Proficiency test SPIL-4 (2022)

Nitrogen parameters in wastewater (effluent)

Quality Documentation
January 2023

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CONTENTS

1 INTRODUCTION

A proficiency test on the analysis of nitrogen parameters in wastewater was conducted on 17 November 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 20 December 2022.

2 FEATURES OF THE PROFICIENCY TEST

Participants in the proficiency test were a total of 54 laboratories from Denmark, Norway and Sweden. A list of participants is shown in Appendix A.

The closing date for submission of results was 2 December 2022. All participants except laboratory no. 51 had submitted their results before the deadline.

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 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	4.6	0.093	0.8
Ammonium	NH_4	mg/L N	0.1-2	0.108	0.0058	0.231
Nitrite+nitrate	NO_{2+3}	mg/L N	1-5	3.87	0.062	0.50
Nitrate	NO_3	mg/L N	1-5	4.00	0.061	0.50
Conductivity	γ_{25}	mS/m	50-300	69	1.1	1
pH	pH		6-9	7.57	0.046	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 conductivity and pH 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, 3, 4 and 5 (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 NH_4, NO_{2+3} and pH, but the test revealed a significant difference between the two for TN, NO_3 and γ_{25}.

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, 51, 71, 71A and 72 and now showed no significant difference. The assigned spike value is therefore kept unchanged.

The difference for NO_3 and γ_{25} was significant and could not be attributed to specific methods or other conditions. However, the difference is numerically small and has insignificant influence on the general quality of analyses estimated from the data as well as on the evaluation of accuracy of participating laboratories.

2.3.3 Test of assigned values

The assigned value and the average of the results obtained from all laboratories were also compared (t-test, 95% confidence level), see Appendix D. The test showed no significant difference between the two and the control of assigned value at Eurofins confirmed the value (Appendix E).

3 HOMOGENEITY AND STABILITY OF SAMPLES

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

NH_4	Combined homogeneity and stability test
NO_3	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)

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/. The 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.

The tests for stability for NO_3 shows that the samples are stable.

The tests for stability for NH_4 and pH shows that the samples are not stable from the date of production to the day of analysis. Since the recoveries for the proficiency test were not significant different from 100 % and the proficiency should be performed on a specific date, the instability should not affect the validity of the proficiency test.

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 NO_3 and γ_{25} 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 TN the participants could not recover the spike value. The difference could be attributed to laboratories using methods other than that prescribed by the Danish EPA.

The tests for stability for NO_3 shows that the samples are stable.

The tests for stability for NH_4 and pH shows that the samples are not stable from the date of production to the date of analysis. The instability can give different results for laboratories analysing on other dates than the one set by the proficiency test.

5 REFERENCES

/1/ Eurofins A/S, *Proficiency test SPIL-4 (2022)*, Report to participants, December 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
AquaDjurs A/S	Grenaa	Denmark
BIOFOS Renseanlæg, Avedøre Spildevands- og driftslaboratoriet	Hvidovre	Denmark
Bjergmarken RA, Fors Spildevand Roskilde	Roskilde	Denmark
BlueKolding A/S	Kolding	Denmark
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
RGS Nordic A/S	Skælskør	Denmark
Ringkøbing-Skjern Forsyning A/S	Skjern	Denmark
SK Spildevand A/S, Slagelse Renseanlæg (2 participants)	Slagelse	Denmark
Svendborg Spildevand A/S, Svenborg Centralrense-anlæg	Skårup Fyn	Denmark
Vandmiljø Randers A/S	Randers SØ	Denmark
Vejle Spildevand	Vejle	Denmark
Aalborg Forsyning, Renseanlæg Øst	Aalborg Øst	Denmark
SGS Analytics Norway AS (Hamar)	Hamar	Norway
AB Lennart Månsson International	Helsingborg	Sweden

