	0.02	2.2	13
Mg	mg/l	A1K		-1.17	0.84	10	0.79	0.82	0.82	0.03	3.5	13
	mg/l	D2K		-0.71	1.68	10	1.62	1.69	1.68	0.04	2.6	13
	mg/l	G3K		-0.90	1.33	10	1.27	1.33	1.33	0.04	3.2	14
Mn	µg/l	A1Fe		0.63	43.1	10	44.5	43.0	42.9	1.9	4.5	17
	µg/l	D2Fe		0.23	25.4	15	25.8	25.6	25.4	1.1	4.3	18
	µg/l	G3Fe		0.39	57.0	10	58.1	57.1	56.8	2.0	3.6	18
Na	mg/l	A1K		-0.98	1.22	10	1.16	1.18	1.18	0.06	4.7	15
	mg/l	D2K		-0.35	7.40	10	7.27	7.36	7.40	0.27	3.6	15
	mg/l	G3K		0.09	4.43	10	4.45	4.46	4.43	0.21	4.8	15
NH_4	mg/l	A1N		0.91	0.22	10	0.23	0.23	0.22	0.03	12.1	21
	mg/l	D2N		0.72	0.092	15	0.097	0.093	0.092	0.008	8.2	19
	mg/l	G3N		0.00	0.13	15	0.13	0.13	0.13	0.01	5.5	19
NO_2	mg/l	A1N		1.73	0.22	10	0.24	0.22	0.22	0.01	4.8	17
	mg/l	D2N		1.22	0.18	10	0.19	0.18	0.18	0.01	3.7	16
	mg/l	G3N		0.04	0.078	20	0.078	0.078	0.078	0.001	1.5	16
NO_3	mg/l	A1N		-1.22	4.75	10	4.46	4.75	4.75	0.14	3.0	18
	mg/l	D2N		-2.50	2.64	10	2.31	2.70	2.65	0.12	4.5	18
	mg/l	G3N		-0.07	5.61	10	5.59	5.59	5.61	0.24	4.2	17
pH		A1P		0.20	7.28	2,7	7.30	7.28	7.28	0.04	0.6	31
		D2PJ		0.71	7.93	2,5	8.00	7.93	7.93	0.08	1.0	29
		G3PJ		-0.20	7.22	2,8	7.20	7.20	7.22	0.08	1.1	27
SO_4	mg/l	A1S		0.16	6.17	10	6.22	6.13	6.13	0.20	3.3	21
	mg/l	D2S		0.30	26.7	10	27.1	26.8	26.8	0.7	2.7	22
	mg/l	G3S		0.28	9.37	10	9.50	9.29	9.34	0.33	3.5	21

Participant 19												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Ca	mg/l	A1K		1.64	4.54	10	4.91	4.51	4.50	0.28	6.3	16
	mg/l	G3K		-17.71	7.33	10	0.84	7.32	7.29	0.25	3.4	13
Cl	mg/l	A1S		6.10	12.1	10	15.8	11.9	12.0	0.4	3.1	22
	mg/l	G3S		2.18	3.67	10	4.07	3.68	3.67	0.21	5.6	23
COD_{Mn}	mg/l	A1C		59.60	4.02	10	16.00	4.00	4.00	0.08	2.0	19
	mg/l	G3C		38.55	2.57	15	10.00	2.54	2.58	0.15	6.0	17
Conductivity	µS/cm	G3PJ		-0.64	81.6	5	80.3	81.8	81.5	1.3	1.6	25
Hardness	mmol/l	A1K		0.43	0.14	10	0.14	0.14	0.14	0.01	4.5	16
	mmol/l	G3K		0.17	0.23	10	0.23	0.24	0.23	0.01	4.5	17
K	mg/l	A1K		1.96	0.70	10	0.77	0.69	0.69	0.04	5.5	11
	mg/l	G3K		1.87	1.09	10	1.19	1.09	1.09	0.02	2.2	13
Mg	mg/l	A1K		171.17	0.84	10	8.03	0.82	0.82	0.03	3.5	13
	mg/l	G3K		-0.14	1.33	10	1.32	1.33	1.33	0.04	3.2	14
Na	mg/l	A1K		-0.41	1.22	10	1.20	1.18	1.18	0.06	4.7	15
	mg/l	G3K		-1.56	4.43	10	4.09	4.46	4.43	0.21	4.8	15
NH_4	mg/l	A1N		-4.91	0.22	10	0.17	0.23	0.22	0.03	12.1	21
	mg/l	G3N		-3.49	0.13	15	0.10	0.13	0.13	0.01	5.5	19
NO_2	mg/l	A1N		-13.64	0.22	10	0.07	0.22	0.22	0.01	4.8	17
	mg/l	G3N		-7.31	0.078	20	0.021	0.078	0.078	0.001	1.5	16
NO_3	mg/l	A1N		-17.62	4.75	10	0.57	4.75	4.75	0.14	3.0	18
	mg/l	G3N		-17.12	5.61	10	0.81	5.59	5.61	0.24	4.2	17
pH		A1P		0.20	7.28	2,7	7.30	7.28	7.28	0.04	0.6	31
		G3PJ		-3.07	7.22	2,8	6.91	7.20	7.22	0.08	1.1	27
SO_4	mg/l	A1S		0.55	6.17	10	6.34	6.13	6.13	0.20	3.3	21
	mg/l	G3S		1.28	9.37	10	9.97	9.29	9.34	0.33	3.5	21

Participant 20												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Conductivity	µS/cm	A1J		0.27	291	5	293	292	291	4	1.4	27
	µS/cm	D2PJ		0.25	162	5	163	163	162	3	1.7	26
	µS/cm	G3PJ		0.34	81.6	5	82.3	81.8	81.5	1.3	1.6	25
pH		A1P		-0.10	7.28	2,7	7.27	7.28	7.28	0.04	0.6	31
		D2PJ		-0.30	7.93	2,5	7.90	7.93	7.93	0.08	1.0	29
		G3PJ		0.00	7.22	2,8	7.22	7.20	7.22	0.08	1.1	27

Participant 21												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Ca	mg/l	A1K		0.09	4.54	10	4.56	4.51	4.50	0.28	6.3	16
	mg/l	D2K		0.00	19.7	10	19.7	19.8	19.9	1.0	5.1	16
	mg/l	G3K		-0.05	7.33	10	7.31	7.32	7.29	0.25	3.4	13
Cl	mg/l	A1S		0.99	12.1	10	12.7	11.9	12.0	0.4	3.1	22
	mg/l	D2S		-0.52	5.74	10	5.59	5.78	5.73	0.25	4.3	24
	mg/l	G3S		-0.76	3.67	10	3.53	3.68	3.67	0.21	5.6	23
COD_{Mn}	mg/l	A1C		0.60	4.02	10	4.14	4.00	4.00	0.08	2.0	19
	mg/l	D2C		1.23	3.26	15	3.56	3.28	3.25	0.25	7.8	20
	mg/l	G3C		0.47	2.57	15	2.66	2.54	2.58	0.15	6.0	17
Conductivity	µS/cm	A1J		0.27	291	5	293	292	291	4	1.4	27
	µS/cm	D2PJ		-3.95	162	5	146	163	162	3	1.7	26
	µS/cm	G3PJ		2.35	81.6	5	86.4	81.8	81.5	1.3	1.6	25

Participant 21												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
F	mg/l	A1F		1.93	1.35	10	1.48	1.38	1.38	0.07	5.3	19
	mg/l	D2F		-1.84	0.32	20	0.26	0.31	0.32	0.03	9.4	19
	mg/l	G3F		-1.42	0.46	15	0.41	0.46	0.45	0.04	8.6	19
Fe	µg/l	A1Fe		0.14	56.0	15	56.6	52.7	52.5	4.6	8.8	19
	µg/l	D2Fe		1.97	34.6	15	39.7	34.7	34.7	2.2	6.3	20
	µg/l	G3Fe		0.49	81.3	15	84.3	80.9	81.4	4.0	4.9	20
Hardness	mmol/l	A1K		1.29	0.14	10	0.15	0.14	0.14	0.01	4.5	16
	mmol/l	D2K		0.14	0.56	10	0.56	0.56	0.56	0.01	2.3	18
	mmol/l	G3K		0.87	0.23	10	0.24	0.24	0.23	0.01	4.5	17
K	mg/l	A1K		3.71	0.70	10	0.83	0.69	0.69	0.04	5.5	11
	mg/l	D2K		0.14	1.38	10	1.39	1.40	1.38	0.04	2.9	13
	mg/l	G3K		-0.73	1.09	10	1.05	1.09	1.09	0.02	2.2	13
Mg	mg/l	A1K		0.31	0.84	10	0.85	0.82	0.82	0.03	3.5	13
	mg/l	D2K		0.60	1.68	10	1.73	1.69	1.68	0.04	2.6	13
	mg/l	G3K		0.75	1.33	10	1.38	1.33	1.33	0.04	3.2	14
Mn	µg/l	A1Fe		-0.05	43.1	10	43.0	43.0	42.9	1.9	4.5	17
	µg/l	D2Fe		0.42	25.4	15	26.2	25.6	25.4	1.1	4.3	18
	µg/l	G3Fe		-0.18	57.0	10	56.5	57.1	56.8	2.0	3.6	18
Na	mg/l	A1K		-1.31	1.22	10	1.14	1.18	1.18	0.06	4.7	15
	mg/l	D2K		-1.19	7.40	10	6.96	7.36	7.40	0.27	3.6	15
	mg/l	G3K		-0.81	4.43	10	4.25	4.46	4.43	0.21	4.8	15
NH_4	mg/l	A1N		0.91	0.22	10	0.23	0.23	0.22	0.03	12.1	21
	mg/l	D2N		-0.43	0.092	15	0.089	0.093	0.092	0.008	8.2	19
	mg/l	G3N		0.41	0.13	15	0.13	0.13	0.13	0.01	5.5	19
NO_2	mg/l	A1N		1.00	0.22	10	0.23	0.22	0.22	0.01	4.8	17
	mg/l	D2N		1.44	0.18	10	0.19	0.18	0.18	0.01	3.7	16
	mg/l	G3N		0.65	0.078	20	0.083	0.078	0.078	0.001	1.5	16
NO_3	mg/l	A1N		0.21	4.75	10	4.80	4.75	4.75	0.14	3.0	18
	mg/l	D2N		0.45	2.64	10	2.70	2.70	2.65	0.12	4.5	18
	mg/l	G3N		0.00	5.61	10	5.61	5.59	5.61	0.24	4.2	17
pH		A1P		0.31	7.28	2,7	7.31	7.28	7.28	0.04	0.6	31
		D2PJ		1.31	7.93	2,5	8.06	7.93	7.93	0.08	1.0	29
		G3PJ		1.39	7.22	2,8	7.36	7.20	7.22	0.08	1.1	27
SO_4	mg/l	A1S		-0.23	6.17	10	6.10	6.13	6.13	0.20	3.3	21
	mg/l	D2S		-0.60	26.7	10	25.9	26.8	26.8	0.7	2.7	22
	mg/l	G3S		-0.55	9.37	10	9.11	9.29	9.34	0.33	3.5	21

Participant 22												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Ca	mg/l	A1K		0.79	4.54	10	4.72	4.51	4.50	0.28	6.3	16
	mg/l	D2K		1.93	19.7	10	21.6	19.8	19.9	1.0	5.1	16
	mg/l	G3K		0.74	7.33	10	7.60	7.32	7.29	0.25	3.4	13
Cl	mg/l	A1S		0.33	12.1	10	12.3	11.9	12.0	0.4	3.1	22
	mg/l	D2S		0.17	5.74	10	5.79	5.78	5.73	0.25	4.3	24
	mg/l	G3S		-0.54	3.67	10	3.57	3.68	3.67	0.21	5.6	23
Conductivity	µS/cm	A1J		-37.88	291	5	15	292	291	4	1.4	27
	µS/cm	D2PJ		-38.10	162	5	8	163	162	3	1.7	26
	µS/cm	G3PJ		-26.52	81.6	5	27.5	81.8	81.5	1.3	1.6	25

Participant 22												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
F	mg/l	A1F		1.78	1.35	10	1.47	1.38	1.38	0.07	5.3	19
	mg/l	D2F		-0.63	0.32	20	0.30	0.31	0.32	0.03	9.4	19
	mg/l	G3F		0.00	0.46	15	0.46	0.46	0.45	0.04	8.6	19
Fe	µg/l	A1Fe		-0.95	56.0	15	52.0	52.7	52.5	4.6	8.8	19
	µg/l	D2Fe		-0.23	34.6	15	34.0	34.7	34.7	2.2	6.3	20
	µg/l	G3Fe		-0.54	81.3	15	78.0	80.9	81.4	4.0	4.9	20
K	mg/l	A1K		-0.86	0.70	10	0.67	0.69	0.69	0.04	5.5	11
	mg/l	D2K		0.43	1.38	10	1.41	1.40	1.38	0.04	2.9	13
	mg/l	G3K		0.18	1.09	10	1.10	1.09	1.09	0.02	2.2	13
Mg	mg/l	A1K		-0.48	0.84	10	0.82	0.82	0.82	0.03	3.5	13
	mg/l	D2K		0.36	1.68	10	1.71	1.69	1.68	0.04	2.6	13
	mg/l	G3K		0.30	1.33	10	1.35	1.33	1.33	0.04	3.2	14
Mn	µg/l	A1Fe		-1.30	43.1	10	40.3	43.0	42.9	1.9	4.5	17
	µg/l	D2Fe		-0.63	25.4	15	24.2	25.6	25.4	1.1	4.3	18
	µg/l	G3Fe		-1.30	57.0	10	53.3	57.1	56.8	2.0	3.6	18
Na	mg/l	A1K		0.66	1.22	10	1.26	1.18	1.18	0.06	4.7	15
	mg/l	D2K		0.78	7.40	10	7.69	7.36	7.40	0.27	3.6	15
	mg/l	G3K		0.90	4.43	10	4.63	4.46	4.43	0.21	4.8	15
NH_4	mg/l	A1N		-1.82	0.22	10	0.20	0.23	0.22	0.03	12.1	21
	mg/l	D2N		-1.30	0.092	15	0.083	0.093	0.092	0.008	8.2	19
	mg/l	G3N		-1.03	0.13	15	0.12	0.13	0.13	0.01	5.5	19
NO_3	mg/l	A1N		-15.49	4.75	10	1.07	4.75	4.75	0.14	3.0	18
	mg/l	D2N		-15.91	2.64	10	0.54	2.70	2.65	0.12	4.5	18
	mg/l	G3N		-15.54	5.61	10	1.25	5.59	5.61	0.24	4.2	17
pH		A1P		-0.10	7.28	2,7	7.27	7.28	7.28	0.04	0.6	31
		D2PJ		-0.30	7.93	2,5	7.90	7.93	7.93	0.08	1.0	29
		G3PJ		0.30	7.22	2,8	7.25	7.20	7.22	0.08	1.1	27
SO_4	mg/l	A1S		-1.20	6.17	10	5.80	6.13	6.13	0.20	3.3	21
	mg/l	D2S		0.30	26.7	10	27.1	26.8	26.8	0.7	2.7	22
	mg/l	G3S		-0.79	9.37	10	9.00	9.29	9.34	0.33	3.5	21

Participant 23												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Cl	mg/l	A1S		1.49	12.1	10	13.0	11.9	12.0	0.4	3.1	22
	mg/l	D2S		1.25	5.74	10	6.10	5.78	5.73	0.25	4.3	24
	mg/l	G3S		0.71	3.67	10	3.80	3.68	3.67	0.21	5.6	23
COD_{Mn}	mg/l	A1C		-0.10	4.02	10	4.00	4.00	4.00	0.08	2.0	19
	mg/l	D2C		-1.06	3.26	15	3.00	3.28	3.25	0.25	7.8	20
	mg/l	G3C			2.57	15	*<1*	2.54	2.58	0.15	6.0	17
Conductivity	µS/cm	A1J		-35.99	291	5	29	292	291	4	1.4	27
	µS/cm	D2PJ		-36.00	162	5	16	163	162	3	1.7	26
	µS/cm	G3PJ		-36.03	81.6	5	8.1	81.8	81.5	1.3	1.6	25
F	mg/l	A1F		0.74	1.35	10	1.40	1.38	1.38	0.07	5.3	19
	mg/l	D2F		-0.31	0.32	20	0.31	0.31	0.32	0.03	9.4	19
	mg/l	G3F		0.29	0.46	15	0.47	0.46	0.45	0.04	8.6	19
NH_4	mg/l	A1N		0.00	0.22	10	0.22	0.23	0.22	0.03	12.1	21
	mg/l	D2N		-0.43	0.092	15	0.089	0.093	0.092	0.008	8.2	19
	mg/l	G3N		-2.05	0.13	15	0.11	0.13	0.13	0.01	5.5	19

Participant 23												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
NO_2	mg/l	A1N		-1.82	0.22	10	0.20	0.22	0.22	0.01	4.8	17
	mg/l	D2N		-1.11	0.18	10	0.17	0.18	0.18	0.01	3.7	16
	mg/l	G3N		-2.44	0.078	20	0.059	0.078	0.078	0.001	1.5	16
NO_3	mg/l	A1N		0.21	4.75	10	4.80	4.75	4.75	0.14	3.0	18
	mg/l	D2N		0.45	2.64	10	2.70	2.70	2.65	0.12	4.5	18
	mg/l	G3N		1.03	5.61	10	5.90	5.59	5.61	0.24	4.2	17
pH		A1P		0.20	7.28	2,7	7.30	7.28	7.28	0.04	0.6	31
		D2PJ		0.71	7.93	2,5	8.00	7.93	7.93	0.08	1.0	29
		G3PJ		-0.20	7.22	2,8	7.20	7.20	7.22	0.08	1.1	27
SO_4	mg/l	A1S		1.07	6.17	10	6.50	6.13	6.13	0.20	3.3	21
	mg/l	D2S		0.97	26.7	10	28.0	26.8	26.8	0.7	2.7	22
	mg/l	G3S		0.92	9.37	10	9.80	9.29	9.34	0.33	3.5	21

Participant 24												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Ca	mg/l	A1K		3.35	4.54	10	5.30	4.51	4.50	0.28	6.3	16
	mg/l	D2K		1.12	19.7	10	20.8	19.8	19.9	1.0	5.1	16
	mg/l	G3K		5.92	7.33	10	9.50	7.32	7.29	0.25	3.4	13
Cl	mg/l	A1S		2.64	12.1	10	13.7	11.9	12.0	0.4	3.1	22
	mg/l	D2S		7.53	5.74	10	7.90	5.78	5.73	0.25	4.3	24
	mg/l	G3S		11.61	3.67	10	5.80	3.68	3.67	0.21	5.6	23
Conductivity	µS/cm	A1J		0.07	291	5	292	292	291	4	1.4	27
	µS/cm	D2PJ		-0.88	162	5	158	163	162	3	1.7	26
	µS/cm	G3PJ		-0.74	81.6	5	80.1	81.8	81.5	1.3	1.6	25
F	mg/l	A1F		1.76	1.35	10	1.47	1.38	1.38	0.07	5.3	19
	mg/l	D2F		-0.74	0.32	20	0.30	0.31	0.32	0.03	9.4	19
	mg/l	G3F		1.14	0.46	15	0.50	0.46	0.45	0.04	8.6	19
Fe	µg/l	A1Fe		3.88	56.0	15	72.3	52.7	52.5	4.6	8.8	19
	µg/l	D2Fe		0.04	34.6	15	34.7	34.7	34.7	2.2	6.3	20
	µg/l	G3Fe		1.54	81.3	15	90.7	80.9	81.4	4.0	4.9	20
Hardness	mmol/l	A1K		14.29	0.14	10	0.24	0.14	0.14	0.01	4.5	16
	mmol/l	D2K		2.86	0.56	10	0.64	0.56	0.56	0.01	2.3	18
	mmol/l	G3K		9.57	0.23	10	0.34	0.24	0.23	0.01	4.5	17
Mg	mg/l	A1K		41.90	0.84	10	2.60	0.82	0.82	0.03	3.5	13
	mg/l	D2K		14.52	1.68	10	2.90	1.69	1.68	0.04	2.6	13
	mg/l	G3K		17.59	1.33	10	2.50	1.33	1.33	0.04	3.2	14
Mn	µg/l	A1Fe		13.67	43.1	10	72.6	43.0	42.9	1.9	4.5	17
	µg/l	D2Fe		20.45	25.4	15	64.4	25.6	25.4	1.1	4.3	18
	µg/l	G3Fe		7.49	57.0	10	78.4	57.1	56.8	2.0	3.6	18
NH_4	mg/l	A1N		-6.82	0.22	10	0.15	0.23	0.22	0.03	12.1	21
	mg/l	D2N		-6.09	0.092	15	0.050	0.093	0.092	0.008	8.2	19
	mg/l	G3N		-5.12	0.13	15	0.08	0.13	0.13	0.01	5.5	19
NO_2	mg/l	A1N		-13.62	0.22	10	0.07	0.22	0.22	0.01	4.8	17
	mg/l	D2N		-13.70	0.18	10	0.06	0.18	0.18	0.01	3.7	16
	mg/l	G3N		-6.79	0.078	20	0.025	0.078	0.078	0.001	1.5	16
NO_3	mg/l	A1N		-16.00	4.75	10	0.95	4.75	4.75	0.14	3.0	18
	mg/l	D2N		-13.64	2.64	10	0.84	2.70	2.65	0.12	4.5	18
	mg/l	G3N		-16.68	5.61	10	0.93	5.59	5.61	0.24	4.2	17

Participant 24												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
pH		A1P		4.21	7.28	2,7	7.69	7.28	7.28	0.04	0.6	31
		D2PJ		-3.48	7.93	2,5	7.59	7.93	7.93	0.08	1.0	29
		G3PJ		3.95	7.22	2,8	7.62	7.20	7.22	0.08	1.1	27
SO_4	mg/l	A1S		3.01	6.17	10	7.10	6.13	6.13	0.20	3.3	21
	mg/l	D2S		-1.80	26.7	10	24.3	26.8	26.8	0.7	2.7	22
	mg/l	G3S		7.11	9.37	10	12.70	9.29	9.34	0.33	3.5	21

Participant 25												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Conductivity	µS/cm	A1J		0.55	291	5	295	292	291	4	1.4	27
	µS/cm	D2PJ		0.99	162	5	166	163	162	3	1.7	26
	µS/cm	G3PJ		0.69	81.6	5	83.0	81.8	81.5	1.3	1.6	25
Fe	µg/l	A1Fe		2.60	56.0	15	66.9	52.7	52.5	4.6	8.8	19
	µg/l	D2Fe		5.51	34.6	15	48.9	34.7	34.7	2.2	6.3	20
	µg/l	G3Fe		2.44	81.3	15	96.2	80.9	81.4	4.0	4.9	20
Hardness	mmol/l	A1K		-0.14	0.14	10	0.14	0.14	0.14	0.01	4.5	16
	mmol/l	D2K		0.00	0.56	10	0.56	0.56	0.56	0.01	2.3	18
	mmol/l	G3K		0.52	0.23	10	0.24	0.24	0.23	0.01	4.5	17
Mn	µg/l	A1Fe		-2.18	43.1	10	38.4	43.0	42.9	1.9	4.5	17
	µg/l	D2Fe		2.99	25.4	15	31.1	25.6	25.4	1.1	4.3	18
	µg/l	G3Fe		2.91	57.0	10	65.3	57.1	56.8	2.0	3.6	18
NH_4	mg/l	A1N		0.09	0.22	10	0.22	0.23	0.22	0.03	12.1	21
	mg/l	D2N		-1.16	0.092	15	0.084	0.093	0.092	0.008	8.2	19
	mg/l	G3N		-1.13	0.13	15	0.12	0.13	0.13	0.01	5.5	19
NO_2	mg/l	A1N		1.18	0.22	10	0.23	0.22	0.22	0.01	4.8	17
	mg/l	D2N		1.00	0.18	10	0.19	0.18	0.18	0.01	3.7	16
	mg/l	G3N		0.13	0.078	20	0.079	0.078	0.078	0.001	1.5	16
NO_3	mg/l	A1N		0.34	4.75	10	4.83	4.75	4.75	0.14	3.0	18
	mg/l	D2N		1.74	2.64	10	2.87	2.70	2.65	0.12	4.5	18
	mg/l	G3N		0.64	5.61	10	5.79	5.59	5.61	0.24	4.2	17
pH		A1P		-0.51	7.28	2,7	7.23	7.28	7.28	0.04	0.6	31
		D2PJ		0.00	7.93	2,5	7.93	7.93	7.93	0.08	1.0	29
		G3PJ		-0.20	7.22	2,8	7.20	7.20	7.22	0.08	1.1	27

Participant 26												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Cl	mg/l	A1S		-0.33	12.1	10	11.9	11.9	12.0	0.4	3.1	22
	mg/l	D2S		-1.81	5.74	10	5.22	5.78	5.73	0.25	4.3	24
	mg/l	G3S		-1.36	3.67	10	3.42	3.68	3.67	0.21	5.6	23
COD_{Mn}	mg/l	A1C		-0.30	4.02	10	3.96	4.00	4.00	0.08	2.0	19
	mg/l	D2C		-1.15	3.26	15	2.98	3.28	3.25	0.25	7.8	20
	mg/l	G3C		-0.52	2.57	15	2.47	2.54	2.58	0.15	6.0	17
Conductivity	µS/cm	A1J		-0.41	291	5	288	292	291	4	1.4	27
	µS/cm	D2PJ		-0.25	162	5	161	163	162	3	1.7	26
	µS/cm	G3PJ		-0.49	81.6	5	80.6	81.8	81.5	1.3	1.6	25
F	mg/l	A1F		-0.74	1.35	10	1.30	1.38	1.38	0.07	5.3	19
	mg/l	D2F		-0.16	0.32	20	0.32	0.31	0.32	0.03	9.4	19
	mg/l	G3F		-1.77	0.46	15	0.40	0.46	0.45	0.04	8.6	19

Participant 26												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
pH		A1P		-0.51	7.28	2,7	7.23	7.28	7.28	0.04	0.6	31
		D2PJ		-1.51	7.93	2,5	7.78	7.93	7.93	0.08	1.0	29
		G3PJ		-0.40	7.22	2,8	7.18	7.20	7.22	0.08	1.1	27
SO_4	mg/l	A1S		0.29	6.17	10	6.26	6.13	6.13	0.20	3.3	21
	mg/l	D2S		0.60	26.7	10	27.5	26.8	26.8	0.7	2.7	22
	mg/l	G3S		0.43	9.37	10	9.57	9.29	9.34	0.33	3.5	21

Participant 27												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Cl	mg/l	A1S		-0.17	12.1	10	12.0	11.9	12.0	0.4	3.1	22
	mg/l	D2S		0.56	5.74	10	5.90	5.78	5.73	0.25	4.3	24
	mg/l	G3S		0.16	3.67	10	3.70	3.68	3.67	0.21	5.6	23
COD_{Mn}	mg/l	A1C		-0.10	4.02	10	4.00	4.00	4.00	0.08	2.0	19
	mg/l	D2C		0.98	3.26	15	3.50	3.28	3.25	0.25	7.8	20
	mg/l	G3C		0.16	2.57	15	2.60	2.54	2.58	0.15	6.0	17
Conductivity	µS/cm	A1J		-36.11	291	5	28	292	291	4	1.4	27
	µS/cm	D2PJ		-36.07	162	5	16	163	162	3	1.7	26
	µS/cm	G3PJ		-36.13	81.6	5	7.9	81.8	81.5	1.3	1.6	25
NH_4	mg/l	A1N		16343.64	0.22	10	180.00	0.23	0.22	0.03	12.1	21
	mg/l	D2N		9986.67	0.092	15	69.000	0.093	0.092	0.008	8.2	19
	mg/l	G3N		11268.72	0.13	15	110.00	0.13	0.13	0.01	5.5	19
NO_2	mg/l	A1N		6252.73	0.22	10	69.00	0.22	0.22	0.01	4.8	17
	mg/l	D2N		6313.33	0.18	10	57.00	0.18	0.18	0.01	3.7	16
	mg/l	G3N		3066.92	0.078	20	24.000	0.078	0.078	0.001	1.5	16
pH		A1P		0.20	7.28	2,7	7.30	7.28	7.28	0.04	0.6	31
		D2PJ		-0.30	7.93	2,5	7.90	7.93	7.93	0.08	1.0	29
		G3PJ		0.79	7.22	2,8	7.30	7.20	7.22	0.08	1.1	27
SO_4	mg/l	A1S		0.10	6.17	10	6.20	6.13	6.13	0.20	3.3	21
	mg/l	D2S		-2.02	26.7	10	24.0	26.8	26.8	0.7	2.7	22
	mg/l	G3S		-1.64	9.37	10	8.60	9.29	9.34	0.33	3.5	21

Participant 28												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Cl	mg/l	A1S		-0.36	12.1	10	11.9	11.9	12.0	0.4	3.1	22
	mg/l	D2S		0.28	5.74	10	5.82	5.78	5.73	0.25	4.3	24
	mg/l	G3S		0.08	3.67	10	3.68	3.68	3.67	0.21	5.6	23
F	mg/l	A1F		1.54	1.35	10	1.45	1.38	1.38	0.07	5.3	19
	mg/l	D2F		1.28	0.32	20	0.36	0.31	0.32	0.03	9.4	19
	mg/l	G3F		1.68	0.46	15	0.52	0.46	0.45	0.04	8.6	19
NO_2	mg/l	A1N		5.36	0.22	10	0.28	0.22	0.22	0.01	4.8	17
	mg/l	D2N		6.89	0.18	10	0.24	0.18	0.18	0.01	3.7	16
	mg/l	G3N		8.72	0.078	20	0.146	0.078	0.078	0.001	1.5	16
NO_3	mg/l	A1N		-0.38	4.75	10	4.66	4.75	4.75	0.14	3.0	18
	mg/l	D2N		-0.95	2.64	10	2.51	2.70	2.65	0.12	4.5	18
	mg/l	G3N		-0.57	5.61	10	5.45	5.59	5.61	0.24	4.2	17
SO_4	mg/l	A1S		0.55	6.17	10	6.34	6.13	6.13	0.20	3.3	21
	mg/l	D2S		-0.06	26.7	10	26.6	26.8	26.8	0.7	2.7	22
	mg/l	G3S		0.39	9.37	10	9.55	9.29	9.34	0.33	3.5	21

Participant 29												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Ca	mg/l	A1K		0.62	4.54	10	4.68	4.51	4.50	0.28	6.3	16
	mg/l	D2K		0.30	19.7	10	20.0	19.8	19.9	1.0	5.1	16
	mg/l	G3K		1.17	7.33	10	7.76	7.32	7.29	0.25	3.4	13
Cl	mg/l	A1S		0.00	12.1	10	12.1	11.9	12.0	0.4	3.1	22
	mg/l	D2S		0.56	5.74	10	5.90	5.78	5.73	0.25	4.3	24
	mg/l	G3S		0.33	3.67	10	3.73	3.68	3.67	0.21	5.6	23
COD_{Mn}	mg/l	A1C		-0.50	4.02	10	3.92	4.00	4.00	0.08	2.0	19
	mg/l	D2C		0.20	3.26	15	3.31	3.28	3.25	0.25	7.8	20
	mg/l	G3C		0.78	2.57	15	2.72	2.54	2.58	0.15	6.0	17
Conductivity	µS/cm	A1J		0.27	291	5	293	292	291	4	1.4	27
	µS/cm	D2PJ		0.49	162	5	164	163	162	3	1.7	26
	µS/cm	G3PJ		0.00	81.6	5	81.6	81.8	81.5	1.3	1.6	25
F	mg/l	A1F		0.30	1.35	10	1.37	1.38	1.38	0.07	5.3	19
	mg/l	D2F		-0.22	0.32	20	0.31	0.31	0.32	0.03	9.4	19
	mg/l	G3F		-0.70	0.46	15	0.44	0.46	0.45	0.04	8.6	19
Fe	µg/l	A1Fe		-0.26	56.0	15	54.9	52.7	52.5	4.6	8.8	19
	µg/l	D2Fe		0.89	34.6	15	36.9	34.7	34.7	2.2	6.3	20
	µg/l	G3Fe		-0.28	81.3	15	79.6	80.9	81.4	4.0	4.9	20
Hardness	mmol/l	A1K		1.57	0.14	10	0.15	0.14	0.14	0.01	4.5	16
	mmol/l	D2K		0.32	0.56	10	0.57	0.56	0.56	0.01	2.3	18
	mmol/l	G3K		1.65	0.23	10	0.25	0.24	0.23	0.01	4.5	17
K	mg/l	A1K		-0.91	0.70	10	0.67	0.69	0.69	0.04	5.5	11
	mg/l	D2K		0.29	1.38	10	1.40	1.40	1.38	0.04	2.9	13
	mg/l	G3K		-0.18	1.09	10	1.08	1.09	1.09	0.02	2.2	13
Mg	mg/l	A1K		-0.14	0.84	10	0.83	0.82	0.82	0.03	3.5	13
	mg/l	D2K		0.12	1.68	10	1.69	1.69	1.68	0.04	2.6	13
	mg/l	G3K		0.00	1.33	10	1.33	1.33	1.33	0.04	3.2	14
Mn	µg/l	A1Fe		0.32	43.1	10	43.8	43.0	42.9	1.9	4.5	17
	µg/l	D2Fe		0.47	25.4	15	26.3	25.6	25.4	1.1	4.3	18
	µg/l	G3Fe		-0.04	57.0	10	56.9	57.1	56.8	2.0	3.6	18
Na	mg/l	A1K		-1.15	1.22	10	1.15	1.18	1.18	0.06	4.7	15
	mg/l	D2K		-0.27	7.40	10	7.30	7.36	7.40	0.27	3.6	15
	mg/l	G3K		0.14	4.43	10	4.46	4.46	4.43	0.21	4.8	15
NH_4	mg/l	A1N		0.55	0.22	10	0.23	0.23	0.22	0.03	12.1	21
	mg/l	D2N		-0.36	0.092	15	0.090	0.093	0.092	0.008	8.2	19
	mg/l	G3N		0.31	0.13	15	0.13	0.13	0.13	0.01	5.5	19
NO_2	mg/l	A1N		0.09	0.22	10	0.22	0.22	0.22	0.01	4.8	17
	mg/l	D2N		0.56	0.18	10	0.19	0.18	0.18	0.01	3.7	16
	mg/l	G3N		0.18	0.078	20	0.079	0.078	0.078	0.001	1.5	16
NO_3	mg/l	A1N		-0.21	4.75	10	4.70	4.75	4.75	0.14	3.0	18
	mg/l	D2N		-0.15	2.64	10	2.62	2.70	2.65	0.12	4.5	18
	mg/l	G3N		-1.57	5.61	10	5.17	5.59	5.61	0.24	4.2	17
pH		A1P		0.10	7.28	2,7	7.29	7.28	7.28	0.04	0.6	31
		D2PJ		-0.20	7.93	2,5	7.91	7.93	7.93	0.08	1.0	29
		G3PJ		-0.49	7.22	2,8	7.17	7.20	7.22	0.08	1.1	27
SO_4	mg/l	A1S		-1.23	6.17	10	5.79	6.13	6.13	0.20	3.3	21
	mg/l	D2S		-0.15	26.7	10	26.5	26.8	26.8	0.7	2.7	22
	mg/l	G3S		-0.38	9.37	10	9.19	9.29	9.34	0.33	3.5	21

Participant 30												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Ca	mg/l	A1K		0.09	4.54	10	4.56	4.51	4.50	0.28	6.3	16
	mg/l	D2K		0.51	19.7	10	20.2	19.8	19.9	1.0	5.1	16
	mg/l	G3K		0.25	7.33	10	7.42	7.32	7.29	0.25	3.4	13
Cl	mg/l	A1S		-0.33	12.1	10	11.9	11.9	12.0	0.4	3.1	22
	mg/l	D2S		0.10	5.74	10	5.77	5.78	5.73	0.25	4.3	24
	mg/l	G3S		0.71	3.67	10	3.80	3.68	3.67	0.21	5.6	23
F	mg/l	A1F		2.22	1.35	10	1.50	1.38	1.38	0.07	5.3	19
	mg/l	D2F		-0.88	0.32	20	0.29	0.31	0.32	0.03	9.4	19
	mg/l	G3F		-0.67	0.46	15	0.44	0.46	0.45	0.04	8.6	19
Fe	µg/l	A1Fe		-0.33	56.0	15	54.6	52.7	52.5	4.6	8.8	19
	µg/l	D2Fe		-0.15	34.6	15	34.2	34.7	34.7	2.2	6.3	20
	µg/l	G3Fe		0.03	81.3	15	81.5	80.9	81.4	4.0	4.9	20
Hardness	mmol/l	A1K		1.11	0.14	10	0.15	0.14	0.14	0.01	4.5	16
	mmol/l	D2K		0.45	0.56	10	0.57	0.56	0.56	0.01	2.3	18
	mmol/l	G3K		0.93	0.23	10	0.24	0.24	0.23	0.01	4.5	17
K	mg/l	A1K		-0.74	0.70	10	0.67	0.69	0.69	0.04	5.5	11
	mg/l	D2K		0.00	1.38	10	1.38	1.40	1.38	0.04	2.9	13
	mg/l	G3K		-0.37	1.09	10	1.07	1.09	1.09	0.02	2.2	13
Mg	mg/l	A1K		-0.24	0.84	10	0.83	0.82	0.82	0.03	3.5	13
	mg/l	D2K		0.12	1.68	10	1.69	1.69	1.68	0.04	2.6	13
	mg/l	G3K		0.30	1.33	10	1.35	1.33	1.33	0.04	3.2	14
Mn	µg/l	A1Fe		-0.19	43.1	10	42.7	43.0	42.9	1.9	4.5	17
	µg/l	D2Fe		0.26	25.4	15	25.9	25.6	25.4	1.1	4.3	18
	µg/l	G3Fe		0.18	57.0	10	57.5	57.1	56.8	2.0	3.6	18
Na	mg/l	A1K		-0.16	1.22	10	1.21	1.18	1.18	0.06	4.7	15
	mg/l	D2K		0.81	7.40	10	7.70	7.36	7.40	0.27	3.6	15
	mg/l	G3K		1.08	4.43	10	4.67	4.46	4.43	0.21	4.8	15
SO_4	mg/l	A1S		-0.29	6.17	10	6.08	6.13	6.13	0.20	3.3	21
	mg/l	D2S		0.07	26.7	10	26.8	26.8	26.8	0.7	2.7	22
	mg/l	G3S		-0.38	9.37	10	9.19	9.29	9.34	0.33	3.5	21

Participant 31												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Ca	mg/l	A1K		-0.88	4.54	10	4.34	4.51	4.50	0.28	6.3	16
	mg/l	D2K		-0.20	19.7	10	19.5	19.8	19.9	1.0	5.1	16
	mg/l	G3K		-0.35	7.33	10	7.20	7.32	7.29	0.25	3.4	13
Cl	mg/l	A1S		0.50	12.1	10	12.4	11.9	12.0	0.4	3.1	22
	mg/l	D2S		0.17	5.74	10	5.79	5.78	5.73	0.25	4.3	24
	mg/l	G3S		-0.44	3.67	10	3.59	3.68	3.67	0.21	5.6	23
COD_{Mn}	mg/l	A1C		-0.50	4.02	10	3.92	4.00	4.00	0.08	2.0	19
	mg/l	D2C		0.29	3.26	15	3.33	3.28	3.25	0.25	7.8	20
	mg/l	G3C		-0.57	2.57	15	2.46	2.54	2.58	0.15	6.0	17
Conductivity	µS/cm	A1J		0.41	291	5	294	292	291	4	1.4	27
	µS/cm	D2PJ		0.25	162	5	163	163	162	3	1.7	26
	µS/cm	G3PJ		0.05	81.6	5	81.7	81.8	81.5	1.3	1.6	25
F	mg/l	A1F		0.74	1.35	10	1.40	1.38	1.38	0.07	5.3	19
	mg/l	D2F		-0.22	0.32	20	0.31	0.31	0.32	0.03	9.4	19
	mg/l	G3F		-0.46	0.46	15	0.44	0.46	0.45	0.04	8.6	19

Participant 31												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Fe	µg/l	A1Fe		-0.48	56.0	15	54.0	52.7	52.5	4.6	8.8	19
	µg/l	D2Fe		1.16	34.6	15	37.6	34.7	34.7	2.2	6.3	20
	µg/l	G3Fe		0.11	81.3	15	82.0	80.9	81.4	4.0	4.9	20
Hardness	mmol/l	A1K		0.14	0.14	10	0.14	0.14	0.14	0.01	4.5	16
	mmol/l	D2K		-0.25	0.56	10	0.55	0.56	0.56	0.01	2.3	18
	mmol/l	G3K		0.17	0.23	10	0.23	0.24	0.23	0.01	4.5	17
K	mg/l	A1K		-2.03	0.70	10	0.63	0.69	0.69	0.04	5.5	11
	mg/l	D2K		-1.30	1.38	10	1.29	1.40	1.38	0.04	2.9	13
	mg/l	G3K		-0.55	1.09	10	1.06	1.09	1.09	0.02	2.2	13
Mg	mg/l	A1K		-1.21	0.84	10	0.79	0.82	0.82	0.03	3.5	13
	mg/l	D2K		-0.60	1.68	10	1.63	1.69	1.68	0.04	2.6	13
	mg/l	G3K		-1.05	1.33	10	1.26	1.33	1.33	0.04	3.2	14
Mn	µg/l	A1Fe		-0.46	43.1	10	42.1	43.0	42.9	1.9	4.5	17
	µg/l	D2Fe		-0.10	25.4	15	25.2	25.6	25.4	1.1	4.3	18
	µg/l	G3Fe		-0.28	57.0	10	56.2	57.1	56.8	2.0	3.6	18
Na	mg/l	A1K		-1.80	1.22	10	1.11	1.18	1.18	0.06	4.7	15
	mg/l	D2K		-0.78	7.40	10	7.11	7.36	7.40	0.27	3.6	15
	mg/l	G3K		-0.81	4.43	10	4.25	4.46	4.43	0.21	4.8	15
NH_4	mg/l	A1N		0.36	0.22	10	0.22	0.23	0.22	0.03	12.1	21
	mg/l	D2N		-1.61	0.092	15	0.081	0.093	0.092	0.008	8.2	19
	mg/l	G3N		0.21	0.13	15	0.13	0.13	0.13	0.01	5.5	19
NO_2	mg/l	A1N		-0.09	0.22	10	0.22	0.22	0.22	0.01	4.8	17
	mg/l	D2N		0.22	0.18	10	0.18	0.18	0.18	0.01	3.7	16
	mg/l	G3N		0.09	0.078	20	0.079	0.078	0.078	0.001	1.5	16
NO_3	mg/l	A1N		-0.25	4.75	10	4.69	4.75	4.75	0.14	3.0	18
	mg/l	D2N		0.08	2.64	10	2.65	2.70	2.65	0.12	4.5	18
	mg/l	G3N		-0.32	5.61	10	5.52	5.59	5.61	0.24	4.2	17
pH		A1P		-0.20	7.28	2,7	7.26	7.28	7.28	0.04	0.6	31
		D2PJ		-5.55	7.93	2,5	7.38	7.93	7.93	0.08	1.0	29
		G3PJ		-2.67	7.22	2,8	6.95	7.20	7.22	0.08	1.1	27
SO_4	mg/l	A1S		0.71	6.17	10	6.39	6.13	6.13	0.20	3.3	21
	mg/l	D2S		0.07	26.7	10	26.8	26.8	26.8	0.7	2.7	22
	mg/l	G3S		-0.36	9.37	10	9.20	9.29	9.34	0.33	3.5	21

Participant 32												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Ca	mg/l	A1K		-0.31	4.54	10	4.47	4.51	4.50	0.28	6.3	16
	mg/l	D2K		-0.10	19.7	10	19.6	19.8	19.9	1.0	5.1	16
	mg/l	G3K		-0.33	7.33	10	7.21	7.32	7.29	0.25	3.4	13
Cl	mg/l	A1S		-0.17	12.1	10	12.0	11.9	12.0	0.4	3.1	22
	mg/l	D2S		0.10	5.74	10	5.77	5.78	5.73	0.25	4.3	24
	mg/l	G3S		-0.38	3.67	10	3.60	3.68	3.67	0.21	5.6	23
COD_{Mn}	mg/l	A1C		0.30	4.02	10	4.08	4.00	4.00	0.08	2.0	19
	mg/l	D2C		-0.12	3.26	15	3.23	3.28	3.25	0.25	7.8	20
	mg/l	G3C		-0.42	2.57	15	2.49	2.54	2.58	0.15	6.0	17
Conductivity	µS/cm	A1J		-1.51	291	5	280	292	291	4	1.4	27
	µS/cm	D2PJ		-1.23	162	5	157	163	162	3	1.7	26
	µS/cm	G3PJ		-0.59	81.6	5	80.4	81.8	81.5	1.3	1.6	25

Participant 32												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
F	mg/l	A1F		0.00	1.35	10	1.35	1.38	1.38	0.07	5.3	19
	mg/l	D2F		1.34	0.32	20	0.36	0.31	0.32	0.03	9.4	19
	mg/l	G3F		-2.90	0.46	15	0.36	0.46	0.45	0.04	8.6	19
Fe	µg/l	A1Fe		-0.79	56.0	15	52.7	52.7	52.5	4.6	8.8	19
	µg/l	D2Fe		-0.81	34.6	15	32.5	34.7	34.7	2.2	6.3	20
	µg/l	G3Fe		-0.84	81.3	15	76.2	80.9	81.4	4.0	4.9	20
Hardness	mmol/l	A1K		0.86	0.14	10	0.15	0.14	0.14	0.01	4.5	16
	mmol/l	D2K		0.00	0.56	10	0.56	0.56	0.56	0.01	2.3	18
	mmol/l	G3K		0.43	0.23	10	0.24	0.24	0.23	0.01	4.5	17
K	mg/l	A1K		-0.43	0.70	10	0.69	0.69	0.69	0.04	5.5	11
	mg/l	D2K		0.43	1.38	10	1.41	1.40	1.38	0.04	2.9	13
	mg/l	G3K		0.18	1.09	10	1.10	1.09	1.09	0.02	2.2	13
Mg	mg/l	A1K		0.17	0.84	10	0.85	0.82	0.82	0.03	3.5	13
	mg/l	D2K		0.24	1.68	10	1.70	1.69	1.68	0.04	2.6	13
	mg/l	G3K		0.15	1.33	10	1.34	1.33	1.33	0.04	3.2	14
Mn	µg/l	A1Fe		-0.42	43.1	10	42.2	43.0	42.9	1.9	4.5	17
	µg/l	D2Fe		-0.63	25.4	15	24.2	25.6	25.4	1.1	4.3	18
	µg/l	G3Fe		-0.98	57.0	10	54.2	57.1	56.8	2.0	3.6	18
Na	mg/l	A1K		-0.16	1.22	10	1.21	1.18	1.18	0.06	4.7	15
	mg/l	D2K		0.11	7.40	10	7.44	7.36	7.40	0.27	3.6	15
	mg/l	G3K		0.86	4.43	10	4.62	4.46	4.43	0.21	4.8	15
NH_4	mg/l	A1N		0.64	0.22	10	0.23	0.23	0.22	0.03	12.1	21
	mg/l	D2N		-1.74	0.092	15	0.080	0.093	0.092	0.008	8.2	19
	mg/l	G3N		0.51	0.13	15	0.14	0.13	0.13	0.01	5.5	19
NO_2	mg/l	A1N		0.18	0.22	10	0.22	0.22	0.22	0.01	4.8	17
	mg/l	D2N		0.56	0.18	10	0.19	0.18	0.18	0.01	3.7	16
	mg/l	G3N		0.13	0.078	20	0.079	0.078	0.078	0.001	1.5	16
NO_3	mg/l	A1N		0.00	4.75	10	4.75	4.75	4.75	0.14	3.0	18
	mg/l	D2N		0.15	2.64	10	2.66	2.70	2.65	0.12	4.5	18
	mg/l	G3N		-0.07	5.61	10	5.59	5.59	5.61	0.24	4.2	17
pH		A1P		0.00	7.28	2,7	7.28	7.28	7.28	0.04	0.6	31
		D2PJ		0.30	7.93	2,5	7.96	7.93	7.93	0.08	1.0	29
		G3PJ		0.20	7.22	2,8	7.24	7.20	7.22	0.08	1.1	27
SO_4	mg/l	A1S		-0.13	6.17	10	6.13	6.13	6.13	0.20	3.3	21
	mg/l	D2S		0.30	26.7	10	27.1	26.8	26.8	0.7	2.7	22
	mg/l	G3S		0.00	9.37	10	9.37	9.29	9.34	0.33	3.5	21

