Proficiency test SPIL-3 (2025)

Organic matter, phosphorus, chloride, sulphate and suspended solids in wastewater (synthetic wastewater, effluent)

Quality Documentation
November 2025

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Project	Project No
Proficiency test SPIL-3 (2025)	20405-53
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1	Quality Documentation Report	FYE3	DPRE/ HT5M	28-11-2025
Revision	Description	By	Approved	Date

Key words	Classification
Analytical quality, assigned value, precision, trueness, homogeneity, stability, COD_{Cr}, BOD_5 (w. ATU), BOD_7 (w. ATU), NVOC/TOC, total phosphorus, chloride, sulphate, total suspended solids, wastewater	☒ Open ☐ Internal ☐ Proprietary

Distribution	
Available online:	www.eurofins.dk
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1 INTRODUCTION

A proficiency test on the analysis of organic matter, phosphorus, chloride, sulphate and suspended solids in wastewater was conducted on 11 September 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 10. October 2025.

2 FEATURES OF THE PROFICIENCY TEST

Participants in the proficiency test were a total of 47 laboratories from Brazil, Croatia, Denmark, Finland, Germany, Greece, Japan, Netherlands, Spain and Sweden.

The closing date for submission of results was 26 September 2025. All participants except laboratory no. 5, 11, 17 and 32 had submitted their results before the deadline. Two of the four which did not submit results were due to sample delivery problems.

2.1 Sample preparation

The parameters covered in the proficiency test are listed in Table 2 as are the abbreviations used in this report.

Six samples were dispatched for the proficiency test. The samples were sample pairs covering the parameters as described in Table 1. The matrix of the samples represented wastewater, in this case synthetic effluent wastewater. Sample preparation is described in Appendix A.

Table 1 Samples in the proficiency test

Sample name	Parameters
A1/B1	COD_{Cr}, BOD (w. ATU) and NVOC/TOC
A2/B2	TP, Cl and SO_4
A3/B3	TSS

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, but NVOC/TOC and TSS, hence the statistical model used for data analysis for NVOC/TOC and TSS were using either assumed unequal variance or the data analysis were performed on both samples.

2.3 Assigned and spike values

An overview of the concentrations in the samples (the assigned values) and the difference in concentration between the two samples of a sample pair (spike value) are shown in Table 2 compared to the range of concentrations normally encountered in synthetic wastewater, effluent. The table also gives the expanded uncertainty of the assigned values. 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
Chemical oxygen demand – dichromate method	COD_{Cr}	mg/L O_2	5-75	38	0.77	9
Five day biochemical oxygen demand (w. ATU)	BOD_5 (w. ATU)	mg/L O_2	2-6	3.5	0.48	0.6
Seven day biochemical oxygen demand (w. ATU)	BOD_7 (w. ATU)	mg/L O_2	2-6	4.0	0.22	0.6
Non-volatile/Total organic carbon	NVOC/TOC	mg/L C	2-30	15.0	0.30	3.7
Total phosphorus	TP	mg/L P	0.2-2	1.21	0.014	0.21
Chloride	Cl	mg/L	50-700	73	0.94	14
Sulphate	SO_4	mg/L	20-200	81	0.94	16
Total suspended solids	TSS	mg/L	20-100	49.4	0.58	3.0

2.3.1 Assigned and spike values

The content of each parameter in each sample is given an assigned value for the sample with the lower content and a spike value, the spike value being the difference in concentration between the two samples of the sample pair. The assigned and spike values are both calculated from sample preparation except for BOD where spike values are calculated from sample preparation and assigned values are consensus values for laboratories using standardised methods (method no. 1 - 4), 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 (*d*), see Appendix B.

The test showed no significant difference between the spike value and *d* except for BOD_7 (w. ATU). Scrutiny of documentation from the sample preparation showed no indications of mistakes in sample preparation and the test for COD_{Cr}, BOD_5 (w. ATU) and NVOC showed no significant difference between the spike values and *d*'s.

2.3.3 Test of assigned values

The assigned value (μ) and the average of the results obtained from all laboratories (m) were also compared (t-test, 95% confidence level), see Appendix C. Results from the t-tests are summarized in table 3 with the calculated recoveries for each parameter.