Laboratory	Town	Country
Arctic Paper Munkedals AB	Munkedal	Sweden
Ernemar Laboratorium	Oskarshamn	Sweden
Fiskeby Board AB	Norrköping	Sweden
GRYAAB AB	Göteborg	Sweden
Holmen Paper Braviken AB, Bravikens Pappersbruk	Norrköping	Sweden
Kalmar Vatten AB, VA-lab	Kalmar	Sweden
Kristianstad Kommun	Kristianstad	Sweden
Käppalaverket	Lidingö	Sweden
MittSweden Vatten och Avfall AB, Fillanverket Laboratoriet	Sundsvall	Sweden
Mjölby Kommun (2 participants)	Mjölby	Sweden
Motala Kommun, Tekniska Förvaltningen, Vatten och Avfall	Motala	Sweden
Nordic Sugar AB, Örtofta Sockerbruk	Eslöv	Sweden
Preemraff AB Göteborg	Göteborg	Sweden
Preemraff Lysekil	Lysekil	Sweden
Reningsverket Aggerud	Karlskoga	Sweden
Smurfit Kappa Piteå	Piteå	Sweden
St1 Refinery AB	Göteborg	Sweden
Södra Cell AB Mönsterås	Mönsterås	Sweden
Södra Cell AB, Värö	Väröbacka	Sweden
Vallviks Bruk AB	Vallvik	Sweden
VIVAB	Varberg	Sweden
Västervik Miljö & Energi AB, Vattenlaboratoriet	Västervik	Sweden
Växjö Kommun, Tekniska Förvaltningen/VA-Lab.	Växjö	Sweden
Yara AB	Köping	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	0.999 g	Ammonium chloride (NH_4Cl) milli-Q water up to 1000.0 g	NH_4: 261.8 mg/kg N
Stock NO_3	2.499 g	Potassium nitrate (KNO_3) milli-Q water up to 1000.0 g	NO_3: 346.3 mg/kg N

Sample	**Sample prepared from**	**TN mg/L N**	**NH_4 mg/L N**	**NO_3 mg/L N**	**γ25 mS/m**
A1	0 g stock TN 0 g stock NH_4 300.0 g stock NO_3 300.0 g stock NaCl Filtered water from Holsted sewage treatment plant up to 65.00 kg	a+4.60	b+0.109	c+4.00	d
B1	10.00 g stock TN 30.00 g stock NH_4 50.00 g stock NO_3 Sample A1 up to 34.00 kg	0.997 · (a+4.60) + 0.795	0.997 · (b+0.109) + 0.231	0.997 · (c+4.00) + 0.499	e

Sample	**Sample prepared from**	**pH**
A2/B2	Filtered water from Holsted 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	0.200	
2	0.020	
3	-0.020	
4	-0.120	
5	0.240	
6	0.170	
7	-0.040	
8	0.000	
9	-0.030	
10	0.020	
11	-	
12	0.220	
13	-0.050	
14	-0.100	
15	-	
16	0.310	
17	-0.190	
18	0.070	
19	-0.120	
20	0.110	
21	-	
22	0.000	
23	0.040	
24	0.420	
25	0.073	
26	0.230	
27	-0.350	
28	0.020	
29	0.125	
30	0.000	
31	-0.140	
32	0.370	
33	0.190	
34	0.060	
35	-0.110	
36	0.230	
37	-0.040	
38	-0.230	
39	0.120	
40	0.320	
41	0.037	
42	0.160	
43	-0.070	
44	-1.200	UC
45	0.240	
46	-0.140	
47	-0.060	
48	-0.040	
49	0.420	
50	0.160	
52	0.380	

Laboratory	Difference AB	
53	0.630	
54	-	
No of labs., p	48	
No of repl., n	2	
d	0.078	
s^2	0.037	
s	0.193	
$t = \sqrt{p} \cdot (d/s)$	2.7992	
Sign. level, p(t)	0.0074	**

* 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	-0.0080	
2	0.0100	
3	0.0110	
4	0.0070	
5	-	
6	0.0140	
7	-0.0350	
8	0.0310	
9	-0.0190	
10	-0.0050	
11	-	
12	-0.0090	
13	-0.0010	
14	-0.0030	
15	-0.0250	
16	-0.0020	
17	-0.0100	
18	-0.0040	
19	-	
20	0.0010	
21	-	
22	0.0060	
23	0.0120	
24	-	
25	-0.0110	
26	0.0010	
27	0.1100	UC
28	0.0000	
29	-0.0280	
30	0.0910	UC
31	-0.0030	
32	0.0180	
33	-0.0100	
34	-0.0053	
35	0.0000	
36	-0.0010	
37	0.0010	
38	-0.0090	
39	-0.0190	
40	-0.0010	
41	0.0640	UC
42	0.0330	
43	-	
44	-0.0200	
45	0.0010	
46	0.0080	
47	-0.0150	
48	-0.0020	
49	-0.0180	
50	-	
52	0.0190	
53	-	
54	-	

No of labs., p	41
No of repl., n	2
d	-0.0022
s^2	0.0002
s	0.0143
$t = \sqrt{p} \cdot (d/s)$	-0.9849
Sign. level, p(t)	0.3306