Participant 33												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Ca	mg/l	A1K		-1.15	4.54	10	4.28	4.51	4.50	0.28	6.3	16
	mg/l	D2K		-0.51	19.7	10	19.2	19.8	19.9	1.0	5.1	16
	mg/l	G3K		-0.90	7.33	10	7.00	7.32	7.29	0.25	3.4	13
Cl	mg/l	A1S		-0.50	12.1	10	11.8	11.9	12.0	0.4	3.1	22
	mg/l	D2S		0.07	5.74	10	5.76	5.78	5.73	0.25	4.3	24
	mg/l	G3S		-0.71	3.67	10	3.54	3.68	3.67	0.21	5.6	23
COD_{Mn}	mg/l	A1C		-0.15	4.02	10	3.99	4.00	4.00	0.08	2.0	19
	mg/l	D2C		-0.37	3.26	15	3.17	3.28	3.25	0.25	7.8	20
	mg/l	G3C		-0.21	2.57	15	2.53	2.54	2.58	0.15	6.0	17

Participant 33												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Conductivity	µS/cm	A1J		-2.89	291	5	270	292	291	4	1.4	27
	µS/cm	D2PJ		-1.73	162	5	155	163	162	3	1.7	26
	µS/cm	G3PJ		-1.96	81.6	5	77.6	81.8	81.5	1.3	1.6	25
F	mg/l	A1F		0.30	1.35	10	1.37	1.38	1.38	0.07	5.3	19
	mg/l	D2F		0.94	0.32	20	0.35	0.31	0.32	0.03	9.4	19
	mg/l	G3F		1.16	0.46	15	0.50	0.46	0.45	0.04	8.6	19
Fe	µg/l	A1Fe		-1.17	56.0	15	51.1	52.7	52.5	4.6	8.8	19
	µg/l	D2Fe		-0.96	34.6	15	32.1	34.7	34.7	2.2	6.3	20
	µg/l	G3Fe		-0.82	81.3	15	76.3	80.9	81.4	4.0	4.9	20
Hardness	mmol/l	A1K		0.00	0.14	10	0.14	0.14	0.14	0.01	4.5	16
	mmol/l	D2K		-0.36	0.56	10	0.55	0.56	0.56	0.01	2.3	18
	mmol/l	G3K		0.00	0.23	10	0.23	0.24	0.23	0.01	4.5	17
Mg	mg/l	A1K		-1.43	0.84	10	0.78	0.82	0.82	0.03	3.5	13
	mg/l	D2K		-0.36	1.68	10	1.65	1.69	1.68	0.04	2.6	13
	mg/l	G3K		-0.75	1.33	10	1.28	1.33	1.33	0.04	3.2	14
Mn	µg/l	A1Fe		-0.79	43.1	10	41.4	43.0	42.9	1.9	4.5	17
	µg/l	D2Fe		-0.58	25.4	15	24.3	25.6	25.4	1.1	4.3	18
	µg/l	G3Fe		-0.49	57.0	10	55.6	57.1	56.8	2.0	3.6	18
Na	mg/l	A1K		-2.62	1.22	10	1.06	1.18	1.18	0.06	4.7	15
	mg/l	D2K		-1.00	7.40	10	7.03	7.36	7.40	0.27	3.6	15
	mg/l	G3K		-1.22	4.43	10	4.16	4.46	4.43	0.21	4.8	15
NH_4	mg/l	A1N		1.82	0.22	10	0.24	0.23	0.22	0.03	12.1	21
	mg/l	D2N		1.16	0.092	15	0.100	0.093	0.092	0.008	8.2	19
	mg/l	G3N		0.00	0.13	15	0.13	0.13	0.13	0.01	5.5	19
NO_2	mg/l	A1N		0.00	0.22	10	0.22	0.22	0.22	0.01	4.8	17
	mg/l	D2N		0.00	0.18	10	0.18	0.18	0.18	0.01	3.7	16
	mg/l	G3N		0.00	0.078	20	0.078	0.078	0.078	0.001	1.5	16
NO_3	mg/l	A1N		0.97	4.75	10	4.98	4.75	4.75	0.14	3.0	18
	mg/l	D2N		0.45	2.64	10	2.70	2.70	2.65	0.12	4.5	18
	mg/l	G3N		0.82	5.61	10	5.84	5.59	5.61	0.24	4.2	17
pH		A1P		-0.51	7.28	2,7	7.23	7.28	7.28	0.04	0.6	31
		D2PJ		0.40	7.93	2,5	7.97	7.93	7.93	0.08	1.0	29
		G3PJ		1.09	7.22	2,8	7.33	7.20	7.22	0.08	1.1	27
SO_4	mg/l	A1S		2.69	6.17	10	7.00	6.13	6.13	0.20	3.3	21
	mg/l	D2S		1.42	26.7	10	28.6	26.8	26.8	0.7	2.7	22
	mg/l	G3S		1.77	9.37	10	10.20	9.29	9.34	0.33	3.5	21

Participant 34												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Ca	mg/l	A1K		-0.09	4.54	10	4.52	4.51	4.50	0.28	6.3	16
	mg/l	D2K		0.10	19.7	10	19.8	19.8	19.9	1.0	5.1	16
	mg/l	G3K		0.19	7.33	10	7.40	7.32	7.29	0.25	3.4	13
Cl	mg/l	A1S		1.65	12.1	10	13.1	11.9	12.0	0.4	3.1	22
	mg/l	D2S		3.17	5.74	10	6.65	5.78	5.73	0.25	4.3	24
Conductivity	µS/cm	A1J		-1.10	291	5	283	292	291	4	1.4	27
	µS/cm	G3PJ		-3.48	81.6	5	74.5	81.8	81.5	1.3	1.6	25
F	mg/l	A1F		3.26	1.35	10	1.57	1.38	1.38	0.07	5.3	19
	mg/l	G3F		5.65	0.46	15	0.66	0.46	0.45	0.04	8.6	19
K	mg/l	A1K		-0.37	0.70	10	0.69	0.69	0.69	0.04	5.5	11
	mg/l	D2K		0.43	1.38	10	1.41	1.40	1.38	0.04	2.9	13
	mg/l	G3K		0.55	1.09	10	1.12	1.09	1.09	0.02	2.2	13
Mg	mg/l	A1K		-0.88	0.84	10	0.80	0.82	0.82	0.03	3.5	13
	mg/l	D2K		-0.36	1.68	10	1.65	1.69	1.68	0.04	2.6	13
	mg/l	G3K		-0.45	1.33	10	1.30	1.33	1.33	0.04	3.2	14
Na	mg/l	A1K		-0.98	1.22	10	1.16	1.18	1.18	0.06	4.7	15
	mg/l	D2K		-0.11	7.40	10	7.36	7.36	7.40	0.27	3.6	15
	mg/l	G3K		0.00	4.43	10	4.43	4.46	4.43	0.21	4.8	15
pH		A1P		-0.41	7.28	2,7	7.24	7.28	7.28	0.04	0.6	31
		G3PJ		-1.48	7.22	2,8	7.07	7.20	7.22	0.08	1.1	27
SO_4	mg/l	A1S		0.00	6.17	10	6.17	6.13	6.13	0.20	3.3	21
	mg/l	D2S		0.15	26.7	10	26.9	26.8	26.8	0.7	2.7	22

Participant 35												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Ca	mg/l	A1K		-1.54	4.54	10	4.19	4.51	4.50	0.28	6.3	16
	mg/l	D2K		-0.81	19.7	10	18.9	19.8	19.9	1.0	5.1	16
	mg/l	G3K		0.03	7.33	10	7.34	7.32	7.29	0.25	3.4	13
Cl	mg/l	A1S		-1.98	12.1	10	10.9	11.9	12.0	0.4	3.1	22
	mg/l	D2S		-1.46	5.74	10	5.32	5.78	5.73	0.25	4.3	24
	mg/l	G3S		-1.74	3.67	10	3.35	3.68	3.67	0.21	5.6	23
COD_{Mn}	mg/l	A1C		-0.10	4.02	10	4.00	4.00	4.00	0.08	2.0	19
	mg/l	D2C		0.86	3.26	15	3.47	3.28	3.25	0.25	7.8	20
	mg/l	G3C		-0.57	2.57	15	2.46	2.54	2.58	0.15	6.0	17
Conductivity	µS/cm	A1J		0.55	291	5	295	292	291	4	1.4	27
	µS/cm	D2PJ		0.74	162	5	165	163	162	3	1.7	26
	µS/cm	G3PJ		0.74	81.6	5	83.1	81.8	81.5	1.3	1.6	25
F	mg/l	A1F		-1.19	1.35	10	1.27	1.38	1.38	0.07	5.3	19
	mg/l	D2F		-1.88	0.32	20	0.26	0.31	0.32	0.03	9.4	19
	mg/l	G3F		-0.58	0.46	15	0.44	0.46	0.45	0.04	8.6	19
Fe	µg/l	A1Fe		-0.88	56.0	15	52.3	52.7	52.5	4.6	8.8	19
	µg/l	D2Fe		-0.85	34.6	15	32.4	34.7	34.7	2.2	6.3	20
	µg/l	G3Fe		-0.07	81.3	15	80.9	80.9	81.4	4.0	4.9	20
Hardness	mmol/l	A1K		0.00	0.14	10	0.14	0.14	0.14	0.01	4.5	16
	mmol/l	D2K		0.36	0.56	10	0.57	0.56	0.56	0.01	2.3	18
	mmol/l	G3K		0.87	0.23	10	0.24	0.24	0.23	0.01	4.5	17

Participant 35												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
K	mg/l	A1K		-1.43	0.70	10	0.65	0.69	0.69	0.04	5.5	11
	mg/l	D2K		-0.14	1.38	10	1.37	1.40	1.38	0.04	2.9	13
	mg/l	G3K		0.00	1.09	10	1.09	1.09	1.09	0.02	2.2	13
Mg	mg/l	A1K		-0.48	0.84	10	0.82	0.82	0.82	0.03	3.5	13
	mg/l	D2K		-0.24	1.68	10	1.66	1.69	1.68	0.04	2.6	13
	mg/l	G3K		0.00	1.33	10	1.33	1.33	1.33	0.04	3.2	14
Mn	µg/l	A1Fe		-1.07	43.1	10	40.8	43.0	42.9	1.9	4.5	17
	µg/l	D2Fe		-0.63	25.4	15	24.2	25.6	25.4	1.1	4.3	18
	µg/l	G3Fe		-1.02	57.0	10	54.1	57.1	56.8	2.0	3.6	18
Na	mg/l	A1K		-0.66	1.22	10	1.18	1.18	1.18	0.06	4.7	15
	mg/l	D2K		-0.59	7.40	10	7.18	7.36	7.40	0.27	3.6	15
	mg/l	G3K		0.14	4.43	10	4.46	4.46	4.43	0.21	4.8	15
NH_4	mg/l	A1N		1.73	0.22	10	0.24	0.23	0.22	0.03	12.1	21
	mg/l	D2N		1.45	0.092	15	0.102	0.093	0.092	0.008	8.2	19
	mg/l	G3N		1.33	0.13	15	0.14	0.13	0.13	0.01	5.5	19
NO_2	mg/l	A1N		-0.18	0.22	10	0.22	0.22	0.22	0.01	4.8	17
	mg/l	D2N		0.22	0.18	10	0.18	0.18	0.18	0.01	3.7	16
	mg/l	G3N		-0.26	0.078	20	0.076	0.078	0.078	0.001	1.5	16
NO_3	mg/l	A1N		0.29	4.75	10	4.82	4.75	4.75	0.14	3.0	18
	mg/l	D2N		0.45	2.64	10	2.70	2.70	2.65	0.12	4.5	18
	mg/l	G3N		0.86	5.61	10	5.85	5.59	5.61	0.24	4.2	17
pH		A1P		-2.85	7.28	2,7	7.00	7.28	7.28	0.04	0.6	31
		D2PJ		-1.82	7.93	2,5	7.75	7.93	7.93	0.08	1.0	29
		G3PJ		0.10	7.22	2,8	7.23	7.20	7.22	0.08	1.1	27
SO_4	mg/l	A1S		-0.58	6.17	10	5.99	6.13	6.13	0.20	3.3	21
	mg/l	D2S		-0.22	26.7	10	26.4	26.8	26.8	0.7	2.7	22
	mg/l	G3S		-0.41	9.37	10	9.18	9.29	9.34	0.33	3.5	21

Participant 36												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Cl	mg/l	A1S		-0.66	12.1	10	11.7	11.9	12.0	0.4	3.1	22
	mg/l	D2S		-0.24	5.74	10	5.67	5.78	5.73	0.25	4.3	24
	mg/l	G3S		-0.54	3.67	10	3.57	3.68	3.67	0.21	5.6	23
COD_{Mn}	mg/l	A1C		-0.20	4.02	10	3.98	4.00	4.00	0.08	2.0	19
	mg/l	D2C		-0.29	3.26	15	3.19	3.28	3.25	0.25	7.8	20
	mg/l	G3C		0.26	2.57	15	2.62	2.54	2.58	0.15	6.0	17
Conductivity	µS/cm	A1J		0.26	291	5	293	292	291	4	1.4	27
	µS/cm	D2PJ		0.10	162	5	162	163	162	3	1.7	26
	µS/cm	G3PJ		-0.05	81.6	5	81.5	81.8	81.5	1.3	1.6	25
F	mg/l	A1F		-0.30	1.35	10	1.33	1.38	1.38	0.07	5.3	19
	mg/l	D2F		0.19	0.32	20	0.33	0.31	0.32	0.03	9.4	19
	mg/l	G3F		0.12	0.46	15	0.46	0.46	0.45	0.04	8.6	19
Fe	µg/l	A1Fe		-1.45	56.0	15	49.9	52.7	52.5	4.6	8.8	19
	µg/l	D2Fe		-0.19	34.6	15	34.1	34.7	34.7	2.2	6.3	20
	µg/l	G3Fe		-0.41	81.3	15	78.8	80.9	81.4	4.0	4.9	20
K	mg/l	A1K		-5.29	0.70	10	0.52	0.69	0.69	0.04	5.5	11
	mg/l	D2K		-2.75	1.38	10	1.19	1.40	1.38	0.04	2.9	13
	mg/l	G3K		-4.15	1.09	10	0.86	1.09	1.09	0.02	2.2	13

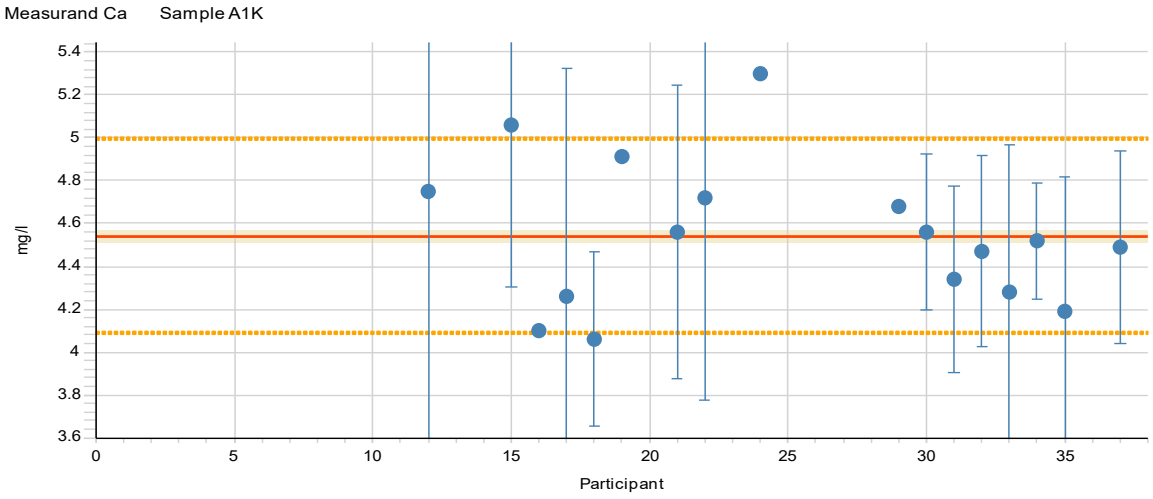
Participant 36												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Mn	µg/l	A1Fe		4.45	43.1	10	52.7	43.0	42.9	1.9	4.5	17
	µg/l	D2Fe		5.14	25.4	15	35.2	25.6	25.4	1.1	4.3	18
	µg/l	G3Fe		1.58	57.0	10	61.5	57.1	56.8	2.0	3.6	18
Na	mg/l	A1K		-4.48	1.22	10	0.95	1.18	1.18	0.06	4.7	15
	mg/l	D2K		-0.11	7.40	10	7.36	7.36	7.40	0.27	3.6	15
	mg/l	G3K		-1.35	4.43	10	4.13	4.46	4.43	0.21	4.8	15
NH_4	mg/l	A1N		1.00	0.22	10	0.23	0.23	0.22	0.03	12.1	21
	mg/l	D2N		0.36	0.092	15	0.095	0.093	0.092	0.008	8.2	19
	mg/l	G3N		0.62	0.13	15	0.14	0.13	0.13	0.01	5.5	19
NO_2	mg/l	A1N		1.00	0.22	10	0.23	0.22	0.22	0.01	4.8	17
	mg/l	D2N		1.11	0.18	10	0.19	0.18	0.18	0.01	3.7	16
	mg/l	G3N		0.13	0.078	20	0.079	0.078	0.078	0.001	1.5	16
NO_3	mg/l	A1N		1.14	4.75	10	5.02	4.75	4.75	0.14	3.0	18
	mg/l	D2N		0.91	2.64	10	2.76	2.70	2.65	0.12	4.5	18
	mg/l	G3N		1.46	5.61	10	6.02	5.59	5.61	0.24	4.2	17
pH		A1P		-0.41	7.28	2,7	7.24	7.28	7.28	0.04	0.6	31
		D2PJ		-1.11	7.93	2,5	7.82	7.93	7.93	0.08	1.0	29
		G3PJ		-0.20	7.22	2,8	7.20	7.20	7.22	0.08	1.1	27
SO_4	mg/l	A1S		-0.42	6.17	10	6.04	6.13	6.13	0.20	3.3	21
	mg/l	D2S		-0.37	26.7	10	26.2	26.8	26.8	0.7	2.7	22
	mg/l	G3S		-0.43	9.37	10	9.17	9.29	9.34	0.33	3.5	21

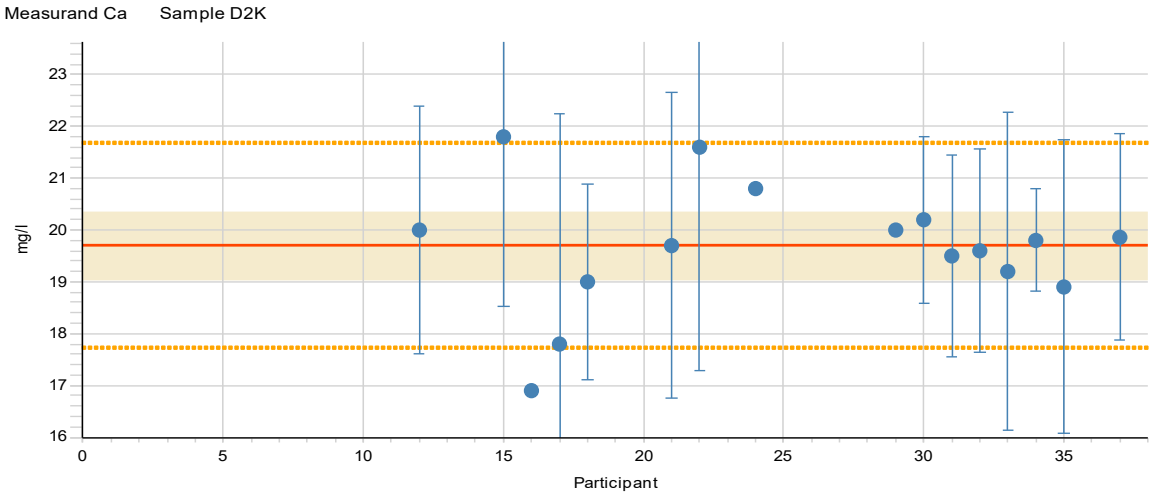
Participant 37												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Ca	mg/l	A1K		-0.22	4.54	10	4.49	4.51	4.50	0.28	6.3	16
	mg/l	D2K		0.16	19.7	10	19.9	19.8	19.9	1.0	5.1	16
	mg/l	G3K		0.00	7.33	10	7.33	7.32	7.29	0.25	3.4	13
Fe	µg/l	A1Fe		-0.43	56.0	15	54.2	52.7	52.5	4.6	8.8	19
	µg/l	D2Fe		0.54	34.6	15	36.0	34.7	34.7	2.2	6.3	20
	µg/l	G3Fe		-0.07	81.3	15	80.9	80.9	81.4	4.0	4.9	20
Hardness	mmol/l	A1K		1.00	0.14	10	0.15	0.14	0.14	0.01	4.5	16
	mmol/l	D2K		0.36	0.56	10	0.57	0.56	0.56	0.01	2.3	18
	mmol/l	G3K		1.04	0.23	10	0.24	0.24	0.23	0.01	4.5	17
K	mg/l	A1K		-0.29	0.70	10	0.69	0.69	0.69	0.04	5.5	11
	mg/l	D2K		0.58	1.38	10	1.42	1.40	1.38	0.04	2.9	13
	mg/l	G3K		0.55	1.09	10	1.12	1.09	1.09	0.02	2.2	13
Mg	mg/l	A1K		0.55	0.84	10	0.86	0.82	0.82	0.03	3.5	13
	mg/l	D2K		0.71	1.68	10	1.74	1.69	1.68	0.04	2.6	13
	mg/l	G3K		0.90	1.33	10	1.39	1.33	1.33	0.04	3.2	14
Mn	µg/l	A1Fe		-0.05	43.1	10	43.0	43.0	42.9	1.9	4.5	17
	µg/l	D2Fe		0.10	25.4	15	25.6	25.6	25.4	1.1	4.3	18
	µg/l	G3Fe		0.14	57.0	10	57.4	57.1	56.8	2.0	3.6	18
Na	mg/l	A1K		0.00	1.22	10	1.22	1.18	1.18	0.06	4.7	15
	mg/l	D2K		0.76	7.40	10	7.68	7.36	7.40	0.27	3.6	15
	mg/l	G3K		1.04	4.43	10	4.66	4.46	4.43	0.21	4.8	15

Appendix 9. Results of participants and their uncertainties

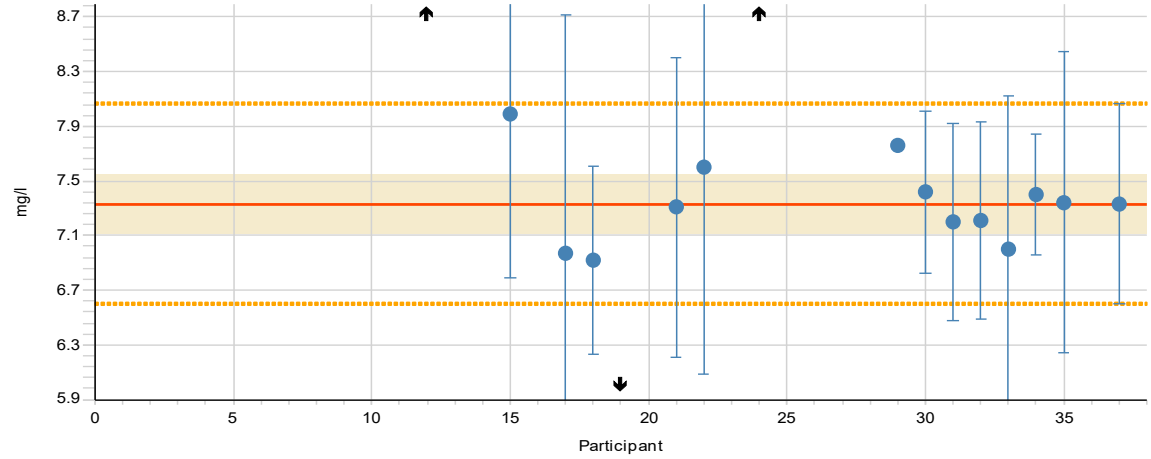
In figures:

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

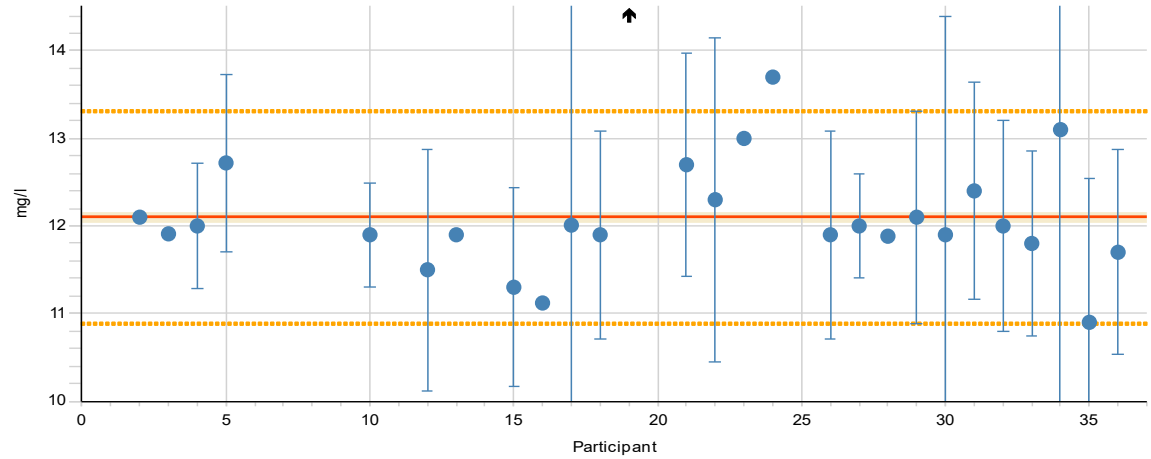




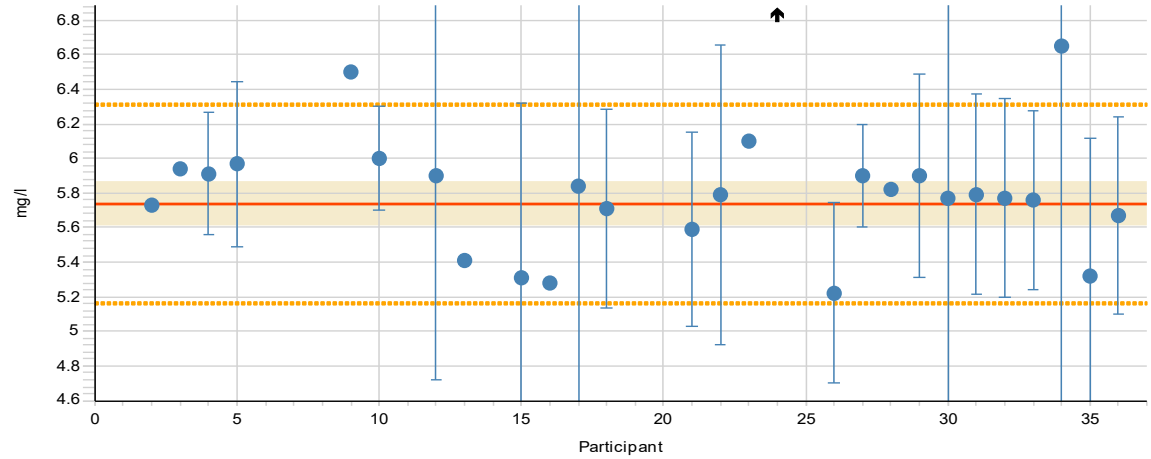
Measurand Ca Sample G3K



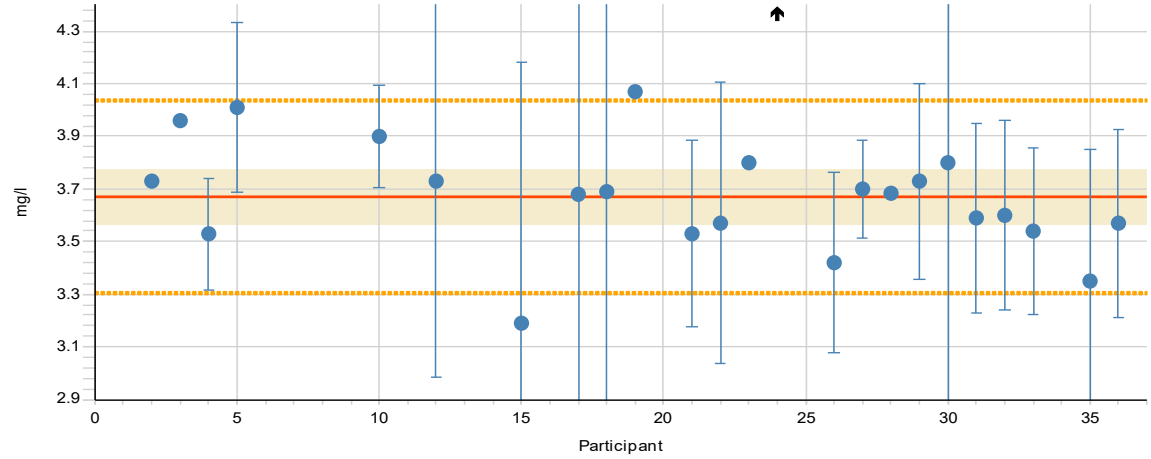
Measurand Cl Sample A1S



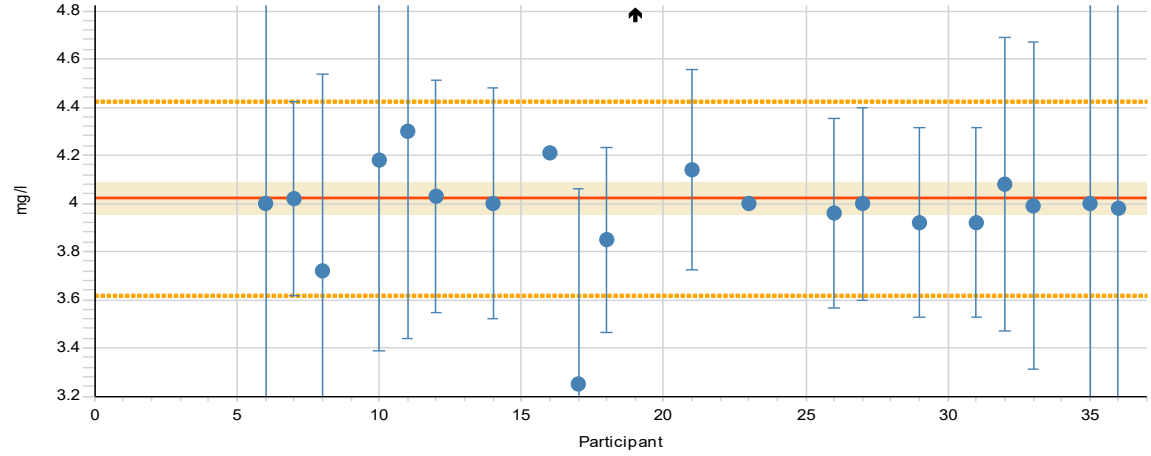
Measurand Cl Sample D2S



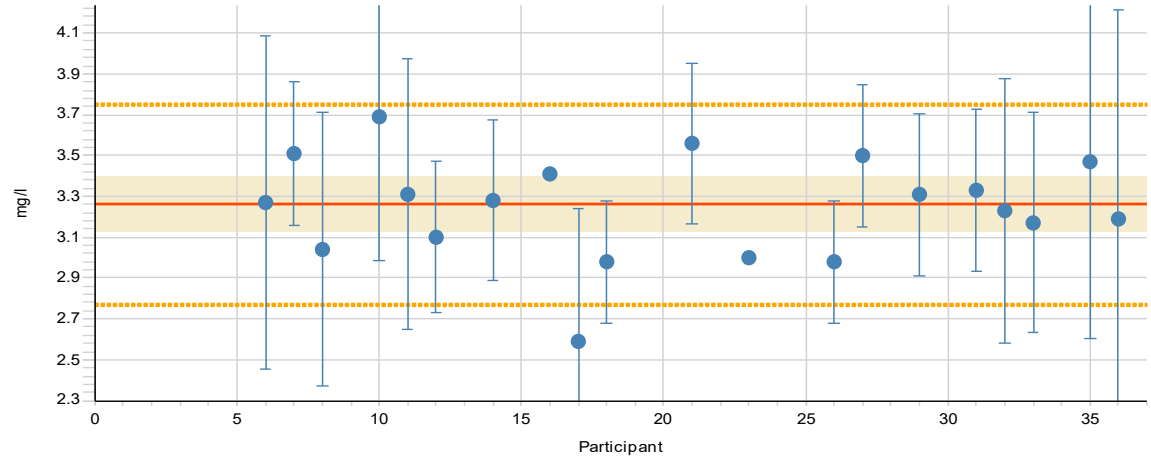
Measurand Cl Sample G3S



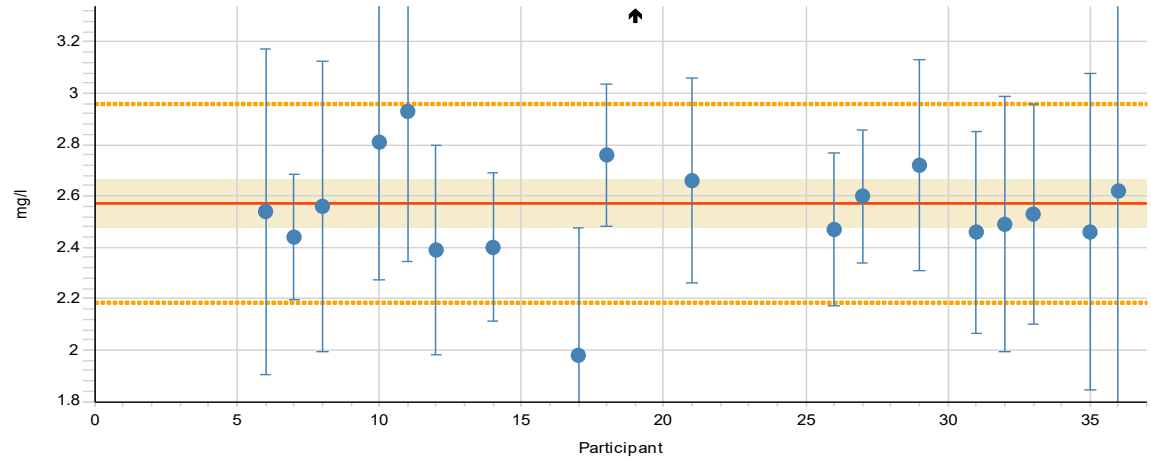
Measurand COD_{Mn} Sample A1C



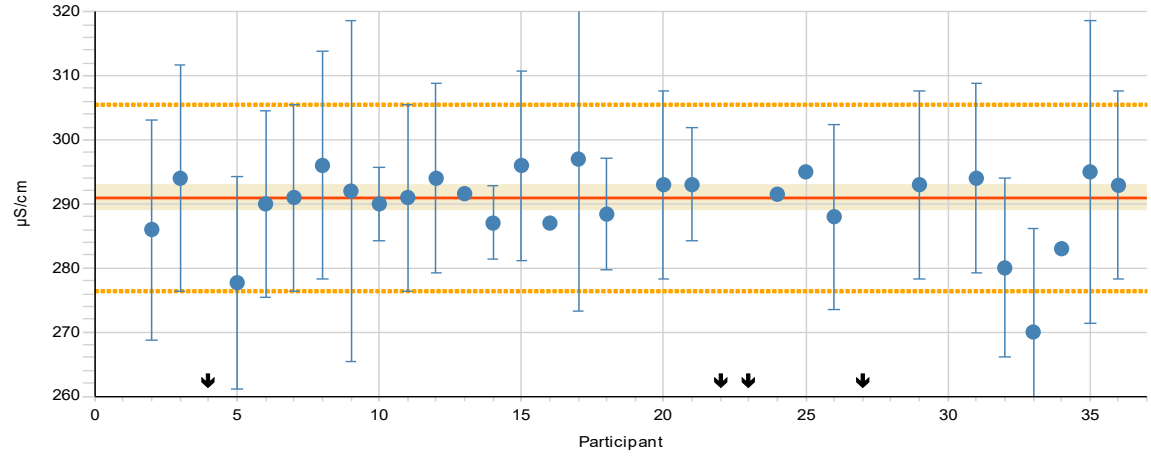
Measurand COD_{Mn} Sample D2C



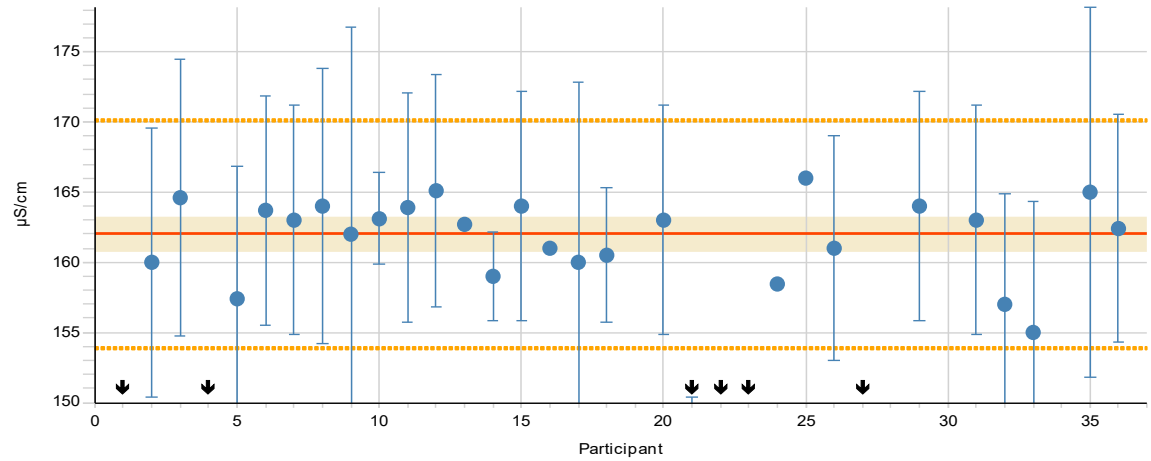
Measurand COD_{Mn} Sample G3C



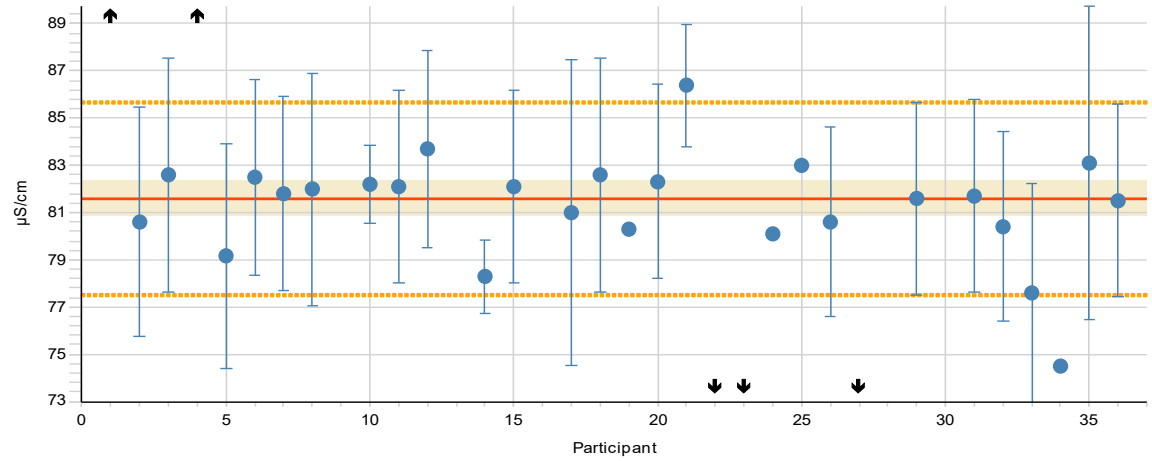
Measurand Conductivity Sample A1J



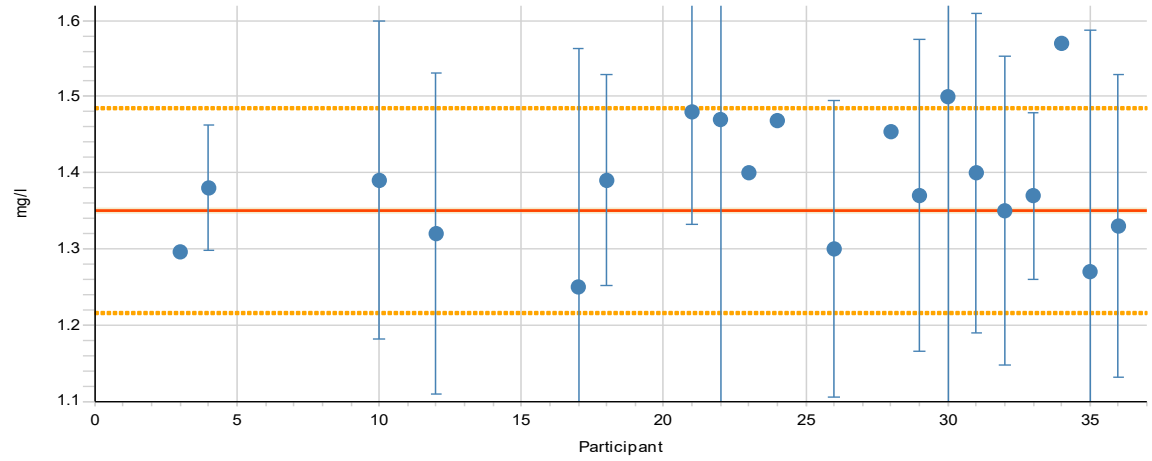
Measurand Conductivity Sample D2PJ



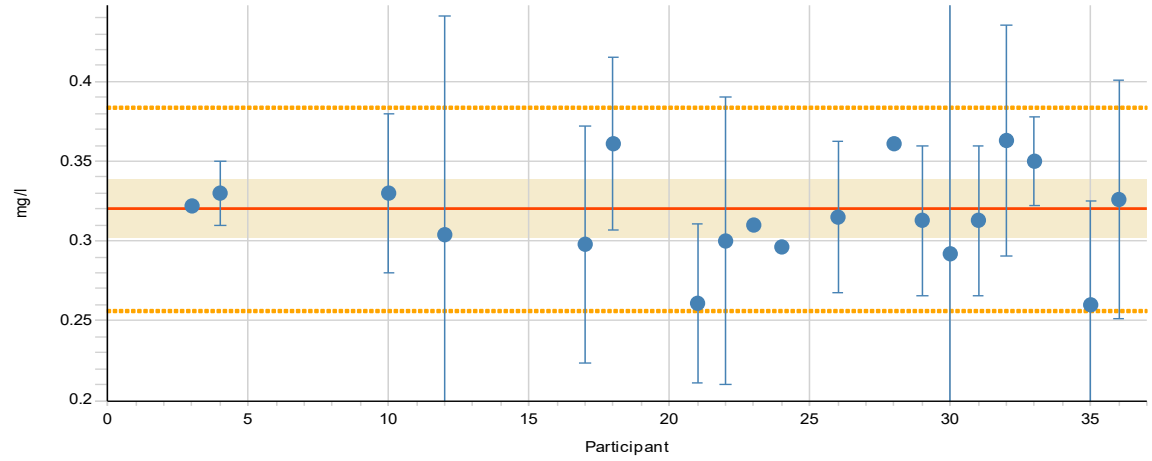
Measurand Conductivity Sample G3PJ



Measurand F Sample A1F



Measurand F Sample D2F



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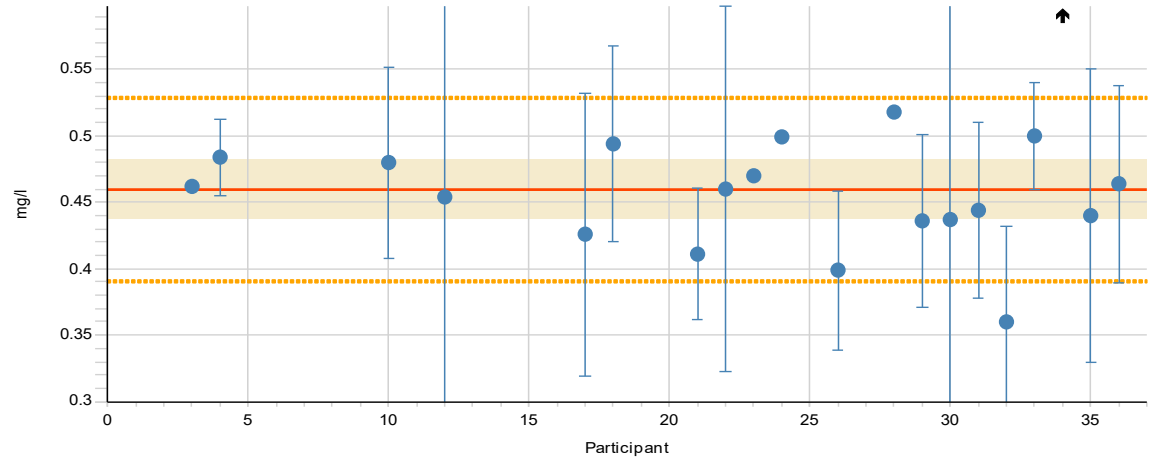
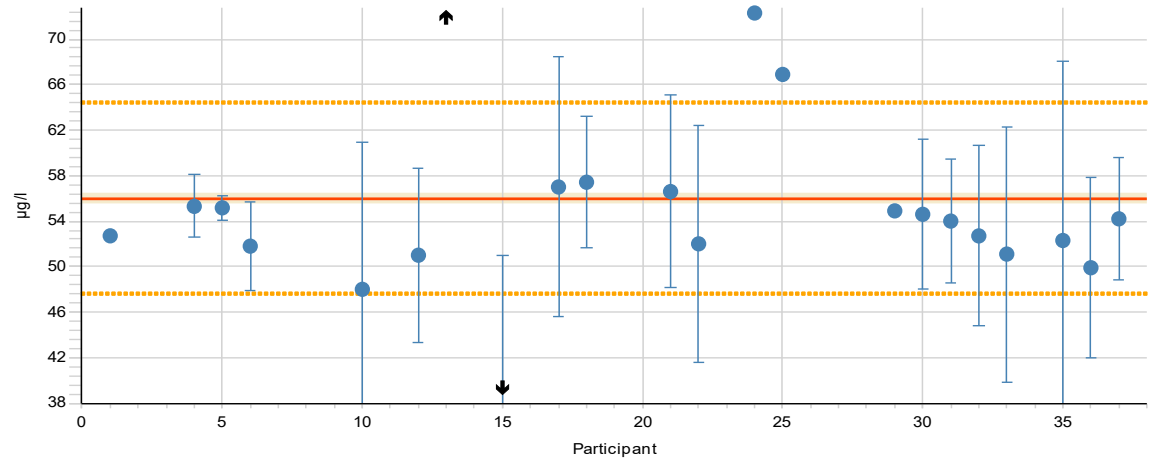
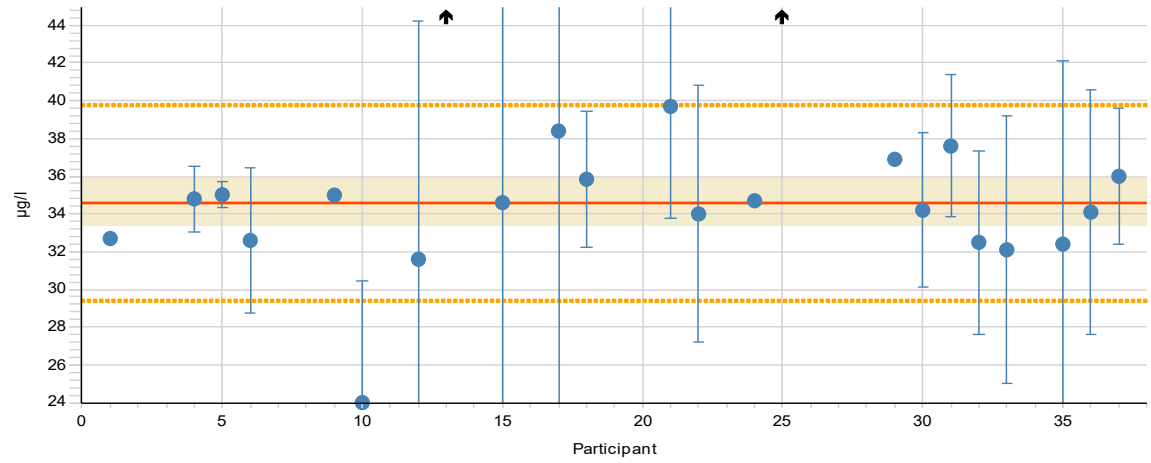


