

Proficiency test SPIL-3 (2013)


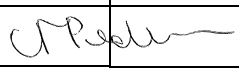
**Organic matter, phosphorus, chloride,
sulphate and suspended matter in
wastewater (synthetic wastewater, effluent)**

Proficiency test SPIL-3 (2013) 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 2013. 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 and DANAK /1/ on 8 October 2013.

2. FEATURES OF THE PROFICIENCY TEST

Participants in the proficiency test were a total of 69 laboratories from Denmark, Sweden and Aaland. A list of participants is shown in Appendix A.

The closing date for submission of results was 30 September 2013. All participants 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.

Four 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-BOD/B1-BOD	BOD5 (w ATU); BOD7 (w ATU)
A1-COD/NVOC /B1-COD/NVOC	COD, NVOC
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	COD _{Cr}	mg/L O ₂	5 – 75	35.4	0.25	9.9
Biochemical oxygen demand, 5 days	BOD ₅ (w. ATU)	mg/L O ₂	2 – 6	1.6*	0.22*	0.3
Biochemical oxygen demand, 7 days	BOD ₇ (w. ATU)	mg/L O ₂	2 – 6	2.1	0.24	0.3
Non-volatile/total organic carbon	NVOC/ TOC	mg/L C	2 – 30	14.0	0.095	3.9
Total phosphorus	TP	mg/L P	0.2 – 2	0.325	0.0021	0.051
Chloride	Cl	mg/L	50 – 700	69.3	0.44	6.8
Sulphate	SO ₄	mg/L	20 – 200	29.0	0.18	3.8
Total suspended solids	TSS	mg/L	20 - 100	29.9	0.23	6.0

*: 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 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.

Only four laboratories used standardised methods for BOD₅ (w ATU). Therefore the value indicated in Table 2 is indicative only.

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. The test revealed a significant difference between the two for TP. However, the difference is numerically small (0.002 mg/L P) and has insignificant influence on the general quality of analyses estimated from the data as well as on the evaluation of accuracy of participating laboratories.

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. The test revealed a significant difference between the two for COD, NVOC, Cl and TSS. Average recovery was 94% (COD), 102% (NVOC), 92% (Cl) and 94% (TSS). The difference could be attributed to influence from laboratories using methods other than those prescribed by the Danish EPA or methods previously shown to give deviation results (method 52 for Cl). The test was repeated after exclusion of the results for the non-approved methods and now showed no significant difference with the exception of TSS. Furthermore, the results of control measurements at Eurofins confirmed the assigned value for all parameters (Appendix E). The assigned values are therefore kept unchanged.

The difference between assigned value and average for TSS is attributed to difficulties for some laboratories to homogenise the samples. This is illustrated by the plot in Figure 1.

