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Proficiency test SPIL-2 (2020)

Nitrogen parameters in wastewater (synthetic wastewater, effluent)

Quality Documentation
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Proficiency test SPIL-2 (2020)
Quality Documentation

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CONTENTS

1 INTRODUCTION

A proficiency test on the analysis of nitrogen parameters in wastewater was conducted on 14 May 2020. 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 16 June 2020.

2 FEATURES OF THE PROFICIENCY TEST

Participants in the proficiency test were a total of 46 laboratories from Denmark, Norway and Sweden. A list of participants is shown in Appendix A.

The closing date for submission of results was 28 May 2020. All participants except laboratory no. 26, 30 and 38 had submitted their results before the dead-line.

2.1 Sample preparation

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

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/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 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
Total nitrogen	TN	mg/l N	2-10	6.97	0.024	1.86
Ammonium	NH_4	mg/l N	0.1-2	0.786	0.0066	0.171
Nitrite+nitrate	NO_{2+3}	mg/l N	1-5	2.43	0.020	0.45
Nitrate	NO_3	mg/l N	1-5	2.38	0.020	0.42
Conductivity	γ_{25}	mS/m	50-300	105.7	1.6	20
pH	pH		6-9	6.90	0.013	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. The assigned and spike values are both calculated from sample preparation for TN, NH_4 and NO_{2+3}. For NO_3, conductivity and pH the assigned value is a consensus value for all laboratories based on the median and the spike value for the two samples in the sample pair.

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 for NO_{2+3}, NO_3 and pH. The test revealed a significant difference between the two for TN, NH_4 and conductivity. For TN 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. 6, 9, 71, 71A and 71B and now showed no significant difference. The spike value is therefore kept unchanged. For NH_4 and conductivity 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. For most of the parameters the test showed no significant difference between the two and the control of assigned value at Eurofins confirmed the value (Appendix E). The test revealed a significant difference between the two for TN. Average recovery was 96,8 %. 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. 6, 9, 71, 71A and 71B and now showed no significant difference. 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	Homogeneity 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 TN 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.

5 REFERENCES

/1/ Eurofins A/S, *Proficiency test SPIL-2 (2020)*, Report to participants, June 2020.

/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 and Food, regulation no. 1071 on *quality criteria for environmental measurements,* 30 October 2019 (in Danish).

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

A N N E X E S

ANNEX A LIST OF PARTICIPANTS

Laboratory	**Town**	**Country**
Analyseenheden, Institut for Agroøkologi, Aarhus Universitet	Tjele	Denmark
AquaDjurs A/S	Grenaa	Denmark
Biofos A/S	København K	Denmark
Bjergmarken RA, Fors Spildevand Roskilde	Roskilde	Denmark
BlueKolding A/S	Kolding	Denmark
CP Kelco, QC Analyselab.	Ll. Skensved	Denmark
Eurofins Miljø A/S (2 participants)	Vejen	Denmark
Hillerød Spildevand	Hillerød	Denmark
Holbæk RA, Fors Spildevand Holbæk	Holbæk	Denmark
Holstebro Renseanlæg, Vestforsyning Spildevand	Holstebro	Denmark
Kerteminde Forsyning - Spildevand A/S	Kerteminde	Denmark
Klarforsyning, Køge-Egnens Renseanlæg	Køge	Denmark
Melby Renseanlæg	Liseleje	Denmark
NK-Forsyning A/S	Næstved	Denmark
Nyborg Forsyning & Service	Nyborg	Denmark
Provas - Haderslev Forsyningsservice A/S	Haderslev	Denmark
Ringkøbing-Skjern Forsyning A/S	Skjern	Denmark
Rønne Renseanlæg	Rønne	Denmark
SK Spildevand A/S, Slagelse Renseanlæg (5 participants)	Slagelse	Denmark
Spildevandslaboratoriet (2 participants)	Esbjerg	Denmark
Vandmiljø Randers A/S	Randers SØ	Denmark
Vejle Spildevand	Vejle	Denmark
SYNLAB AS (Hamar)	Hamar	Norway
AB Borlänge Energi, Borlänge Reningsverk	Borlänge	Sweden
AB Lennart Månsson International	Helsingborg	Sweden
Arctic Paper Munkedals AB	Munkedal	Sweden
GRYAAB AB	Göteborg	Sweden
Kalmar Vatten AB, VA-lab	Kalmar	Sweden
Klippans Reningsverk	Klippan	Sweden
Laboratoriet vid Smedjeholms avolppsreningsverk	Falkenberg	Sweden
Ljungby Kommun, Avloppsreningsverket	Ljungby	Sweden
Mjölby Kommun	Mjölby	Sweden

