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Proficiency test SPIL-3 (2019)

Organic matter, phosphorus, chloride, sulphate and suspended matter in wastewater (synthetic wastewater, effluent)

Quality Documentation
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1 INTRODUCTION

A proficiency test on the analysis of organic matter, phosphorus, chloride, sulphate and suspended matter in wastewater was conducted on 12 September 2019. The proficiency test was organised by Eurofins Miljø A/S.

The present report contains Eurofins' documentation for the quality of the proficiency test. Results of the proficiency test including data from participating laboratories and statistical analysis of these data were issued in a report to all participants /1/ on 14 October 2019.

2 FEATURES OF THE PROFICIENCY TEST

Participants in the proficiency test were a total of 55 laboratories from Denmark and Sweden. A list of participants is shown in Appendix A.

One laboratory did not receive the samples. The closing date for submission of results was 27 September 2019. All participants except laboratory no 9 and 38 had submitted their results before the dead-line.

2.1 Sample preparation

The parameters covered in the proficiency test are listed in Table 2 as are the abbreviations used in this report.

Six samples were dispatched for the proficiency test. The samples were sample pairs covering the parameters as described in Table 1. The matrix of the samples represented wastewater, in this case synthetic wastewater, effluent. Sample preparation is described in Appendix B.

Table 1 Samples in the proficiency test

Sample name	Parameters
A1/B1	COD_{Cr}, NVOC/TOC, BOD (w. ATU)
A2/B2	TP, Cl, SO_4
A3/B3	TSS

2.2 Statistical analysis of participants' data

A split-level design was used. The data analysis was performed in accordance with ISO 5725: "Accuracy (trueness and precision) of measurement methods and results" (1994) /2/ and as described in detail in Spliid (1992) /3/. A short introduction to the statistics and a list of symbols and abbreviations used is given in Eurofins document "Schedule for a proficiency test", which is available at Eurofins' home page /4/.

The statistical model used is based on the assumption that the variances for the two samples in a sample pair are identical. The assumption was tested (F-test, 95% confidence level) and the result was that the two variances may be assumed to be identical for all parameters.

2.3 Assigned and spike value

An overview of the concentrations in the samples (the assigned values) and the difference in concentration between the two samples of a sample pair (spike value) are shown in Table 2 compared to the range of concentrations normally encountered in synthetic wastewater, effluent. The table also gives the expanded uncertainty of the assigned values.

Table 2 Assigned and spike value

Parameter	Abbreviation	Unit	Typical Range	Assigned value	Uncertainty of assigned value	Spike value
Chemical oxygen demand – dichromate method	COD_{Cr}	mg/L O_2	5-75	15,1	0,33	3,7
Five day biochemical oxygen demand	BOD_5 w. ATU	mg/L O_2	2-6	2,0*	0,28	0,2
Seven day biochemical oxygen demand	BOD_7 w. ATU	mg/L O_2	2-6	2,0	0,28	0,2
Non-volatile organic carbon	NVOC/TOC	mg/L C	2-30	6,0	0,13	1,5
Total phosphorus	TP	mg/L P	0,2-2	0,65	0,013	0,17
Chloride	Cl	mg/L	50-700	349	4,4	19
Sulphate	SO_4	mg/L	20-200	87	1,0	15
Total Suspended matter	TSS	mg/L	20-100	48	1,8	4

*Indicative value

2.3.1 Assigned and spike values

The content of each parameter in each sample is given an assigned value for the sample with the lower content and a spike value, the spike value being the difference in concentration between the two samples of the sample pair.

The content of each parameter in each sample is given an assigned value for the sample with the lower content and a spike value, the spike value being the difference in concentration between the two samples of the sample pair. The assigned and spike values are both calculated from sample preparation Except for BOD where spike values are calculated from sample preparation and assigned values are consensus values for laboratories using standardised methods (method no. 1 - 4), based on the median. Since only one laboratory have used a standardised method for BOD_5 an indicative value from BOD_7 are used.

2.3.2 Test of spike values

A comparison was made (t-test, 95% confidence level) between the spike value and the difference in concentration between the two samples in the sample pair found from the laboratories' results, see Appendix C. The test showed no significant difference between the two.

2.3.3 Test of assigned values

The assigned value and the average of the results obtained from all laboratories were also compared (t-test, 95% confidence level), see Appendix D. For most parameters the test showed no significant difference between the two and the control of assigned value at Eurofins confirmed the value (Appendix E). The test revealed a significant difference between the two for COD_{Cr}, NVOC and TSS. Average recovery was for COD_{Cr} 108,2 %, for NVOC 104,8 % and for TSS 96,4 %.

The difference for COD is numerically small and could be attributed to influence from methods with measurement range above the results. The test was repeated after exclusion of the results for method no. 74 and 78 and now showed no significant differences. Furthermore the results of control measurements at Eurofins confirmed the assigned value (Appendix E).

The test revealed a significant difference between the two for NVOC. However, the numerical value was consistent with the measurement of COD found in control meas-

urements at Eurofins, and scrutiny of documentation from the sample preparation showed no indications of mistakes in sample preparation. The assigned value is therefore kept unchanged.

