**Proficiency test SPIL-1
(2025)**

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

Proficiency test SPIL-1 (2025)
Quality Documentation

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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 13 March 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 15 April 2025 and a 2nd version of the report were issued to all participants on 23 April 2025.

2 FEATURES OF THE PROFICIENCY TEST

Participants in the proficiency test were a total of 52 laboratories from Brazil, Croatia, Denmark, Finland, Germany, Greece, Japan, the Netherlands, Spain and Sweden.

The closing date for submission of results was 28 March 2025. All participants 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.

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 effluent. 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 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. Assigned values, spike values and uncertainty of the assigned values were calculated in accordance to 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	35	2.1	4
Five day biochemical oxygen demand (w. ATU)	BOD_5 (w. ATU)	mg/L O_2	2-6	4.2	0.46	0.6
Seven day biochemical oxygen demand (w. ATU)	BOD_7 (w. ATU)	mg/L O_2	2-6	4.9	0.27	0.7
Non-volatile/Total organic carbon	NVOC/TOC	mg/L C	2-30	14.1	0.48	1.5
Total phosphorus	TP	mg/L P	0.2-2	0.56	0.013	0.15
Chloride	Cl	mg/L	50-700	114	1.9	14
Sulphate	SO_4	mg/L	20-200	102	1.5	20
Total suspended solids	TSS	mg/L	20-100	24.7	1.5	6.0

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.

The assigned values for all parameters except NVOC/TOC, Cl and SO_4 are operationally defined and are consensus values based upon the median for method no. 3, 76, 77, 91, 92, and similar methods (COD_{Cr}), method no. 1, 2, 5 and similar methods (TP), or method no. 2 (TSS), which are the methods required by the Danish EPA /6/. Assigned values for BOD are based upon standardised methods (method no. 1 – 4 or other standardised methods registered as method 9). A list of method identification numbers is found in the report to participants /1/. Assigned values for NVOC/TOC, Cl and SO_4 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 most parameters. The test revealed a significant difference between the two for TP. 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. 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. The test showed no significant difference between the assigned value and the average value and the control of assigned value at Eurofins confirmed the value (Appendix D).

The test revealed a significant difference between the two for COD_{Cr}. Average recovery was 104 %. 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. 3, 76, 77, 91, 92 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 were tested using the following parameters as indicators:

COD_{Cr}	Combined homogeneity and stability test
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 TP 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.

Furthermore, for COD_{Cr} 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-1 (2025)*, Report to participants, April 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 Equality regulation no. 811 on Quality criteria for environmental measurements, 19 June 2024 (in Danish).

A N N E X E S

APPENDIX A   SAMPLE PREPARATION

Stock solution	Prepared from		Concentration
Concentrate A1	0.925 g 0.925 g	D-glucose L-glutamic acid milli-Q water up to 1000 g	COD_{Cr}: 1.892 g/kg NVOC: 0.747 g/kg BOD: 1.295 g/kg
Concentrate B1	1.154 g 1.154 g	D-glucose L-glutamic acid milli-Q water up to 1000 g	COD_{Cr}: 2.360 g/kg NVOC: 0.932 g/kg BOD: 1.615 g/kg
Stock TP	1.502 g	Na-B.glycerophosphate milli-Q water up to 1000.0 g	TP: 152.0 mg/kg
Stock Cl	10.001 g	Sodium chloride (NaCl) milli-Q water up to 1000.0 g	Cl: 6.072 g/kg
Stock SO_4	10.006 g	Sodium sulphate (Na_2SO_4) milli-Q water up to 1000.0 g	SO_4: 6.7671 g/kg
Stock TSS	15.012 g	Microcrystalline cellulose milli-Q water up to 1000.0 g	TSS: 15.012 g/kg