Table 3 Recovery test of assigned value

Parameter	**Recovery**	**t-test**
COD_{Cr}	95.3 %	Significant - 99.9 % confidence level.
BOD_5 (w. ATU)	101.9 %	Not significant - 95 % confidence level
BOD_7 (w. ATU)	102.9 %	Not significant - 95 % confidence level
NVOC/TOC	A1: 98.8 % B1: 98.9 %	Not significant - 95 % confidence level
TP	98.5 %	Significant - 95 % confidence level
Cl	98.7 %	Not significant - 95 % confidence level
SO_4	97.6 %	Not significant - 95 % confidence level
TSS	A3: 98.2 % B3: 98.3 %	Significant - 95 % confidence level Significant - 99.9 % confidence level.

The difference between μ and m for COD_{Cr} could be attributed to influence from one laboratory. The test was repeated after exclusion of the results from laboratory no. 45 and now showed no significant difference. Scrutiny of documentation from the sample preparation showed no indications of mistakes in sample preparation. The assigned value is kept unchanged.

The difference between μ and m for BOD_5 (w. ATU) and BOD_7 (w. ATU) is not significant, but only indicative values were assigned, this was partly due to significant difference between the split value and d for BOD_7 (w. ATU) and the size of the calculated standard deviation with laboratories compared to the standard deviation between laboratories.

The difference between μ and m for TP was significant on a 95 % confidence level. The results of control measurements at Eurofins did not indicate error in preparation (Appendix D), and scrutiny of documentation from the sample preparation showed no indications of mistakes in sample preparation Furthermore recovery was close to 100 %. The assigned value is therefore kept unchanged.

The difference between μ and m for TSS was significant on a 99.9 % confidence level. The results of control measurements at Eurofins did not indicate error in preparation (Appendix D), and scrutiny of documentation from the sample preparation showed no indications of mistakes in sample preparation. Furthermore, recovery was close to 100%. 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:

COD_{Cr}	Homogeneity
TP	Combined homogeneity and stability test
TSS	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 * 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 $0.3 * \hat{\sigma} + 2\sqrt{u_x^2 + u_y^2}$ 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 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 BOD_7 (w. ATU) the participants could not recover the spike value. The difference between μ and m for BOD_5 (w. ATU) and BOD_7 (w. ATU) is not significant, but only indicative values were assigned, this was partly due to significant difference between the split value and d for BOD7 (w. ATU) and the size of the calculated standard deviation with laboratories compared to the standard deviation between laboratories.

For COD_{Cr}, TP and TS the participants did not recover the assigned value. Eurofins' scrutiny of the combined evidence gave the conclusion that the assigned value is correct. 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-3 (2025)*, Report to participants, October 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. 811 on *quality criteria for environmental measurements,* 19/06/2024 (in Danish).

A N N E X E S

APPENDIX A SAMPLE PREPARATION

Stock solution	**Prepared from**	**Concentration**
Concentrate A1	1.154 g D-glucose 1.154 g L-glutamic acid milli-Q water up to 1000 g	COD_{Cr}: 2.359 g/kg NVOC: 0.9325 g/kg BOD_5: 1.523 g/kg BOD_7: 1.581 g/kg
Concentrate B1	0.9250 g D-glucose 0.9250 g L-glutamic acid milli-Q water up to 1000 g	COD_{Cr}: 1.891 g/kg NVOC: 0.7476 g/kg BOD_5: 1.221 g/kg BOD_7: 1.2673 g/kg
Stock TP	1.506 g Na-B.glycerophosphate milli-Q water up to 1000.0 g	TP: 152.4 mg/kg
Stock Cl	10.000 g Sodium chloride (NaCl) milli-Q water up to 1000.0 g	Cl: 6.067 g/kg
Stock SO_4	10.002 g Sodium sulphate (Na_2SO_4) milli-Q water up to 1000.0 g	SO_4: 6.764 g/kg
Stock TSS	15.013 g Microcrystalline cellulose milli-Q water up to 1000.0 g	TSS: 15.013 g/kg