The difference for TSS could be attributed to influence from laboratories using methods other than those prescribed by the Danish EPA. The test was repeated after exclusion of the results for method no. 9 (TSS) and now showed less significant difference (on a 5 % level) after the exclusion the average recovery was 98,4 % and close to 100 %. Furthermore, the results of control measurements at Eurofins confirmed the assigned value (Appendix E). The assigned value is therefore kept unchanged.

3 HOMOGENEITY AND STABILITY OF SAMPLES

The homogeneity and stability of samples were tested using the following parameters as indicators:

NVOC	Homogeneity test (ampoule diluted x100)
TP	Combined homogeneity and stability test
TSS	Combined homogeneity and stability test

The results of control measurements are shown in Appendix F. The appendix also gives the results of the statistical evaluation of the control data. The data are analysed by analysis of variance (ANOVA) giving:

1. the standard deviation/variance for replicates (the contribution from analytical variability),

2. the between bottle standard deviation/variance (the contribution from heterogeneity) and

3. the between days concentration difference (the contribution from instability).

Homogeneity is evaluated by comparing the between bottle variance to 0.3 * the standard deviation for evaluation of participants' performance ($0.3 \cdot \hat{\sigma}$) specified by the Danish EPA /5/, whereas the stability is evaluated by comparing the concentration change of the samples to $0.3 \cdot \hat{\sigma}$. This test ensures that heterogeneity and instability will not have negative influence on the evaluation of participant performance /6/.

The appendix also shows the standard deviation within and between laboratories from the proficiency test to allow comparison between tests performed and average quality from participating laboratories.

The tests for stability and homogeneity show that the samples are stable and homogeneous.

4 CONCLUSION

The quality control performed, including test of sample stability and homogeneity as well as test of recovery of spike and assigned values, shows that the samples and their assigned values are suitable for testing the proficiency of the participating laboratories for all parameters. The results are also suitable for estimation of the general quality of analyses among all participating laboratories.

For COD, NVOC and TSS the participants did not recover the assigned value. Eurofins' scrutiny of the combined evidence gave the conclusion that the assigned value is correct. The assigned value is therefore kept unchanged and it is recommended as the basis for evaluation of participating laboratories.

5 REFERENCES

/1/ Eurofins A/S, *Proficiency test SPIL-3 (2019)*, Report to participants, October 2019.

/2/ ISO 5725-2, *Accuracy (trueness and precision) of measurement methods and results – Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method*, 1994.

/3/ Spliid, H., *Procedure and analysis of data for proficiency tests and environmental analyses*, Report to Danish Environmental Protection Agency, 1994 (in Danish).

/4/ Eurofins A/S, *Schedule for a proficiency test*, document may be downloaded from www.eurofins.dk/proficiencytest.

/5/ Ministry of Environment regulation no. 681 on *quality criteria for environmental measurements,* 2 July 2019 (in Danish).

/6/ ISO 13528, *Statistical methods for use in proficiency testing by interlaboratory comparison*, 2015.

A N N E X E S

ANNEX A LIST OF PARTICIPANTS

Laboratory	**Town**	**Country**
Spildevandslaboratoriet - 2 participants	Esbjerg	Denmark
Faxe Forsyning	Faxe	Denmark
AquaDjurs A/S	Grenaa	Denmark
Provas	Haderslev	Denmark
Hillerød Forsyning, Spildevand	Hillerød	Denmark
Fors Spildevand Holbæk	Holbæk	Denmark
Holstebro Centralrenseanlæg, Vestforsyning Spildevand	Holstebro	Denmark
Kerteminde Forsyning - Spildevand A/S	Kerteminde	Denmark
BlueKolding A/S	Kolding	Denmark
Biofos A/S	København K	Denmark
Klarforsyning, Køge-Egnens Renseanlæg	Køge	Denmark
Melby Renseanlæg	Liseleje	Denmark
CP Kelco, Spildevandslaboratoriet	Ll. Skensved	Denmark
NK-Spildevand A/S	Næstved	Denmark
Vandmiljø Randers A/S	Randers SØ	Denmark
Bjergmarken R/A, Fors Spildevand Roskilde	Roskilde	Denmark
Rønne Renseanlæg	Rønne	Denmark
Ringkøbing-Skjern Forsyning A/S	Skjern	Denmark
RGS Nordic A/S	Skælskør	Denmark
SK Spildevand, Slagelse Renseanlæg - 5 participants	Slagelse	Denmark
Eurofins Miljø A/S	Vejen	Denmark
Vejle Spildevand	Vejle	Denmark
Aalborg Forsyning, Renseanlæg Øst	Aalborg Øst	Denmark
SYNLAB AS (Hamar)	Hamar	Norway
Laboratoriet på Vatten och Avloppsavdelningen, SBF, Enköpings Kommun	Enköping	Sweden
Laboratoriet vid Smedjeholms avolppsreningsverk	Falkenberg	Sweden
Preem AB Göteborg	Göteborg	Sweden
St1 Refinery AB	Göteborg	Sweden
GRYAAB AB	Göteborg	Sweden
Hallsta Pappersbruk	Hallstavik	Sweden