Laboratory	Town	Country
Nordic Sugar, Örtofta Sockerbruk	Eslöv	Sweden
Preem AB Göteborg	Göteborg	Sweden
Preemraff Lysekil	Lysekil	Sweden
Smurfit Kappa Piteå	Piteå	Sweden
St1 Refinery AB	Göteborg	Sweden
Uddebo Laboratorium	Luleå	Sweden
Vallviks Bruk AB	Vallvik	Sweden
Västervik Miljö & Energi AB, Vattenlaboratoriet	Västervik	Sweden

ANNEX B SAMPLE PREPARATION

Stock solution	**Prepared from**		**Concentration**
Stock TN	25.00 g	Disodium edetate, $2H_2O$ milli-Q water up to 1000.0 g	TN: 1882 mg/kg N
Stock NH_4	10.0 g	Ammonium chloride (NH_4Cl) milli-Q water up to 1000.0 g	NH_4: 2619 mg/kg N
Stock NO_3	2.500 g	Potassium nitrate (KNO_3) milli-Q water up to 1000.0 g	NO_3: 346.4 mg/kg N
Stock NaCl	50.000 g	Sodium chloride (NaCl) milli-Q water up to 1000.0 g	conductivity: c. 10679 mS/m

Sample	**Sample prepared from**	**TN mg/L N**	**NH_4 mg/L N**	**NO_3 mg/L N**	**Conductivity mS/m**
A1	100 g stock TN 15 g stock NH_4 350 g stock NO_3 500 g stock NaCl milli-Q water up to 50.00 kg	6.97	0.786	2.43	118.3
B1	20 g stock TN 2,0 g stock NH_4 40.00 g stock NO_3 60.0 g stock NaCl Sample A1 up to 30.00 kg	0.996 · 6.97 + 1.86	0.996 · 0.786 + 0.171	0.996 · 2.43 + 0,452	0.996 · 118.3 + 21.4

Sample	**Sample prepared from**		**pH**
A2/B2	42.50 g	Potassium dihydrogen phosphate (KH_2PO_4) Disodium hydrogen phosphate, $2H_2O$ (Na_2HPO_4, $2H_2O$) milli-Q water up to 12500 g	c. 6.90
	55.65 g		

ANNEX C CONTROL OF SPIKE VALUES

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

Laboratory	Difference AB	
1	-0.040	
2	0.010	
3	0.140	
4	0.130	
5	0.190	
6	0.130	
7	-0.060	
8	0.010	
9	0.140	
10	0.270	
11	0.100	
12	0.441	
13	0.310	
14	0.780	
15	-0.120	
16	0.000	
17	0.240	
18	0.230	
18A	0.170	
19	1.300	UC
20	0.980	
21	-	
22	0.130	
23	0.150	
24	0.840	
25	0.420	
27	0.280	
28	0.040	
29	-0.049	
31	0.360	
32	-	
33	0.190	
34	0.150	
35	0.030	
36	0.050	
37	-	
39	0.290	
40	-0.140	
41	0.010	
42	0.290	
43	-0.060	
44	0.190	
45	0.200	
46	0.150	
47	0.420	

No of labs., p	41	
No of repl., n	2	
d	0.195	
s^2	0.058	
s	0.241	
$t = \sqrt{p} \cdot (d/s)$	5.1886	
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

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.

Ammonium, mg/L N
Control of differences within sample pairs

Laboratory	Difference AB	
1	-	
2	-0.0110	
3	-0.0130	
4	-0.0020	
5	-0.0020	
6	-0.0100	
7	-0.0090	
8	0.0410	
9	-0.0060	
10	0.0020	
11	-0.0120	
12	-0.0280	
13	0.0010	
14	-0.0050	
15	-0.0040	
16	-0.0250	
17	-0.0140	
18	-0.0210	
18A	-0.0120	
19	0.0070	
20	0.0050	
21	-0.0450	UG
22	0.0100	
23	-	
24	-	
25	-0.0120	
27	0.0010	
28	-0.0130	
29	0.0000	
31	-0.0150	
32	-	
33	-	
34	-0.0280	
35	-	
36	-0.0230	
37	0.0250	
39	-0.0140	
40	-0.0060	
41	-0.0120	
42	0.0040	
43	-0.0160	
44	0.0050	
45	0.0750	UC
46	-0.0050	
47	-0.0110	

No of labs., p	37	
No of repl., n	2	
d	-0.0062	
s^2	0.0002	
s	0.0136	
$t = \sqrt{p} \cdot (d/s)$	-2.7597	
Sign. level, p(t)	0.0090	**

* 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.