Sample	Sample prepared from	COD_{Cr} mg/L O_2	NVOC mg/L C	BOD_5 (w. ATU) mg/L O_2	TP mg/L P	Cl mg/L	SO_4 mg/L	TSS mg/L
A1-COD/NVOC	At the laboratory 5.00 mL of concentrate A1 is diluted up to 250.0 mL with pure water	47.1	18.7					
B1-COD/NVOC	At the laboratory 5.00 mL of concentrate B1 is diluted up to 250.0 mL with pure water	37.8	15.0					
A1-BOD	At the laboratory 2.00 mL of concentrate A1 is diluted up to 1000.0 mL with filtered water from sewage treatment plant			c +3.046				
B1-BOD	At the laboratory 2.00 mL of concentrate B1 is diluted up to 1000.0 mL with filtered water from sewage treatment plant			c + 2.442				
A2	400.0 g stock TP 600.0 g stock Cl 600.0 g stock SO_4 Pure water up to 50.0 kg				1.214	72.80	81.15	
B2	35.01 g stock TP 60.00 g stock Cl 60.02 g stock SO_4 Sample A2 up to 25.0 kg				0.994· 1.214 + 0.2134	0.994·72.80 + 14.56	0.994·81.15 + 16.24	
A3	At the laboratory 1000.0 mL of pure water is added to 3.3 mL stock TSS							49.3
B3	At the laboratory 1000.0 mL of pure water is added to 3.5 mL stock TSS							52.4

APPENDIX B CONTROL OF SPIKE VALUES

COD_{Cr}, mg/L O_2

Control of differences within sample pairs

Laboratory	Difference AB	Outlier
1	0.6	
2	0.0	
3	-2.6	
4	-2.0	
7	-1.6	
8	2.8	
9	-1.4	
10	-3.2	
13	0.0	
14	-1.5	
15	0.6	
18	-1.2	
19	-0.8	
20	0.6	
21	3.0	
25	1.5	
26	1.3	

Laboratory	Difference AB	Outlier
27	-10.0	C
28	3.0	
29	1.3	
31	-1.7	
33	1.1	
35	0.0	
36	-0.3	
37	0.1	
38	-0.2	
40	-4.0	
41	0.9	
42	-1.3	
43	0.7	
44	-0.1	
45	-0.4	
46	0.8	
47	1.2	

Statistical data – Control of spike value		
No of labs	33	**Notes**
No of repl	2	No test statistics were found to be significant C denotes a Cochran outlier
d	-0.0848	
s^2	2.7388	
s	1.6549	
t	-0.2945	
Sign. level 99.9%	3.6218	
Sign. level 99%	2.7385	
Sign. level 95%	2.0369	

BOD_5 (w. ATU), mg/L O_2

Control of differences within sample pairs

Laboratory	Difference AB	Outlier
1	0.00	
3	0.42	
4	0.30	
15	0.04	
19	0.12	
20	-0.70	G
21	-	
27	0.31	
28	-0.60	
31	-0.30	
33	1.30	
36	-1.70	
38	-	
42	-0.16	
46	0.33	
47	0.10	

Statistical data – Control of spike value		
No of labs	13	**Notes**
No of repl	2	No test statistics were found to be significant G denotes a Grubbs outlier
d	0.0123	
s^2	0.4626	
s	0.6801	
t	0.0652	
Sign. level 99.9%	4.3178	
Sign. level 99%	3.0545	
Sign. level 95%	2.1788	

BOD_7 (w. ATU), mg/L O_2

Control of differences within sample pairs

Laboratory	Difference AB	Outlier
3	0.38	
6	0.40	
16	1.10	
24	0.00	
27	0.34	
30	0.19	
33	1.10	
35	0.20	
37	-0.20	
42	-0.27	
43	0.20	
46	0.39	

Statistical data – Control of spike value			
No of labs	12		**Notes**
No of repl	2		* denotes that there is a significant difference (t-test, 5 %-level)
d	0.3192		
s^2	0.1817		
s	0.4263		
t	2.5938	*	
Sign. level 99.9%	4.4370		
Sign. level 99%	3.1058		
Sign. level 95%	2.2010		

