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Proficiency test SPIL-2 (2022)

Nitrogen parameters in wastewater (synthetic 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 19 May 2022. 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 21 June 2022.

2 FEATURES OF THE PROFICIENCY TEST

Participants in the proficiency test were a total of 42 laboratories from Denmark and Sweden. A list of participants is shown in Appendix A.

The closing date for submission of results was 3 June 2022. All participants except laboratory no. 10, 16 and 33 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" (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 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	7.0	0.081	1.6
Ammonium	NH_4	mg/l N	0.1-2	0.917	0.011	0.213
Nitrite+nitrate	NO_{2+3}	mg/l N	1-5	3.46	0.040	0.79
Nitrate	NO_3	mg/l N	1-5	3.35	0.063	0.71
Conductivity	γ_{25}	mS/m	50-300	127	1.5	26
pH	pH		6-9	8.09	0.020	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 NH_4, NO_{2+3}, conductivity and pH, but the test revealed a significant difference between the two for TN and NO_3.

For TN the difference could be attributed to laboratories using methods other than that prescribed by the Danish EPA. The test was repeated after exclusion of the results for method no. 6, 9, 51, 71, 71A, 71B and 72 and now showed no significant difference. The assigned spike value is therefore kept unchanged.

The difference for NO_3 was significant and could not be attributed to specific methods or other conditions. Eurofins' control measurements supported the difference between calculated and measured spike. Furthermore, the difference had a significant influence on the general quality of analyses. It was therefore decided to change the spike value from the calculated value to a value based on consensus between participating laboratories, i.e. the difference between the medians for sample A1 and B1.

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 95,7 %. 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, 51, 71, 71A, 71B and 72 and now showed no significant difference. The assigned value is therefore kept unchanged.

3 HOMOGENEITY OF SAMPLES

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

NH_4	Homogeneity 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) and

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

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/. This test ensures that heterogeneity 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.

4 CONCLUSION

The quality control performed, including test of 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.

For NO_3 the participants could not recover the spike value calculated from sample preparation and Eurofins' control measurements supported this. The difference between the calculated spike value and that found by the participants as well the influence on evaluation of participant performance or estimation of general quality of analyses was found to be significant. It was therefore decided to base the spike value for NO_3 upon participant data. The final spike value is the difference between medians for sample A1 and B1.

5 REFERENCES

/1/ Eurofins A/S, *Proficiency test SPIL-2 (2022)*, Report to participants, June 2022.

/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. 2362 on *quality criteria for environmental measurements,* 26 November 2021 (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
Bornholms Spildevand A/S	Rønne	Denmark
Cheminova A/S	Harboøre	Denmark
CP Kelco, QC Analyselab.	Ll. Skensved	Denmark
DIN Forsyning, Laboratorium Rens Øst-Esbjerg	Esbjerg	Denmark
Eurofins Miljø A/S (2 participants)	Vejen	Denmark
Hillerød Spildevand (2 participants)	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
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
Svendborg Spildevand A/S, Svenborg Centralrense-anlæg	Skårup Fyn	Denmark
Vandmiljø Randers A/S	Randers SØ	Denmark
Vejle Spildevand	Vejle	Denmark
AB Lennart Månsson International	Helsingborg	Sweden
Arctic Paper Munkedals AB	Munkedal	Sweden
GRYAAB AB	Göteborg	Sweden
Hallsta Pappersbruk	Hallstavik	Sweden
Käppalaverket	Lidingö	Sweden
Laboratoriet vid Smedjeholms avloppsreningsverk	Falkenberg	Sweden
Ljungby Kommun, Avloppsreningsverket, VA-labb	Ljungby	Sweden
Mjölby Kommun (2 participants)	Mjölby	Sweden
NSVA/Öresundsverket	Helsingborg	Sweden
Perstorp Oxo AB	Ödsmål	Sweden
Preemraff AB Göteborg	Göteborg	Sweden
Preemraff Lysekil	Lysekil	Sweden
Reningsverket Aggerud	Karlskoga	Sweden
Smurfit Kappa Piteå	Piteå	Sweden
St1 Refinery AB	Göteborg	Sweden