Nitrite+nitrate, mg/L N
Control of differences within sample pairs

Laboratory	Difference AB	
1	-	
2	-0.030	
3	-0.006	
4	-	
5	-	
6	-	
7	-	
8	-	
9	-	
10	-	
11	-	
12	0.050	
13	0.020	
14	-	
15	0.030	
16	-	
17	0.040	
18	-	
18A	-	
19	-	
20	0.010	
21	-	
22	-	
23	-	
24	-	
25	-	
27	-	
28	-	
29	-0.065	
31	-	
32	-	
33	0.047	
34	-	
35	-	
36	-	
37	-469.550	UC
39	-	
40	-	
41	-	
42	-	
43	0.140	
44	0.010	
45	-	
46	0.050	
47	-	

No of labs., p	12
No of repl., n	2
d	0.025
s^2	0.003
s	0.050
$t = \sqrt{p} \cdot (d/s)$	1.7007
Sign. level, p(t)	0.1171

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

Nitrate, mg/L N
Control of differences within sample pairs

Laboratory	Difference AB
1	-
2	-
3	-
4	-0.130
5	0.040
6	0.000
7	-
8	-
9	0.000
10	-0.130
11	-0.100
12	0.015
13	-
14	0.160
15	-
16	-0.090
17	-
18	0.100
18A	-0.000
19	-0.020
20	-
21	0.030
22	-
23	-
24	-
25	-0.020
27	0.100
28	0.020
29	-0.095
31	-0.050
32	-
33	-
34	-0.010
35	-
36	0.000
37	-
39	0.070
40	0.020
41	0.160
42	0.020
43	-
44	-0.020
45	0.030
46	-
47	0.040
No of labs., p	27
No of repl., n	2
d	0.005
s^2	0.006
s	0.075
$t = \sqrt{p} \cdot (d/s)$	0.3589
Sign. level, p(t)	0.7226

No test statistics were found to be significant

Conductivity, mS/m
Control of differences within sample pairs

Laboratory	Difference AB	
1	-1.10	UG
2	-	
3	-0.50	
4	-	
5	-0.10	
6	-0.70	
7	-	
8	-	
9	-	
10	-	
11	-	U
12	-	
13	-0.70	
14	-	
15	-	
16	0.10	
17	-	
18	-	
18A	-	
19	-	
20	-	
21	-	
22	-	
23	-	
24	0.00	
25	-	
27	-	
28	-	
29	-	U
31	0.10	
32	-0.60	
33	-0.70	
34	-	
35	2.30	UG
36	-	
37	5.00	UC
39	-	
40	-	
41	-	
42	-	
43	-	
44	-	
45	-	U
46	-	
47	-	

No of labs., p	9	
No of repl., n	2	
d	-0.34	
s^2	0.13	
s	0.36	
$t = \sqrt{p} \cdot (d/s)$	-2.8629	
Sign. level, p(t)	0.0211	*

* 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
U denotes data excluded from the data file

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.

pH,
Control of differences within sample pairs

Laboratory	Difference AB	
1	0.000	
2	0.000	
3	0.010	
4	0.020	
5	-0.020	
6	0.010	
7	0.000	
8	-	
9	0.000	
10	0.010	
11	0.000	
12	0.000	
13	-0.030	
14	0.010	
15	0.000	
16	0.030	
17	0.000	
18	-0.010	
18A	-	
19	0.021	
20	0.020	
21	0.010	
22	0.000	
23	0.000	
24	-0.010	
25	-0.030	
27	0.000	
28	-0.020	
29	-0.010	
31	-0.050	
32	-0.010	
33	0.000	
34	0.060	
35	0.020	
36	0.000	
37	0.000	
39	0.000	
40	-0.010	
41	-0.020	
42	-0.030	
43	0.050	
44	0.010	
45	-0.020	
46	0.010	UG
47	-0.020	

