



Proficiency test SPIL-4 (2025)

Nitrogen parameters in wastewater (effluent)

Proficiency test SPIL-4 (2025) Quality Documentation

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1 INTRODUCTION

A proficiency test on the analysis of nitrogen parameters in wastewater was conducted on 13 November 2025. 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 December 2025.

2 FEATURES OF THE PROFICIENCY TEST

Participants in the proficiency test were a total of 38 laboratories from Denmark, Norway, Spain and Sweden.

The closing date for submission of results was 28 November 2025. All participants except laboratory no. 2 and 11 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 A.

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/, ISO 13528:2022 /3/ and as described in detail in Spliid (1992) /4/. 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 /5/.

The statistical model used assumes 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.

It is assumed that the samples have been stored as prescribed and that the analyses have been initiated on the correct date.

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. Assigned values, spike values and uncertainty of the assigned values were calculated in accordance with ISO 13528:2022 /3/. The Uncertainty of the assigned values are the expanded uncertainty with coverage factor, $k = 2$.

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	4.4	0.12	0.8
Ammonium	NH ₄	mg/L N	0.1 – 2	0.435	0.0088	0,153
Nitrite+nitrate	NO ₂₊₃	mg/L N	1 – 5	3.0	0.10	0.5
Nitrate	NO ₃	mg/L N	1 – 5	3.11	0.068	0.5
Conductivity	γ ₂₅	mS/m	50 – 300	37.0	0.20	0.5
pH			6 – 9	7.55	0.050	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 where the spike value is the difference between median values for the two samples in the sample pair.

Assigned values for TN, NH₄, NO₂₊₃, NO₃, 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 B. The test showed no significant difference between the two for TN, NH₄, NO₂₊₃, NO₃ and conductivity.

The test revealed a significant difference between the two for pH. However, the difference is numerically small and has insignificant influence on the general quality of analyses estimated from the data as well as on the evaluation of accuracy of participating laboratories.

2.3.3 Test of assigned values

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

3 **HOMOGENEITY AND STABILITY OF SAMPLES**

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

TN	Combined homogeneity and stability test
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 E. 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 $0.3 \cdot \hat{\sigma}$ the standard deviation for evaluation of participants' performance ($0.3 \cdot \hat{\sigma}$) specified by the Danish EPA /6/ whereas the stability is evaluated by comparing the concentration change of the samples to $0.3 \cdot \hat{\sigma}$ or $0.3 \cdot \hat{\sigma} + 2 \sqrt{u_x^2 + u_y^2}$ where the precision of the measurement method contribute to the inability to meet the criterion. This test ensures that heterogeneity and instability will not have negative influence on the evaluation of participant performance /3/.

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 sample pairs for NH₄, NO₃ and pH are stable and homogeneous.

The test for stability and homogeneity for TN shows that the samples are stable but indicates that they are not homogeneous. This trend is also seen in the participants results.

Therefore, it is concluded that the found indication of inhomogeneity gives reason to make reservations on the evaluation of the participants performance for TN.

4 CONCLUSION

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

For pH the participants could not recover the spike value. 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.

Homogeneity test for TN indicates inhomogeneity. Eurofins Environment Testing Denmark's scrutiny of the combined evidence gave the conclusion that the found indication of inhomogeneity gives reason to make reservations on the evaluation of the participants performance for TN.

5 REFERENCES

- /1/ Eurofins A/S, *Proficiency test SPIL-4 (2025)*, Report to participants, December 2025.
- /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/ ISO 13528, *Statistical methods for use in proficiency testing by interlaboratory comparison*, 2022.
- /4/ Spliid, H., *Procedure and analysis of data for proficiency tests and environmental analyses*, Report to Danish Environmental Protection Agency, 1994 (in Danish).
- /5/ Eurofins A/S, *Schedule for a proficiency test*, document may be downloaded from www.eurofins.dk/proficiencytest.
- /6/ Ministry of Environment and Gender Equality's regulation no. 1275 on *quality criteria for environmental measurements*, 31/10/2025 (in Danish).

