



Proficiency test SPIL-4 (2023)

Nitrogen parameters in wastewater (effluent)



Proficiency test SPIL-4 (2023) Quality Documentation

January 2024

Eurofins Miljø A/S
Smedeskovvej 38
DK-8464 Galten
Denmark

Tel: +45 7022 4266
e-mail: proficiency@eurofins.com
Web: www.eurofins.dk

Client	Client's representative
Environmental laboratories	

Project	Project No
Proficiency test SPIL-4 (2023)	20405-34

Authors	Date
	2024-01-30
Peter Rerup	Approved by
	Rikke Mikkelsen

	Quality Documentation Report	DPRE	FYE3	2024-01-29
--	------------------------------	------	------	------------

Revision	Description	By	Approved	Date
----------	-------------	----	----------	------

Key words	Classification
Analytical quality, assigned value, precision, trueness, homogeneity, stability, total nitrogen, ammonium, nitrite+nitrate, conductivity, pH, wastewater	☒ Open
	☐ Internal
	☐ Proprietary

Distribution	
Available online:	www.eurofins.dk
Eurofins:	Peter Rerup, Rikke Mikkelsen

CONTENTS

1	INTRODUCTION.....	1
2	FEATURES OF THE PROFICIENCY TEST	2
2.1	Sample preparation.....	2
2.2	Statistical analysis of participants' data	2
2.3	Assigned and spike value.....	2
2.3.1	Assigned and spike values.....	3
2.3.2	Test of spike values	3
2.3.3	Test of assigned values.....	3
3	HOMOGENEITY AND STABILITY OF SAMPLES.....	4
4	CONCLUSION	5
5	REFERENCES	6
ANNEX A	SAMPLE PREPARATION	8
ANNEX B	CONTROL OF SPIKE VALUES	9
ANNEX C	CONTROL OF RECOVERY.....	15
ANNEX D	CONCENTRATION LEVEL.....	21
ANNEX E	HOMOGENEITY AND STABILITY	22

1 INTRODUCTION

A proficiency test on the analysis of nitrogen parameters in wastewater was conducted on 16 November 2023. 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 19 December 2023.

2 FEATURES OF THE PROFICIENCY TEST

Participants in the proficiency test were a total of 47 laboratories from Brazil, Denmark, Lithuania, Norway and Sweden.

The closing date for submission of results was 1 December 2023. All participants except laboratory no. 30 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 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 untreated sewage. 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	5.7	0.20	1
Ammonium	NH ₄	mg/L N	0.1-2	1.17	0.021	0.23
Nitrite+nitrate	NO ₂₊₃	mg/L N	1-5	2.9	0.11	0.5
Nitrate	NO ₃	mg/L N	1-5	3.02	0.065	0.5
Conductivity	γ_{25}	mS/m	50 – 300	132	1.2	1
pH	pH	-	6 – 9	7.64	0.043	1

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 (methods prescribed by the Danish EPA). A list of method identification numbers is found in the report to participants /1/. Assigned values for NH_4 , NO_{2+3} , NO_3 , γ_{25} and pH are consensus values for all laboratories based on the median. The assigned value for NO_3 (3.02 mg/L N) is higher than the assigned value for NO_{2+3} (2.9 mg/L N). This is due to differences in results obtained from different methods.

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.

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 for most parameters showed no significant difference between the two and the control of assigned value at Eurofins confirmed the value (Appendix D).

The test revealed a significant difference between the two for TN. Average recover was 95.9 %. 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. other than 1, 2 and 3 and now showed no significant difference. Furthermore, the results of control measurements at Eurofins confirmed the assigned value (Appendix E). The assigned value is therefore kept unchanged.

3 **HOMOGENEITY AND STABILITY OF SAMPLES**

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

NH ₄	Homogeneity test
NO ₃	Homogeneity test
TN	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 $0.3 \cdot \hat{\sigma}$ specified by the Danish EPA /5/, whereas the stability is evaluated by comparing the concentration change of the samples to $0.3 \cdot \hat{\sigma}$. This test ensures that heterogeneity and instability will not have negative influence on the evaluation of participant performance /6/.