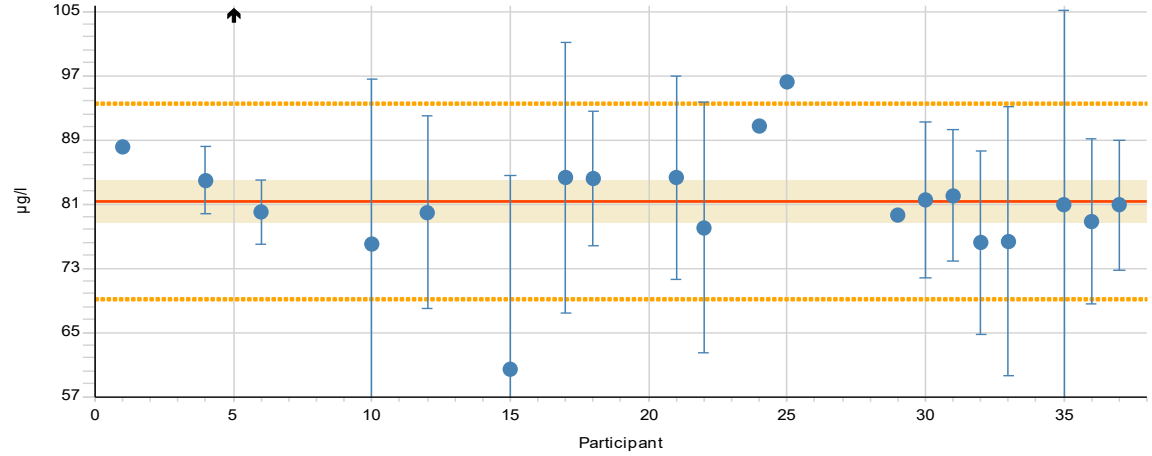
Measurand Fe Sample A1Fe



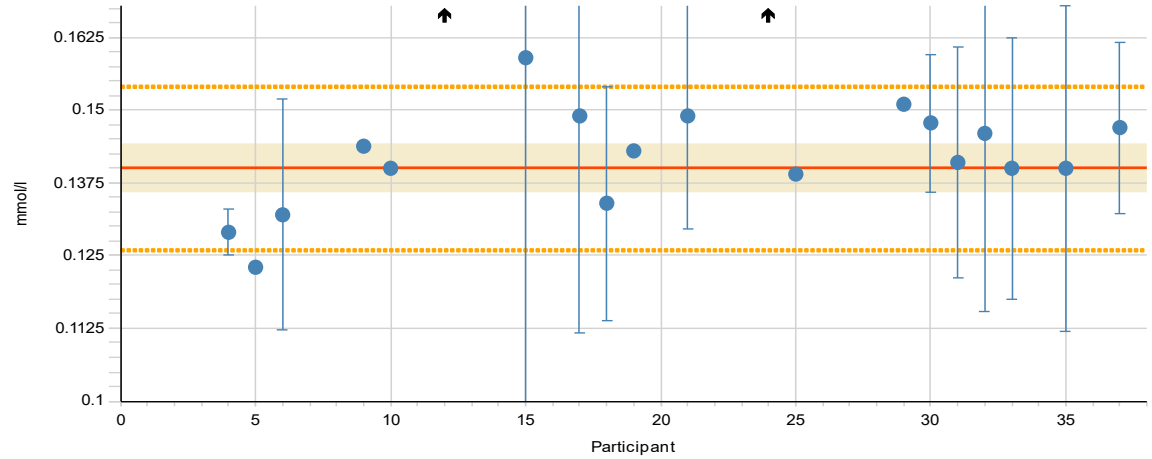
Measurand Fe Sample D2Fe



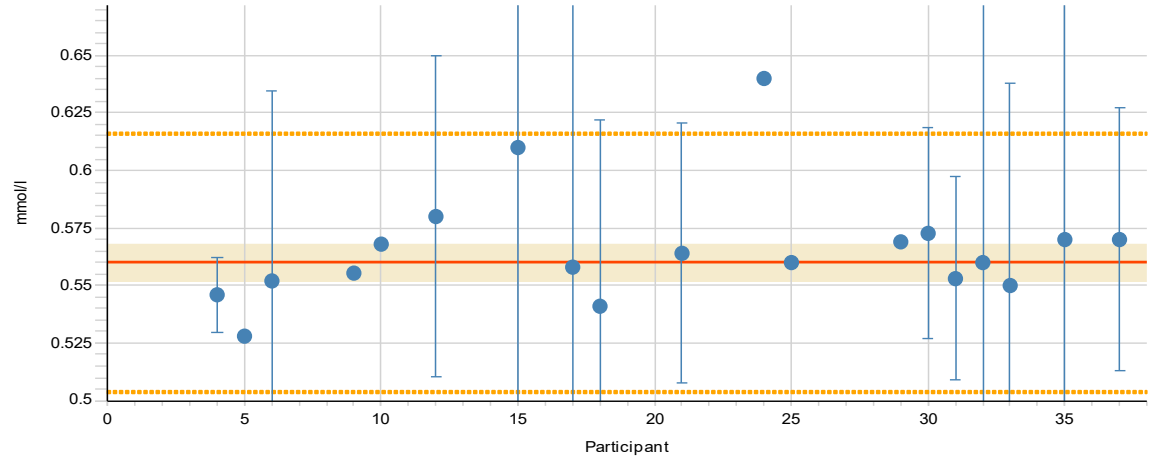
Measurand Fe Sample G3Fe



Measurand Hardness Sample A1K



Measurand Hardness Sample D2K



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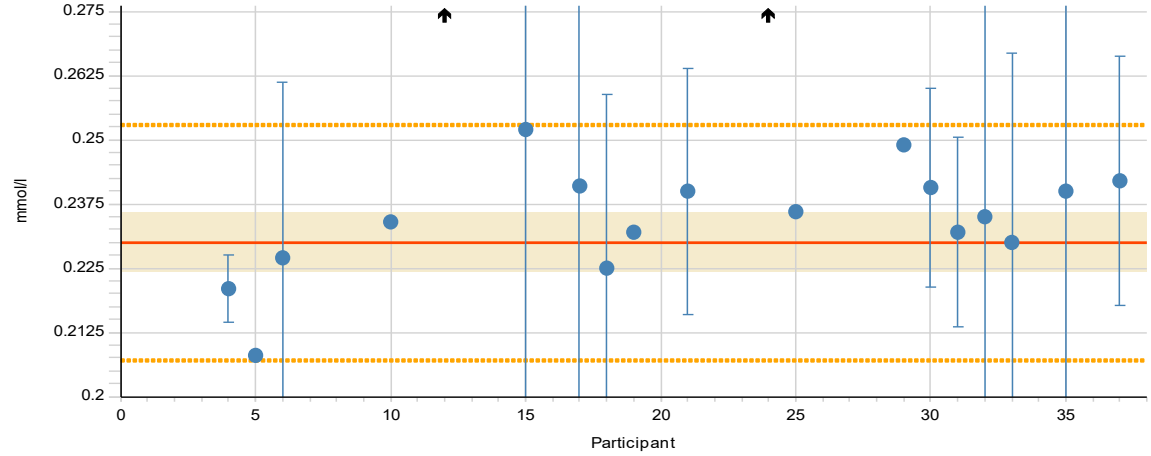

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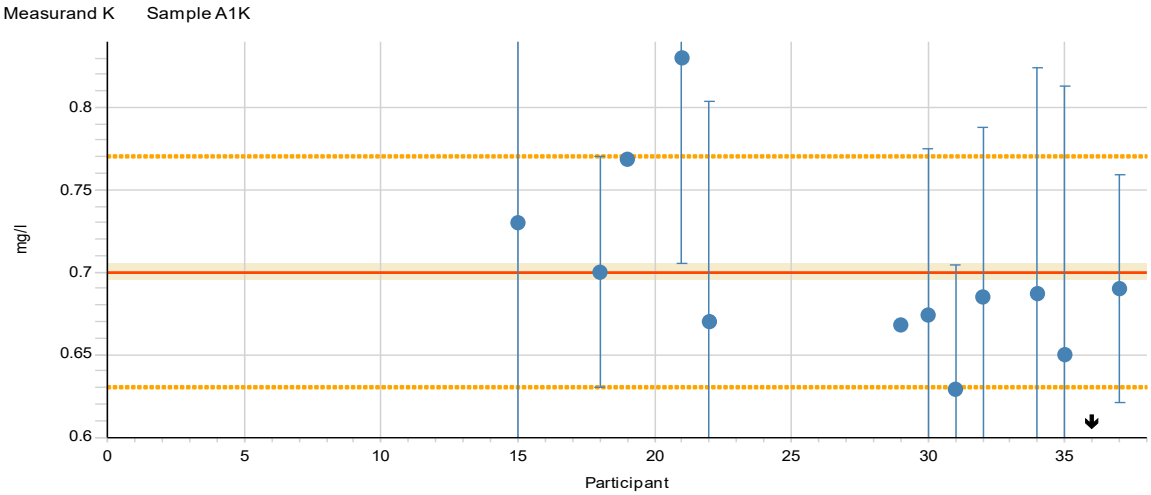

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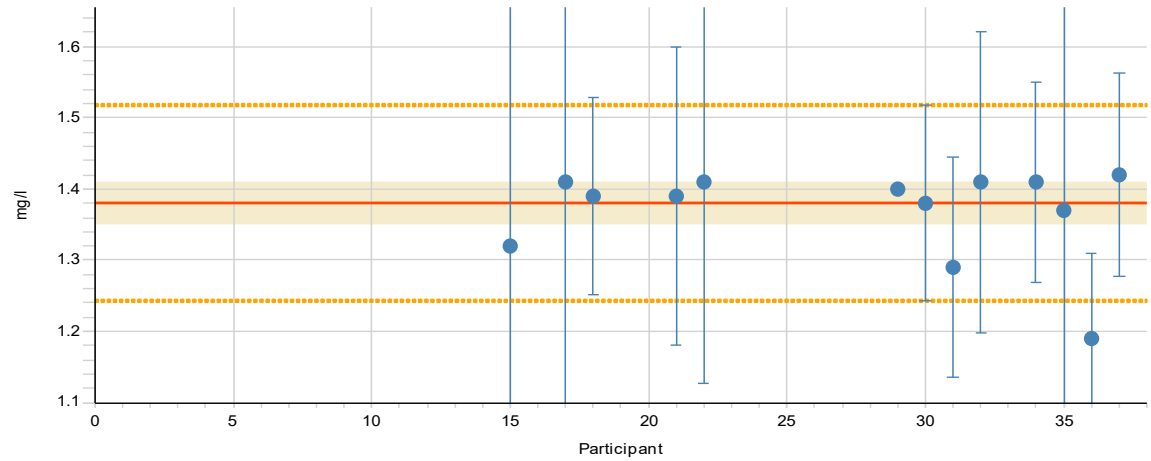

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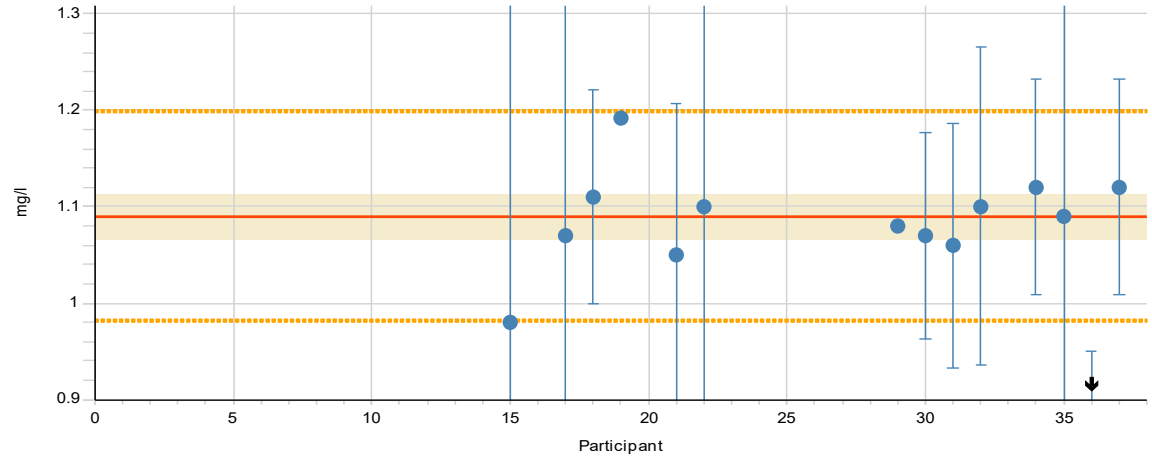
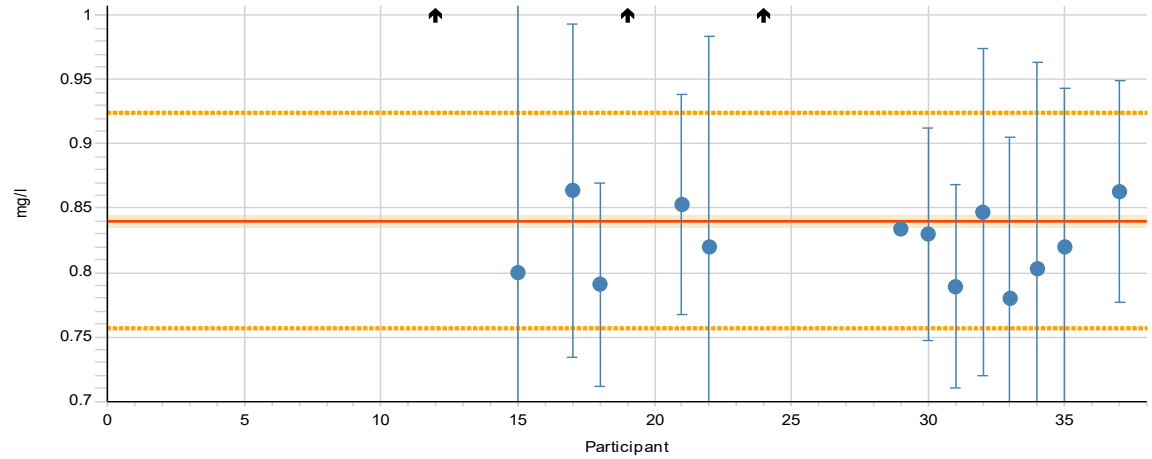
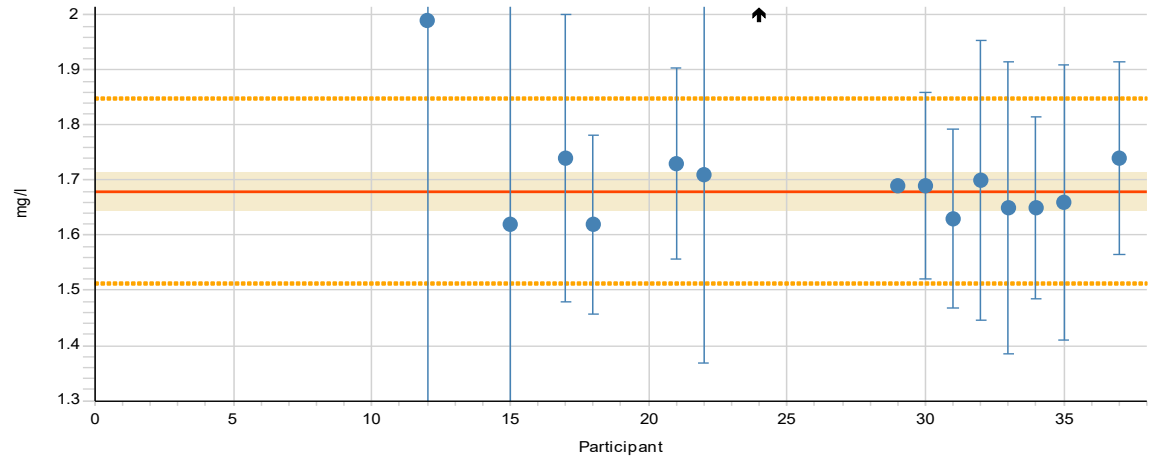


Measurand Mg Sample A1K



Measurand Mg Sample D2K



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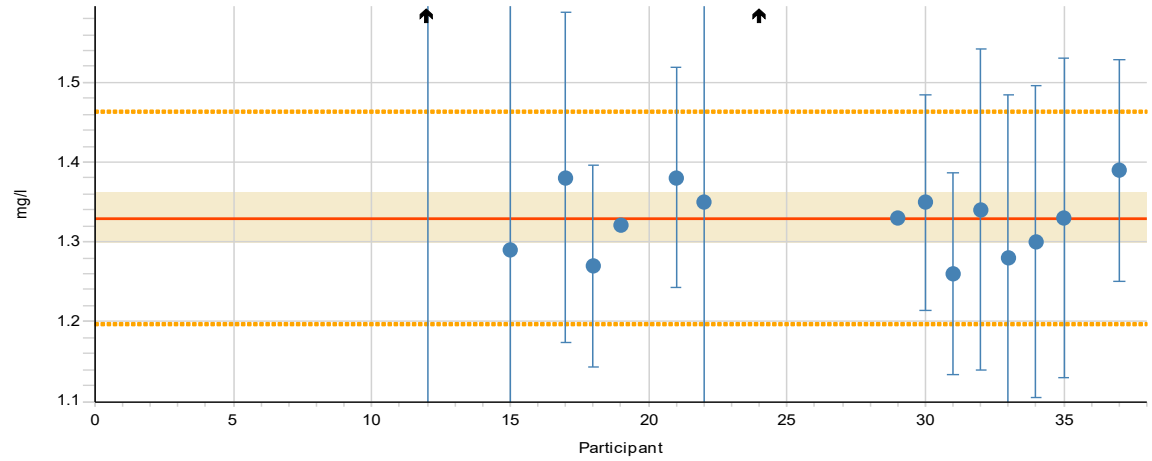
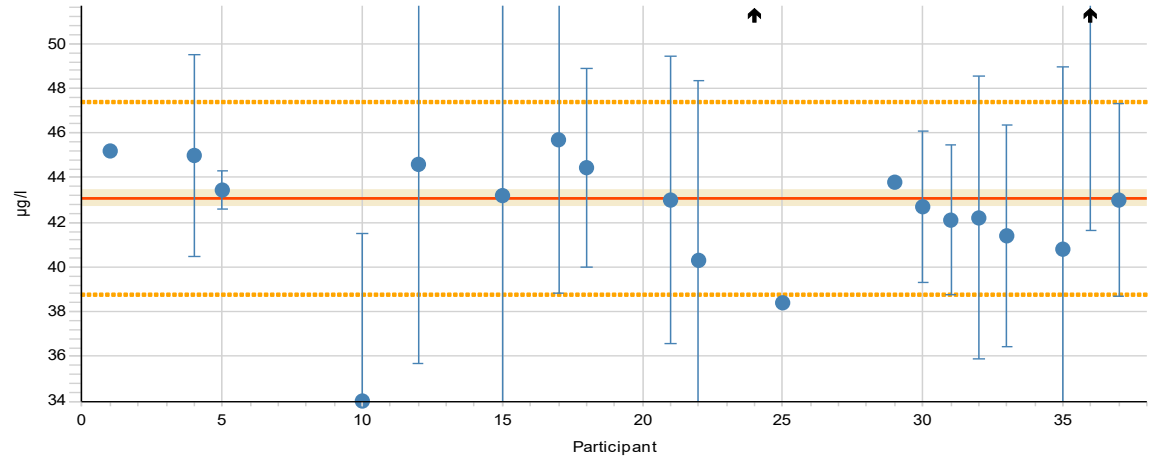
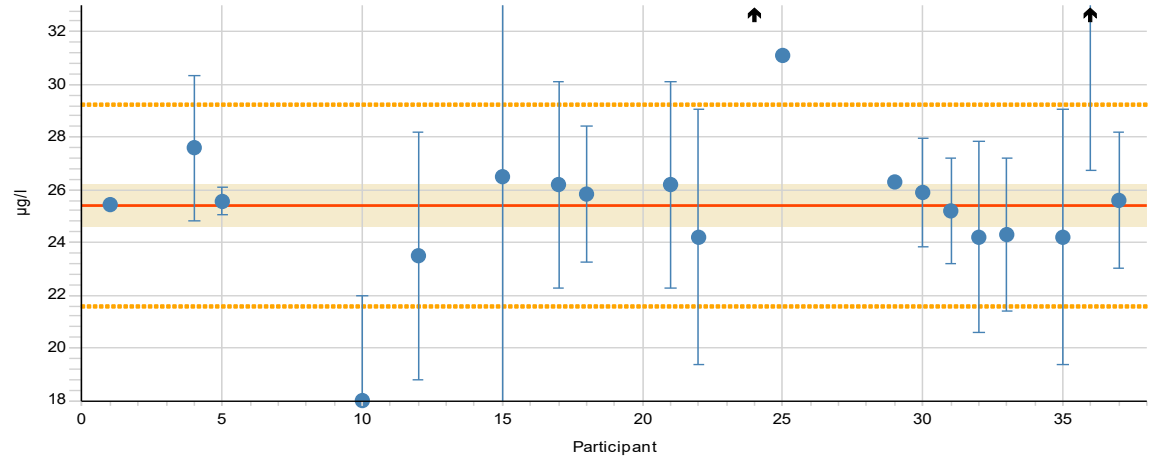


Measurand Mn Sample A1Fe



Measurand Mn Sample D2Fe



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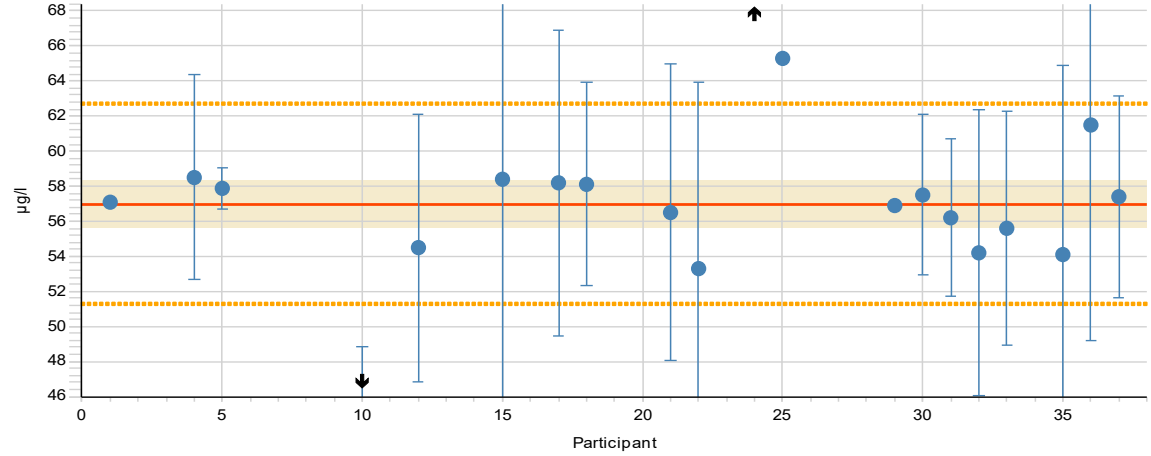
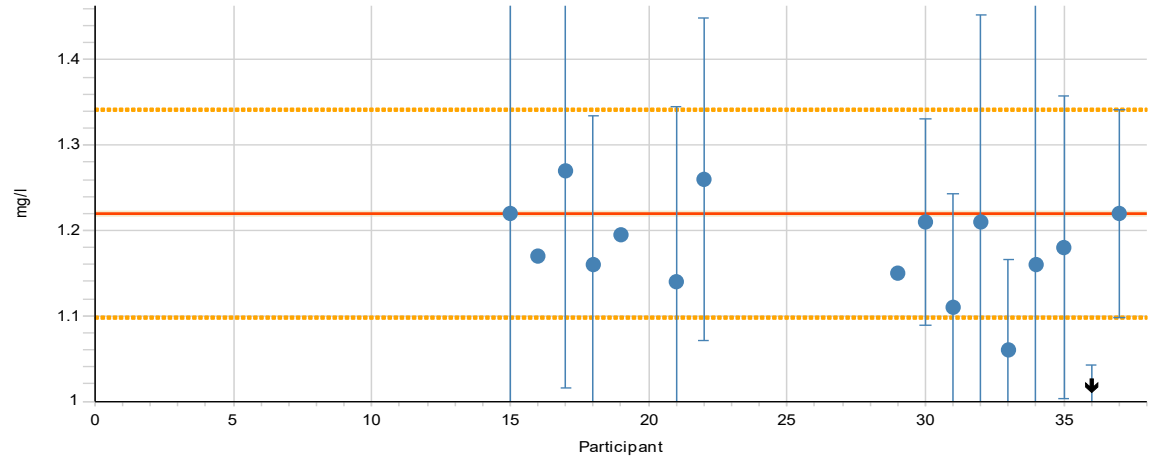


Measurand Na Sample A1K



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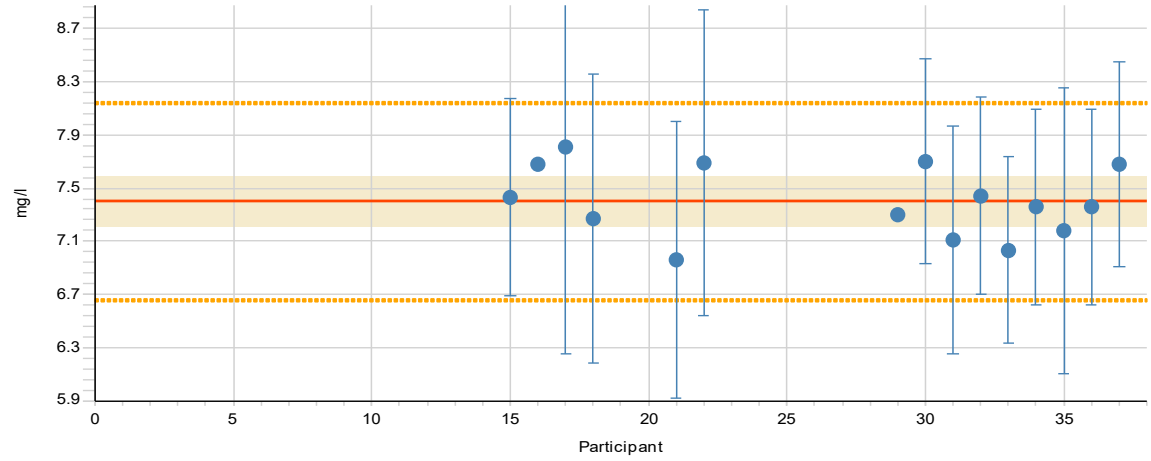

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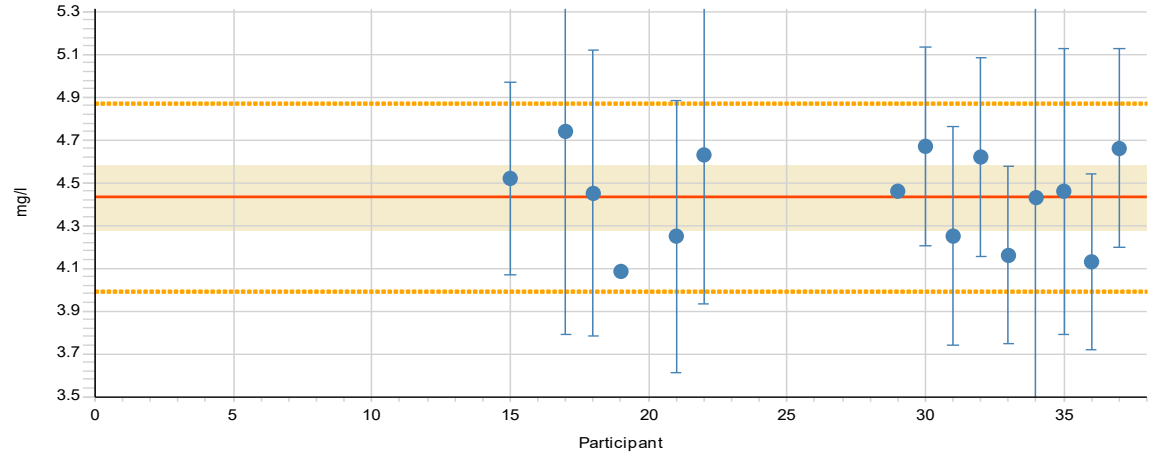
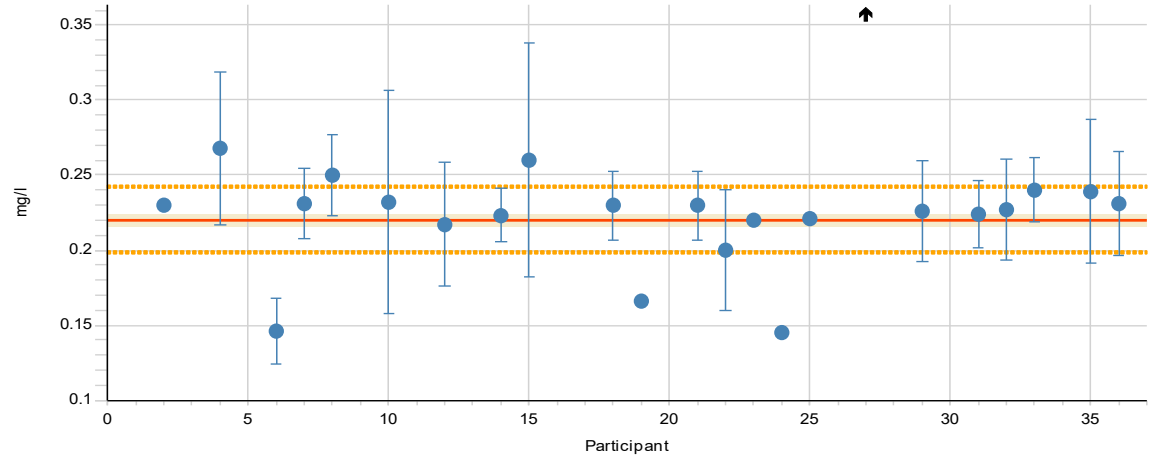


Measurand NH_4 Sample A1N



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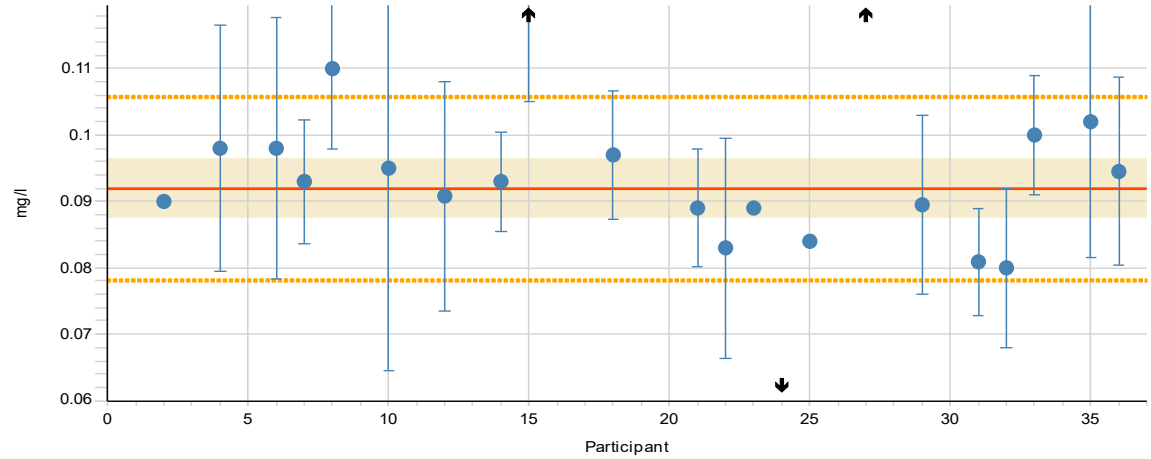
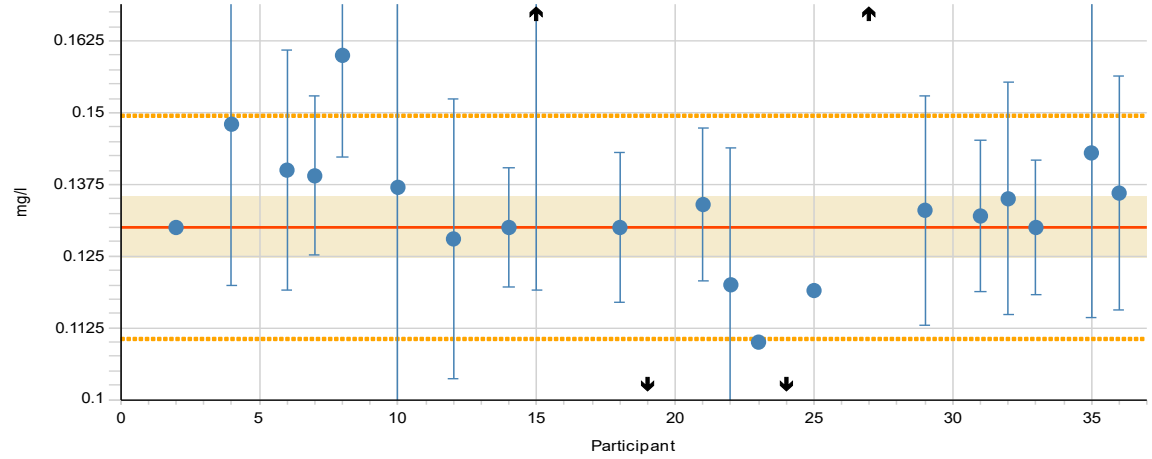
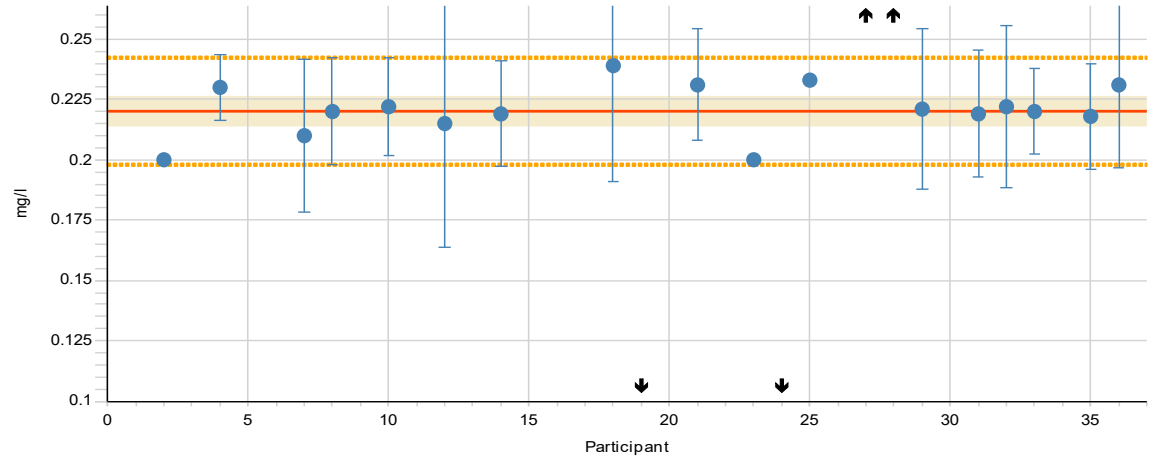


Measurand NH_4 Sample G3N



Measurand NO_2 Sample A1N



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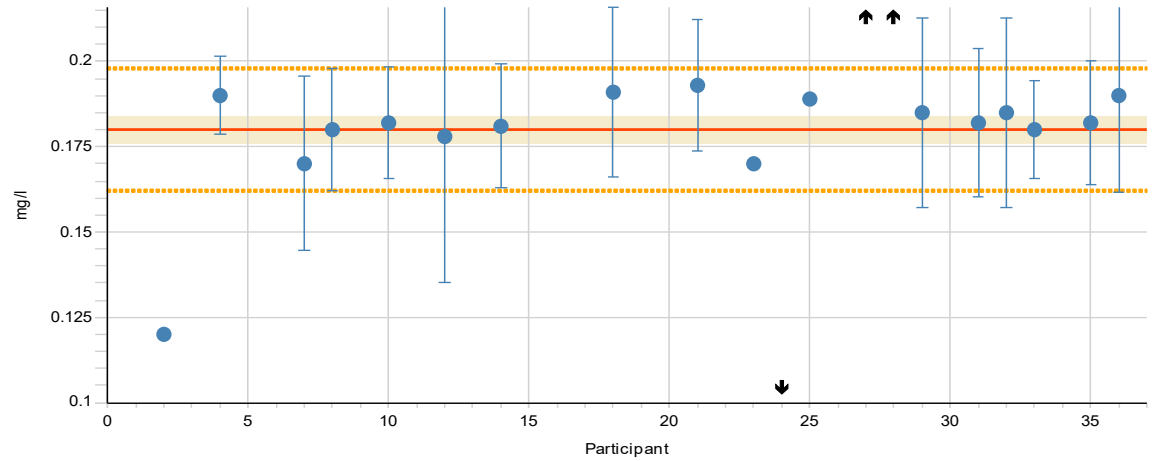

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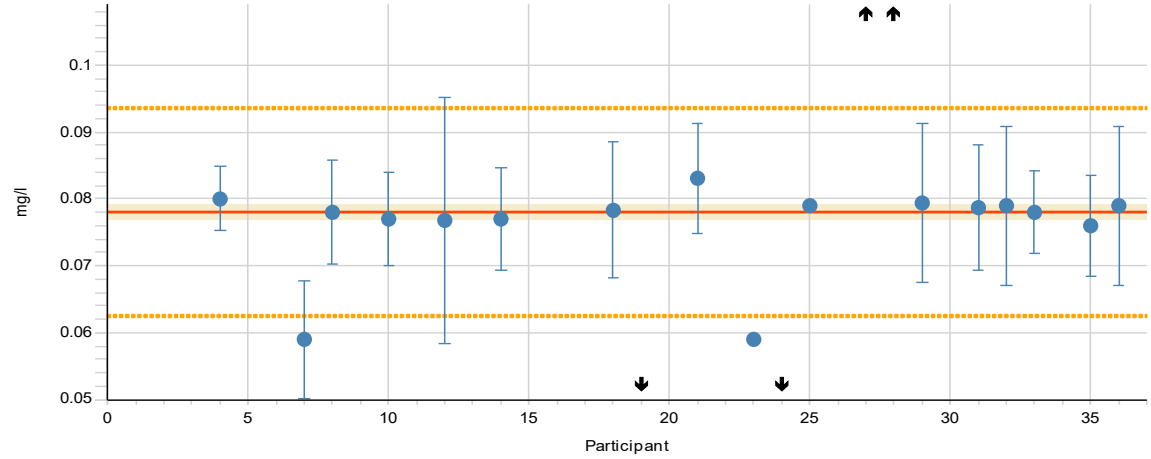
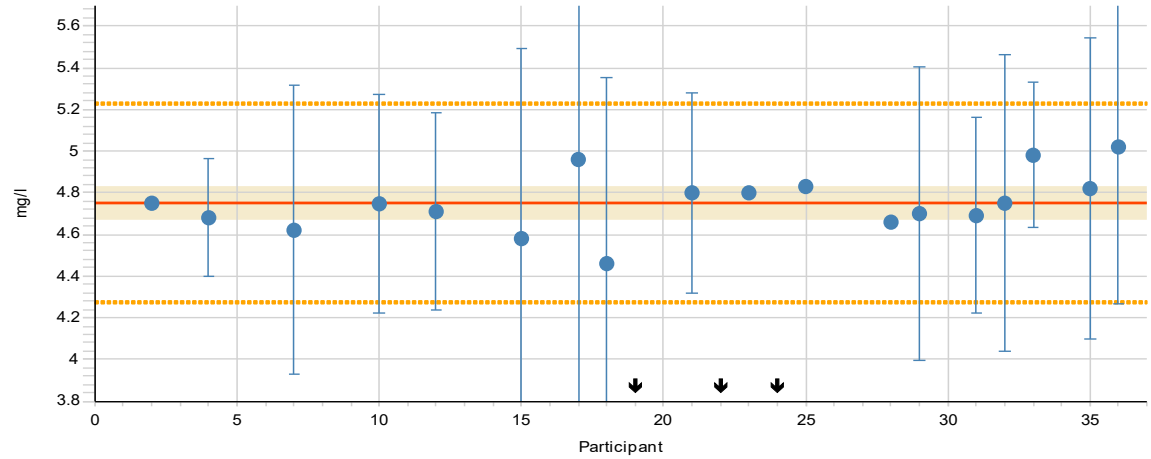
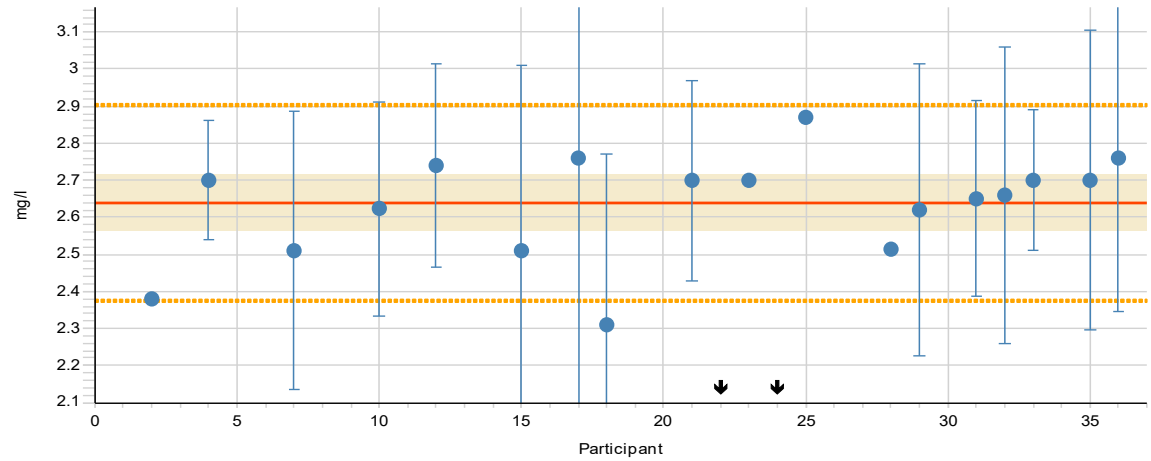