NVOC/TOC, mg/L C

Control of differences within sample pairs

Laboratory	Difference AB	Outlier
1	-0.10	
2	-0.14	
3	-0.30	
6	-0.04	
8	-0.40	
12	0.10	
15	-0.49	
16	2.90	C
19	-0.10	
21	-0.70	
22	1.26	
23	-0.40	G
24	-1.82	C
26	0.07	

Laboratory	Difference AB	Outlier
27	-3.90	C
28	-0.10	G
30	0.70	
31	-0.57	
33	0.07	
37	0.20	
38	-0.16	G
39	0.10	
40	-0.20	
41	-0.09	
42	-0.06	
43	-0.60	
46	0.00	
47	0.20	G

Statistical data – Control of spike value		
No of labs	21	**Notes**
No of repl	2	Test performed as Two-Sample t-test with unequal variance No test statistics were found to be significant C denotes a Cochran outlier G denotes a Grubbs outlier
d	-0.0614	
s^2 (A)	0.3714	
s^2 (B)	0.1709	
t	-0.3822	
Sign. level 99.9%	3.5911	
Sign. level 99%	2.7238	
Sign. level 95%	2.0301	

TP, mg/L P

Control of differences within sample pairs

Laboratory	Difference AB	Outlier
1	0.000	
2	0.020	
3	0.000	
4	0.010	
6	-0.005	
7	0.080	
8	0.010	
9	-0.050	
10	-0.050	
12	0.010	
13	0.020	
15	0.010	
16	0.030	
18	0.030	
19	-0.030	
20	0.030	
22	0.000	
23	-0.090	
24	0.020	
25	-0.002	

Laboratory	Difference AB	Outlier
26	0.040	
27	0.010	
28	0.000	
29	0.020	
30	0.000	
31	0.190	C
33	0.021	
36	0.020	
37	-0.090	
38	0.000	
39	-0.010	
40	0.010	
41	0.000	
42	0.030	
43	0.013	
44	0.020	
45	-0.010	
46	0.020	
47	-0.000	

Statistical data – Control of spike value		
No of labs	38	**Notes**
No of repl	2	No test statistics were found to be significant C denotes a Cochran outlier
d	0.0036	
s^2	0.0010	
s	0.0318	
t	0.6986	
Sign. level 99.9%	3.5737	
Sign. level 99%	2.7154	
Sign. level 95%	2.0262	

Cl, mg/L

Control of differences within sample pairs

Laboratory	Difference AB	Outlier
1	-0.5	
2	-1.0	
3	1.8	
4	-2.0	
7	0.6	G
10	4.0	
13	2.0	
15	-1.5	
18	-5.7	
19	8.9	C
21	-2.0	
22	0.3	
23	0.7	
27	-1.2	

Laboratory	Difference AB	Outlier
28	0.4	
31	0.5	
33	-1.1	
34	0.2	
36	-3.4	G
38	0.0	
40	-0.7	
41	-0.2	
42	0.1	
44	5.0	
45	-1.2	
46	-0.7	
47	0.2	

Statistical data – Control of spike value		
No of labs	24	**Notes**
No of repl	2	No test statistics were found to be significant C denotes a Cochran outlier G denotes a Grubbs outlier
d	-0.1096	
s^2	4.2731	
s	2.0671	
t	-0.2598	
Sign. level 99.9%	3.7676	
Sign. level 99%	2.8073	
Sign. level 95%	2.0687	

SO_4, mg/L

Control of differences within sample pairs

Laboratory	Difference AB	Outlier
1	0.2	
3	3.6	
8	1.1	
15	0.3	
19	-1.9	
21	-2.0	
22	-0.5	G
27	-0.7	
28	0.6	
31	1.0	
33	-1.6	
34	1.0	
38	6.0	
40	0.5	
41	0.6	
42	0.7	
44	0.3	
46	4.2	
47	0.6	