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

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

Laboratory	Difference AB	
1	-	
2	-	
3	-	
4	0.130	
5	-	
6	-	
7	-	
8	-	
9	0.020	
10	-	
11	-	
12	-	
13	-	
14	-	
15	0.128	
16	-	
17	-	
18	-	
19	-	
20	-0.330	UC
21	-	
22	-	
23	-	
24	-	
25	-	
26	0.020	
27	0.030	
28	-	
29	-	
30	-0.010	
31	-	
32	-	
33	-	
34	0.085	
35	0.010	
36	0.020	
37	-	
38	-0.030	
39	-	
40	0.010	
41	-0.067	
42	-	
43	-	
44	-	
45	-	
46	-	
47	-	
48	-	
49	-	
50	-	
52	-	
53	-	
54	-	

No of labs., p	12
No of repl., n	2
d	0.029
s^2	0.003
s	0.059
$t = \sqrt{p} \cdot (d/s)$	1.6922
Sign. level, p(t)	0.1187

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	-0.010	
2	0.100	
3	-0.020	
4	-	
5	-	
6	0.000	
7	0.100	
8	0.060	
9	0.020	
10	0.050	
11	-	
12	0.010	
13	0.020	
14	-	
15	-	
16	0.060	
17	0.090	
18	0.020	
19	-	
20	-	
21	-	
22	-0.040	
23	0.070	
24	-	
25	-0.060	
26	-	
27	-	
28	-0.070	
29	-0.078	
30	-	
31	0.010	
32	-0.050	
33	0.010	
34	-	
35	0.011	
36	-	
37	-	
38	-	
39	0.200	UG
40	-	
41	-	
42	0.000	
43	-	
44	-0.030	
45	0.050	
46	0.060	
47	-	
48	0.040	
49	0.070	
50	-	
52	0.110	
53	-	
54	-	

No of labs., p	29	
No of repl., n	2	
d	0.021	
s^2	0.003	
s	0.052	
$t = \sqrt{p} \cdot (d/s)$	2.1413	
Sign. level, p(t)	0.0411	*

* denotes that there is a significant difference (t-test, 5%-level)
** denotes that there is a significant difference (t-test, 1%-level)
*** denotes that there is a significant difference (t-test, 0.1%-level)
UG denotes a Grubbs outlier

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.

Conductivity, mS/m
Control of differences within sample pairs

Laboratory	Difference AB	
1	-	
2	-	
3	-	
4	0.10	
5	-	
6	-	
7	-	
8	-0.10	
9	-	
10	-	
11	-	
12	-	
13	0.30	
14	-	
15	-	
16	0.60	
17	0.20	
18	-	
19	-	
20	-	
21	1.00	
22	0.20	
23	0.20	
24	-	
25	-0.10	
26	-	
27	0.25	
28	-	
29	-0.30	
30	0.25	
31	-13.50	UC
32	-	
33	-	
34	-	
35	-0.30	
36	-	
37	-	
38	-1.80	UC
39	0.40	
40	0.70	
41	0.40	
42	0.30	
43	0.05	UG
44	0.40	
45	-	
46	-	
47	-	
48	-	
49	-	
50	0.10	
52	0.00	
53	-	
54	-	

No of labs., p	20	
No of repl., n	2	
d	0.23	
s^2	0.10	
s	0.32	
$t = \sqrt{p} \cdot (d/s)$	3.2382	
Sign. level, p(t)	0.0043	**

* 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.

pH,
Control of differences within sample pairs

Laboratory	Difference AB	
1	0.010	
2	0.377	
3	-0.030	
4	-0.020	
5	-	
6	-0.039	
7	-0.130	
8	0.240	
9	-	
10	-0.150	
11	0.010	
12	0.000	
13	-0.070	
14	-0.010	
15	-0.010	
16	-0.182	
17	-0.030	
18	0.260	
19	-	
20	-0.150	
21	-0.020	
22	-0.050	
23	-0.040	
24	-	
25	0.000	
26	-0.040	
27	-0.040	
28	-0.010	
29	-0.010	
30	-	
31	0.040	
32	0.140	
33	-0.030	
34	-	
35	-0.080	
36	-0.060	
37	-0.030	
38	0.020	
39	-0.190	
40	-0.030	
41	-0.150	
42	0.590	UC
43	0.030	
44	-0.020	
45	-0.020	
46	-	
47	0.010	
48	-0.230	
49	0.020	
50	0.040	
52	-0.050	
53	-	
54	0.000	