A N N E X E S

APPENDIX A SAMPLE PREPARATION

Stock solution	Prepared from	Concentration
Stock TN	3.0041 g Disodium edetate, 2H ₂ O milli-Q water up to 1000.0 g	TN: 226.1 mg/kg N
Stock NH ₄	0.9986 g Ammonium chloride (NH ₄ Cl) milli-Q water up to 1000.0 g	NH ₄ : 261.6 mg/kg N
Stock NO ₃	2.5015 g Potassium nitrate (KNO ₃) milli-Q water up to 1000.0 g	NO ₃ : 346.6 mg/kg N

Sample	Sample prepared from	TN mg/L N	NH ₄ mg/L N	NO ₃ mg/L N
A1	19.99 g stock TN 20.00 g stock NH ₄ 50.00 g stock NO ₃ Sample B1 up to 34.0 kg	0.997 · (a+2.506) +1.404	0.997 · (b+.0.374) +0.154	0.997 · (c+1.486) +0.510
B1	200.01 g stock TN 100.09 g stock NH ₄ 300.01 g stock NO ₃ filtered water from Holsted sewage treatment plant up to 70.0 kg	a+2.506	b+0.374	c+1.486

Sample	Sample prepared from	pH
A2/B2	Filtered water from Holsted sewage treatment plant	d

APPENDIX B CONTROL OF SPIKE VALUES

TOTAL NITROGEN (TN), mg/L N

Control of differences within sample pairs

Laboratory	Sample pair AB	Outlier
1	0.29	
3	-0.05	
4	-0.11	
5	-0.09	
7	0.08	
8	0.08	
9	-0.19	
10	-0.11	
12	-0.08	
14	0.07	
15	-0.18	
16	-0.13	
17	0.04	
18	-0.52	C
19	0.01	
20	0.03	
21	-0.16	

Laboratory	Sample pair AB	Outlier
22	0.22	
23	-0.01	
24	-0.12	
26	0.14	
27	0.06	
29	-0.02	
30	0.01	
31	-0.15	
32	0.08	
33	-0.17	
34	-0.14	
35	-0.16	
36	-0.10	
37	0.03	
38	-0.13	
39	-0.05	

Statistical data – Control of spike value		
No of labs	32	<p style="text-align: center;">Notes</p> <p>No test statistics were found to be significant</p> <p>* denotes that there is a significant difference (t-test, 5 %-level)</p> <p>** denotes that there is a significant difference (t-test, 1 %-level)</p> <p>*** denotes that there is a significant difference (t-test, 0.1%-level)</p> <p>U denote a manual selected outlier</p> <p>C denotes a Cochran outlier</p> <p>G denotes a Grubbs outlier</p>
No of repl	2	
d	-0.0313	
s ²	0.0144	
s	0.1200	
t	-1.4770	
Sign. level 99.9%	3.6335	
Sign. level 99%	2.7440	
Sign. level 95%	2.0395	

AMMONIUM-N (NH₄-N), mg/L N

Control of differences within sample pairs

Laboratory	Sample pair AB	Outlier
4	0.0060	
8	-0.0030	
9	-0.0030	
10	0.0070	
12	-0.0130	
14	0.0030	
15	-0.0380	
17	0.0015	
18	-0.0290	
19	0.0020	
20	0.0190	
21	-0.0120	
22	-0.0030	
23	-0.0070	
24	-0.0030	

Laboratory	Sample pair AB	Outlier
25	0.0115	G
26	-0.0000	
27	0.0010	
28	-0.0110	
29	-0.0000	
30	-0.0040	
31	-0.0330	
32	-0.0110	
33	-0.0040	
34	0.0290	
36	-0.0080	
37	-0.0020	
38	0.0120	
39	0.0070	

Statistical data – Control of spike value		
No of labs	28	<p style="text-align: center;">Notes</p> <p>No test statistics were found to be significant * 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)</p> <p style="text-align: center;">U denote a manual selected outlier C denotes a Cochran outlier G denotes a Grubbs outlier</p>
No of repl	2	
d	-0.0034	
s ²	0.0002	
s	0.0140	
t	-1.3044	
Sign. level 99.9%	3.6896	
Sign. level 99%	2.7707	
Sign. level 95%	2.0518	

