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Proficiency test SPIL-4 (2020)

Nitrogen parameters in wastewater (effluent)

Quality Documentation
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CONTENTS

1 INTRODUCTION

A proficiency test on the analysis of nitrogen parameters in wastewater was conducted on 12 November. 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 14 December 2020.

2 FEATURES OF THE PROFICIENCY TEST

Participants in the proficiency test were a total of 52 laboratories from Denmark, Norway and Sweden. A list of participants is shown in Appendix A.

The closing date for submission of results was 26 November. All participants except laboratory no. 6 and 25 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, NH4, NO_{2+3}, NO_3 and 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" (2019) /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	5.3	0.16	0.9
Ammonium	NH_4	mg/L N	0.1-2	1.09	0.015	0.26
Nitrite+nitrate	NO_{2+3}	mg/L N	1-5	2.99	0.035	0.58
Nitrate	NO_3	mg/L N	1-5	3.07	0.029	0.58
Conductivity	γ_{25}	mS/m	50-300	68	1.0	1
pH	pH		6-9	7.79	0.040	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. 1, 2 and 3 (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 for most parameters.

The test revealed a significant difference between the two for γ_{25}. 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 for most parameters 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 γ_{25}. Average recovery was 97.7 %. The difference could be attributed to influence from a few laboratories. The test was repeated after exclusion of the results from laboratory no. 11 and 27 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 was/were tested using the following parameters as indicators:

NH4	Combined homogeneity and stability test
pH	Combined homogeneity and stability test

The results of control measurements are shown in Appendix F. The appendix also gives the results of the statistical evaluation of the control data. The data are analysed by analysis of variance (ANOVA) giving:

1. the standard deviation/variance for replicates (the contribution from analytical variability),

2. the between bottle standard deviation/variance (the contribution from heterogeneity) and

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

Homogeneity is evaluated by comparing the between bottle variance to 0.3 * 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 homogeneity show that the samples are homogeneous.

The tests for stability show that the samples are unstable. The result for NH_4 decreases from production week to the date of the proficiency test. The results found on the date for the proficiency test deviated less than $0.3 \cdot \hat{\sigma}$ from the nominal found using the consensus values for all laboratories based on the median. It is therefore concluded that the above found instability had no effect on the evaluation of the participants' results. The change in pH is insignificant compared to the standard deviation of the parameter. Since the proficiency test is set to a specific date the change in pH is estimated not to influence the evaluation of the participating laboratories.

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 γ_{25} the participants could not recover the spike value or 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. Also the 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.

The test performed at the laboratory making Proficiency testing at Eurofins found instability in the tested parameters. The change in parameters are larger than the acceptable limit $0.3 \cdot \hat{\sigma}$, but as described in the above chapter the change is estimated to have insignificant influence on the evaluation of the participants' performance.

5 REFERENCES

/1/ Eurofins A/S, *Proficiency test SPIL-4 (2020)*, Report to participants, December 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*, 2019.

/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. 1770 on *quality criteria for environmental measurements,* 28 October 2020 (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
Spildevandslaboratoriet (2 participants)	Esbjerg	Denmark
AquaDjurs A/S	Grenaa	Denmark
Provas - Haderslev Forsyningsservice A/S	Haderslev	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
BlueKolding A/S	Kolding	Denmark
Biofos A/S	København K	Denmark
Klarforsyning, Køge-Egnens Renseanlæg	Køge	Denmark
Melby Renseanlæg	Liseleje	Denmark
CP Kelco, QC Analyselab.	Ll. Skensved	Denmark
Nyborg Forsyning & Service	Nyborg	Denmark
NK-Forsyning A/S	Næstved	Denmark
VandCenter Syd A/S	Odense C	Denmark
Vandmiljø Randers A/S	Randers SØ	Denmark
Bjergmarken RA, Fors Spildevand Roskilde	Roskilde	Denmark
Rønne Renseanlæg	Rønne	Denmark
Ringkøbing-Skjern Forsyning A/S	Skjern	Denmark
RGS Nordic A/S	Skælskør	Denmark
Svendborg Spildevand A/S, Egsmade/Svenborg Centralrenseanlæg	Skårup Fyn	Denmark
SK Spildevand A/S, Slagelse Renseanlæg (5 participants)	Slagelse	Denmark
Eurofins Miljø A/S (2 participants)	Vejen	Denmark
Vejle Spildevand	Vejle	Denmark
Aalborg Forsyning, Renseanlæg Øst	Aalborg Øst	Denmark
SYNLAB AS (Hamar)	Hamar	Norway
VIVAB	Falkenberg	Sweden
Preem AB Göteborg	Göteborg	Sweden
St1 Refinery AB	Göteborg	Sweden
GRYAAB AB	Göteborg	Sweden
Hallsta Pappersbruk	Hallstavik	Sweden
AB Lennart Månsson International	Helsingborg	Sweden
Kalmar Vatten AB, VA-lab	Kalmar	Sweden
Kristianstad Kommun	Kristianstad	Sweden
Yara AB	Köping	Sweden
Käppalaförbundet	Lidingö	Sweden
Preemraff Lysekil	Lysekil	Sweden
Mjölby Kommun	Mjölby	Sweden
Motala Kommun, Tekniska Förvaltningen, Vatten och Avfall	Motala	Sweden
Fiskeby Board AB	Norrköping	Sweden