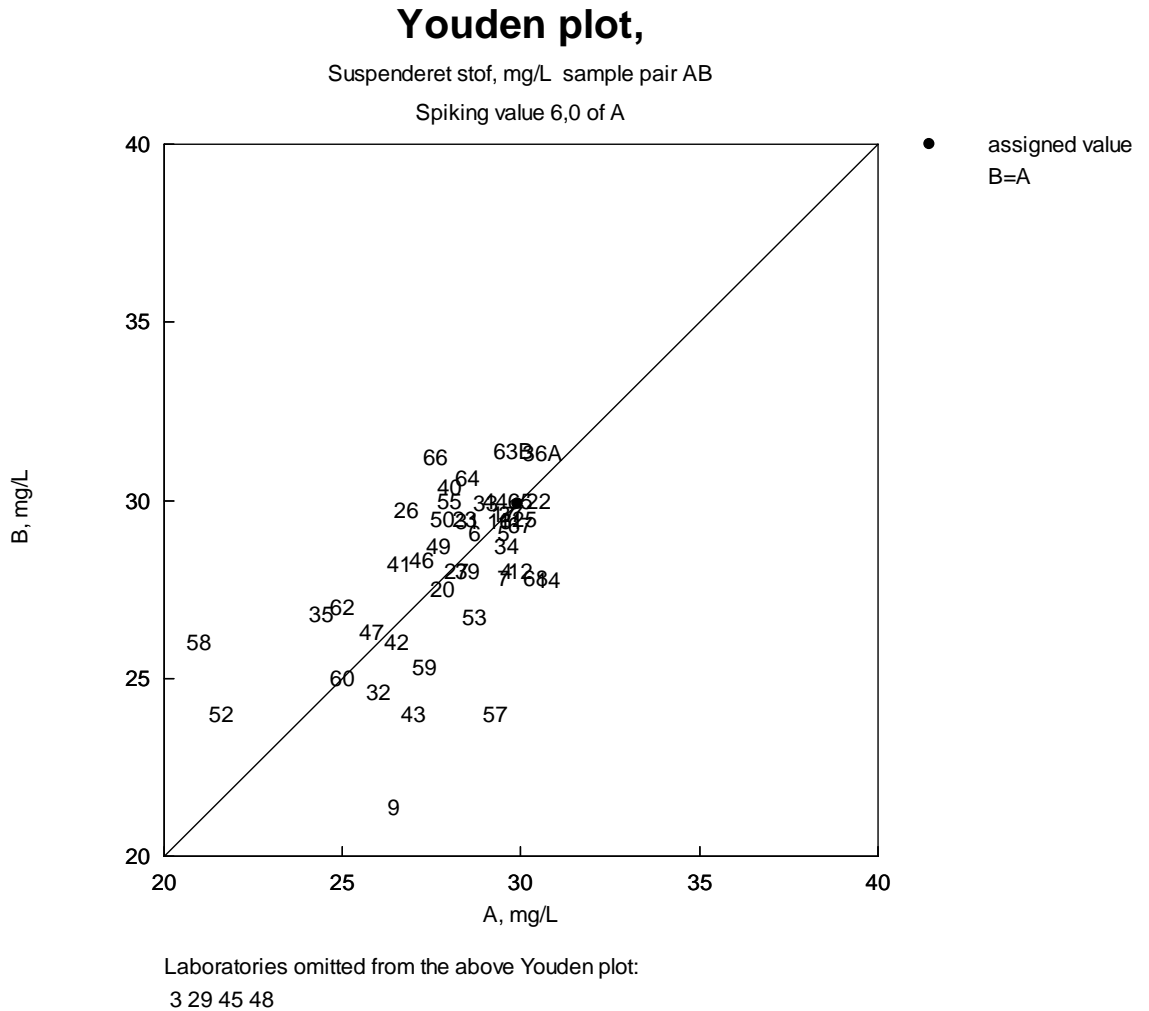


Figure 1 Youden plot for total suspended solids (TSS)

The plot shows a concentration of results around the assigned value and scattered results below the assigned value. The assigned value for TSS is therefore also kept unchanged.

The test of recovery of the assigned value was not performed for BOD₅ (w ATU) since this value is indicative and based upon data from only four participants.

3. **HOMOGENEITY AND STABILITY OF SAMPLES**

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

TP	Homogeneity 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 $0.3 \cdot \sigma$ the standard deviation for evaluation of participants' performance (0.3 · σ) specified by the Danish EPA /5/, whereas the stability is evaluated by comparing the concentration change of the samples to $0.3 \cdot \sigma$. 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 TP the participants could not recover the spike value. The difference between the calculated spike value and that found by the participants is small and the influence on evaluation of participant performance or estimation of general quality of analyses is insignificant.

For COD, NVOC, CI 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 (2013)*, Report to participants, 2013.
- /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. 900 on *quality criteria for environmental measurements*, 17 August 2011 (in Danish).
- /6/ ISO 13528, *Statistical methods for use in proficiency testing by interlaboratory comparison*, 2005.

A P P E N D I C E S

A P P E N D I X A

List of participants

Laboratory	Town	Country
Analyseenheden	Tjele	Denmark
AquaDjurs - Fornæs Renseanlæg	Grenaa	Denmark
Bjergmarken R/A, Roskilde Forsyning	Roskilde	Denmark
CP Kelco ApS, Spildevandslaboratoriet	Ll. Skensved	Denmark
Dianalund Renseanlæg	Dianalund	Denmark
Eurofins Miljø A/S	Vejen	Denmark
Faxe Forsyning, 2 deltagere	Faxe	Denmark
Greve Solrød Forsyning	Greve	Denmark
Grundfos, Process Laboratory, Afd. 3920	Bjerringbro	Denmark
Hach Lange ApS	Brønshøj	Denmark
Halsnæs Kommunale Forsyning A/S	Liseleje	Denmark
Hedensted Spildevand A/S, 2 deltagere	Daugård	Denmark
Hillerød Forsyning Spildevand A/S	Hillerød	Denmark
Holstebro Centralrenseanlæg, Vestforsyning A/S	Holstebro	Denmark
Højmarklaboratoriet	Lem St.	Denmark
Højvang Miljølaboratorium	Dianalund	Denmark
Kerteminde Forsyning - Spildevand A/S	Kerteminde	Denmark
Kolding Spildevand A/S	Kolding	Denmark
Køge-Egnens Renseanlæg	Køge	Denmark
Lynettefællesskabet I/S	København K	Denmark
Mølleåværkets Driftslaboratorium	Lyngby	Denmark
Nyborg Renseanlæg	Nyborg	Denmark
Næstved Centralrenseanlæg	Næstved	Denmark
Provas Haderslev Forsyningservice A/S	Haderslev	Denmark
Randers Spildevand A/S	Randers NØ	Denmark
Rensningsanlæg Øst, Esbjerg	Esbjerg	Denmark
Rensningsanlæg Øst, Esbjerg, Spildevandslaboratoriet	Esbjerg	Denmark
Ringkøbing-Skjern Forsyning A/S, Spildevand	Skjern	Denmark
Ringsted Renseanlæg	Ringsted	Denmark
Rønne Renseanlæg	Rønne	Denmark
SK Forsyning, Slagelse Renseanlæg, 5 deltagere	Slagelse	Denmark
Sun Chemicals, E30	Køge	Denmark
Svendborg Centralrenseanlæg	Skårup Fyn	Denmark
Sønderborg Renseanlæg	Sønderborg	Denmark
Vandsamarbejdet A/S	Holstebro	Denmark
Vejle Spildevand A/S	Vejle	Denmark
Arctic Paper Munkedals AB	Munkedal	Sweden

