



Proficiency test SPIL-4 (2024)

**Nitrogen parameters in wastewater
(wastewater, effluent)**

January 2025

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Client Environmental laboratories		Client's representative			
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1 INTRODUCTION

A proficiency test on the analysis of nitrogen parameters in wastewater, effluent was conducted on 14 November 2024. 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 17 December 2024.

2 **FEATURES OF THE PROFICIENCY TEST**

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

The closing date for submission of results was 29 November 2024. All participants except laboratory no. 6, 9, 11, 13 and 28 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, 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/ 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	9.8	0.26	1.8
Ammonium	NH ₄	mg/L N	0.1 - 2	0.167	0.0096	0.225
Nitrite+nitrate	NO ₂₊₃	mg/L N	1 – 5	8.8	0.46	1.5
Nitrate	NO ₃	mg/L N	1 – 5	8.79	0.085	1.20
Conductivity	γ ₂₅	mS/m	50 – 300	58.8	0.39	1.3
pH			6 – 9	7.72	0.052	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 spike value is the difference between the two median values. The assigned value is calculated as the average of the median for both samples in the sample pair after spike correction.

The assigned value and spike value for TN is operationally defined and is a consensus value based upon the median for method no. 1-5+9 (TN). A list of method identification numbers is found in the report to participants /1/.

Assigned values and spike value for 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 NH₄, NO₂₊₃, NO₃, conductivity and pH, but the test revealed a significant difference between the two for TN. 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 not obtained by method no. 1, 2, 3 and 9 and now showed no significant difference. The spike value is therefore kept unchanged.

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.

For NH₄, NO₂₊₃, NO₃, conductivity and pH 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 95.4%. 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 not obtained by method no. 1, 2, 3 and 9 and now showed no significant difference. Furthermore, the results of control measurements at Eurofins confirmed the assigned value (Appendix D). The assigned value is therefore kept unchanged.

3 **HOMOGENEITY AND STABILITY OF SAMPLES**

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

NH ₄	Combined homogeneity and stability test
NO ₃	Combined homogeneity and stability test
TN	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 multiplied with the standard deviation for evaluation of participants' performance ($0.3 \cdot \hat{\sigma}$) specified by the Danish EPA /5/, whereas the stability is evaluated by comparing the concentration change of the samples to $0.3 \cdot \hat{\sigma}$ 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 /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.

For TN the participants did not recover the spike value and the assigned value. The difference could be attributed to laboratories using methods other than that prescribed by the Danish EPA. The spike value and the assigned value is therefore kept unchanged and it is recommended as the basis for evaluation of participating laboratories.

5 REFERENCES

- /1/ Eurofins A/S, *Proficiency test SPIL-4 (2024)*, Report to participants, December 2024.
- /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 and Equality regulation no. 811 on *Quality criteria for environmental measurements*, 19 June 2024 (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	3.0003 g Disodium edetate, 2H ₂ O milli-Q water up to 1000.0 g	TN: 225.8 mg/kg N
Stock NH ₄	1.0007 g Ammonium chloride (NH ₄ Cl) milli-Q water up to 1000.0 g	NH ₄ : 262.1 mg/kg N
Stock NO ₃	2.4998 g Potassium nitrate (KNO ₃) milli-Q water up to 1000.0 g	NO ₃ : 346.4 mg/kg N

Sample	Sample prepared from	TN mg/L N	NH ₄ mg/L N	NO ₃ mg/L N	Conductivity mS/m
A1	0 g stock TN 0 g stock NH ₄ 0 g stock NO ₃ filtered water from Vejen sewage treatment plant up to 65* kg	a	b	c	d
B1	50 g stock TN 30 g stock NH ₄ 130 g stock NO ₃ Sample A1 up to 34* kg	0.994 · a+10.5	0.994 · b+0.164	0.994 · c+8.7	e

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

*Malfunctional weight – amounts are approximate and is not used directly for assigning values in proficiency test.

