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Proficiency test SPIL-4 (2017)

Nitrogen parameters in wastewater (effluent)

Quality Documentation
August 2018

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CONTENTS

1 INTRODUCTION

A proficiency test on the analysis of nitrogen parameters in wastewater was conducted on 16 November 2017. The proficiency test was organised by Eurofins Miljø A/S.

The present report contains Eurofins' documentation for the quality of the proficiency test. Results of the proficiency test including data from participating laboratories and statistical analysis of these data were issued in a report to all participants /1/ on 18 December 2017.

2 FEATURES OF THE PROFICIENCY TEST

Participants in the proficiency test were a total of 56 laboratories from Denmark, Norway and Sweden. A list of participants is shown in Appendix A.

The closing date for submission of results was 1 December 2017. 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 effluent. Sample preparation is described in Appendix B.

Table 1 Samples in the proficiency test

Sample name	Parameters
A1/B1	TN, NH_4, NO_{2+3}, NO_3, γ_{25}
A2/B2	pH

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
Total nitrogen	TN	mg/L N	2-10	5.4	0.12	1.2
Ammonium	NH_4	mg/L N	0.1-2	0.876	0.0092	0.189
Nitrite+nitrate	NO_{2+3}	mg/L N	1-5	2.93	0.078	0.60
Nitrate	NO_3	mg/L N	1-5	3.07	0.032	0.60
Conductivity	γ_{25}	mS/m	50-300	81.2	0.67	0.7
pH	pH		6-9	8.04	0.052	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 except for γ_{25} where the spike value is the difference between median values for the two samples in the sample pair.

The assigned value for TN is operationally defined and is a consensus value based upon the median for method no. 2 (TN). A list of method identification numbers is found in the report to participants /1/. Assigned values for NH_4, NO_{2+3}, NO_3, conductivity and pH 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 showed no significant difference between the two. The test revealed a significant difference between the two for pH. 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 revealed a significant difference between the two for pH. Average recovery was 99.0 %. Scrutiny of the documentation showed no indication of mistake in sample preparation. The difference has insignificant influence on the general quality of analyses estimated from the data as well as on the evaluation of participating laboratories. The assigned value is therefore kept unchanged.

3 HOMOGENEITY AND STABILITY OF SAMPLES

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

NH_4	Combined homogeneity and stability test
NO_3	Combined homogeneity and stability test
pH	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) and

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

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

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

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

4 CONCLUSION

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

For pH the participants could not recover the spike value and the assigned 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. 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-4 (2017)*, Report to participants, December 2017.

/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. 1146 on *quality criteria for environmental measurements,* 24 October 2017 (in Danish).

/6/ 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 A/S	Grenaa	Denmark
Biofos A/S	København K	Denmark
Bjergmarken R/A, Fors Spildevand Roskilde	Roskilde	Denmark
BlueKolding A/S	Kolding	Denmark
CP Kelco ApS, Spildevandslaboratoriet	Ll. Skensved	Denmark
Eurofins Miljø A/S	Vejen	Denmark
Faxe Forsyning	Faxe	Denmark
Fors Spildevand Holbæk	Holbæk	Denmark
Hedensted Spildevand A/S	Daugård	Denmark
Hillerød Forsyning Spildevand A/S	Hillerød	Denmark
Holstebro renseanlæg, Vestforsyning, erhverv	Holstebro	Denmark
Højvang	Holstebro	Denmark
Kerteminde Forsyning - Spildevand A/S	Kerteminde	Denmark
Klarforsyning, Greve Spildevand	Køge	Denmark
Melby Renseanlæg	Liseleje	Denmark
Nyborg Renseanlæg	Nyborg	Denmark
Næstved Central Renseanlæg, NK-Spildevand	Næstved	Denmark
Provas	Haderslev	Denmark
RGS 90	Skælskør	Denmark
Ringkøbing-Skjern Forsyning A/S	Skjern	Denmark
Rønne Renseanlæg	Rønne	Denmark
Slagelse Renseanlæg (5 participants)	Slagelse	Denmark
Spildevandslaboratoriet (2 participants)	Esbjerg	Denmark
Svendborg Centralrenseanlæg	Skårup Fyn	Denmark
Vandmiljø Randers A/S	Randers SØ	Denmark
Vejle Spildevand A/S	Vejle	Denmark
Ålborg Renseanlæg Øst	Ålborg Øst	Denmark
AlControl Hamar	Hamar	Norway
NGIs Miljølaboratorium	Oslo	Norway
AB Lennart Månsson International	Helsingborg	Sweden
Arctic Paper Munkedals AB	Munkedal	Sweden
Ernemar Laboratorium	Oskarshamn	Sweden
GRYAAB AB	Göteborg	Sweden

