

**Proficiency test SPIL-1
(2015)**

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

Proficiency test SPIL-1 (2015) 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 March 2015. 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 first issued in a report to all participants /1/ on 20 April 2015. On 13 May 2015 a revised report was issued /2/ in which the assigned values for COD_{Cr} and total suspended solids were changed. The revised report was sent to the affected laboratories.

2 FEATURES OF THE PROFICIENCY TEST

Participants in the proficiency test were a total of 73 laboratories from Denmark, Norway and Sweden. A list of participants is shown in Appendix A.

The closing date for submission of results was 27 March 2015. All participants except laboratory no. 53 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.

Eight 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 effluent. Sample preparation is described in Appendix B.

Table 1 Samples in the proficiency test

Sample name	Parameters
A1/B1 COD _{Cr} /NVOC	COD _{Cr} , NVOC
A1/B1 BOD	BOD ₅ , BOD ₇
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) /3/ and as described in detail in Spliid (1992) /4/. 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 /5/.

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 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	45	7.9	8
Five days biochemical oxygen demand	BOD ₅ (w. ATU)	mg/L O ₂	2 - 6	3.8	0.61	0.7
Seven days biochemical oxygen demand	BOD ₇ (w. ATU)	mg/L O ₂	2 - 6	4.1	0.24	0.7
Non-volatile/total organic carbon	NVOC/TOC	mg/L C	2 - 30	19.3	0.56	3.7
Total phosphorus	TP	mg/L P	0.2 - 2	0.75	0.014	0.11
Chloride	Cl	mg/L	50 - 700	193	2.9	23
Sulphate	SO ₄	mg/L	20 - 200	69	1.8	7
Suspended matter	TSS	mg/L	20 - 100	39.6	0.73	6.0

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.

In order to ensure optimal use of the data, the assigned value is calculated as the average of the median for both samples in the sample pair after subtraction of the spike value. The spike values are calculated from sample preparation.

The assigned values for all parameters except Cl and SO₄ are operationally defined and are consensus values based upon the median for method no. 77 and 77A (COD_{Cr}), method no. 1 (NVOC), method no. 1 and 2 (TP), or method no. 2 (TSS), which are the methods required by the Danish EPA /6/. Assigned values for BOD are based upon standardised methods (method no. 1 - 4). A list of method identification numbers is found in the report to participants /1/ /2/. Assigned values for Cl and SO₄ are consensus values for all laboratories based on the median.

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 revealed a significant difference between the two for NVOC and TP.

In the case of NVOC the difference could not be attributed to specific methods or other conditions. Furthermore, the difference had a significant influence on the general quality of analyses. It was therefore decided to change the spike value from the calculated value based on sample preparation to a value based on consensus between participating laboratories, i.e. the difference between the medians for sample A1 and B1.

For TP the difference 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. 3, 4, 6, 41, 42, 42A, and 9 and now showed no significant difference.

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 showed no

significant difference between the two and the control of assigned value at Eurofins confirmed the value (Appendix E).

3 **HOMOGENEITY OF SAMPLES**

The homogeneity of samples was tested using the following parameters as indicators:

COD_{Cr} Homogeneity test

TP Homogeneity 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).

Homogeneity is evaluated by comparing the between bottle variance to $0.3 \cdot \hat{\sigma}$ the standard deviation for evaluation of participants' performance ($0.3 \cdot \hat{\sigma}$) specified by the Danish EPA /6/. This test ensures that heterogeneity will not have negative influence on the evaluation of participant performance /7/.

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 homogeneity show that the samples are homogeneous.

4 CONCLUSION

The quality control performed, including test of sample 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 NVOC and TP the participants could not recover the spike value. For NVOC the difference between the calculated spike value and that found by the participants as well the influence on evaluation of participant performance or estimation of general quality of analyses was found to be significant. It was therefore decided to base the spike value for NVOC upon participant data. The final spike value is the difference between medians for sample A1 and B1. In the case of TP the difference 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. 3, 4, 6, 41, 42, 42A, and 9 and now showed no significant difference.

5 REFERENCES

- /1/ Eurofins A/S, *Proficiency test SPIL-1 (2015)*, Report to participants, April 2015.
- /2/ Eurofins A/S, *Proficiency test SPIL-1 (2015)*, Revised report to participants, May 2015.
- /3/ 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.
- /4/ Spliid, H., *Procedure and analysis of data for proficiency tests and environmental analyses*, Report to Danish Environmental Protection Agency, 1994 (in Danish).
- /5/ Eurofins A/S, *Schedule for a proficiency test*, document may be downloaded from www.eurofins.dk/proficiencytest.
- /6/ Ministry of Environment regulation no. 231 on *quality criteria for environmental measurements*, 5 March 2014 (in Danish).
- /7/ ISO 13528, *Statistical methods for use in proficiency testing by interlaboratory comparison*, 2005.