Laboratory	Town	Country
AB Lennart Månsson International	Helsingborg	Sweden
Kalmar Vatten AB, VA-lab	Kalmar	Sweden
Reningsverket Aggerud	Karlskoga	Sweden
Kristianstad Kommun	Kristianstad	Sweden
Yara AB	Köping	Sweden
Käppalaverket	Lidingö	Sweden
Tekniska Verken i Linköping AB (publ), Laboratoriet Avloppsreningsverket	Linköping	Sweden
Preemraff Lysekil	Lysekil	Sweden
Mjölby Kommun	Mjölby	Sweden
Motala Kommun, Tekniska Förvaltningen, Vatten & Avfall	Motala	Sweden
Arctic Paper Munkedals AB	Munkedal	Sweden
Södra Cell Mörrum	Mörrum	Sweden
Fiskeby Board AB	Norrköping	Sweden
Holmen Paper AB, Bravikens Pappersbruk Bravikens Pappersbruk	Norrköping	Sweden
Vatten och Avloppslaboratoriet VAL AB	Norrtälje	Sweden
Ernemar Laboratorium	Oskarshamn	Sweden
Rottneros Bruk AB	Rottneros	Sweden
Vallviks Bruk AB	Vallvik	Sweden
Kretslopp & Vattens laboratorium , Vänersborgs kommun	Vänersborg	Sweden
Västervik Miljö & Energi AB, Vattenlaboratoriet	Västervik	Sweden
Perstorp Oxo AB	Ödsmål	Sweden

ANNEX B SAMPLE PREPARATION

Stock solution	**Prepared from**		**Concentration**
Concentrate A1	22.20 g 22.20 g 	D-glucose L-glutamic acid milli-Q water up to 24000 g	COD_{Cr}: 1.892 g/kg NVOC: 0.747 g/kg BOD: 1.295 g/kg
Concentrate B1	15.00 g 15.00 g 	D-glucose L-glutamic acid milli-Q water up to 13000 g	COD_{Cr}: 2.360 g/kg NVOC: 0.932 g/kg BOD: 1.615 g/kg
Stock TP	1.50 g 	Na-B.glycerophosphate milli-Q water up to 1000.1 g	TP: 151.8 mg/kg
Stock Cl	50.00 g 	Sodium chloride (NaCl) milli-Q water up to 2500.0 g	Cl: 12.13 g/kg
Stock SO_4	10.00 g 	Sodium sulphate (Na_2SO_4) milli-Q water up to 1000.2 g	SO_4: 6.76 g/kg
Stock TSS	15.00 g 	Microcrystalline cellulose milli-Q water up to 1000.0 l	TSS: 15.00 g/l

Sample	Sample prepared from	COD_{Cr} mg/L O_2	NVOC mg/L C	BOD (w. ATU) mg/L O_2	TP mg/L P	Cl mg/L	SO_4 mg/L	TSS mg/L
A1-COD/NVOC	At the laboratory 2.00 mL of concentrate A1 is diluted up to 250 mL with Milli-Q water	15.1	5.98					
B1-COD/NVOC	At the laboratory 2.00 mL of concentrate B1 is diluted up to 250 mL with Milli-Q water	18.9	7.46					
A1-BOD	At the laboratory 1.50 mL of concentrate A1 is diluted up to 2000 mL with filtered water from Holsted sewage treatment plant			a + 0.971				
B1-BOD	At the laboratory 1.50 mL of concentrate B1 is diluted up to 2000 mL with filtered water from Holsted sewage treatment plant			a + 1.21				
A2	300,0 g stock TP 2000.0 g stock Cl 900.0 g stock SO_4 Milli-Q water up to 70.00 kg				0.651	347	87.0	
B2	39.99 g stock TP 59.99 g stock Cl 79.99 g stock SO_4 A2 up to 35.00 kg				0.821	366	102	
A3	At the laboratory 1000.0 mL of Milli-Q water is added to 3.2 mL stock TSS							47.8
B3	At the laboratory 1000.0 mL of Milli-Q water is added to 3.5 mL stock TSS							52.3

ANNEX C CONTROL OF SPIKE VALUES

COD, mg/L O_2
Control of differences within sample pairs

Laboratory	Difference AB
1	-
2	-1.30
3	3.00
4	-2.20
5A	3.40
5B	1.90
5C	0.20
5C1	3.00
5D	-1.90
5D1	-0.20
6	-1.40
7	1.70
8	-
11	5.40
13	-
14	0.30
15	0.00
16	-0.20
17	-
18	1.30
20	-
22	-4.40
23A	0.10
23B	-
24	2.80
25A	0.70
25B	0.50
26	-
27	3.50
28	-
29	-
30	-4.40
31	-3.30
32	1.40
33	-
34	-
35	1.70
36	0.50
37	-2.00
39	-1.30
40	-
41	-
42	1.90
43	-1.00
44	-2.30
46	-
47	0.50
48	-
49	0.10
50	-0.30
51	6.70
52	-
53	-
54	0.70
55	-
No of labs., p	37
No of repl., n	2
d	0.41
s^2	5.83
s	2.41
$t = \sqrt{p} \cdot (d/s)$	1.0280
Sign. level, p(t)	0.3108