ANNEX B CONTROL OF SPIKE VALUES

Total Nitrogen, mg/L N

Control of differences within sample pairs

Laboratory	Difference AB	Outlier
1	0.35	
2	0.66	
3	0.18	
4	0.03	
7	-0.10	
8	0.11	
10	0.40	
12	0.27	
14	0.33	
15	1.10	
16	0.27	
17	-0.03	
18	0.10	
19	0.39	
20	-0.03	
21	0.30	
23	0.28	
24	0.02	
25	0.14	
26	0.32	
27	1.30	
29	0.21	
30	0.21	
31	0.47	
32	0.15	
34	0.00	
35	0.00	
36	-0.22	
37	0.05	
38	0.30	

No of labs, p	30
No of repl, n	2
d	0.2519
s ²	0.1017
s	0.3190
t	4.3259 ***
Sign. level 99.9%	3.6594
Sign. level 99%	2.7564
Sign. level 95%	2.0452

*** denotes that there is a significant difference (t-test, 0.01 %-level)

Ammonium, mg/L N

Control of differences within sample pairs

Laboratory	Difference AB	Outlier
1	0.0030	
2	0.0060	
3	0.0050	
4	0.0160	
7	-0.0150	
8	0.0050	
12	0.0150	
15	-0.0450	
16	-0.0020	
17	0.0160	
18	-0.0160	
19	0.0024	
20	0.0090	
22	-0.1160	C
23	0.0170	
24	-0.0090	
25	-0.0040	
26	-0.0070	
27	0.0220	
29	0.0150	
31	-0.0090	
32	0.0040	
33	-0.0270	
34	0.0040	
36	-0.0290	
37	0.0110	
38	-0.0040	

No of labs, p	26
No of repl, n	2
d	-0.0006
s ²	0.0003
s	0.0160
t	-0.2038
Sign. level 99.9%	3.7251
Sign. level 99%	2.7874
Sign. level 95%	2.0595

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

Nitrite+Nitrate, mg/L N

Control of differences within sample pairs

Laboratory	Difference AB	Outlier
15	0.82	
16	0.77	
18	0.06	
22	0.38	
31	-0.13	
33	0.05	
34	0.25	

No of labs, p	7
No of repl, n	2
d	0.3129
s ²	0.1336
s	0.3655
t	2.2654
Sign. level 99.9%	5.9588
Sign. level 99%	3.7074
Sign. level 95%	2.4469

No test statistics were found to be significant

Nitrate, mg/L N

Control of differences within sample pairs

Laboratory	Difference AB	Outlier
1	-0.010	
2	-0.550	
3	0.050	
4	0.210	
7	-0.070	
8	0.010	
12	-0.010	
14	0.060	
15	0.530	
16	0.472	
17	-0.010	
20	0.000	
23	-0.010	
24	-0.000	
25	0.190	
26	-0.199	
27	0.740	
32	-0.000	
35	-0.030	
38	-0.040	

No of labs, p	20
No of repl, n	2
d	0.0666
s ²	0.0736
s	0.2713
t	1.0984
Sign. level 99.9%	3.8834
Sign. level 99%	2.8609
Sign. level 95%	2.0930

No test statistics were found to be significant

Conductivity, mS/m

Control of differences within sample pairs

Laboratory	Difference AB	Outlier
2	1.30	
3	-0.70	
4	*)	U
5	0.20	
10	-1.20	
14	1.75	
15	0.30	
17	0.10	
18	0.20	
20	0.73	
21	0.10	
23	-0.20	
24	0.27	
25	-0.02	
26	0.12	
31	0.60	
32	-0.25	
33	-0.10	
35	0.20	
37	0.25	
38	*)	U

No of labs, p	19
No of repl, n	2
d	0.1921
s ²	0.4093
s	0.6397
t	1.3089
Sign. level 99.9%	3.9216
Sign. level 99%	2.8784
Sign. level 95%	2.1009

No test statistics were found to be significant
U denote a manual selected outlier

*) Not calculated as the result is excluded

pH

Control of differences within sample pairs

Laboratory	Difference AB	Outlier
1	0.000	
2	0.040	
3	-0.060	
4	-0.015	
5	-0.060	
7	-0.060	
8	-0.040	
10	-0.050	
12	0.040	
14	0.290	C
15	0.000	
16	0.000	
17	-0.390	C
18	0.010	
19	0.051	
20	-0.100	
21	*)	U
22	-0.040	
23	-0.012	
24	0.050	
25	0.090	
26	-0.010	
27	0.003	
29	-0.060	
31	0.020	
32	-0.150	
33	-0.060	
35	-0.080	
36	0.020	
37	0.010	
38	0.120	

No of labs, p	28
No of repl, n	2
d	-0.0123
s ²	0.0034
s	0.0580
t	-1.1185
Sign. level 99.9%	3.6896
Sign. level 99%	2.7707
Sign. level 95%	2.0518