A N N E X E S

ANNEX A LIST OF PARTICIPANTS

Laboratory	Town	Country
AquaDjurs - Fornæs Renseanlæg	Grenaa	Denmark
Bjergmarken R/A, Roskilde Forsyning	Roskilde	Denmark
CP Kelco ApS, Spildevandslaboratoriet	Ll. Skensved	Denmark
Esbjerg Forsyning Spildevandslaboratorium	Esbjerg	Denmark
Esbjerg Forsyning Spildevandslaboratorium	Esbjerg	Denmark
Eurofins Miljø A/S	Vejen	Denmark
Faxe Forsyning	Faxe	Denmark
Faxe Forsyning	Faxe	Denmark
FORCE Technology	Holstebro	Denmark
Frederikssund Forsyning	Frederikssund	Denmark
Greve Solrød Forsyning	Greve	Denmark
Halsnæs Kommunale Forsyning A/S	Liseleje	Denmark
Hedensted Spildevand A/S	Daugård	Denmark
Hedensted Spildevand A/S	Daugård	Denmark
Holbæk Forsyning	Holbæk	Denmark
Holstebro Centralrenseanlæg, Vestforsyning A/S	Holstebro	Denmark
Kerteminde Forsyning - Spildevand A/S	Kerteminde	Denmark
Kolding Spildevand A/S	Bjert	Denmark
Køge-Egnens Renseanlæg	Køge	Denmark
Middelfart Spildevand A/S	Middelfart	Denmark
Mølleåværkets Driftslaboratorium	Lyngby	Denmark
Nyborg Renseanlæg	Nyborg	Denmark
NK-Spildevand Lab	Næstved	Denmark
Provas Haderslev Forsyningservice A/S	Haderslev	Denmark
Randers Spildevand A/S	Randers SØ	Denmark
Rønne Renseanlæg	Rønne	Denmark
SK Forsyning, Slagelse Renseanlæg	Slagelse	Denmark
SK Forsyning, Slagelse Renseanlæg	Slagelse	Denmark
SK Forsyning, Slagelse Renseanlæg	Slagelse	Denmark
SK Forsyning, Slagelse Renseanlæg	Slagelse	Denmark
SK Forsyning, Slagelse Renseanlæg	Slagelse	Denmark
Svendborg Centralrenseanlæg	Skårup Fyn	Denmark
Vandrens - Stignæs Industripark A/S	Skælskør	Denmark
Vejle Spildevand A/S	Vejle	Denmark

Biofos A/S	København K	Denmark
Eurofins Environment Testing Norway AS	Moss	Norway
AB Borlänge Energi, Reningsverket	Borlänge	Sweden
Akzo Nobel Functional Chemicals AB Cellulosic Specialties QHSE	Domsjö	Sweden
Ernemar Laboratoriet	Oskarshamn	Sweden
Eurofins Environment Testing Sweden AB	Lidköping	Sweden
Fiskeby Board AB	Norrköping	Sweden
GRYAAB AB	Göteborg	Sweden
Hallsta Pappersbruk	Norrköping	Sweden
Holmen Paper AB	Hallstavik	Sweden
Iggesund Paperboard, Cell & Miljölab	Iggesund	Sweden
Ineos Sweden AB	Stenungsund	Sweden
Kalmar Vatten AB, VA-lab, Avloppsreningsverket	Kalmar	Sweden
Kristianstad Kommun	Kristianstad	Sweden
Käppalaverket	Lidingö	Sweden
Laboratoriet vid Smedjeholms	Falkenberg	Sweden
MittSverige Vatten AB, Fillanverket lab.	Sundsvall	Sweden
Mjölby Kommun	Mjölby	Sweden
Motala Kommun	Motala	Sweden
Nordic Sugar	Eslöv	Sweden
NSVA/Öresundsverket	Helsingborg	Sweden
Nyköpings Kommun	Nyköping	Sweden
Nynäshamn Kommun, VA-avdelningen	Nynäshamn	Sweden
Piteå Renhållning & Vatten AB	Öjebyn	Sweden
Preemraff Lysekil	Lysekil	Sweden
Reningsverket Aggerud	Karlskoga	Sweden
SAKAB AB	Kumla	Sweden
Smurfit Kappa Kraftliner	Piteå	Sweden
St1 Refinery AB	Göteborg	Sweden
Stora Enso Paper	Hyltebruk	Sweden
Södra Cell AB Mönsterås	Mönsterås	Sweden
Södra Cell Mörrum	Mörrum	Sweden
Södra Cell AB, Värö	Väröbacka	Sweden
Tekniska förvaltningen, Avloppsverket, Laboratoriet	Örebro	Sweden
Uddebo Laboratorium	Luleå	Sweden

Vallviks Bruk AB	Vallvik	Sweden
Vimmerby Energi o. Miljö, Vattenlab	Vimmerby	Sweden
VIVAB	Varberg	Sweden
Västerviks Miljö & Energi AB, Vattenlaboratoriet	Västervik	Sweden