No test statistics were found to be significant

BOD_5, mg/L O_2
Control of differences within sample pairs

Laboratory	Difference AB
1	-
2	-
3	-
4	-
5A	-
5B	-0.13
5C	-0.82
5C1	-
5D	-0.49
5D1	-
6	-
7	-0.37
8	-
11	-
13	-
14	-
15	-
16	-
17	-
18	-
20	-
22	-
23A	-
23B	-
24	-
25A	0.30
25B	0.30
26	-
27	-
28	-
29	-
30	-
31	-0.10
32	0.20
33	-
34	-
35	-
36	-
37	-
39	-
40	-
41	-
42	-
43	0.30
44	-
46	-
47	-0.80
48	-
49	-
50	-
51	-
52	-
53	-
54	-
55	-
No of labs., p	10
No of repl., n	2
d	-0.16
s^2	0.20
s	0.44
$t = \sqrt{p} \cdot (d/s)$	-1.1490
Sign. level, p(t)	0.2802

No test statistics were found to be significant

BOD_7, mg/L O_2
Control of differences within sample pairs

Laboratory	Difference AB	
1	0.100	
2	-	
3	-	
4	-	
5A	-	
5B	-	
5C	-	
5C1	-	
5D	-	
5D1	-	
6	-	
7	-	
8	-	
11	-	
13	-	
14	-	
15	-	
16	-	
17	0.020	
18	-	
20	-	
22	-	
23A	-	
23B	-	
24	-	
25A	-	
25B	-	
26	-	
27	-	
28	0.100	
29	-	
30	-0.150	
31	-	
32	-	
33	0.100	
34	-	
35	-	
36	-	
37	-	
39	0.200	
40	-0.660	UC

Laboratory	Difference AB
41	-
42	-
43	-
44	-
46	-
47	-
48	-
49	-
50	-
51	-
52	-
53	0.010
54	0.010
55	-
No of labs., p	8
No of repl., n	2
d	0.049
s^2	0.011
s	0.103
$t = \sqrt{p} \cdot (d/s)$	1.3403
Sign. level, p(t)	0.2220

No test statistics were found to be significant
UC denotes a Cochran outlier

NVOC, mg/L C

Control of differences within sample pairs

Laboratory	Difference AB	
1	-0.030	
2	-0.640	
3	-	
4	1.800	UG
5A	-	
5B	-	
5C	-	
5C1	-	
5D	-	
5D1	-	
6	-	
7	-1.370	
8	-	
11	-	
13	0.200	
14	-	
15	-	
16	-	
17	0.360	
18	-	
20	0.304	
22	-	
23A	-	
23B	-	
24	0.610	
25A	0.320	
25B	0.120	
26	0.100	
27	0.450	
28	0.210	
29	-0.110	
30	-	
31	-	
32	0.440	
33	-0.050	
34	-	
35	0.220	
36	0.056	
37	-	
39	0.200	
40	0.230	

Laboratory	Difference AB
41	-0.052
42	-
43	0.100
44	0.430
46	0.730
47	-
48	0.704
49	-
50	-
51	-
52	0.570
53	0.410
54	-0.460
55	-0.090
No of labs., p	28
No of repl., n	2
d	0.142
s^2	0.186
s	0.431
$t = \sqrt{p} \cdot (d/s)$	1.7355
Sign. level, p(t)	0.0941

No test statistics were found to be significant

UG denotes a Grubbs outlier

Total phosphorous, mg/L P
Control of differences within sample pairs

Laboratory	Difference AB	
1	0.0040	
2	0.0080	
3	-0.0070	
4	-0.0020	
5A	0.3630	UC
5B	-0.0090	
5C	0.0030	
5C1	0.0270	
5D	-0.1070	UC
5D1	-	
6	-0.0750	UC
7	0.0080	
8	0.0100	
11	-0.0100	
13	0.0000	
14	0.0230	
15	0.0440	UC
16	0.0100	
17	-0.0140	
18	-0.0040	
20	0.0000	
22	0.0130	
23A	0.0000	
23B	0.0050	
24	0.0100	
25A	-0.0130	
25B	-0.0100	
26	-0.0150	
27	0.0980	UC
28	0.0090	
29	-0.0020	
30	-0.0010	
31	0.0010	
32	0.0010	
33	-0.0030	
34	-0.0040	
35	-0.0120	
36	0.0050	
37	-0.0010	
39	0.0080	
40	-0.0220	

Laboratory	Difference AB	
41	-0.0020	
42	-0.0500	UC
43	-0.0100	
44	-0.0070	
46	-	
47	-0.0040	
48	0.0000	
49	-0.0120	UG
50	0.0150	
51	0.0000	
52	-	
53	-0.0210	
54	-	
55	0.0020	
No of labs., p	44	
No of repl., n	2	
d	-0.0002	
s^2	0.0001	
s	0.0102	
$t = \sqrt{p} \cdot (d/s)$	-0.1619	
Sign. level, p(t)	0.8722	

No test statistics were found to be significant
UC denotes a Cochran outlier
UG denotes a Grubbs outlier