No of labs., p	42
No of repl., n	2
d	-0.000
s^2	0.000
s	0.020
$t = \sqrt{p} \cdot (d/s)$	-0.0683
Sign. level, p(t)	0.9459

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

ANNEX D CONTROL OF RECOVERY

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

Laboratory	Sample pair AB	
1	6.470	
2	7.165	
3	6.570	
4	6.465	
5	6.625	
6	6.705	
7	6.700	
8	7.115	
9	6.420	
10	5.855	
11	6.910	
12	6.229	
13	7.105	
14	6.560	
15	7.170	
16	7.080	
17	6.160	
18	6.295	
18A	6.765	
19	5.710	UC
20	6.780	
21	-	
22	6.685	
23	5.795	
24	6.210	
25	6.410	
27	6.850	
28	7.000	
29	6.910	
31	6.670	
32	-	
33	7.096	
34	7.275	
35	6.935	
36	7.085	
37	-	
39	6.755	
40	6.740	
41	7.255	
42	7.745	
43	7.020	
44	7.015	
45	6.940	
46	6.795	
47	6.420	

No of labs., p	41	
No of repl., n	2	
m	6.750	
s^2	0.156	
s	0.395	
Assigned value, μ	6.97	
Recovery, %	96.8	
$t = \sqrt{p} \cdot (m-\mu)/s$	-3.5682	
Sign. level, p(t)	0.0010	***

* 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

Ammonium, mg/L N
Control of recovery, average of results

Laboratory	Sample pair AB	
1	-	
2	0.8635	
3	0.8035	
4	0.8130	
5	0.8160	
6	0.8150	
7	0.8145	
8	0.7695	
9	0.8130	
10	0.8150	
11	0.8170	
12	0.7681	
13	0.7805	
14	0.7395	
15	0.7790	
16	0.7945	
17	0.7580	
18	0.8285	
18A	0.8210	
19	0.7445	
20	0.8055	
21	0.6085	UG
22	0.7560	
23	-	
24	-	
25	0.8330	
27	0.7895	
28	0.8085	
29	0.7900	
31	0.7525	
32	-	
33	-	
34	0.7920	
35	-	
36	0.8175	
37	0.6805	
39	0.8060	
40	0.7790	
41	0.8020	
42	0.7480	
43	0.8050	
44	0.7355	
45	0.9465	UC
46	0.8065	
47	0.8235	

No of labs., p	37
No of repl., n	2
m	0.7915
s^2	0.0012
s	0.0348
Assigned value, μ	0.786
Recovery, %	100.7
$t = \sqrt{p} \cdot (m-\mu)/s$	0.9541
Sign. level, p(t)	0.3464

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

Nitrite and nitrate, mg/L N
Control of recovery, average of results

Laboratory	Sample pair AB	
1	-	
2	2.625	
3	2.520	
4	-	
5	-	
6	-	
7	-	
8	-	
9	-	
10	-	
11	-	
12	2.481	
13	2.270	
14	-	
15	2.375	
16	-	
17	2.530	
18	-	
18A	-	
19	-	
20	2.255	
21	-	
22	-	
23	-	
24	-	
25	-	
27	-	
28	-	
29	2.481	
31	-	
32	-	
33	2.327	
34	-	
35	-	
36	-	
37	2614.775	UC
39	-	
40	-	
41	-	
42	-	
43	2.280	
44	2.225	
45	-	
46	2.315	
47	-	

No of labs., p	12
No of repl., n	2
m	2.390
s^2	0.017
s	0.131
Assigned value, μ	2.43
Recovery, %	98.4
$t = \sqrt{p} \cdot (m-\mu)/s$	-1.0450
Sign. level, p(t)	0.3185

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

Nitrate, mg/L N
Control of recovery, average of results

Laboratory	Sample pair AB
1	-
2	-
3	-
4	2.415
5	2.260
6	2.410
7	-
8	-
9	2.390
10	2.415
11	2.660
12	2.487
13	-
14	2.630
15	-
16	2.745
17	-
18	2.470
18A	2.260
19	2.250
20	-
21	2.205
22	-
23	-
24	-
25	2.420
27	2.280
28	2.320
29	2.497
31	2.205
32	-
33	-
34	2.385
35	-
36	2.470
37	-
39	2.315
40	2.440
41	2.180
42	2.420
43	-
44	2.240
45	2.435
46	-
47	2.290