Laboratory	Town	Country
Holmen Paper AB Bravikens Pappersbruk	Norrköping	Sweden
Kalmar Vatten AB, VA-lab	Kalmar	Sweden
Kristianstad Kommun	Kristianstad	Sweden
Käppalaverket	Lidingö	Sweden
Mjölby Kommun	Mjölby	Sweden
Motala Kommun	Motala	Sweden
Perstorp Oxo AB	Stenungsund	Sweden
Preem AB Göteborg	Göteborg	Sweden
Preemraff Lysekil	Lysekil	Sweden
Rottneros Bruk AB	Rottneros	Sweden
Smurfit Kappa Piteå	Piteå	Sweden
St1 Refinery AB	Göteborg	Sweden
Södra Cell AB, Värö	Väröbacka	Sweden
Södra Cell Mörrum	Mörrum	Sweden
Tekniska förvaltningen, Verksamhetsstöd VA, Laboratoriet	Örebro	Sweden
Vallviks Bruk	Vallvik	Sweden
Västerviks Miljö & Energi AB, Vattenlaboratoriet	Västervik	Sweden
Yara AB	Köping	Sweden

ANNEX B SAMPLE PREPARATION

Stock solution	**Prepared from**	**Concentration**
Stock TN	2.9985 g Disodium edetate, $2H_2O$ milli-Q water up to 1000 g	TN: 225.7 mg/kg N
Stock NH_4	1. 004 g Ammonium chloride (NH_4Cl) milli-Q water up to 1000 g	NH_4: 263.0 mg/kg N
Stock NO_3	2.5016 g Potassium nitrate (KNO_3) milli-Q water up to 1000 g	NO_3: 346.7 mg/kg N

Sample	**Sample prepared from**	**TN mg/L N**	**NH_4 mg/L N**	**NO_3 mg/L N**	**Conductivity mS/m**
A1	70.03 g stock TN 25.00 g stock NH_4 60.03 g stock NO_3 Sample B1 up to 34.00 kg	0.995 · (a+2.81) + 1.270	0.995 · (b+0.809) + 0.193	0.995 · (c+0.960) + 0.612	e
B1	300.03 g stock TN 200.08 g stock NH_4 180.00 g stock NO_3 filtered water from Stegholt sewage treatment plant up to 65.00 kg	a+2.81	b+0.809	c+0.960	d

Sample	**Sample prepared from**	**pH**
A2/B2	Filtered treated wastewater from Stegholt sewage treatment plant.	f

ANNEX C CONTROL OF SPIKE VALUES

Total nitrogen, mg/L N
Control of differences within sample pairs

Laboratory	Difference AB	
1	0.410	
2	0.090	
3	-0.040	
4	-0.140	
5	-0.150	
6	-	
7	0.148	
8	-0.080	
9	-0.080	
10	-0.010	
11	-0.070	
12	0.080	
13	-0.090	
14	-0.670	
15	-0.400	
16	0.170	
17	-0.050	
18	0.160	
19	0.120	
20	-0.200	
21	-0.390	
22	0.200	
23	-0.010	
24A	0.090	
24B	-0.120	
25	0.150	
26	-0.500	
27	0.060	
28	0.020	
29	0.090	
30	-0.110	
31	-0.080	
32	0.200	
33	0.010	
34	-0.040	
35	-0.130	
36	-65.745	UC
37	-	
38	0.050	
39A	-0.290	
39B	-0.020	
40	0.020	
41	0.020	
42	0.090	
43	4.100	UC
44	0.140	
45	-0.420	
46	-0.420	
47	0.010	
48A	-0.590	
48B	-	
49	0.040	
50	0.300	
51	-0.090	
52	0.240	
53	-1.010	UC
54	-0.010	
55	-0.010	
56	-0.050	
No of labs., p	53	
No of repl., n	2	
d	-0.044	
s^2	0.047	
s	0.217	
$t = \sqrt{p} \cdot (d/s)$	-1.4905	
Sign. level, p(t)	0.1421	