ANNEX B SAMPLE PREPARATION

Stock solution	Prepared from	Concentration
Concentrate A1	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
Concentrate B1	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
Stock TP	1.507 g Na-beta.glycerophosphate, 5 H ₂ O milli-Q water up to 1000.0 g	TP: 152.5 mg/kg
Stock Cl	10.0288 g Sodium chloride (NaCl) milli-Q water up to 1000.0 g	Cl: 6.084 g/kg
Stock SO ₄	5.0041 g Sodium sulphate (Na ₂ SO ₄) milli-Q water up to 1000.0 g	SO ₄ : 3.384 g/kg
Stock TSS	14.999 g Microcrystalline cellulose milli-Q water up to 1000.0 g	TSS: 14.999 g/kg

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 2.5 mL of concentrate A1 is diluted up to 100 mL with filtered water from Varde sewage treatment plant	a + 29.5	b + 11.7					
B1-COD/NVOC	At the laboratory 2.5 mL of concentrate B1 is diluted up to 100 mL with filtered water from Varde sewage treatment plant	a + 37.7	b + 14.9					
A1-BOD	At the laboratory 6 mL of concentrate A1 is diluted up to 2000 mL with filtered water from Varde sewage treatment plant			c + 2.4				
B1-BOD	At the laboratory 6 mL of concentrate B1 is diluted up to 2000.0 mL with filtered water from Varde sewage treatment plant			c + 3.1				
A2	100.03 g stock TP 600.0 g stock Cl 600.0 g stock SO ₄ Filtered water from Varde sewage treatment plant up to 70.00 kg				d + 0.218	e + 52.1	f + 29.0	
B2	30.0023 g stock TP 159.99 g stock Cl 89.99 g stock SO ₄ Sample A2 up to 40.00 kg				0.993 · (d+0.218) + 0.114	0.993 · (e + 52.1) + 24.3	0.993 · (f + 29.0) + 7.61	
A3	At the laboratory 1000.0 mL of filtered water from Varde sewage treatment plant is added to 3.2 mL stock TSS							g + 47.8
B3	At the laboratory 1000.0 mL of filtered water from Varde sewage treatment plant is added to 2.8 mL stock TSS							g + 41.9

ANNEX C CONTROL OF SPIKE VALUES

COD_{Cr}, mg/L O₂

Control of differences within sample pairs

Laboratory	Difference AB	
1	-0.30	
2	-2.65	
3	-0.60	
4	-	
5	-8.00	
6	-	
7	-	
8	0.90	
9	1.20	
10A	0.40	
10B	-0.20	
11	-	
12	-1.80	
13	-	
14	-0.70	
15	-	
16	-2.50	
17	-2.00	
18	-	
19	1.90	
20	-1.00	
21	0.60	
22	-	
23	-0.10	
24	-2.00	
25A	-	
25B	-	
26	8.70	
27	-	
28	2.00	
29	-0.10	
30A	4.00	
30B	1.20	
31	3.30	
32	-0.80	
33	-1.80	
34	-0.50	
35	4.80	
36	-3.00	
37	-	
38	1.10	
39	-	
40	1.60	
41	103.83	UC
42	0.50	
43	-2.50	
44	-	
45	-	
46	-4.00	
47	2.20	
48	-1.00	

49	-8.50	
50A	10.90	
50B	-	
50C	-	
51	-1.00	
52	0.00	
54	2.40	
55	-6.20	
56	-	
57	-	
58	0.40	
59	0.00	
60	0.50	
61	-	
62	-1.00	
63	-	
64	-	
65	0.78	
66	-	
67	-3.60	
68A	-0.90	
68B	1.30	
68C	2.50	
69	0.40	
70	-	
71	-3.50	UG
72	-1.30	
73	-2.80	
No of labs., p	53	
No of repl., n	2	
d	-0.14	
s ²	10.42	
s	3.23	
t = $\sqrt{p} \cdot (d/s)$	-0.3093	
Sign. level, p(t)	0.7583	

No test statistics were found to be significant

UC denotes a Cochran outlier

UG denotes a Grubbs outlier

BOD₅, mg/L O₂
Control of differences within sample pairs

Laboratory	Difference AB
1	0.460
2	-
3	-0.630
4	-
5	1.790
6	-
7	0.470
8	-
9	-1.830
10A	-
10B	-
11	-
12	-
13	-
14	-
15	-
16	-
17	-
18	-
19	0.850
20	-
21	-0.300
22	-
23	-0.350
24	-
25A	-
25B	-
26	0.110
27	-
28	-
29	0.010
30A	-
30B	-
31	-0.080
32	-
33	-
34	-
35	-
36	1.910
37	-
38	-
39	-
40	0.200
41	-
42	-
43	-
44	-
45	-
46	-0.390
47	3.200
48	-0.320
49	-
50A	0.040
50B	-
50C	-
51	-1.200

52	-
54	-
55	-
56	-
57	-
58	-
59	-
60	0.040
61	-
62	-
63	-
64	-
65	-
66	-
67	-
68A	-0.100
68B	0.050
68C	-
69	-
70	-
71	-
72	-
73	-
No of labs., p	21
No of repl., n	2
d	0.187
s ²	1.162
s	1.078
t = $\sqrt{p} \cdot (d/s)$	0.7956
Sign. level, p(t)	0.4356