Laboratory	Town	Country
Eskilstuna Energi och Miljö AB, VA-Laboratoriet	Eskilstuna	Sweden
Eurofins Environment Testing Sweden AB	Lidköping	Sweden
Fiskeby Board AB	Norrköping	Sweden
GRYAAB AB	Göteborg	Sweden
Gästrike Vatten AB	Skutskär	Sweden
Holmen Paper	Norrköping	Sweden
Holmen Paper AB	Hallstavik	Sweden
Kalmar Vatten AB, VA-lab, Avloppsreningsverket	Kalmar	Sweden
Kristianstad Kommun	Kristianstad	Sweden
MittSweden Vatten AB, Fyllanverket lab.	Sundsvall	Sweden
Mjölby Kommun	Mjölby	Sweden
Motala Kommun	Motala	Sweden
Perstorp Oxo AB	Stenungsund	Sweden
Preem AB Göteborg	Göteborg	Sweden
Rottneros Bruk AB	Rottneros	Sweden
SAKAB AB	Kumla	Sweden
Smurfit Kappa Kraftliner	Piteå	Sweden
St1 Refinery AB	Göteborg	Sweden
Södra Cell AB Mönsterås	Mönsterås	Sweden
Södra Cell Mörrum	Mörrum	Sweden
Södra Cell AB, Värö	Väröbacka	Sweden
Vallviks Bruk AB	Vallvik	Sweden
Vattenfall AB, Heat Generation Uppsala	Uppsala	Sweden
Vimmerby Energi o. Miljö, Vattenlab	Vimmerby	Sweden
Västerviks Miljö & Energi AB, Vattenlaboratoriet	Västervik	Sweden
ÅMHM laboratoriet	Jomala	Aaland

A P P E N D I X B

Sample preparation

Stock solution	Prepared from	Concentration
Concentrate A1	17.70 g D-glucose 17.70 g L-glutamic acid milli-Q water up to 24000 g	COD _{Cr} : 1.508 g/kg NVOC: 0.596 g/kg BOD: 1.033 g/kg
Concentrate B1	7.50 g D-glucose 7.50 g L-glutamic acid milli-Q water up to 13000 g	COD _{Cr} : 1.180 g/kg NVOC: 0.466 g/kg BOD: 0.808 g/kg
Stock TP	1.500 g Na-B.glycerophosphate milli-Q water up to 1000.0 g	TP: 151.8 mg/kg
Stock Cl	10.000 g Sodium chloride (NaCl) milli-Q water up to 1000.0 g	Cl: 6.067 g/kg
Stock SO ₄	5.000 g Sodium sulphate (Na ₂ SO ₄) milli-Q water up to 1000.0 g	SO ₄ : 3.381 g/kg
Stock TSS	15.000 g Microcrystalline cellulose milli-Q water up to 1000.0 g	TSS: 15.000 g/kg

A P P E N D I X C

Control of spike value

COD_{Cr}, mg/L O₂
Control of differences within sample pairs

Laboratory	Difference AB	
1	-2.30	
2	0.50	
3	1.30	
4	-1.60	
5	-4.90	
6	-	
7	-1.50	
8	-3.80	
9	-3.50	
10	-	
11	-	
12	0.50	
13	1.10	
14	-	
15	-3.80	
16	-	
17	-0.30	
18	0.30	
19	-0.20	
20	-1.90	
21	-	
22	1.30	
23	0.10	
24	-	
25	-1.60	
26	18.70	UC
27	-1.30	
28	-1.10	
29	-	
30	1.00	
31	-2.10	
32	-2.00	
33	-3.20	
34	-0.80	
35	-9.90	UG
36A	-1.00	
36B	-1.50	
37	0.70	
38	-	
39	-	
40	-2.40	
41	-1.10	
42	0.00	
43	-2.20	
44	0.40	
45	0.10	
46	-1.90	
47	-7.90	
48	5.30	
49	-16.90	UC
50	-	
51	-	
52	5.30	
53	-	
54	-3.80	
55	2.10	

Laboratory	Difference AB
56	-9.30
57	0.20
58	-2.30
59	-0.70
60	5.40
61A	-0.10
61B	6.30
62	-0.40
63A	0.50
63B	1.00
64	-0.50
65	-
66	-1.20
67	1.05
68	-1.40
69	-1.60
No of labs., p	55
No of repl., n	2
d	-0.74
s ²	7.53
s	2.74
t = $\sqrt{p} \cdot (d/s)$	-2.0030
Sign. level, p(t)	0.0502