No of labs., p	27
No of repl., n	2
m	2.389
s^2	0.020
s	0.141
Assigned value, μ	2.38
Recovery, %	100.4
$t = \sqrt{p} \cdot (m-\mu)/s$	0.3187
Sign. level, p(t)	0.7525

No test statistics were found to be significant

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

Laboratory	Sample pair AB	
1	89.35	UG
2	-	
3	109.65	
4	-	
5	103.95	
6	105.55	
7	-	
8	-	
9	-	
10	-	
11	-	U
12	-	
13	107.85	
14	-	
15	-	
16	105.65	
17	-	
18	-	
18A	-	
19	-	
20	-	
21	-	
22	-	
23	-	
24	104.80	
25	-	
27	-	
28	-	
29	-	U
31	108.45	
32	106.50	
33	106.15	
34	-	
35	94.75	UG
36	-	
37	105.50	UC
39	-	
40	-	
41	-	
42	-	
43	-	
44	-	
45	-	U
46	-	
47	-	

No of labs., p		9
No of repl., n		2
	m	106.51
	s^2	3.34
	s	1.83
Assigned value, μ		105.7
Recovery, %		100.8
$t = \sqrt{p} \cdot (m-\mu)/s$		1.3232
Sign. level, p(t)		0.2223

No test statistics were found to be significant
UC denotes a Cochran outlier
UG denotes a Grubbs outlier
U denotes data excluded from the data file

pH,
Control of recovery, average of results

Laboratory	Sample pair AB	
1	6.810	
2	6.850	
3	6.845	
4	6.920	
5	6.890	
6	6.875	
7	6.880	
8	-	
9	6.910	
10	6.935	
11	6.890	
12	6.890	
13	6.835	
14	6.955	
15	6.870	
16	6.835	
17	6.870	
18	6.915	
18A	-	
19	6.861	
20	6.910	
21	7.015	
22	6.900	
23	6.890	
24	6.855	
25	6.905	
27	6.920	
28	6.740	
29	6.875	
31	6.965	
32	6.865	
33	6.890	
34	6.960	
35	6.890	
36	6.880	
37	6.950	
39	6.870	
40	6.935	
41	6.920	
42	6.895	
43	6.875	
44	6.795	
45	7.040	
46	7.205	UG
47	6.970	

No of labs., p	42
No of repl., n	2
m	6.894
s^2	0.003
s	0.055
Assigned value, μ	6.90
Recovery, %	99.9
$t = \sqrt{p} \cdot (m-\mu)/s$	-0.7139
Sign. level, p(t)	0.4793

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

ANNEX E CONCENTRATION LEVEL

Concentration level **SPIL-2 (2020)**

Parameter	Unit	Sample	Bottle no.	I	II	Bottle Average	Sample Average	Assigned value	Spike Measured	Spike Assigned
Total nitrogen	mg/L N	A1	11	6,77	6,81	6,79	6,74	6,97	1,64	1,86
			26	6,79	6,73	6,76				
			53	6,67	6,69	6,68				
		B1	6	8,36	8,35	8,36	8,38	8,83		
			3	8,38	8,39	8,39				
			63	8,39	8,41	8,40				
Ammonium	mg/L N	A1	11	0,809	0,812	0,81	0,809	0,786	0,182	0,171
			26	0,806	0,807	0,81				
			53	0,807	0,810	0,81				
		B1	6	0,986	0,987	0,99	0,991	0,979		
			3	0,985	0,986	0,99				
			63	1,000	1,000	1,00				
Nitrite+nitrate / Nitrate	mg/L N	A1	11	2,44	2,41	2,43	2,41	2,43	0,33	0,45
			26	2,40	2,43	2,42				
			53	2,36	2,41	2,39				
		B1	6	2,65	2,64	2,65	2,74	2,81		
			3	2,78	2,81	2,80				
			63	2,78	2,79	2,79				
pH		A2	10	6,89	6,88	6,88	6,88	6,89	0,00	0
			28	6,88	6,88	6,88				
			62	6,89	6,88	6,88				
		B2	18	6,88	6,87	6,88	6,88	6,89		
			40	6,89	6,88	6,88				
			65	6,88	6,88	6,88				