NITRITE+NITRATE-N (NO₂+NO₃-N), mg/L N

Control of differences within sample pairs

Laboratory	Sample pair AB	Outlier
10	-0.10	
12	-0.06	
16	0.18	
22	0.11	
25	0.08	
34	-0.05	

Statistical data – Control of spike value		
No of labs	6	Notes
No of repl	2	<p>No test statistics were found to be significant * 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)</p> <p>U denote a manual selected outlier C denotes a Cochran outlier G denotes a Grubbs outlier</p>
d	0.0273	
s ²	0.0125	
s	0.1119	
t	0.5981	
Sign. level 99.9%	6.8688	
Sign. level 99%	4.0321	
Sign. level 95%	2.5706	

NITRATE-N (NO₃-N), mg/L N

Control of differences within sample pairs

Laboratory	Sample pair AB	Outlier
8	0.090	
9	-0.016	
10	0.090	
12	-0.060	
15	0.070	
17	-0.005	
18	-0.090	
19	0.060	
20	0.000	
22	0.110	

Laboratory	Sample pair AB	Outlier
23	0.030	
26	-0.020	
27	-0.110	
29	-0.020	
30	0.010	
31	0.020	
32	0.030	
36	0.050	
38	0.040	

Statistical data – Control of spike value		
No of labs	19	<p style="text-align: center;">Notes</p> <p>No test statistics were found to be significant</p> <p>* denotes that there is a significant difference (t-test, 5 %-level)</p> <p>** denotes that there is a significant difference (t-test, 1 %-level)</p> <p>*** denotes that there is a significant difference (t-test, 0.1%-level)</p> <p>U denote a manual selected outlier</p> <p>C denotes a Cochran outlier</p> <p>G denotes a Grubbs outlier</p>
No of repl	2	
d	0.0147	
s ²	0.0036	
s	0.0596	
t	1.0718	
Sign. level 99.9%	3.9216	
Sign. level 99%	2.8784	
Sign. level 95%	2.1009	

CONDUCTIVITY, mS/m

Control of differences within sample pairs

Laboratory	Sample pair AB	Outlier
5	0.10	
7	0.30	
8	0.10	
9	-0.10	
10	-	U
13	0.00	
15	-0.40	
16	-0.10	
17	0.90	

Laboratory	Sample pair AB	Outlier
19	0.10	
20	0.00	
22	-	U
23	-0.10	
26	-1.10	
29	0.03	
34	0.10	
37	0.20	

Statistical data – Control of spike value		
No of labs	15	<p style="text-align: center;">Notes</p> <p>No test statistics were found to be significant</p> <p>* denotes that there is a significant difference (t-test, 5 %-level)</p> <p>** denotes that there is a significant difference (t-test, 1 %-level)</p> <p>*** denotes that there is a significant difference (t-test, 0.1%-level)</p> <p>U denote a manual selected outlier</p> <p>C denotes a Cochran outlier</p> <p>G denotes a Grubbs outlier</p>
No of repl	2	
d	0.0020	
s ²	0.1701	
s	0.4124	
t	0.0188	
Sign. level 99.9%	4.1405	
Sign. level 99%	2.9768	
Sign. level 95%	2.1448	

pH

Control of differences within sample pairs

Laboratory	Sample pair AB	Outlier
1	-0.210	
5	0.030	
7	0.100	
8	-0.370	
9	-0.010	
10	-0.100	
12	-0.020	
13	-0.050	
14	-0.014	
15	-0.073	
16	0.000	
17	-0.070	
18	-0.030	
19	-0.020	
20	-0.146	G
21	-0.040	

Laboratory	Sample pair AB	Outlier
22	0.068	
23	-0.020	
24	0.800	C
25	-0.110	
26	-0.100	
27	0.010	
29	0.020	
30	0.980	C
31	-0.050	
32	-0.070	
33	0.080	
34	-0.060	
36	-0.151	
37	-0.250	
38	0.420	G
39	0.010	