No test statistics were found to be significant

UC denotes a Cochran outlier

UG denotes a Grubbs outlier

BOD₇ (w. ATU), mg/L O₂
Control of differences within sample pairs

Laboratory	Difference AB
1	-
2	-
3	-
4	-
5	-0.040
6	-
7	-
8	-
9	-
10	-
11	0.290
12	-
13	-
14	-
15	-
16	-
17	-
18	-
19	-
20	-
21	-
22	0.050
23	-
24	-0.300
25	-
26	-
27	-
28	-
29	0.100
30	-
31	0.160
32	-
33	-
34	-
35	0.100
36A	-
36B	-
37	-
38	-
39	-
40	-
41	-
42	-
43	-
44	-
45	-
46	-
47	-
48	-
49	-
50	0.220
51	-
52	-
53	-
54	-
55	-

Laboratory	Difference AB
56	-
57	-
58	-
59	-
60	-
61A	-
61B	-
62	0.060
63A	-
63B	-
64	-
65	-
66	-
67	0.260
68	-
69	-
No of labs., p	10
No of repl., n	2
d	0.090
s ²	0.029
s	0.171
t = $\sqrt{p} \cdot (d/s)$	1.6668
Sign. level, p(t)	0.1299

No test statistics were found to be significant

NVOC, mg/L C
Control of differences within sample pairs

Laboratory	Difference AB	
1	-0.40	
2	-0.30	
3	-	
4	-	
5	-0.10	
6	-	
7	-	
8	-	
9	-7.90	UC
10	-	
11	-0.00	
12	-0.20	
13	-	
14	-	
15	-	
16	0.10	
17	-	
18	-	
19	-	
20	-	
21	-	
22	-	
23	-	
24	-	
25	-	
26	-	
27	0.10	
28	0.50	
29	-0.06	
30	-	
31	-0.00	
32	-	
33	-	
34	-	
35	1.70	UC
36A	-	
36B	-	
37	-0.10	
38	-0.60	UG
39	0.01	
40	-0.10	
41	0.20	
42	0.10	
43	-	
44	0.40	
45	-	
46	-0.10	
47	-0.10	
48	0.40	
49	-	
50	0.30	
51	-	
52	-	
53	-0.30	
54	-	
55	-	

Laboratory	Difference AB
56	-
57	-0.36
58	0.10
59	0.10
60	0.10
61A	-0.20
61B	-
62	0.30
63A	-
63B	0.30
64	-
65	-4.00
66	-
67	0.17
68	-
69	-
No of labs., p	29
No of repl., n	2
d	0.03
s ²	0.06
s	0.24
t = $\sqrt{p} \cdot (d/s)$	0.6795
Sign. level, p(t)	0.5024

No test statistics were found to be significant

UC denotes a Cochran outlier

UG denotes a Grubbs outlier

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

Laboratory	Difference AB
1	0.0010
2	0.0200
3	0.0020
4	0.0000
5	-0.0020
6	-
7	0.0040
8	0.0010
9	0.0170
10	-
11	-0.0010
12	0.0110
13	-0.0010
14	-
15	0.0020
16	0.0050
17	0.0260
18	0.0070
19	0.0010
20	0.1040
21	-
22	0.0010
23	0.0090
24	-0.0010
25	-0.0020
26	0.0090
27	0.0020
28	0.0040
29	0.0000
30	-0.0040
31	-0.0140
32	-0.0010
33	0.0070
34	-0.0010
35	-0.0060
36A	0.0040
36B	0.0030
37	-0.0030
38	-
39	0.0160
40	-0.0010
41	-0.0050
42	0.0010
43	-0.0050
44	-0.0010
45	-0.0090
46	0.0040
47	0.0010
48	0.0040
49	-0.0090
50	0.0020
51	0.0000
52	0.0090
53	-0.0070
54	0.0040
55	0.0010

UC

Laboratory	Difference AB
56	0.0110
57	0.0080
58	0.0060
59	0.0100
60	0.0080
61A	0.0010
61B	-0.0030
62	0.0060
63A	-
63B	0.0050
64	-0.0030
65	0.0010
66	-0.0150
67	0.0010
68	0.0090
69	0.0030
No of labs., p	65
No of repl., n	2
d	0.0024
s ²	0.0000
s	0.0071
t = $\sqrt{p} \cdot (d/s)$	2.6876
Sign. level, p(t)	0.0092 **

* 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)
 UC denotes a Cochran outlier

Difference for sample pair AB is significantly different from 0,
 and data should be corrected with the difference (in spike value),
 during execution of Cochran's test.