Statistical data – Control of spike value		
No of labs	18	**Notes**
No of repl	2	No test statistics were found to be significant G denotes a Grubbs outlier
d	0.8021	
s^2	4.1716	
s	2.0425	
t	1.6660	
Sign. level 99.9%	3.9651	
Sign. level 99%	2.8982	
Sign. level 95%	2.1098	

TSS, mg/L

Control of differences within sample pairs

Laboratory	Difference AB	Outlier
1	-2.00	
2	0.70	
3	0.00	
4	-1.00	
6	0.87	
8	0.00	
10	1.30	
13	0.30	
14	0.50	
15	-1.00	
16	0.70	
19	3.80	
20	3.80	G
21	0.00	
22	0.40	
23	0.80	
24	0.40	
25	-0.51	

Laboratory	Difference AB	Outlier
26	0.00	
27	-1.00	
28	-0.10	
29	0.70	
30	-2.30	
31	0.40	
33	0.50	
35	-3.30	
36	1.00	
37	0.60	
38	-4.60	
39	-0.30	
41	2.00	
42	-0.80	
43	-2.50	G
44	2.00	G
46	2.10	
47	0.60	

Statistical data – Control of spike value		
No of labs	33	**Notes**
No of repl	2	Test performed as Two-Sample t-test with unequal variance No test statistics were found to be significant G denotes a Grubbs outlier
d	0.0230	
s^2 (A)	3.39	
s^2 (B)	1.34	
s	-	
t	-0.0608	
Sign. level 99.9%	3.4800	
Sign. level 99%	2.6700	
Sign. level 95%	2.0049	

APPENDIX C CONTROL OF RECOVERY

COD_{Cr}, mg/L O_2

Control of recovery, average of results

Laboratory	Sample pair AB	Outlier
1	34.4	
2	38.6	
3	33.5	
4	38.0	
7	36.8	
8	35.3	
9	31.7	
10	33.2	
13	34.0	
14	35.2	
15	35.9	
18	36.5	
19	37.7	
20	38.6	
21	37.5	
25	35.9	
26	33.8	

Laboratory	Sample pair AB	Outlier
27	35.0	C
28	34.1	
29	35.0	
31	38.6	
33	35.8	
35	34.0	
36	40.7	
37	38.5	
38	35.3	
40	32.6	
41	39.2	
42	39.3	
43	39.1	
44	41.7	
45	28.2	
46	38.9	
47	37.4	

Statistical data – Control of recovery			
No of labs	33		**Notes**
No of repl	2		*** denotes that there is a significant difference (t-test, 0.1%-level) C denotes a Cochran outlier
m	36.1979		
s^2	8.0001		
s	2.8284		
Assigned value	38		
Recovery	95.3		
t	-3.6601	***	
Sign. level 99.9%	3.6218		
Sign. level 99%	2.7385		
Sign. level 95%	2.0369		

BOD_5 (w. ATU), mg/L O_2

Control of recovery, average of results

Laboratory	Sample pair AB	Outlier
1	3.40	
3	3.40	
4	3.75	
15	3.40	
19	4.48	
20	0.15	G
21	-	
27	3.57	
28	2.80	
31	4.65	
33	3.95	
36	3.05	
38	-	
42	3.74	
46	3.36	
47	2.83	

Statistical data – Control of recovery		
No of labs	13	**Notes**
No of repl	2	No test statistics were found to be significant G denotes a Grubbs outlier
m	3.5669	
s^2	0.3120	
s	0.5586	
Indicative value	3.5	
Recovery	101.9	
t	0.4320	
Sign. level 99.9%	4.3178	
Sign. level 99%	3.0545	
Sign. level 95%	2.1788	

BOD_7 (w. ATU), mg/L O_2

Control of recovery, average of results

Laboratory	Sample pair AB	Outlier
3	4.71	
6	3.90	
16	4.95	
24	3.80	
27	3.61	
30	4.08	
33	4.25	
35	4.00	
37	3.80	
42	4.72	
43	3.80	
46	3.80	