Chloride, mg/L
Control of differences within sample pairs

Laboratory	Difference AB	
1	0.0	
2	-5.0	
3	8.0	
4	-	
5A	6.0	
5B	0.0	
5C	2.0	
5C1	8.0	
5D	-7.0	
5D1	-	
6	32.0	UC
7	-16.0	
8	-	
11	-	
13	-	
14	5.0	
15	-0.8	
16	-	
17	-	
18	0.0	
20	-	
22	-	
23A	-	
23B	-	
24	-	
25A	-1.0	
25B	-5.0	
26	-	
27	15.0	
28	-	
29	-	
30	-	
31	21.0	
32	-	
33	-	
34	-	
35	-	
36	4.6	
37	-	
39	-	
40	-	

Laboratory	Difference AB
41	-
42	-3.0
43	1.0
44	-1.4
46	-
47	-10.0
48	-
49	-3.0
50	-
51	4.0
52	-
53	-
54	-
55	5.6
No of labs., p	24
No of repl., n	2
d	1.2
s^2	59.7
s	7.7
$t = \sqrt{p} \cdot (d/s)$	0.7407
Sign. level, p(t)	0.4664

No test statistics were found to be significant
UC denotes a Cochran outlier

Sulphate, mg/L
Control of differences within sample pairs

Laboratory	Difference AB
1	-1.70
2	1.00
3	-
4	-
5A	-0.40
5B	1.40
5C	2.80
5C1	-
5D	1.20
5D1	-
6	-
7	0.60
8	-
11	-
13	-
14	-
15	-
16	-
17	-
18	-
20	-
22	-
23A	-
23B	-
24	-
25A	-
25B	-
26	-
27	-
28	-
29	-
30	-
31	-
32	-
33	-
34	-
35	1.40
36	-
37	-
39	-
40	-
41	-
42	-
43	0.00
44	1.40
46	-
47	-
48	-
49	-
50	-
51	-
52	-
53	-
54	-
55	-0.81
No of labs., p	11
No of repl., n	2
d	0.63
s^2	1.59
s	1.26
$t = \sqrt{p} \cdot (d/s)$	1.6458
Sign. level, p(t)	0.1308

No test statistics were found to be significant

SS, mg/L
Control of differences within sample pairs

Laboratory	Difference AB	
1	2.90	
2	-	
3	-5.00	
4	-0.40	
5A	3.90	
5B	-0.50	
5C	-1.70	
5C1	-	
5D	-1.10	
5D1	-	
6	-	
7	0.00	
8	-	
11	-	
13	0.50	
14	0.70	
15	-0.50	
16	1.00	UG
17	-1.90	
18	-	
20	-3.70	
22	-5.00	
23A	-0.70	
23B	-	
24	-1.00	
25A	4.00	
25B	3.00	
26	6.80	
27	-	
28	-1.40	
29	-0.90	
30	-0.70	
31	0.00	
32	-0.20	
33	-0.20	
34	-	
35	-3.00	
36	-0.90	
37	-	
39	-0.40	
40	-0.60	

Laboratory	Difference AB
41	-0.70
42	-1.50
43	-1.00
44	-2.50
46	7.80
47	-5.50
48	-0.80
49	-0.80
50	-
51	-
52	0.50
53	-0.10
54	-
55	-
No of labs., p	39
No of repl., n	2
d	-0.32
s^2	7.40
s	2.72
$t = \sqrt{p} \cdot (d/s)$	-0.7415
Sign. level, p(t)	0.4630

No test statistics were found to be significant
UG denotes a Grubbs outlier

ANNEX D CONTROL OF RECOVERY

COD, mg/L O_2
Control of recovery, average of results

Laboratory	Sample pair AB
1	-
2	17.35
3	17.60
4	13.70
5A	13.00
5B	12.05
5C	12.20
5C1	13.20
5D	11.55
5D1	15.20
6	18.60
7	16.55
8	-
11	17.30
13	-
14	16.75
15	16.20
16	21.30
17	-
18	14.45
20	-
22	19.30
23A	18.45
23B	-
24	24.60
25A	15.05
25B	15.15
26	-
27	14.95
28	-
29	-
30	14.00
31	14.35
32	13.00
33	-
34	-
35	17.45
36	18.25
37	17.70
39	16.65
40	12.50

Laboratory	Sample pair AB	
41	-	
42	24.35	
43	14.60	
44	18.55	
46	-	
47	19.25	
48	-	
49	16.95	
50	14.05	
51	15.65	
52	-	
53	-	
54	15.45	
55	-	
No of labs., p	37	
No of repl., n	2	
m	16.34	
s^2	9.06	
s	3.01	
Assigned value, μ	15.1	
Recovery, %	108.2	
$t = \sqrt{p} \cdot (m-\mu)/s$	2.5154	
Sign. level, p(t)	0.0165	*

* denotes that there is a significant difference (t-test, 5%-level)
** denotes that there is a significant difference (t-test, 1%-level)
*** denotes that there is a significant difference (t-test, 0.1%-level)