Laboratory	Town	Country
Vallviks Bruk AB	Vallvik	Sweden
Yara AB	Köping	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	5.0 g	Ammonium chloride (NH_4Cl) milli-Q water up to 1000.0 g	NH_4: 1310 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	70 g stock TN 35 g stock NH_4 500 g stock NO_3 600 g stock NaCl milli-Q water up to 50.00 kg	7.02	0.917	3.46	140.2
B1	10 g stock TN 5.0 g stock NH_4 70.00 g stock NO_3 80.0 g stock NaCl Sample A1 up to 30.00 kg	0.994 · 7.02 + 1.62	0.917 + 0.213	0.994 · 3.46 + 0.789	0.994 · 140.2 + 28.5

Sample	**Sample prepared from**	**pH**
A2/B2	88.51 g Potassium dihydrogen phosphate (KH_2PO_4) 637.5 g Sodium hydroxide 1 M milli-Q water up to 12500 g	c. 8.08

ANNEX C CONTROL OF SPIKE VALUES

Total Nitrogen, mg/l N
Control of differences within sample pairs

Laboratory	Difference AB
1	-0.020
2	0.750
3	-0.080
4	0.370
5	1.260
6	-0.200
7	0.200
8	0.200
9	0.130
11	-0.160
12	0.350
13	0.120
14	-0.140
15	0.340
17	-
18	-
19	0.230
20	0.160
21	-0.200
22	0.224
23	0.863
24	-0.000
25	-0.010
26	0.070
27	0.180
28	-0.304
29	-0.180
30	0.040
31	0.260
32	-1.410
34	0.020
35	-0.230
36	0.120
37	-
38	0.100
39	0.760
40	0.010
41	0.990
42	0.120
No of labs., p	36
No of repl., n	2
d	0.137
s^2	0.195
s	0.442
$t = \sqrt{p} \cdot (d/s)$	1.8604
Sign. level, p(t)	0.0712

No test statistics were found to be significant

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

Laboratory	Difference AB
1	-0.005
2	-
3	-
4	0.003
5	0.021
6	-0.003
7	-0.007
8	-0.001
9	0.003
11	0.006
12	0.048
13	-0.006
14	0.005
15	0.003
17	-
18	-
19	-0.027
20	0.013
21	-0.008
22	-
23	-
24	-0.045
25	-0.022
26	-0.008
27	0.002
28	-0.006
29	-0.016
30	-0.017
31	-0.002
32	0.005
34	-
35	0.023
36	-0.027
37	0.038
38	-0.003
39	0.018
40	-0.008
41	0.053
42	-0.007
No of labs., p	32
No of repl., n	2
d	0.001
s^2	0.000
s	0.021
$t = \sqrt{p} \cdot (d/s)$	0.1974
Sign. level, p(t)	0.8448

No test statistics were found to be significant

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

Laboratory	Difference AB	
1	0.010	
2	-	
3	-	
4	-	
5	-	
6	-	
7	-	
8	-	
9	-0.010	
11	-	
12	-	
13	-	
14	-	
15	-	
17	0.130	
18	-	
19	0.790	UC
20	-	
21	-	
22	-	
23	-	
24	0.036	
25	-	
26	-	
27	-	
28	-0.026	
29	-	
30	-	
31	0.069	
32	0.060	
34	-	
35	-	
36	-	
37	0.018	
38	-	
39	-	
40	-	
41	-	
42	-0.080	
No of labs., p	9	
No of repl., n	2	
d	0.023	
s^2	0.004	
s	0.061	
$t = \sqrt{p} \cdot (d/s)$	1.1400	
Sign. level, p(t)	0.2873	

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	-0.010	
5	0.120	
6	0.010	
7	0.030	
8	0.150	
9	-0.040	
11	0.030	
12	-0.020	
13	-0.000	
14	0.000	
15	0.010	
17	-	
18	-	
19	0.030	
20	-0.040	
21	-	
22	-	
23	-	
24	-0.055	
25	-0.030	
26	0.040	
27	-0.220	
28	-0.106	
29	-0.020	
30	-	
31	-0.011	
32	-	
34	-	
35	0.080	UG
36	-0.060	
37	-	
38	-0.090	
39	-	
40	-0.050	
41	-	
42	-	
No of labs., p	23	
No of repl., n	2	
d	-0.014	
s^2	0.005	
s	0.073	
$t = \sqrt{p} \cdot (d/s)$	-0.9429	
Sign. level, p(t)	0.3560	

