

Proficiency test SPIL-1 (2012)

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

Proficiency test SPIL-1 (2012) 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 15 March 2012. The proficiency test was organised by Eurofins A/S according to agreement with Danish Accreditation, DANAK.

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 23 April 2012.

2 FEATURES OF THE PROFICIENCY TEST

Participants in the proficiency test were a total of 79 laboratories from Denmark, Faroe Islands, Norway and Sweden. A list of participants is shown in Appendix A.

The closing date for submission of results was 2 April 2012. 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.

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 effluent. Sample preparation is described in Appendix B.

Table 1 Samples in the proficiency test

Sample name	Parameters
A1/B1	COD, BOD ₅ (w. ATU), BOD ₇ (w.ATU), TOC/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 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	mg/L O ₂	5 – 75	29	2.2	3
5 days biochemical oxygen demand	BOD ₅ (w. ATU)	mg/L O ₂	2 – 6	2.4	0.26	0.6
7 days biochemical oxygen demand	BOD ₇ (w. ATU)	mg/L O ₂	2 – 6	3.0	0.15	0.6
Total organic carbon	NVOC/TOC	mg/L C	2 – 30	12	1.7	1
Total phosphorus	TP	mg/L P	0.2 - 2	0.400	0.0086	0.055
Chloride	Cl	mg/L	50 – 700	91	2.9	10
Sulphate	SO ₄	mg/L	20 – 200	55	3.4	7
Total suspended solids	TSS	mg/L	20 - 100	42.9	0.93	0.0

2.3.1 Assigned and spike values

The results for all parameters except Cl and SO₄ are operationally defined. Assigned values for Cl and SO₄ are consensus values for all laboratories based on the median. The assigned values for operationally defined parameters are consensus values based upon the median for method no. 1, 76, 77, 91, 92 (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 /5/. 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/. 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.

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 BOD₇ (w. ATU) and NVOC/TOC. However, the difference is numerically small 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 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 BOD₅ (w. ATU), TP and TSS.

Average recovery was for BOD₅ (w. ATU) was 136%. 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 methods no. 51, 52 and 61 and now showed no significant difference and a recovery of 98%.

For TP the recovery was 103%, and the significant difference from 100% could also be explained by influence from results from methods other than those prescribed by the Danish EPA. After exclusion of methods 41 and 42 the recovery was 101% and not significantly different from 100%.

The recovery for TSS was 98%. This was still the case when analysing only data from laboratories using the prescribed method. The samples have been shown to be homogeneous (see section 3) and an additional test was made to see if the order of filling of the sample bottles had an influence on the size of the measurement result. This additional test showed no connection between measurement result and the sample bottles position in the order of filling. The difference is attributed to a slightly skewed distribution resulting in an average slightly lower than the median.

The assigned values for all three parameters are therefore kept unchanged.

3 HOMOGENEITY AND STABILITY OF SAMPLES

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

NVOC	Homogeneity test
TP	Homogeneity test
TSS	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), and
2. the between bottle standard deviation/variance (the contribution from heterogeneity)

Homogeneity is evaluated by comparing the between bottle variance to $0.15 \cdot$ the maximum tolerated deviation from the assigned value specified by the Danish EPA /5/ (“sigma” in the calculations is 0.5 times the maximum tolerated deviation), whereas the stability is evaluated by comparing the concentration change of the samples to $0.15 \cdot$ the maximum tolerated deviation from the assigned value specified by the Danish EPA /5/. 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 homogeneity show that the samples are homogeneous. Analyses were also made to indicate stability of TSS. The test showed that the samples are stable.

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 BOD₇ (w. ATU) and NVOC/TOC 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 BOD₅ (w. ATU), TP and TSS the participants did not recover the assigned value. Eurofins' scrutiny of the combined evidence gave the conclusion that the assigned values are correct. The assigned values are therefore kept unchanged and they are recommended as the basis for evaluation of participating laboratories.