Statistical data – Control of recovery		
No of labs	12	**Notes**
No of repl	2	No test statistics were found to be significant
m	4.1171	
s^2	0.1951	
s	0.4416	
Indicative value	4.0	
Recovery	102.9	
t	0.9184	
Sign. level 99.9%	4.4370	
Sign. level 99%	3.1058	
Sign. level 95%	2.2010	

NVOC/TOC, mg/L C

Control of recovery, average of results

Laboratory	Sample pair AB	Outlier
1	14.85	
2	14.98	
3	14.95	
6	14.35	
8	14.10	
12	15.74	
15	14.23	
16	16.15	C
19	14.85	
21	14.65	
22	15.83	
23	12.50	G
24	16.14	C
26	15.17	

Laboratory	Sample pair AB	Outlier
27	12.85	C
28	17.75	G
30	14.55	
31	14.52	
33	14.20	
37	14.80	
38	13.42	G
39	15.35	
40	14.90	
41	14.52	
42	14.34	
43	14.90	
46	15.20	
47	17.10	G

Statistical data – Control of recovery			
	A1	B1	
No of labs	21	21	**Notes**
No of repl	2	2	No test statistics were found to be significant C denotes a Cochran outlier G denotes a Grubbs outlier
m	18.4767	14.8381	
s^2	0.3714	0.1709	
s	0.6094	0.4135	
Assigned value	18.7	15.0	
Recovery	98.8	98.9	
t	-1.6793	-1.7945	
Sign. level 99.9%	3.8495	3.8495	
Sign. level 99%	2.8453	2.8453	
Sign. level 95%	2.0860	2.0860	

TP, mg/L P

Control of recovery, average of results

Laboratory	Sample pair AB	Outlier
1	1.200	
2	1.200	
3	1.220	
4	1.165	
6	1.223	
7	1.240	
8	1.185	
9	1.165	
10	1.285	
12	1.245	
13	1.210	
15	1.265	
16	1.185	
18	1.125	
19	1.235	
20	1.175	
22	1.240	
23	1.125	
24	1.180	
25	1.157	

Laboratory	Sample pair AB	Outlier
26	1.270	
27	1.095	
28	1.090	
29	1.170	
30	1.180	
31	1.055	C
33	1.208	
36	1.190	
37	1.155	
38	1.230	
39	1.175	
40	1.245	
41	1.190	
42	1.145	
43	1.233	
44	1.160	
45	1.225	
46	1.180	
47	1.140	

Statistical data – Control of recovery			
No of labs	38		**Notes**
No of repl	2		* denotes that there is a significant difference (t-test, 5 %-level) C denotes a Cochran outlier
m	1.1922		
s^2	0.0021		
s	0.0462		
Assigned value	1.21		
Recovery	98.5		
t	-2.3701	*	
Sign. level 99.9%	3.5737		
Sign. level 99%	2.7154		
Sign. level 95%	2.0262		

Cl, mg/L

Control of recovery, average of results

Laboratory	Sample pair AB	Outlier
1	71.4	
2	69.8	
3	73.3	
4	77.0	
7	56.9	G
10	69.7	
13	73.0	
15	73.8	
18	68.3	
19	79.0	C
21	74.0	
22	81.9	
23	69.4	
27	75.1	

Laboratory	Sample pair AB	Outlier
28	69.1	
31	70.5	
33	70.4	
34	71.8	
36	55.7	G
38	73.8	
40	73.4	
41	73.5	
42	70.3	
44	71.5	
45	63.5	
46	71.5	
47	73.8	

Statistical data – Control of recovery		
No of labs	24	**Notes**
No of repl	2	No test statistics were found to be significant C denotes a Cochran outlier G denotes a Grubbs outlier
m	72.0654	
s^2	11.8772	
s	3.4463	
Assigned value	73	
Recovery	98.7	
t	-1.3285	
Sign. level 99.9%	3.7676	
Sign. level 99%	2.8073	
Sign. level 95%	2.0687	

SO_4, mg/L

Control of recovery, average of results

Laboratory	Sample pair AB	Outlier
1	81.0	
3	80.7	
8	73.8	
15	77.8	
19	80.8	
21	83.0	
22	96.6	G
27	81.9	
28	76.4	
31	77.7	
33	77.8	
34	79.8	
38	69.3	
40	81.4	
41	76.9	
42	78.4	
44	85.1	
46	79.5	
47	81.5	