Sample	Sample prepared from	COD$_{Cr}$ mg/L O$_2$	NVOC mg/L C	BOD (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 2.00 mL of concentrate A1 is diluted up to 250.0 mL with filtered water from Holsted sewage treatment plant	a + 15.1	b + 5.98					
B1-COD/NVOC	At the laboratory 2.00 mL of concentrate B1 is diluted up to 250.0 mL with filtered water from Holsted sewage treatment plant	a + 18.9	b + 7.46					
A1-BOD	At the laboratory 4.00 mL of concentrate A1 is diluted up to 2000.0 mL with filtered water from Holsted sewage treatment plant			c + 2.59				
B1-BOD	At the laboratory 4.00 mL of concentrate B1 is diluted up to 2000.0 mL with filtered water from Holsted sewage treatment plant			c + 3.23				
A2	40.1 g stock TP 100.0 g stock Cl 125.1 g stock SO$_4$ Sample B2 up to 40.0 kg				0.993· (d+0.326) + 0.152	0.993· (e+17.35) + 15.18	0.993· (f+67.75) + 21.16	
B2	150.0 g stock TP 200.0 g stock Cl 700.8 g stock SO$_4$ filtered water from Holsted sewage treatment plant up to 70.0 kg				d + 0.326	e + 17.35	f + 67.75	
A3	At the laboratory 1000.0 mL of filtered water from Holsted sewage treatment plant is added to 1.7 mL stock TSS							g + 25.5
B3	At the laboratory 1000.0 mL of filtered water from Holsted sewage treatment plant is added to 2.1 mL stock TSS							g + 31.5

APPENDIX B   CONTROL OF SPIKE VALUES

COD_{Cr}, mg/L O_2
Control of differences within sample pairs

Laboratory	Difference AB	Outlier
1	1.9	
2	-2.3	
3	3.0	
4	-4.0	
5	-0.3	
6	-2.2	
7	-2.7	
10	5.8	
13	-0.3	
15	-3.5	
16	8.0	
17	0.5	
19	0.5	
20	0.1	
22	-1.0	
24	1.3	
25	2.2	
26	-2.1	
27	-4.2	
29	0.4	
30	-1.0	
31	-3.1	
33	0.0	
34	-2.3	
36	0.8	
37	-0.1	

Laboratory	Difference AB	Outlier
38	2.6	
39	1.9	
41	0.7	
42	1.0	
43	0.0	
44	5.0	
45	-0.4	
49	-	U
51	-2.0	
52	-2.4	

No of labs, p	35
No of repl, n	2
d	0.0520
s²	7.3476
s	2.7106
t	0.1135
Sign. level 99.9%	3.6007
Sign. level 99%	2.7284
Sign. level 95%	2.0322

No test statistics were found to be significant

U denote a manual selected outlier

BOD₅ (w. ATU), mg/L O₂

Control of differences within sample pairs

Laboratory	Difference AB	Outlier
4	-0.04	
5	0.09	
6	0.43	
15	0.80	
16	0.40	
25	0.69	
29	-0.10	
30	-	
33	-	
34	0.04	
35	0.20	
36	-0.10	
38	0.09	
41	0.10	
44	-0.53	
47	0.25	
52	-0.40	

No of labs, p	15
No of repl, n	2
d	0.1277
s²	0.1292
s	0.3594
t	1.3757
Sign. level 99.9%	4.1405
Sign. level 99%	2.9768
Sign. level 95%	2.1448

No test statistics were found to be significant

BOD$_7$ (w. ATU), mg/L O$_2$
Control of differences within sample pairs

Laboratory	Difference AB	Outlier
2	-0.04	
4	0.02	
6	0.28	
8	-0.30	
11	-0.07	
15	0.20	
21	0.15	
23	0.41	
25	0.70	
31	-0.10	
32	-0.02	
34	-0.06	
37	0.00	
40	-0.04	
42	0.45	

No of labs, p	15
No of repl, n	2
d	0.1053
s²	0.0677
s	0.2602
t	1.5681
Sign. level 99.9%	4.1405
Sign. level 99%	2.9768
Sign. level 95%	2.1448

No test statistics were found to be significant

NVOC/TOC, mg/l C
Control of differences with sample pairs

Laboratory	Difference AB	Outlier
3	0.42	
4	0.00	
5	0.10	
6	0.00	
7	0.20	
8	-0.10	
10	-0.52	
11	-1.30	
12	-0.77	
15	0.06	
18	-0.10	
20	0.28	
21	1.43	
23	0.20	
25	-0.10	
26	0.81	
27	-0.20	
28	-0.40	
29	-1.31	
30	0.50	
31	0.60	
32	-0.35	
34	-0.32	
35	-0.43	
38	0.30	
40	0.11	
41	0.00	
43	0.32	
44	0.78	
45	0.50	
46	0.41	
47	0.37	
48	0.30	
52	-1.00	