5 REFERENCES

- /1/ Eurofins A/S, *Proficiency test SPIL-1 (2012)*, Report to participants, April 2012.
- /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
AquaDjurs - Fornæs Renseanlæg	Grenaa	Danmark
Bjergmarken R/A, Roskilde Forsyning	Roskilde	Danmark
CP Kelco ApS, Spildevandslaboratoriet	Ll. Skensved	Danmark
Eurofins Miljø A/S	Vejen	Danmark
Faxe Spildevand	Faxe	Danmark
Faxe Spildevand	Faxe	Danmark
Fredericia Spildevand A/S	Fredericia	Danmark
Greve Solrød Forsyning	Greve	Danmark
Hach Lange ApS	Brønshøj	Danmark
Halsnæs Kommunale Forsyning A/S	Liseleje	Danmark
Hedensted Spildevand A/S	Daugård	Danmark
Hedensted Spildevand A/S	Daugård	Danmark
Holstebro Centralrenseanlæg, Vestforsyning A/S	Holstebro	Danmark
Ikast-Brande Spildevand	Ikast	Danmark
Kerteminde Forsyning - Spildevand A/S	Kerteminde	Danmark
Kolding Spildevand A/S	Bjert	Danmark
Køge-Egnens Renseanlæg	Køge	Danmark
Lynettefællesskabet I/S	København K	Danmark
Mølleåværkets Driftslaboratorium	Lyngby	Danmark
Måløv Renseanlæg	Måløv	Danmark
Nyborg Renseanlæg	Nyborg	Danmark
Næstved Centralrenseanlæg	Næstved	Danmark
Provas Haderslev Forsyningsservice	Haderslev	Danmark
Randers Spildevand A/S	Randers NØ	Danmark
Rensningsanlæg Øst, Esbjerg	Esbjerg	Danmark
Rensningsanlæg Øst, Esbjerg, Spildevandslaboratoriet	Esbjerg	Danmark
Ringkøbing-Skjern Forsyning A/S, Spildevand	Skjern	Danmark
Ringsted Renseanlæg	Ringsted	Danmark
Rønne Renseanlæg	Rønne	Danmark
SK Forsyning, Slagelse Renseanlæg	Slagelse	Danmark
SK Forsyning, Slagelse Renseanlæg	Slagelse	Danmark
SK Forsyning, Slagelse Renseanlæg	Slagelse	Danmark
SK Forsyning, Slagelse Renseanlæg	Slagelse	Danmark
Sun Chemicals, E30	Køge	Danmark
Svendborg Centralrenseanlæg	Skårup Fyn	Danmark

Laboratory	Town	Country
Sønderborg Renseanlæg	Sønderborg	Danmark
Vandrens - Stignæs Industripark A/S	Skælskør	Danmark
Vandsamarbejdet A/S	Holstebro	Danmark
Vejle Spildevand A/S	Vejle	Danmark
Ålborg Renseanlæg Vest	Ålborg	Danmark
Ålborg Renseanlæg Øst	Ålborg Øst	Danmark
Heilsufrøðiliga starvsstovan	Tórshavn	Færøerne
Eurofins Norsk Miljøanalyse, avd. Moss	Moss	Norge
Akzo Nobel Functional Chemicals AB Cellulosic Specialties, QHSE	Örnsköldsvik	Sverige
Eksjö Kommunala Laboratorium	Eksjö	Sverige
Ernemar Laboratoriet	Oskarshamn	Sverige
Eurofins Environment Testing Sweden AB	Lidköping	Sverige
Fiskeby Board AB	Norrköping	Sverige
GRYAAB AB	Göteborg	Sverige
Gästrike Vatten AB	Skutskär	Sverige
Hallsta Pappersbruk	Hallstavik	Sverige
Holmen Paper	Norrköping	Sverige
Iggesund Paperboard, Cell & Miljölab	Iggesund	Sverige
Ineos Sverige AB	Stenungsund	Sverige
Kalmar Vatten AB, VA-lab, Avloppsreningsverket	Kalmar	Sverige
Kristianstad Kommun, C4 Teknik, Kommunteknik	Kristianstad	Sverige
Käppalaverket	Lidingö	Sverige
Laboratoriet vid Smedjeholms Arv	Falkenberg	Sverige
MittSverige Vatten AB, Fillanverket lab.	Sundsvall	Sverige
Mjölby Kommun	Mjölby	Sverige
Motala Kommun	Motala	Sverige
Nordic Sugar	Eslöv	Sverige
NSVA/Öresundsverket	Helsingborg	Sverige
Piteå Renhållning & Vatten AB	Öjebyn	Sverige
Preem AB Göteborg	Göteborg	Sverige
Preemraff Lysekil	Lysekil	Sverige
Rottneros Bruk AB	Rottneros	Sverige
SAKAB AB	Kumla	Sverige
St1 Refinery AB	Göteborg	Sverige
Stora Enso Publication Paper	Hyltebruk	Sverige

Laboratory	Town	Country
Södra Cell AB Mönsterås	Mönsterås	Sverige
Tekniska förvaltningen, Verksamhetsstöd VA, Laboratoriet	Örebro	Sverige
Tekniska Verken i Linköping AB (publ), Laboratoriet Avloppsreningsverket	Linköping	Sverige
Uddebo Laboratorium	Luleå	Sverige
Uppsala Vatten o. Avfall AB, Vattenlaboratoriet	Uppsala	Sverige
VA SYD Klaghamns Avloppsreningsverk	Malmö	Sverige
VA SYD Källby Avloppsreningsverk	Malmö	Sverige
VA SYD Sjölundalaboratoriet	Malmö	Sverige
VA-SYD, Ellingelaboratoriet	Malmö	Sverige
Vattenfall AB, Heat Generation Uppsala	Uppsala	Sverige
VIVAB	Varberg	Sverige
Västerviks Miljö & Energi AB, Vattenlaboratoriet	Västervik	Sverige