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

Ammonium, mg/L N

Control of differences within sample pairs

Laboratory	Difference AB	
1	0.003	
2	-	
3	-0.028	
4	-0.059	
5	-0.052	
6	-0.004	
7	-0.114	UC
8	0.001	
9	-0.079	UC
10	0.001	
11	0.121	UC
12	0.014	
13	-0.010	
14	-0.002	
15	-0.009	
16	0.002	
17	-	
18	0.017	
19	0.041	
20	-	
21	0.002	
22	0.017	
23	-0.002	
24A	0.008	
24B	-	
25	0.000	
26	-0.019	
27	-0.002	
28	-	
29	-0.014	
30	0.041	UG
31	0.004	
32	-0.009	
33	-0.009	
34	0.015	
35	0.011	UG
36	0.021	
37	-	
38	-0.002	
39A	0.012	
39B	-0.005	
40	-0.041	
41	-0.017	
42	-0.010	
43	-0.020	
44	-	
45	0.021	
46	-0.009	
47	0.011	
48A	-0.196	UC
48B	-	
49	-0.026	
50	-	
51	0.007	
52	0.003	
53	1.351	UC

Laboratory	Difference AB
54	0.001
55	0.014
56	-
No of labs., p	42
No of repl., n	2
d	-0.003
s^2	0.000
s	0.019
$t = \sqrt{p} \cdot (d/s)$	-1.0844
Sign. level, p(t)	0.2845

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

Nitrite+nitrate, mg/L N

Control of differences within sample pairs

Laboratory	Difference AB
1	0.030
2	-
3	-
4	-
5	-
6	-0.080
7	-
8	-
9	-
10	-0.000
11	0.050
12	-
13	-
14	-
15	-
16	-
17	-
18	0.030
19	0.010
20	-
21	-
22	-0.080
23	-
24A	-0.030
24B	-
25	-
26	-
27	-
28	-
29	-
30	-
31	-
32	-
33	-
34	-
35	-
36	-0.180
37	-
38	-
39A	-
39B	-
40	0.000
41	-0.040
42	-
43	-
44	-
45	0.080
46	-
47	-
48A	-
48B	-
49	0.002
50	-
51	-
52	-
53	0.010
54	0.140
55	-
56	-
No of labs., p	15
No of repl., n	2
d	-0.004
s^2	0.006
s	0.075
$t = \sqrt{p} \cdot (d/s)$	-0.2007
Sign. level, p(t)	0.8439

No test statistics were found to be significant

Nitrate, mg/L N

Control of differences within sample pairs

Laboratory	Difference AB	
1	-	
2	-	
3	-0.040	
4	-	
5	0.040	
6	-	
7	-0.010	
8	-0.060	
9	-0.100	
10	-0.010	
11	-	
12	-0.010	
13	-0.030	
14	0.110	
15	-0.120	
16	-0.050	
17	-	
18	-	
19	-	
20	-	
21	-0.080	UG
22	-	
23	-0.010	
24A	-0.030	
24B	-	
25	-	
26	0.070	
27	-0.020	
28	-	
29	0.010	
30	-0.130	UG
31	-0.030	
32	-0.030	
33	0.020	
34	0.030	
35	0.030	
36	-0.181	
37	-	
38	-0.060	
39A	-0.020	
39B	0.180	
40	0.000	
41	-	
42	-0.020	
43	0.100	
44	-	
45	-	
46	0.310	UC
47	-0.050	
48A	-0.580	UC
48B	-	
49	0.000	
50	-	
51	-0.020	
52	-0.010	
53	-	
54	0.140	
55	0.020	
56	-	
No of labs., p	34	
No of repl., n	2	
d	-0.005	
s^2	0.005	
s	0.069	
$t = \sqrt{p} \cdot (d/s)$	-0.3975	
Sign. level, p(t)	0.6935	