No of labs., p	44
No of repl., n	2
d	-0.016
s^2	0.012
s	0.110
$t = \sqrt{p} \cdot (d/s)$	-0.9930
Sign. level, p(t)	0.3262

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	5.080	
2	4.680	
3	4.390	
4	4.780	
5	4.270	
6	4.325	
7	4.700	
8	4.370	
9	4.555	
10	4.640	
11	-	
12	4.980	
13	4.555	
14	4.250	
15	-	
16	4.135	
17	4.985	
18	4.705	
19	4.590	
20	4.635	
21	-	
22	4.760	
23	5.000	
24	3.730	
25	4.453	
26	4.725	
27	4.565	
28	4.360	
29	3.785	
30	4.870	
31	4.700	
32	4.515	
33	4.325	
34	4.080	
35	5.365	
36	5.025	
37	4.290	
38	4.625	
39	4.180	
40	3.690	
41	5.431	
42	5.090	
43	4.845	
44	4.020	UC
45	4.230	
46	4.460	
47	4.620	
48	4.420	
49	4.510	
50	4.050	
52	4.690	

Laboratory	Sample pair AB
53	4.155
54	4.330
No of labs., p	48
No of repl., n	2
m	4.545
s^2	0.144
s	0.379
Assigned value, μ	4.60
Recovery, %	98.8
$t = \sqrt{p} \cdot (m-\mu)/s$	-1.0013
Sign. level, p(t)	0.3218

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	0.0980	
2	0.0900	
3	0.1345	
4	0.0855	
5	-	
6	0.1000	
7	0.1205	
8	0.1945	
9	0.1695	
10	0.1085	
11	-	
12	0.1065	
13	0.1145	
14	0.1075	
15	0.1381	
16	0.0980	
17	0.1110	
18	0.1120	
19	-	
20	0.1095	
21	-	
22	0.1200	
23	0.0580	
24	-	
25	0.1095	
26	0.0995	
27	0.0050	UC
28	0.0980	
29	0.1370	
30	0.2545	UC
31	0.1005	
32	0.0800	
33	0.1110	
34	0.1571	
35	0.0940	
36	0.0965	
37	0.0995	
38	0.1105	
39	0.1095	
40	0.1385	
41	0.1990	UC
42	0.0645	
43	-	
44	0.1240	
45	0.0795	
46	0.0870	
47	0.1185	
48	0.0970	
49	0.1130	
50	-	
52	0.0875	
53	-	
54	0.1690	

No of labs., p	41
No of repl., n	2
m	0.1095
s^2	0.0007
s	0.0257
Assigned value, μ	0.108
Recovery, %	101.4
$t = \sqrt{p} \cdot (m-\mu)/s$	0.3654
Sign. level, p(t)	0.7167

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

Nitrite/nitrate, mg/l N
Control of recovery, average of results

Laboratory	Sample pair AB	
1	-	
2	-	
3	-	
4	3.775	
5	-	
6	-	
7	-	
8	-	
9	4.070	
10	-	
11	-	
12	-	
13	-	
14	-	
15	3.996	
16	-	
17	-	
18	-	
19	-	
20	3.755	UC
21	-	
22	-	
23	-	
24	-	
25	-	
26	3.850	
27	3.455	
28	-	
29	-	
30	3.875	
31	-	
32	-	
33	-	
34	3.821	
35	3.737	
36	3.870	
37	-	
38	3.915	
39	-	
40	3.915	
41	3.952	
42	-	
43	-	
44	-	
45	-	
46	-	
47	-	
48	-	
49	-	
50	-	
52	-	
53	-	
54	3.630	

No of labs., p	12
No of repl., n	2
m	3.853
s^2	0.024
s	0.155
Assigned value, μ	3.87
Recovery, %	99.6
$t = \sqrt{p} \cdot (m-\mu)/s$	-0.3885
Sign. level, p(t)	0.7051

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	4.045	
2	3.860	
3	4.260	
4	-	
5	-	
6	3.850	
7	4.050	
8	4.190	
9	4.060	
10	3.965	
11	-	
12	4.065	
13	3.840	
14	-	
15	-	
16	3.920	
17	4.075	
18	4.020	
19	-	
20	-	
21	-	
22	4.040	
23	3.895	
24	-	
25	4.080	
26	-	
27	-	
28	3.865	
29	4.087	
30	-	
31	4.045	
32	3.865	
33	4.065	
34	-	
35	3.732	
36	-	
37	-	
38	-	
39	3.000	UG
40	-	
41	-	
42	3.990	
43	-	
44	4.095	
45	3.715	
46	3.690	
47	-	
48	4.030	
49	3.925	
50	-	
52	3.875	
53	-	
54	3.630	