No test statistics were found to be significant

U denote a manual selected outlier

C denotes a Cochran outlier

*) Not calculated as the result is excluded

ANNEX C CONTROL OF RECOVERY

Total Nitrogen, mg/L N

Control of recovery, average of results

Laboratory	Sample pair AB	Outlier
1	9.68	
2	8.03	
3	9.24	
4	9.12	
7	10.45	
8	9.25	
10	9.90	
12	9.04	
14	9.67	
15	8.65	
16	9.34	
17	9.79	
18	9.55	
19	8.45	
20	9.86	
21	9.35	
23	9.54	
24	8.78	
25	8.15	
26	8.12	
27	8.95	
29	9.41	
30	9.38	
31	9.02	
32	9.91	
34	10.50	
35	9.90	
36	9.49	
37	9.81	
38	10.05	

No of labs, p	30
No of repl, n	2
m	9.3447
s ²	0.4021
s	0.6341
Assigned value, μ	9.8
Recovery, %	95.4
t	-3.9326 ***
Sign. level 99.9%	3.6594
Sign. level 99%	2.7564
Sign. level 95%	2.0452

*** denotes that there is a significant difference
(t-test, 0.01 %-level)

Ammonium, mg/L N

Control of recovery, average of results

Laboratory	Sample pair AB	Outlier
1	0.1685	
2	0.1470	
3	0.1555	
4	0.1430	
7	0.1475	
8	0.1725	
12	0.1525	
15	0.2225	
16	0.1820	
17	0.2180	
18	0.1250	
19	0.1694	
20	0.1625	
22	0.4132	C
23	0.1555	
24	0.1805	
25	0.1900	
26	0.2305	
27	0.1510	
29	0.1545	
31	0.1865	
32	0.1650	
33	0.1385	
34	0.1760	
36	0.1685	
37	0.1565	
38	0.1850	

No of labs, p	26
No of repl, n	2
m	0.1694
s ²	0.0007
s	0.0255
Assigned value, μ	0.167
Recovery, %	101.4
t	0.4757
Sign. level 99.9%	3.7251
Sign. level 99%	2.7874
Sign. level 95%	2.0595

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

Nitrite+Nitrate, mg/L N

Control of recovery, average of results

Laboratory	Sample pair AB	Outlier
15	7.73	
16	7.87	
18	9.23	
22	9.56	
31	8.68	
33	8.82	
34	9.03	

No of labs, p	7
No of repl, n	2
m	8.7013
s ²	0.4605
s	0.6786
Assigned value, μ	8.8
Recovery, %	98.9
t	-0.3847
Sign. level 99.9%	5.9588
Sign. level 99%	3.7074
Sign. level 95%	2.4469

No test statistics were found to be significant

Nitrate, mg/L N

Control of recovery, average of results

Laboratory	Sample pair AB	Outlier
1	8.895	
2	7.785	
3	8.585	
4	8.825	
7	8.865	
8	8.805	
12	8.795	
14	8.810	
15	7.835	
16	7.972	
17	8.705	
20	8.740	
23	8.895	
24	8.930	
25	8.105	
26	8.742	
27	9.270	
32	8.790	
35	8.985	
38	8.630	

No of labs, p	20
No of repl, n	2
m	8.6482
s ²	0.1608
s	0.4010
Assigned value, μ	8.79
Recovery, %	98.4
t	-1.5813
Sign. level 99.9%	3.8834
Sign. level 99%	2.8609
Sign. level 95%	2.0930

No test statistics were found to be significant

Conductivity, mS/m

Control of recovery, average of results

Laboratory	Sample pair AB	Outlier
2	59.05	
3	58.45	
4	*)	U
5	59.30	
10	57.10	
14	61.39	
15	60.05	
17	58.55	
18	57.38	
20	59.96	
21	58.75	
23	59.10	
24	59.45	
25	60.05	
26	58.75	
31	59.20	
32	58.65	
33	58.75	
35	58.60	
37	57.91	
38	*)	U

No of labs, p	19
No of repl, n	2
m	58.9692
s ²	0.9744
s	0.9871
Assigned value, μ	58.8
Recovery, %	100.3
t	0.7472
Sign. level 99.9%	3.9216
Sign. level 99%	2.8784
Sign. level 95%	2.1009