No of labs, p	34
No of repl, n	2
d	0.0233
s^2	0.3337
s	0.5776
t	0.2355
Sign. level 99.9%	3.6109
Sign. level 99%	2.7333
Sign. level 95%	2.0345

No test statistics were found to be significant

TP, mg/l P
Control of differences within sample pairs

Laboratory	Difference AB	Outlier
1	-0.005	
2	0.006	
3	-0.009	
4	-0.014	
5	0.000	
6	-0.007	
7	0.006	
8	-0.012	
10	-0.013	
11	-0.002	
12	-0.064	
13	-0.010	
14	-0.020	
15	0.000	
16	-0.005	
17	0.002	
18	-0.017	
19	-0.016	
20	-0.020	
21	0.003	
22	-0.324	C
23	0.038	
24	-0.005	
25	0.007	
26	-0.007	
27	-0.004	
28	-0.020	
29	0.050	
30	-0.060	
31	-0.004	
33	0.040	
34	-0.031	
35	0.014	
36	-0.021	
37	-0.008	
38	-0.070	
39	-0.004	
40	-0.021	
41	0.000	
43	-0.050	G

Laboratory	Difference AB	Outlier
44	-0.047	
45	0.001	
46	0.017	
47	0.004	
48	-0.014	
49	-0.013	
51	-0.016	
52	-0.010	

No of labs, p	46
No of repl, n	2
d	-0.0083
s²	0.0005
s	0.0227
t	-2.4759 *
Sign. level 99.9%	3.5203
Sign. level 99%	2.6896
Sign. level 95%	2.0141

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

C denotes a Cochran outlier
G denotes a Grubbs outlier

Cl, mg/L

Control of differences within sample pairs

Laboratory	Difference AB	Outlier
1	0.0	
4	5.0	
5	0.5	
6	-1.0	
9	4.9	
10	0.5	
13	12.4	C
15	1.5	
16	0.0	
20	1.8	
22	-0.4	
24	11.0	C
25	0.0	
26	0.8	
29	0.5	
30	2.0	
33	0.2	
34	0.5	
35	3.5	
36	0.0	
38	2.0	
39	0.2	
40	2.0	
41	0.0	
44	0.1	
46	-2.0	
47	-0.6	
49	-3.9	
50	0.0	
52	0.0	

No of labs, p	28
No of repl, n	2
d	0.6442
s^2	3.3199
s	1.8221
t	1.8707
Sign. level 99.9%	3.6896
Sign. level 99%	2.7707
Sign. level 95%	2.0518

No test statistics were found to be significant

C denotes a Cochran outlier

SO$_4$, mg/L
Control of differences within sample pairs

Laboratory	Difference AB	Outlier
4	-0.4	
5	4.8	
6	0.0	
7	-2.0	
9	11.3	
15	1.2	
16	1.0	
20	-4.0	
25	1.7	
26	-1.0	
29	0.1	
30	3.0	
34	0.8	
35	-9.2	
38	1.0	
39	0.2	
41	-1.0	
44	-0.0	
46	-2.3	
50	0.0	
52	-3.0	

No of labs, p	21
No of repl, n	2
d	0.1011
s²	14.3431
s	3.7872
t	0.1223
Sign. level 99.9%	3.8495
Sign. level 99%	2.8453
Sign. level 95%	2.0860

No test statistics were found to be significant

TSS, mg/L
Control of differences within sample pairs

Laboratory	Difference AB	Outlier
2	0.10	
3	1.00	
4	0.00	
5	-0.44	
6	-0.40	
7	0.40	
8	-1.70	
9	-0.50	
10	0.50	
11	-1.30	
12	0.10	
15	2.83	
16	0.00	
17	0.00	
18	-0.10	
20	0.50	
21	-1.10	
23	1.10	
25	0.00	
26	-2.00	
27	2.40	
28	0.00	
29	0.30	
30	0.00	
31	1.50	
32	0.10	
33	1.80	
34	0.70	
36	0.40	