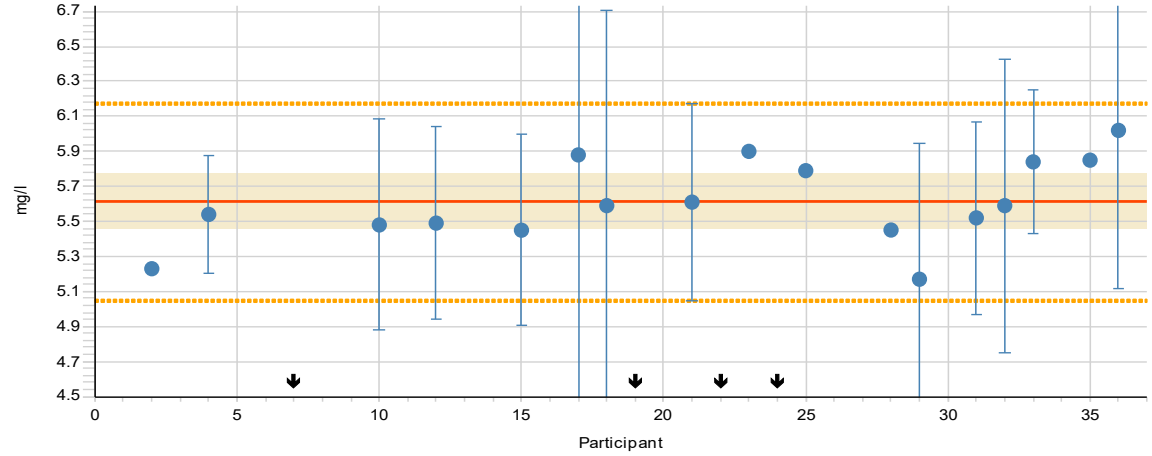
Measurand NO_3 Sample A1N



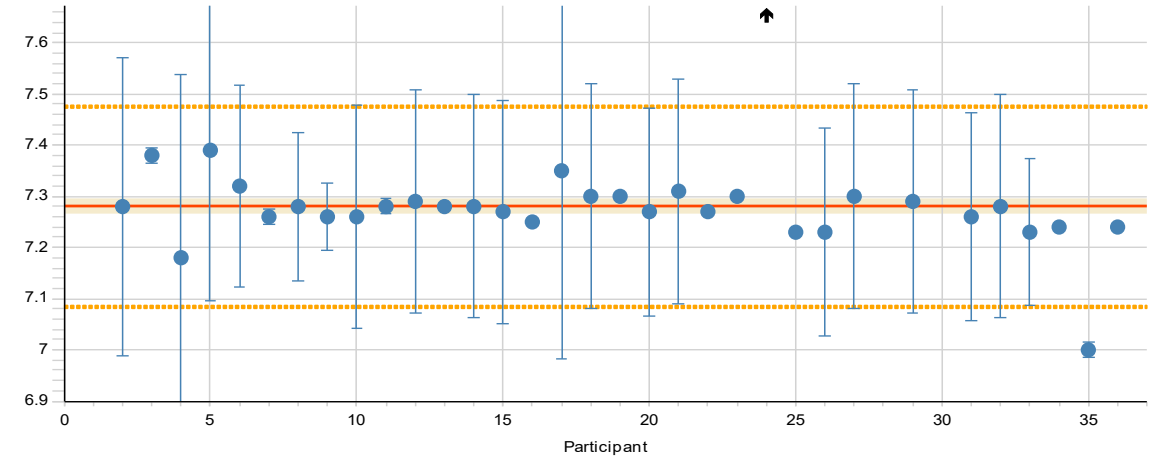
Measurand NO_3 Sample D2N



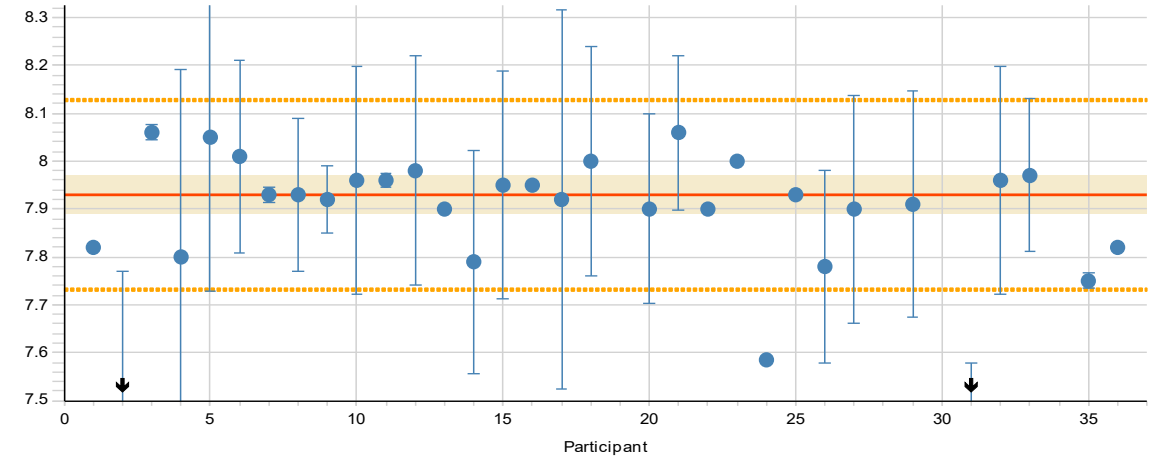
Measurand NO_3 Sample G3N



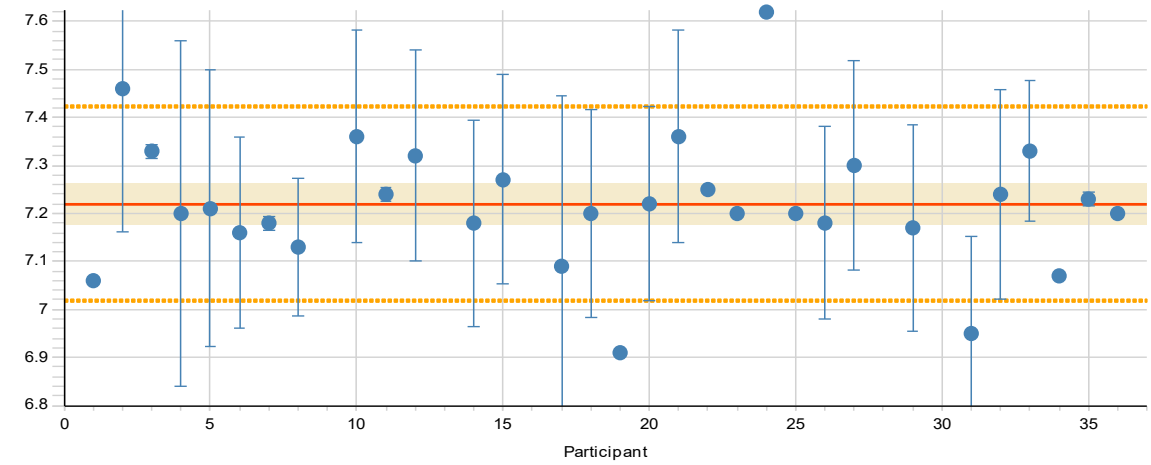
Measurand pH Sample A1P



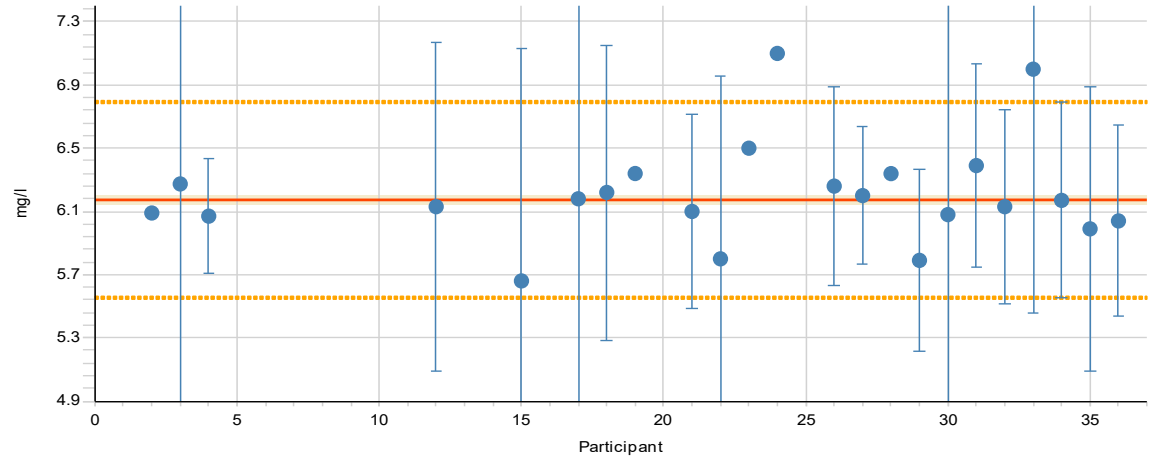
Measurand pH Sample D2PJ



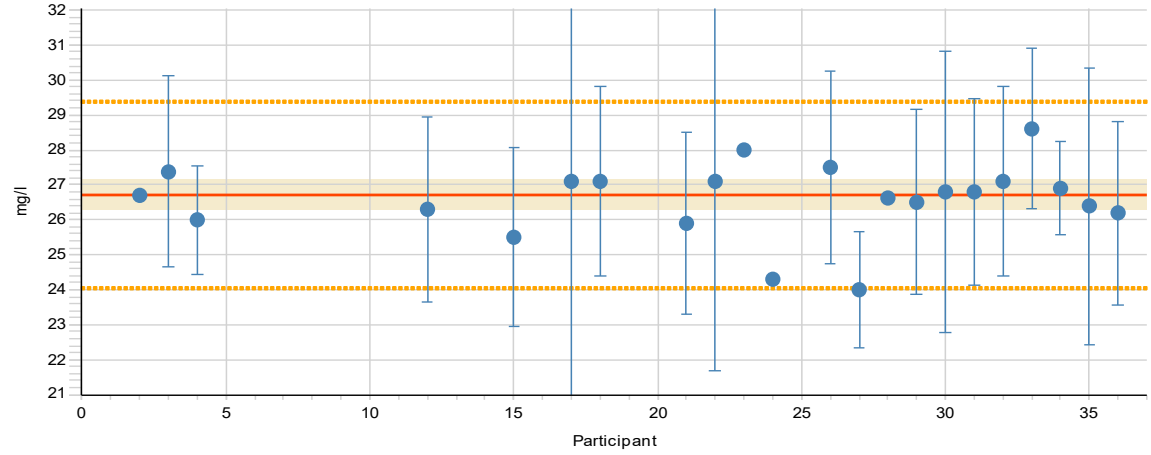
Measurand pH Sample G3PJ

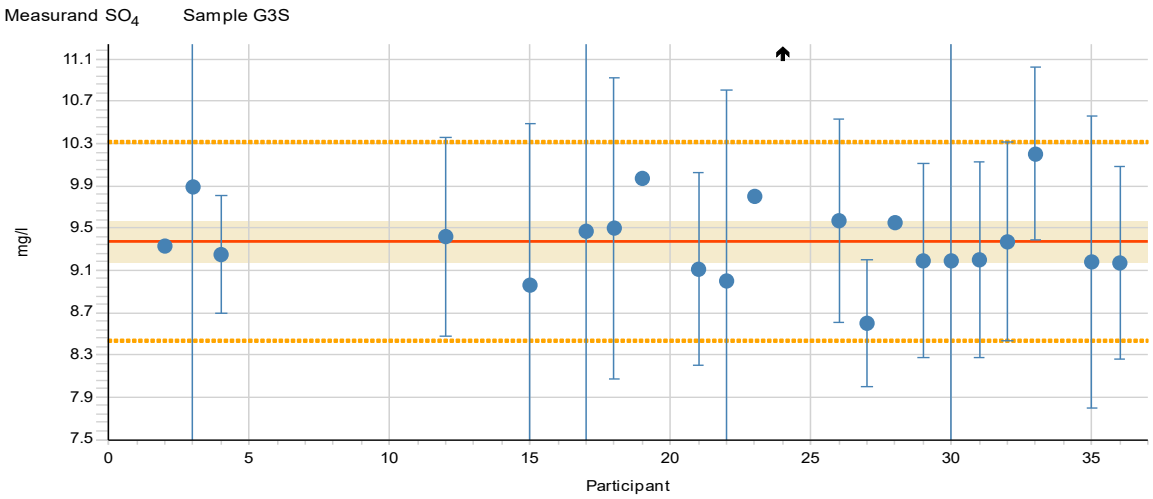


Measurand SO_4 Sample A1S



Measurand SO_4 Sample D2S




Measurand SO_4
Sample G3S
11.1
10.7
10.3
9.9
9.5
9.1
8.7
8.3
7.9
7.5
mg/l
0
5
10
15
20
25
30
35
Participant

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	%
Ca	A1K	.	.	.	.	.	.	.	.	.	.	.	S	.	.	Q	S	S	q	S	.	S	S	.	82.4
	D2K	.	.	.	.	.	.	.	.	.	.	.	S	.	.	Q	q	S	S	.	.	S	S	.	87.5
	G3K	.	.	.	.	.	.	.	.	.	.	.	U	.	.	S	.	S	S	u	.	S	S	.	81.3
Cl	A1S	.	S	S	S	S	.	.	.	.	S	.	S	S	.	S	S	S	S	U	.	S	S	S	92.6
	D2S	.	S	S	S	S	.	.	.	Q	S	.	S	S	.	S	S	S	S	.	.	S	S	S	88.9
	G3S	.	S	S	S	S	.	.	.	.	S	.	S	.	.	q	.	S	S	Q	.	S	S	S	87.5
COD_{Mn}	A1C	.	.	.	.	.	S	S	S	.	S	S	S	.	S	.	S	u	S	U	.	S	.	S	90.5
	D2C	.	.	.	.	.	S	S	S	.	S	S	S	.	S	.	S	q	S	.	.	S	.	S	95.0
	G3C	.	.	.	.	.	S	S	S	.	S	S	S	.	S	.	.	u	S	U	.	S	.	.	89.5
Conductivity	A1J	.	S	S	u	S	S	S	S	S	S	S	S	S	S	S	S	S	S	.	S	S	u	u	84.4
	D2PJ	u	S	S	u	S	S	S	S	S	S	S	S	S	S	S	S	S	S	.	S	u	u	u	81.3
	G3PJ	U	S	S	U	S	S	S	S	.	S	S	S	.	S	S	.	S	S	S	S	Q	u	u	77.4
F	A1F	.	.	S	S	.	.	.	.	.	S	.	S	.	.	.	.	S	S	.	.	S	S	S	90.0
	D2F	.	.	S	S	.	.	.	.	.	S	.	S	.	.	.	.	S	S	.	.	S	S	S	100
	G3F	.	.	S	S	.	.	.	.	.	S	.	S	.	.	.	.	S	S	.	.	S	S	S	90.0
Fe	A1Fe	S	.	.	S	S	S	.	.	.	S	.	S	U	.	u	.	S	S	.	.	S	S	.	81.8
	D2Fe	S	.	.	S	S	S	.	.	S	u	.	S	U	.	S	.	S	S	.	.	S	S	.	87.0
	G3Fe	S	.	.	S	U	S	.	.	.	S	.	S	.	.	u	.	S	S	.	.	S	S	.	85.7
Hardness	A1K	.	.	.	S	q	S	.	.	S	S	.	U	.	.	Q	.	S	S	S	.	S	.	.	80.0
	D2K	.	.	.	S	S	S	.	.	S	S	.	S	.	.	S	.	S	S	.	.	S	.	.	94.7
	G3K	.	.	.	S	S	S	.	.	.	S	.	U	.	.	S	.	S	S	S	.	S	.	.	89.5
K	A1K	.	.	.	.	.	.	.	.	.	.	.	.	.	.	S	.	.	S	S	.	U	S	.	76.9
	D2K	.	.	.	.	.	.	.	.	.	.	.	.	.	.	S	.	S	S	.	.	S	S	.	92.3
	G3K	.	.	.	.	.	.	.	.	.	.	.	.	.	.	q	.	S	S	S	.	S	S	.	85.7
Mg	A1K	.	.	.	.	.	.	.	.	.	.	.	U	.	.	S	.	S	S	U	.	S	S	.	81.3
	D2K	.	.	.	.	.	.	.	.	.	.	.	U	.	.	S	.	S	S	.	.	S	S	.	86.7
	G3K	.	.	.	.	.	.	.	.	.	.	.	U	.	.	S	.	S	S	S	.	S	S	.	87.5
Mn	A1Fe	S	.	.	S	S	.	.	.	.	u	.	S	.	.	S	.	S	S	.	.	S	S	.	80.0
	D2Fe	S	.	.	S	S	.	.	.	.	u	.	S	.	.	S	.	S	S	.	.	S	S	.	80.0
	G3Fe	S	.	.	S	S	.	.	.	.	u	.	S	.	.	S	.	S	S	.	.	S	S	.	85.0
Na	A1K	.	.	.	.	.	.	.	.	.	.	.	.	.	.	S	S	S	S	S	.	S	S	.	87.5
	D2K	.	.	.	.	.	.	.	.	.	.	.	.	.	.	S	S	S	S	.	.	S	S	.	100
	G3K	.	.	.	.	.	.	.	.	.	.	.	.	.	.	S	.	S	S	S	.	S	S	.	100
NH_4	A1N	.	S	.	U	.	u	S	Q	.	S	.	S	.	S	U	.	.	S	u	.	S	S	S	69.6
	D2N	.	S	.	S	.	S	S	Q	.	S	.	S	.	S	U	.	.	S	.	.	S	S	S	81.8
	G3N	.	S	.	S	.	S	S	U	.	S	.	S	.	S	U	.	.	S	u	.	S	S	q	73.9
NO_2	A1N	.	S	.	S	.	.	S	S	.	S	.	S	.	S	.	.	.	S	u	.	S	.	S	81.0
	D2N	.	u	.	S	.	.	S	S	.	S	.	S	.	S	.	.	.	S	.	.	S	.	S	80.0
	G3N	.	.	.	S	.	.	q	S	.	S	.	S	.	S	.	.	.	S	u	.	S	.	q	70.0
NO_3	A1N	.	S	.	S	.	.	S	.	.	S	.	S	.	.	S	.	S	S	u	.	S	u	S	85.7
	D2N	.	S	.	S	.	.	S	.	.	S	.	S	.	.	S	.	S	q	.	.	S	u	S	85.0
	G3N	.	S	.	S	.	.	u	.	.	S	.	S	.	.	S	.	S	S	u	.	S	u	S	81.0

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	%
pH	A1P	.	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	93.9
	D2PJ	S	u	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	.	S	S	S	S	90.6
	G3PJ	S	Q	S	S	S	S	S	S	.	S	S	S	.	S	S	.	S	S	u	S	S	S	S	87.1
SO_4	A1S	.	S	S	S	.	.	.	.	.	.	.	S	.	.	S	.	S	S	S	.	S	S	S	91.3
	D2S	.	S	S	S	.	.	.	.	.	.	.	S	.	.	S	.	S	S	.	.	S	S	S	95.5
	G3S	.	S	S	S	.	.	.	.	.	.	.	S	.	.	S	.	S	S	S	.	S	S	S	95.5
%		80	85	100	88	89	94	89	80	88	88	100	86	75	100	74	92	93	96	48	100	94	85	81	
accredited		8					18	15	14		30	9	36		15	27		28	44	1	6	48	33	24	

Measurand	Sample	24	25	26	27	28	29	30	31	32	33	34	35	36	37										%
Ca	A1K	U	.	.	.	.	S	S	S	S	S	S	S	.	S	.	.	.	.	.	.	.	.	.	82.4
	D2K	S	.	.	.	.	S	S	S	S	S	S	S	.	S	.	.	.	.	.	.	.	.	.	87.5
	G3K	U	.	.	.	.	S	S	S	S	S	S	S	.	S	.	.	.	.	.	.	.	.	.	81.3
Cl	A1S	Q	.	S	S	S	S	S	S	S	S	S	S	S	.	.	.	.	.	.	.	.	.	.	92.6
	D2S	U	.	S	S	S	S	S	S	S	S	U	S	S	.	.	.	.	.	.	.	.	.	.	88.9
	G3S	U	.	S	S	S	S	S	S	S	S	.	S	S	.	.	.	.	.	.	.	.	.	.	87.5
COD_{Mn}	A1C	.	.	S	S	.	S	.	S	S	S	.	S	S	.	.	.	.	.	.	.	.	.	.	90.5
	D2C	.	.	S	S	.	S	.	S	S	S	.	S	S	.	.	.	.	.	.	.	.	.	.	95.0
	G3C	.	.	S	S	.	S	.	S	S	S	.	S	S	.	.	.	.	.	.	.	.	.	.	89.5
Conductivity	A1J	S	S	S	u	.	S	.	S	S	q	S	S	S	.	.	.	.	.	.	.	.	.	.	84.4
	D2PJ	S	S	S	u	.	S	.	S	S	S	.	S	S	.	.	.	.	.	.	.	.	.	.	81.3
	G3PJ	S	S	S	u	.	S	.	S	S	S	u	S	S	.	.	.	.	.	.	.	.	.	.	77.4
F	A1F	S	.	S	.	S	S	Q	S	S	S	U	S	S	.	.	.	.	.	.	.	.	.	.	90.0
	D2F	S	.	S	.	S	S	S	S	S	S	.	S	S	.	.	.	.	.	.	.	.	.	.	100
	G3F	S	.	S	.	S	S	S	S	q	S	U	S	S	.	.	.	.	.	.	.	.	.	.	90.0
Fe	A1Fe	U	Q	.	.	.	S	S	S	S	S	.	S	S	S	.	.	.	.	.	.	.	.	.	81.8
	D2Fe	S	U	.	.	.	S	S	S	S	S	.	S	S	S	.	.	.	.	.	.	.	.	.	87.0
	G3Fe	S	Q	.	.	.	S	S	S	S	S	.	S	S	S	.	.	.	.	.	.	.	.	.	85.7
Hardness	A1K	U	S	.	.	.	S	S	S	S	S	.	S	.	S	.	.	.	.	.	.	.	.	.	80.0
	D2K	Q	S	.	.	.	S	S	S	S	S	.	S	.	S	.	.	.	.	.	.	.	.	.	94.7
	G3K	U	S	.	.	.	S	S	S	S	S	.	S	.	S	.	.	.	.	.	.	.	.	.	89.5
K	A1K	.	.	.	.	.	S	S	q	S	.	S	S	u	S	.	.	.	.	.	.	.	.	.	76.9
	D2K	.	.	.	.	.	S	S	S	S	.	S	S	q	S	.	.	.	.	.	.	.	.	.	92.3
	G3K	.	.	.	.	.	S	S	S	S	.	S	S	u	S	.	.	.	.	.	.	.	.	.	85.7
Mg	A1K	U	.	.	.	.	S	S	S	S	S	S	S	.	S	.	.	.	.	.	.	.	.	.	81.3
	D2K	U	.	.	.	.	S	S	S	S	S	S	S	.	S	.	.	.	.	.	.	.	.	.	86.7
	G3K	U	.	.	.	.	S	S	S	S	S	S	S	.	S	.	.	.	.	.	.	.	.	.	87.5
Mn	A1Fe	U	q	.	.	.	S	S	S	S	S	.	S	U	S	.	.	.	.	.	.	.	.	.	80.0
	D2Fe	U	Q	.	.	.	S	S	S	S	S	.	S	U	S	.	.	.	.	.	.	.	.	.	80.0
	G3Fe	U	Q	.	.	.	S	S	S	S	S	.	S	S	S	.	.	.	.	.	.	.	.	.	85.0
Na	A1K	.	.	.	.	.	S	S	S	S	q	S	S	u	S	.	.	.	.	.	.	.	.	.	87.5
	D2K	.	.	.	.	.	S	S	S	S	S	S	S	S	S	.	.	.	.	.	.	.	.	.	100
	G3K	.	.	.	.	.	S	S	S	S	S	S	S	S	S	.	.	.	.	.	.	.	.	.	100

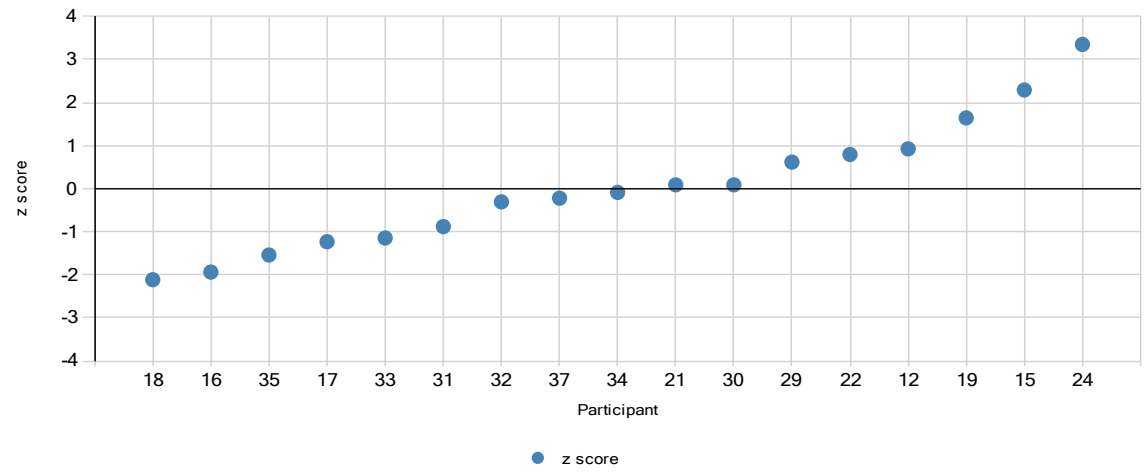
Measurand	Sample	24	25	26	27	28	29	30	31	32	33	34	35	36	37										%
NH_4	A1N	*u*	*S*	.	**U**	.	**S**	.	**S**	**S**	**S**	.	**S**	**S**	.	.	.	.	.	.	.	.	.	.	69.6
	D2N	*u*	*S*	.	**U**	.	**S**	.	**S**	**S**	**S**	.	**S**	**S**	.	.	.	.	.	.	.	.	.	.	81.8
	G3N	*u*	*S*	.	**U**	.	**S**	.	**S**	**S**	**S**	.	**S**	**S**	.	.	.	.	.	.	.	.	.	.	73.9
NO_2	A1N	*u*	*S*	.	**U**	*U*	**S**	.	**S**	**S**	**S**	.	**S**	**S**	.	.	.	.	.	.	.	.	.	.	81.0
	D2N	*u*	*S*	.	**U**	*U*	**S**	.	**S**	**S**	**S**	.	**S**	**S**	.	.	.	.	.	.	.	.	.	.	80.0
	G3N	*u*	*S*	.	**U**	*U*	**S**	.	**S**	**S**	**S**	.	**S**	**S**	.	.	.	.	.	.	.	.	.	.	70.0
NO_3	A1N	*u*	*S*	.	.	*S*	**S**	.	**S**	**S**	**S**	.	**S**	**S**	.	.	.	.	.	.	.	.	.	.	85.7
	D2N	*u*	*S*	.	.	*S*	**S**	.	**S**	**S**	**S**	.	**S**	**S**	.	.	.	.	.	.	.	.	.	.	85.0
	G3N	*u*	*S*	.	.	*S*	**S**	.	**S**	**S**	**S**	.	**S**	**S**	.	.	.	.	.	.	.	.	.	.	81.0
pH	A1P	*U*	*S*	**S**	**S**	.	**S**	.	**S**	**S**	**S**	*S*	**q**	**S**	.	.	.	.	.	.	.	.	.	.	93.9
	D2PJ	*u*	*S*	**S**	**S**	.	**S**	.	**u**	**S**	**S**	.	**S**	**S**	.	.	.	.	.	.	.	.	.	.	90.6
	G3PJ	*U*	*S*	**S**	**S**	.	**S**	.	**q**	**S**	**S**	*S*	**S**	**S**	.	.	.	.	.	.	.	.	.	.	87.1
SO_4	A1S	*U*	.	**S**	**S**	*S*	**S**	**S**	**S**	**S**	**Q**	*S*	**S**	**S**	.	.	.	.	.	.	.	.	.	.	91.3
	D2S	*S*	.	**S**	**q**	*S*	**S**	**S**	**S**	**S**	**S**	*S*	**S**	**S**	.	.	.	.	.	.	.	.	.	.	95.5
	G3S	*U*	.	**S**	**S**	*S*	**S**	**S**	**S**	**S**	**S**	.	**S**	**S**	.	.	.	.	.	.	.	.	.	.	95.5
%		26	75	100	52	80	100	97	94	98	93	82	98	85	100										
accredited				18	21		48	29	48	48	45		48	39	21										

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

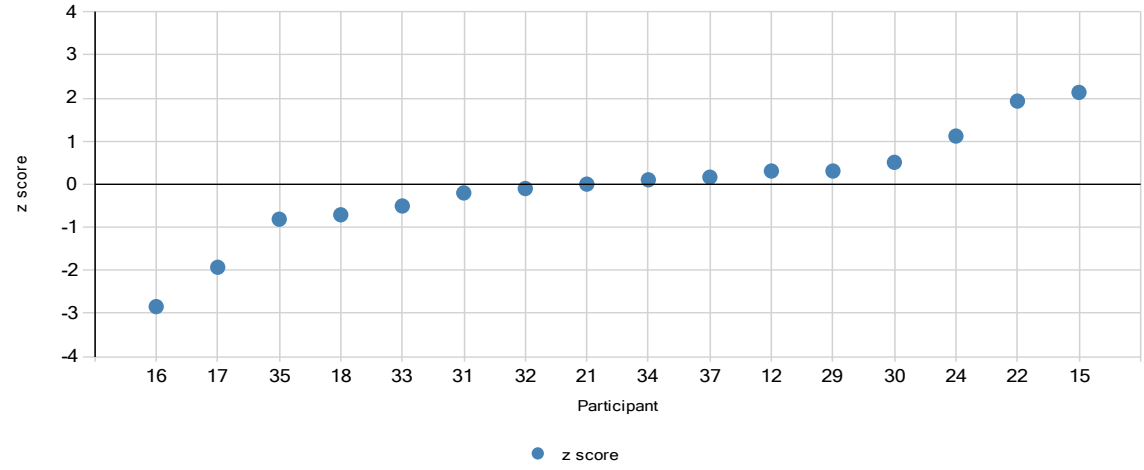
Satisfactory results, in total %: 86 in accredited %: 92 in non-accredited %: 71