Laboratory	Town	Country
Holmen Paper AB, Bravikens Pappersbruk	Norrköping	Sweden
Nodra AB, Laboratoriet Slottshagens Reningsverk	Norrköping	Sweden
Ernemar Laboratorium	Oskarshamn	Sweden
Perstorp Specialty Chemicals AB	Perstorp	Sweden
Smurfit Kappa Piteå	Piteå	Sweden
Vallviks Bruk AB	Vallvik	Sweden
Västervik Miljö & Energi AB, Vattenlaboratoriet	Västervik	Sweden
Växjö Kommun, Tekniska Förvaltningen/VA-Lab.	Växjö	Sweden
Perstorp Oxo AB	Ödsmål	Sweden
Östersunds Provningslaboratorium, Göviken reningsverk	Östersund	Sweden

ANNEX B SAMPLE PREPARATION

Stock solution	**Prepared from**		**Concentration**
Stock TN	3.000 g	Disodium edetate, $2H_2O$ milli-Q water up to 1000.0 g	TN: 225.8 mg/kg N
Stock NH_4	1. 000 g	Ammonium chloride (NH_4Cl) milli-Q water up to 1000.0 g	NH_4: 261.9 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

Sample	**Sample prepared from**	**TN mg/L N**	**NH_4 mg/L N**	**NO_3 mg/L N**	γ_{25} **mS/m**
A1	10.00 g stock TN 25.00 g stock NH_4 60.00 g stock NO_3 Sample B1 up to 34.00 kg	0.997 · (a+1.39) + 0.0664	0.997 · (b+0.605) + 0.193	0.997 · (c+2.66) + 0.611	d
B1	400.0 g stock TN 150.0 g stock NH_4 500.0 g stock NO_3 filtered water from Vejen sewage treatment plant up to 65.0 kg	a+1.39	b+0.605	c+2.66	e

Sample	**Sample prepared from**	**pH**
A2/B2	Filtered water from Vejen 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	-0.110
2	-0.200
3	-0.000
4	-0.010
5	0.190
7	-0.020
8	0.050
9	-0.650
10	0.060
11	-0.100
12	-0.070
13	0.220
14	0.371
15	-0.000
16	0.540
17	-0.046
18	-0.050
19	0.180
20	-0.140
21	0.310
22	-0.390
23	0.010
24	0.000
26	-0.030
27	-0.018
28	-0.090
29	-0.090
30	0.260
31	0.100
32	0.020
33	-0.072
34	-0.210
35	0.070
36	-
37	0.165
38	-0.080
39	-0.700
40	-0.050
41	0.120
42	-0.010
43	-
44	0.040
45	-0.050
46	-0.060
47	0.170
48	-0.240
49	-0.090
50	-0.080
51	-0.150
52	0.040

No of labs., p	48
No of repl., n	2
d	-0.019
s^2	0.045
s	0.212
$t = \sqrt{p} \cdot (d/s)$	-0.6047
Sign. level, p(t)	0.5483