A P P E N D I X B

Sample preparation

Stock solution	Prepared from	Concentration
Concentrate A1	7.500 g D-glucose 7.500 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} : 1.509 g/kg NVOC: 0.596 g/kg BOD: 1.033 g/kg
Stock TP	1.5000 g Na-β.glycerophosphate milli-Q water up to 10000 g	TP: 0.152 g/kg
Stock Cl	10.00 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	0.90
1B	-
2	2.30
3	-0.35
4	1.00
5	1.00
6	0.10
7	0.20
8	0.40
9	-0.40
10	-
11	-0.20
12	-
13	0.60
14	1.85
15	-7.00
16	0.20
17	1.70
18	1.00
19	-2.20
20	-0.20
21	0.90
22	-
23	-2.90
24	-
25	0.30
26	-0.20
27	-1.20
28	0.70
29	-
30	-2.00 UG
31	1.30
32	1.80
33	-0.10
34	-7.00
35	0.70
36	-10.80 UC
37	0.30
38	2.80
39	0.00
40	0.20
41A	-0.30
41B	-
42	1.00
43	-
44	-0.60
45	1.90
46	3.00 UG
47	0.60
48	2.30
49	-
50	-
51	1.00
52	-
53	-2.00
54	0.50

55	2.50
56	-
57	-1.60
58	0.10
59	3.10
60	0.80
61	-
62	0.30
63A	0.20
63B	-0.10
64	-3.10 UG
65	-
66	-1.50
67	1.50
68	-1.00
69	0.30
70	1.80
71	-0.40
72	-4.15
73	-
74	-
75	1.60
76	-
77	-
78	1.20
79	1.70
No of labs., p	60
No of repl., n	2
d	0.15
s ²	3.57
s	1.89
$t = \sqrt{p} \cdot (d/s)$	0.6318
Sign. level, p(t)	0.5299

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

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

Laboratory	Difference AB
1	0.350
1B	-0.150
2	-
3	-
4	-
5	-0.340
6	-0.050
7	0.450
8	-0.460
9	-0.330
10	-
11	0.820
12	-
13	-
14	-
15	-0.900
16	-
17	-
18	-
19	-
20	0.120
21	-0.140
22	0.140
23	-
24	-
25	-
26	-
27	-
28	-
29	-
30	-
31	-
32	-
33	0.100
34	0.180
35	-
36	1.140
37	-
38	-
39	-
40	-
41A	-
41B	-
42	-
43	-
44	-
45	-1.280
46	-
47	-
48	-
49	-
50	-
51	-
52	-
53	-
54	-

55	1.600	
56	-	
57	-	
58	-	
59	-	
60	-3.970	UC
61	-	
62	-1.400	
63A	0.300	
63B	-	
64	-	
65	-	
66	-	
67	-	
68	-	
69	-0.100	
70	-	
71	-	
72	0.120	
73	-	
74	-	
75	-0.040	
76	-	
77	-	
78	-	
79	-	
No of labs., p	22	
No of repl., n	2	
d	0.006	
s ²	0.473	
s	0.688	
$t = \sqrt{p} \cdot (d/s)$	0.0403	
Sign. level, p(t)	0.9682	

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

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

Laboratory	Difference AB
1	-
1B	-
2	-
3	-
4	-
5	-
6	-
7	-
8	-
9	-
10	0.000
11	-
12	-
13	-
14	-
15	-
16	0.310
17	-
18	0.370
19	-0.300
20	-
21	-
22	-
23	0.000
24	0.300
25	0.400
26	-
27	-
28	0.150
29	-
30	-
31	-
32	-
33	-
34	0.100
35	-
36	-
37	0.400
38	-
39	-
40	-
41A	-0.410
41B	-
42	0.400
43	-
44	-
45	-
46	-
47	-
48	-
49	-0.070
50	-
51	-
52	-
53	-
54	-

55	-
56	-0.340
57	0.060
58	-
59	-
60	-
61	-
62	-
63A	-
63B	-
64	0.300
65	-
66	-
67	-
68	-
69	-
70	-
71	0.300
72	-
73	0.100
74	0.260
75	-
76	0.820
77	-
78	-
79	-
No of labs., p	20
No of repl., n	2
d	0.158
s ²	0.087
s	0.295
$t = \sqrt{p} \cdot (d/s)$	2.3890
Sign. level, p(t)	0.0274 *

* 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)

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

Laboratory	Difference AB
1	-0.40
1B	-
2	-
3	-
4	-
5	-
6	-0.55
7	-
8	-0.60
9	-0.50
10	-0.10
11	-
12	-
13	-
14	-
15	-
16	0.10
17	-
18	0.00
19	-
20	-0.20
21	-
22	-
23	-
24	-0.40
25	-
26	-
27	-
28	-0.23
29	-
30	1.00 UG
31	-
32	-
33	-0.15
34	0.00
35	-
36	-
37	-1.20
38	-
39	-
40	-0.70
41A	-0.10
41B	-0.20
42	-
43	0.50
44	-
45	-
46	-
47	-
48	-
49	-0.70
50	-
51	-
52	-0.86
53	0.68
54	-0.10