The appendix also shows the standard deviation within and between laboratories from the proficiency test to allow comparison between tests performed and average quality from participating laboratories.

The tests for stability and homogeneity show that the samples are stable and homogeneous.

4 CONCLUSION

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

5 REFERENCES

- /1/ Eurofins A/S, *Proficiency test SPIL-4 (2023)*, Report to participants, December 2023.
- /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. 529 on *quality criteria for environmental measurements*, 14 May 2023 (in Danish).
- /6/ ISO 13528, *Statistical methods for use in proficiency testing by interlaboratory comparison*, 2022.

A N N E X E S

ANNEX A *SAMPLE PREPARATION*

Stock solution	Prepared from	Concentration
Stock TN	3.000 g Disodium edetate, 2H ₂ O milli-Q water up to 1000.1 g	TN: 226 mg/kg N
Stock NH ₄	1.000 g Ammonium chloride (NH ₄ Cl) milli-Q water up to 1000.0 g	NH ₄ : 262 mg/kg N
Stock NO ₃	2.500 g Potassium nitrate (KNO ₃) milli-Q water up to 1000.0 g	NO ₃ : 346 mg/kg N

Sample	Sample prepared from	TN mg/kg N	NH ₄ mg/kg N	NO ₃ mg/kg N	Conductivity mS/m
A1	250.0 g stock TN 250.0 g stock NH ₄ 300.0 g stock NO ₃ Filtered effluent from Brørup sewage treatment plant up to 65.00 kg	a+3.475	b+1.007	c+1.599	d
B1	40.0 g stock TN 30.0 g stock NH ₄ 50.0 g stock NO ₃ Sample A1 up to 34.00 kg	0.996· (a+3.475) +1.006	0.996· (b+1.007) +0.231	0.996· (c+1.599) +0.509	e

Sample	Sample prepared from	pH
A2/B2	Filtered effluent from Brørup sewage treatment plant.	f

ANNEX B CONTROL OF SPIKE VALUES

Total Nitrogen, mg/L N

Control of differences within sample pairs

Laboratory	Difference AB	Outlier
3	-0.08	
4	0.51	
5	-0.18	UG
6	0.19	
7	0.07	
9	0.04	
10	0.31	
11	-0.25	
3	0.18	
4	1.10	
5	-0.31	
6	0.00	
7	0.32	
9	0.06	
10	-0.09	
11	0.29	
12	-0.57	
13	-0.08	
14	0.36	
15	0.39	
16	0.07	
17	1.39	UC
18	-0.08	
19	-0.01	
20	0.14	
21	0.00	
23	0.01	
25	-0.22	
26	-0.05	
27	-1.02	
28	-0.02	
31	0.04	
32	0.20	
34	0.10	
35	0.11	
36	0.31	
37	0.32	
38	0.12	
39	0.20	
40	-0.08	

Laboratory	Difference AB	Outlier
41	0.51	UG
42	-0.18	
43	0.19	
44	0.07	
45	0.04	
46	0.31	
47	-0.25	

No of labs	37
No of repl	2
d	0.072
s ²	0.107
s	0.328
t	1.333
Sign. level 99.9 %	3.582
Sign. level 99 %	2.719
Sign. level 95 %	2.028

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

Ammonium-N, mg/L N

Control of differences within sample pairs

Laboratory	Difference AB	Outlier
3	0.01	
5	-0.03	
6	-0.03	
7	-0.01	
8	-0.01	
9	-0.04	
10	-0.02	
11	0.02	
14	-0.03	
15	0.00	
16	-0.01	
17	0.00	
18	-0.02	
19	0.00	
20	-0.02	
21	-0.02	
23	-0.01	
24	-0.01	
25	0.00	
26	0.01	
28	0.00	
29	0.04	
31	-0.07	
32	0.02	
34	-0.03	
36	0.03	
37	0.00	
38	-0.02	
40	-0.03	
41	0.03	
42	-0.02	
43	0.00	
44	0.04	
46	-0.02	
47	-0.01	