No of labs., p	29
No of repl., n	2
m	3.972
s^2	0.019
s	0.137
Assigned value, μ	4.00
Recovery, %	99.3
$t = \sqrt{p} \cdot (m-\mu)/s$	-1.0929
Sign. level, p(t)	0.2837

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	-	
4	70.35	
5	-	
6	-	
7	-	
8	66.25	
9	-	
10	-	
11	-	
12	-	
13	70.35	
14	-	
15	-	
16	70.20	
17	70.50	
18	-	
19	-	
20	-	
21	71.20	
22	69.50	
23	70.60	
24	-	
25	68.25	
26	-	
27	68.36	
28	-	
29	66.45	
30	68.17	
31	74.95	UC
32	-	
33	-	
34	-	
35	66.15	
36	-	
37	-	
38	66.00	UC
39	69.60	
40	68.15	
41	69.00	
42	66.65	
43	61.69	UG
44	70.10	
45	-	
46	-	
47	-	
48	-	
49	-	
50	69.95	
52	71.00	
53	-	
54	-	

No of labs., p	20
No of repl., n	2
m	69.04
s^2	2.71
s	1.65
Assigned value, μ	69
Recovery, %	100.1
$t = \sqrt{p} \cdot (m-\mu)/s$	0.1059
Sign. level, p(t)	0.9168

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	7.555	
2	7.783	
3	7.755	
4	7.600	
5	-	
6	7.615	
7	7.695	
8	8.210	
9	-	
10	7.675	
11	8.123	
12	7.680	
13	7.465	
14	7.795	
15	7.395	
16	7.315	
17	7.305	
18	7.890	
19	-	
20	7.585	
21	7.580	
22	7.585	
23	7.480	
24	-	
25	7.570	
26	7.450	
27	7.550	
28	7.355	
29	7.515	
30	-	
31	7.520	
32	7.910	
33	7.495	
34	-	
35	7.520	
36	7.470	
37	7.665	
38	7.610	
39	8.085	
40	7.685	
41	7.325	
42	7.725	UC
43	7.565	
44	7.380	
45	7.400	
46	-	
47	7.825	
48	7.445	
49	7.620	
50	7.510	
52	7.445	
53	-	
54	7.580	

No of labs., p	44
No of repl., n	2
m	7.604
s^2	0.043
s	0.207
Assigned value, μ	7.57
Recovery, %	100.5
$t = \sqrt{p} \cdot (m-\mu)/s$	1.0936
Sign. level, p(t)	0.2802

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

ANNEX E CONCENTRATION LEVEL

Concentration level **SPIL-4 (2022)**

Parameter	Unit	Sample	Bottle no.	I	II	Bottle Average	Sample Average	Assigned value	Spike Measured	Spike Assigned
Total nitrogen	mg/L N	A1	10	4,69	4,71	4,70	4,75	4,60	0,75	0,80
			42	4,83	4,84	4,84				
			61	4,72	4,69	4,71				
		B1	15	5,51	5,54	5,53	5,49	5,35		
			45	5,49	5,49	5,49				
			81	5,49	5,44	5,47				
Ammonium	mg/L N	A1	10	0,101	0,103	0,10	0,100	0,108	0,24	0,231
			42	0,097	0,098	0,10				
			61	0,099	0,100	0,10				
		B1	15	0,352	0,354	0,35	0,345	0,339		
			45	0,339	0,339	0,34				
			81	0,341	0,342	0,34				
Nitrite+nitrate / Nitrate	mg/L N	A1	10	4,09	4,10	4,10	4,07	3,87	0,47	0,50
			42	4,05	4,05	4,05				
			61	4,07	4,05	4,06				
		B1	15	4,53	4,53	4,53	4,54	4,50		
			45	4,55	4,53	4,54				
			81	4,57	4,54	4,56				
pH		A2	6	7,61	7,60	7,61	7,60	7,57	0,00	0,00
			37	7,61	7,58	7,60				
			64	7,62	7,60	7,61				
		B2	12	7,62	7,59	7,61	7,61	7,57		
			45	7,62	7,59	7,61				
			78	7,61	7,60	7,61				