Chloride, mg/L
Control of differences within sample pairs

Laboratory	Difference AB	
1	1.80	
2	0.20	
3	3.80	
4	-	
5	0.00	
6	-	
7	-2.30	
8	-	
9	-	
10	-	
11	-	
12	-43.20	UC
13	0.00	
14	-	
15	-6.50	
16	2.10	
17	-	
18	-2.00	
19	-	
20	7.90	
21	-	
22	-	
23	0.60	
24	-0.70	
25	-36.20	UC
26	-8.00	
27	-3.70	
28	4.30	
29	-	
30	-	
31	1.90	
32	1.00	
33	2.10	
34	-	
35	48.00	UC
36A	0.90	
36B	2.60	UG
37	-	
38	-2.20	
39	-	
40	-0.54	
41	0.10	
42	-1.20	
43	-	
44	-0.11	
45	2.70	
46	-2.50	
47	-	
48	-	
49	0.10	
50	-	
51	-0.42	
52	-	
53	-	
54	-	
55	1.80	

Laboratory	Difference AB
56	-
57	-0.25
58	0.16
59	-3.20
60	-
61A	-0.80
61B	-1.30
62	-
63A	-
63B	-0.80
64	2.80
65	-
66	-0.80
67	-
68	-
69	3.50
No of labs., p	38
No of repl., n	2
d	0.01
s ²	8.12
s	2.85
t = $\sqrt{p} \cdot (d/s)$	0.0252
Sign. level, p(t)	0.9801

No test statistics were found to be significant

UC denotes a Cochran outlier

UG denotes a Grubbs outlier

Sulphate, mg/L
Control of differences within sample pairs

Laboratory	Difference AB
1	-
2	-1.20
3	-
4	-
5	0.20
6	-
7	3.00
8	-
9	-
10	-
11	-
12	-
13	-
14	-
15	-0.30
16	-
17	-
18	-
19	-
20	-
21	-
22	-
23	-
24	-
25	-
26	5.90
27	-74.60 UC
28	-
29	-
30	-
31	-
32	-
33	-3.20
34	-
35	47.80 UC
36A	1.10
36B	-
37	-
38	15.80 UC
39	-
40	7.47
41	-0.10
42	-
43	-
44	0.19
45	-
46	-
47	-
48	-
49	-
50	-
51	-0.03
52	-
53	-
54	-
55	-

Laboratory	Difference AB
56	-
57	1.00
58	-2.00
59	-
60	2.30
61A	0.91
61B	-
62	-
63A	-
63B	-
64	-
65	-
66	1.20
67	-
68	-
69	-
No of labs., p	16
No of repl., n	2
d	1.03
s ²	7.22
s	2.69
t = $\sqrt{p} \cdot (d/s)$	1.5292
Sign. level, p(t)	0.1470

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

Total suspended solids, mg/L
Control of differences within sample pairs

Laboratory	Difference AB	
1	-	
2	-	
3	4.00	UG
4	1.60	
5	0.40	
6	-0.40	
7	1.70	
8	-	
9	5.05	
10	-	
11	0.30	
12	2.00	
13	-	
14	2.99	
15	-	
16	0.00	
17	-0.10	
18	-	
19	-	
20	0.30	
21	-	
22	0.50	
23	-1.08	
24	-	
25	0.60	
26	-2.90	
27	0.20	
28	-	
29	66.00	UC
30	-	
31	-0.90	
32	1.40	
33	-0.90	
34	0.90	
35	-2.40	
36A	-0.70	
36B	-	
37	0.10	
38	-	
39	0.50	
40	-2.41	
41	-1.60	
42	0.50	
43	3.00	
44	-0.73	
45	-7.40	UG
46	-1.10	
47	-0.50	
48	-5.50	UG
49	-1.00	
50	-1.70	
51	-	
52	-2.40	
53	2.00	
54	-	
55	-2.00	

Laboratory	Difference AB
56	-
57	5.30
58	-5.00
59	2.00
60	0.00
61A	-
61B	-
62	-2.00
63A	-
63B	-1.60
64	-2.10
65	0.00
66	-3.60
67	0.70
68	2.60
69	-
No of labs., p	47
No of repl., n	2
d	-0.05
s ²	4.15
s	2.04
t = $\sqrt{p} \cdot (d/s)$	-0.1776
Sign. level, p(t)	0.8598

No test statistics were found to be significant

UC denotes a Cochran outlier

UG denotes a Grubbs outlier

A P P E N D I X D

Control of recovery

COD_{Cr}, mg/L O₂
Control of recovery, average of results

Laboratory	Sample pair AB
1	30.25
2	32.85
3	35.35
4	29.80
5	36.55
6	-
7	28.25
8	35.20
9	40.45
10	-
11	-
12	30.05
13	29.55
14	-
15	29.10
16	-
17	33.75
18	31.95
19	33.00
20	29.75
21	-
22	38.05
23	29.85
24	-
25	29.50
26	22.95 UC
27	23.15
28	30.65
29	-
30	34.90
31	35.35
32	34.10
33	29.20
34	31.30
35	3.05 UG
36A	29.60
36B	36.15
37	33.35
38	-
39	-
40	34.95
41	31.95
42	32.10
43	31.60
44	31.30
45	40.05
46	32.75
47	30.05
48	36.45
49	24.85 UC
50	-
51	-
52	38.35
53	-
54	34.90
55	39.05