No test statistics were found to be significant

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

Laboratory	Difference AB
1	-0.010
2	-0.000
3	-0.010
4	0.010
5	0.040
7	-0.070
8	-
9	0.060
10	0.010
11	-
12	-0.010
13	0.000
14	0.019
15	-0.010
16	-0.020
17	-
18	-0.050
19	-0.010
20	0.000
21	0.000
22	0.018
23	-
24	0.050
26	-0.020
27	-0.015
28	-0.000
29	0.000
30	-0.020
31	-0.010
32	-0.010
33	0.010
34	0.000
35	-0.030
36	-
37	-
38	0.010
39	0.010
40	-0.020
41	-0.010
42	0.010
43	-0.060
44	0.040
45	0.000
46	0.010
47	0.078
48	0.000
49	-0.010
50	0.060
51	-0.030
52	-0.020

No of labs., p	44
No of repl., n	2
d	-0.000
s^2	0.001
s	0.029
$t = \sqrt{p} \cdot (d/s)$	-0.0540
Sign. level, p(t)	0.9572

No test statistics were found to be significant

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

Laboratory	Difference AB
1	0.020
2	-
3	-
4	-0.010
5	0.030
7	-
8	-
9	-
10	-
11	-
12	-0.260
13	-
14	-0.209
15	-
16	-0.080
17	0.041
18	-
19	-
20	-
21	-
22	-
23	-
24	0.030
26	-
27	-0.038
28	-
29	-
30	-0.010
31	-
32	-
33	-
34	-
35	0.030
36	-
37	-
38	-
39	-
40	-
41	-
42	-
43	-0.030
44	-
45	-
46	-
47	-
48	-
49	0.000
50	-
51	-
52	-0.040

No of labs., p	14
No of repl., n	2
d	-0.038
s^2	0.008
s	0.091
$t = \sqrt{p} \cdot (d/s)$	-1.5507
Sign. level, p(t)	0.1450

No test statistics were found to be significant

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

Laboratory	Difference AB	
1	-0.040	
2	0.020	
3	0.040	
4	-0.010	
5	-	
7	-	
8	-	
9	-	
10	0.010	
11	-	
12	-0.270	
13	-0.000	
14	-0.210	
15	-0.020	
16	-	
17	-	
18	-0.110	
19	-0.020	
20	0.020	
21	-	
22	-0.060	UG
23	-	
24	-	
26	0.000	
27	-0.024	
28	-0.540	UC
29	-0.040	
30	-	
31	-0.040	
32	0.030	
33	-	
34	0.020	
35	-	
36	-	
37	-	
38	-0.040	
39	0.060	
40	0.060	
41	-	
42	-0.240	
43	-	
44	-0.070	
45	-	
46	-0.020	
47	0.166	
48	-0.050	
49	-	
50	-0.040	
51	0.030	
52	-	

No of labs., p	28
No of repl., n	2
d	-0.028
s^2	0.008
s	0.091
$t = \sqrt{p} \cdot (d/s)$	-1.6451
Sign. level, p(t)	0.1116

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

Conductivity, mS/m
Control of differences within sample pairs

Laboratory	Difference AB	
1	-	
2	-	
3	-	
4	-	
5	-0.50	
7	-	
8	-	
9	-0.40	
10	-	
11	-0.45	
12	-0.80	
13	-	
14	-	
15	-0.50	
16	-	
17	0.33	
18	-	
19	-	
20	-0.20	
21	-	
22	-	
23	-0.30	
24	-	
26	3.80	UC
27	-0.27	
28	-	
29	-0.20	
30	-	
31	-	
32	-0.40	
33	-	
34	-	
35	-1.10	
36	-0.30	
37	0.00	
38	-	
39	-0.40	
40	-0.50	
41	-	
42	-0.60	
43	-	
44	0.10	
45	-	
46	-	
47	-0.40	
48	-	
49	-0.20	
50	-	
51	-	
52	-	

No of labs., p	20	
No of repl., n	2	
d	-0.35	
s^2	0.09	
s	0.31	
$t = \sqrt{p} \cdot (d/s)$	-5.1783	
Sign. level, p(t)	0.0001	***

* 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.