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

Conduktivity, mS/m

Control of differences within sample pairs

Laboratory	Difference AB	
1	-0.09	
2	-	
3	-0.20	
4	-	
5	-	
6	0.30	
7	-0.50	
8	-0.60	
9	-	
10	0.70	
11	-	
12	-	
13	-	
14	-	
15	-	
16	0.60	
17	-	
18	-	
19	0.10	
20	-	
21	-	
22	-0.40	
23	0.10	
24A	-0.30	
24B	-	
25	-	
26	-0.80	
27	-	
28	0.40	
29	-	
30	-0.60	
31	-	
32	2.30	UC
33	-0.20	UG
34	-	
35	-0.40	
36	-	
37	-0.30	
38	-	
39A	-	
39B	-	
40	0.00	
41	-0.50	
42	-	
43	0.10	
44	-0.30	
45	-	
46	-	
47	-	
48A	-	
48B	-	
49	-0.50	
50	-	
51	-0.70	
52	0.23	
53	-	

Laboratory	Difference AB
54	-
55	-
56	-
No of labs., p	23
No of repl., n	2
d	-0.16
s^2	0.17
s	0.42
$t = \sqrt{p} \cdot (d/s)$	-1.8270
Sign. level, p(t)	0.0813

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

pH,
Control of differences within sample pairs

Laboratory	Difference AB	
1	-0.030	
2	0.110	
3	-0.250	
4	-0.040	
5	-0.100	
6	0.000	
7	0.030	
8	0.000	
9	-0.220	
10	0.020	
11	-0.060	
12	0.070	
13	-0.020	
14	-0.040	
15	0.010	
16	-0.050	
17	0.030	
18	-	
19	-0.011	
20	-	
21	-0.150	
22	0.070	
23	-0.050	
24A	-0.030	
24B	-	
25	-0.150	
26	-0.070	UG
27	0.050	
28	-0.040	
29	-0.020	
30	-0.010	
31	-0.170	
32	1.000	UC
33	0.130	
34	-0.230	
35	0.080	
36	-0.010	
37	-0.040	
38	-0.080	
39A	-0.130	
39B	-	
40	-0.050	
41	0.040	
42	-0.020	
43	-0.070	
44	-0.010	
45	0.170	
46	-0.120	
47	-0.060	
48A	0.130	
48B	0.070	
49	0.000	
50	-	
51	0.000	
52	0.010	
53	-0.060	
54	-0.110	
55	0.100	
56	-	
No of labs., p	51	
No of repl., n	2	
d	-0.026	
s^2	0.008	
s	0.090	
$t = \sqrt{p} \cdot (d/s)$	-2.0292	
Sign. level, p(t)	0.0478	*

* 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.

ANNEX D CONTROL OF RECOVERY

Total nitrogen, mg/L N
Control of recovery, average of results

Laboratory	Sample pair AB	
1	5.535	
2	5.215	
3	6.090	
4	4.500	
5	4.955	
6	-	
7	5.223	
8	4.370	
9	5.320	
10	5.325	
11	4.745	
12	5.550	
13	5.395	
14	4.675	
15	5.080	
16	5.505	
17	5.015	
18	6.390	
19	5.840	
20	4.500	
21	4.035	
22	5.200	
23	5.395	
24A	5.345	
24B	5.240	
25	5.425	
26	6.930	
27	5.630	
28	5.750	
29	5.385	
30	4.815	
31	5.500	
32	5.400	
33	5.215	
34	5.280	
35	5.525	
36	38.147	UC
37	-	
38	4.755	
39A	4.785	
39B	4.790	
40	5.630	
41	5.650	
42	5.305	
43	4.100	UC
44	5.450	
45	5.090	
46	4.840	
47	5.095	
48A	6.065	
48B	-	
49	5.680	
50	5.070	
51	4.705	
52	5.760	
53	0.365	UC
54	5.265	
55	5.625	
56	4.985	
No of labs., p	53	
No of repl., n	2	
m	5.280	
s^2	0.255	
s	0.505	
Assigned value, μ	5.4	
Recovery, %	97.8	
$t = \sqrt{p} \cdot (m-\mu)/s$	-1.7301	
Sign. level, p(t)	0.0895	