Laboratory	Sample pair AB
56	37.85
57	38.50
58	29.90
59	32.45
60	42.50
61A	37.25
61B	24.75
62	31.10
63A	33.25
63B	29.80
64	33.25
65	-
66	29.70
67	36.38
68	33.50
69	36.50
No of labs., p	55
No of repl., n	2
m	33.11
s ²	14.89
s	3.86
Assigned value, μ	35.4
Recovery, %	93.5
$t = \sqrt{p} \cdot (m - \mu) / s$	-4.3962
Sign. level, p(t)	0.0001 ***

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

BOD₇ (w. ATU), mg/L O₂
Control of recovery, average of results

Laboratory	Sample pair AB
1	-
2	-
3	-
4	-
5	1.790
6	-
7	-
8	-
9	-
10	-
11	1.875
12	-
13	-
14	-
15	-
16	-
17	-
18	-
19	-
20	-
21	-
22	2.265
23	-
24	2.850
25	-
26	-
27	-
28	-
29	2.050
30	-
31	2.090
32	-
33	-
34	-
35	3.150
36A	-
36B	-
37	-
38	-
39	-
40	-
41	-
42	-
43	-
44	-
45	-
46	-
47	-
48	-
49	-
50	2.430
51	-
52	-
53	-
54	-
55	-

Laboratory	Sample pair AB
56	-
57	-
58	-
59	-
60	-
61A	-
61B	-
62	1.840
63A	-
63B	-
64	-
65	-
66	-
67	2.230
68	-
69	-
No of labs., p	10
No of repl., n	2
m	2.257
s ²	0.199
s	0.446
Assigned value, μ	2.1
Recovery, %	107.5
$t = \sqrt{p} \cdot (m - \mu) / s$	1.1137
Sign. level, p(t)	0.2943

No test statistics were found to be significant

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

Laboratory	Sample pair AB	
1	14.70	
2	15.05	
3	-	
4	-	
5	14.05	
6	-	
7	-	
8	-	
9	13.85	UC
10	-	
11	14.80	
12	14.90	
13	-	
14	-	
15	-	
16	13.65	
17	-	
18	-	
19	-	
20	-	
21	-	
22	-	
23	-	
24	-	
25	-	
26	-	
27	13.65	
28	13.95	
29	14.19	
30	-	
31	14.50	
32	-	
33	-	
34	-	
35	14.65	UC
36A	-	
36B	-	
37	14.45	
38	11.57	UG
39	14.31	
40	14.42	
41	13.60	
42	14.95	
43	-	
44	14.60	
45	-	
46	14.85	
47	14.65	
48	13.80	
49	-	
50	14.35	
51	-	
52	-	
53	13.65	
54	-	
55	-	

Laboratory	Sample pair AB	
56	-	
57	15.08	
58	13.79	
59	14.85	
60	13.75	
61A	14.80	
61B	-	
62	14.25	
63A	-	
63B	14.15	
64	-	
65	15.30	UC
66	-	
67	13.35	
68	-	
69	-	
No of labs., p	29	
No of repl., n	2	
m	14.31	
s ²	0.26	
s	0.51	
Assigned value, μ	14.0	
Recovery, %	102.2	
$t = \sqrt{p} \cdot (m-\mu)/s$	3.3229	
Sign. level, p(t)	0.0025	**

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 UG denotes a Grubbs outlier

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

Laboratory	Sample pair AB
1	0.3025
2	0.3180
3	0.3340
4	0.3230
5	0.3480
6	-
7	0.3400
8	0.3095
9	0.3215
10	-
11	0.3165
12	0.3725
13	0.3125
14	-
15	0.3540
16	0.3245
17	0.3600
18	0.3135
19	0.3015
20	0.3300
21	-
22	0.3295
23	0.3165
24	0.3285
25	0.3120
26	0.3385
27	0.3250
28	0.3040
29	0.3170
30	0.3370
31	0.2970
32	0.3425
33	0.3365
34	0.3035
35	0.3240
36A	0.3500
36B	0.3215
37	0.3325
38	-
39	0.3200
40	0.3325
41	0.3285
42	0.2995
43	0.3395
44	0.3255
45	0.3345
46	0.3310
47	0.3195
48	0.2860
49	0.3245
50	0.3170
51	0.3170
52	0.2905
53	0.3475
54	0.3130
55	0.3295

UC

Laboratory	Sample pair AB
56	0.3545
57	0.3120
58	0.3290
59	0.3010
60	0.3230
61A	0.3215
61B	0.3005
62	0.3150
63A	-
63B	0.3755
64	0.3295
65	0.3295
66	0.3505
67	0.3185
68	0.3235
69	0.3225
No of labs., p	65
No of repl., n	2
m	0.3251
s ²	0.0003
s	0.0180
Assigned value, μ	0.325
Recovery, %	100.0
$t = \sqrt{p} \cdot (m - \mu) / s$	0.0242
Sign. level, p(t)	0.9808