No test statistics were found to be significant

BOD₇, mg/L O₂
Control of differences within sample pairs

Laboratory	Difference AB
1	-
2	-
3	-
4	-
5	2.120 UG
6	-
7	-
8	-
9	-
10A	-
10B	-
11	-
12	-
13	-
14	-
15	0.000
16	-
17	-0.150
18	-
19	-
20	-
21	-
22	-
23	-
24	0.000
25A	-
25B	-
26	-
27	-0.210
28	-
29	-
30A	-
30B	-
31	-
32	0.260
33	-1.240 UG
34	-
35	-
36	-
37	-
38	-
39	-
40	-
41	-
42	-
43	-
44	0.155
45	0.100
46	-
47	-
48	1.200
49	-
50A	-
50B	-
50C	-
51	-

52	-
54	-
55	-
56	0.190
57	-
58	-
59	-
60	-
61	-
62	-
63	-
64	0.350
65	-
66	0.010
67	-
68A	-
68B	-
68C	-
69	-
70	-
71	-
72	-
73	-
No of labs., p	11
No of repl., n	2
d	0.173
s ²	0.144
s	0.379
t = $\sqrt{p} \cdot (d/s)$	1.5152
Sign. level, p(t)	0.1607

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

NVOC, mg/L C

Control of differences within sample pairs

Laboratory	Difference AB	
1	-	
2	-	
3	-	
4	-	
5	0.40	
6	0.10	
7	3.08	UC
8	-	
9	-	
10A	-	
10B	-0.10	
11	-	
12	0.20	
13	0.10	
14	-	
15	-1.10	
16	0.48	UG
17	-0.30	UG
18	0.47	
19	-	
20	-	
21	-0.10	
22	-0.30	
23	-	
24	-0.23	
25A	-0.61	
25B	-	
26	-	
27	-0.10	
28	-	
29	0.30	
30A	-	
30B	-	
31	-	
32	0.10	
33	0.10	
34	-	
35	-	
36	-0.50	UG
37	0.40	
38	-	
39	0.20	
40	-	
41	-	
42	0.20	
43	-	
44	-0.67	
45	-0.26	
46	-	
47	-	
48	-0.09	UG
49	-0.80	
50A	-0.40	
50B	-	
50C	-	
51	-	

52	-
54	-0.30
55	-0.10
56	0.70
57	0.10
58	0.50
59	0.70
60	-
61	-0.10
62	-0.10
63	0.10
64	-0.20
65	-
66	-0.00
67	-
68A	1.20
68B	-
68C	-
69	-
70	1.00
71	-
72	-0.10
73	-
No of labs., p	36
No of repl., n	2
d	0.04
s ²	0.22
s	0.47
t = $\sqrt{p} \cdot (d/s)$	0.4627
Sign. level, p(t)	0.6465

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	0.0080	
2	0.0040	
3	0.0300	
4	0.0080	
5	0.0140	
6	0.0220	
7	-0.0020	
8	-0.0080	
9	0.1750	UC
10A	-0.0060	
10B	0.0010	
11	0.0140	
12	0.0190	
13	0.0100	
14	0.0250	
15	-0.0100	
16	0.0300	
17	-0.0250	
18	0.0230	
19	0.0620	UG
20	0.0200	
21	0.0200	
22	0.0100	
23	0.0110	
24	-0.0100	
25A	-	
25B	-	
26	-0.0060	
27	-0.0050	
28	0.0380	
29	0.0220	
30A	0.0000	
30B	0.0100	
31	0.0060	
32	0.0070	
33	-0.0100	
34	0.0190	
35	0.0100	
36	-0.0400	
37	0.0250	
38	0.0260	
39	-	
40	0.0300	
41	-0.1400	UC
42	0.0100	
43	0.0230	
44	0.0100	
45	-0.0470	
46	0.0500	
47	0.0470	
48	0.0100	UG
49	0.1100	UC
50A	0.0250	
50B	0.0240	
50C	0.0280	
51	0.0080	

52	-0.0080	
54	0.0150	
55	0.0880	
56	0.0090	
57	0.0180	
58	0.0090	
59	0.0200	
60	0.0090	
61	0.0350	
62	0.0170	
63	0.0340	
64	0.0070	
65	0.0160	
66	0.0060	
67	0.0790	UG
68A	0.0040	
68B	-	
68C	-	
69	0.0300	
70	0.0250	
71	0.2700	UC
72	0.0220	
73	0.0070	
No of labs., p	67	
No of repl., n	2	
d	0.0131	
s ²	0.0004	
s	0.0195	
t = $\sqrt{p} \cdot (d/s)$	5.5171	
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)

UC denotes a Cochran outlier

UG denotes a Grubbs 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	-3.0	
2	-	
3	0.0	
4	-	
5	0.8	
6	-	
7	1.0	
8	56.0	UC
9	-3.0	
10A	-4.0	
10B	0.0	
11	-	
12	-	
13	-	
14	-	
15	-	
16	-	
17	3.0	
18	-	
19	-1.0	
20	-1.0	
21	-6.0	
22	-	
23	1.0	
24	-	
25A	0.1	
25B	-1.2	
26	9.0	
27	-	
28	-	
29	4.0	
30A	-1.0	
30B	-8.0	
31	0.0	
32	-	
33	1.0	
34	1.3	
35	-11.0	
36	0.0	
37	0.0	
38	-9.0	
39	2.3	
40	-5.0	
41	2.0	
42	-	
43	-	
44	-	
45	-	
46	8.0	
47	5.0	
48	-6.9	
49	-4.0	
50A	2.0	
50B	0.0	
50C	-	
51	-	