BOD_5, mg/L O_2
Control of recovery, average of results

Laboratory	Sample pair AB
1	-
2	-
3	-
4	-
5A	-
5B	2.34
5C	3.14
5C1	-
5D	2.72
5D1	-
6	-
7	0.93
8	-
11	-
13	-
14	-
15	-
16	-
17	-
18	-
20	-
22	-
23A	-
23B	-
24	-
25A	2.25
25B	2.25
26	-
27	-
28	-
29	-
30	-
31	1.65
32	2.70
33	-
34	-
35	-
36	-
37	-
39	-
40	-

Laboratory	Sample pair AB
41	-
42	-
43	1.35
44	-
46	-
47	4.90
48	-
49	-
50	-
51	-
52	-
53	-
54	-
55	-
No of labs., p	10
No of repl., n	2
m	2.42
s^2	1.21
s	1.10
Assigned value, μ	2.0
Recovery, %	121.2
$t = \sqrt{p} \cdot (m-\mu)/s$	1.2182
Sign. level, p(t)	0.2541

No test statistics were found to be significant

BOD_7, mg/L O_2
Control of recovery, average of results

Laboratory	Sample pair AB	
1	1.950	
2	-	
3	-	
4	-	
5A	-	
5B	-	
5C	-	
5C1	-	
5D	-	
5D1	-	
6	-	
7	-	
8	-	
11	-	
13	-	
14	-	
15	-	
16	-	
17	2.260	
18	-	
20	-	
22	-	
23A	-	
23B	-	
24	-	
25A	-	
25B	-	
26	-	
27	-	
28	2.050	
29	-	
30	2.955	
31	-	
32	-	
33	1.950	
34	-	
35	-	
36	-	
37	-	
39	1.200	
40	1.600	UC

Laboratory	Sample pair AB
41	-
42	-
43	-
44	-
46	-
47	-
48	-
49	-
50	-
51	-
52	-
53	2.035
54	2.705
55	-
No of labs., p	8
No of repl., n	2
m	2.138
s^2	0.282
s	0.531
Assigned value, μ	2.0
Recovery, %	106.9
$t = \sqrt{p} \cdot (m-\mu)/s$	0.7359
Sign. level, p(t)	0.4857

No test statistics were found to be significant
UC denotes a Cochran outlier

NVOC, mg/L C
Control of recovery, average of results

Laboratory	Sample pair AB	
1	6.265	
2	6.870	
3	-	
4	12.500	UG
5A	-	
5B	-	
5C	-	
5C1	-	
5D	-	
5D1	-	
6	-	
7	4.995	
8	-	
11	-	
13	6.300	
14	-	
15	-	
16	-	
17	5.700	
18	-	
20	7.442	
22	-	
23A	-	
23B	-	
24	5.755	
25A	6.900	
25B	6.880	
26	6.210	
27	6.405	
28	5.665	
29	5.865	
30	-	
31	-	
32	6.050	
33	5.435	
34	-	
35	6.130	
36	6.400	
37	-	
39	6.500	
40	5.785	

Laboratory	Sample pair AB	
41	6.453	
42	-	
43	5.850	
44	6.025	
46	6.605	
47	-	
48	6.135	
49	-	
50	-	
51	-	
52	7.645	
53	6.185	
54	7.310	
55	6.375	
No of labs., p	28	
No of repl., n	2	
m	6.291	
s^2	0.360	
s	0.600	
Assigned value, μ	6.0	
Recovery, %	104.8	
$t = \sqrt{p} \cdot (m-\mu)/s$	2.5622	
Sign. level, p(t)	0.0163	*

* denotes that there is a significant difference (t-test, 5%-level)
** denotes that there is a significant difference (t-test, 1%-level)
*** denotes that there is a significant difference (t-test, 0.1%-level)
UG denotes a Grubbs outlier

Total phosphorous, mg/L P
Control of recovery, average of results

Laboratory	Sample pair AB	
1	0.6160	
2	0.6400	
3	0.6745	
4	0.6460	
5A	0.7025	UC
5B	0.6815	
5C	0.6755	
5C1	0.6385	
5D	0.7705	UC
5D1	0.7180	
6	0.6915	UC
7	0.6550	
8	0.5850	
11	0.7150	
13	0.6600	
14	0.6685	
15	0.5710	UC
16	0.6360	
17	0.6330	
18	0.6860	
20	0.6680	
22	0.6395	
23A	0.6700	
23B	0.6465	
24	0.6540	
25A	0.6895	
25B	0.6950	
26	0.6815	
27	0.1840	UC
28	0.6295	
29	0.6450	
30	0.6465	
31	0.6695	
32	0.6585	
33	0.6365	
34	0.6500	
35	0.6600	
36	0.6625	
37	0.6965	
39	0.6500	
40	0.6740	

Laboratory	Sample pair AB	
41	0.6570	
42	0.6650	UC
43	0.6350	
44	0.6475	
46	-	
47	0.6760	
48	0.6440	
49	0.7820	UG
50	0.6735	
51	0.6600	
52	-	
53	0.6185	
54	-	
55	0.6460	
No of labs., p	44	
No of repl., n	2	
m	0.6566	
s^2	0.0006	
s	0.0239	
Assigned value, μ	0.65	
Recovery, %	101.0	
$t = \sqrt{p} \cdot (m-\mu)/s$	1.8307	
Sign. level, p(t)	0.0741	