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

Ammonium, mg/L N

Control of recovery, average of results

Laboratory	Sample pair AB	
1	0.899	
2	-	
3	0.905	
4	0.780	
5	0.857	
6	0.853	
7	0.833	UC
8	0.901	
9	0.670	UC
10	0.911	
11	0.900	UC
12	0.834	
13	0.886	
14	0.872	
15	0.885	
16	0.890	
17	-	
18	0.923	
19	0.980	
20	-	
21	0.880	
22	0.883	
23	0.872	
24A	0.887	
24B	-	
25	0.861	
26	0.841	
27	0.872	
28	-	
29	0.878	
30	1.000	UG
31	0.889	
32	0.815	
33	0.845	
34	0.893	
35	1.035	UG
36	0.851	
37	-	
38	0.882	
39A	0.885	
39B	0.853	
40	0.891	
41	0.869	
42	0.876	
43	0.776	
44	0.851	
45	0.891	
46	0.875	
47	0.895	
48A	0.714	UC
48B	-	
49	0.840	
50	-	
51	0.847	
52	0.889	
53	6.226	UC
54	0.851	
55	0.934	
56	-	

No of labs., p	42
No of repl., n	2
m	0.874
s^2	0.001
s	0.036
Assigned value, μ	0.876
Recovery, %	99.7
$t = \sqrt{p} \cdot (m-\mu)/s$	-0.3931
Sign. level, p(t)	0.6963

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

Nitrite+nitrate, mg/L N

Control of recovery, average of results

Laboratory	Sample pair AB
1	2.945
2	-
3	-
4	-
5	-
6	2.930
7	-
8	-
9	-
10	2.910
11	2.815
12	-
13	-
14	-
15	-
16	-
17	-
18	2.945
19	2.915
20	-
21	-
22	3.070
23	-
24A	2.925
24B	-
25	-
26	-
27	-
28	-
29	-
30	-
31	-
32	-
33	-
34	-
35	-
36	3.059
37	-
38	-
39A	-
39B	-
40	3.120
41	2.680
42	-
43	-
44	-
45	3.140
46	-
47	-
48A	-
48B	-
49	2.843
50	-
51	-
52	-
53	2.945
54	2.710
55	-
56	-
No of labs., p	15
No of repl., n	2
m	2.930
s^2	0.018
s	0.133
Assigned value, μ	2.93
Recovery, %	100.0
$t = \sqrt{p} \cdot (m-\mu)/s$	0.0039
Sign. level, p(t)	0.9970

No test statistics were found to be significant

Nitrate, mg/L N

Control of recovery, average of results

Laboratory	Sample pair AB	
1	-	
2	-	
3	3.010	
4	-	
5	3.130	
6	-	
7	3.015	
8	3.160	
9	3.100	
10	2.905	
11	-	
12	3.115	
13	3.045	
14	3.165	
15	3.130	
16	3.135	
17	-	
18	-	
19	-	
20	-	
21	2.520	UG
22	-	
23	3.035	
24A	2.925	
24B	-	
25	-	
26	3.235	
27	3.050	
28	-	
29	3.065	
30	2.585	UG
31	3.145	
32	3.065	
33	3.190	
34	3.435	
35	3.245	
36	3.055	
37	-	
38	3.070	
39A	3.080	
39B	3.020	
40	3.120	
41	-	
42	3.050	
43	3.070	
44	-	
45	-	
46	3.275	UC
47	3.215	
48A	2.730	UC
48B	-	
49	2.840	
50	-	
51	2.850	
52	3.005	
53	-	
54	2.710	
55	3.130	
56	-	

No of labs., p	34
No of repl., n	2
m	3.074
s^2	0.017
s	0.131
Assigned value, μ	3.07
Recovery, %	100.1
$t = \sqrt{p} \cdot (m-\mu)/s$	0.1776
Sign. level, p(t)	0.8601