Statistical data – Control of spike value			
No of labs	28	<p align="center">Notes</p> <p align="center">No test statistics were found to be significant</p> <p>* denotes that there is a significant difference (t-test, 5 %-level)</p> <p>** denotes that there is a significant difference (t-test, 1 %-level)</p> <p>*** denotes that there is a significant difference (t-test, 0.1%-level)</p> <p align="center">U denote a manual selected outlier C denotes a Cochran outlier G denotes a Grubbs outlier</p>	
No of repl	2		
d	-0.0536		
s ²	0.0099		
s	0.0997		
t	-2.8437		**
Sign. level 99.9%	3.6896		
Sign. level 99%	2.7707		
Sign. level 95%	2.0518		

APPENDIX C CONTROL OF RECOVERY

TOTAL NITROGEN (TN), mg/L N

Control of recovery, average of results

Laboratory	Sample pair AB	Outlier
1	4.03	
3	4.21	
4	4.16	
5	4.22	
7	4.62	
8	4.58	
9	3.40	
10	3.87	
12	4.32	
14	4.45	
15	3.18	
16	4.90	
17	4.82	
18	3.93	C
19	4.52	
20	4.40	
21	3.69	

Laboratory	Sample pair AB	Outlier
22	5.88	
23	4.78	
24	3.89	
26	4.49	
27	4.86	
29	4.52	
30	4.69	
31	4.21	
32	4.40	
33	3.79	
34	4.36	
35	3.74	
36	4.21	
37	4.51	
38	4.64	
39	4.57	

Statistical data – Control of recovery		
No of labs	32	<p style="text-align: center;">Notes</p> <p>No test statistics were found to be significant</p> <p>* denotes that there is a significant difference (t-test, 5 %-level)</p> <p>** denotes that there is a significant difference (t-test, 1 %-level)</p> <p>*** denotes that there is a significant difference (t-test, 0.1%-level)</p> <p>U denote a manual selected outlier</p> <p>C denotes a Cochran outlier</p> <p>G denotes a Grubbs outlier</p>
No of repl	2	
m	4.3388	
s ²	0.2533	
s	0.5033	
Assigned value	4.4	
Recovery	98.6	
t	-0.6875	
Sign. level 99.9%	3.6335	
Sign. level 99%	2.7440	
Sign. level 95%	2.0395	

AMMONIUM-N (NH₄-N), mg/L N

Control of recovery, average of results

Laboratory	Sample pair AB	Outlier
4	0.4310	
8	0.4485	
9	0.4855	
10	0.4035	
12	0.4735	
14	0.4375	
15	0.3330	
17	0.4468	
18	0.4045	
19	0.4790	
20	0.5395	
21	0.4070	
22	0.4375	
23	0.4165	
24	0.4305	

Laboratory	Sample pair AB	Outlier
25	0.6429	G
26	0.4360	
27	0.4395	
28	0.4415	
29	0.4250	
30	0.4360	
31	0.3735	
32	0.3865	
33	0.4350	
34	0.4035	
36	0.4040	
37	0.4310	
38	0.4310	
39	0.4635	

Statistical data – Control of recovery		
No of labs	28	<p align="center">Notes</p> <p align="center">No test statistics were found to be significant</p> <p>* denotes that there is a significant difference (t-test, 5 %-level)</p> <p>** denotes that there is a significant difference (t-test, 1 %-level)</p> <p>*** denotes that there is a significant difference (t-test, 0.1%-level)</p> <p align="center">U denote a manual selected outlier</p> <p align="center">C denotes a Cochran outlier</p> <p align="center">G denotes a Grubbs outlier</p>
No of repl	2	
m	0.4314	
s ²	0.0015	
s	0.0382	
Assigned value	0.435	
Recovery	99.2	
t	-0.4956	
Sign. level 99.9%	3.6896	
Sign. level 99%	2.7707	
Sign. level 95%	2.0518	

NITRITE+NITRATE-N (NO₂+NO₃-N), mg/L N

Control of recovery, average of results

Laboratory	Sample pair AB	Outlier
10	2.95	
12	2.93	
16	2.92	
22	3.14	
25	3.22	
34	3.02	

Statistical data – Control of recovery		
No of labs	6	Notes
No of repl	2	<p>No test statistics were found to be significant * 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)</p> <p>U denote a manual selected outlier C denotes a Cochran outlier G denotes a Grubbs outlier</p>
m	3.0291	
s ²	0.0155	
s	0.1246	
Assigned value	3.0	
Recovery	101.0	
t	0.5719	
Sign. level 99.9%	6.8688	
Sign. level 99%	4.0321	
Sign. level 95%	2.5706	