No test statistics were found to be significant

UC denotes a Cochran outlier

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

Laboratory	Sample pair AB	
1	62.30	
2	78.30	
3	50.10	
4	-	
5	67.90	
6	-	
7	66.35	
8	-	
9	-	
10	-	
11	-	
12	536.60	UC
13	69.30	
14	-	
15	43.75	
16	70.15	
17	-	
18	67.40	
19	-	
20	63.75	
21	-	
22	-	
23	66.80	
24	67.15	
25	511.10	UC
26	62.30	
27	68.05	
28	61.75	
29	-	
30	-	
31	69.75	
32	65.60	
33	41.55	
34	-	
35	45.70	UC
36A	41.75	
36B	22.80	UG
37	-	
38	64.10	
39	-	
40	68.00	
41	68.25	
42	73.60	
43	-	
44	68.75	
45	58.85	
46	68.15	
47	-	
48	-	
49	66.65	
50	-	
51	77.61	
52	-	
53	-	
54	-	
55	63.10	

Laboratory	Sample pair AB
56	-
57	66.03
58	69.24
59	75.60
60	-
61A	66.80
61B	49.65
62	-
63A	-
63B	66.20
64	63.80
65	-
66	44.80
67	-
68	-
69	63.55
No of labs., p	38
No of repl., n	2
m	63.86
s ²	84.44
s	9.19
Assigned value, μ	69.3
Recovery, %	92.2
$t = \sqrt{p} \cdot (m - \mu) / s$	-3.6488
Sign. level, p(t)	0.0008 ***

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

Laboratory	Sample pair AB
1	-
2	25.60
3	-
4	-
5	29.70
6	-
7	8.90
8	-
9	-
10	-
11	-
12	-
13	-
14	-
15	32.35
16	-
17	-
18	-
19	-
20	-
21	-
22	-
23	-
24	-
25	-
26	27.95
27	67.20 UC
28	-
29	-
30	-
31	-
32	-
33	29.70
34	-
35	52.40 UC
36A	32.55
36B	-
37	-
38	15.10 UC
39	-
40	26.82
41	27.55
42	-
43	-
44	27.09
45	-
46	-
47	-
48	-
49	-
50	-
51	28.94
52	-
53	-
54	-
55	-

Laboratory	Sample pair AB
56	-
57	32.17
58	29.00
59	-
60	61.35
61A	5.45
61B	-
62	-
63A	-
63B	-
64	-
65	-
66	26.70
67	-
68	-
69	-
No of labs., p	16
No of repl., n	2
m	28.24
s ²	137.29
s	11.72
Assigned value, μ	29.0
Recovery, %	97.4
$t = \sqrt{p} \cdot (m-\mu)/s$	-0.2599
Sign. level, p(t)	0.7985

No test statistics were found to be significant

UC denotes a Cochran outlier

Total suspended solids, mg/L
Control of recovery, average of results

Laboratory	Sample pair AB	
1	-	
2	-	
3	42.00	UG
4	28.80	
5	29.30	
6	28.90	
7	28.65	
8	-	
9	23.93	
10	-	
11	29.55	
12	29.00	
13	-	
14	29.27	
15	-	
16	29.40	
17	29.55	
18	-	
19	-	
20	27.65	
21	-	
22	30.25	
23	28.95	
24	-	
25	29.80	
26	28.25	
27	28.10	
28	-	
29	313.00	UC
30	-	
31	28.95	
32	25.30	
33	29.45	
34	29.15	
35	25.60	
36A	30.95	
36B	-	
37	29.65	
38	-	
39	28.25	
40	29.19	
41	27.40	
42	26.25	
43	25.50	
44	29.64	
45	5.00	UG
46	27.75	
47	26.05	
48	-1.95	UG
49	28.20	
50	28.65	
51	-	
52	22.80	
53	27.70	
54	-	
55	29.00	

Laboratory	Sample pair AB
56	-
57	26.65
58	23.50
59	26.30
60	25.00
61A	-
61B	-
62	26.00
63A	-
63B	30.60
64	29.55
65	30.00
66	29.40
67	29.65
68	29.10
69	-
No of labs., p	47
No of repl., n	2
m	28.10
s ²	3.71
s	1.93
Assigned value, μ	29.9
Recovery, %	94.0
$t = \sqrt{p} \cdot (m-\mu)/s$	-6.4224
Sign. level, p(t)	0.0000 ***