ANNEX F HOMOGENEITY AND STABILITY

PT:	SPIL-2
Parameter:	NH4
Unit:	mg/L N
Sigma:	0,053

Responsible for tests: HBP/S7MS

Homogeneity test Date: 2020-04-28

Sample	x(a)	x(b)	aver-age	sd	sd^2
B1-4	0,975	0,977	1,0	0,001	0,000
B1-19	0,999	1,000	1,0	0,001	0,000
B1-27	0,969	0,972	1,0	0,002	0,000
B1-30	0,986	0,988	1,0	0,001	0,000
B1-39	0,998	0,999	1,0	0,001	0,000
B1-43	0,980	0,980	1,0	0,000	0,000
B1-52	0,998	0,998	1,0	0,000	0,000
B1-56	0,990	0,991	1,0	0,001	0,000
B1-62	0,992	0,992	1,0	0,000	0,000
B1-65	0,999	0,999	1,0	0,000	0,000

For homogeneity

General average (x)	0,9891
Sample average sd (s_x)	0,0105
Within-sample sd (s_w):	0,0010
Between-samples sd (ss):	0,0105
S_L in the Proficiency Test:	0,034
S_R in the Proficiency Test:	0,036

Stability test Date: 2020-05-14

Sample	x(a)	x(b)
B1-6	0,986	0,967
B1-37	0,985	0,986
B1-63	1,000	1,000

For stability

General average (y):	0,9873333
/x-y/ =	0,0017667

Conclusions

ss = 0,0105 0.3*sigma= 0,0160

/x-y/ = 0,0017667

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

PT: SPIL-2
Parameter: NO3
Unit: mg/L N
Sigma: 0,155

Responsible for tests: HBP/S7MS

Homogeneity test Date: 2020-04-28

Sample	x(a)	x(b)	average	sd	sd^2
B1-4	2,87	2,89	2,9	0,014	0,000
B1-19	2,89	2,86	2,9	0,021	0,00
B1-27	2,87	2,89	2,9	0,014	0,000
B1-30	2,89	2,88	2,9	0,007	0,000
B1-34	2,88	2,88	2,9	0,000	0,000
B1-39	2,83	2,86	2,8	0,021	0,000
B1-43	2,86	2,93	2,9	0,049	0,002
B1-52	2,87	2,84	2,9	0,021	0,000
B1-56	2,90	2,88	2,9	0,014	0,000
B1-62	2,85	2,84	2,8	0,007	0,000
B1-65	2,87	2,88	2,9	0,007	0,000
B1-74	2,93	2,92	2,9	0,007	0,000

For homogeneity

General average (x)	2,88
Sample average sd (s_x)	0,022
Within-sample sd (s_w):	0,020
Between-samples sd (ss):	0,0174
S_L in the Proficiency Test:	0,136
S_R in the Proficiency Test:	0,146

Conclusions

ss =0,017 0.3*sigma=0,0466
/x-y/ =0,1358333

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

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

PT:	SPIL-2
Parameter:	pH
Unit:	
Sigma:	0,1

Responsible for tests: HBP/S7MS

Homogeneity test Date: 2020-04-28

Sample	x(a)	x(b)	average	sd	sd^2
B2-2	6,96	6,96	7,0	0,000	0,000
B2-11	6,98	6,98	7,0	0,000	0,00
B2-21	6,97	6,95	7,0	0,014	0,000
B2-25	6,99	6,94	7,0	0,035	0,001
B2-29	6,93	6,96	6,9	0,021	0,000
B2-39	6,94	6,93	6,9	0,007	0,000
B2-48	6,96	6,97	7,0	0,007	0,000
B2-53	6,96	6,93	6,9	0,021	0,000
B2-57	6,96	6,92	6,9	0,028	0,001
B2-61	6,95	6,93	6,9	0,014	0,000
B2-67	6,94	6,96	7,0	0,014	0,000
B2-73	6,96	6,94	7,0	0,014	0,000

For homogeneity

General average (x)	6,95
Sample average sd (s_x)	0,013
Within-sample sd (s_w):	0,018
Between-samples sd (ss):	0,0038
S_L in the Proficiency Test:	0,054
S_R in the Proficiency Test:	0,056

Conclusions

ss = 0,004 0.3*sigma= 0,02

/x-y/ = 0,0725833

Homogeneity: Is ss < 0.3*sigma?

YES