No test statistics were found to be significant
UC denotes a Cochran outlier
UG denotes a Grubbs outlier

Chloride, mg/L
Control of recovery, average of results

Laboratory	Sample pair AB	
1	349.0	
2	361.5	
3	307.0	
4	-	
5A	295.0	
5B	360.0	
5C	391.0	
5C1	306.0	
5D	386.5	
5D1	393.0	
6	373.0	UC
7	388.0	
8	-	
11	-	
13	-	
14	313.5	
15	341.1	
16	-	
17	-	
18	351.0	
20	-	
22	-	
23A	-	
23B	-	
24	-	
25A	360.5	
25B	356.5	
26	-	
27	299.5	
28	-	
29	-	
30	-	
31	346.5	
32	-	
33	-	
34	-	
35	-	
36	327.9	
37	-	
39	-	
40	-	

Laboratory	Sample pair AB
41	-
42	307.5
43	348.5
44	365.0
46	-
47	366.0
48	-
49	292.5
50	-
51	306.0
52	-
53	-
54	-
55	340.2
No of labs., p	24
No of repl., n	2
m	340.3
s^2	933.3
s	30.6
Assigned value, μ	347
Recovery, %	98.1
$t = \sqrt{p} \cdot (m-\mu)/s$	-1.0810
Sign. level, p(t)	0.2909

No test statistics were found to be significant
UC denotes a Cochran outlier

Sulphate, mg/L
Control of recovery, average of results

Laboratory	Sample pair AB
1	87.15
2	88.50
3	-
4	-
5A	89.80
5B	89.70
5C	89.40
5C1	-
5D	90.60
5D1	92.00
6	-
7	81.30
8	-
11	-
13	-
14	-
15	-
16	-
17	-
18	-
20	-
22	-
23A	-
23B	-
24	-
25A	-
25B	-
26	-
27	-
28	-
29	-
30	-
31	-
32	-
33	-
34	-
35	82.90
36	-
37	-
39	-
40	-

Laboratory	Sample pair AB
41	-
42	-
43	87.00
44	98.20
46	-
47	-
48	-
49	-
50	-
51	-
52	-
53	-
54	-
55	86.83
No of labs., p	11
No of repl., n	2
m	88.31
s^2	19.21
s	4.38
Assigned value, μ	87
Recovery, %	101.5
$t = \sqrt{p} \cdot (m-\mu)/s$	0.9895
Sign. level, p(t)	0.3457

No test statistics were found to be significant

SS, mg/L
Control of recovery, average of results

Laboratory	Sample pair AB	
1	44.45	
2	-	
3	46.50	
4	47.30	
5A	46.85	
5B	45.95	
5C	45.55	
5C1	-	
5D	47.25	
5D1	-	
6	-	
7	47.00	
8	-	
11	-	
13	45.15	
14	47.15	
15	47.05	
16	37.50	UG
17	46.05	
18	-	
20	45.75	
22	42.50	
23A	47.55	
23B	-	
24	43.50	
25A	43.00	
25B	46.50	
26	43.40	
27	-	
28	46.00	
29	47.85	
30	47.95	
31	47.60	
32	46.60	
33	47.70	
34	46.30	
35	48.50	
36	47.85	
37	-	
39	46.90	
40	48.30	

Laboratory	Sample pair AB	
41	47.85	
42	46.05	
43	47.50	
44	46.05	
46	43.40	
47	45.35	
48	45.60	
49	46.60	
50	-	
51	-	
52	47.55	
53	45.85	
54	-	
55	-	
No of labs., p	39	
No of repl., n	2	
m	46.29	
s^2	2.35	
s	1.53	
Assigned value, μ	48	
Recovery, %	96.4	
$t = \sqrt{p} \cdot (m-\mu)/s$	-6.9510	
Sign. level, p(t)	0.0000	***

* denotes that there is a significant difference (t-test, 5%-level)
** denotes that there is a significant difference (t-test, 1%-level)
*** denotes that there is a significant difference (t-test, 0.1%-level)
UG denotes a Grubbs outlier

ANNEX E CONCENTRATION LEVEL

Parameter	Unit	Sample	Bottle no.	I	II	Bottle Average	Sample Average	Assigned value	Spike Measured	Spike Assigned
COD	mg/L O2	A1	32	14,9	14,5	14,7	14,7	15,1	2,9	3,7
			38	15,0	14,2	14,6				
			62	14,8	15,0	14,9				
		B1	23	18,0	17,2	17,6	17,6	18,8		
			38	17,9	17,8	17,9				
			40	17,6	17,3	17,5				
Total phosphorus	mg/L P	A2	9	0,662	0,662	0,66	0,66	0,65	0,17	0,17
			40	0,661	0,661	0,66				
			64	0,660	0,662	0,66				
		B2	11	0,816	0,817	0,82	0,83	0,82		
			43	0,833	0,834	0,83				
			59	0,831	0,830	0,83				
Chloride	mg/L	A2	9	356	356	356	352	347	21	19
			40	350	351	351				
			64	348	348	348				
		B2	11	372	371	372	372	366		
			43	372	371	372				
			59	373	374	374				
Sulphate	mg/L	A2	9	76	76	76	77	87	15	15
			40	79	76	78				
			64	77	76	76				
		B2	11	94	92	93	92	102		
			43	90	90	90				
			59	93	92	93				
Total suspended solids	mg/L	A3	14	48		48	47	48	5	4
			38	47		47				
			68	47		47				
		B3	7	52		52	52	52		
			25	52		52				
			51	53		53				