pH,
Control of differences within sample pairs

Laboratory	Difference AB	
1	0.120	
2	-0.180	
3	-0.070	
4	-0.020	
5	-0.060	
7	-	
8	-0.010	
9	0.010	
10	-0.010	
11	-0.020	
12	0.000	
13	-0.070	
14	-0.050	
15	-0.030	
16	-0.040	
17	0.030	
18	-0.240	
19	-	
20	0.030	
21	0.000	
22	-0.080	
23	-0.020	
24	0.050	
26	-0.010	
27	-0.087	
28	-0.430	UC
29	0.090	
30	-0.030	
31	-	
32	-0.020	
33	-	
34	-0.060	
35	-0.020	
36	0.070	
37	0.010	
38	0.100	
39	-0.008	
40	-0.190	
41	-0.050	
42	0.000	
43	-0.470	UC
44	0.010	
45	-0.170	
46	0.020	
47	-0.020	
48	0.020	
49	0.240	
50	0.070	
51	0.020	
52	-0.100	

No of labs., p	44
No of repl., n	2
d	-0.018
s^2	0.007
s	0.083
$t = \sqrt{p} \cdot (d/s)$	-1.4007
Sign. level, p(t)	0.1685

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

ANNEX D CONTROL OF RECOVERY

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

Laboratory	Sample pair AB
1	5.025
2	4.930
3	5.160
4	5.275
5	5.215
7	5.090
8	5.195
9	5.955
10	5.420
11	5.530
12	5.085
13	5.350
14	4.950
15	5.370
16	4.960
17	4.992
18	5.425
19	5.410
20	5.210
21	5.555
22	4.955
23	4.948
24	4.800
26	5.475
27	4.855
28	5.225
29	5.195
30	5.570
31	5.350
32	5.400
33	4.312
34	5.785
35	5.345
36	-
37	5.269
38	4.590
39	4.310
40	5.405
41	4.580
42	5.185
43	-
44	5.640
45	5.525
46	5.230
47	5.067
48	5.350
49	5.225
50	6.240
51	5.645
52	5.090

No of labs., p	48
No of repl., n	2
m	5.222
s^2	0.135
s	0.367
Assigned value, μ	5.3
Recovery, %	98.5
$t = \sqrt{p} \cdot (m-\mu)/s$	-1.4673
Sign. level, p(t)	0.1489

No test statistics were found to be significant

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

Laboratory	Sample pair AB
1	1.025
2	1.120
3	1.125
4	1.315
5	1.100
7	1.045
8	-
9	0.950
10	1.115
11	-
12	1.075
13	1.100
14	1.071
15	1.125
16	1.130
17	-
18	1.175
19	1.095
20	1.110
21	1.110
22	0.861
23	-
24	1.195
26	1.010
27	1.038
28	1.120
29	1.080
30	0.980
31	1.095
32	1.095
33	1.065
34	1.110
35	1.075
36	-
37	-
38	1.105
39	1.045
40	1.110
41	1.065
42	1.115
43	1.160
44	1.330
45	1.060
46	1.085
47	1.085
48	1.040
49	0.915
50	1.090
51	1.105
52	1.030

No of labs., p	44
No of repl., n	2
m	1.088
s^2	0.007
s	0.081
Assigned value, μ	1.09
Recovery, %	99.8
$t = \sqrt{p} \cdot (m-\mu)/s$	-0.2035
Sign. level, p(t)	0.8397

No test statistics were found to be significant

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

Laboratory	Sample pair AB
1	3.010
2	-
3	-
4	3.045
5	2.945
7	-
8	-
9	-
10	-
11	-
12	2.870
13	-
14	3.216
15	-
16	2.620
17	2.938
18	-
19	-
20	-
21	-
22	-
23	-
24	3.025
26	-
27	3.006
28	-
29	-
30	2.915
31	-
32	-
33	-
34	-
35	3.025
36	-
37	-
38	-
39	-
40	-
41	-
42	-
43	3.235
44	-
45	-
46	-
47	-
48	-
49	2.980
50	-
51	-
52	2.980

No of labs., p	14
No of repl., n	2
m	2.986
s^2	0.021
s	0.147
Assigned value, μ	2.99
Recovery, %	99.9
$t = \sqrt{p} \cdot (m-\mu)/s$	-0.0912
Sign. level, p(t)	0.9287