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

Conduktivity, mS/m
Control of recovery, average of results

Laboratory	Sample pair AB	
1	81.66	
2	-	
3	78.10	
4	-	
5	-	
6	81.05	
7	82.45	
8	82.10	
9	-	
10	80.15	
11	-	
12	-	
13	-	
14	-	
15	-	
16	78.00	
17	-	
18	-	
19	81.75	
20	-	
21	-	
22	82.70	
23	81.15	
24A	82.35	
24B	-	
25	-	
26	75.00	
27	-	
28	79.90	
29	-	
30	76.10	
31	-	
32	73.15	UC
33	92.70	UG
34	-	
35	78.50	
36	-	
37	82.25	
38	-	
39A	-	
39B	-	
40	81.00	
41	81.75	
42	-	
43	82.45	
44	81.95	
45	-	
46	-	
47	-	
48A	-	
48B	-	
49	80.95	
50	-	
51	80.95	
52	80.84	
53	-	
54	-	
55	-	
56	-	
No of labs., p	23	
No of repl., n	2	
m	80.57	
s^2	4.34	
s	2.08	
Assigned value, μ	81.2	
Recovery, %	99.2	
$t = \sqrt{p} \cdot (m-\mu)/s$	-1.4507	
Sign. level, p(t)	0.1610	

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

pH,
Control of recovery, average of results

Laboratory	Sample pair AB	
1	8.145	
2	8.025	
3	7.325	
4	8.120	
5	7.850	
6	8.060	
7	8.025	
8	8.070	
9	7.560	
10	7.850	
11	8.050	
12	7.945	
13	8.130	
14	8.100	
15	7.835	
16	8.115	
17	8.205	
18	-	
19	7.870	
20	-	
21	7.845	
22	8.135	
23	8.035	
24A	8.045	
24B	-	
25	8.105	
26	7.025	UG
27	7.825	
28	8.120	
29	7.610	
30	8.065	
31	7.745	
32	7.500	UC
33	8.205	
34	7.938	
35	8.100	
36	8.045	
37	8.020	
38	8.010	
39A	7.725	
39B	-	
40	8.155	
41	8.150	
42	7.590	
43	8.045	
44	8.065	
45	7.725	
46	8.110	
47	7.770	
48A	7.985	
48B	8.015	
49	8.050	
50	-	
51	8.110	
52	8.015	
53	7.400	
54	8.015	
55	7.870	
56	-	
No of labs., p	51	
No of repl., n	2	
m	7.959	
s^2	0.040	
s	0.200	
Assigned value, μ	8.04	
Recovery, %	99.0	
$t = \sqrt{p} \cdot (m-\mu)/s$	-2.8846	
Sign. level, p(t)	0.0058	**

* 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

ANNEX E CONCENTRATION LEVEL

Concentration level **SPIL-4 (2017)**

Parameter	Unit	Sample	Bottle no.	I	II	Bottle Average	Sample Average	Assigned value	Spike Measured	Spike Assigned
Ammonium	mg/L N	A1	9	1,070	1,070	1,07	1,075	1,065	0,201	0,189
			37	1,060	1,090	1,08				
			66	1,070	1,090	1,08				
		B1	6	0,880	0,874	0,88	0,874	0,876		
			36	0,876	0,876	0,88				
			62	0,874	0,866	0,87				
Nitrate	mg/L N	A1	9	3,81	3,78	3,78	3,79	3,67	0,59	0,60
			37	3,78	3,78	3,78				
			66	3,80	3,81	3,81				
		B1	6	3,17	3,21	3,19	3,20	3,07		
			36	3,18	3,20	3,19				
			62	3,23	3,19	3,21				
pH		A2	17	7,78	7,82	7,80	7,80	8,04	0,10	0
			35	7,79	7,83	7,81				
			68	7,76	7,79	7,78				
		B2	27	7,81	7,87	7,84	7,89	8,04		
			48	7,94	7,97	7,96				
			57	7,86	7,90	7,88				

ANNEX F HOMOGENEITY AND STABILITY

PT:	SPIL-4
Parameter:	NH4
Unit:	mg/L N
Sigma:	0,4

Responsible for tests: IRL

Homogeneity test Date: 2017-10-31

Sample	x(a)	x(b)	average	sd	sd^2
A1-8	1,07	1,07	1,1	0,000	0,000
A1-18	1,06	1,07	1,1	0,007	0,00
A1-28	1,07	1,08	1,1	0,007	0,000
A1-33	1,07	1,07	1,1	0,000	0,000
A1-38	1,07	1,06	1,1	0,007	0,000
A1-45	1,06	1,07	1,1	0,007	0,000
A1-49	1,07	1,07	1,1	0,000	0,000
A1-60	1,07	1,06	1,1	0,007	0,000
A1-65	1,08	1,07	1,1	0,007	0,000
A1-70	1,05	1,08	1,1	0,021	0,000
A1-75	1,07	1,08	1,1	0,007	0,000
A1-79	1,06	1,08	1,1	0,014	0,000