No test statistics were found to be significant

U denote a manual selected outlier

*) Not calculated as the result is excluded

pH

Control of recovery, average of results

Laboratory	Sample pair AB	Outlier
1	7.470	
2	7.640	
3	7.670	
4	7.558	
5	7.620	
7	7.680	
8	7.830	
10	7.575	
12	7.370	
14	7.835	C
15	7.900	
16	7.780	
17	7.595	C
18	7.695	
19	7.787	
20	7.450	
21	*)	U
22	7.640	
23	7.763	
24	7.785	
25	8.045	
26	7.735	
27	7.690	
29	7.810	
31	7.840	
32	7.385	
33	7.790	
35	7.710	
36	7.820	
37	7.775	
38	7.600	

No of labs, p	28
No of repl, n	2
m	7.6933
s ²	0.0239
s	0.1546
Assigned value, μ	7.72
Recovery, %	99.7
t	-0.9149
Sign. level 99.9%	3.6896
Sign. level 99%	2.7707
Sign. level 95%	2.0518

No test statistics were found to be significant

U denote a manual selected outlier

C denotes a Cochran outlier

*) Not calculated as the result is excluded

ANNEX 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	4	9.61	9.62	9.62	9.72	9.80	1.73	1.8
			25	9.65	9.65	9.65				
			50	9.88	9.89	9.89				
		B1	14	11.3	11.40	11.35	11.45	11.60		
			42	11.50	11.50	11.50				
			59	11.50	11.50	11.50				
Ammonium	mg/L N	A1	4	0.172	0.173	0.17	0.172	0.167	0.22	0.225
			25	0.175	0.176	0.18				
			50	0.168	0.168	0.17				
		B1	14	0.396	0.396	0.40	0.395	0.392		
			42	0.39	0.39	0.39				
			59	0.398	0.398	0.40				
Nitrite+nitrate / Nitrate	mg/L N	A1	4	8.902	8.852	8.88	8.91	8.8	1.15	1.5
			25	8.892	8.862	8.88				
			50	8.962	8.982	8.97				
		B1	14	10.158	10.058	10.11	10.06	10.3		
			42	10.057	10.157	10.11				
			59	9.969	9.969	9.97				
pH		A2	12	7.94	7.96	7.95	7.96	7.72	-0.01	0
			31	7.96	7.96	7.96				
			45	7.96	7.97	7.97				
		B2	5	7.93	7.94	7.94	7.95	7.72		
			40	7.95	7.95	7.95				
			64	7.95	7.95	7.95				

ANNEX E HOMOGENEITY AND STABILITY

PT: SPIL-4 2024

Parameter: TN

Unit: mg/L N

Sigma: 0.610

Responsible for tests: HBP/S7MS

Homogeneity test Date: 2024-10-29

Sample	x(a)	x(b)	average	sd	sd^2
4	11.30	11.40	11.4	0.071	0.005
10	11.30	11.30	11.3	0.000	0.00
11	11.20	11.30	11.3	0.071	0.005
18	11.30	11.30	11.3	0.000	0.000
24	11.20	11.20	11.2	0.000	0.000
32	11.30	11.30	11.3	0.000	0.000
33	11.20	11.20	11.2	0.000	0.000
39	11.40	11.40	11.4	0.000	0.000
47	11.30	11.30	11.3	0.000	0.000
52	11.30	11.30	11.3	0.000	0.000
57	11.20	11.20	11.2	0.000	0.000
60	11.40	11.30	11.4	0.071	0.005

For homogeneity

General average (x)	11.29
Sample average sd (s _x)	0.064
Within-sample sd (s _w):	0.035
Between-samples sd (ss):	0.0594
S _L in the Proficiency Test:	0.534
S _R in the Proficiency Test:	0.583

Stability test Date: 2024-11-14

Sample	x(a)	x(b)
14	11.3	11.4
42	11.5	11.5
59	11.5	11.5

For stability

General average (y):	11.45
/x-y/ =	0.1625

Conclusions

ss = 0.059 0.3*sigma= 0.18	
/x-y/ = 0.1625	
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 2024
Parameter:	Ammonium
Unit:	mg/L N
Sigma:	0,036