No test statistics were found to be significant

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

Laboratory	Sample pair AB	
1	2.940	
2	3.030	
3	3.080	
4	3.045	
5	-	
7	-	
8	-	
9	-	
10	3.095	
11	-	
12	2.855	
13	3.180	
14	3.209	
15	3.040	
16	-	
17	-	
18	3.155	
19	3.050	
20	2.910	
21	-	
22	2.580	UG
23	-	
24	-	
26	2.980	
27	2.994	
28	0.880	UC
29	3.060	
30	-	
31	3.060	
32	3.055	
33	-	
34	3.060	
35	-	
36	-	
37	-	
38	3.180	
39	3.040	
40	3.210	
41	-	
42	3.280	
43	-	
44	3.285	
45	-	
46	3.110	
47	3.005	
48	3.115	
49	-	
50	3.120	
51	3.125	
52	-	

No of labs., p	28
No of repl., n	2
m	3.081
s^2	0.010
s	0.102
Assigned value, μ	3.07
Recovery, %	100.4
$t = \sqrt{p} \cdot (m-\mu)/s$	0.5727
Sign. level, p(t)	0.5716

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

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

Laboratory	Sample pair AB	
1	-	
2	-	
3	-	
4	-	
5	67.55	
7	-	
8	-	
9	67.50	
10	-	
11	61.38	
12	67.70	
13	-	
14	-	
15	66.65	
16	-	
17	65.84	
18	-	
19	-	
20	68.40	
21	-	
22	-	
23	67.85	
24	-	
26	71.80	UC
27	61.36	
28	-	
29	67.90	
30	-	
31	-	
32	66.50	
33	-	
34	-	
35	64.35	
36	69.45	
37	63.40	
38	-	
39	69.00	
40	65.25	
41	-	
42	62.50	
43	-	
44	71.15	
45	-	
46	-	
47	69.30	
48	-	
49	66.34	
50	-	
51	-	
52	-	

No of labs., p	20	
No of repl., n	2	
m	66.47	
s^2	7.38	
s	2.72	
Assigned value, μ	68	
Recovery, %	97.7	
$t = \sqrt{p} \cdot (m-\mu)/s$	-2.5214	
Sign. level, p(t)	0.0208	*

* 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

pH,
Control of recovery, average of results

Laboratory	Sample pair AB	
1	7.950	
2	7.260	
3	7.755	
4	7.750	
5	7.770	
7	-	
8	7.955	
9	7.845	
10	7.905	
11	7.860	
12	7.870	
13	7.615	
14	7.845	
15	7.755	
16	7.630	
17	7.855	
18	7.490	
19	-	
20	7.845	
21	7.800	
22	7.790	
23	7.930	
24	7.825	
26	7.745	
27	7.665	
28	7.225	UC
29	7.825	
30	7.925	
31	-	
32	7.760	
33	-	
34	7.710	
35	7.930	
36	7.695	
37	7.775	
38	7.850	
39	7.615	
40	8.165	
41	7.885	
42	7.810	
43	7.445	UC
44	8.155	
45	7.815	
46	8.050	
47	7.790	
48	7.630	
49	7.990	
50	7.725	
51	7.630	
52	7.580	

No of labs., p	44
No of repl., n	2
m	7.796
s^2	0.027
s	0.163
Assigned value, μ	7.79
Recovery, %	100.1
$t = \sqrt{p} \cdot (m-\mu)/s$	0.2412
Sign. level, p(t)	0.8106

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

ANNEX E CONCENTRATION LEVEL

Parameter	Unit	Sample	Bottle no.	I	II	Bottle Average	Sample Average	Assigned value	Spike Measured	Spike Assigned
Total nitrogen	mg/L N	A1	5	6,32	6,35	6,34	6,39	6,177	0,783	0,904
			42	6,40	6,43	6,42				
			75	6,39	6,42	6,41				
		B1	12	5,58	5,52	5,55	5,60	5,273		
			40	5,52	5,52	5,52				
			52	5,75	5,72	5,74				
Ammonium	mg/L N	A1	5	1,35	1,36	1,36	1,36	1,35	0,262	0,260
			42	1,37	1,37	1,37				
			75	1,36	1,36	1,36				
		B1	12	1,11	1,11	1,11	1,10	1,09		
			40	1,09	1,09	1,09				
			52	1,10	1,10	1,10				
Nitrate	mg/L N	A1	5	3,81	3,80	3,81	3,80	3,65	0,60	0,58
			42	3,79	3,80	3,80				
			75	3,81	3,81	3,81				
		B1	12	3,23	3,22	3,23	3,21	3,07		
			40	3,20	3,20	3,20				
			52	3,20	3,20	3,20				
pH		A2	15	7,86	7,88	7,87	7,85	7,79	-0,04	0,00
			33	7,84	7,85	7,85				
			53	7,83	7,84	7,84				
		B2	20	7,80	7,81	7,81	7,81	7,79		
			37	7,82	7,82	7,82				
			61	7,79	7,80	7,80				