No of labs	35
No of repl	2
d	-0.007
s ²	0.001
s	0.023
t	-1.838
Sign. level 99.9 %	3.601
Sign. level 99 %	2.728
Sign. level 95 %	2.032

No test statistics were found to be significant

Nitrite-nitrate-N, mg/L N

Control of differences within sample pairs

Laboratory	Difference AB	Outlier
6	0.06	
8	0.06	
11	0.07	
18	-0.07	
20	-0.01	
28	0.01	
29	-0.14	
34	0.10	
41	0.09	

No of labs	9
No of repl	2
d	0.019
s ²	0.006
s	0.080
t	0.713
Sign. level 99.9 %	5.041
Sign. level 99 %	3.355
Sign. level 95 %	2.306

No test statistics were found to be significant

Nitrate-N, mg/L N

Control of differences within sample pairs

Laboratory	Difference AB	Outlier
1	-0.01	
3	0.00	
5	-0.06	
6	0.06	
7	0.01	
9	0.02	
10	-0.01	
11	0.08	
14	0.25	
16	-0.02	
17	0.11	
18	-0.07	
19	-0.03	
21	0.06	
23	-0.04	
25	0.12	UG
29	-0.14	
32	-0.06	
37	-0.01	
38	-0.10	
40	0.35	
41	0.09	
42	0.03	
43	0.09	
44	-0.40	
46	-0.01	
47	-0.07	

No of labs	26
No of repl	2
d	0.005
s ²	0.017
s	0.132
t	0.182
Sign. level 99.9 %	3.725
Sign. level 99 %	2.787
Sign. level 95 %	2.060

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	Outlier
1	0.70	
2	1.10	
5	2.20	UG
9	1.70	
14	5.20	UC
16	0.90	UG
17	0.40	
18	-1.40	
19	0.70	
20	0.00	
23	0.90	
25	-1.90	
28	-1.00	UG
29	0.70	
31	0.10	
32	1.00	
34	*)	U
35	0.80	
36	-2.10	
37	0.60	
39	0.10	
41	1.00	UG
44	*)	U
46	1.00	
47	1.30	

No of labs	18
No of repl	2
d	0.317
s ²	1.143
s	1.069
t	1.257
Sign. level 99.9 %	3.965
Sign. level 99 %	2.898
Sign. level 95 %	2.110

No test statistics were found to be significant

U denote a manual selected outlier

UC denotes a Cochran outlier

UG denotes a Grubbs outlier

*) Not calculated as the result is excluded

pH

Control of differences within sample pairs

Laboratory	Difference AB	Outlier
2	-0.02	
3	0.04	
5	-0.01	UG
6	0.10	
7	0.03	
8	0.04	
9	-0.02	
10	-0.05	
11	-0.03	
13	-0.04	
14	0.00	
15	-0.01	
16	-0.01	
17	0.02	
18	-0.05	
19	-0.01	
20	-0.10	
21	0.02	
22	0.03	
23	-0.07	
25	-0.01	
26	-0.06	
27	0.02	
28	0.05	
29	0.00	
31	-0.03	
32	0.10	
34	-0.23	
35	0.04	
36	0.06	
37	0.00	
38	0.18	
39	-0.10	
40	0.00	
41	-0.10	
42	0.39	UC
43	-0.02	
44	-0.01	
46	0.05	
47	0.27	

No of labs	39
No of repl	2
d	0.002
s ²	0.006
s	0.080
t	0.146
Sign. level 99.9 %	3.566
Sign. level 99 %	2.712
Sign. level 95 %	2.024