ANNEX F HOMOGENEITY AND STABILITY

PT: SPIL-3
Parameter: NVOC
Unit: mg/L C
Sigma: 0,531

Homogeneity test Date: 2017-03-02

Sample	x(a)	x(b)	average	sd	sd^2
A1-x	7,300	7,300	7,3	0,000	0,000
A1-x	7,300	7,300	7,3	0,000	0,00
A1-x	7,300	7,400	7,4	0,071	0,005
A1-x	7,300	7,300	7,3	0,000	0,000
A1-x	7,400	7,400	7,4	0,000	0,000
A1-x	7,300	7,400	7,4	0,071	0,005
A1-x	7,400	7,400	7,4	0,000	0,000
A1-x	7,400	7,400	7,4	0,000	0,000
A1-x	7,500	7,400	7,5	0,071	0,005
A1-x	7,400	7,500	7,5	0,071	0,005
A1-x	7,500	7,400	7,5	0,071	0,005
A1-x	7,400	7,400	7,4	0,000	0,000

For homogeneity

General average (x)	7,38
Sample average sd (s_x)	0,058
Within-sample sd (s_w):	0,046
Between-samples sd (ss):	0,0485
S_L in the Proficiency Test:	0,560
S_R in the Proficiency Test:	0,638

Conclusions

ss =0,048 0.3*sigma=0,16
/x-y/ =0

Analytical quality Is s_w < 0,15*sigma **YES**

Homogeneity: Is ss < 0.3*sigma? **YES**

PT:	SPIL-3
Parameter:	TP
Unit:	mg/L P
Sigma:	0,036

Responsible for tests: S7MS

Homogeneity test Date: 2019-08-27

Sample	x(a)	x(b)	average	sd	sd^2
A2-7	0,646	0,642	0,64	0,003	0,000
A2-13	0,662	0,662	0,66	0,000	0,00
A2-18	0,660	0,659	0,66	0,001	0,000
A2-26	0,659	0,656	0,66	0,002	0,000
A2-33	0,659	0,658	0,66	0,001	0,000
A2-37	0,660	0,661	0,66	0,001	0,000
A2-42	0,668	0,666	0,67	0,001	0,000
A2-48	0,664	0,665	0,66	0,001	0,000
A2-54	0,658	0,658	0,66	0,000	0,000
A2-56	0,662	0,661	0,66	0,001	0,000
A2-66	0,661	0,660	0,66	0,001	0,000
A2-79	0,656	0,655	0,66	0,001	0,000

For homogeneity

General average (x)	0,66
Sample average sd (s_x)	0,006
Within-sample sd (s_w):	0,001
Between-samples sd (ss):	0,0056
S_L in the Proficiency Test:	0,0234
S_R in the Proficiency Test:	0,0245

Stability test Date: 2019-09-12

Sample	x(a)	x(b)
A2-9	0,662	0,662
A2-40	0,661	0,661
A2-64	0,660	0,662

For stability

General average (y):	0,6613333
/x-y/ =	0,00225

Conclusions

ss =	0,006	0.3*sigma=	0,01
/x-y/ =	0,00225		

Analytical quality	Is s_w < 0,15*sigma **YES**
Homogeneity:	Is ss < 0.3*sigma? **YES**
Stability:	/x-y/ < 0.3*sigma? **YES**

PT:	SPIL-3
Parameter:	TSS
Unit:	mg/L
Sigma:	3,6

Responsible for tests: S7MS

Homogeneity test Date: 2019-08-27

Sample	x(a)	x(b)	average	sd	sd^2
A3-7	47,9		47,9		
A3-12	47,3		47,3		
A-317	47,1		47,1		
A3-24	48,0		48,0		
A3-29	48,4		48,4		
A3-32	48,2		48,2		
A3-37	48,4		48,4		
A3-43	48,4		48,4		
A3-53	48,2		48,2		
A3-60	48,4		48,4		
A3-64	48,0		48,0		
A3-70	48,2		48,2		

For homogeneity

General average (x)	48,0
Sample average sd (s_x)	0,453
Within-sample sd (s_w):	
Between-samples sd (ss):	0,453
S_L in the Proficiency Test:	0,70
S_R in the Proficiency Test:	2,05

Stability test Date: 2019-09-12

Sample	x(a)	x(b)
A3-14	47,84	
A3-38	47,14	
A3-68	46,75	

For stability

General average (y):	47,243333
/x-y/ =	0,7708333

Conclusions

ss = 0,45 0.3*sigma= 1,08

/x-y/ = 0,7708333

Homogeneity: Is ss < 0.3*sigma?
YES

Stability: /x-y/ < 0.3*sigma?
YES