ANNEX F HOMOGENEITY AND STABILITY

PT:	SPIL-4
Parameter:	NH4
Unit:	mg/L N
Sigma:	0,1

Responsible for tests: HBP/S7MS

Homogeneity test Date: 2020-10-27

Sample	x(a)	x(b)	average	sd	sd^2
A1-2	1,40	1,40	1,40	0,000	0,000
A1-9	1,42	1,42	1,42	0,000	0,000
A1-20	1,42	1,43	1,43	0,007	0,000
A1-30	1,41	1,41	1,41	0,000	0,000
A1-35	1,41	1,42	1,42	0,007	0,000
A1-39	1,40	1,40	1,40	0,000	0,000
A1-47	1,41	1,41	1,41	0,000	0,000
A1-52	1,43	1,43	1,43	0,000	0,000
A1-58	1,44	1,44	1,44	0,000	0,000
A1-64	1,43	1,43	1,43	0,000	0,000
A1-70	1,42	1,43	1,43	0,007	0,000
A1-78	1,41	1,41	1,41	0,000	0,000

For homogeneity

General average (x)	1,42
Sample average sd (s_x)	0,013
Within-sample sd (s_w):	0,004
Between-samples sd (ss):	0,012
S_L in the Proficiency Test:	0,080
S_R in the Proficiency Test:	0,082

Stability test Date: 2020-11-12

Sample	x(a)	x(b)
A1-5	1,35	1,36
A1-75	1,36	1,36
A1-42	1,37	1,37

For stability

General average (y):	1,36
/x-y/ =	0,056

Conclusions

ss =	0,012	0.3*sigma=	0,023
/x-y/ =	0,056		
Analytical quality	Is s_w < 0,15*sigma **YES**		
Homogeneity:	Is ss < 0.3*sigma? **YES**		
Stability:	/x-y/ < 0.3*sigma? **NO**		

PT:	SPIL-4
Parameter:	pH
Unit:	
Sigma:	0,072

Responsible for tests: HBP/S7MS

Homogeneity test Date: 2020-10-27

Sample	x(a)	x(b)	average	sd	sd^2
B2-2	7,78	7,81	7,8	0,021	0,000
B2-6	7,78	7,80	7,8	0,014	0,00
B2-16	7,77	7,79	7,8	0,014	0,000
B2-21	7,77	7,78	7,8	0,007	0,000
B2-28	7,76	7,77	7,8	0,007	0,000
B2-35	7,76	7,78	7,8	0,014	0,000
B2-42	7,77	7,78	7,8	0,007	0,000
B2-47	7,77	7,79	7,8	0,014	0,000
B2-56	7,77	7,78	7,8	0,007	0,000
B2-63	7,78	7,78	7,8	0,000	0,000
B2-71	7,77	7,77	7,8	0,000	0,000
B2-77	7,77	7,77	7,8	0,000	0,000

For homogeneity

General average (x)	7,777
Sample average sd (s_x)	0,009
Within-sample sd (s_w):	0,011
Between-samples sd (ss):	0,0038
S_L in the Proficiency Test:	0,157
S_R in the Proficiency Test:	0,168

Stability test Date: 2020-11-12

Sample	x(a)	x(b)
B2-20	7,80	7,81
B2-37	7,82	7,82
B2-61	7,79	7,80

For stability

General average (y):	7,807
/x-y/ =	0,030

Conclusions

ss =	0,004	0.3*sigma=	0,02
/x-y/ =	0,0295833		

Analytical quality	ls s_w < 0,15*sigma **NO**
Homogeneity:	ls ss < 0.3*sigma? **YES**
Stability:	/x-y/ < 0.3*sigma? **NO**