Laboratory	Difference AB	Outlier
37	0.30	
38	0.20	
40	0.20	
41	3.80	
42	0.00	
43	2.40	
44	8.00	C
45	0.20	
46	0.50	
47	0.00	
48	-1.60	
49	1.00	
51	0.60	
52	0.20	

No of labs, p	42
No of repl, n	2
d	0.3331
s^2	1.2991
s	1.1398
t	1.8940
Sign. level 99.9%	3.5442
Sign. level 99%	2.7012
Sign. level 95%	2.0195

No test statistics were found to be significant

C denotes a Cochran outlier

APPENDIX C   CONTROL OF RECOVERY

COD_{Cr}, mg/L O_2
Control of recovery, average of results

Laboratory	Sample pair AB	Outlier
1	34.8	
2	38.1	
3	43.4	
4	33.0	
5	33.1	
6	31.7	
7	37.8	
10	38.7	
13	35.4	
15	38.3	
16	30.0	
17	42.5	
19	33.6	
20	34.3	
22	36.2	
24	34.7	
25	34.5	
26	44.2	
27	38.5	
29	38.9	
30	34.5	
31	31.6	
33	34.9	
34	41.2	
36	37.9	
37	39.3	
38	38.4	
39	36.2	
41	34.3	
42	31.5	
43	33.0	
44	37.5	
45	40.8	
49	-	U
51	32.0	
52	39.6	

No of labs, p	35
No of repl, n	2
m	36.3954
s^2	12.8201
s	3.5805
Assigned value, μ	35
Recovery, %	104.0
t	2.3057 *
Sign. level 99.9%	3.6007
Sign. level 99%	2.7284
Sign. level 95%	2.0322

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

U denote a manual selected outlier

BOD$_5$ (w. ATU), mg/L O$_2$
Control of recovery, average of results

Laboratory	Sample pair AB	Outlier
4	4.71	
5	3.64	
6	3.84	
15	5.70	
16	4.70	
25	3.72	
29	4.15	
30	-	
33	-	
34	4.41	
35	5.21	
36	4.45	
38	3.73	
41	3.25	
44	4.14	
47	4.48	
52	3.10	

No of labs, p	15
No of repl, n	2
m	4.2140
s²	0.4989
s	0.7063
Assigned value, µ	4.2
Recovery, %	100.3
t	0.0770
Sign. level 99.9%	4.1405
Sign. level 99%	2.9768
Sign. level 95%	2.1448

No test statistics were found to be significant

BOD$_7$ (w. ATU), mg/L O$_2$
Control of recovery, average of results

Laboratory	Sample pair AB	Outlier
2	5.02	
4	5.01	
6	3.92	
8	4.20	
11	5.36	
15	6.40	
21	5.19	
23	4.93	
25	4.49	
31	4.55	
32	5.10	
34	4.69	
37	5.30	
40	4.30	
42	5.04	

No of labs, p	15
No of repl, n	2
m	4.8987
s²	0.3520
s	0.5933
Assigned value, µ	4.9
Recovery, %	100.0
t	-0.0087
Sign. level 99.9%	4.1405
Sign. level 99%	2.9768
Sign. level 95%	2.1448

No test statistics were found to be significant

NVOC/TOC, mg/l C
Control of recovery, average of results

Laboratory	Sample pair AB	Outlier
3	16.11	
4	14.70	
5	13.64	
6	13.60	
7	13.80	
8	13.75	
10	16.34	
11	15.15	
12	14.13	
15	14.79	
18	15.55	
20	13.78	
21	14.61	
23	13.20	
25	13.05	
26	15.30	
27	13.40	
28	14.00	
29	15.11	
30	17.75	
31	13.70	
32	14.67	
34	14.08	
35	14.96	

Laboratory	Sample pair AB	Outlier
38	12.95	
40	16.22	
41	13.90	
43	13.67	
44	11.58	
45	13.85	
46	15.66	
47	14.17	
48	13.45	
52	14.70	