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

Conductivity, mS/m
Control of differences within sample pairs

Laboratory	Difference AB	
1	-	
2	-	
3	1.10	
4	0.60	
5	0.60	
6	-2.60	
7	-0.30	
8	-	
9	-	
11	1.90	
12	-0.30	
13	-	
14	-1.00	
15	-0.00	
17	-	
18	-0.60	
19	-	
20	-0.80	
21	-	
22	-0.50	
23	-	
24	-1.40	
25	-	
26	-	
27	-0.30	
28	2.00	
29	-	
30	-	
31	-	
32	-	
34	-	
35	-226.00	UC
36	-	
37	-	
38	-	
39	-	
40	-0.10	
41	-	
42	-	
No of labs., p	16	
No of repl., n	2	
d	-0.11	
s^2	1.37	
s	1.17	
$t = \sqrt{p} \cdot (d/s)$	-0.3626	
Sign. level, p(t)	0.7220	

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

pH,
Control of differences within sample pairs

Laboratory	Difference AB	
1	0.010	
2	0.000	
3	0.020	
4	-0.010	UG
5	-0.035	
6	-0.020	
7	0.000	
8	0.000	UG
9	-0.130	UC
11	-	
12	-0.074	
13	-0.010	
14	-0.030	
15	-0.020	
17	-	
18	-0.010	
19	-0.010	
20	0.000	
21	0.000	
22	-0.020	
23	0.010	
24	0.000	
25	-0.030	
26	-0.010	
27	-0.035	
28	0.040	
29	0.100	UC
30	-0.020	
31	0.000	
32	0.010	
34	-	
35	0.030	
36	0.000	
37	0.010	
38	0.000	
39	0.002	
40	0.020	
41	0.050	
42	-0.050	
No of labs., p	32	
No of repl., n	2	
d	-0.005	
s^2	0.001	
s	0.025	
$t = \sqrt{p} \cdot (d/s)$	-1.2121	
Sign. level, p(t)	0.2346	

No test statistics were found to be significant
UC denotes a Cochran outlier
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	7.240	
2	5.935	
3	7.170	
4	7.695	
5	5.500	
6	7.120	
7	5.860	
8	6.780	
9	6.315	
11	8.420	
12	6.505	
13	6.880	
14	6.930	
15	6.380	
17	-	
18	-	
19	6.385	
20	6.580	
21	6.590	
22	5.746	
23	4.989	
24	6.620	
25	7.075	
26	6.875	
27	6.240	
28	8.513	
29	6.950	
30	6.510	
31	5.880	
32	7.465	
34	5.640	
35	6.955	
36	6.920	
37	-	
38	6.890	
39	5.790	
40	6.545	
41	7.385	
42	7.780	
No of labs., p	36	
No of repl., n	2	
m	6.696	
s^2	0.586	
s	0.765	
Assigned value, μ	7.0	
Recovery, %	95.7	
$t = \sqrt{p} \cdot (m-\mu)/s$	-2.3837	
Sign. level, p(t)	0.0227	*

* 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)

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

Laboratory	Sample pair AB
1	0.924
2	-
3	-
4	0.928
5	0.848
6	0.906
7	0.934
8	0.946
9	0.899
11	0.910
12	0.881
13	0.934
14	0.860
15	0.889
17	-
18	-
19	0.884
20	1.014
21	0.953
22	-
23	-
24	0.923
25	0.916
26	0.943
27	0.868
28	0.867
29	0.909
30	1.018
31	0.967
32	0.910
34	-
35	0.958
36	0.964
37	0.967
38	0.946
39	1.046
40	0.923
41	0.824
42	0.894
No of labs., p	32
No of repl., n	2
m	0.923
s^2	0.002
s	0.049
Assigned value, μ	0.917
Recovery, %	100.7
$t = \sqrt{p} \cdot (m-\mu)/s$	0.7418
Sign. level, p(t)	0.4638

No test statistics were found to be significant

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

Laboratory	Sample pair AB	
1	3.405	
2	-	
3	-	
4	-	
5	-	
6	-	
7	-	
8	-	
9	3.705	
11	-	
12	-	
13	-	
14	-	
15	-	
17	3.475	
18	-	
19	-0.395	UC
20	-	
21	-	
22	-	
23	-	
24	3.301	
25	-	
26	-	
27	-	
28	3.376	
29	-	
30	-	
31	3.303	
32	3.300	
34	-	
35	-	
36	-	
37	3.585	
38	-	
39	-	
40	-	
41	-	
42	3.380	
No of labs., p	9	
No of repl., n	2	
m	3.425	
s^2	0.020	
s	0.140	
Assigned value, μ	3.46	
Recovery, %	99.0	
$t = \sqrt{p} \cdot (m-\mu)/s$	-0.7388	
Sign. level, p(t)	0.4811	