No test statistics were found to be significant

UC denotes a Cochran outlier

UG denotes a Grubbs outlier

ANNEX C CONTROL OF RECOVERY

Total Nitrogen, mg/L N

Control of recovery, average of results

Laboratory	Sample pair AB	Outlier
3	5.59	
4	4.4495	
5	9.26	UG
6	5.885	
7	5.375	
9	5.59	
10	5.495	
11	6.125	
12	5.159	
13	4.4	
14	5.915	
15	5.8	
16	5.47	
17	5.35	
18	5.815	
19	6.145	
20	5.685	
21	5.77	
23	5.59	
25	5.075	
26	5.325	
27	7.155	UC
28	5.59	
31	5.565	
32	5.01	
34	5.4	
35	5.395	
36	6.5175	
37	5.355	
38	7.12	
39	5.68	
40	5.47	
41	5.8	
42	5.41	
43	5.095	
44	4.695	
45	4.25	

Laboratory	Sample pair AB	Outlier
46	4.978	
47	4.84	

No of labs, p	37
No of repl., n	2
m	5.464
s ²	0.3125
s	0.5590
Assigned value, μ	5.7
Recovery %	95.9
t	-2.565 *
Sign. level 99.9 %	3.582
Sign. level 99 %	2.719
Sign. level 95 %	2.028

* Denotes that there is a significant difference (t-test, 5 %-level)

UC denotes a Cochran outlier

UG denotes a Grubbs outlier

Ammonium, mg/L N

Control of recovery, average of results

Laboratory	Sample pair AB	Outlier
3	1.075	
5	1.245	
6	1.195	
7	1.175	
8	1.1792	
9	1.13	
10	1.16	
11	1.103	
14	1.115	
15	1.19	
16	1.135	
17	1.14	
18	1.17	
19	1.09	
20	1.21	
21	1.16	
23	1.185	
24	1.165	
25	1.13	
26	1.055	
28	1.17	
29	1.1455	
31	1.195	
32	1.14	
34	1.165	
36	1.32	
37	1.12	
38	1.14	
40	1.255	
41	1.185	
42	1.19	
43	1.09	
44	1.134	
46	1.2	
47	1.185	

No of labs, p	35
No of repl., n	2
m	1.161
s ²	0.003
s	0.052
Assigned value, μ	1.17
Recovery %	99.2
t	-1.000
Sign. level 99.9 %	3.601
Sign. level 99 %	2.728
Sign. level 95 %	2.032

No test statistics were found to be significant

Nitrite + nitrate, mg/L N

Control of recovery, average of results

Laboratory	Sample pair AB	Outlier
6	2.85	
8	3.2739	
11	2.875	
18	3.155	
20	2.875	
28	3.005	
29	3.0835	
34	2.75	
41	2.855	

No of labs, p	9
No of repl., n	2
m	2.969
s ²	0.029
s	0.171
Assigned value, μ	2.9
Recovery %	102.4
t	1.211
Sign. level 99.9 %	5.041
Sign. level 99 %	3.355
Sign. level 95 %	2.306

No test statistics were found to be significant

Nitrate, mg/L N

Control of recovery, average of results

Laboratory	Sample pair AB	Outlier
1	3.095	
3	3.12	
5	3.0809	
6	2.85	
7	3.105	
9	3.17	
10	3.025	
11	2.87	
14	2.935	
16	2.91	
17	2.905	
18	3.155	
19	2.995	
21	2.94	
23	3.14	
25	2.32	UG
29	3.0745	
32	3.33	
37	3.085	
38	2.98	
40	2.795	
41	2.845	
42	3.045	
43	2.895	
44	3.2	
46	3.095	
47	2.675	

No of labs, p	26
No of repl., n	2
m	3.012
s ²	0.021
s	0.146
Assigned value, μ	3.02
Recovery %	99.7
t	-0.275
Sign. level 99.9 %	3.725
Sign. level 99 %	2.787
Sign. level 95 %	2.060

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	Outlier
1	132.65	
2	133.55	
5	117.7	
9	133.25	
14	129.5	UC
16	113.75	
17	132.3	
18	128.9	
19	135.95	
20	132	
23	133.65	
25	133.65	
28	124.5	
29	133.35	
31	128.75	
32	133.5	
34	0.8565	UG
35	130.5	
36	132.516	
37	133.3	
39	129.65	
41	107.8	
44	1116.5	UC
46	131.3	
47	133.85	