55	-0.30	
56	-0.60	
57	0.10	
58	-0.40	
59	-	
60	-	
61	0.40	
62	-	
63A	-0.50	
63B	-	
64	-	
65	-0.30	
66	-0.20	
67	-0.20	
68	2.00	UG
69	-	
70	-	
71	-0.50	
72	-0.19	
73	0.50	
74	-0.10	
75	-	
76	-0.14	
77	-0.20	
78	-0.60	
79	-1.10	
No of labs., p	38	
No of repl., n	2	
d	-0.26	
s ²	0.16	
s	0.40	
$t = \sqrt{p} \cdot (d/s)$	-4.0368	
Sign. level, p(t)	0.0003	***

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

Laboratory	Difference AB
1	-0.0010
1B	-
2	-0.0010
3	0.0030
4	-0.0120
5	0.0050
6	0.0100
7	-0.0000
8	0.0030
9	0.0060
10	0.0240
11	0.0050
12	-
13	-0.0140
14	0.0350
15	0.0310
16	-0.0100
17	-0.0050
18	-0.0110
19	-0.0080
20	-0.0140
21	-0.0100
22	-0.0050
23	-0.0165
24	-
25	0.0150
26	0.0030
27	0.0180
28	-0.0110
29	-
30	-0.0090
31	-0.0050
32	0.0190
33	0.0010
34	0.0170
35	0.0000
36	0.0060
37	-0.0150
38	-0.0030
39	-0.0050
40	0.0040
41A	-0.0120
41B	-
42	-0.0100
43	-
44	-0.0040
45	-0.0050
46	0.0140
47	-0.0150
48	0.0030
49	0.0030
50	-0.0010
51	0.0090
52	0.0090
53	-0.0010
54	-0.0130

55	0.0100
56	0.0050
57	0.0080
58	0.0040
59	0.0170
60	0.0030
61	-0.0080
62	0.0080
63A	-0.0050
63B	-
64	-0.0270
65	0.0020
66	-0.0030
67	0.0960
68	-0.0050
69	0.0120
70	0.0050
71	0.0070
72	0.0067
73	-0.0080
74	-0.0010
75	0.1010
76	-0.0150
77	0.0250
78	0.0100
79	0.0130
No of labs., p	71
No of repl., n	2
d	0.0016
s ²	0.0001
s	0.0116
t = $\sqrt{p} \cdot (d/s)$	1.1248
Sign. level, p(t)	0.2645

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	0.00	
1B	-	
2	-	
3	1.20	
4	1.10	
5	0.00	
6	2.00	
7	-0.80	
8	-0.40	
9	-6.00	
10	1.10	
11	-6.80	
12	-	
13	6.00	
14	-	
15	-3.00	
16	-	
17	15.00	UC
18	-	
19	-	
20	-2.30	
21	1.00	
22	-	
23	-0.60	
24	-0.17	
25	-	
26	-	
27	-	
28	-	
29	-	
30	5.00	
31	-2.00	
32	0.10	
33	2.00	
34	2.90	
35	1.00	
36	1.80	
37	-	
38	-1.80	
39	0.00	
40	-2.00	
41A	-	
41B	-	
42	5.00	
43	-0.13	
44	0.10	
45	1.10	
46	-	
47	-3.00	
48	-3.80	
49	-	
50	0.28	
51	-	
52	-	
53	19.50	UC
54	1.05	

55	25.70	UC
56	-	
57	-	
58	-0.90	
59	5.20	
60	3.00	
61	-0.30	
62	0.90	
63A	-2.60	
63B	-	
64	-	
65	-	
66	-	
67	-0.60	
68	5.00	
69	-0.90	
70	-0.30	
71	-	
72	1.31	
73	-	
74	-	
75	3.00	
76	-	
77	2.00	
78	-	
79	-	
No of labs., p	47	
No of repl., n	2	
d	0.31	
s ²	7.11	
s	2.67	
t = $\sqrt{p} \cdot (d/s)$	0.8062	
Sign. level, p(t)	0.4243	

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	0.90
1B	-
2	-
3	-
4	-3.40
5	-
6	-
7	-
8	2.10
9	-3.90
10	-
11	1.00
12	-
13	-
14	-
15	-
16	-
17	0.20
18	-
19	-
20	3.70
21	-
22	-
23	0.50
24	-3.50
25	-
26	-
27	-
28	-
29	-
30	-
31	4.70
32	-
33	-
34	0.30
35	-
36	-
37	-
38	-0.80
39	-
40	1.30
41A	-
41B	-
42	-
43	-
44	-
45	1.10
46	-
47	-
48	-
49	-
50	-
51	-
52	-
53	10.00
54	-