NITRATE-N (NO₃-N), mg/L N

Control of recovery, average of results

Laboratory	Sample pair AB	Outlier
8	3.245	
9	3.085	
10	2.685	
12	2.930	
15	2.865	
17	3.198	
18	3.055	
19	3.240	
20	3.100	
22	3.133	

Laboratory	Sample pair AB	Outlier
23	3.115	
26	3.230	
27	3.165	
29	3.200	
30	3.175	
31	3.260	
32	2.985	
36	3.065	
38	3.280	

Statistical data – Control of recovery		
No of labs	19	<p align="center">Notes</p> <p align="center">No test statistics were found to be significant</p> <p>* denotes that there is a significant difference (t-test, 5 %-level)</p> <p>** denotes that there is a significant difference (t-test, 1 %-level)</p> <p>*** denotes that there is a significant difference (t-test, 0.1%-level)</p> <p align="center">U denote a manual selected outlier</p> <p align="center">C denotes a Cochran outlier</p> <p align="center">G denotes a Grubbs outlier</p>
No of repl	2	
m	3.1058	
s ²	0.0233	
s	0.1525	
Assigned value	3.11	
Recovery	99.9	
t	-0.1194	
Sign. level 99.9%	3.9216	
Sign. level 99%	2.8784	
Sign. level 95%	2.1009	

CONDUCTIVITY, mS/m

Control of recovery, average of results

Laboratory	Sample pair AB	Outlier
5	36.95	
7	37.90	
8	36.93	
9	35.25	
10	-	U
13	37.20	
15	37.30	
16	37.25	
17	35.85	

Laboratory	Sample pair AB	Outlier
19	36.65	
20	37.30	
22	-	U
23	36.55	
26	36.75	
29	37.16	
34	37.05	
37	36.80	

Statistical data – Control of recovery		
No of labs	15	<p>Notes</p> <p>No test statistics were found to be significant * 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)</p> <p>U denote a manual selected outlier C denotes a Cochran outlier G denotes a Grubbs outlier</p>
No of repl	2	
m	36.8590	
s ²	0.4029	
s	0.6348	
Assigned value	37	
Recovery	99.6	
t	-0.8603	
Sign. level 99.9%	4.1405	
Sign. level 99%	2.9768	
Sign. level 95%	2.1448	

pH

Control of recovery, average of results

Laboratory	Sample pair AB	Outlier
1	7.875	
5	7.515	
7	7.650	
8	7.105	
9	7.425	
10	7.650	
12	7.600	
13	7.405	
14	7.500	
15	7.699	
16	7.700	
17	7.455	
18	7.385	
19	7.580	
20	6.754	G
21	7.560	

Laboratory	Sample pair AB	Outlier
22	7.557	
23	7.590	
24	8.400	C
25	7.535	
26	7.650	
27	7.605	
29	7.570	
30	6.310	C
31	7.525	
32	7.415	
33	7.670	
34	7.590	
36	7.441	
37	7.355	
38	6.230	G
39	7.495	

Statistical data – Control of recovery		
No of labs	28	<p align="center">Notes</p> <p align="center">No test statistics were found to be significant</p> <p>* denotes that there is a significant difference (t-test, 5 %-level)</p> <p>** denotes that there is a significant difference (t-test, 1 %-level)</p> <p>*** denotes that there is a significant difference (t-test, 0.1%-level)</p> <p align="center">U denote a manual selected outlier</p> <p align="center">C denotes a Cochran outlier</p> <p align="center">G denotes a Grubbs outlier</p>
No of repl	2	
m	7.5393	
s ²	0.0203	
s	0.1425	
Assigned value	7.55	
Recovery	99.9	
t	-0.3965	
Sign. level 99.9%	3.6896	
Sign. level 99%	2.7707	
Sign. level 95%	2.0518	