For homogeneity

General average (x)	1,07
Sample average sd (s_x)	0,004
Within-sample sd (s_w):	0,009
Between-samples sd (ss):	0
S_L in the Proficiency Test:	0,035
S_R in the Proficiency Test:	0,037

Stability test Date: 2017-11-16

Sample	x(a)	x(b)
A1-9	1,07	1,07
A1-37	1,06	1,09
A1-66	1,07	1,09

For stability

General average (y):	1,075
/x-y/ =	0,005833

Conclusions

ss =	0	0.3*sigma=	0,11
/x-y/ =	0,005833		
Analytical quality	Is s_w < 0,15*sigma **YES**		
Homogeneity:	Is ss < 0.3*sigma? **YES**		
Stability:	/x-y/ < 0.3*sigma? **YES**		

PT:	SPIL-4
Parameter:	NO3
Unit:	mg/L N
Sigma:	0,4

Responsible for tests: IRL

Homogeneity test Date: 2017-10-31

Sample	x(a)	x(b)	average	sd	sd^2
A1-8	3,82	3,88	3,9	0,042	0,002
A1-18	3,80	3,83	3,8	0,021	0,00
A1-28	3,78	3,85	3,8	0,049	0,002
A1-33	3,84	3,88	3,9	0,028	0,001
A1-38	3,85	3,87	3,9	0,014	0,000
A1-45	3,89	3,88	3,9	0,007	0,000
A1-49	3,86	3,85	3,9	0,007	0,000
A1-60	3,85	3,86	3,9	0,007	0,000
A1-65	3,86	3,82	3,8	0,028	0,001
A1-70	3,84	3,86	3,9	0,014	0,000
A1-75	3,87	3,84	3,9	0,021	0,000
A1-79	3,85	3,80	3,8	0,035	0,001

For homogeneity

General average (x)	3,85
Sample average sd (s_x)	0,020
Within-sample sd (s_w):	0,027
Between-samples sd (ss):	0,0077
S_L in the Proficiency Test:	0,126
S_R in the Proficiency Test:	0,135

Stability test Date: 2017-11-16

Sample	x(a)	x(b)
A1-9	3,81	3,78
A1-37	3,78	3,78
A1-66	3,8	3,81

For stability

General average (y):	3,793333
/x-y/ =	0,05375

Conclusions

ss =	0,008	0.3*sigma=	0,11
/x-y/ =	0,05375		

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

PT:	SPIL-4
Parameter:	pH
Unit:	-
Sigma:	0,1

Responsible for tests: IRL

Homogeneity test Date: 2017-10-31

Sample	x(a)	x(b)	average	sd	sd^2
B2-4	8,21	8,21	8,2	0,000	0,000
B2-10	8,20	8,20	8,2	0,000	0,000
B2-18	8,22	8,21	8,2	0,007	0,000
B2-24	8,21	8,21	8,2	0,000	0,000
B2-32	8,20	8,19	8,2	0,007	0,000
B2-38	8,20	8,22	8,2	0,014	0,000
B2-46	8,20	8,22	8,2	0,014	0,000
B2-52	8,21	8,22	8,2	0,007	0,000
B2-60	8,20	8,23	8,2	0,021	0,000
B2-66	8,22	8,22	8,2	0,000	0,000
B2-73	8,22	8,24	8,2	0,014	0,000
B2-79	8,21	8,25	8,2	0,028	0,001

For homogeneity

General average (x)	8,2
Sample average sd (s_x)	0,010
Within-sample sd (s_w):	0,013
Between-samples sd (ss):	0,005
S_L in the Proficiency Test:	0,195
S_R in the Proficiency Test:	0,205

Stability test Date: 2017-11-16

Sample	x(a)	x(b)
B2-27	7,81	7,87
B2-48	7,94	7,97
B2-57	7,86	7,9

Conclusions

ss = 0,00 0.3*sigma= 0,02

/x-y/ = 0

Homogeneity: Is ss < 0.3*sigma?

YES