55	-2.40
56	-
57	-
58	-0.10
59	-
60	-
61	-3.50
62	-
63A	-
63B	-
64	-
65	-
66	-
67	-0.90
68	10.70
69	5.70
70	-
71	-
72	0.70
73	-
74	-
75	-
76	-
77	4.00
78	-
79	-
No of labs., p	23
No of repl., n	2
d	1.23
s ²	15.10
s	3.89
$t = \sqrt{p} \cdot (d/s)$	1.5240
Sign. level, p(t)	0.1418

No test statistics were found to be significant

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

Laboratory	Difference AB
1	-1.10
1B	-
2	-0.40
3	1.00
4	12.00
5	-2.00
6	-2.25
7	0.10
8	5.00
9	-1.60
10	0.00
11	11.60
12	-4.60
13	-2.00
14	0.00
15	-10.00
16	1.85
17	-
18	-1.00 UG
19	0.60
20	-
21	12.00
22	-
23	0.60
24	-0.50
25	0.75
26	-
27	1.00
28	2.60
29	-0.30
30	-
31	-
32	-
33	-3.30
34	1.30
35	-3.80
36	-0.70
37	1.70
38	-
39	-1.00
40	0.00
41A	0.30
41B	-
42	3.40
43	-
44	-2.10
45	-2.40
46	1.10
47	-
48	0.10
49	-0.30
50	2.00
51	0.90
52	3.40
53	-
54	0.60

55	3.80
56	1.00
57	0.90
58	-
59	-0.60
60	1.60
61	0.72
62	-0.40
63A	-2.40
63B	-
64	0.50
65	0.60
66	0.10
67	-
68	0.00
69	5.00
70	-
71	0.00
72	0.37
73	0.50
74	1.30
75	0.10
76	0.00
77	0.00
78	-0.80
79	0.70
No of labs., p	64
No of repl., n	2
d	0.60
s ²	11.14
s	3.34
$t = \sqrt{p} \cdot (d/s)$	1.4432
Sign. level, p(t)	0.1539

No test statistics were found to be significant

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	26.95
1B	-
2	16.25
3	27.98
4	26.30
5	22.50
6	29.00
7	28.10
8	26.60
9	26.80
10	-
11	26.30
12	-
13	28.60
14	25.43
15	31.50
16	31.30
17	27.35
18	32.50
19	32.10
20	31.20
21	29.45
22	-
23	27.85
24	-
25	30.30
26	24.00
27	27.90
28	34.15
29	-
30	55.60 UG
31	27.85
32	30.15
33	29.75
34	29.50
35	28.15
36	32.20 UC
37	22.75
38	26.30
39	41.00
40	32.50
41A	29.35
41B	-
42	37.00
43	-
44	32.10
45	25.55
46	62.70 UG
47	32.60
48	29.35
49	-
50	-
51	27.50
52	-
53	34.00
54	31.55

55	24.05
56	-
57	32.20
58	26.25
59	31.90
60	26.00
61	-
62	29.35
63A	25.00
63B	26.75
64	53.15 UG
65	-
66	35.05
67	26.75
68	33.50
69	25.35
70	29.10
71	31.60
72	27.77
73	-
74	-
75	25.60
76	-
77	-
78	34.80
79	34.05
No of labs., p	60
No of repl., n	2
m	29.04
s ²	15.60
s	3.95
Assigned value, μ	29
Recovery, %	100.1
$t = \sqrt{p} \cdot (m-\mu)/s$	0.0793
Sign. level, p(t)	0.9371

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

BOD₅ w. ATU, mg/L O₂
Control of recovery, average of results

Laboratory	Sample pair AB
1	2.675
1B	2.855
2	-
3	-
4	-
5	2.840
6	2.765
7	2.445
8	2.110
9	2.325
10	-
11	4.820
12	-
13	-
14	-
15	4.450
16	-
17	-
18	-
19	-
20	2.820
21	3.370
22	2.260
23	-
24	-
25	-
26	-
27	-
28	-
29	-
30	-
31	-
32	-
33	2.700
34	2.210
35	-
36	5.000
37	-
38	-
39	-
40	-
41A	-
41B	-
42	-
43	-
44	-
45	4.110
46	-
47	-
48	-
49	-
50	-
51	-
52	-
53	-
54	-

55	2.200	
56	-	
57	-	
58	-	
59	-	
60	6.795	UC
61	-	
62	6.800	
63A	3.450	
63B	-	
64	-	
65	-	
66	-	
67	-	
68	-	
69	4.360	
70	-	
71	-	
72	1.680	
73	-	
74	-	
75	3.390	
76	-	
77	-	
78	-	
79	-	
No of labs., p	22	
No of repl., n	2	
m	3.256	
s ²	1.496	
s	1.223	
Assigned value, μ	2.4	
Recovery, %	135.7	
$t = \sqrt{p} \cdot (m-\mu)/s$	3.2827	
Sign. level, p(t)	0.0036	**