52	-	
54	6.0	
55	-	
56	-	
57	-	
58	-	
59	-4.0	
60	-1.0	
61	-5.0	
62	-	
63	-	
64	-	
65	-	
66	-	
67	2.6	UG
68A	-	
68B	-	
68C	-	
69	-4.0	
70	-	
71	-6.0	
72	-	
73	-6.5	
No of labs., p	41	
No of repl., n	2	
d	-1.1	
s ²	19.2	
s	4.4	
t = $\sqrt{p} \cdot (d/s)$	-1.5733	
Sign. level, p(t)	0.1235	

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	-
3	-0.10
4	-
5	-0.20
6	-
7	-
8	-
9	1.90
10A	-
10B	1.70
11	-
12	-
13	-
14	-
15	-
16	2.30
17	1.00
18	-
19	-
20	-
21	-
22	-
23	-
24	-
25A	-1.30
25B	-
26	-
27	-
28	-
29	8.20
30A	-5.00
30B	-
31	-
32	-
33	-
34	-1.10
35	-
36	0.10
37	0.30
38	1.20
39	-
40	4.00
41	1.00
42	-
43	-
44	-
45	-
46	-1.00
47	-
48	-4.07
49	-2.90
50A	0.10
50B	-0.10
50C	-
51	-

52	-
54	-1.30
55	-
56	-
57	-
58	-
59	2.00
60	-
61	2.00
62	-
63	-
64	-
65	-
66	-
67	-
68A	-
68B	-
68C	-
69	-
70	-
71	-2.30
72	-
73	-
No of labs., p	24
No of repl., n	2
d	0.27
s ²	7.21
s	2.68
t = $\sqrt{p} \cdot (d/s)$	0.4889
Sign. level, p(t)	0.6295

No test statistics were found to be significant

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

Laboratory	Difference AB
1	1.50
2	3.00
3	0.00
4	-0.70
5	1.00
6	-0.50
7	-
8	-6.80
9	0.80
10A	-
10B	-0.40 UG
11	-0.80
12	-7.20
13	0.40
14	3.00
15	-0.90
16	-2.00
17	0.20
18	-1.60
19	11.40
20	-2.00
21	1.00
22	-9.60
23	-1.80
24	0.00
25A	-
25B	-
26	1.00
27	2.27
28	-4.00
29	1.00
30A	0.55
30B	-
31	0.50
32	0.50
33	-0.90
34	0.20
35	-
36	0.00
37	0.70
38	-
39	-
40	-0.80
41	-

42	0.20
43	-
44	-1.40
45	-0.60
46	-1.00
47	-4.70
48	-0.40
49	-
50A	10.40
50B	-
50C	-
51	-0.50
52	-1.70
54	-
55	-0.10
56	-3.80
57	0.20
58	-1.50
59	10.00
60	-1.50
61	1.30
62	6.10
63	0.00
64	-0.50
65	2.00
66	0.10
67	0.30
68A	-1.60
68B	-
68C	-
69	3.20
70	0.80
71	-
72	-3.80
73	-
No of labs., p	60
No of repl., n	2
d	0.02
s ²	12.07
s	3.47
t = $\sqrt{p} \cdot (d/s)$	0.0342
Sign. level, p(t)	0.9728

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

ANNEX D CONTROL OF RECOVERY

COD_{Cr}, mg/L O₂

Control of recovery, average of results

Laboratory	Sample pair AB
1	43.45
2	33.17
3	43.30
4	-
5	48.00
6	-
7	-
8	44.35
9	39.90
10A	44.40
10B	48.00
11	-
12	51.50
13	-
14	51.05
15	-
16	52.05
17	27.50
18	-
19	66.75
20	34.50
21	41.40
22	-
23	43.25
24	49.00
25A	-
25B	-
26	15.85
27	-
28	42.00
29	46.70
30A	47.20
30B	41.30
31	41.85
32	41.50
33	51.10
34	50.05
35	41.90
36	24.70
37	-
38	40.35
39	-
40	47.60
41	44.88
42	50.05
43	42.55
44	-
45	-
46	43.00
47	44.00
48	54.50

UC

49	47.25
50A	26.65
50B	-
50C	-
51	46.80
52	43.30
54	43.00
55	54.40
56	-
57	-
58	49.40
59	54.50
60	44.25
61	-
62	53.50
63	-
64	-
65	49.34
66	-
67	45.90
68A	46.05
68B	46.15
68C	40.75
69	42.40
70	-
71	90.75
72	53.95
73	49.65
No of labs., p	53
No of repl., n	2
m	44.62
s ²	68.19
s	8.26
Assigned value, μ	45
Recovery, %	99.2
$t = \sqrt{p} \cdot (m - \mu) / s$	-0.3324
Sign. level, p(t)	0.7409