ANNEX F HOMOGENEITY AND STABILITY

PT: SPIL-4
Parameter: NH_4
Unit: mg/L N
Sigma: 0,036

Responsible for tests: DHBP/S7MS

Homogeneity test Date: 2022-11-01

Sample	x(a)	x(b)	average	sd	sd^2
1	0,352	0,354	0,4	0,001	0,000
11	0,367	0,368	0,4	0,001	0,00
22	0,368	0,369	0,4	0,001	0,000
26	0,364	0,365	0,4	0,001	0,000
33	0,364	0,365	0,4	0,001	0,000
40	0,37	0,371	0,4	0,001	0,000
49	0,354	0,356	0,4	0,001	0,000
52	0,366	0,366	0,4	0,000	0,000
62	0,365	0,365	0,4	0,000	0,000
67	0,365	0,365	0,4	0,000	0,000
74	0,366	0,366	0,4	0,000	0,000
85	0,339	0,337	0,3	0,001	0,000

For homogeneity

General average (x)	0,36
Sample average sd (s_x)	0,009
Within-sample sd (s_w):	0,001
Between-samples sd (ss):	0,0091
S_L in the Proficiency Test:	0,025
S_R in the Proficiency Test:	0,027

Stability test Date: 2022-22-17

Sample	x(a)	x(b)
15	0,352	0,354
45	0,339	0,339
81	0,341	0,342

For stability

General average (y):	0,3445
/x-y/ =	0,017458

Conclusions

ss =0,009 0.3*sigma=0,01
/x-y/ =0,017458

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:	NO_3
Unit:	mg/L N
Sigma:	0,25

Responsible for tests: DHBP/S7MS

Homogeneity test Date: 2022-11-01

Sample	x(a)	x(b)	average	sd	sd^2
1	4,5	4,55	4,5	0,007	0,000
11	4,6	4,62	4,6	0,014	0,000
22	4,6	4,56	4,6	0,007	0,000
26	4,7	4,59	4,6	0,057	0,003
33	4,6	4,64	4,6	0,000	0,000
40	4,7	4,65	4,7	0,000	0,000
49	4,6	4,61	4,6	0,007	0,000
52	4,6	4,59	4,6	0,014	0,000
62	4,6	4,64	4,6	0,007	0,000
67	4,6	4,58	4,6	0,014	0,000
74	4,6	4,59	4,6	0,007	0,000
85	4,6	4,62	4,6	0,028	0,001

For homogeneity

General average (x)	4,6
Sample average sd (s_x)	0,033
Within-sample sd (s_w):	0,020
Between-samples sd (ss):	0,030
S_L in the Proficiency Test:	0,134
S_R in the Proficiency Test:	0,139

Stability test Date: 2022-11-17

Sample	x(a)	x(b)
15	4,53	4,53
45	4,55	4,53
81	4,57	4,54

For stability

General average (y):	4,541667
/x-y/ =	0,062083

Conclusions

ss =	0,03	0.3*sigma= 0,07
/x-y/ =	0,062083	
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:	0,072

Responsible for tests: DHBP/S7MS

Homogeneity test Date: 2022-11-01

Sample	x(a)	x(b)	average	sd	sd^2
4	7,54	7,55	7,55	0,007	0,000
14	7,51	7,55	7,53	0,028	0,00
17	7,52	7,56	7,54	0,028	0,001
29	7,51	7,54	7,53	0,021	0,000
32	7,51	7,56	7,54	0,035	0,001
42	7,55	7,53	7,54	0,014	0,000
47	7,52	7,54	7,53	0,014	0,000
57	7,54	7,54	7,54	0,000	0,000
61	7,53	7,54	7,54	0,007	0,000
68	7,52	7,54	7,53	0,014	0,000
77	7,55	7,53	7,54	0,014	0,000
85	7,54	7,51	7,53	0,021	0,000

For homogeneity

General average (x)	7,53
Sample average sd (s_x)	0,007
Within-sample sd (s_w):	0,020
Between-samples sd (ss):	0
S_L in the Proficiency Test:	0,199
S_R in the Proficiency Test:	0,214

Stability test Date: 2022-11-17

Sample	x(a)	x(b)
12	7,62	7,59
45	7,62	7,59
78	7,61	7,6

For stability

General average (y):	7,605
/x-y/ =	0,070417

Conclusions

ss =	0	0.3*sigma= 0,02
/x-y/ =	0,070417	
Analytical quality	Is s_w < 0,15*sigma	**NO**
Homogeneity:	Is ss < 0.3*sigma?	**YES**
Stability:	/x-y/ < 0.3*sigma?	**NO**