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 ** 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

BOD₇ w. ATU, mg/L O₂

Control of recovery, average of results

Laboratory	Sample pair AB
1	-
1B	-
2	-
3	-
4	-
5	-
6	-
7	-
8	-
9	-
10	2.200
11	-
12	-
13	-
14	-
15	-
16	3.305
17	-
18	3.075
19	3.450
20	-
21	-
22	-
23	3.100
24	2.750
25	2.420
26	-
27	-
28	3.055
29	-
30	-
31	-
32	-
33	-
34	2.840
35	-
36	-
37	2.300
38	-
39	-
40	-
41A	2.805
41B	-
42	2.900
43	-
44	-
45	-
46	-
47	-
48	-
49	3.515
50	-
51	-
52	-
53	-
54	-

55	-
56	2.720
57	3.600
58	-
59	-
60	-
61	-
62	-
63A	-
63B	-
64	3.050
65	-
66	-
67	-
68	-
69	-
70	-
71	2.850
72	-
73	3.240
74	2.980
75	-
76	3.030
77	-
78	-
79	-
No of labs., p	20
No of repl., n	2
m	2.959
s ²	0.141
s	0.375
Assigned value, μ	3.0
Recovery, %	98.6
$t = \sqrt{p} \cdot (m-\mu)/s$	-0.4861
Sign. level, p(t)	0.6325

No test statistics were found to be significant

NVOC/TOC, mg/L C

Control of recovery, average of results

Laboratory	Sample pair AB
1	12.40
1B	-
2	-
3	-
4	-
5	-
6	13.07
7	-
8	11.30
9	11.15
10	15.55
11	-
12	-
13	-
14	-
15	-
16	11.95
17	-
18	11.00
19	-
20	11.40
21	-
22	-
23	-
24	12.00
25	-
26	-
27	-
28	11.69
29	-
30	34.40 UG
31	-
32	-
33	12.93
34	10.50
35	-
36	-
37	13.50
38	-
39	-
40	14.96
41A	11.25
41B	11.50
42	-
43	12.05
44	-
45	-
46	-
47	-
48	-
49	12.15
50	-
51	-
52	15.67
53	7.51
54	12.25

55	11.65
56	11.10
57	11.55
58	12.20
59	-
60	-
61	11.30
62	-
63A	10.95
63B	-
64	-
65	14.25
66	11.40
67	11.90
68	27.00 UG
69	-
70	-
71	10.75
72	10.46
73	11.65
74	12.15
75	-
76	11.78
77	13.20
78	11.30
79	12.05
No of labs., p	38
No of repl., n	2
m	11.98
s ²	2.15
s	1.47
Assigned value, μ	12
Recovery, %	99.9
$t = \sqrt{p} \cdot (m - \mu) / s$	-0.0653
Sign. level, p(t)	0.9483

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

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

Laboratory	Sample pair AB
1	0.4205
1B	-
2	0.4285
3	0.4615
4	0.4240
5	0.4275
6	0.4080
7	0.4120
8	0.4035
9	0.4170
10	0.4000
11	0.4345
12	-
13	0.4420
14	0.4525
15	0.3925
16	0.4010
17	0.3925
18	0.4075
19	0.3980
20	0.4320
21	0.4330
22	0.3815
23	0.3863
24	-
25	0.4225
26	0.4075
27	0.4220
28	0.3925
29	-
30	0.4355
31	0.3925
32	0.4105
33	0.4135
34	0.4265
35	0.4050
36	0.4330
37	0.4325
38	0.4335
39	0.5625 UG
40	0.4020
41A	0.3900
41B	-
42	0.3940
43	-
44	0.4210
45	0.4225
46	0.4020
47	0.5775 UG
48	0.3985
49	0.3905
50	0.4375
51	0.4105
52	0.3975
53	0.4145
54	0.3805

55	0.4350
56	0.3985
57	0.3880
58	0.4020
59	0.4295
60	0.4265
61	0.4010
62	0.4430
63A	0.4325
63B	-
64	0.3995
65	0.3920
66	0.3775
67	0.3940 UC
68	0.4025
69	0.4210
70	0.4375
71	0.3965
72	0.4292
73	0.3920
74	0.3875
75	0.3875 UC
76	0.3795
77	0.4075
78	0.4130
79	0.4065
No of labs., p	71
No of repl., n	2
m	0.4119
s ²	0.0004
s	0.0191
Assigned value, μ	0.400
Recovery, %	103.0
$t = \sqrt{p} \cdot (m-\mu)/s$	5.2365
Sign. level, p(t)	0.0000 ***

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 ** 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