Appendix 11. z scores in ascending order

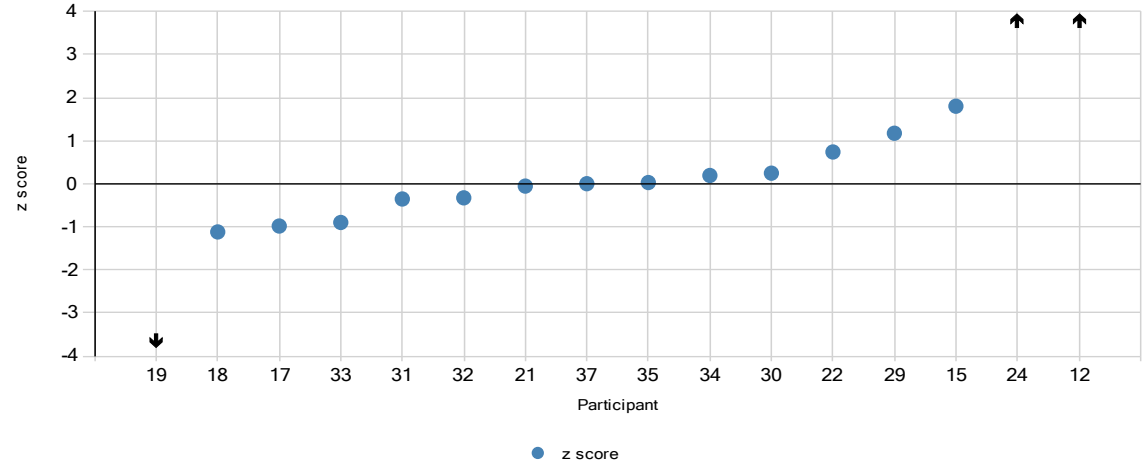
Measurand Ca Sample A1K



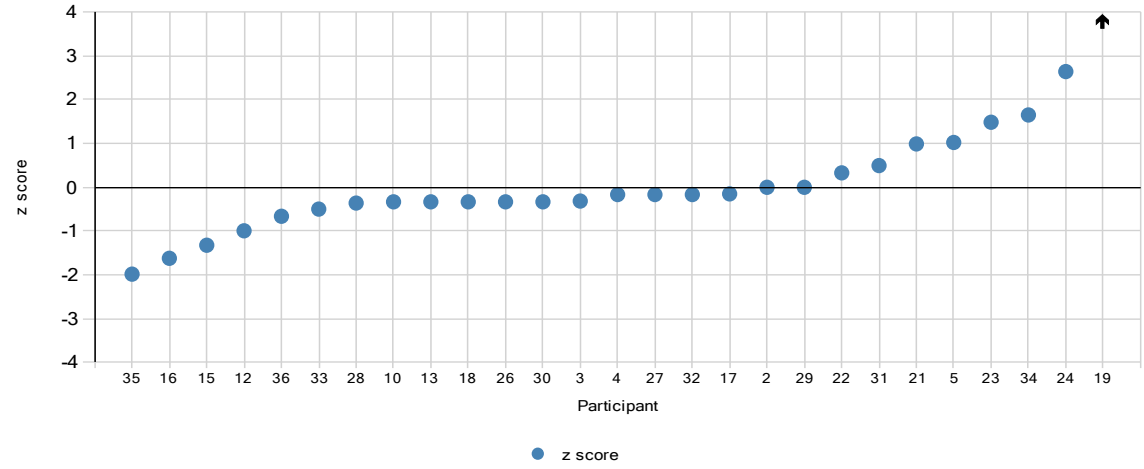
Measurand Ca Sample D2K



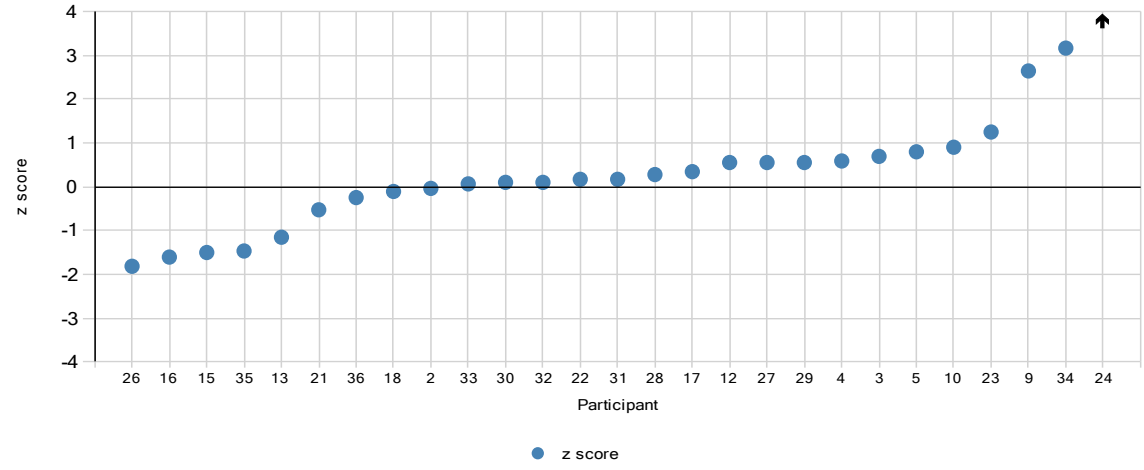
Measurand Ca Sample G3K



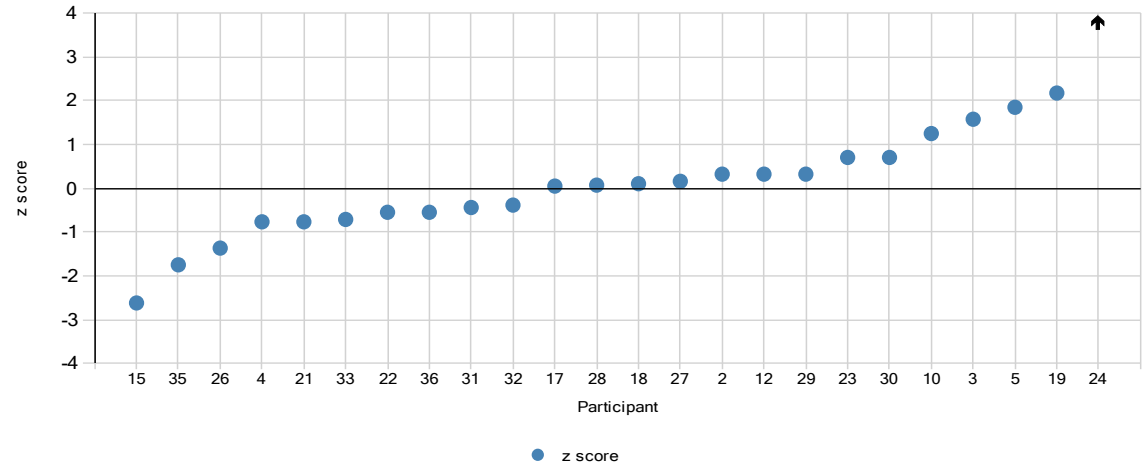
Measurand Cl Sample A1S



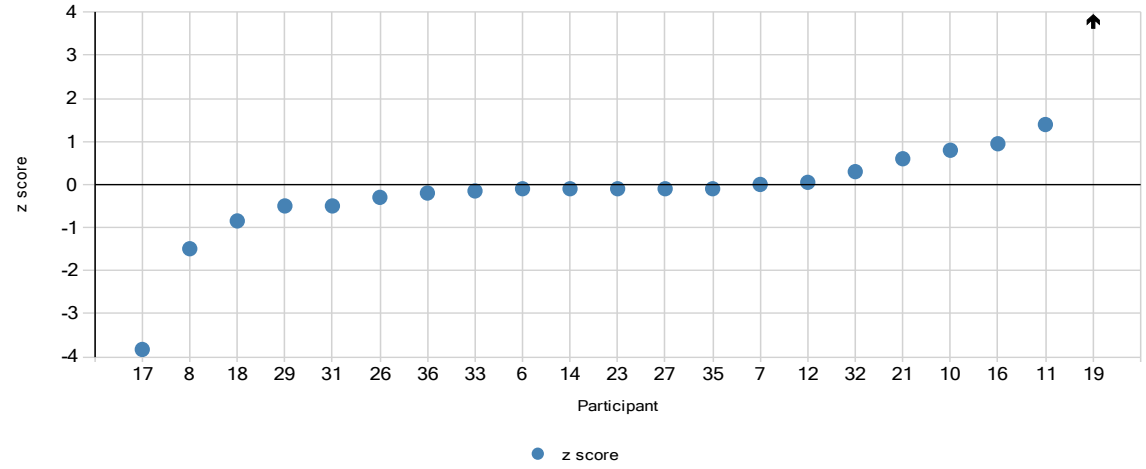
Measurand Cl Sample D2S



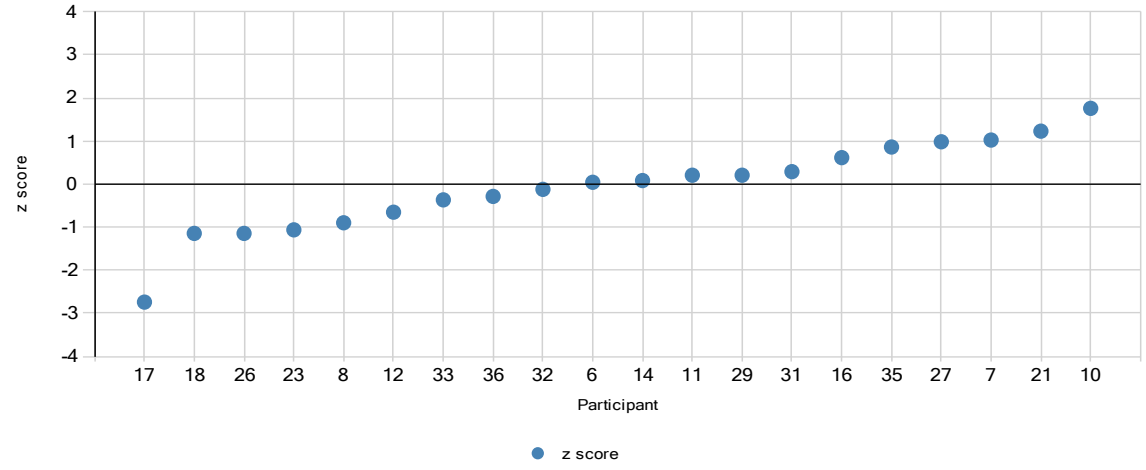
Measurand Cl Sample G3S



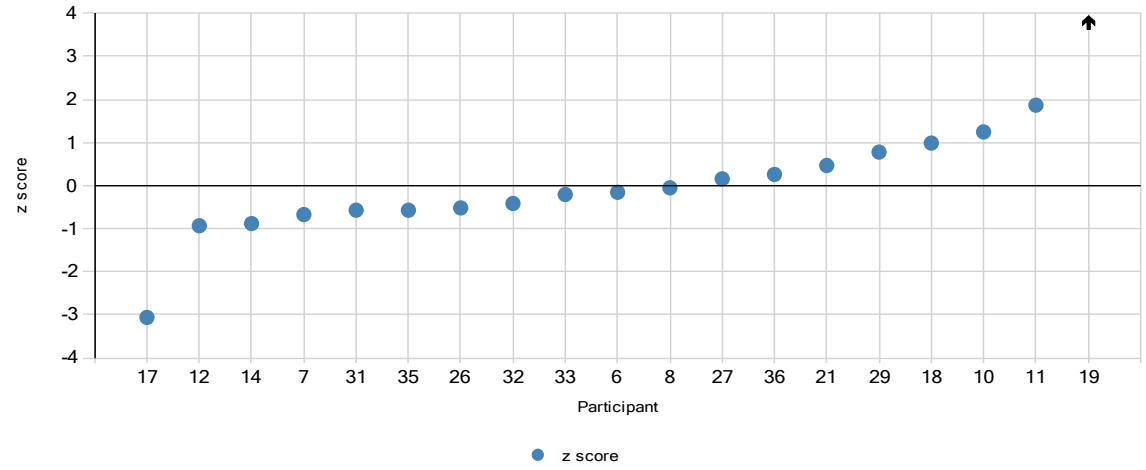
Measurand COD_{Mn} Sample A1C



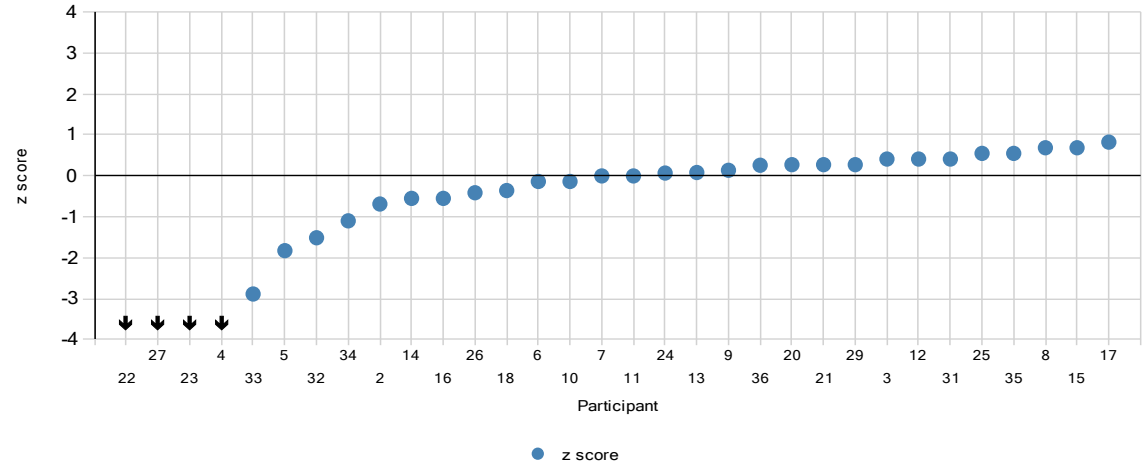
Measurand COD_{Mn} Sample D2C



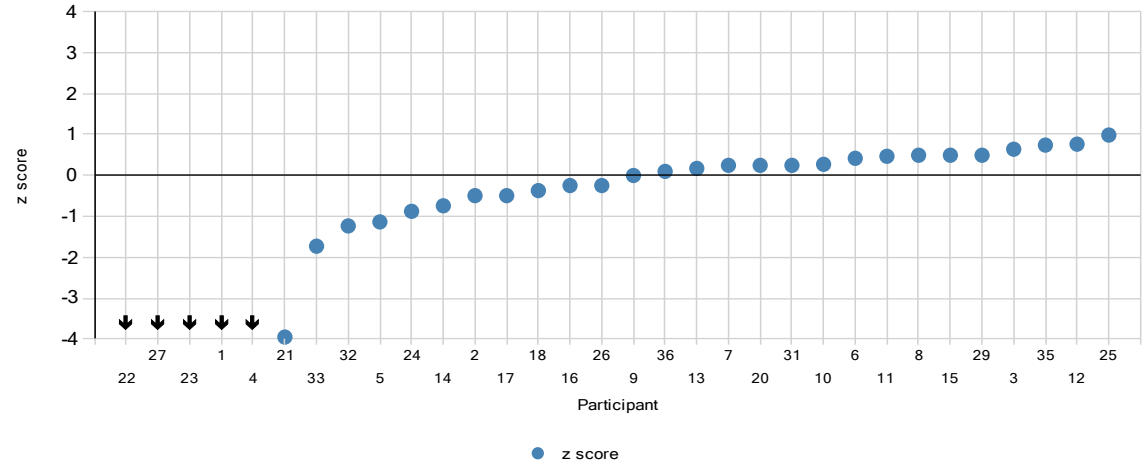
Measurand COD_{Mn} Sample G3C



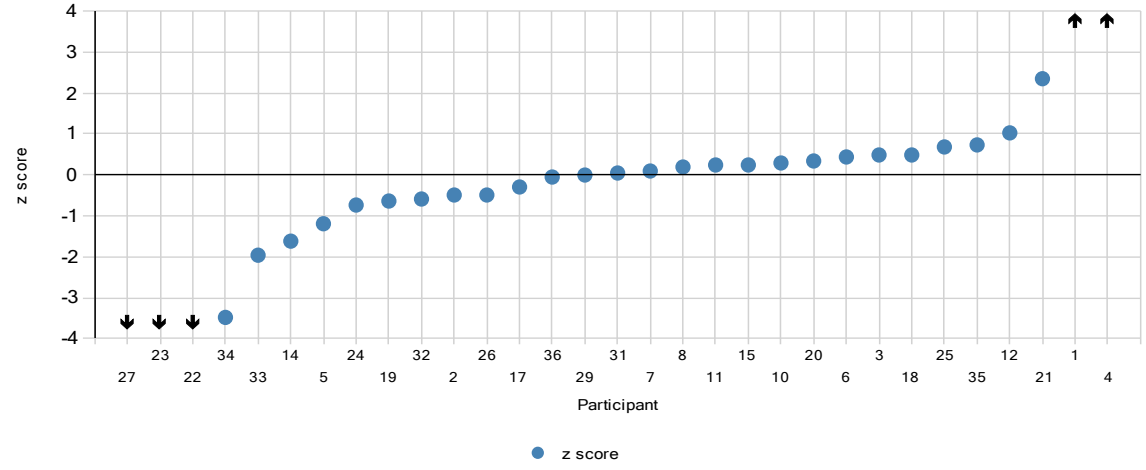
Measurand Conductivity Sample A1J



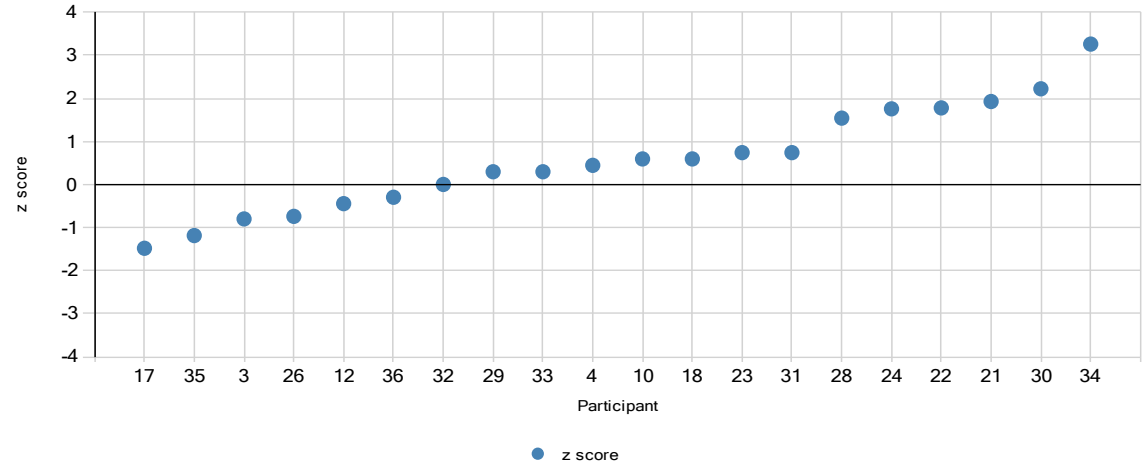
Measurand Conductivity Sample D2PJ



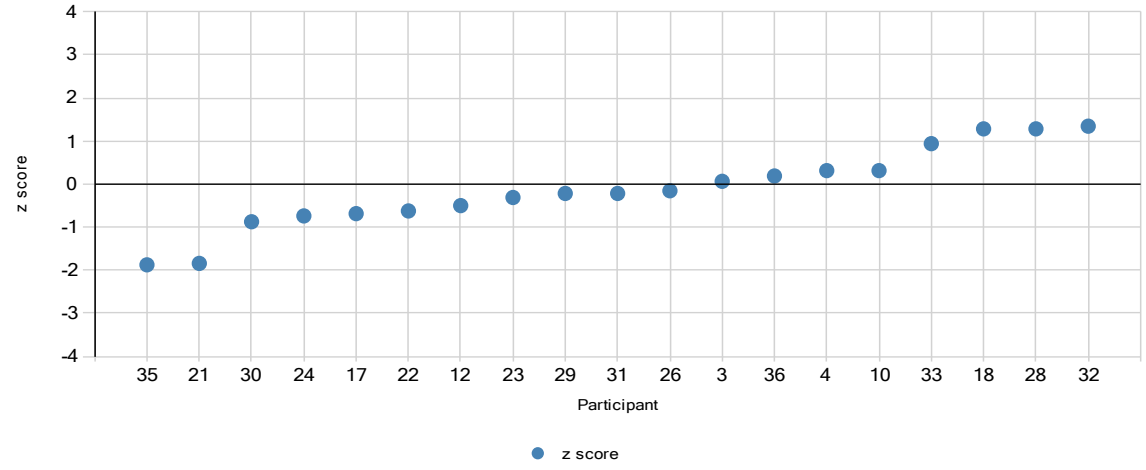
Measurand Conductivity Sample G3PJ



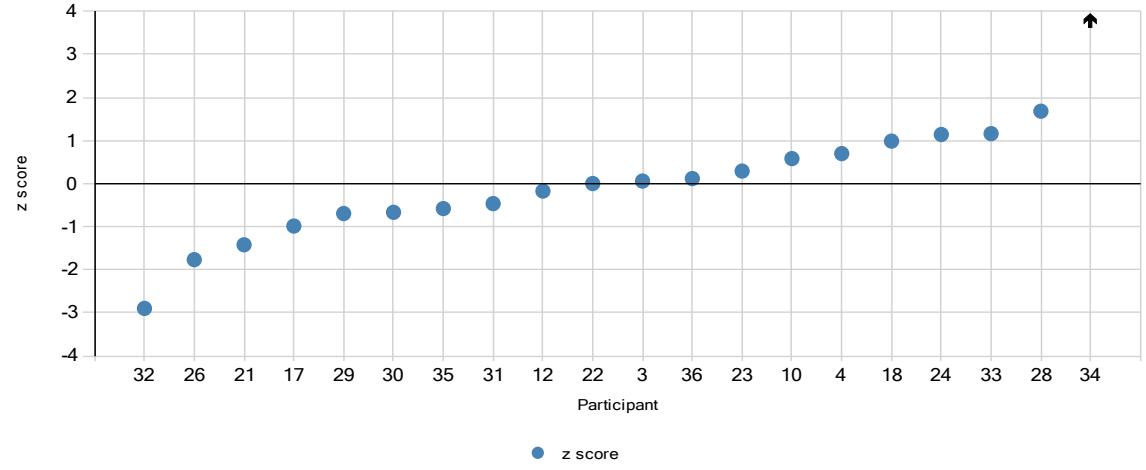
Measurand F Sample A1F

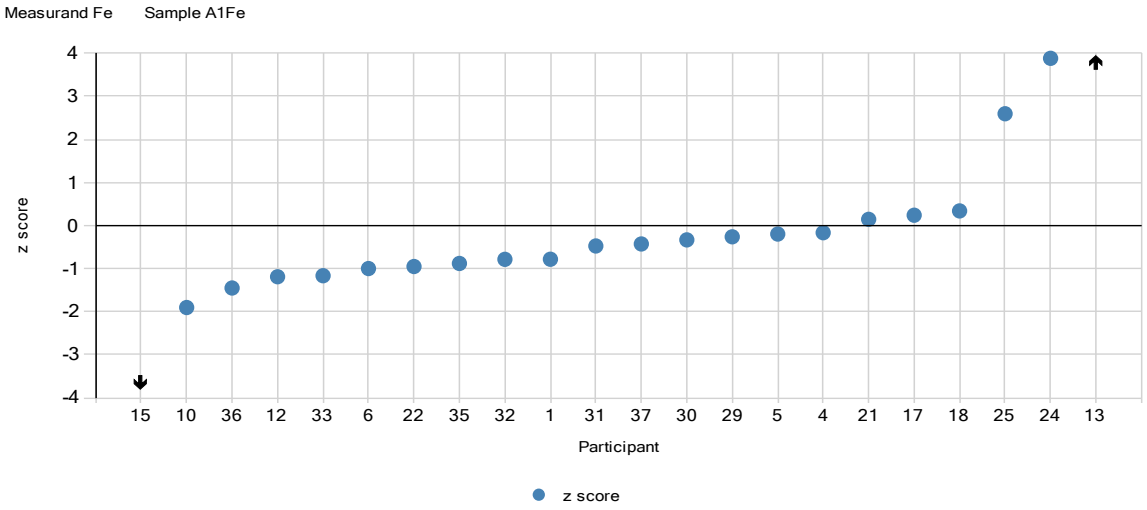


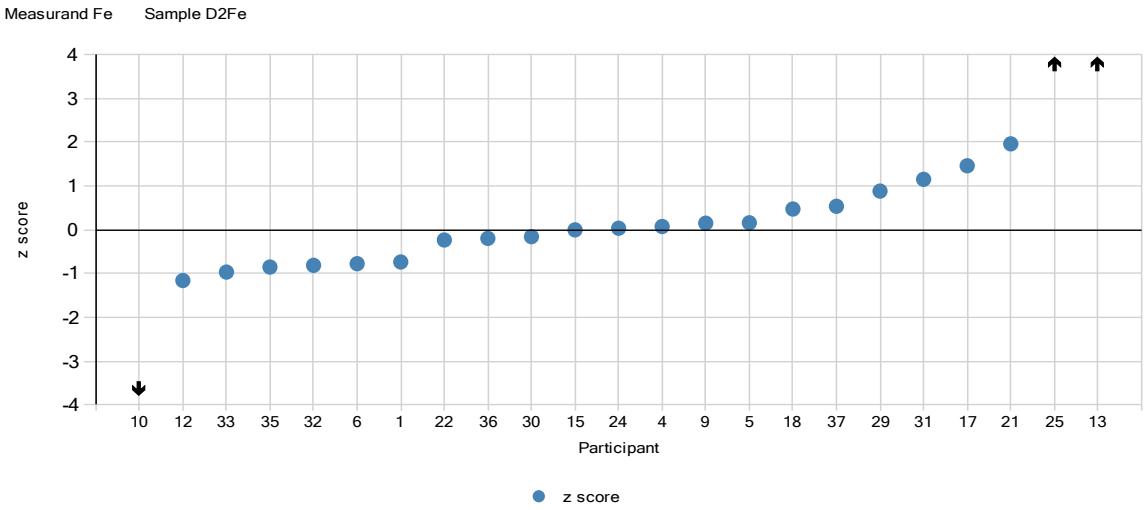
Measurand F Sample D2F

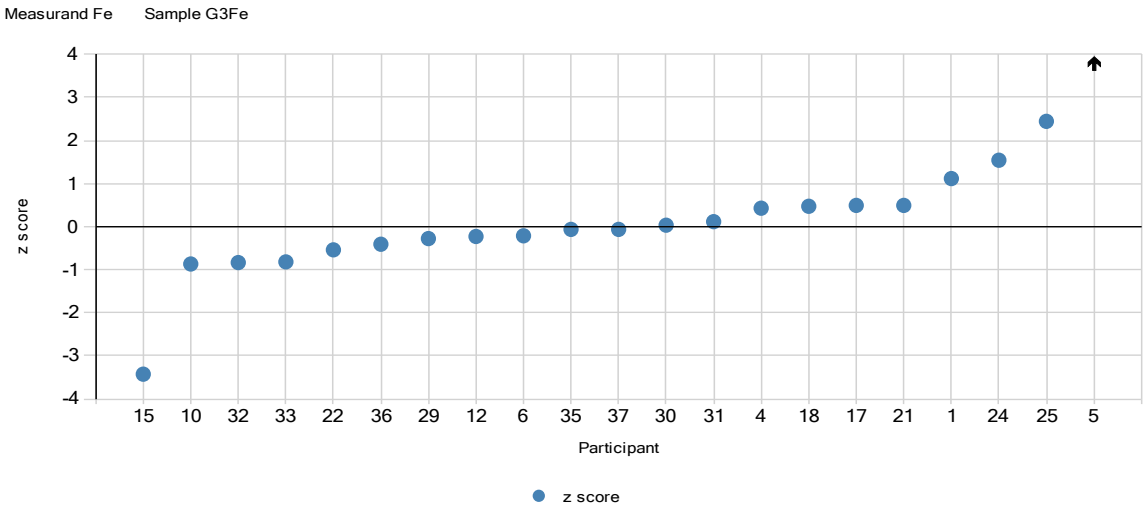


Measurand F Sample G3F

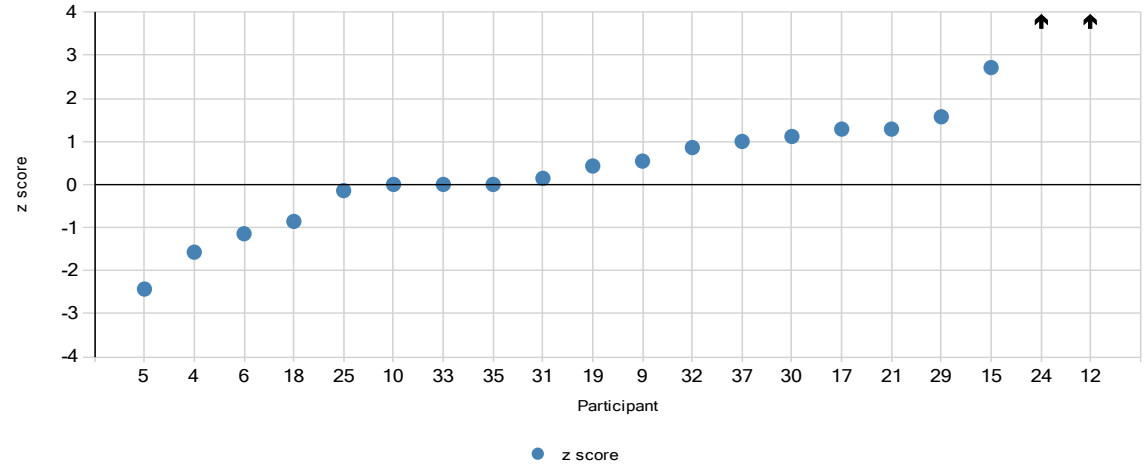



Measurand Fe Sample A1Fe
z score
4
3
2
1
0
-1
-2
-3
-4
15 10 36 12 33 6 22 35 32 1 31 37 30 29 5 4 21 17 18 25 24 13
Participant
z score

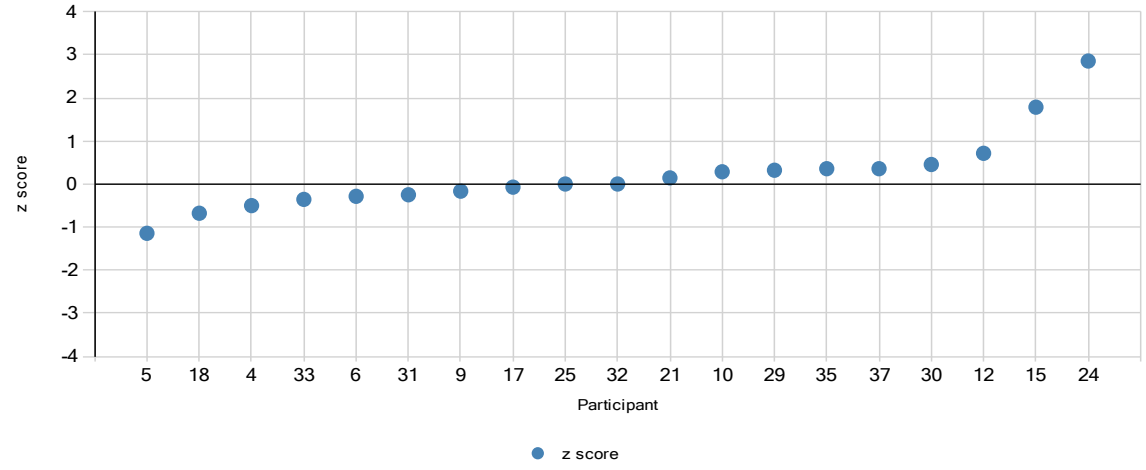

Measurand Fe Sample D2Fe
z score
4
3
2
1
0
-1
-2
-3
-4
10 12 33 35 32 6 1 22 36 30 15 24 4 9 5 18 37 29 31 17 21 25 13
Participant
z score


Measurand Fe Sample G3Fe
z score
4
3
2
1
0
-1
-2
-3
-4
15 10 32 33 22 36 29 12 6 35 37 30 31 4 18 17 21 1 24 25 5
Participant
z score

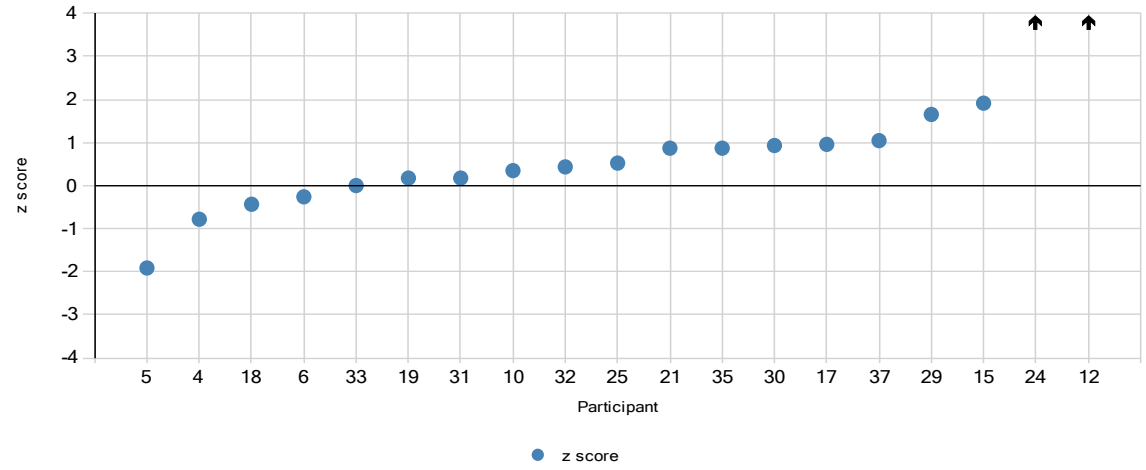
Measurand Hardness Sample A1K

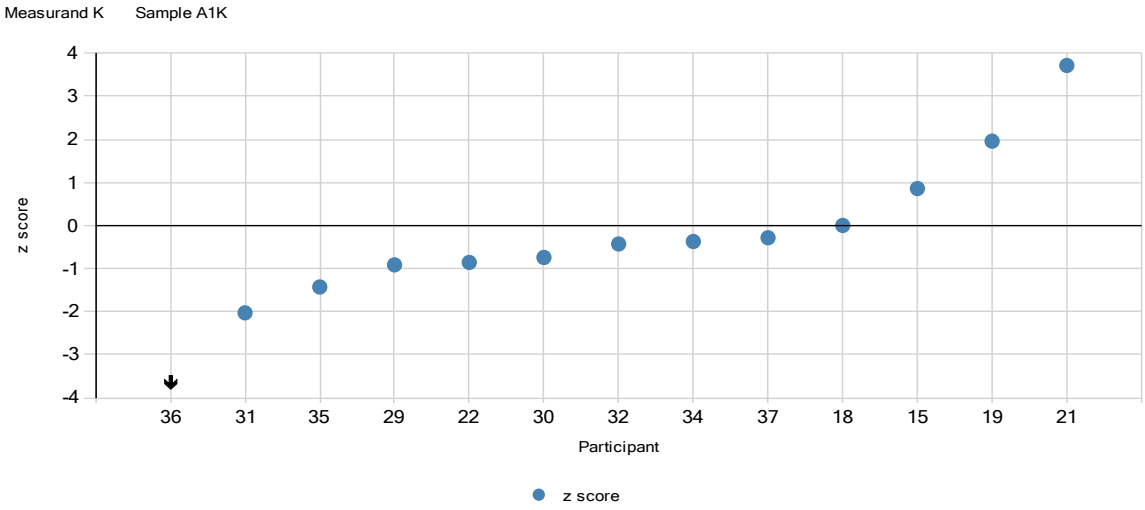


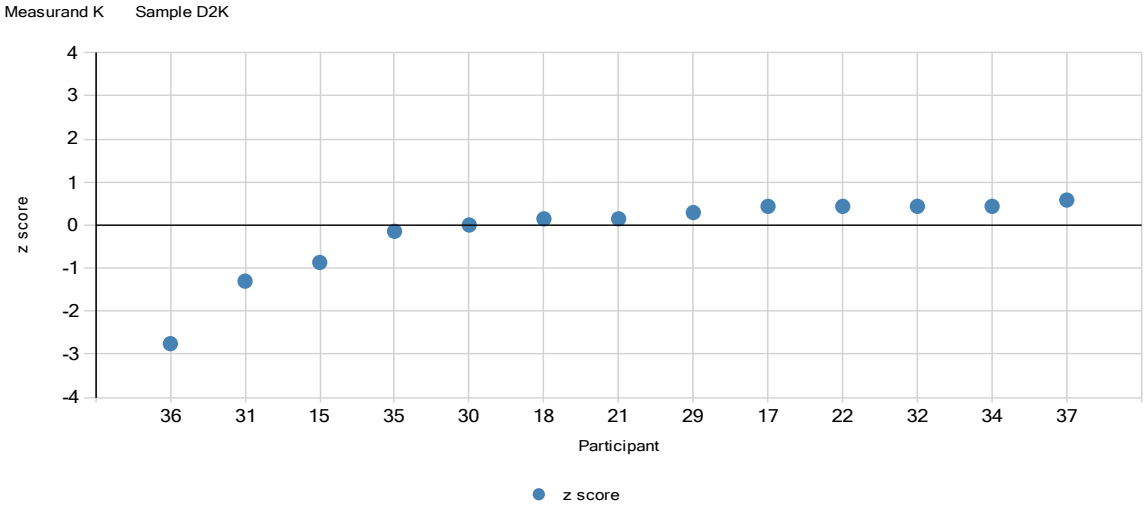
Measurand Hardness Sample D2K

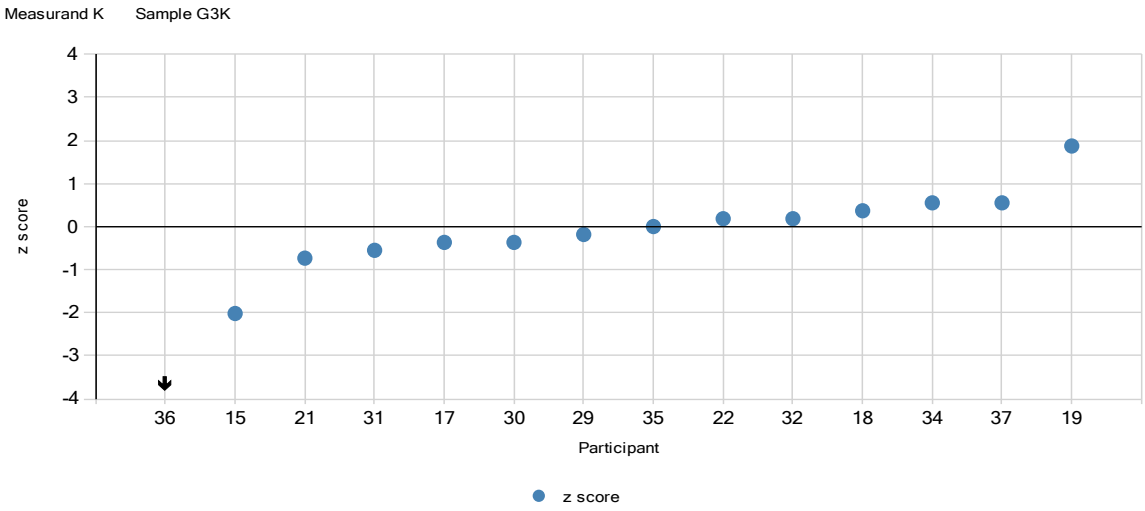


Measurand Hardness Sample G3K

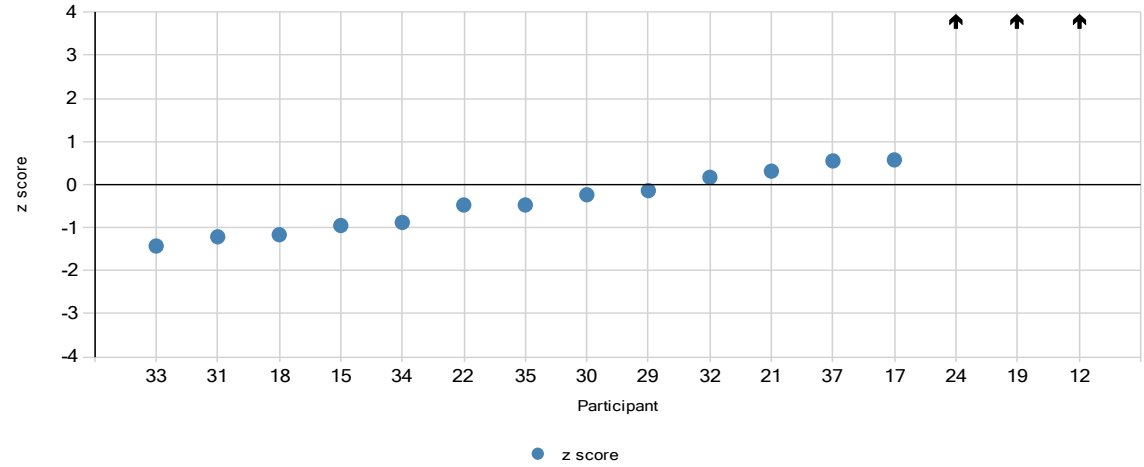



Measurand K
Sample A1K
z score
4
3
2
1
0
-1
-2
-3
-4
36
31
35
29
22
30
32
34
37
18
15
19
21
Participant
z score

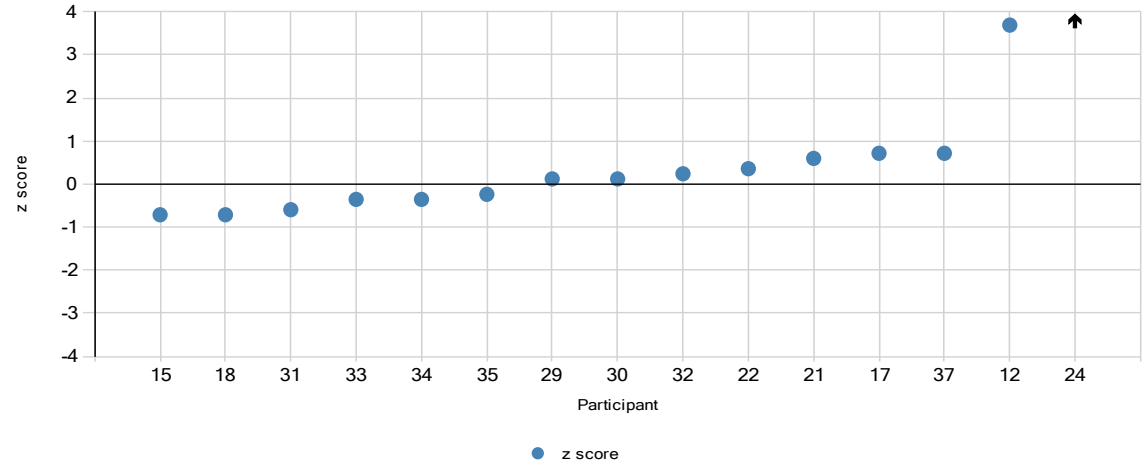

Measurand K
Sample D2K
z score
4
3
2
1
0
-1
-2
-3
-4
36
31
15
35
30
18
21
29
17
22
32
34
37
Participant
z score


Measurand K
Sample G3K
z score
4
3
2
1
0
-1
-2
-3
-4
36
15
21
31
17
30
29
35
22
32
18
34
37
19
Participant
z score

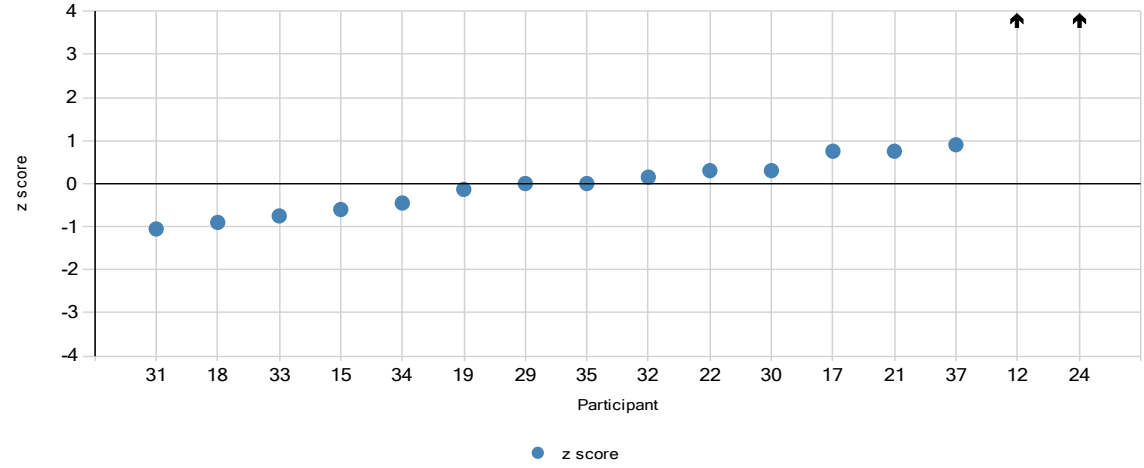
Measurand Mg Sample A1K

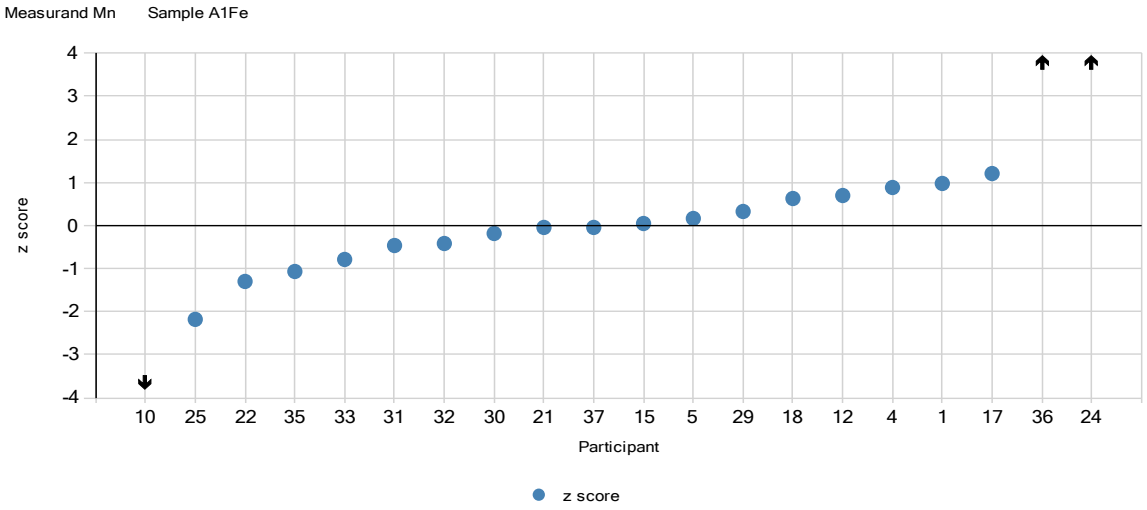


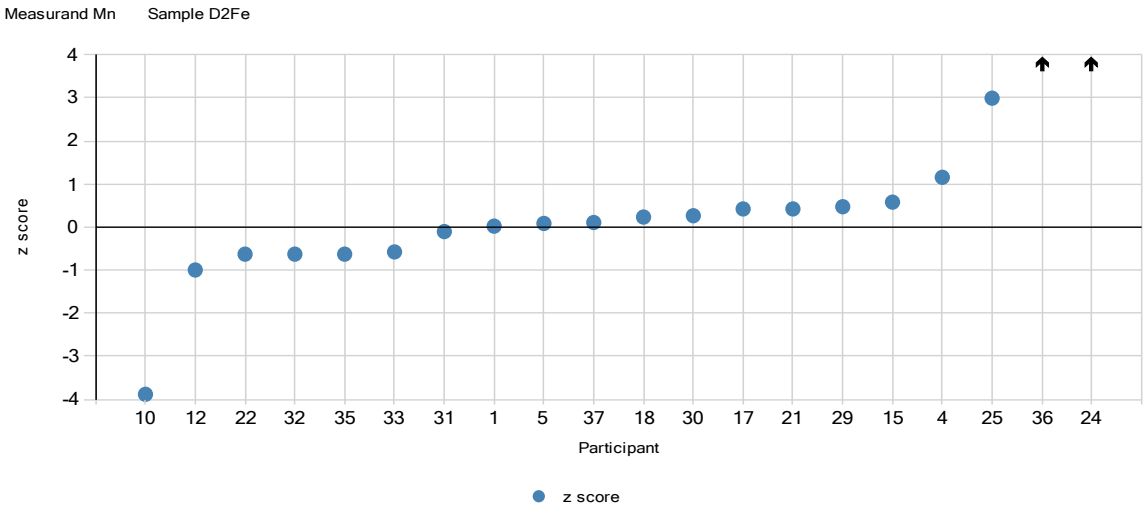
Measurand Mg Sample D2K

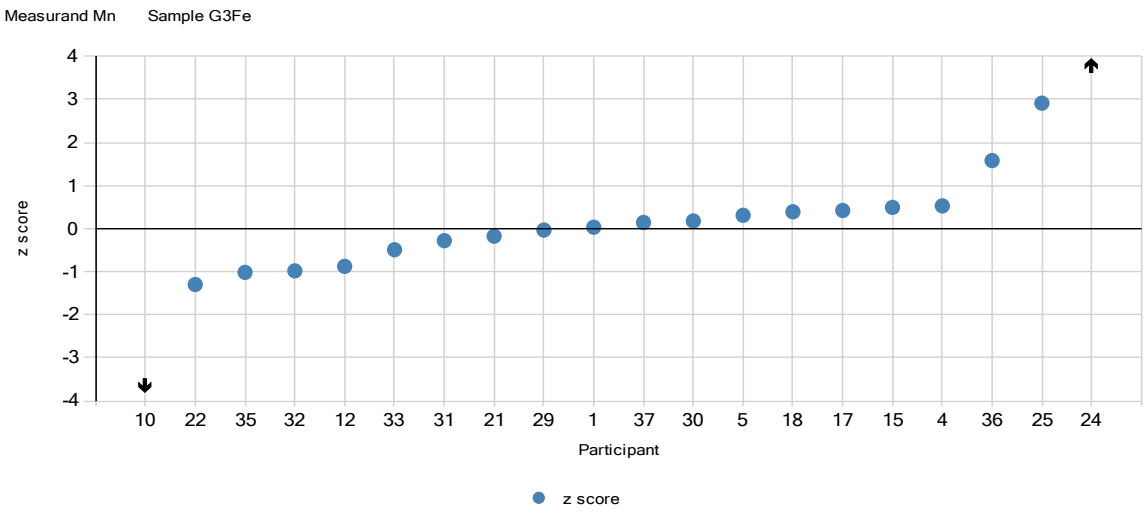


Measurand Mg Sample G3K

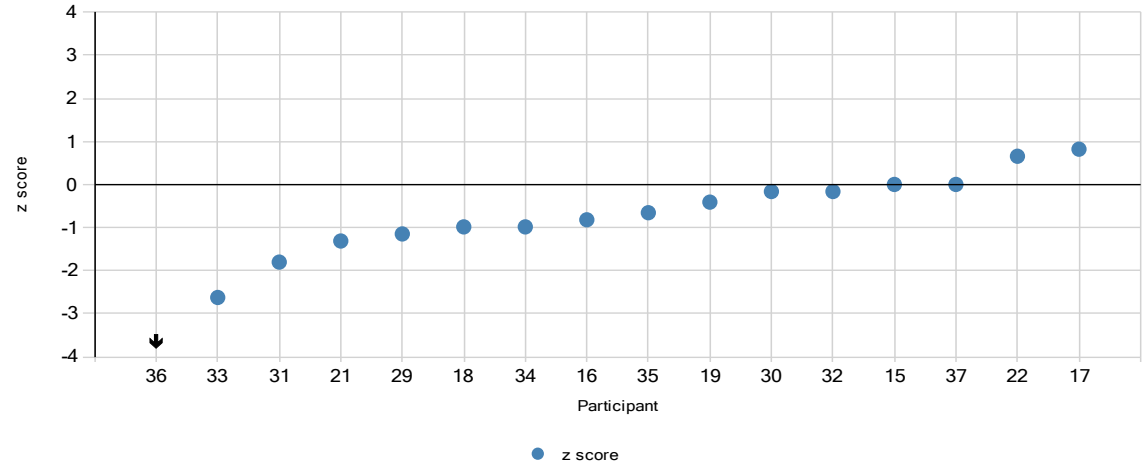



Measurand Mn Sample A1Fe
z score
4
3
2
1
0
-1
-2
-3
-4
10 25 22 35 33 31 32 30 21 37 15 5 29 18 12 4 1 17 36 24
Participant
z score

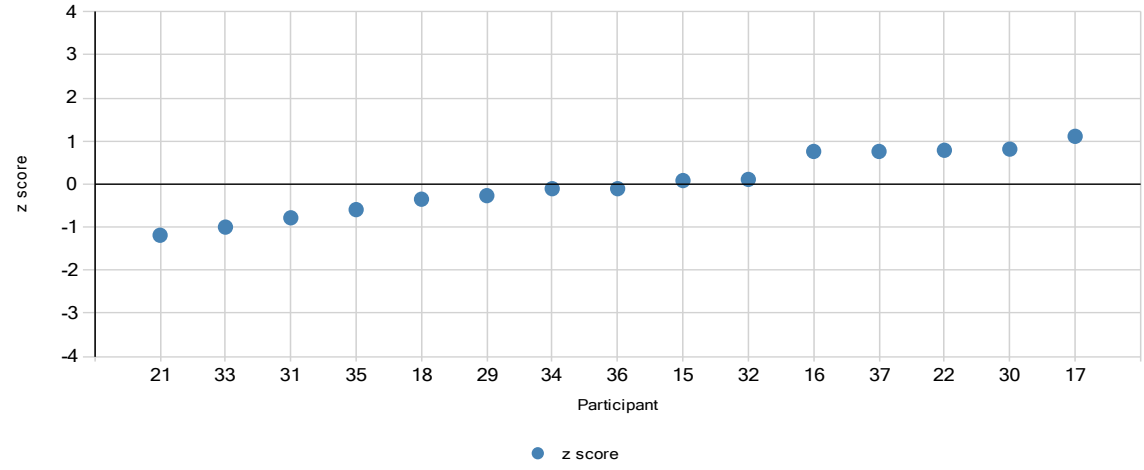

Measurand Mn Sample D2Fe
z score
4
3
2
1
0
-1
-2
-3
-4
10 12 22 32 35 33 31 1 5 37 18 30 17 21 29 15 4 25 36 24
Participant
z score


Measurand Mn Sample G3Fe
z score
4
3
2
1
0
-1
-2
-3
-4
10 22 35 32 12 33 31 21 29 1 37 30 5 18 17 15 4 36 25 24
Participant
z score