Responsible for tests: HBP/S7MS

Homogeneity test Date: 2024-10-29

Sample	x(a)	x(b)	average	sd	sd^2
4	0,40	0,401	0,4	0,002	0,000
10	0,40	0,402	0,4	0,001	0,000
11	0,40	0,402	0,4	0,002	0,000
18	0,41	0,407	0,4	0,001	0,000
24	0,40	0,406	0,4	0,002	0,000
32	0,40	0,402	0,4	0,002	0,000
33	0,40	0,402	0,4	0,001	0,000
39	0,40	0,404	0,4	0,001	0,000
47	0,39	0,396	0,4	0,001	0,000
52	0,40	0,395	0,4	0,000	0,000
57	0,39	0,395	0,4	0,001	0,000
60	0,40	0,398	0,4	0,000	0,000

For homogeneity	
General average (x)	0,4
Sample average sd (s _x)	0,004
Within-sample sd (s _w):	0,002
Between-samples sd (ss):	0,004
S _L in the Proficiency Test:	0,051
S _R in the Proficiency Test:	0,054

Stability test Date: 2024-11-14

Sample	x(a)	x(b)
14	0,396	0,396
42	0,39	0,39
59	0,40	0,40

For stability	
General average (y):	0,3946667
/x-y/ =	0,00525

Conclusions	
ss = 0,00	0.3*sigma= 0,01
/x-y/ = 0,00525	
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 2024
Parameter:	Nitrat
Unit:	mg/L N
Sigma:	0,552

Responsible for tests: HBP/S7MS

Homogeneity test Date: 2024-10-29

Sample	x(a)	x(b)	average	sd	sd^2
4	10,20	10,30	10,3	0,071	0,005
10	10,20	10,20	10,2	0,000	0,00
11	10,30	10,30	10,3	0,000	0,000
18	10,20	10,20	10,2	0,000	0,000
24	10,20	10,30	10,3	0,071	0,005
32	10,20	10,30	10,3	0,071	0,005
33	10,20	10,20	10,2	0,000	0,000
39	10,20	10,20	10,2	0,000	0,000
47	10,20	10,30	10,3	0,071	0,005
52	10,30	10,20	10,3	0,071	0,005
57	10,20	10,20	10,2	0,000	0,000
60	10,20	10,20	10,2	0,000	0,000

For homogeneity
 General average (x) 10,23
 Sample average sd (s_x) 0,033
 Within-sample sd (s_w): 0,046
 Between-samples sd (ss): 0,0087
 S_L in the Proficiency Test: 0,02
 S_R in the Proficiency Test: 0,159

Stability test Date: 2024-11-14

Sample	x(a)	x(b)
14	10,1	10
42	10	10,1
59	9,91	9,91

For stability
 General average (y): 10,0033333
 /x-y/ = 0,22583333

ss = 0,009 0.3*sigma= 0,17 /x-y/ = 0,225833 0,480	
Analytical quality	Is s _w < 0,15*sigma YES
Homogeneity:	Is ss < 0.3*sigma? YES
Stability:	/x-y/ < 0.3*sigma? NO
Stability:	YES

PT: SPIL-4 2024

Parameter: pH

Unit:

Sigma: 0,1

Responsible for tests: DHBP/S7MS

Homogeneity test

Date: 2024-10-29

Sample	x(a)	x(b)	average	sd	sd^2
3	8,01	8,01	8,0	0,000	0,000
6	8,01	7,99	8,0	0,014	0,00
12	8,00	7,98	8,0	0,014	0,000
19	7,96	7,99	8,0	0,021	0,000
23	7,97	7,96	8,0	0,007	0,000
29	7,98	7,99	8,0	0,007	0,000
33	8,00	7,97	8,0	0,021	0,000
38	8,02	8,03	8,0	0,007	0,000
47	7,97	7,98	8,0	0,007	0,000
56	7,99	8,01	8,0	0,014	0,000
59	7,98	8,01	8,0	0,021	0,000
63	7,98	7,97	8,0	0,007	0,000

For homogeneity

General average (x)7,99

Sample average sd (s_x)0,017

Within-sample sd (s_w):0,014

Between-samples sd (ss):0,0141

S_L in the Proficiency Test:0,158

S_R in the Proficiency Test:0,168

Stability test

Date: 2024-11-14

Sample	x(a)	x(b)
5	7,93	7,94
40	7,95	7,95
64	7,95	7,95

For stability

General average (y):7,945

/x-y/ =0,045

Conclusions

ss = 0,014

/x-y/ = 0,045

0.3*sigma= 0,022

0,066

Analytical quality

Is s_w < 0,15*sigma

NO

Homogeneity:

Is ss < 0.3*sigma?

YES

Stability:

/x-y/ < 0.3*sigma?

NO

Stability:

YES