Chloride, mg/L

Control of recovery, average of results

Laboratory	Sample pair AB
1	91.80
1B	-
2	-
3	76.90
4	78.15
5	77.00
6	98.00
7	89.30
8	95.80
9	86.60
10	91.45
11	82.20
12	-
13	102.00
14	-
15	98.50
16	-
17	128.50 UC
18	-
19	-
20	91.85
21	104.50
22	-
23	92.80
24	92.57
25	-
26	-
27	-
28	-
29	-
30	52.10
31	121.00
32	89.35
33	99.00
34	89.55
35	89.50
36	72.40
37	-
38	91.10
39	85.00
40	94.30
41A	-
41B	-
42	86.50
43	94.45
44	93.05
45	71.85
46	-
47	117.50
48	82.60
49	-
50	93.14
51	-
52	-
53	83.65 UC
54	93.18

55	76.75	UC
56	-	
57	-	
58	73.65	
59	91.25	
60	98.50	
61	90.95	
62	84.55	
63A	78.70	
63B	-	
64	-	
65	-	
66	-	
67	75.40	
68	94.50	
69	71.15	
70	95.85	
71	-	
72	91.47	
73	-	
74	-	
75	80.00	
76	-	
77	93.00	
78	-	
79	-	
No of labs., p	47	
No of repl., n	2	
m	89.02	
s ²	137.51	
s	11.73	
Assigned value, μ	91	
Recovery, %	97.8	
$t = \sqrt{p} \cdot (m-\mu)/s$	-1.1572	
Sign. level, p(t)	0.2532	

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	56.35
1B	-
2	-
3	-
4	85.30
5	-
6	-
7	-
8	46.55
9	43.55
10	-
11	87.00
12	-
13	-
14	-
15	-
16	-
17	39.00
18	-
19	-
20	53.65
21	-
22	-
23	55.75
24	57.65
25	-
26	-
27	-
28	-
29	-
30	-
31	34.55
32	-
33	-
34	63.55
35	-
36	-
37	-
38	55.40
39	-
40	57.55
41A	-
41B	-
42	-
43	-
44	-
45	84.25
46	-
47	-
48	-
49	-
50	-
51	-
52	-
53	49.30
54	-

55	54.90
56	-
57	-
58	47.15
59	-
60	-
61	49.85
62	-
63A	-
63B	-
64	-
65	-
66	-
67	50.95
68	8.75
69	77.25
70	-
71	-
72	57.50
73	-
74	-
75	-
76	-
77	53.00
78	-
79	-
No of labs., p	23
No of repl., n	2
m	55.16
s ²	297.55
s	17.25
Assigned value, μ	55
Recovery, %	100.3
$t = \sqrt{p} \cdot (m-\mu)/s$	0.0453
Sign. level, p(t)	0.9643

No test statistics were found to be significant

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

Laboratory	Sample pair AB
1	42.65
1B	-
2	43.70
3	36.50
4	32.40
5	43.00
6	42.09
7	42.85
8	41.50
9	43.10
10	43.00
11	31.40
12	38.60
13	34.00
14	40.00
15	55.00
16	39.42
17	-
18	25.50 UG
19	44.10
20	-
21	44.00
22	-
23	43.30
24	44.15
25	45.13
26	-
27	37.50
28	45.10
29	43.57
30	-
31	-
32	-
33	42.79
34	43.55
35	36.40
36	44.55
37	45.75
38	-
39	40.50
40	37.80
41A	40.95
41B	-
42	42.40
43	-
44	44.05
45	33.20
46	38.75
47	-
48	42.35
49	43.25
50	42.30
51	44.55
52	39.30
53	-
54	43.90

55	42.90
56	44.40
57	43.35
58	-
59	33.40
60	42.50
61	44.19
62	41.60
63A	41.10
63B	-
64	43.95
65	44.20
66	43.85
67	-
68	36.80
69	39.30
70	-
71	41.00
72	44.78
73	43.85
74	43.45
75	44.45
76	42.13
77	44.00
78	43.00
79	45.55
No of labs., p	64
No of repl., n	2
m	41.81
s ²	14.48
s	3.81
Assigned value, μ	42.9
Recovery, %	97.5
$t = \sqrt{p} \cdot (m-\mu)/s$	-2.2814
Sign. level, p(t)	0.0259 *

* 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

A P P E N D I X E

Concentration level

Concentration level **SPIL-1 (2012)**

Parameter	Unit	Sample	Bottle no.	I	II	Bottle Average	Sample Average	Assigned value	Spike	
									Measured	Assigned
COD	mg/L O2	A1		28,6	28,8	28,7	28,7	29	2,6	3
		B1		31,6	30,9	31,3	31,3	32		
Total phosphorus	mg/L P	A2		0,487	0,482	0,485	0,485	0,400	0,074	0,055
		B2		0,565	0,552	0,559	0,559	0,455		
Chloride	mg/L	A2		85,8	85,2	85,5	85,5	91	9,9	10
		B2		95,8	95,0	95,4	95,4	101		
Sulphate	mg/L	A2		43,6	43,4	43,5	43,5	55	3,4	7
		B2		47,0	46,8	46,9	46,9	62		
Total suspended solids	mg/L	A3		44,6		44,6	44,6	42,9	0,4	0,0
		B3		44,2		44,2	44,2	42,9		