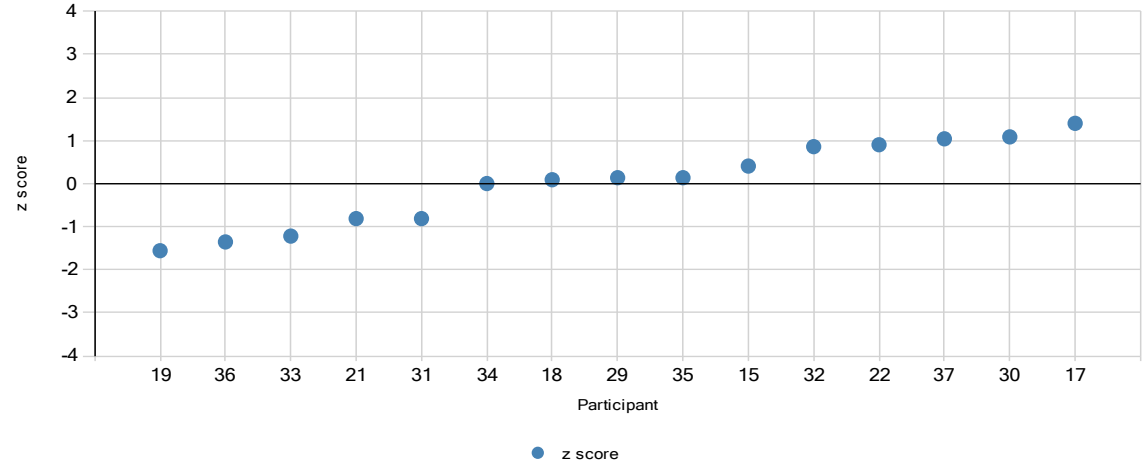
Measurand Na Sample A1K



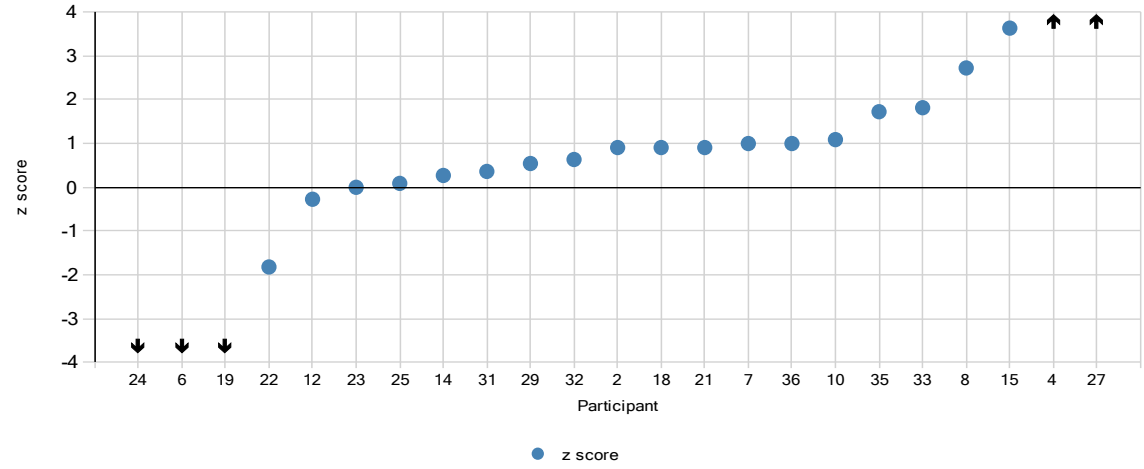
Measurand Na Sample D2K



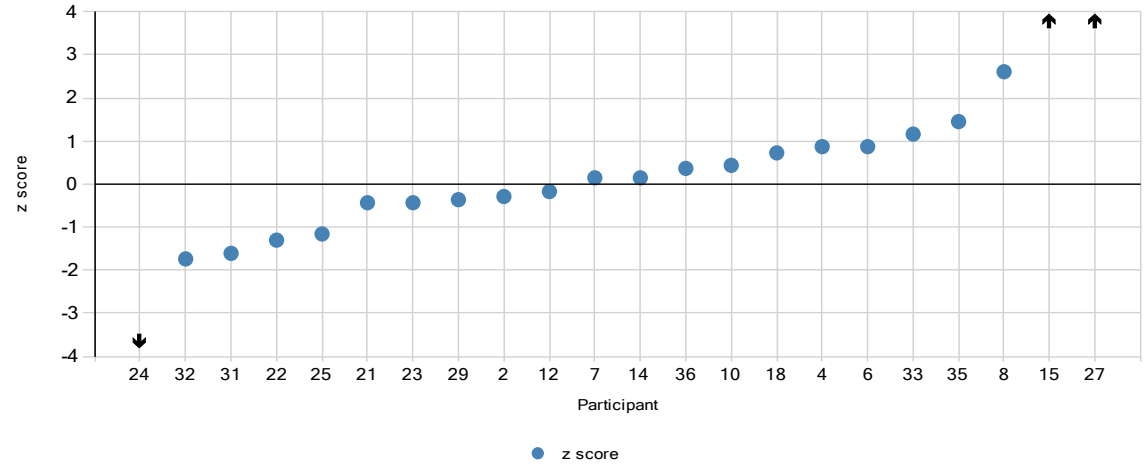
Measurand Na Sample G3K



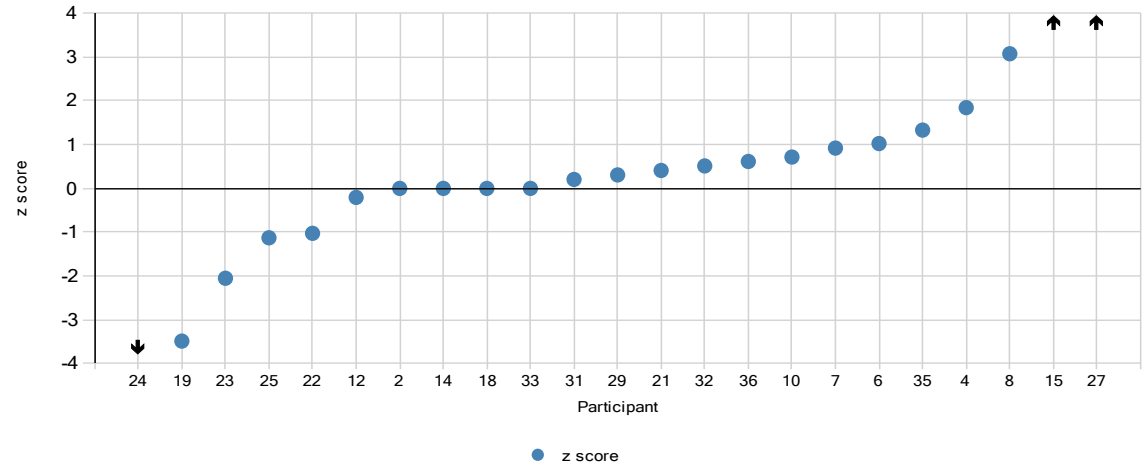
Measurand NH_4 Sample A1N



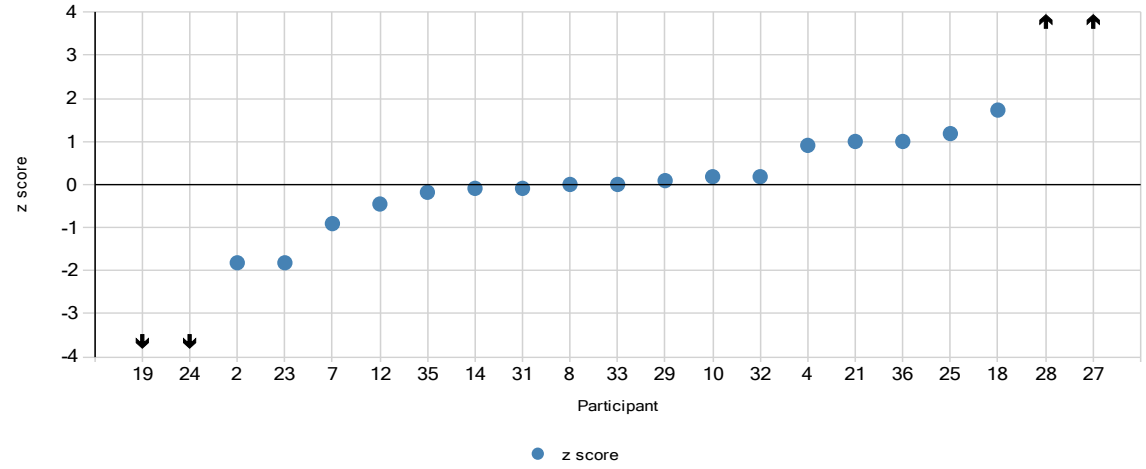
Measurand NH_4 Sample D2N



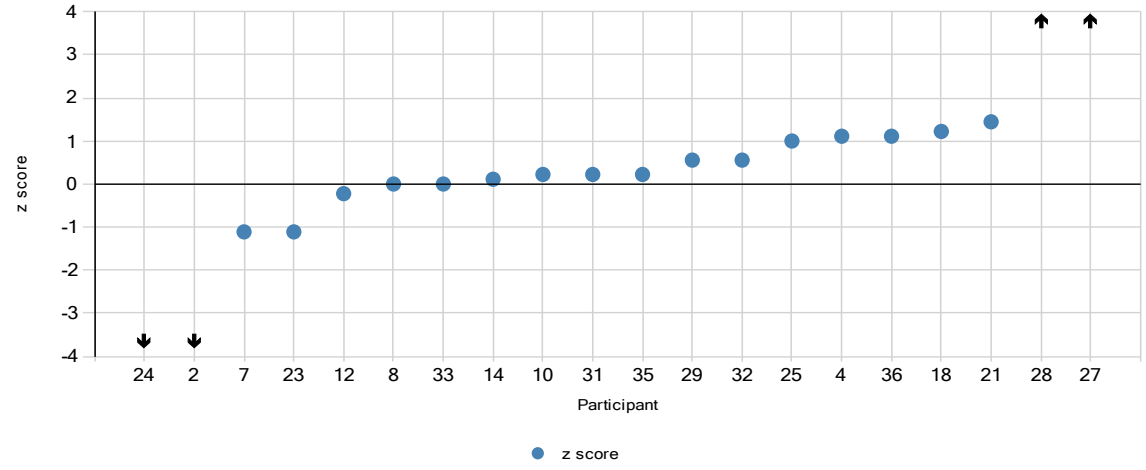
Measurand NH_4 Sample G3N



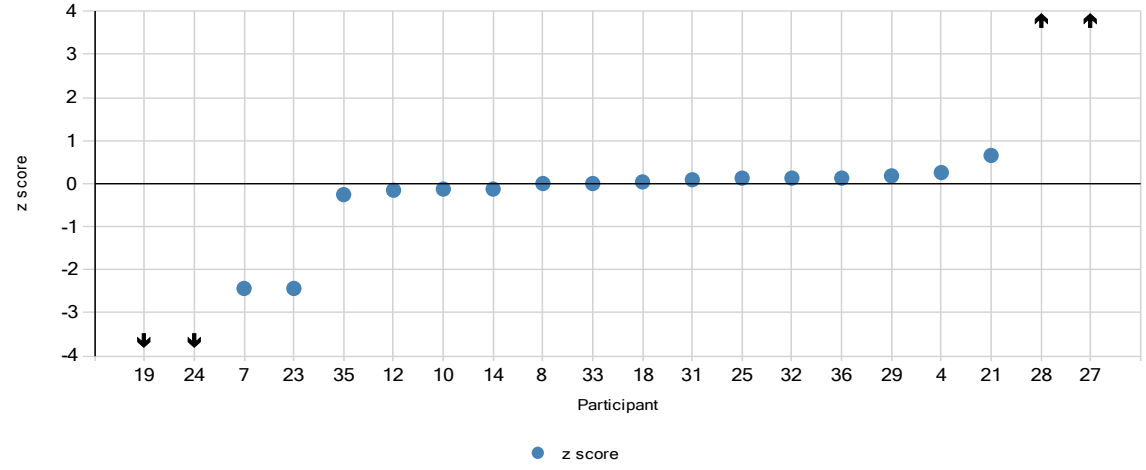
Measurand NO_2 Sample A1N

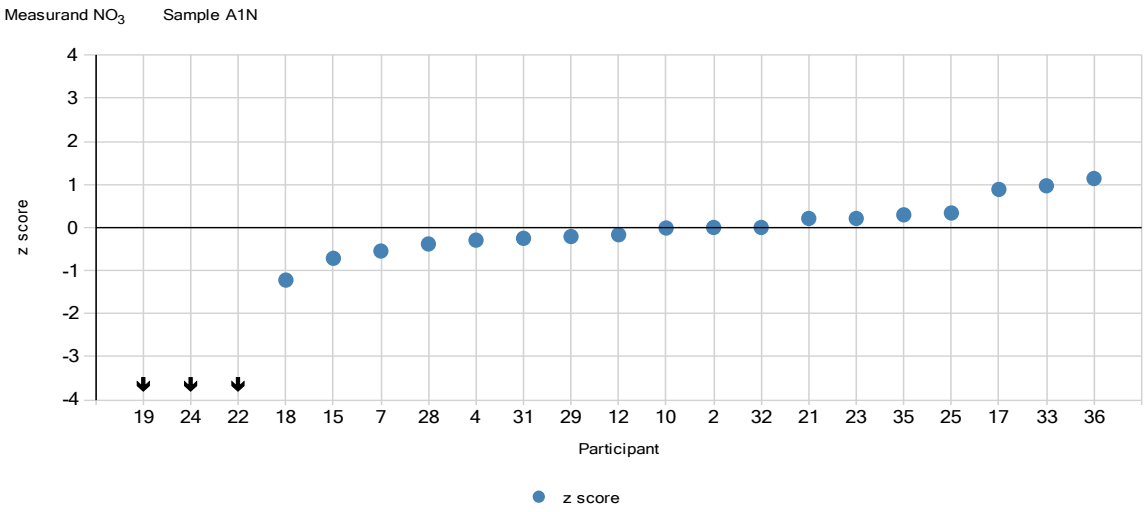


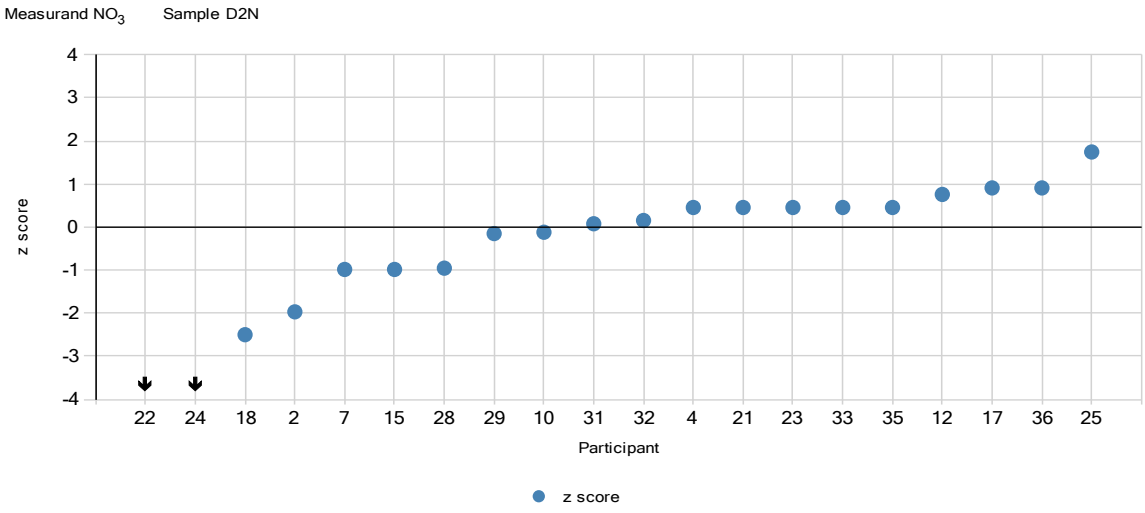
Measurand NO_2 Sample D2N

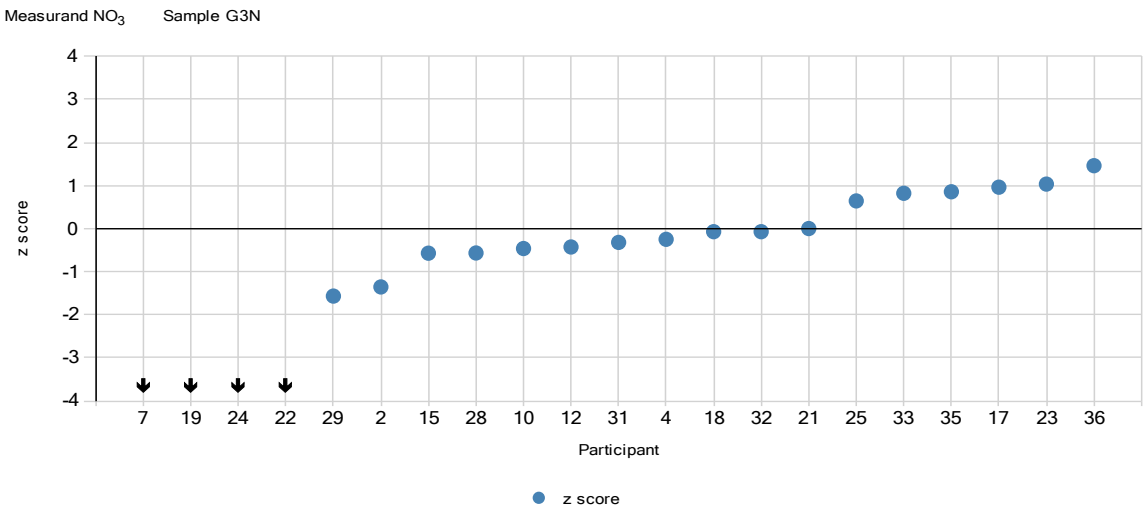


Measurand NO_2 Sample G3N

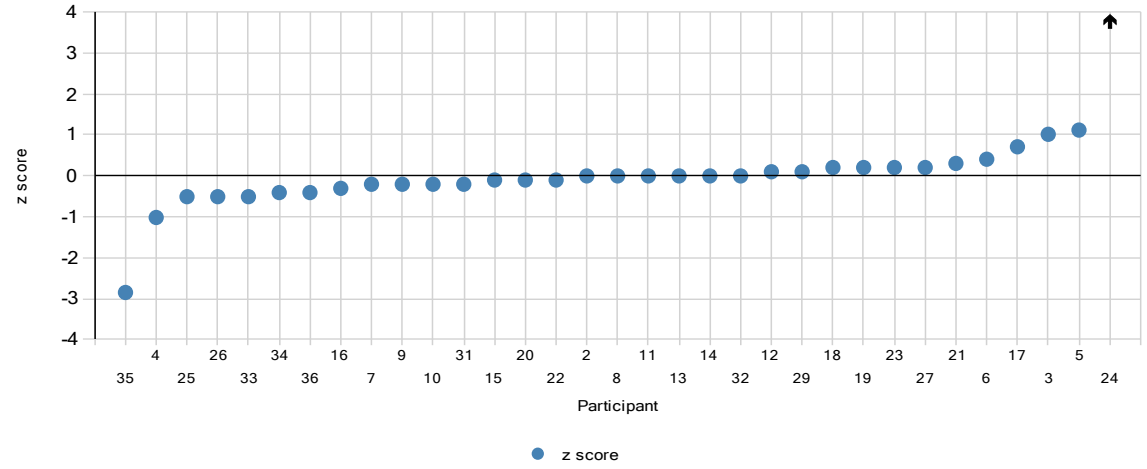



Measurand NO_3 Sample A1N
z score
4
3
2
1
0
-1
-2
-3
-4
19 24 22 18 15 7 28 4 31 29 12 10 2 32 21 23 35 25 17 33 36
Participant
z score

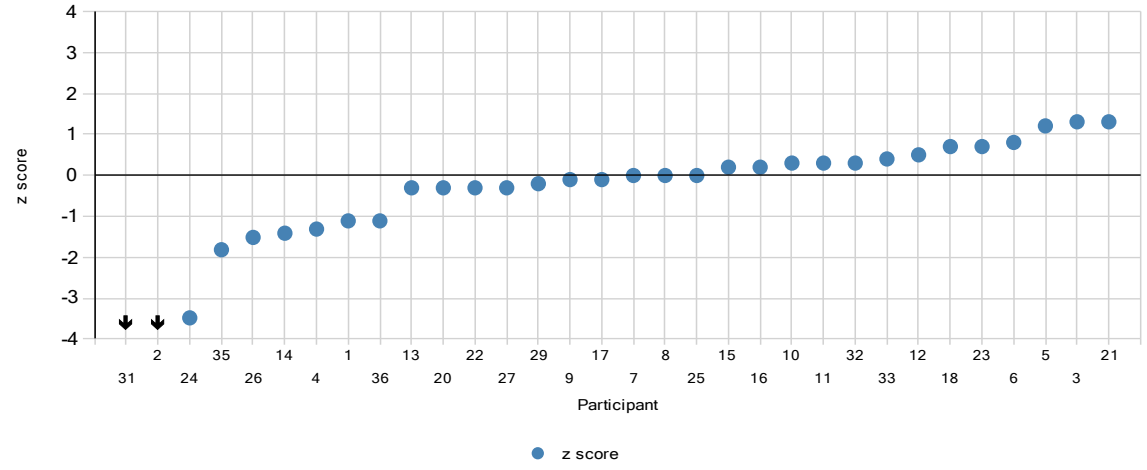

Measurand NO_3 Sample D2N
z score
4
3
2
1
0
-1
-2
-3
-4
22 24 18 2 7 15 28 29 10 31 32 4 21 23 33 35 12 17 36 25
Participant
z score


Measurand NO_3 Sample G3N
z score
4
3
2
1
0
-1
-2
-3
-4
7 19 24 22 29 2 15 28 10 12 31 4 18 32 21 25 33 35 17 23 36
Participant
z score

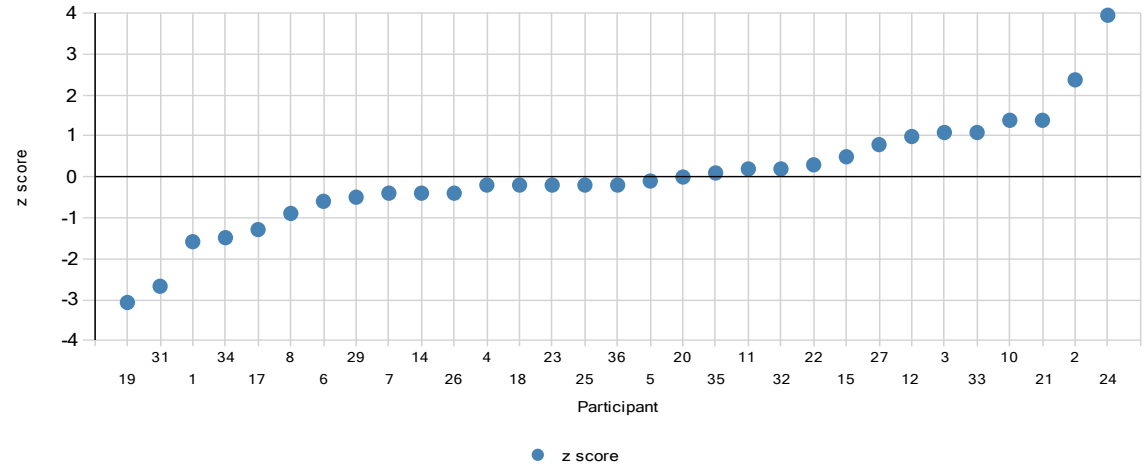
Measurand pH Sample A1P



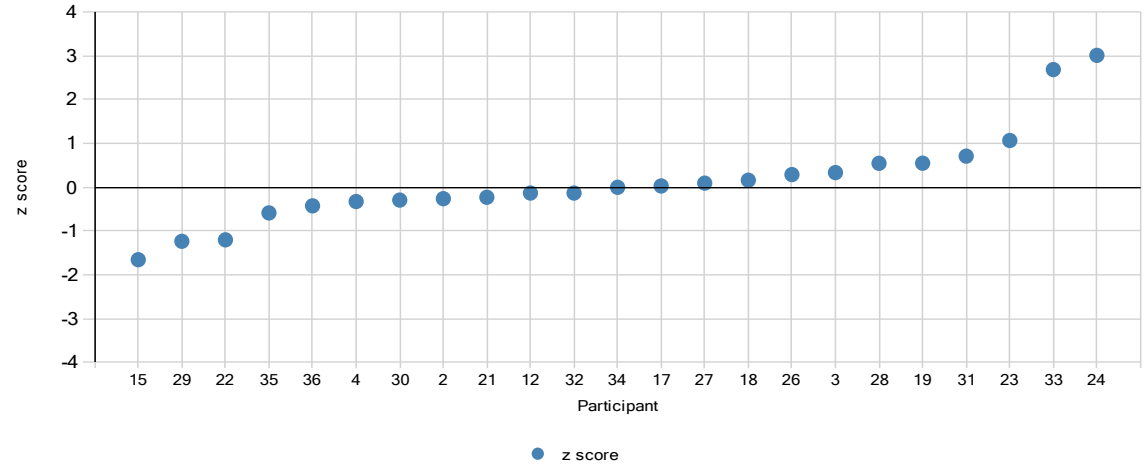
Measurand pH Sample D2PJ



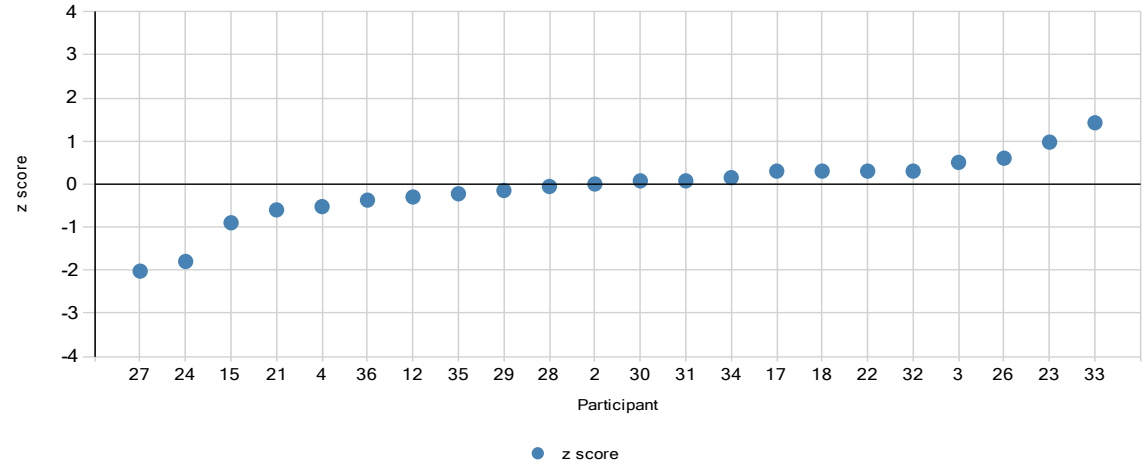
Measurand pH Sample G3PJ



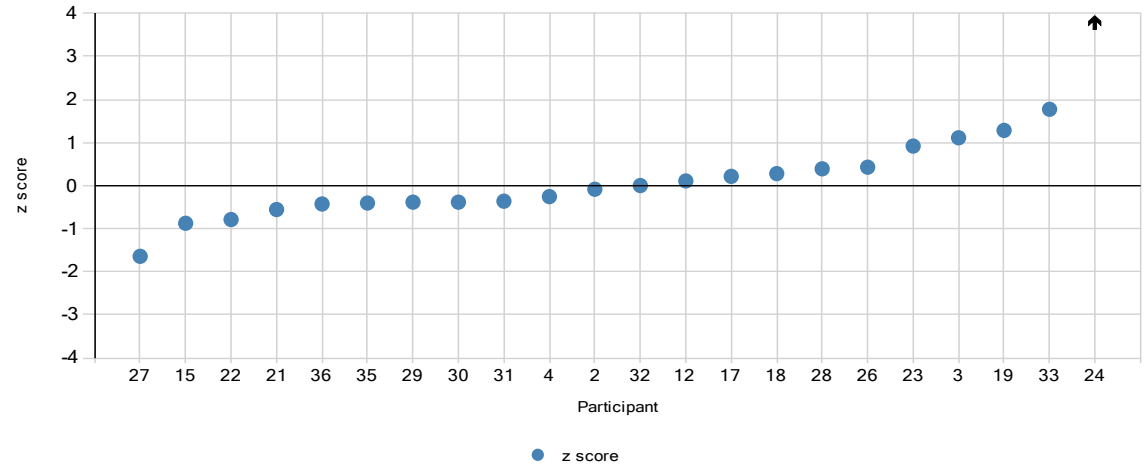
Measurand SO_4 Sample A1S



Measurand SO_4 Sample D2S

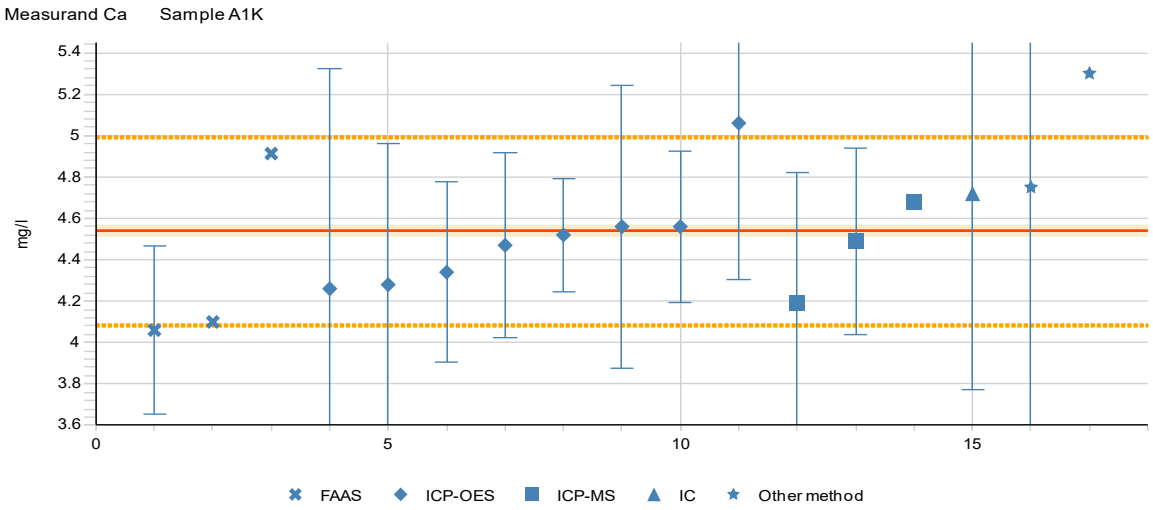


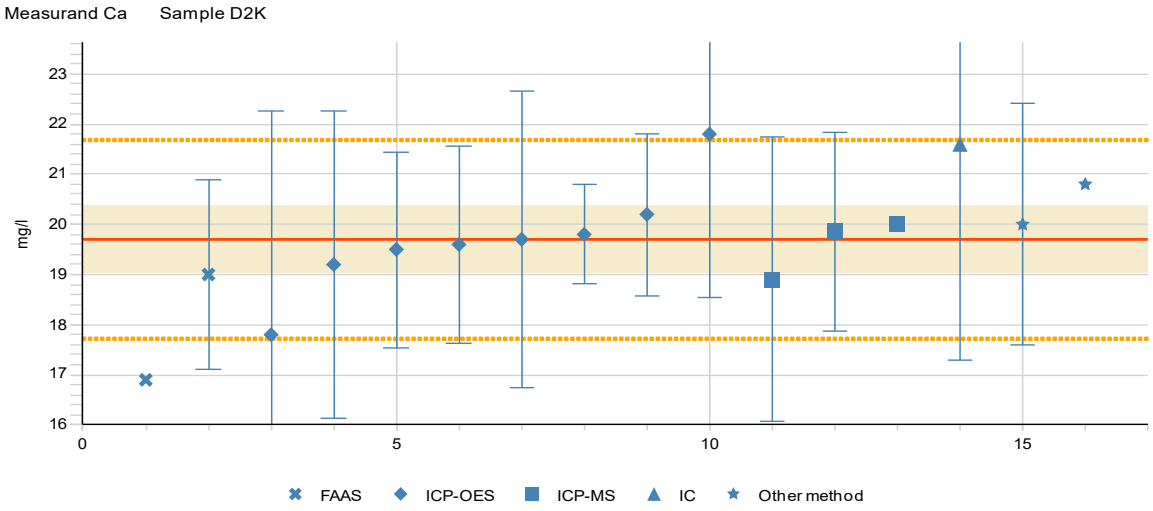
Measurand SO_4 Sample G3S



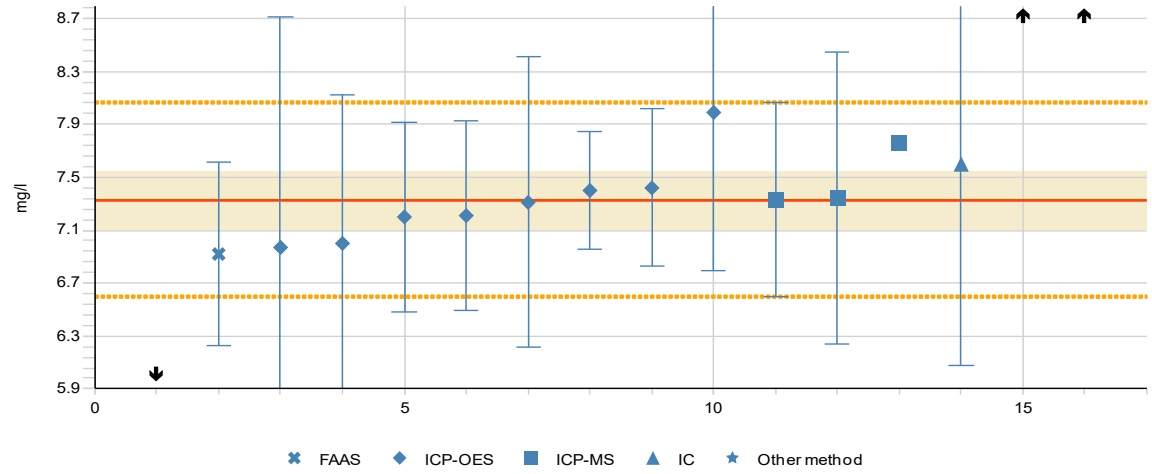
Appendix 12. Results grouped according to the methods