APPENDIX D CONCENTRATION LEVEL

Parameter	Unit	Sample	Bottle no.	I	II	Bottle Average	Sample Average	Assigned value	Spike	
									Measured	Assigned
Total nitrogen	mg/L N	A1	9	5,62	5,61	5,62	5,66	5,2	0,93	0,8
			39	5,79	5,82	5,81				
			52	5,57	5,56	5,57				
		B1	16	4,60	4,62	4,61	4,73	4,4		
			31	4,78	4,79	4,79				
			52	4,79	4,79	4,79				
Ammonium	mg/L N	A1	9	0,59	0,593	0,59	0,590	0,588	0,15	0,153
			39	0,59	0,592	0,59				
			52	0,587	0,589	0,59				
		B1	16	0,437	0,439	0,44	0,438	0,435		
			31	0,439	0,439	0,44				
			52	0,435	0,436	0,44				
Nitrate	mg/L N	A1	9	3,81	3,82	3,82	3,79	3,61	0,54	0,5
			39	3,76	3,77	3,77				
			52	3,79	3,81	3,80				
		B1	16	3,23	3,24	3,24	3,25	3,11		
			31	3,26	3,27	3,27				
			52	3,25	3,26	3,26				
pH		A2	5	7,62	7,62	7,62	7,63	7,55	0,01	0
			24	7,63	7,63	7,63				
			53	7,62	7,63	7,63				
		B2	10	7,65	7,63	7,64	7,64	7,55		
			26	7,64	7,63	7,64				
			62	7,63	7,63	7,63				

APPENDIX E HOMOGENEITY AND STABILITY

PT: SPIL-4
 Parameter: TN
 Unit: mg/L
 Sigma: 0,3

Responsible for tests: O6HJ/DHBP
 Approval of controltest HT5M

Homogeneity test Date: 2025-10-28

Sample	x(a)	x(b)	aver- age	sd	sd^2
2	5,290	5,303	5,3	0,009	0,000
7	5,230	5,240	5,2	0,007	0,00
13	5,320	5,320	5,3	0,000	0,000
18	5,310	5,330	5,3	0,014	0,000
23	5,640	5,660	5,7	0,014	0,000
28	5,340	5,320	5,3	0,014	0,000
32	5,810	5,790	5,8	0,014	0,000
37	5,270	5,350	5,3	0,057	0,003
42	5,340	5,350	5,3	0,007	0,000
46	5,460	5,470	5,5	0,007	0,000
55	5,330	5,340	5,3	0,007	0,000
60	5,340	5,310	5,3	0,021	0,000

For homogeneity

General average (x) 5,39
 Sample average sd (s_x) 0,166
 Within-sample sd (s_w): 0,020
 Between-samples sd (ss): 0,1654
 S_L in the Proficiency Test: 0,500
 S_R in the Proficiency Test: 0,507

Stability test Date: 2025-11-13

Sample	x(a)	x(b)
9	5,62	5,61
39	5,79	5,82
52	5,57	5,56

For stability

General average (y): 5,661667
 /x-y/ = 0,267375

Conclusions

$|x-y| = 0,267$ $ss = 0,165$

 $0.3 \cdot \sigma = 0,087$
 $0.3\sigma_{pt} + 2\sqrt{u^2(x) + u^2(y)} = 1,339$

Analytical quality Is s_w < 0,15*sigma
YES

Homogeneity: Is ss < 0.3*sigma?
NO

Stability: /x-y/ < 0.3*sigma?
NO

$|x - y| \leq 0,3\sigma_{pt} + 2\sqrt{u^2(x) + u^2(y)}$?

Stability*: **YES**

PT: SPIL-4
 Parameter: NH4
 Unit: mg/L
 Sigma: 0,036

Responsible for tests: O6HJ/DHBP

Approval of controltest HT5M

Homogeneity test Date: 2025-10-28

Sample	x(a)	x(b)	average	sd	sd^2
2	0,607	0,608	0,6	0,001	0,000
7	0,599	0,601	0,6	0,001	0,00
13	0,592	0,594	0,6	0,001	0,000
18	0,596	0,598	0,6	0,001	0,000
23	0,595	0,596	0,6	0,001	0,000
28	0,598	0,599	0,6	0,001	0,000
32	0,601	0,601	0,6	0,000	0,000
37	0,598	0,599	0,6	0,001	0,000
42	0,596	0,597	0,6	0,001	0,000
46	0,594	0,595	0,6	0,001	0,000
55	0,597	0,598	0,6	0,001	0,000
60	0,591	0,590	0,6	0,001	0,000