A P P E N D I X F

Homogeneity and stability

PT:SPIL-1 (2012)
Parameter:NVOC
Unit:mg/L C
Sigma:1,2009 10%

Responsible for tests: uol

10% level or $2 \cdot S_{T \max}$

Homogeneity test Date:2012-03-02

Sample	x(a)	x(b)	average	sd	sd^2
A1-1	12,36	12,45	12,41	0,064	0,004
A1-10	12,06	11,87	11,97	0,134	0,02
A1-19	12,00	11,92	11,96	0,057	0,003
A1-28	11,83	11,89	11,86	0,042	0,002
A1-37	11,91	12,04	11,98	0,092	0,008
A1-46	11,85	12,03	11,94	0,127	0,016
A1-55	11,97	12,05	12,01	0,057	0,003
A1-64	11,86	12,19	12,03	0,233	0,054
A1-73	12,14	12,91	12,53	0,544	0,296
A1-83	12,47	11,90	12,19	0,403	0,162
A1-93	11,74	11,73	11,74	0,007	0,000
A1-106	11,57	11,48	11,53	0,064	0,004

For homogeneity

General average (x)	12,01
Sample average sd (s_x)	0,269
Within-sample sd (s_w):	0,218
Between-samples sd (ss):	0,2203
S_L in the Proficiency Test:	1,46
S_R in the Proficiency Test:	1,49

Stability test Date:

Sample	x(a)	x(b)

For stability

General average (y):

$|x-y| =$

$ss = 0,220$ $0.3 \cdot \sigma = 0,36$ $ x-y =$	
Analytical quality	Is $s_w < 0,15 \cdot \sigma$ NO
Homogeneity:	Is $ss < 0.3 \cdot \sigma$? YES
Stability:	$ x-y < 0.3 \cdot \sigma$? No data

PT: SPIL-1 (2012)
Parameter: TP
Unit: mg/L P
Sigma: 0,06 $2 \cdot S_{T \max}$

Responsible for tests: uol

10% level or $2 \cdot S_{T \max}$

Homogeneity test Date: 2012-02-28

Sample	x(a)	x(b)	average	sd	sd ²
B2-1	0,465	0,463	0,464	0,001	0,000
B2-14	0,464	0,457	0,461	0,005	0,00
B2-28	0,455	0,457	0,456	0,001	0,000
B2-36	0,475	0,478	0,477	0,002	0,000
B2-48	0,473	0,469	0,471	0,003	0,000
B2-55	0,417	0,449	0,433	0,023	0,001
B2-62	0,446	0,447	0,447	0,001	0,000
B2-74	0,460	0,456	0,458	0,003	0,000
B2-86	0,470	0,460	0,465	0,007	0,000
B2-91	0,448	0,447	0,448	0,001	0,000
B2-98	0,431	0,454	0,443	0,016	0,000
B2-110	0,452	0,451	0,452	0,001	0,000

For homogeneity

General average (x)	0,456
Sample average sd (s _x)	0,012
Within-sample sd (s _w):	0,009
Between-samples sd (ss):	0,011
S _L in the Proficiency Test:	0,0182
S _R in the Proficiency Test:	0,0199

Stability test Date:

Sample	x(a)	x(b)

For stability

General average (y):

|x-y| =

ss = 0,011		0.3*sigma= 0,018	
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-1 (2012)
 Parameter: TSS
 Unit: mg/L
 Sigma: 6,0 $2 \cdot S_{T \max}$

Responsible for tests: uol

10% level or $2 \cdot S_{T \max}$

Homogeneity test

Date: 2012-02-29

Sample	x(a)	x(b)	average	sd	sd^2
A3-1	41,5		41,5		
A3-72	44,5		44,5		
A3-14	44,7		44,7		
A3-21	44,8		44,8		
A3-28	44,7		44,7		
A3-36	44,9		44,9		
A3-44	45,1		45,1		
A3-52	43,9		43,9		
A3-61	45,1		45,1		
A3-73	45,2		45,2		
A3-87	45,3		45,3		
A3-95	45,1		45,1		

For homogeneity

General average (x)	44,6
Sample average sd (s_x)	1,04
Within-sample sd (s_w):	
Between-samples sd (ss):	1,04
S_L in the Proficiency Test:	3,42
S_R in the Proficiency Test:	4,16

Stability test

Date: 2012-03-15

Sample	x(a)	x(b)
A3	44,6	
B3	44,2	

For stability

General average (y):	44,4
$ x-y =$	0,17

Conclusions

ss = 1,04		0.3*sigma= 1,80	
$ x-y = 0,17$			
Analytical quality	Is $s_w < 0,15 \cdot \sigma$		
	No data		
Homogeneity:	Is ss < 0.3*sigma?		
	YES		
Stability:	$ x-y < 0.3 \cdot \sigma$?		
	YES		