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

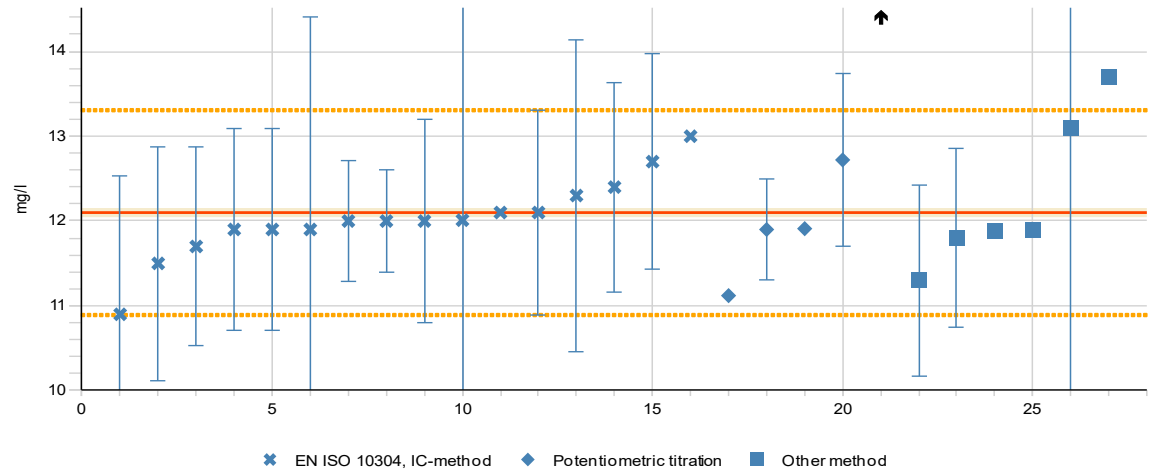




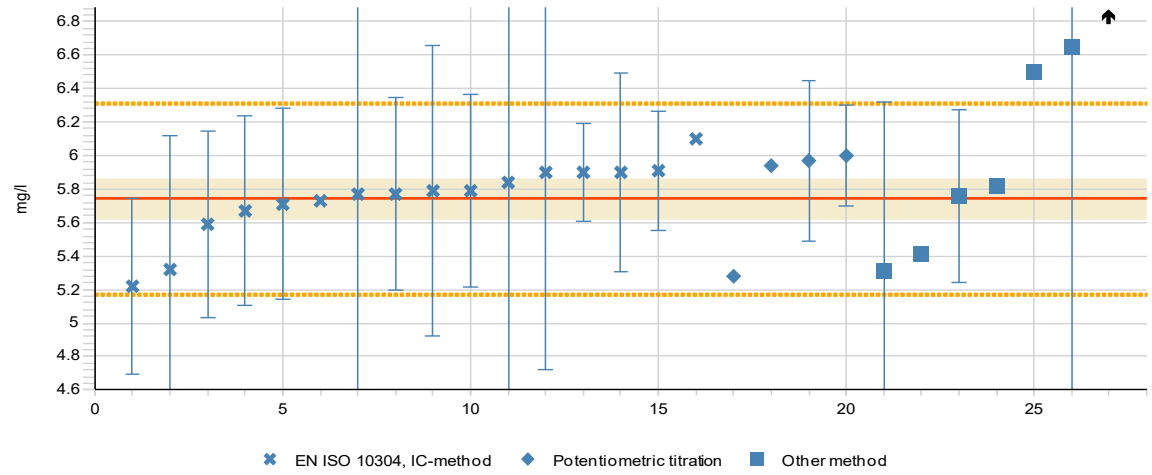
Measurand Ca Sample G3K



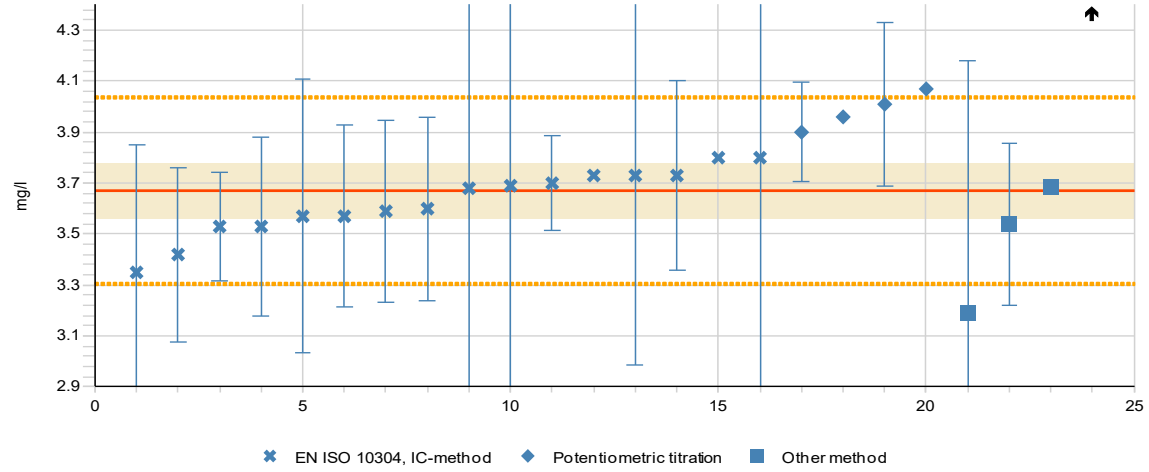
Measurand Cl Sample A1S



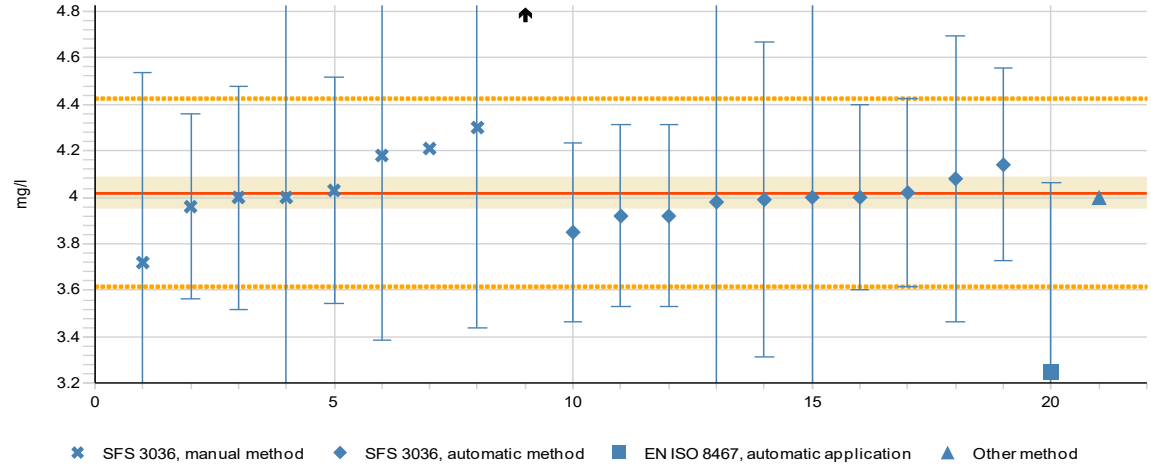
Measurand Cl Sample D2S



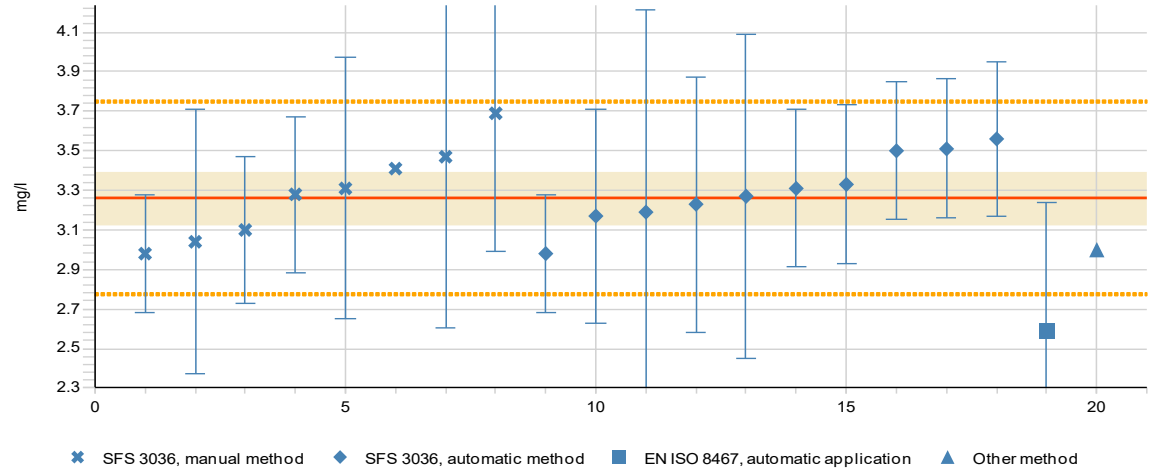
Measurand Cl Sample G3S



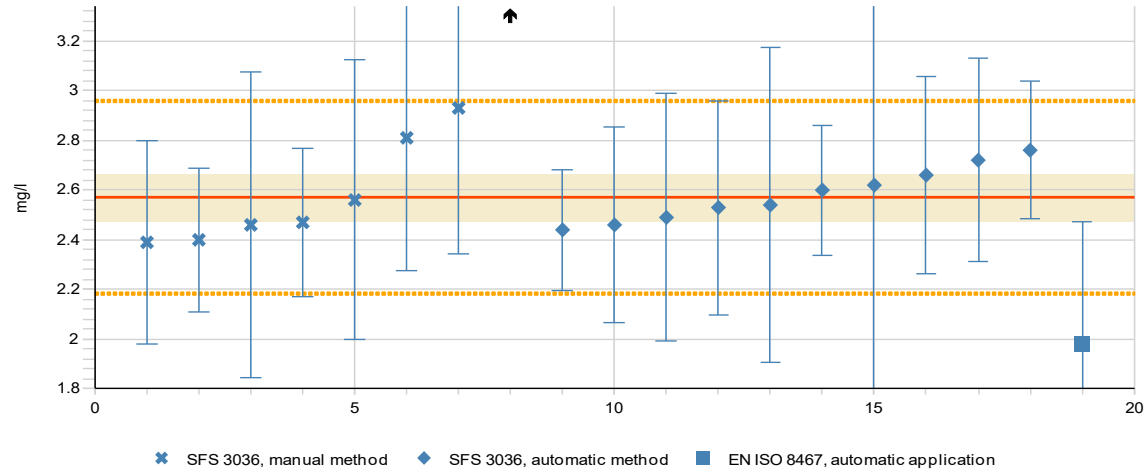
Measurand COD_{Mn} Sample A1C



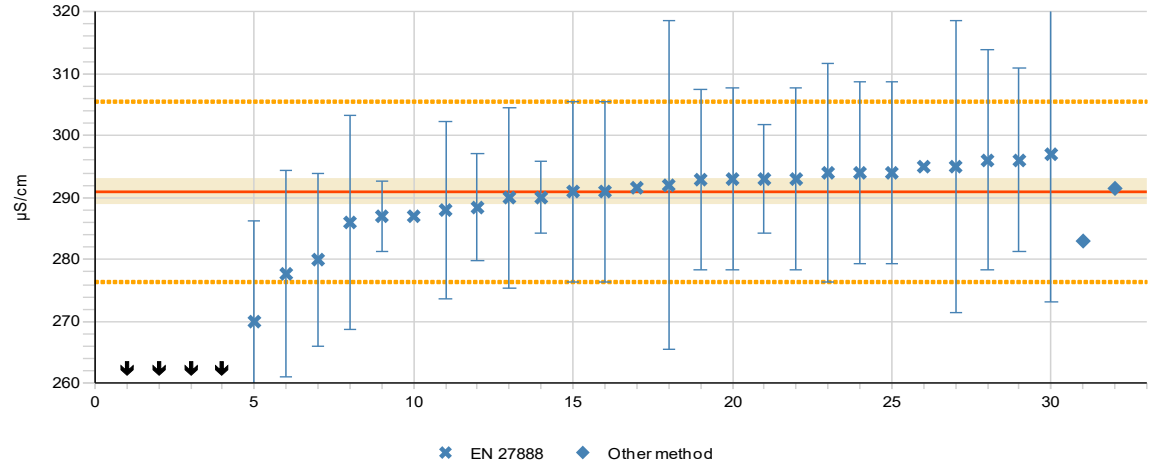
Measurand COD_{Mn} Sample D2C



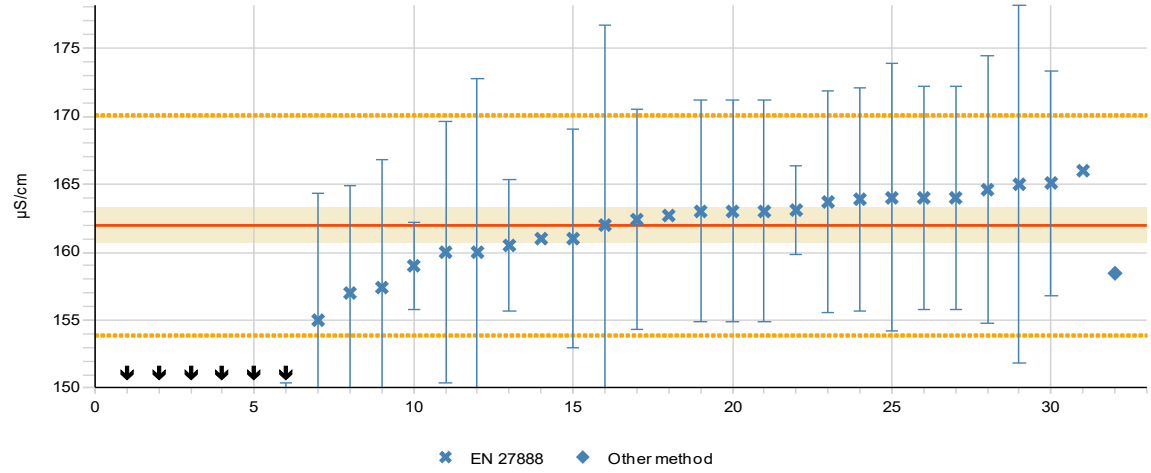
Measurand COD_{Mn} Sample G3C



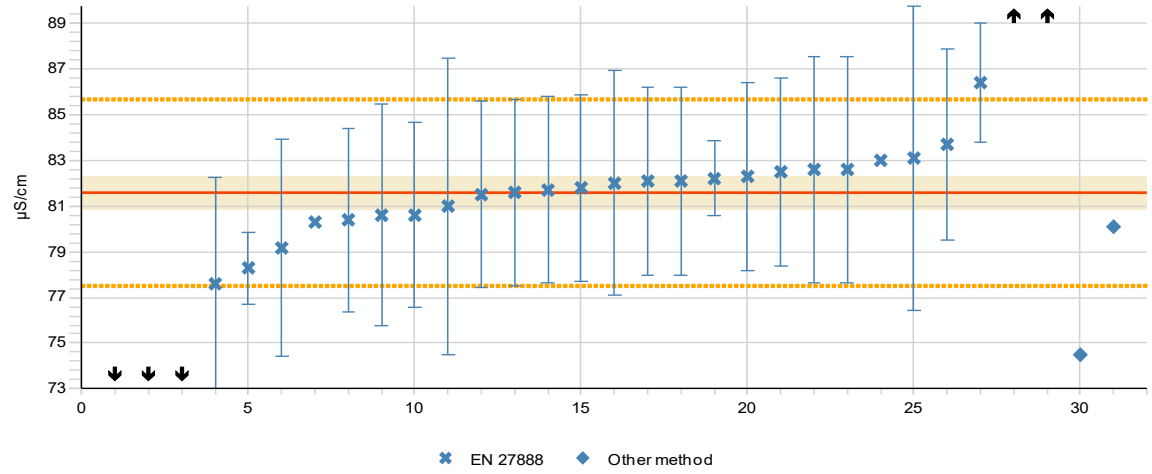
Measurand Conductivity Sample A1J



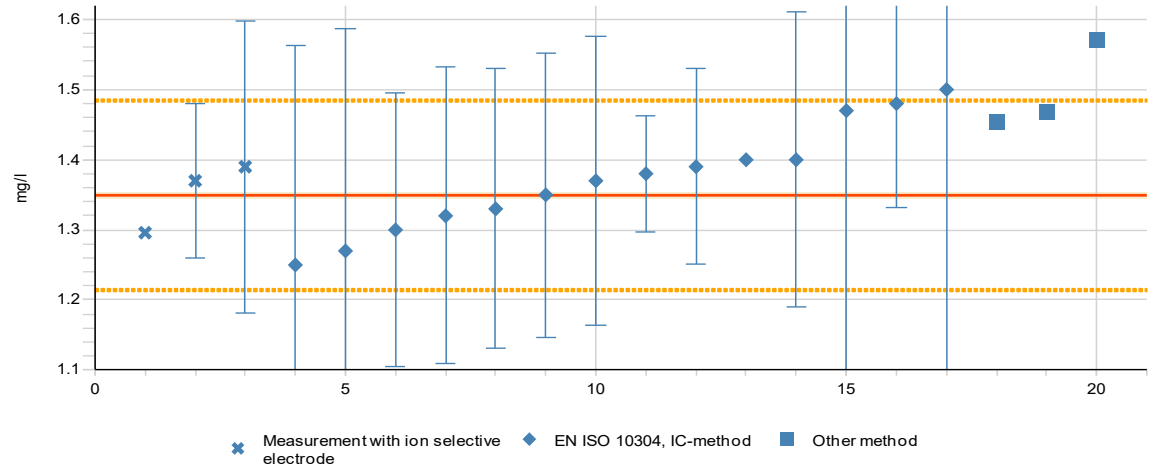
Measurand Conductivity Sample D2PJ



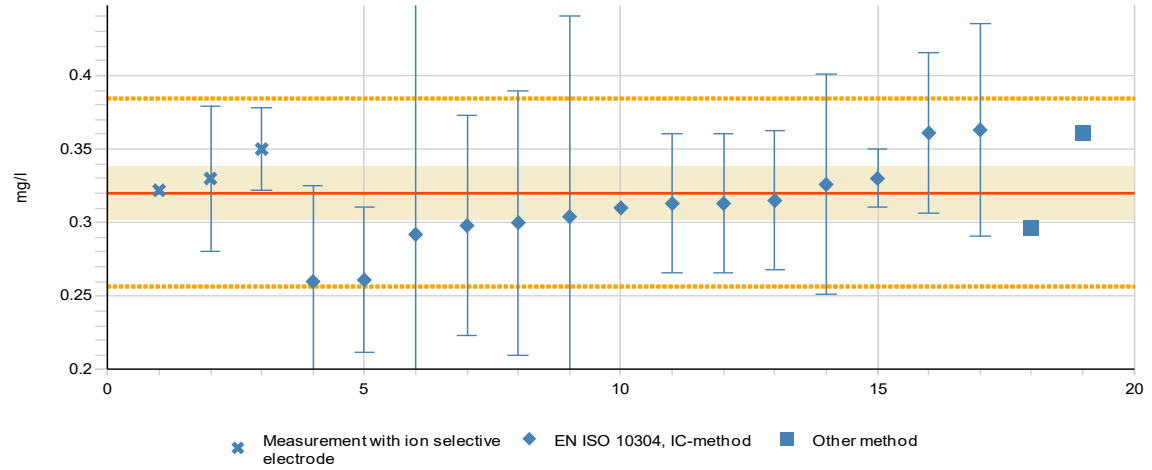
Measurand Conductivity Sample G3PJ



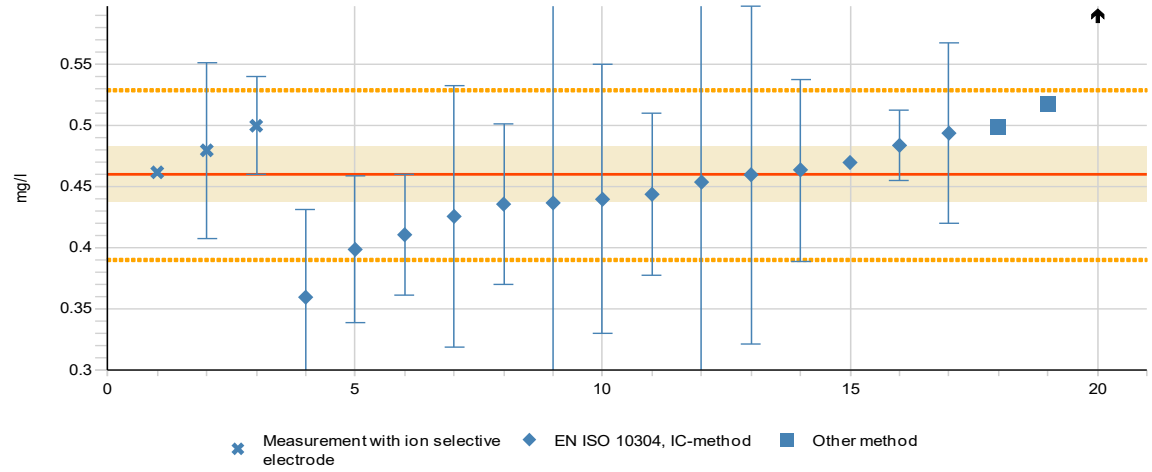
Measurand F Sample A1F



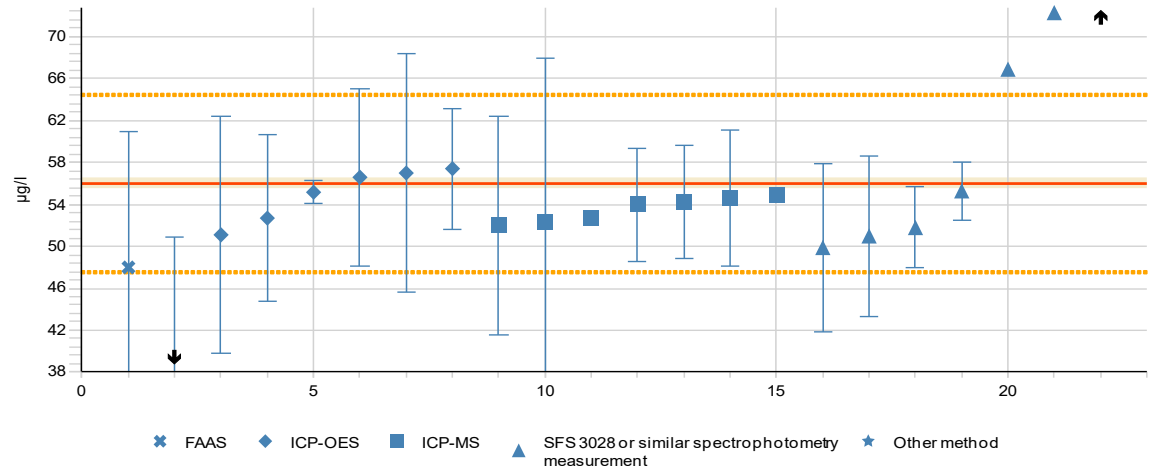
Measurand F Sample D2F



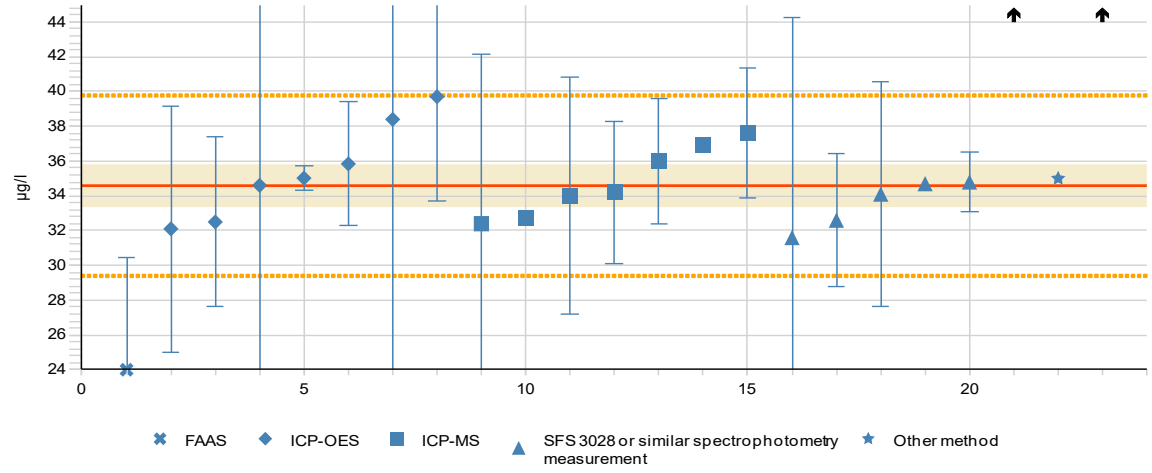
Measurand F Sample G3F



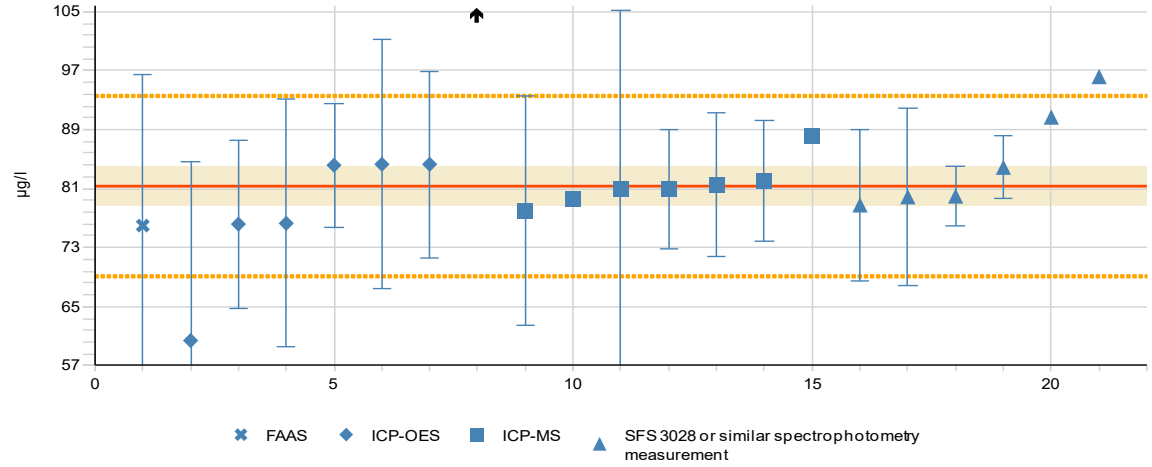
Measurand Fe Sample A1Fe



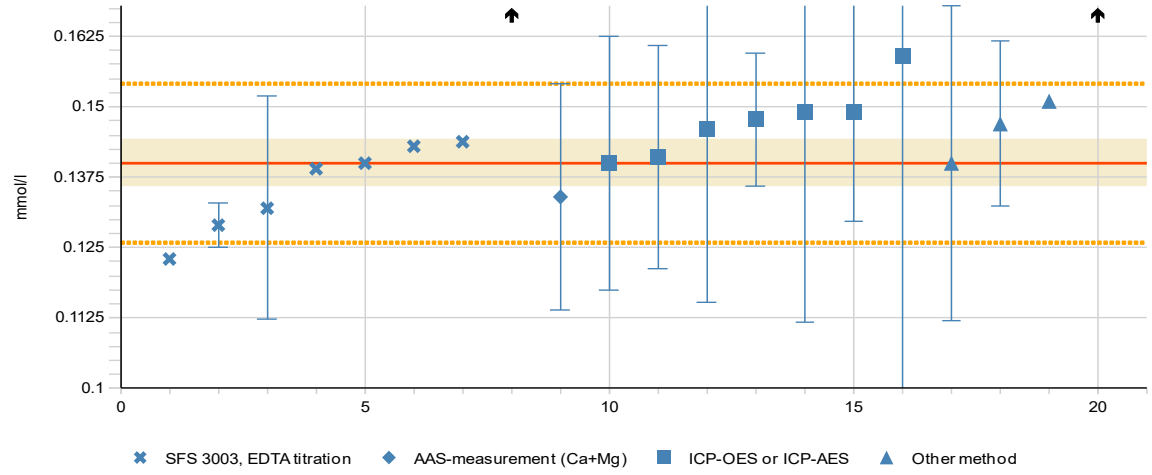
Measurand Fe Sample D2Fe



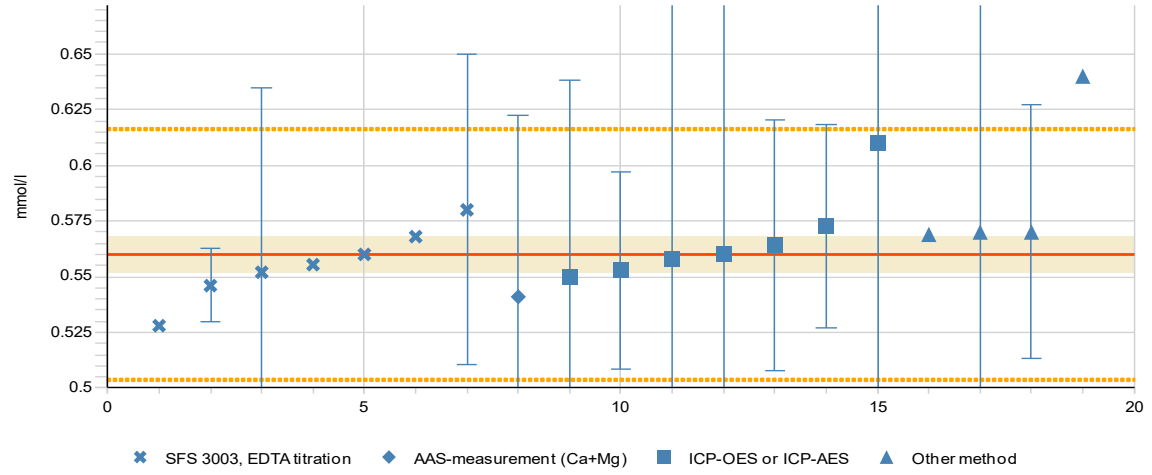
Measurand Fe Sample G3Fe



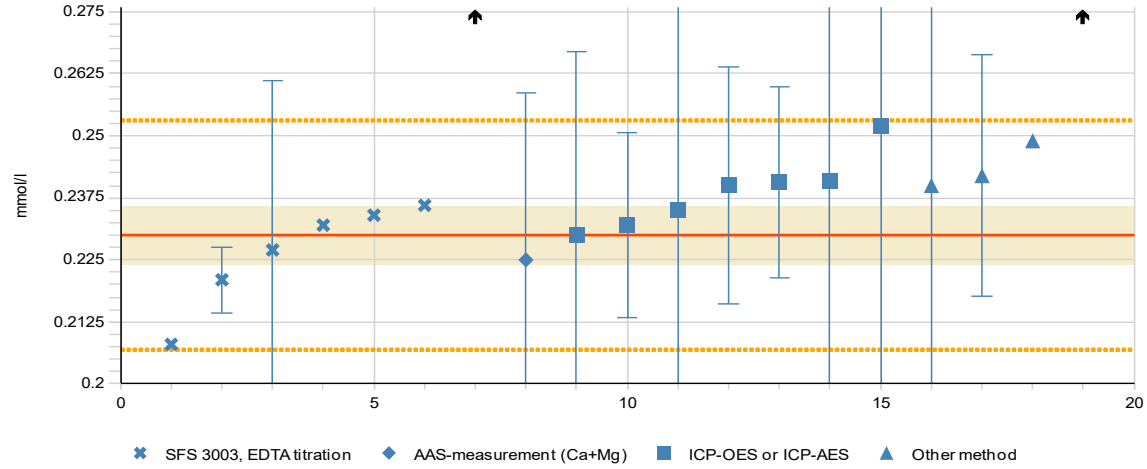
Measurand Hardness Sample A1K



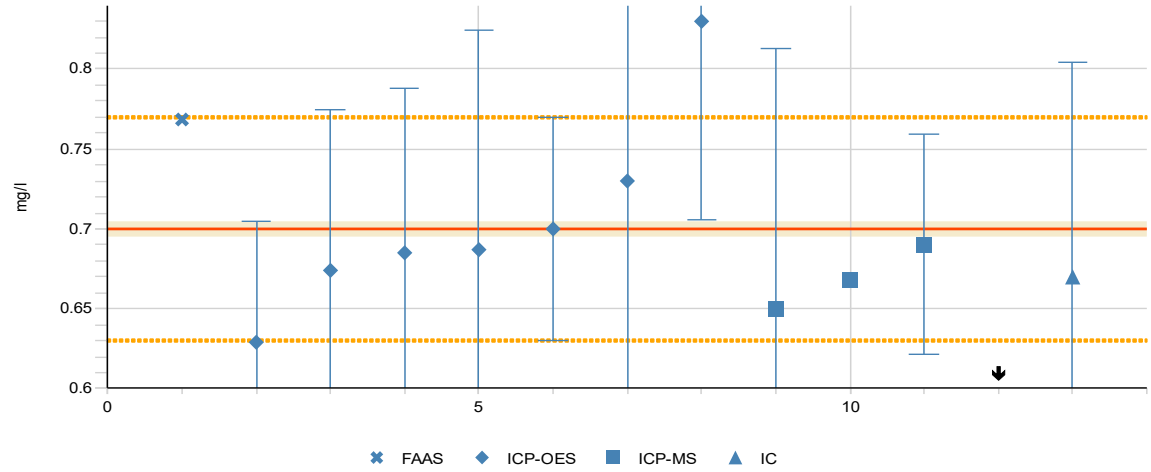
Measurand Hardness Sample D2K



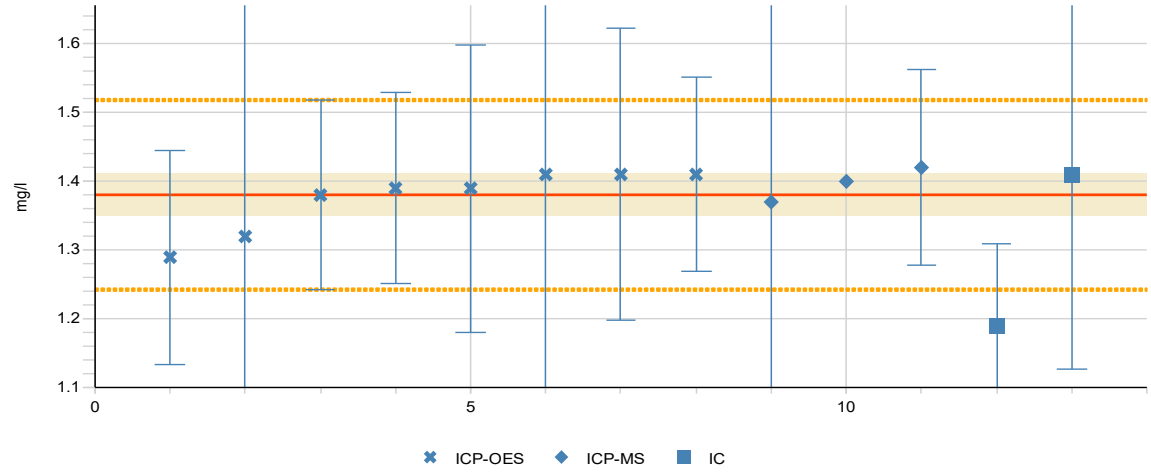
Measurand Hardness Sample G3K



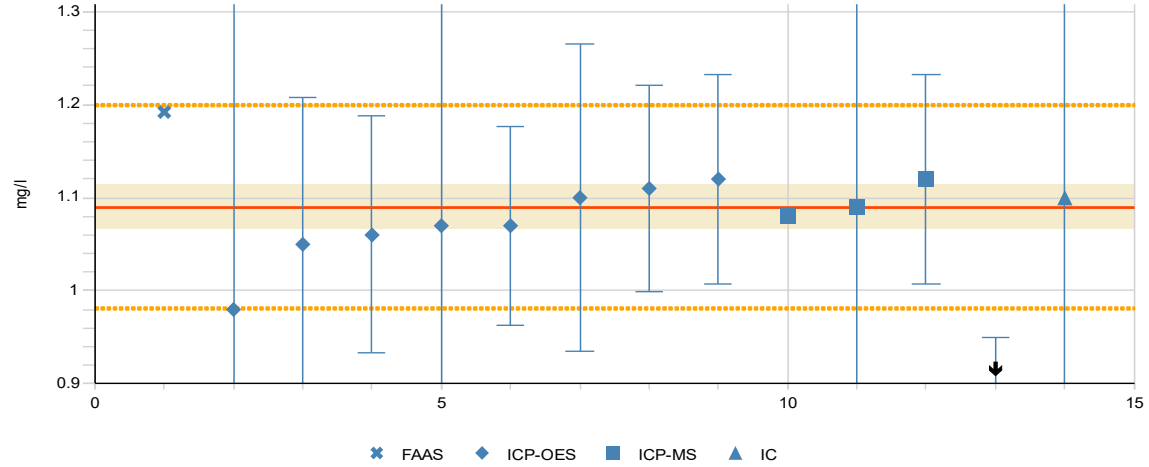
Measurand K Sample A1K



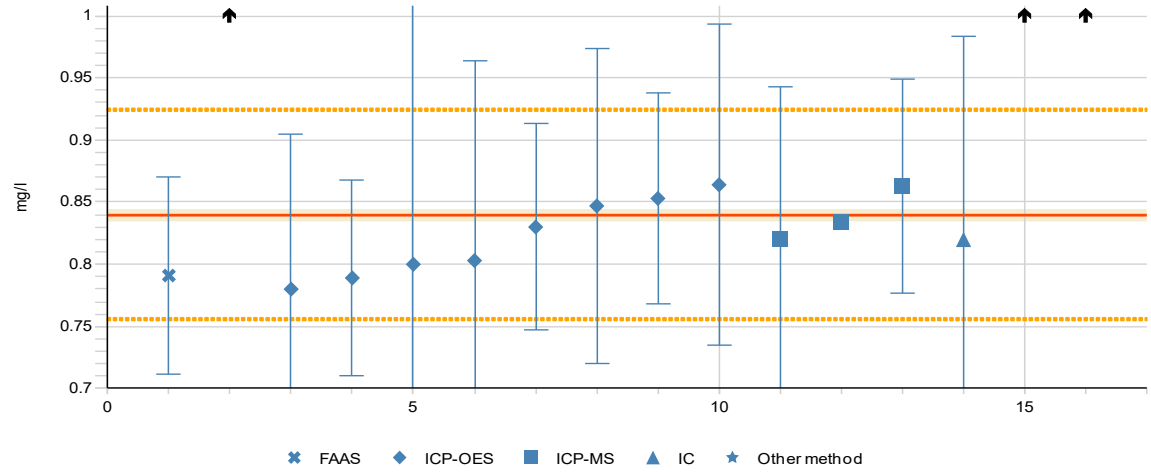
Measurand K Sample D2K



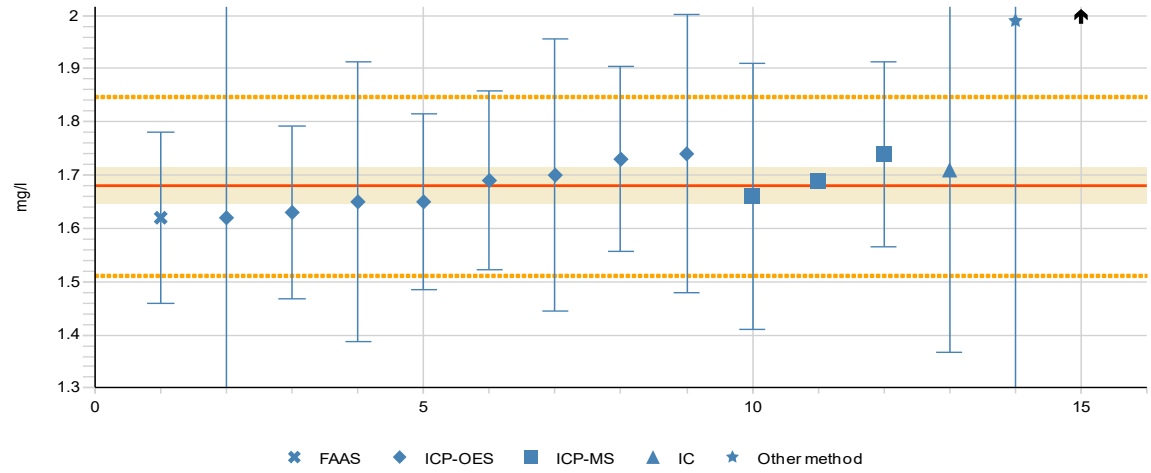
Measurand K Sample G3K



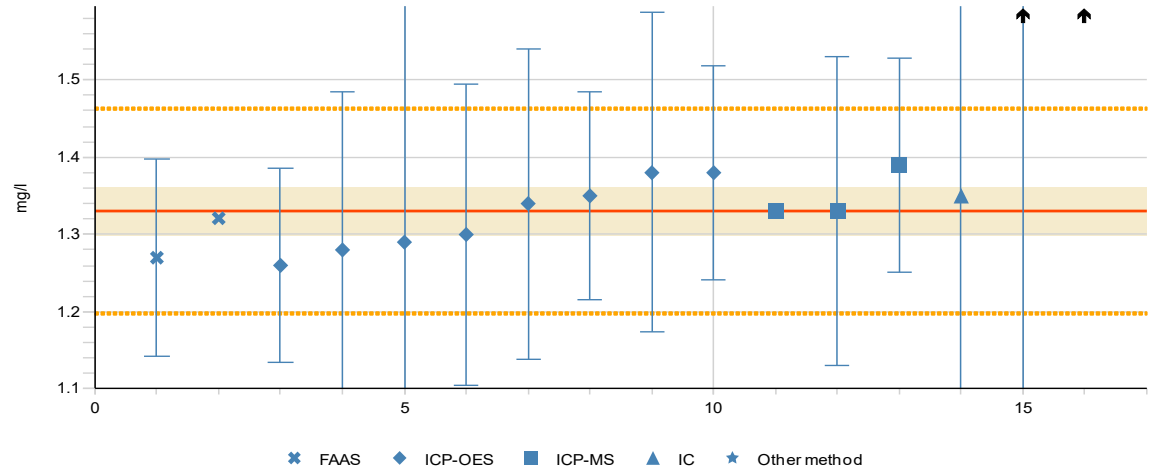
Measurand Mg Sample A1K



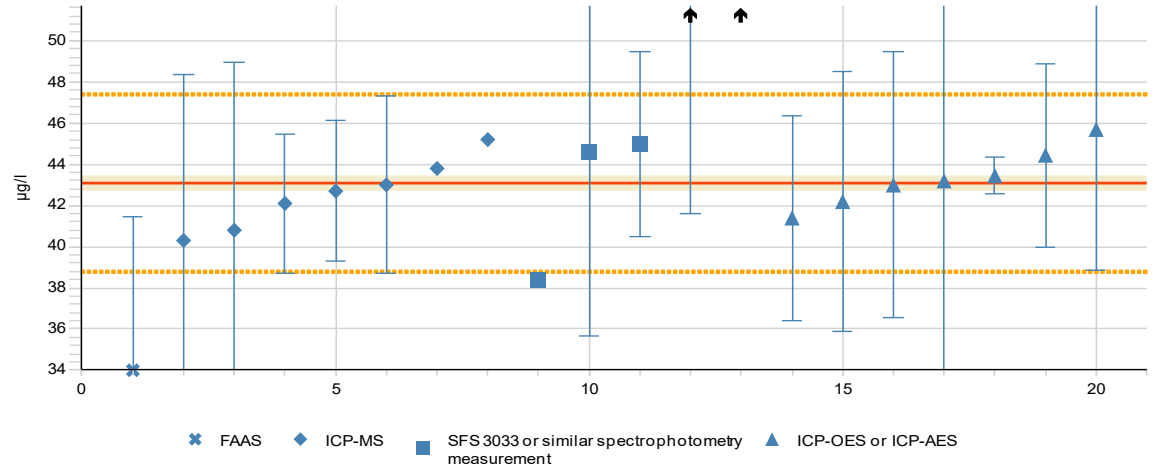
Measurand Mg Sample D2K



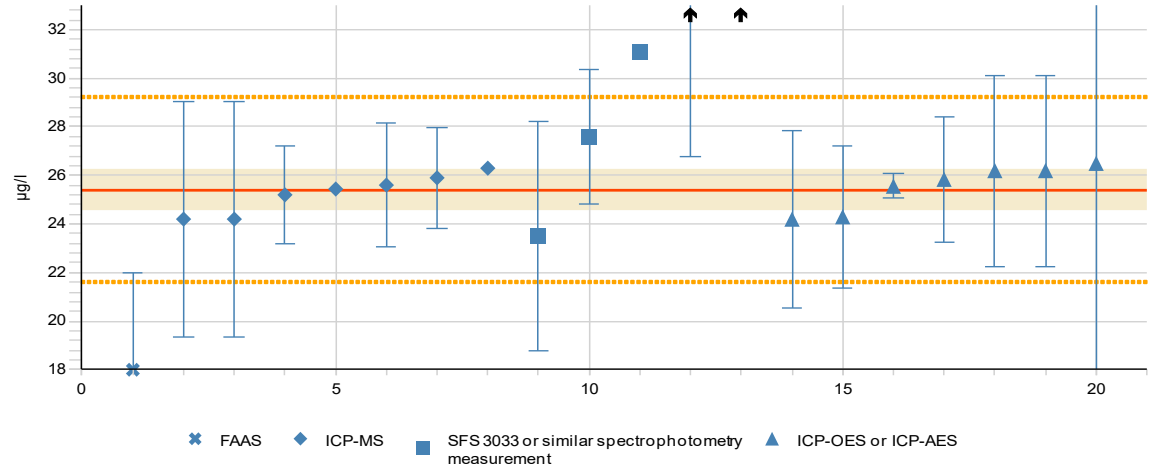
Measurand Mg Sample G3K



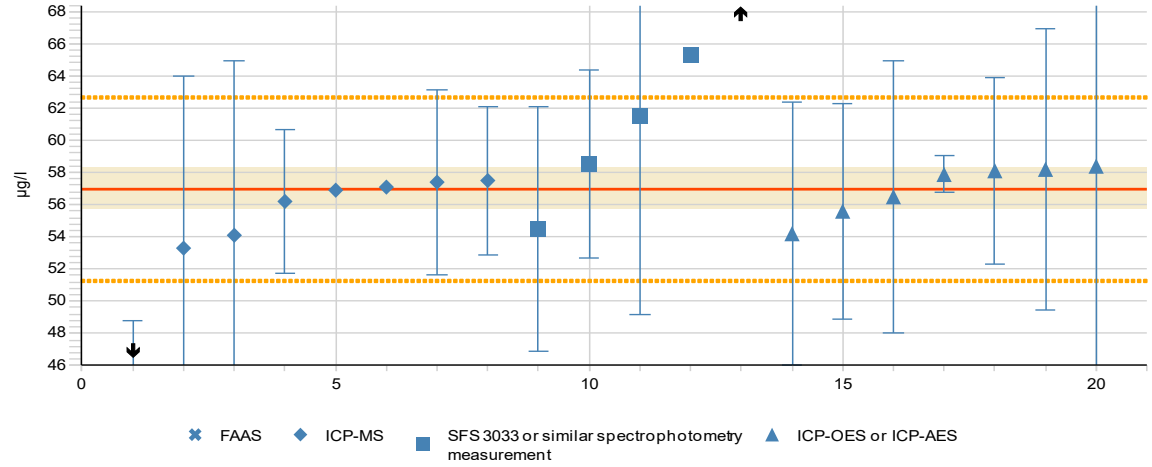
Measurand Mn Sample A1Fe



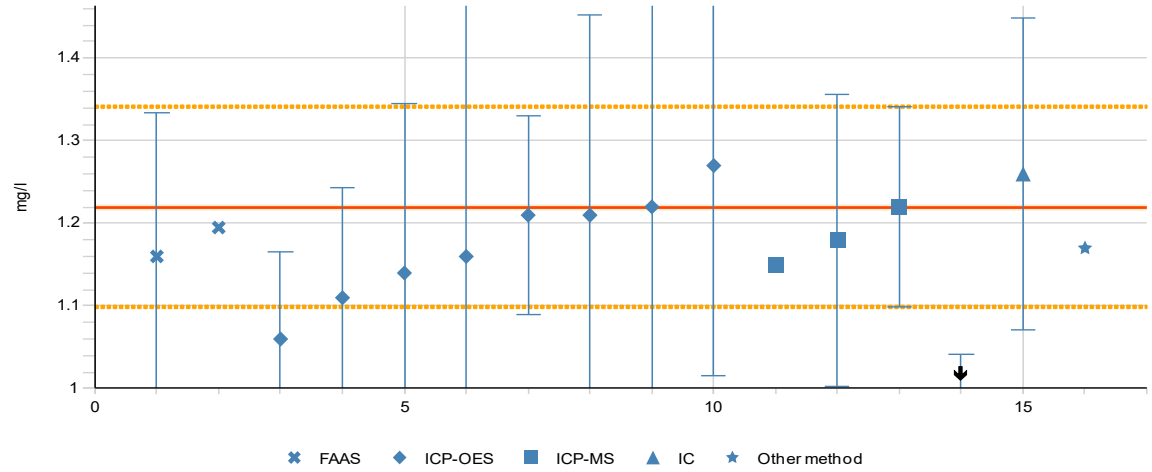
Measurand Mn Sample D2Fe



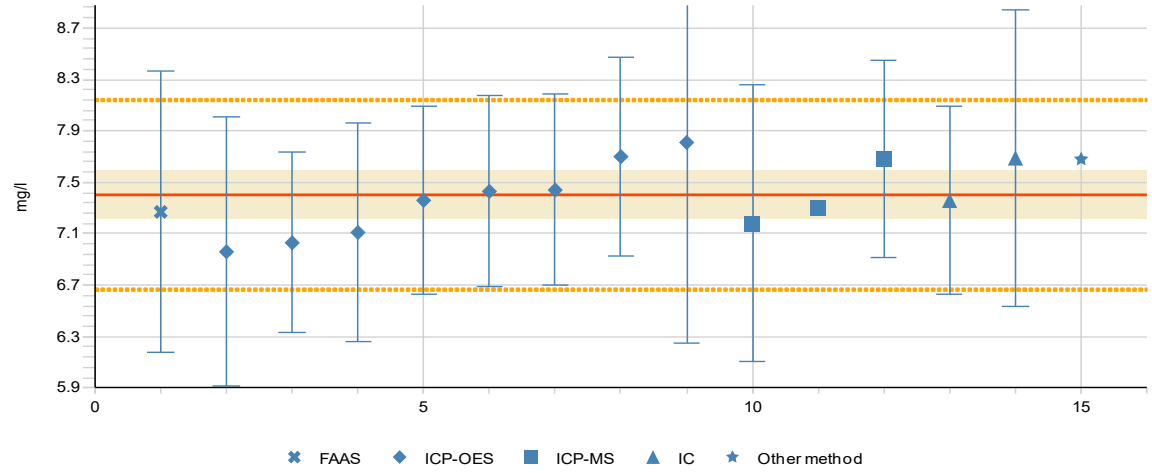
Measurand Mn Sample G3Fe



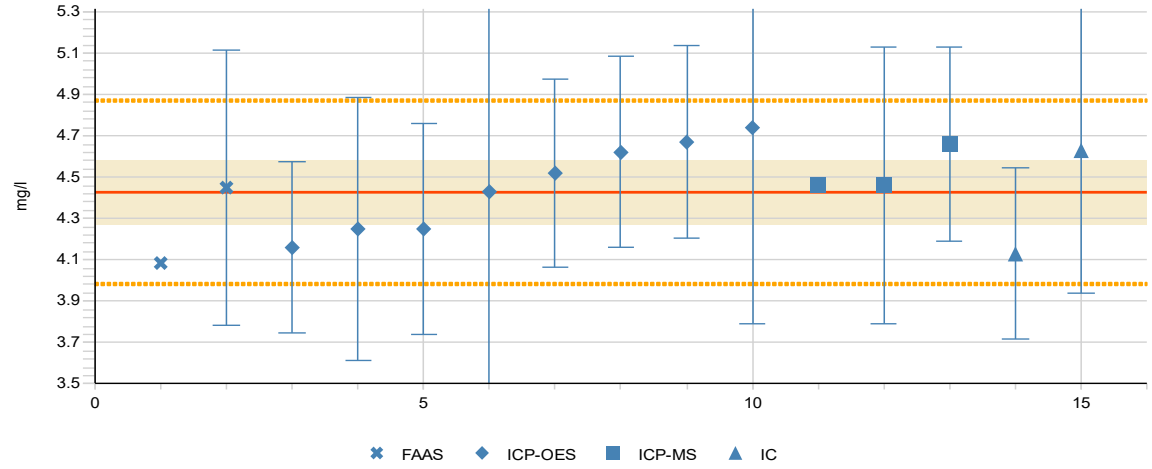
Measurand Na Sample A1K



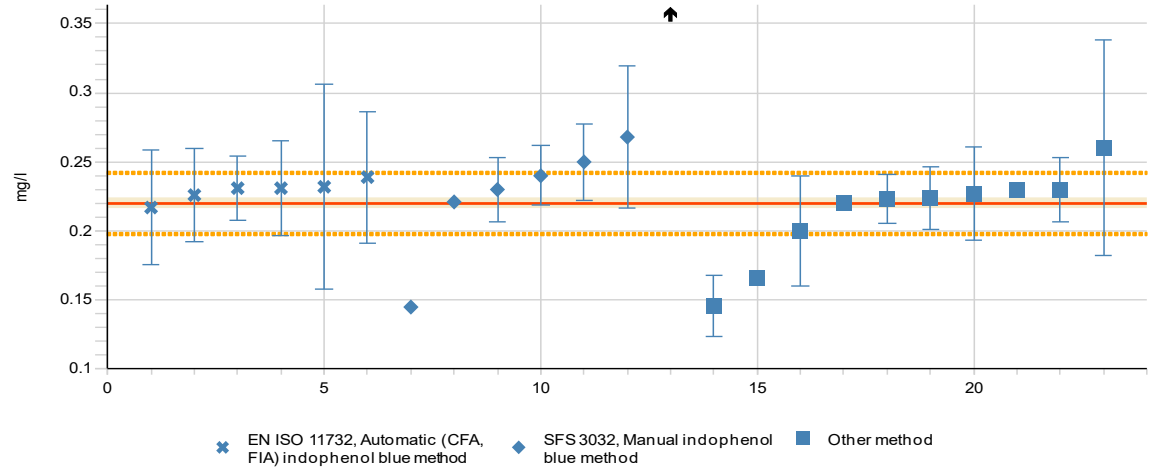
Measurand Na Sample D2K



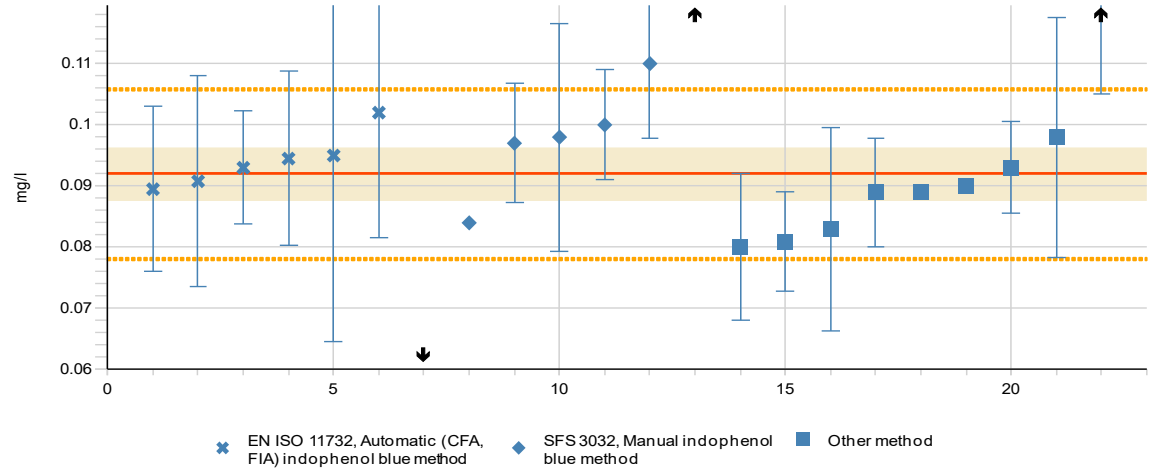
Measurand Na Sample G3K



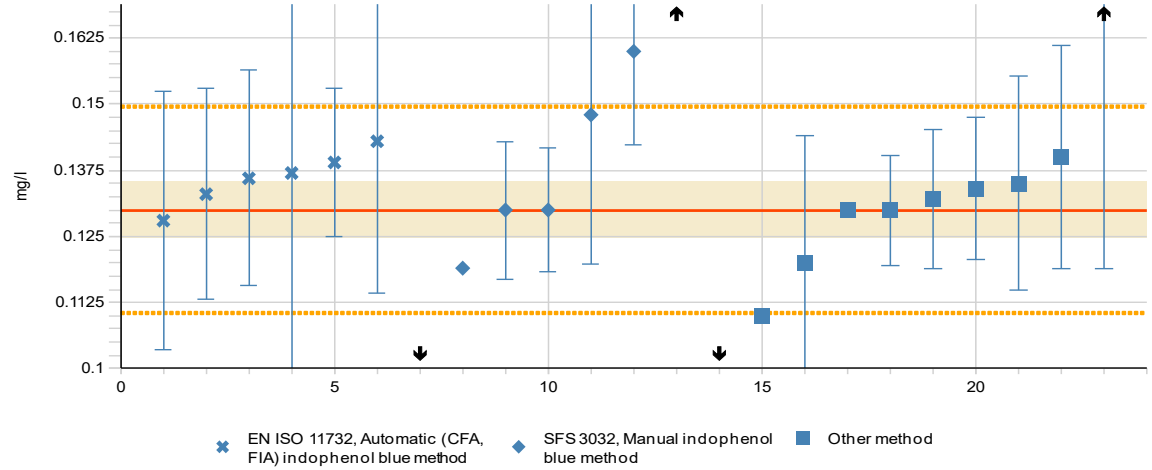
Measurand NH_4 Sample A1N



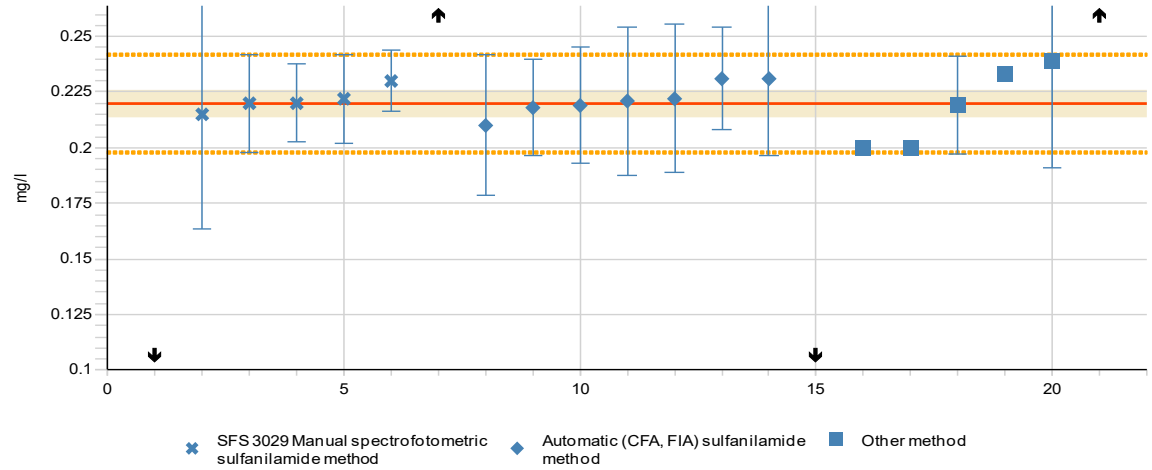
Measurand NH_4 Sample D2N



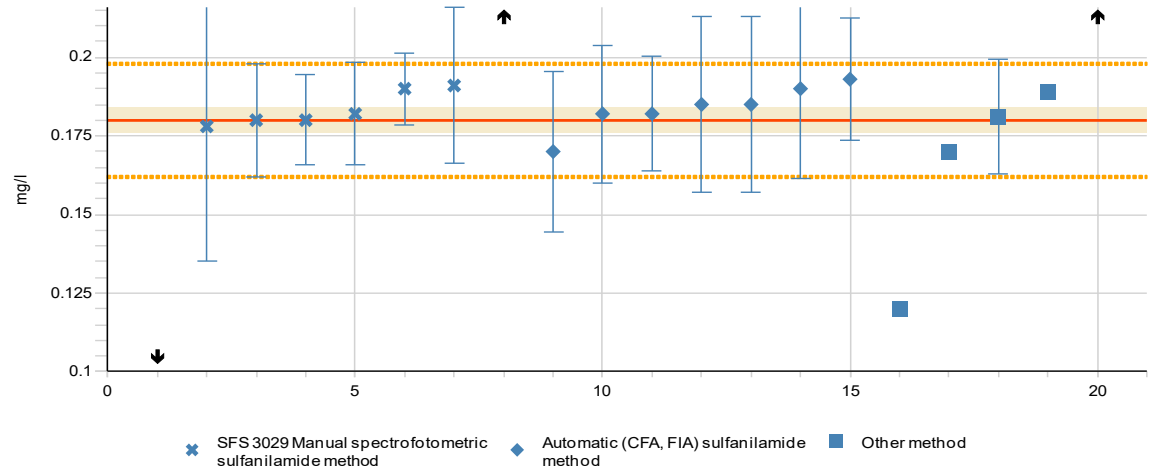
Measurand NH_4 Sample G3N



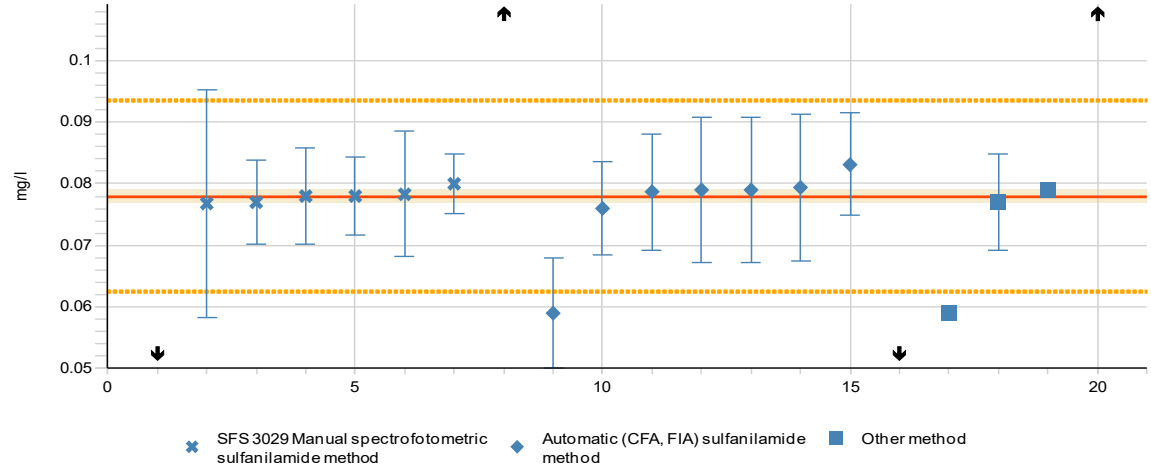
Measurand NO_2 Sample A1N



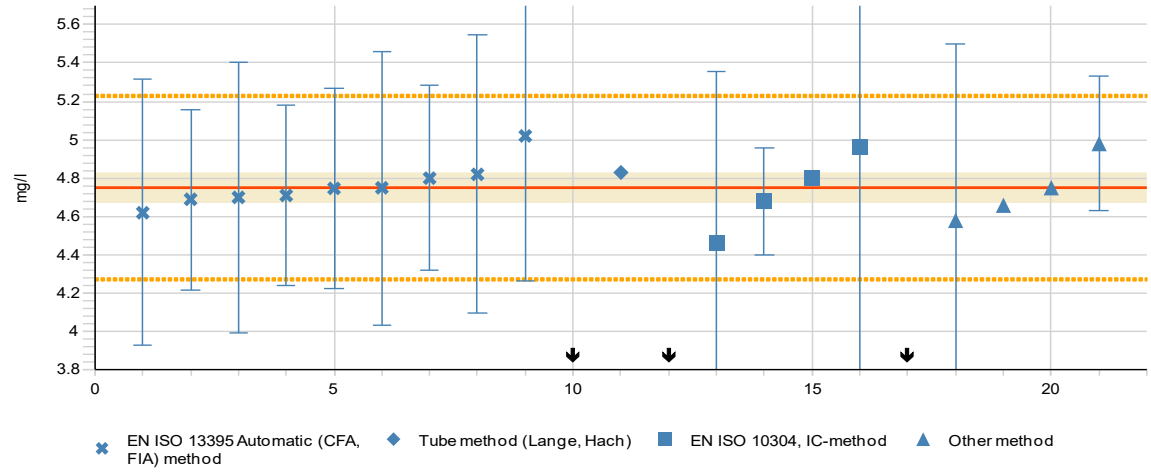
Measurand NO_2 Sample D2N



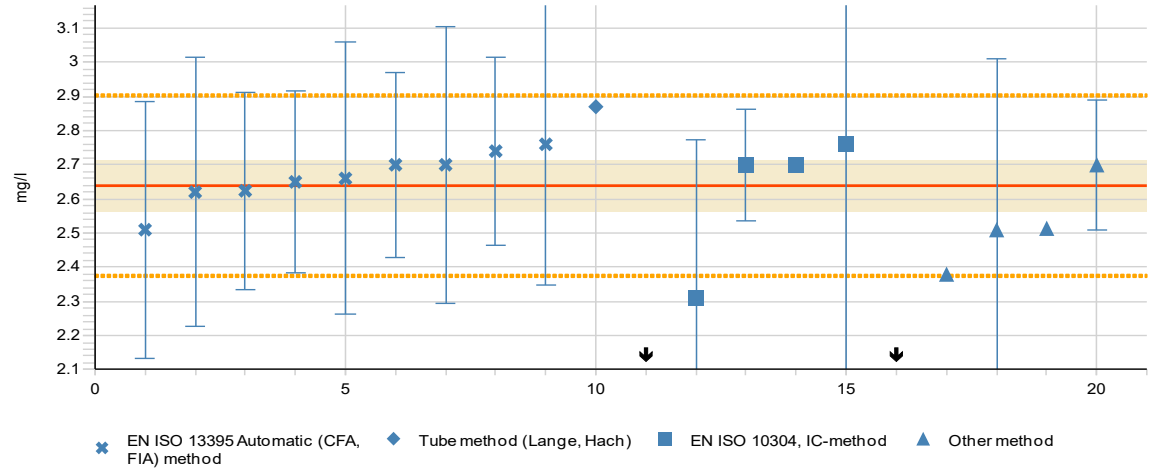
Measurand NO_2 Sample G3N



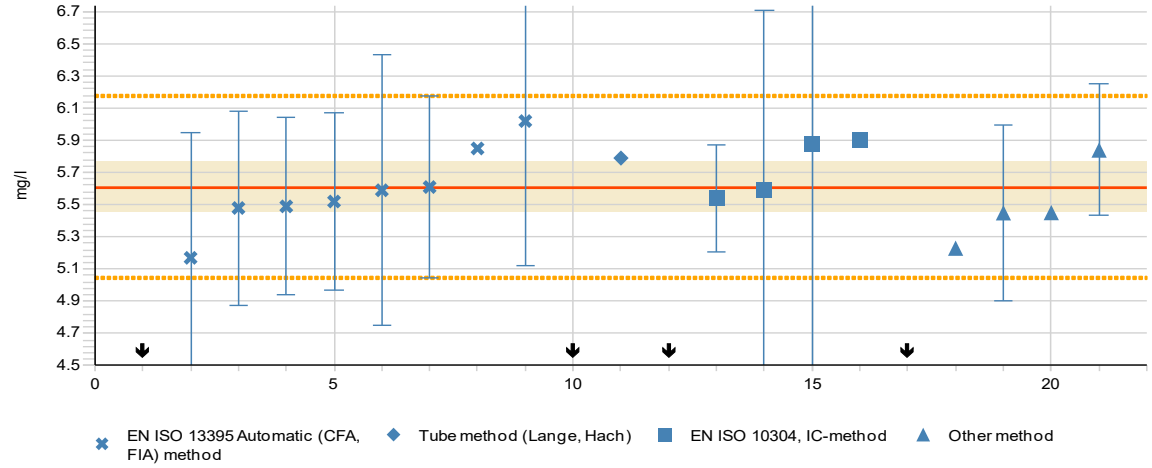
Measurand NO_3 Sample A1N



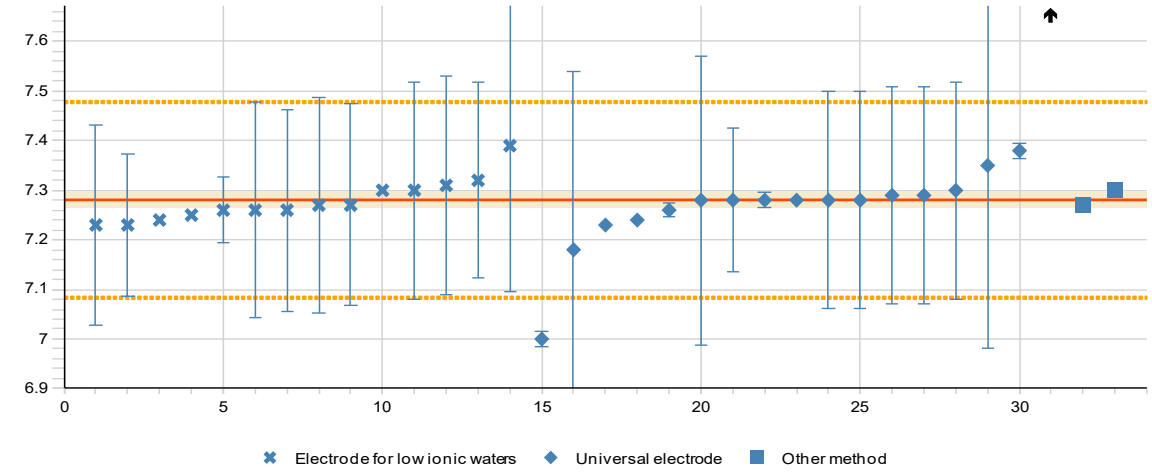
Measurand NO_3 Sample D2N



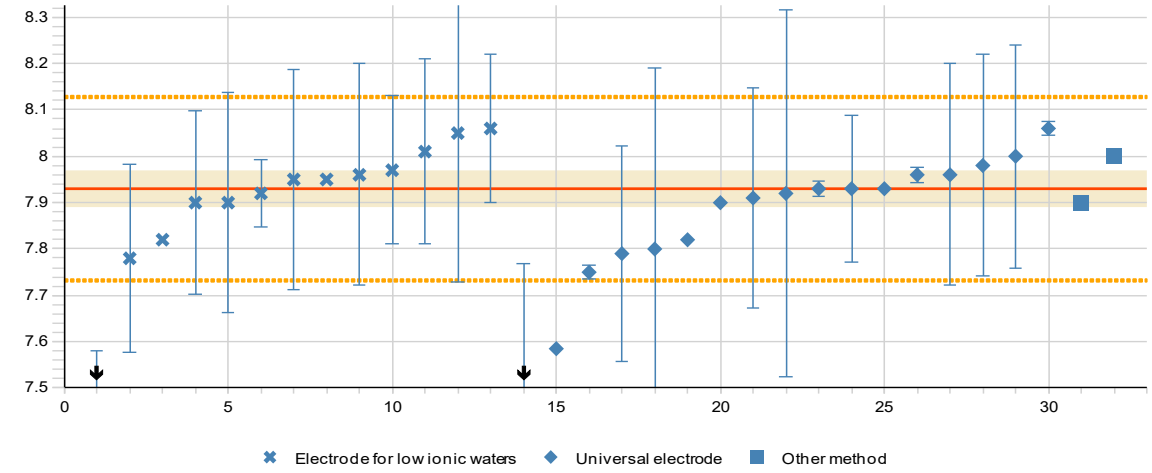
Measurand NO_3 Sample G3N



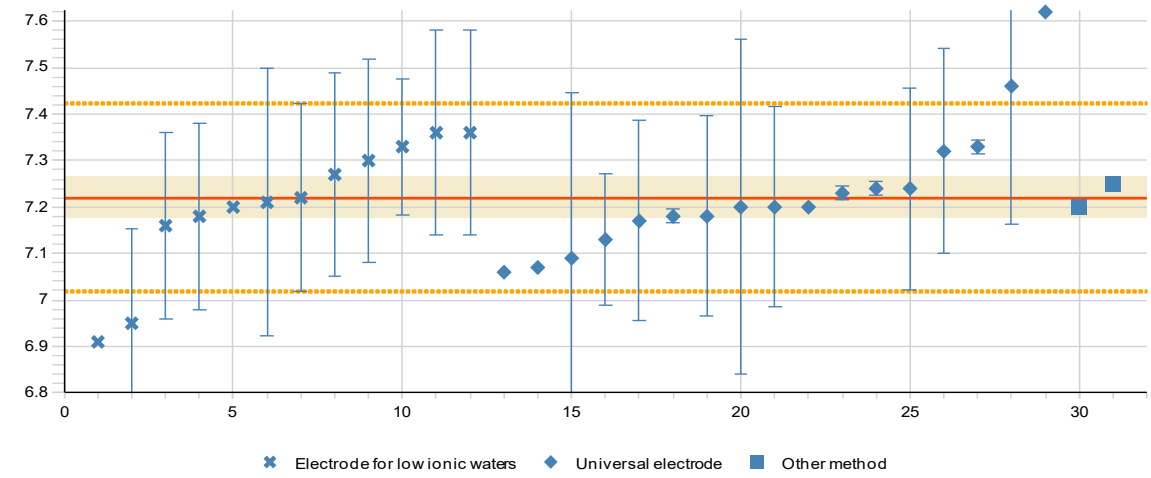
Measurand pH Sample A1P



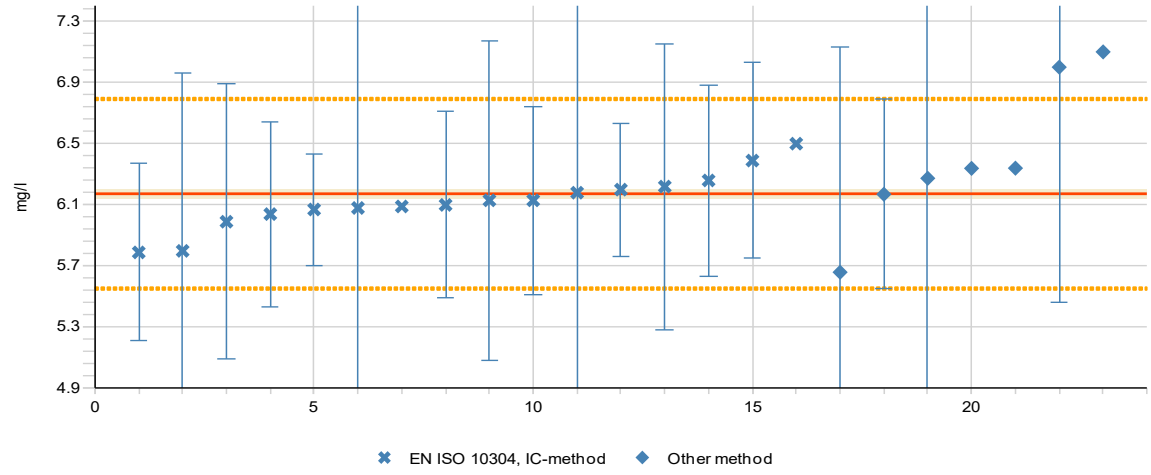
Measurand pH Sample D2PJ



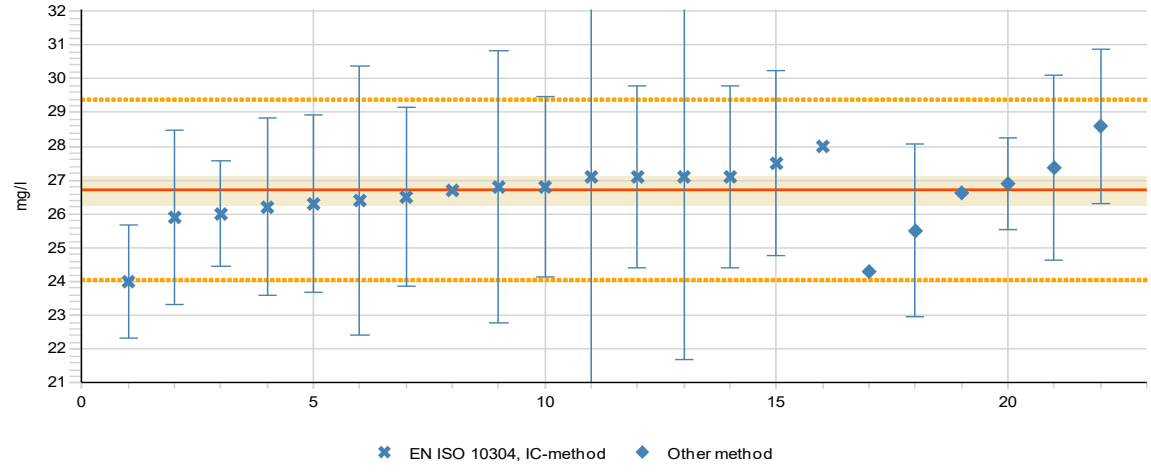
Measurand pH Sample G3PJ

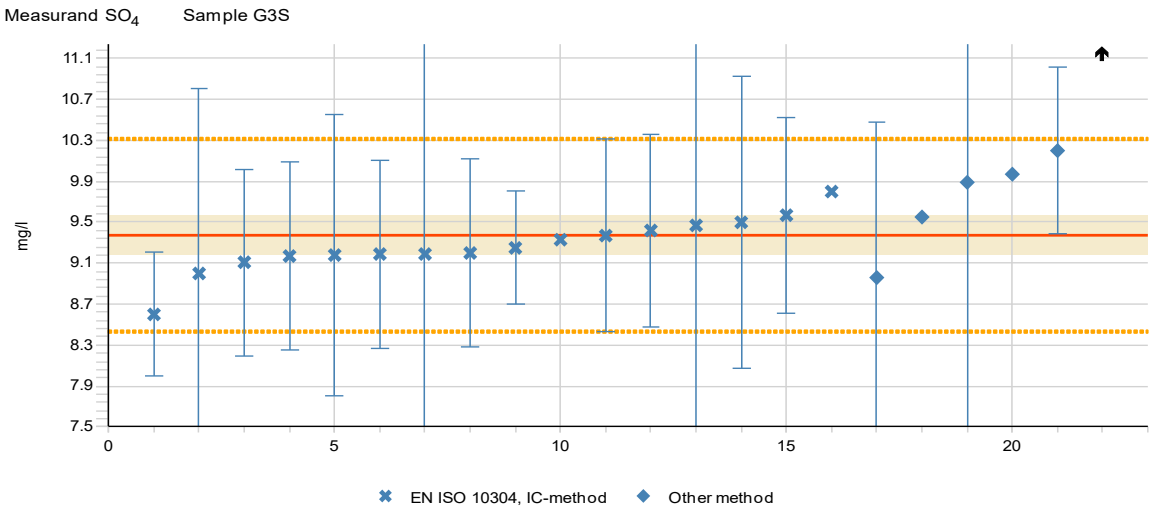


Measurand SO_4 Sample A1S



Measurand SO_4 Sample D2S