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A P P E N D I X E

Concentration level

Concentration level		SPIL-3 (2013)									
Parameter	Unit	Sample	Bottle no.	I	II	Bottle Average	Sample Average	Assigned value	Spike Measured Assigned		
COD	mg/L O ₂	A1	68	45,0	45,4	45,2	45,3	45,2	8,8	9,9	
			70	45,1	46,9	46,0					
			78	45,0	44,6	44,8					
		B1	72	35,7	36,7	36,2	36,6	35,4			
			73	36,3	37,5	36,9					
			75	36,4	36,7	36,6					
Total phosphorus	mg/L P	A2	70	0,309	0,320	0,315	0,319	0,325	0,051	0,051	
			72	0,320	0,319	0,320					
			77	0,324	0,321	0,323					
		B2	76	0,372	0,367	0,370	0,370	0,376			
			68	0,372	0,370	0,371					
			73	0,368	0,371	0,370					
Chloride	mg/L	A2	70	63,4	63,2	63,3	64,62	69,3	33,5	6,8	
			72	64,7	65,5	65,1					
			77	65,3	65,6	65,5					
		B2	76	97,8	100,5	99,2	98,10	76,1			
			68	97,4	99,9	98,7					
			73	96,9	96,1	96,5					
Sulphate	mg/L	A2	70	<40			<40	29,0	-	3,8	
			72	<40							
			77	<40							
		B2	76	<40			<40	32,8			
			68	<40							
			73	<40							
Total suspended solids	mg/L	A3	58	39,2		39,2	37,1	35,9	6,6	6,0	
			60	36,4		36,4					
			62	35,7		35,7					
		B3	59	30,4		30,4	30,5	29,9			
			61	30,8		30,8					
			63	30,4		30,4					

A P P E N D I X F

Homogeneity and stability

PT:	SPIL-3 2013
Parameter:	TP
Unit:	mg/L P
Sigma:	0,039 1,3* $S_{T\max}$

Responsible for tests: agk/suv

6,5% level or 1,3* $S_{T\max}$

Homogeneity test Date: 2013-08-29

Sample	x(a)	x(b)	average	sd	sd^2
A2-1	0,355	0,358	0,357	0,0021	4,5E-06
A2-8	0,335	0,333	0,334	0,0014	2,0E-06
A2-16	0,334	0,335	0,335	0,0007	5,0E-07
A2-24	0,339	0,334	0,337	0,0035	1,3E-05
A2-32	0,335	0,336	0,336	0,0007	5,0E-07
A2-40	0,339	0,345	0,342	0,0042	1,8E-05
A2-48	0,336	0,338	0,337	0,0014	2,0E-06
A2-56	0,337	0,335	0,336	0,0014	2,0E-06
A2-64	0,334	0,336	0,335	0,0014	2,0E-06
A2-72	0,344	0,331	0,338	0,0092	8,4E-05
A2-80	0,338	0,344	0,341	0,0042	1,8E-05
A2-88	0,336	0,337	0,337	0,0007	5,0E-07

For homogeneity

General average (x)	0,339
Sample average sd (s_x)	0,0062
Within-sample sd (s_w):	0,0035
Between-samples sd (ss):	0,0056
S_L in the Proficiency Test:	0,0176
S_R in the Proficiency Test:	0,0183

Stability test Date:

Sample	x(a)	x(b)

For stability

General average (y):

|x-y| =

Conclusions

ss = 0,0056		0.3*sigma= 0,012	
x-y =			
Analytical quality	Is $s_w < 0,15*\sigma$	YES	
Homogeneity:	Is ss < 0.3*sigma?	YES	
Stability:	x-y < 0.3*sigma?	No data	

PT:	SPIL-3 2013
Parameter:	Total suspended solids
Unit:	mg/L
Sigma:	3,9 1,3*S_{T max}

Responsible for tests: agk

6,5% level or 1,3*S_{T max}

Homogeneity test

Date: 2013-08-28

Sample	x(a)	x(b)	average	sd	sd^2
B3-1	30,2		30,2		
B3-8	30,2		30,2		
B3-16	30,3		30,3		
B3-24	31,1		31,1		
B3-32	26,8		26,8		
B3-40	29,7		29,7		
B3-48	30,1		30,1		
B3-56	30,7		30,7		
B3-64	29,9		29,9		
B3-70	30,1		30,1		
B3-72	30,9		30,9		
B3-80	28,4		28,4		

For homogeneity

General average (x)	29,9
Sample average sd (s _x)	1,18
Within-sample sd (s _w):	
Between-samples sd (ss):	1,18
S _L in the Proficiency Test:	1,63
S _R in the Proficiency Test:	2,18

Stability test

Date: 2013-09-12

Sample	x(a)	x(b)
B3-59	30,4	
B3-61	30,8	
B3-63	30,4	

For stability

General average (y):	30,5
x-y =	0,7

Conclusions

ss = 1,2		0.3*sigma= 1,2	
x-y = 0,7			
Analytical quality	Is s _w < 0,15*sigma		
	No data		
Homogeneity:	Is ss < 0.3*sigma?		
	YES		
Stability:	x-y < 0.3*sigma?		
	YES		