Statistical data – Control of recovery			
No of labs	18		**Notes**
No of repl	2		* denotes that there is a significant difference (t-test, 5 %-level) G denotes a Grubbs outlier
m	79.0376		
s^2	13.0546		
s	3.6131		
Assigned value	81		
Recovery	97.6		
t	-2.3043	*	
Sign. level 99.9%	3.9651		
Sign. level 99%	2.8982		
Sign. level 95%	2.1098		

TSS, mg/L

Control of recovery, average of results

Laboratory	Sample pair AB	Outlier
1	48.70	
2	49.15	
3	48.60	
4	48.40	
6	49.89	
8	49.80	
10	48.35	
13	49.85	
14	47.75	
15	46.10	
16	49.15	
19	48.10	
20	40.70	G
21	47.00	
22	50.60	
23	49.10	
24	49.60	
25	47.85	

Laboratory	Sample pair AB	Outlier
26	50.00	
27	48.50	
28	47.95	
29	48.95	
30	48.25	
31	47.70	
33	48.42	
35	45.95	
36	50.00	
37	49.30	
38	44.30	
39	49.65	
41	48.00	
42	48.50	
43	54.75	G
44	34.00	G
46	47.65	
47	50.10	

	Statistical data – Control of recovery		
	A3	B3	
No of labs	33	33	**Notes**
No of repl	2	2	
m	48.53	51.51	
s^2	3.3903	1.3437	
s	1.8413	1.1592	
Assigned value	49.4	52.4	
Recovery	98.2	98.3	
t	-2.7048	-4.4106 */***	
Sign. level 99.9%	3.6218	3.6218	
Sign. level 99%	2.7385	2.7385	
Sign. level 95%	2.0369	2.0369	

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

G denotes a Grubbs outlier

APPENDIX D CONCENTRATION LEVEL

Parameter	Unit	Sample	Bottle no.	I	II	Bottle Average	Sample Average	Assigned value	Spike Measured	Spike Assigned
COD_{Cr}	mg/L O_2	A1	14	40.4	40.5	40.5	40.8	47	7.57	9
			41	40.7	40.9	40.8				
			71	41.1	40.9	41.0				
		B1	10	32.7	33.5	33.1	33.2	38		
			32	33.8	33.8	33.8				
			60	32.5	32.8	32.7				
Total phosphorus	mg/L P	A2	9	1.21	1.21	1.21	1.24	1.21		
			36	1.25	1.25	1.25				
			72	1.25	1.26	1.26				
		B2	11	1.44	1.43	1.44	1.44	1.42	0.20	0.21
			35	1.46	1.45	1.46				
			52	1.42	1.43	1.43				
Chloride	mg/L	A2*	9	-	-	-	-	73.00		
			36	-	-	-				
			72	-	-	-				
		B2	11	79.1	79.6	79.4	78.1	87.00	-	14
			35	79.0	79.1	79.1				
			52	76.0	75.8	75.9				
Sulphate	mg/L	A2	9	80.0	77.1	78.6	75.7	81.00		
			36	78.0	75.7	76.9				
			72	79.0	75.8	77.4				
		B2	11	95.4	93.5	94.5	94.9	97.00	19.17	16
			35	97.1	95.3	96.2				
			52	94.4	93.5	94.0				
Total suspended solids	mg/L	A3	10	48.94		48.94	48.67	49.40		
			40	47.44		47.44				
			64	49.64		49.64				
		B3	9	52.02		52.02	51.88	52.40	3.21	3
			23	52.32		52.32				
			52	51.30		51.30				