No of labs, p	22
No of repl. n	2
m	129.4
s ²	52.0
s	7.21
Assigned value, μ	132
Recovery %	98.0
t	-1.704
Sign. level 99.9 %	3.819
Sign. level 99 %	2.831
Sign. level 95 %	2.080

No test statistics were found to be significant

UG denotes a Grubbs outlier

UC denotes a Cochran outlier

pH

Control of recovery, average of results

Laboratory	Sample pair AB	Outlier
2	7.7	
3	7.79	
5	7.635	
6	7.66	
7	7.295	
8	7.55	
9	7.65	
10	7.635	
11	7.605	
13	7.55	
14	7.35	
15	7.735	
16	7.861	
17	7.59	
18	7.995	
19	7.585	
20	7.71	
21	7.85	
22	7.685	
23	7.565	
25	7.627	
26	7.89	
27	7.65	
28	7.625	
29	7.69	
31	7.555	
32	7.85	
34	7.755	
35	7.66	
36	7.52	
37	7.4635	
38	7.45	
39	7.45	
40	7.73	
41	7.45	
42	7.975	UC
43	7.6	
44	7.785	
46	7.705	
47	7.195	

No of labs, p	39
No of repl., n	2
m	7.632
s ²	0.027
s	0.163
Assigned value, μ	7.64
Recovery %	99.9
t	-0.308
Sign. level 99.9 %	3.566
Sign. level 99 %	2.712
Sign. level 95 %	2.024

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

ANNEX D CONCENTRATION LEVEL

Concentration level SPIL-4 (2023)

Parameter	Unit	Sample	Bottle no.	I	II	Bottle Average	Sample Average	Assigned value	Spike	
									Measured	Assigned
Total nitrogen	mg/L N	A1	2	5.46	5.45	5.46	5.42	5.7	0.92	1.0
			34	5.41	5.41	5.41				
			62	5.40	5.39	5.40				
		B1	6	6.35	6.34	6.35	6.34	6.7		
			39	6.32	6.34	6.33				
			63	6.33	6.34	6.34				
Ammonium	mg/L N	A1	2	1.20	1.20	1.20	1.19	1.17	0.22	0.23
			34	1.17	1.17	1.17				
			62	1.19	1.19	1.19				
		B1	6	1.41	1.41	1.41	1.40	1.40		
			39	1.40	1.40	1.40				
			63	1.40	1.40	1.40				
Nitrite+nitrate / Nitrate	mg/L N	A1	2	3.02	3.03	3.03	3.03	2.9	0.49	0.5
			34	3.04	3.05	3.05				
			62	3.03	3.02	3.03				
		B1	6	3.52	3.51	3.52	3.53	3.40		
			39	3.54	3.52	3.53				
			63	3.53	3.53	3.53				
pH		A2	20	7.57	7.59	7.58	7.59	7.64	0.00	0.00
			31	7.58	7.60	7.59				
			52	7.60	7.60	7.60				
		B2	11	7.60	7.57	7.59	7.59	7.64		
			47	7.58	7.60	7.59				
			69	7.59	7.58	7.59				

ANNEX E HOMOGENEITY AND STABILITY

PT: SPIL-4 2023
Parameter: TN
Unit: mg/L N
Sigma: 0,346

Responsible for tests: HBP/S7MS

Homogeneity test

Date: 2023-10-31

Sample	x(a)	x(b)	average	sd	sd^2
A1-5	6,50	6,51	6,5	0,007	0,000
A1-11	6,20	6,21	6,2	0,007	0,00
A1-17	6,43	6,43	6,4	0,000	0,000
A1-19	6,21	6,21	6,2	0,000	0,000
A1-29	6,49	6,49	6,5	0,000	0,000
A1-37	6,46	6,45	6,5	0,007	0,000
A1-43	6,40	6,44	6,4	0,028	0,001
A1-48	6,47	6,49	6,5	0,014	0,000
A1-54	6,39	6,39	6,4	0,000	0,000
A1-62	6,55	6,56	6,6	0,007	0,000
A1-65	6,34	6,34	6,3	0,000	0,000
A1-74	6,41	6,42	6,4	0,007	0,000