For homogeneity

General average (x) 0,60
 Sample average sd (s_x) 0,004
 Within-sample sd (s_w): 0,001
 Between-samples sd (ss): 0,0043
 S_L in the Proficiency Test: 0,038
 S_R in the Proficiency Test: 0,039

Stability test Date: 2025-11-13

Sample	x(a)	x(b)
9	0,59	0,593
39	0,59	0,592
52	0,587	0,589

For stability

General average (y): 0,590167
 /x-y/ = 0,007333

Conclusions

ss = 0,004 0.3*sigma= 0,011	
/x-y/ = 0,007333	
Analytical quality	Is s _w < 0,15*sigma YES
Homogeneity:	Is ss < 0.3*sigma? YES
Stability:	/x-y/ < 0.3*sigma? YES

PT: SPIL-4
 Parameter: NO3
 Unit: mg/L
 Sigma: 0,2

Responsible for tests: L5VX
 Approval of controltest HT5M

Homogeneity test Date: 2025-10-28

Sample	x(a)	x(b)	average	sd	sd^2
2	3,7	3,77	3,8	0,021	0,000
7	3,8	3,77	3,8	0,014	0,000
13	3,8	3,79	3,8	0,014	0,000
18	3,8	3,79	3,8	0,021	0,000
23	3,7	3,75	3,7	0,014	0,000
28	3,7	3,73	3,7	0,014	0,000
32	3,8	3,8	3,8	0,007	0,000
37	3,7	3,74	3,7	0,000	0,000
42	3,7	3,75	3,7	0,007	0,000
46	3,8	3,82	3,8	0,007	0,000
55	3,7	3,72	3,7	0,014	0,000
60	3,7	3,75	3,7	0,007	0,000

For homogeneity

General average (x) 3,8
 Sample average sd (s_x) 0,030
 Within-sample sd (s_w): 0,013
 Between-samples sd (ss): 0,029
 S_L in the Proficiency Test: 0,150
 S_R in the Proficiency Test: 0,155

Stability test Date: 2025-11-13

Sample	x(a)	x(b)
9	3,81	3,82
39	3,76	3,77
52	3,79	3,81

For stability

General average (y): 3,793333
 /x-y/ = 0,036667

Conclusions

ss = 0,03 0.3*sigma= 0,06
 /x-y/ = 0,036667

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: 0,04

Responsible for tests: S7MS
 Approval of controltest HT5M

Homogeneity test Date: 2025-10-28

Sample	x(a)	x(b)	average	sd	sd^2
2	7,63	7,64	7,6	0,007	0,000
7	7,63	7,64	7,6	0,007	0,00
12	7,61	7,62	7,6	0,007	0,000
16	7,63	7,63	7,6	0,000	0,000
22	7,63	7,64	7,6	0,007	0,000
28	7,63	7,64	7,6	0,007	0,000
31	7,63	7,63	7,6	0,000	0,000
39	7,65	7,65	7,7	0,000	0,000
43	7,65	7,64	7,6	0,007	0,000
52	7,64	7,64	7,6	0,000	0,000
63	7,64	7,64	7,6	0,000	0,000
65	7,65	7,63	7,6	0,014	0,000

For homogeneity

General average (x) 7,64
 Sample average sd (s_x) 0,009
 Within-sample sd (s_w): 0,006
 Between-samples sd (ss): 0,0075
 S_L in the Proficiency Test: 0,131
 S_R in the Proficiency Test: 0,153

Stability test Date: 2025-11-13

Sample	x(a)	x(b)
10	7,65	7,63
26	7,64	7,63
62	7,63	7,63

For stability

General average (y): 7,635
 /x-y/ = 0,000833

Conclusions

ss = 0,007 0.3*sigma= 0,01	
/x-y/ = 0,000833	
Analytical quality	Is s _w < 0,15*sigma NO
Homogeneity:	Is ss < 0.3*sigma? YES
Stability:	/x-y/ < 0.3*sigma? YES