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	3.375	
5	3.280	
6	3.305	
7	3.355	
8	3.175	
9	3.120	
11	3.475	
12	3.280	
13	3.400	
14	3.130	
15	2.895	
17	-	
18	-	
19	3.485	
20	3.600	
21	-	
22	-	
23	-	
24	3.333	
25	3.485	
26	3.380	
27	3.040	
28	3.415	
29	3.310	
30	-	
31	3.343	
32	-	
34	-	
35	4.030	UG
36	3.270	
37	-	
38	3.495	
39	-	
40	3.505	
41	-	
42	-	
No of labs., p	23	
No of repl., n	2	
m	3.324	
s^2	0.028	
s	0.166	
Assigned value, μ	3.35	
Recovery, %	99.2	
$t = \sqrt{p} \cdot (m-\mu)/s$	-0.7529	
Sign. level, p(t)	0.4595	

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

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

Laboratory	Sample pair AB	
1	-	
2	-	
3	115.35	
4	127.60	
5	108.90	
6	128.20	
7	126.55	
8	-	
9	-	
11	120.85	
12	125.65	
13	-	
14	128.50	
15	123.80	
17	-	
18	126.20	
19	-	
20	127.50	
21	-	
22	126.85	
23	-	
24	129.00	
25	-	
26	-	
27	127.95	
28	107.00	
29	-	
30	-	
31	-	
32	-	
34	-	
35	1370.00	UC
36	-	
37	-	
38	-	
39	-	
40	127.75	
41	-	
42	-	
No of labs., p	16	
No of repl., n	2	
m	123.60	
s^2	49.28	
s	7.02	
Assigned value, μ	127	
Recovery, %	97.3	
$t = \sqrt{p} \cdot (m-\mu)/s$	-1.9355	
Sign. level, p(t)	0.0720	

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

pH,
Control of recovery, average of results

Laboratory	Sample pair AB	
1	8.075	
2	8.080	
3	8.100	
4	8.455	UG
5	8.095	
6	8.040	
7	8.150	
8	8.570	UG
9	8.195	UC
11	-	
12	8.193	
13	8.065	
14	8.155	
15	8.110	
17	-	
18	8.065	
19	8.125	
20	8.200	
21	8.090	
22	8.020	
23	8.055	
24	8.060	
25	8.095	
26	8.075	
27	8.110	
28	8.150	
29	8.250	UC
30	8.080	
31	8.060	
32	8.055	
34	-	
35	8.125	
36	8.080	
37	8.045	
38	8.070	
39	8.069	
40	8.150	
41	8.125	
42	8.195	
No of labs., p	32	
No of repl., n	2	
m	8.099	
s^2	0.002	
s	0.047	
Assigned value, μ	8.09	
Recovery, %	100.1	
$t = \sqrt{p} \cdot (m-\mu)/s$	1.0653	
Sign. level, p(t)	0.2950	

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

ANNEX E CONCENTRATION LEVEL

Concentration level **SPIL-2 (2022)**

Parameter	Unit	Sample	Bottle no.	I	II	Bottle Average	Sample Average	Assigned value	Spike Measured	Spike Assigned
Total nitrogen	mg/L N	A1	5	6.77	6.81	6.79	6.74	7.02	1.64	1.62
			30	6.79	6.73	6.76				
			53	6.67	6.69	6.68				
		B1	13	8.36	8.35	8.36	8.38	8.63		
			43	8.38	8.39	8.39				
			65	8.39	8.41	8.40				
Ammonium	mg/L N	A1	5	0.934	0.934	0.93	0.940	0.917	0.23	0.213
			30	0.946	0.948	0.95				
			53	0.940	0.940	0.94				
		B1	13	1.150	1.150	1.15	1.170	1.130		
			43	1.200	1.200	1.20				
			65	1.160	1.160	1.16				
Nitrite+nitrate / Nitrate	mg/L N	A1	5	3.35	3.36	3.36	3.36	3.35	0.76	0.71
			30	3.35	3.36	3.36				
			53	3.38	3.37	3.38				
		B1	13	4.13	4.14	4.14	4.13	2.81		
			43	4.11	4.09	4.10				
			65	4.14	4.15	4.15				
pH		A2	4	8.16	8.16	8.16	8.16	8.09	0.00	0
			44	8.17	8.17	8.17				
			65	8.15	8.17	8.16				
		B2	7	8.17	8.16	8.17	8.16	8.09		
			34	8.15	8.15	8.15				
			66	8.17	8.17	8.17				