UG

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

BOD₅, mg/L O₂

Control of recovery, average of results

Laboratory	Sample pair AB
1	2.840
2	-
3	3.845
4	-
5	4.725
6	-
7	3.415
8	-
9	5.155
10A	-
10B	-
11	-
12	-
13	-
14	-
15	-
16	-
17	-
18	-
19	3.675
20	-
21	5.150
22	-
23	3.475
24	-
25A	-
25B	-
26	2.795
27	-
28	-
29	1.555
30A	-
30B	-
31	3.010
32	-
33	-
34	-
35	-
36	2.175
37	-
38	-
39	-
40	4.160
41	-
42	-
43	-
44	-
45	-
46	4.645
47	4.400
48	4.080
49	-
50A	4.160
50B	-
50C	-
51	3.140

52	-
54	-
55	-
56	-
57	-
58	-
59	-
60	3.340
61	-
62	-
63	-
64	-
65	-
66	-
67	-
68A	5.150
68B	3.105
68C	-
69	-
70	-
71	-
72	-
73	-
No of labs., p	21
No of repl., n	2
m	3.714
s ²	0.962
s	0.981
Assigned value, μ	3.8
Recovery, %	97.7
$t = \sqrt{p} \cdot (m-\mu)/s$	-0.4017
Sign. level, p(t)	0.6922

No test statistics were found to be significant

BOD₇, mg/L O₂

Control of recovery, average of results

Laboratory	Sample pair AB
1	-
2	-
3	-
4	-
5	5.390 UG
6	-
7	-
8	-
9	-
10A	-
10B	-
11	-
12	-
13	-
14	-
15	3.800
16	-
17	4.115
18	-
19	-
20	-
21	-
22	-
23	-
24	4.000
25A	-
25B	-
26	-
27	4.335
28	-
29	-
30A	-
30B	-
31	-
32	3.740
33	4.910 UG
34	-
35	-
36	-
37	-
38	-
39	-
40	-
41	-
42	-
43	-
44	3.874
45	4.230
46	-
47	-
48	4.000
49	-
50A	-
50B	-
50C	-
51	-

52	-
54	-
55	-
56	3.775
57	-
58	-
59	-
60	-
61	-
62	-
63	-
64	4.075
65	-
66	3.985
67	-
68A	-
68B	-
68C	-
69	-
70	-
71	-
72	-
73	-
No of labs., p	11
No of repl., n	2
m	3.994
s ²	0.036
s	0.189
Assigned value, μ	4.1
Recovery, %	97.4
$t = \sqrt{p} \cdot (m-\mu)/s$	-1.8660
Sign. level, p(t)	0.0916

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

NVOC, mg/L C

Control of recovery, average of results

Laboratory	Sample pair AB	
1	-	
2	-	
3	-	
4	-	
5	19.40	
6	18.55	
7	7.47	UC
8	-	
9	-	
10A	-	
10B	18.85	
11	-	
12	19.20	
13	20.15	
14	-	
15	20.05	
16	22.32	UG
17	10.25	UG
18	18.59	
19	-	
20	-	
21	18.90	
22	18.55	
23	-	
24	19.49	
25A	18.68	
25B	-	
26	-	
27	18.75	
28	-	
29	18.50	
30A	-	
30B	-	
31	-	
32	17.65	
33	19.85	
34	-	
35	-	
36	12.75	UG
37	16.20	
38	-	
39	18.60	
40	-	
41	-	
42	19.00	
43	-	
44	19.55	
45	17.97	
46	-	
47	-	
48	21.95	UG
49	19.20	
50A	19.10	
50B	-	
50C	-	
51	-	

52	-
54	19.55
55	19.65
56	18.85
57	19.65
58	19.65
59	19.85
60	-
61	19.35
62	19.15
63	18.35
64	19.60
65	-
66	18.90
67	-
68A	18.90
68B	-
68C	-
69	-
70	20.00
71	-
72	19.45
73	-
No of labs., p	36
No of repl., n	2
m	19.05
s ²	0.58
s	0.76
Assigned value, μ	19.3
Recovery, %	98.7
$t = \sqrt{p} \cdot (m - \mu) / s$	-1.9984
Sign. level, p(t)	0.0535

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 recovery, average of results

Laboratory	Sample pair AB	
1	0.7530	
2	0.7650	
3	0.7020	
4	0.7900	
5	0.7600	
6	0.7390	
7	0.7700	
8	0.7350	
9	0.6755	UC
10A	0.7330	
10B	0.7495	
11	0.7650	
12	0.8115	
13	0.7390	
14	0.7255	
15	0.7280	
16	0.7020	
17	0.7695	
18	0.7245	
19	0.3390	UG
20	0.7500	
21	0.8000	
22	0.7150	
23	0.7395	
24	0.7850	
25A	-	
25B	-	
26	0.7530	
27	0.7285	
28	0.7370	
29	0.8020	
30A	0.7800	
30B	0.6850	
31	0.7830	
32	0.7855	
33	0.7800	
34	0.7335	
35	0.7650	
36	0.8200	
37	0.7245	
38	0.7470	
39	-	
40	0.7950	
41	0.8200	UC
42	0.7650	
43	0.7775	
44	0.7630	
45	0.7635	
46	0.7650	
47	0.7775	
48	0.9050	UG
49	0.7450	UC
50A	0.7515	
50B	0.7390	
50C	0.7420	
51	0.7390	