*: Error in preparation

APPENDIX E HOMOGENEITY AND STABILITY

PT: SPIL-3 2025
Parameter: COD A1*
Unit: mg/L O_2
Sigma: 10.8

Responsible for tests: DHBP/S7MS/L5VX
Approval of control test: FYE3

Homogeneity test* Date: 2025-08-27

Sample	x(a)	x(b)	average	sd	sd^2
2	58	55	56.2	2.404	5.780
10	56	57	56.8	0.778	0.60
13	58	58	57.9	0.212	0.045
18	58	58	57.6	0.000	0.000
28	59	58	58.4	0.141	0.020
34	57	57	57.1	0.141	0.020
37	57	58	57.3	0.424	0.180
47	55	55	54.9	0.354	0.125
53	55	56	55.4	0.778	0.605
57	56	56	55.9	0.071	0.005
67	59	56	57.5	1.626	2.645
76	58	57	57.4	0.354	0.125

For homogeneity

General average (x)	56.84
Sample average sd (s_x)	1.067
Within-sample sd (s_w):	0.920
Between-samples sd (ss):	0.8456
S_L in the Proficiency Test:	2.71
S_R in the Proficiency Test:	2.94

Conclusions

ss = 0.846 0.3*sigma= 3.24
/x-y/ = 16.0875

Analytical quality Is s_w < 0,15*sigma **YES**

Homogeneity: Is ss < 0.3*sigma? **YES**

*The ampoules were not diluted according to the preparation instruction for SPIL-3 2025.
The results are not comparable with the proficiency test results.

PT: SPIL-3 2025
Parameter: TP A2
Unit: mg/L P
Sigma: 0.068

Responsible for tests: DHBP/S7MS/L5VX
Approval of control test: FYE3

Homogeneity test Date: 2025-08-27

Sample	x(a)	x(b)	average	sd	sd^2
3	1.25	1.26	1.26	0.007	0.000
10	1.25	1.25	1.25	0.000	0.00
13	1.26	1.26	1.26	0.000	0.000
23	1.23	1.23	1.23	0.000	0.000
29	1.25	1.25	1.25	0.000	0.000
34	1.25	1.24	1.25	0.007	0.000
37	1.25	1.25	1.25	0.000	0.000
43	1.27	1.27	1.27	0.000	0.000
51	1.24	1.24	1.24	0.000	0.000
54	1.28	1.28	1.28	0.000	0.000
62	1.26	1.25	1.26	0.007	0.000
68	1.25	1.25	1.25	0.000	0.000

For homogeneity

General average (x)	1.25
Sample average sd (s_x)	0.013
Within-sample sd (s_w):	0.004
Between-samples sd (ss):	0.0128
S_L in the Proficiency Test:	0.0435
S_R in the Proficiency Test:	0.0489

Stability test Date: 2025-09-11

Sample	x(a)	x(b)
9	1.21	1.21
36	1.25	1.25
72	1.25	1.26

For stability

General average (y):	1.238333
/x-y/ =	0.014583

Conclusions

ss = 0.013 0.3*sigma= 0.02
/x-y/ = 0.014583

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-3 2025
Parameter: TSS A3
Unit: mg/L
Sigma: 3.6

Responsible for tests: DHBP/S7MS/L5VX
Approval of control test: FYE3

Homogeneity test Date: 2025-08-27

Sample	x(a)	x(b)	average	sd	sd^2
2	47.9		47.9		
6	47.8		47.8		
11	49.8		49.8		
20	49.5		49.5		
23	50.0		50.0		
28	50.0		50.0		
38	49.9		49.9		
42	49.3		49.3		
45	49.2		49.2		
52	49.5		49.5		
59	49.9		49.9		
61	50.1		50.1		

For homogeneity

General average (x)	49.4
Sample average sd (s_x)	0.781
Within-sample sd (s_w):	
Between-samples sd (ss):	0.781
S_L in the Proficiency Test:	1.0976
S_R in the Proficiency Test:	1.5327

Stability test Date: 2025-09-11

Sample	x(a)	x(b)
10	48.939	
40	47.443	
64	49.636	

For stability

General average (y):	48.67267
/x-y/ =	0.772498

Conclusions

ss = 0.78 0.3*sigma= 1.08
/x-y/ = 0.772498

Analytical quality Is s_w < 0.15*sigma
No data

Homogeneity: Is ss < 0.3*sigma?
YES

Stability: /x-y/ < 0.3*sigma?
YES