ANNEX F HOMOGENEITY

PT:	SPIL-2
Parameter:	NH4
Unit:	mg/L N
Sigma:	0,065

Responsible for tests: HBP/S7MS

Homogeneity test Date: 2022-05-03

Sample	x(a)	x(b)	average	sd	sd^2
B1 3	1,190	1,190	1,2	0,000	0,000
B1 11	1,200	1,200	1,2	0,000	0,000
B1 18	1,200	1,200	1,2	0,000	0,000
B1 22	1,190	1,190	1,2	0,000	0,000
B1 28	1,190	1,190	1,2	0,000	0,000
B1 33	1,200	1,200	1,2	0,000	0,000
B1 37	1,200	1,200	1,2	0,000	0,000
B1 42	1,210	1,210	1,2	0,000	0,000
B1 49	1,210	1,210	1,2	0,000	0,000
B1 52	1,200	1,210	1,2	0,007	0,000
B1 58	1,220	1,220	1,2	0,000	0,000
B1 67	1,190	1,190	1,2	0,000	0,000

For homogeneity

General average (x)	1,2004
Sample average sd (s_x)	0,0096
Within-sample sd (s_w):	0,0020
Between-samples sd (ss):	0,0095
S_L in the Proficiency Test:	0,048
S_R in the Proficiency Test:	0,050

Conclusions

ss =	0,0095	0.3*sigma= 0,0194
/x-y/ =	0	
Analytical quality	Is s_w < 0,15*sigma	**YES**
Homogeneity:	Is ss < 0.3*sigma?	**YES**

PT:	SPIL-2
Parameter:	NO3
Unit:	mg/L N
Sigma:	0,232

Responsible for tests: HBP/S7MS

Homogeneity test Date: 2022-05-03

Sample	x(a)	x(b)	average	sd	sd^2
B1 3	4,27	4,26	4,3	0,007	0,000
B1 11	4,25	4,28	4,3	0,021	0,00
B1 18	4,31	4,32	4,3	0,007	0,000
B1 22	4,26	4,28	4,3	0,014	0,000
B1 28	4,30	4,28	4,3	0,014	0,000
B1 33	4,26	4,28	4,3	0,014	0,000
B1 37	4,30	4,29	4,3	0,007	0,000
B1 42	4,29	4,28	4,3	0,007	0,000
B1 49	4,30	4,28	4,3	0,014	0,000
B1 52	4,28	4,30	4,3	0,014	0,000
B1 58	4,31	4,31	4,3	0,000	0,000
B1 67	4,31	4,29	4,3	0,014	0,000

For homogeneity

General average (x)	4,29
Sample average sd (s_x)	0,017
Within-sample sd (s_w):	0,012
Between-samples sd (ss):	0,0144
S_L in the Proficiency Test:	0,162
S_R in the Proficiency Test:	0,170

Conclusions

ss =	0,014	0.3*sigma=	0,0695
/x-y/ =	0		

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: 2022-05-03

Sample	x(a)	x(b)	aver-age	sd	sd^2
B2 1	8,16	8,16	8,2	0,000	0,000
B2 6	8,15	8,15	8,2	0,000	0,00
B2 9	8,17	8,16	8,2	0,007	0,000
B2 14	8,16	8,16	8,2	0,000	0,000
B2 23	8,15	8,15	8,2	0,000	0,000
B2 28	8,16	8,15	8,2	0,007	0,000
B2 36	8,16	8,16	8,2	0,000	0,000
B2 43	8,16	8,17	8,2	0,007	0,000
B2 46	8,17	8,16	8,2	0,007	0,000
B2 53	8,15	8,15	8,2	0,000	0,000
B2 59	8,15	8,16	8,2	0,007	0,000
B2 65	8,17	8,15	8,2	0,014	0,000

For homogeneity

General average (x)	8,16
Sample average sd (s_x)	0,006
Within-sample sd (s_w):	0,006
Between-samples sd (ss):	0,0039
S_L in the Proficiency Test:	0,045
S_R in the Proficiency Test:	0,048

Conclusions

ss =	0,004	0.3*sigma=	0,02
/x-y/ =	0		
Analytical quality	Is s_w < 0,15*sigma **YES**		
Homogeneity:	Is ss < 0.3*sigma? **YES**		