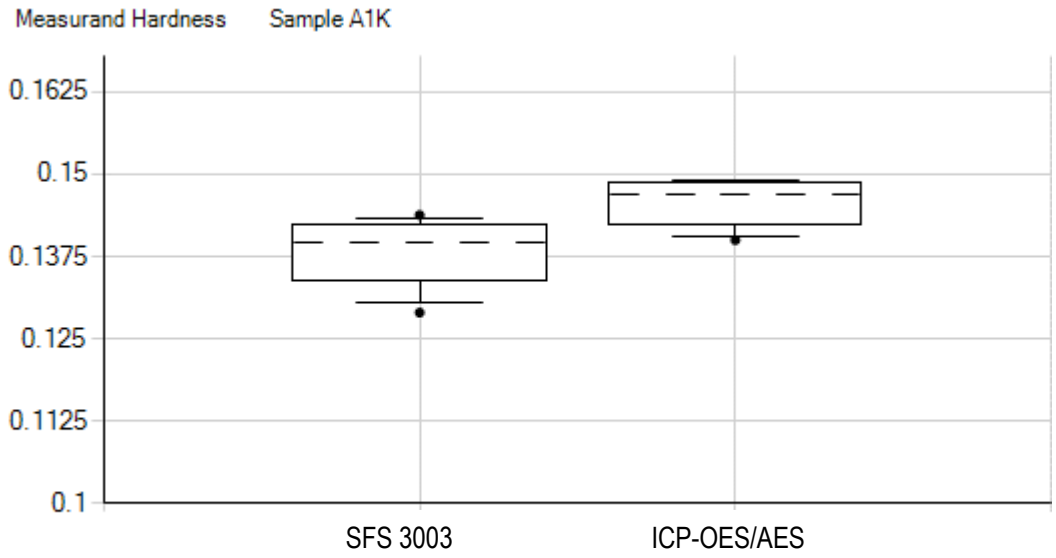



Measurand SO_4
Sample G3S
mg/l
11.1
10.7
10.3
9.9
9.5
9.1
8.7
8.3
7.9
7.5
0
5
10
15
20
EN ISO 10304, IC-method
Other method

Appendix 13. Significant differences in the results reported using different methods

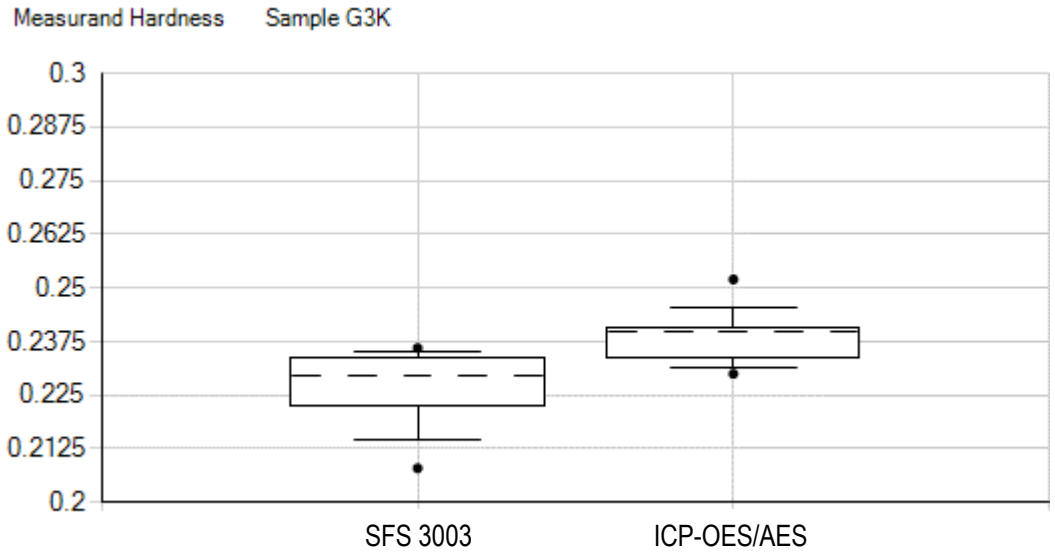
Boxplot figures: In the box the upper and lower limit included 50 % of the results. The dashed vertical line in the middle of the box is the median of the results. The vertical lines above and under the box describe the limits of 80 % of the results. The black dots describe the highest and smallest results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

A1K: Hardness



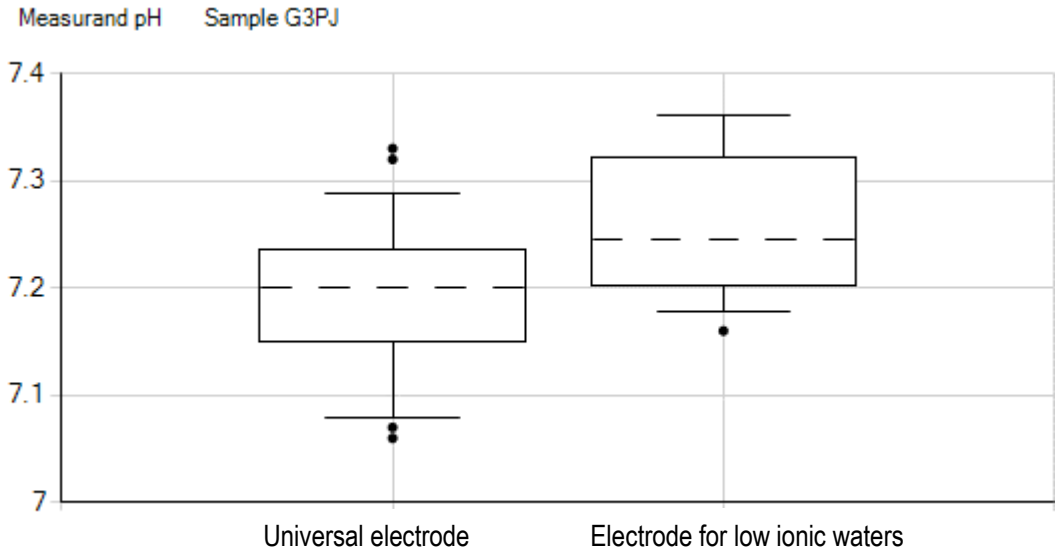
Method	n	Mean (mg/l)	s (mg/l)
SFS 3003, EDTA titration	6	0.14	0.01
ICP-OES or ICP-AES	6	0.15	0.004

G3K: Hardness



Method	n	Mean (mg/l)	s (mg/l)
SFS 3003, EDTA titration	6	0.23	0.01
ICP-OES or ICP-AES	7	0.24	0.01

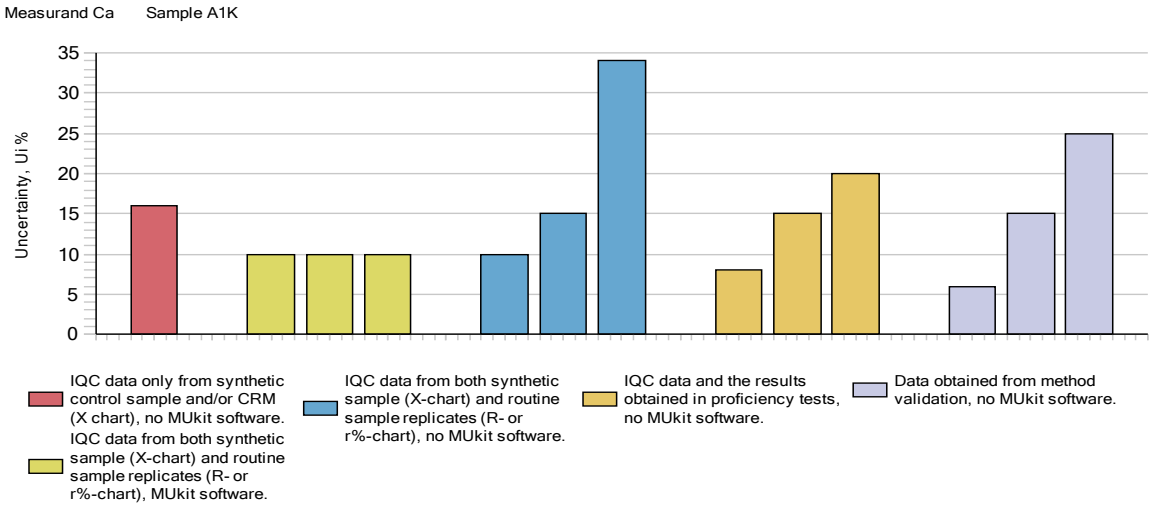
G3PJ: pH

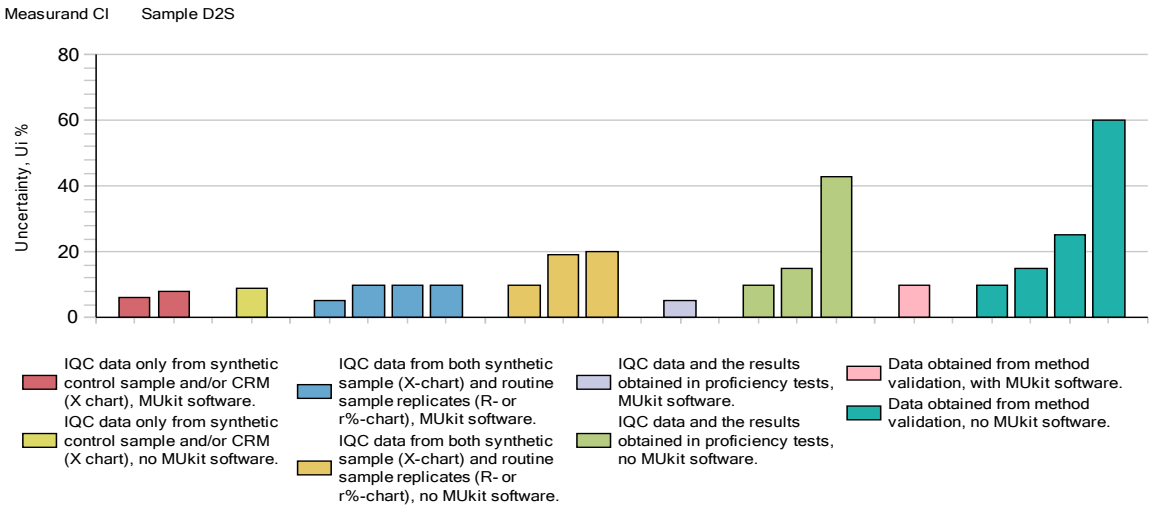


Method	n	Mean (mg/l)	s (mg/l)
Universal electrode	15	7.20	0.08
Electrode for low ionic waters	10	7.26	0.08

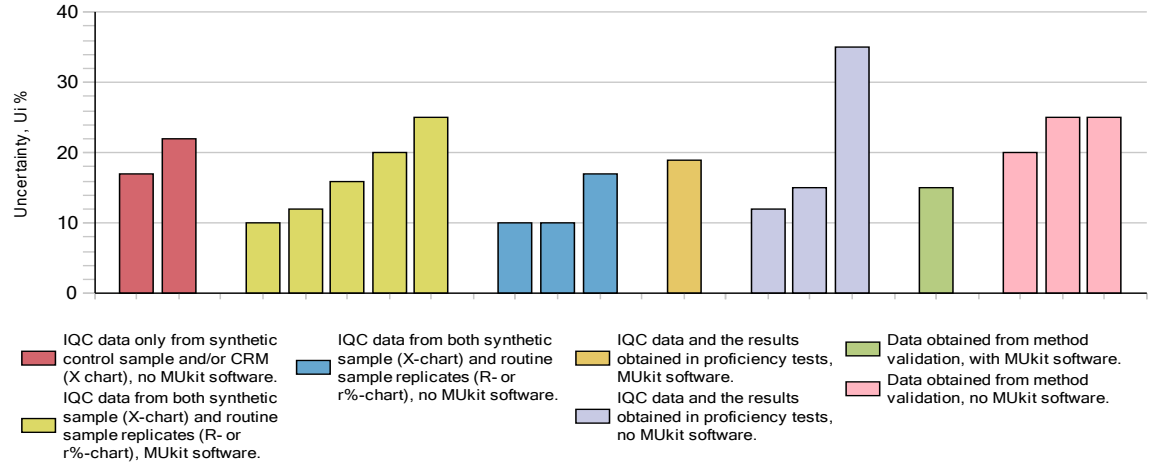
Appendix 14. Examples of measurement uncertainties reported by the participants

In figures, the presented expanded measurement uncertainties are grouped according to the method of evaluation at 95 % confidence level (k=2). The expanded uncertainties were evaluated 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 evaluation [9, 10].

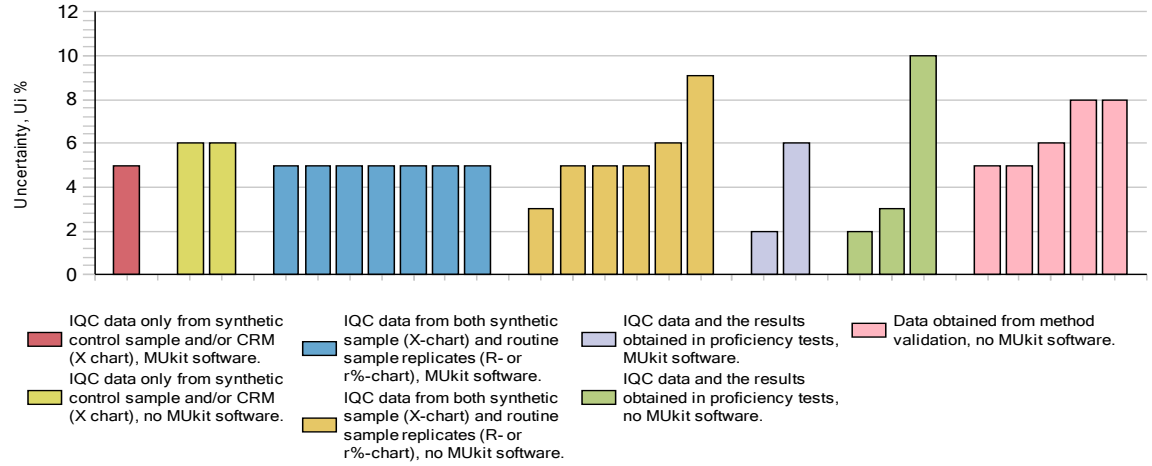




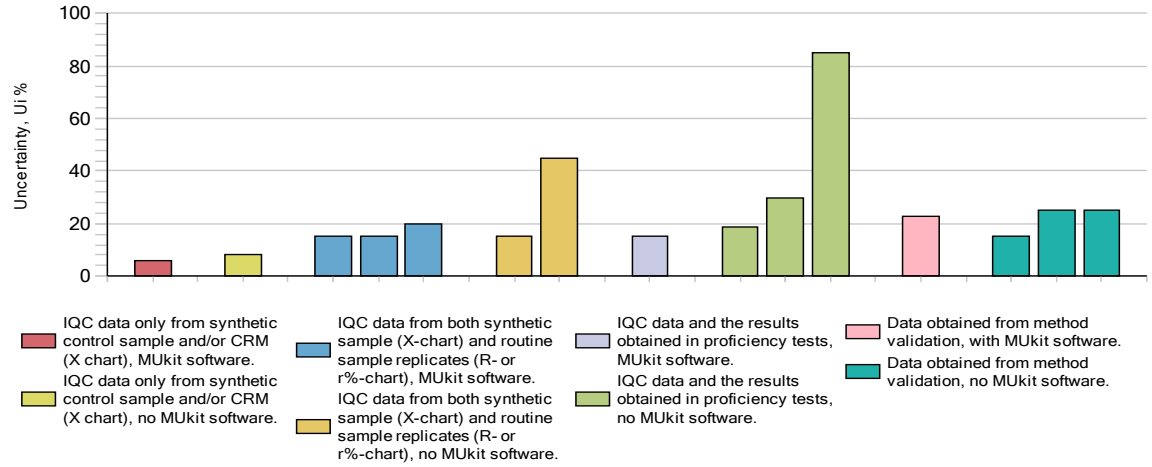
Measurand COD_{Mn} Sample G3C



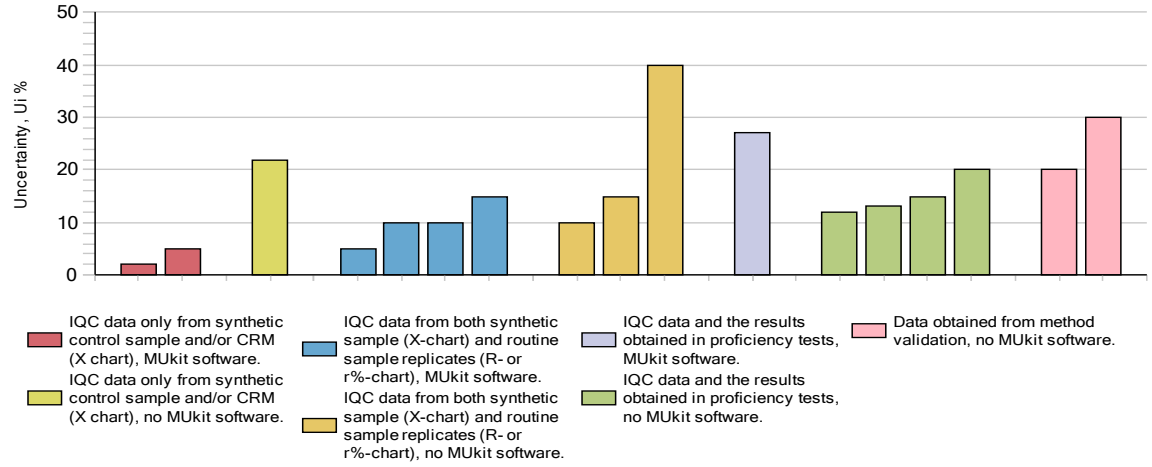
Measurand Conductivity Sample A1J



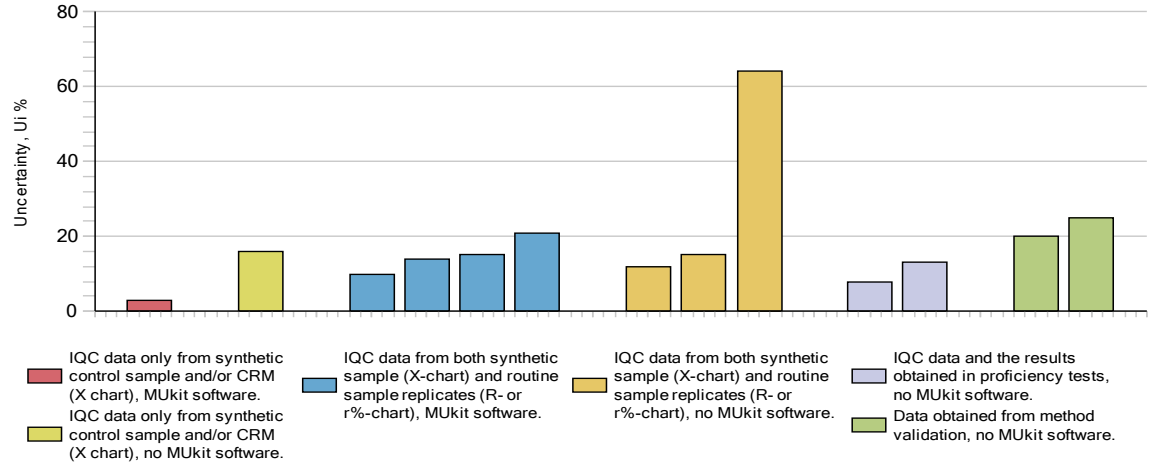
Measurand F Sample D2F



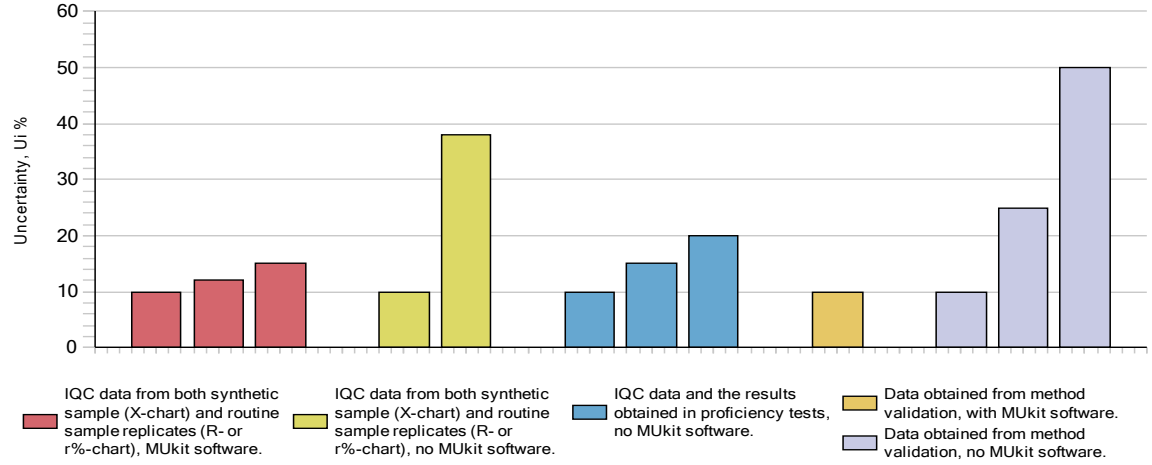
Measurand Fe Sample G3Fe



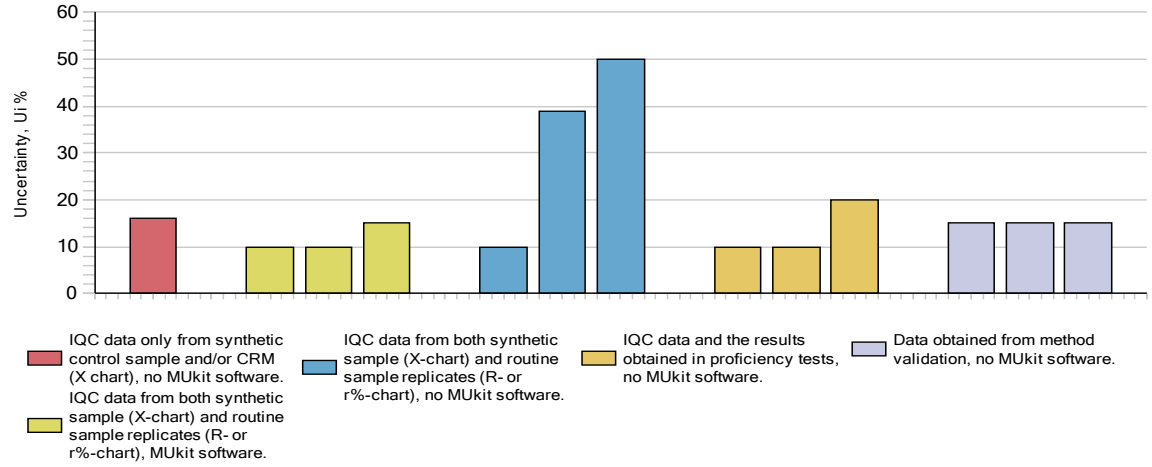
Measurand Hardness Sample A1K



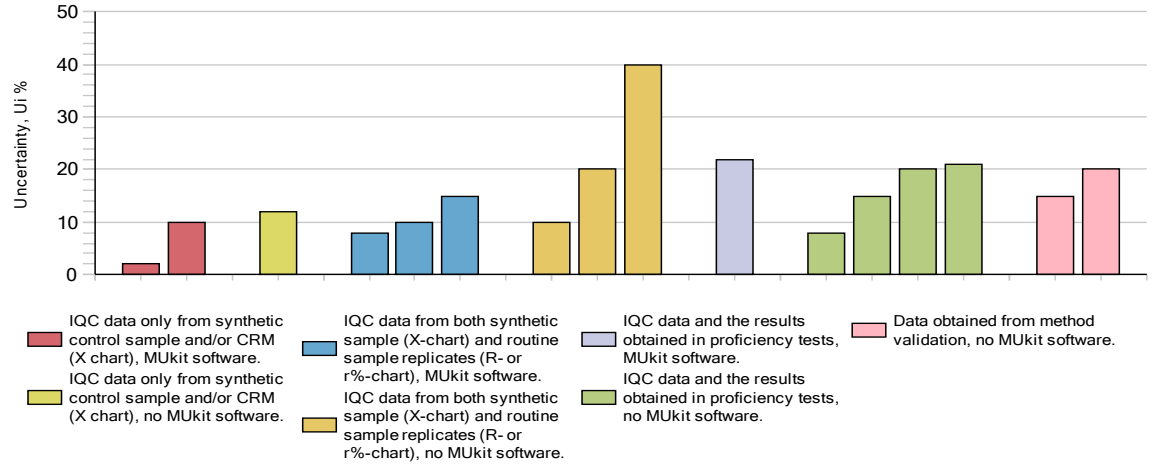
Measurand K Sample D2K



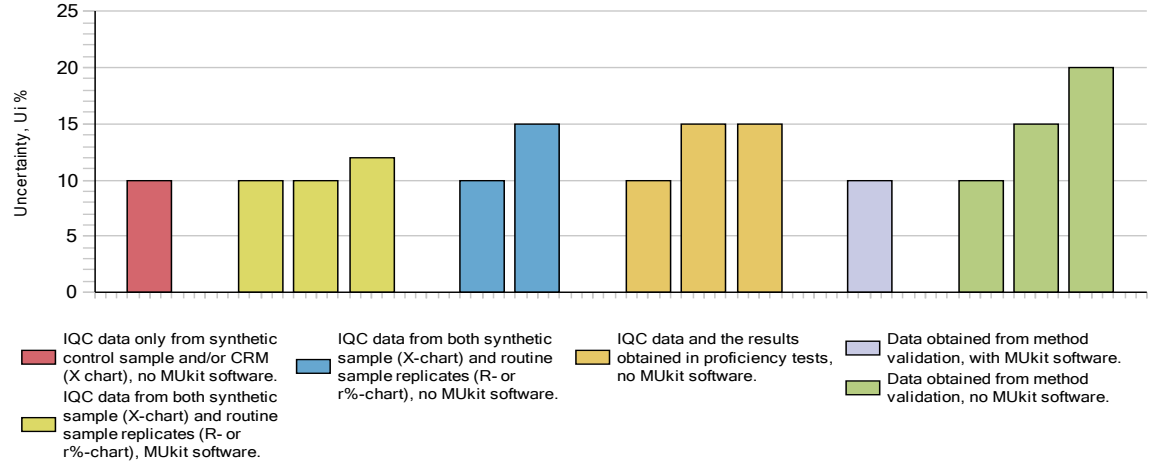
Measurand Mg Sample G3K



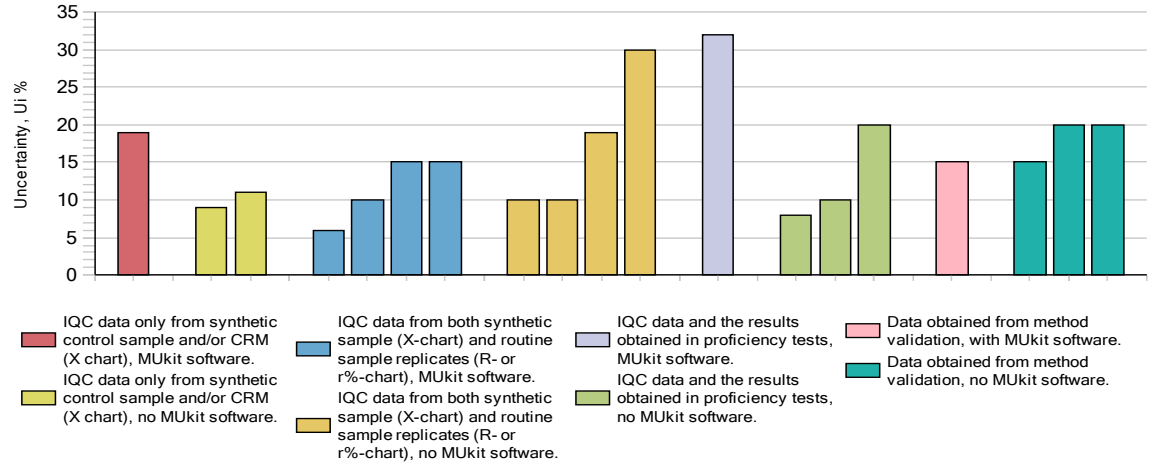
Measurand Mn Sample A1Fe



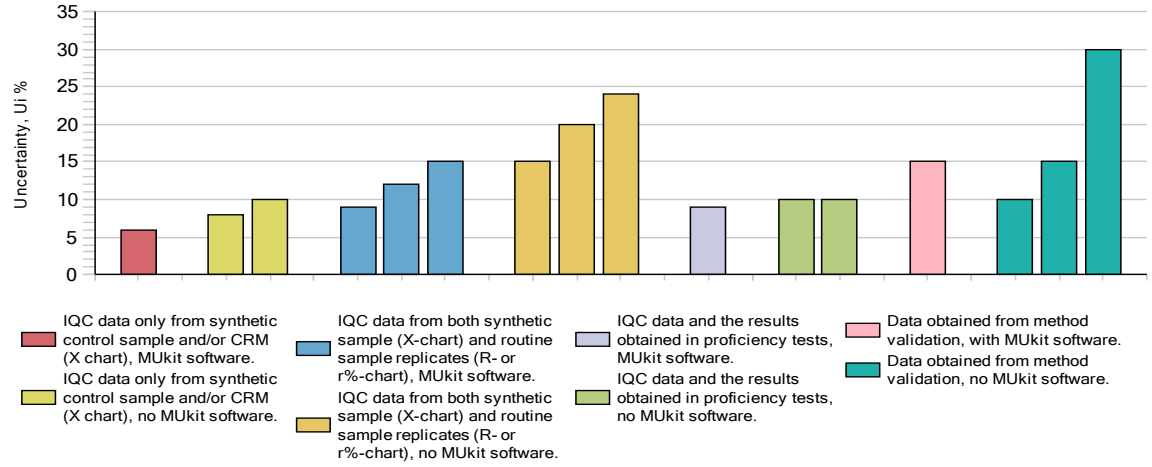
Measurand Na Sample D2K



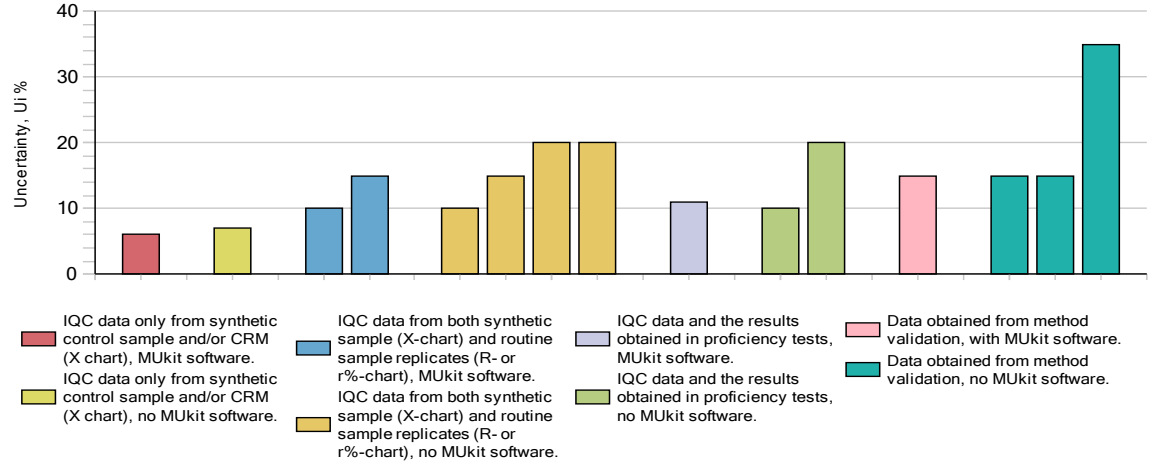
Measurand NH_4 Sample G3N

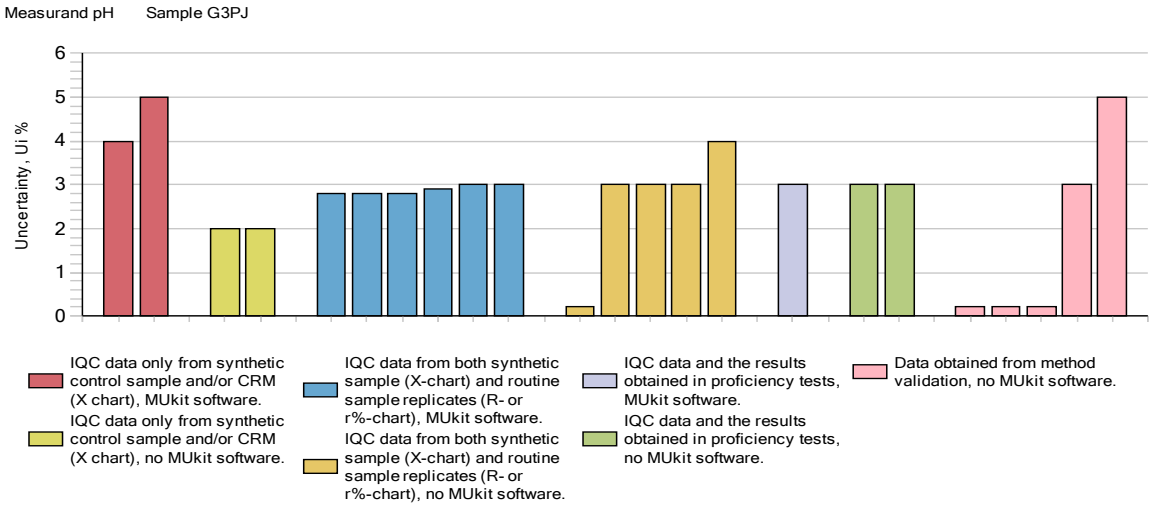


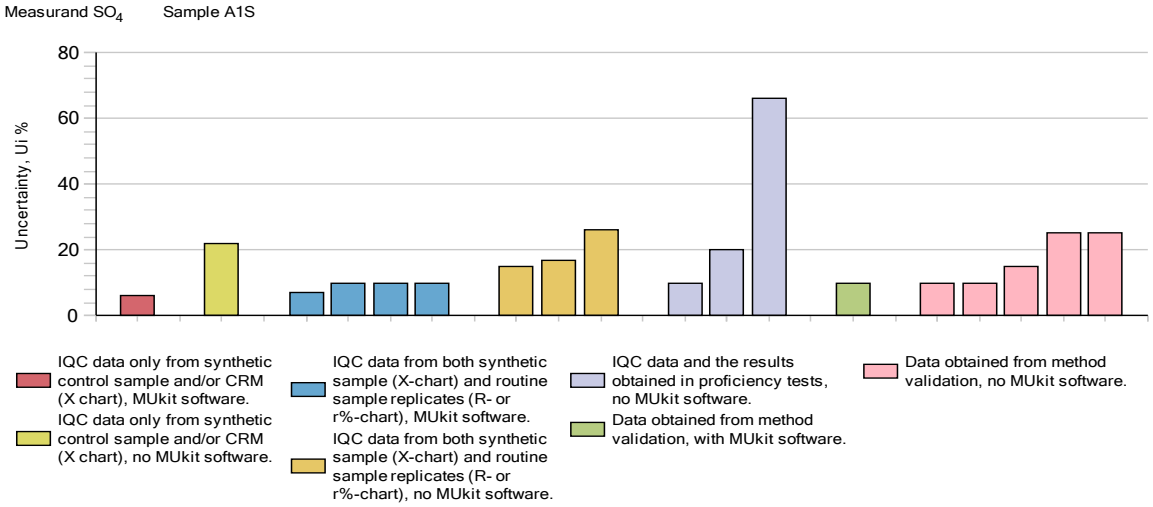
Measurand NO_2 Sample A1N



Measurand NO_3 Sample D2N




Measurand pH
Sample G3PJ
Uncertainty, Ui %
0
1
2
3
4
5
6
IQC data only from synthetic control sample and/or CRM (X chart), MUkit software.
IQC data only from synthetic control sample and/or CRM (X chart), no MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), no MUkit software.
IQC data and the results obtained in proficiency tests, MUkit software.
IQC data and the results obtained in proficiency tests, no MUkit software.
Data obtained from method validation, no MUkit software.


Measurand SO_4
Sample A1S
Uncertainty, Ui %
0
20
40
60
80
IQC data only from synthetic control sample and/or CRM (X chart), MUkit software.
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Data obtained from method validation, with MUkit software.
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