For homogeneity

General average (x)	6,41
Sample average sd (s _x)	0,109
Within-sample sd (s _w):	0,010
Between-samples sd (ss):	0,1090
S _L in the Proficiency Test:	0,534
S _R in the Proficiency Test:	0,583

Stability test

Date: 2023-11-16

Sample	x(a)	x(b)
6	6,35	6,34
39	6,32	6,34
63	6,33	6,34

For stability

General average (y):	6,3366667
x-y =	0,07125

Conclusions

ss = 0,109	0.3*sigma= 0,10
x-y = 0,07125	
Analytical quality	Is s _w < 0,15*sigma YES
Stability:	x-y < 0.3*sigma? YES

PT: SPIL-4 2023
Parameter: Ammonium
Unit: mg/L N
Sigma: 0,1

Responsible for tests: HBP/S7MS

Homogeneity test

Date: 2023-10-31

Sample	x(a)	x(b)	average	sd	sd^2
A1-5	1,45	1,45	1,5	0,000	0,000
A1-11	1,40	1,44	1,4	0,028	0,001
A1-17	1,45	1,44	1,4	0,007	0,000
A1-19	1,46	1,43	1,4	0,021	0,000
A1-29	1,45	1,46	1,5	0,007	0,000
A1-37	1,45	1,46	1,5	0,007	0,000
A1-43	1,44	1,44	1,4	0,000	0,000
A1-48	1,42	1,43	1,4	0,007	0,000
A1-54	1,44	1,44	1,4	0,000	0,000
A1-62	1,44	1,44	1,4	0,000	0,000
A1-65	1,44	1,44	1,4	0,000	0,000
A1-74	1,48	1,48	1,5	0,000	0,000

For homogeneity

General average (x)	1,4
Sample average sd (s _x)	0,015
Within-sample sd (s _w):	0,011
Between-samples sd (ss):	0,013
S _L in the Proficiency Test:	0,051
S _R in the Proficiency Test:	0,054

Conclusions

ss = 0,01 0.3*sigma= 0,02	
/x-y/ = 0	
Analytical quality	Is s _w < 0,15*sigma YES
Homogeneity:	Is ss < 0.3*sigma? YES

PT:	SPIL-4 2023
Parameter:	Nitrat
Unit:	mg/L N
Sigma:	0,195

Responsible for tests:

HBP/S7MS

Homogeneity test

Date: 2023-10-31

Sample	x(a)	x(b)	average	sd	sd^2
A1-5	3,60	3,59	3,6	0,008	0,000
A1-11	3,55	3,58	3,6	0,020	0,00
A1-17	3,57	3,58	3,6	0,006	0,000
A1-19	3,58	3,60	3,6	0,011	0,000
A1-29	3,58	3,62	3,6	0,030	0,001
A1-37	3,66	3,64	3,6	0,009	0,000
A1-43	3,64	3,62	3,6	0,014	0,000
A1-48	3,65	3,64	3,6	0,007	0,000
A1-54	3,67	3,61	3,6	0,040	0,002
A1-62	3,58	3,60	3,6	0,011	0,000
A1-65	3,72	3,64	3,7	0,061	0,004
A1-74	3,67	3,69	3,7	0,010	0,000

For homogeneity

General average (x)	3,62
Sample average sd (s _x)	0,040
Within-sample sd (s _w):	0,025
Between-samples sd (ss):	0,0360
S _L in the Proficiency Test:	0,13
S _R in the Proficiency Test:	0,159

Conclusions

ss = 0,036 0.3*sigma= 0,06	
/x-y/ = 0	
Analytical quality	Is s _w < 0,15*sigma YES
Homogeneity:	Is ss < 0.3*sigma? YES