52	0.7610	
54	0.7285	
55	0.8340	
56	0.7405	
57	0.7360	
58	0.7365	
59	0.7100	
60	0.7365	
61	0.7605	
62	0.7525	
63	0.7240	
64	0.7225	
65	0.7370	
66	0.7370	
67	0.6135	UG
68A	0.7640	
68B	-	
68C	-	
69	0.7430	
70	0.7335	
71	0.8550	UC
72	0.7330	
73	0.7575	
No of labs., p	67	
No of repl., n	2	
m	0.7522	
s ²	0.0008	
s	0.0285	
Assigned value, μ	0.75	
Recovery, %	100.3	
$t = \sqrt{p} \cdot (m-\mu)/s$	0.6452	
Sign. level, p(t)	0.5211	

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	216.5	
2	-	
3	190.0	
4	-	
5	190.4	
6	-	
7	195.5	
8	178.0	UC
9	194.5	
10A	198.0	
10B	182.0	
11	-	
12	-	
13	-	
14	-	
15	-	
16	-	
17	190.5	
18	-	
19	216.5	
20	176.5	
21	165.5	
22	-	
23	201.5	
24	-	
25A	192.8	
25B	190.7	
26	204.5	
27	-	
28	-	
29	181.0	
30A	187.5	
30B	207.0	
31	149.0	
32	-	
33	192.5	
34	194.6	
35	194.5	
36	194.0	
37	186.6	
38	190.5	
39	195.8	
40	192.5	
41	193.0	
42	-	
43	-	
44	-	
45	-	
46	193.0	
47	167.5	
48	192.9	
49	191.0	
50A	195.0	
50B	186.0	
50C	-	
51	-	

52	-	
54	183.0	
55	-	
56	-	
57	-	
58	-	
59	205.0	
60	204.5	
61	191.5	
62	-	
63	-	
64	-	
65	-	
66	-	
67	271.5	UG
68A	-	
68B	-	
68C	-	
69	179.0	
70	-	
71	207.0	
72	-	
73	168.8	
No of labs., p	41	
No of repl., n	2	
m	190.9	
s ²	169.4	
s	13.0	
Assigned value, μ	193	
Recovery, %	98.9	
$t = \sqrt{p} \cdot (m-\mu)/s$	-1.0196	
Sign. level, p(t)	0.3140	

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

Sulphate, mg/L

Control of recovery, average of results

Laboratory	Sample pair AB
1	-
2	-
3	69.75
4	-
5	71.90
6	-
7	-
8	-
9	69.25
10A	-
10B	66.45
11	-
12	-
13	-
14	-
15	-
16	77.05
17	67.50
18	-
19	-
20	-
21	-
22	-
23	-
24	-
25A	68.09
25B	-
26	-
27	-
28	-
29	78.80
30A	71.50
30B	-
31	-
32	-
33	-
34	60.15
35	-
36	68.65
37	65.85
38	64.70
39	-
40	62.50
41	71.20
42	-
43	-
44	-
45	-
46	65.50
47	-
48	67.40
49	62.55
50A	70.55
50B	74.55
50C	-
51	-

52	-
54	64.45
55	-
56	-
57	-
58	-
59	70.00
60	-
61	75.50
62	-
63	-
64	-
65	-
66	-
67	-
68A	-
68B	-
68C	-
69	-
70	-
71	68.05
72	-
73	-
No of labs., p	24
No of repl., n	2
m	68.83
s ²	21.45
s	4.63
Assigned value, μ	69
Recovery, %	99.8
$t = \sqrt{p} \cdot (m - \mu) / s$	-0.1813
Sign. level, p(t)	0.8577

No test statistics were found to be significant

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

Laboratory	Sample pair AB
1	40.05
2	36.50
3	39.60
4	40.45
5	39.80
6	40.65
7	-
8	34.40
9	38.80
10A	-
10B	25.00 UG
11	40.70
12	37.20
13	41.50
14	35.50
15	39.65
16	37.80
17	40.40
18	39.20
19	33.00
20	41.00
21	38.00
22	35.50
23	38.10
24	41.20
25A	-
25B	-
26	35.50
27	41.03
28	32.00
29	38.50
30A	40.17
30B	-
31	40.95
32	38.75
33	40.55
34	41.40
35	-
36	39.90
37	38.55
38	-
39	-
40	38.40
41	-
42	41.00
43	-
44	39.70
45	40.70
46	38.50
47	36.65
48	37.00
49	-
50A	31.30
50B	-
50C	-
51	40.85

52	41.25
54	-
55	41.15
56	37.00
57	38.20
58	41.05
59	45.00
60	36.95
61	38.35
62	37.55
63	41.20
64	39.95
65	43.00
66	40.15
67	40.85
68A	41.30
68B	-
68C	-
69	42.20
70	39.90
71	-
72	39.10
73	-
No of labs., p	60
No of repl., n	2
m	39.08
s ²	6.54
s	2.56
Assigned value, μ	39.6
Recovery, %	98.7
$t = \sqrt{p} \cdot (m - \mu) / s$	-1.5873
Sign. level, p(t)	0.1178

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

ANNEX E CONCENTRATION LEVEL

Parameter	Unit	Sample	Bottle no.	I	II	Bottle Average	Sample	Assigned	Spike		
							Average	value	Measured	Assigned	
COD	mg/L O ₂	A1	77	42,9	44,1	43,5	43,0	45	7,9	8	
			83	42,4	42,8	42,6					
			50	42,7	43,3	43,0					
		B1	19	50,4	50,9	50,7	50,9	53			
			34	51,7	50,8	51,3					
			40	50,1	51,4	50,8					
Total phosphorus	mg/L P	A2	30	0,720	0,713	0,717	0,725	0,75	0,102	0,11	
			2	0,713	0,741	0,727					
			93	0,732	0,733	0,733					
		B2	12	0,827	0,827	0,827	0,827	0,86			
			5	0,826	0,833	0,830					
			34	0,833	0,816	0,825					
Chloride	mg/L	A2	30	170		170	169	193	29	23	
			2	167		167					
			93	171		171					
		B2	12	197		197	199	216			
			5	201		201					
			34	198		198					
Sulphate	mg/L	A2	30	55,5	52,3	53,9	53,5	69	8,4	7	
			2	53,8	54,2	54,0					
			93	52,2	52,7	52,5					
		B2	12	61,4	64,2	62,8	61,9	76			
			5	60,2	59,3	59,8					
			34	64,4	61,8	63,1					
Total suspended solids	mg/L	A3	45	48,1		48,10	48,1	45,6	6,9	6,0	
			B3	61	40,7						40,70
		2	41,6		41,60						
		8	41,4		41,40						

ANNEX F HOMOGENEITY AND STABILITY

PT:	SPIL-1	
Parameter:	COD	
	mg/L	
Unit:	O ₂	
Sigma:	2,9995	6,5% of x

Responsible for tests:

IRL

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

Homogeneity test

Date: 2015-02-24

Sample	x(a)	x(b)	average	sd	sd ²
A1-79	46,8	46,2	46,5	0,424	0,180
A1-34	46,2	45,7	46,0	0,354	0,13
A1-44	46,0	46,7	46,4	0,495	0,245
A1-92	46,3	46,4	46,4	0,071	0,005
A1-39	46,5	46,2	46,4	0,212	0,045
A1-74	46,4	46,4	46,4	0,000	0,000
A1-6	45,8	45,8	45,8	0,000	0,000
A1-86	47,6	45,7	46,7	1,344	1,805
A1-13	45,9	46,0	46,0	0,071	0,005
A1-72	45,6	45,8	45,7	0,141	0,020
A1-59	45,6	45,7	45,7	0,071	0,005
A1-66	46,6	45,6	46,1	0,707	0,500

For homogeneity

General average (x)	46,15
Sample average sd (s _x)	0,332
Within-sample sd (s _w):	0,495
Between-samples sd (ss):	0
S _L in the Proficiency Test:	0,72
S _R in the Proficiency Test:	0,8

Conclusions

$$ss = 0 \quad 0,3 \cdot \sigma = 0,90$$

$$|x-y| = 0$$

Analytical quality Is $s_w < 0,15 \cdot \sigma$
NO

Homogeneity: Is $ss < 0,3 \cdot \sigma$?
YES

PT:	SPIL-1
Parameter:	TP
Unit:	mg/L P
Sigma:	0,0486 x 6,5% of x

Responsible for tests:

IRL

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

Homogeneity test

Date: 2015-02-24

Sample	x(a)	x(b)	average	sd	sd^2
A2-36	0,761	0,759	0,760	0,001	0,000
A2-31	0,748	0,752	0,750	0,003	0,00
A2-14	0,749	0,743	0,746	0,004	0,000
A2-20	0,753	0,752	0,753	0,001	0,000
A2-25	0,740	0,742	0,741	0,001	0,000
A2-89	0,753	0,741	0,747	0,008	0,000
A2-48	0,759	0,754	0,757	0,004	0,000
A2-84	0,755	0,729	0,742	0,018	0,000
A2-76	0,752	0,740	0,746	0,008	0,000
A2-57	0,769	0,733	0,751	0,025	0,001
A2-60	0,758	0,733	0,746	0,018	0,000
A2-85	0,742	0,738	0,740	0,003	0,000

For homogeneity

General average (x)	0,75
Sample average sd (s _x)	0,006
Within-sample sd (s _w):	0,011
Between-samples sd (ss):	0
S _L in the Proficiency Test:	0,027
S _R in the Proficiency Test:	0,030

Conclusions

ss = 0	0.3*sigma= 0,01
x-y = 0	
Analytical quality	Is s _w < 0,15*sigma NO
Homogeneity:	Is ss < 0.3*sigma? YES