No of labs, p	34
No of repl, n	2
m	14.3907
s^2	1.4026
s	1.1843
Assigned value, μ	14.1
Recovery, %	102.1
t	1.4311
Sign. level 99.9%	3.6109
Sign. level 99%	2.7333
Sign. level 95%	2.0345

No test statistics were found to be significant

TP, mg/l P

Control of differences within sample pairs

Laboratory	Sample pair AB	Outlier
1	0.579	
2	0.581	
3	0.548	
4	0.537	
5	0.510	
6	0.561	
7	0.564	
8	0.576	
10	0.567	
11	0.554	
12	0.556	
13	0.558	
14	0.570	
15	0.585	
16	0.546	
17	0.553	
18	0.563	
19	0.536	
20	0.560	
21	0.571	
22	0.742	C
23	0.579	
24	0.563	
25	0.657	
26	0.569	
27	0.566	
28	0.540	
29	0.605	
30	0.620	
31	0.566	
33	0.560	
34	0.524	
35	0.583	
36	0.557	
37	0.568	
38	0.555	
39	0.599	
40	0.544	
41	0.570	
43	0.675	G

Laboratory	Sample pair AB	Outlier
44	0.561	
45	0.533	
46	0.575	
47	0.570	
48	0.536	
49	0.629	
51	0.525	
52	0.575	

No of labs, p	46
No of repl, n	2
m	0.5652
s^2	0.0007
s	0.0268
Assigned value, μ	0.56
Recovery, %	100.9
t	1.3250
Sign. level 99.9%	3.5203
Sign. level 99%	2.6896
Sign. level 95%	2.0141

No test statistics were found to be significant

C denotes a Cochran outlier
G denotes a Grubbs outlier

Cl, mg/L
Control of differences within sample pairs

Laboratory	Sample pair AB	Outlier
1	118.0	
4	117.5	
5	104.5	
6	114.5	
9	123.3	
10	113.7	
13	102.8	C
15	120.2	
16	116.0	
20	97.1	
22	99.2	
24	120.5	C
25	118.0	
26	113.8	
29	113.9	
30	120.0	
33	119.0	
34	114.3	
35	112.7	
36	102.0	
38	106.0	
39	112.9	
40	115.0	

Laboratory	Sample pair AB	Outlier
41	113.0	
44	114.0	
46	109.6	
47	115.0	
49	114.1	
50	118.0	
52	117.0	

No of labs, p	28
No of repl, n	2
m	113.2854
s²	39.7493
s	6.3047
Assigned value, μ	114
Recovery, %	99.4
t	-0.5998
Sign. level 99.9%	3.6896
Sign. level 99%	2.7707
Sign. level 95%	2.0518

No test statistics were found to be significant

C denotes a Cochran outlier

SO$_4$, mg/L
Control of recovery, average of results

Laboratory	Sample pair AB	Outlier
4	99.2	
5	112.2	
6	101.0	
7	108.0	
9	94.3	
15	107.8	
16	104.5	
20	103.0	
25	99.2	
26	96.6	
29	102.6	
30	105.5	
34	104.4	
35	103.7	
38	106.5	
39	100.9	
41	99.5	
44	100.1	
46	93.6	
50	106.0	
52	101.5	

No of labs, p	21
No of repl, n	2
m	102.3782
s²	21.1571
s	4.5997
Assigned value, µ	102
Recovery, %	100.4
t	0.3768
Sign. level 99.9%	3.8495
Sign. level 99%	2.8453
Sign. level 95%	2.0860

No test statistics were found to be significant

TSS, mg/L
Control of recovery, average of results

Laboratory	Sample pair AB	Outlier
2	25.15	
3	23.50	
4	25.00	
5	24.89	
6	23.90	
7	24.90	
8	24.95	
9	23.75	
10	24.45	
11	24.15	
12	24.55	
15	24.59	
16	25.00	
17	22.40	
18	24.05	
20	23.25	
21	26.55	
23	24.15	
25	24.90	
26	26.00	
27	23.80	
28	24.00	
29	25.15	
30	26.00	
31	25.09	
32	24.85	
33	24.70	
34	23.95	
36	26.50	
37	24.75	
38	26.20	
40	24.70	
41	23.10	
42	22.50	
43	25.90	
44	18.10	C
45	24.90	
46	24.65	
47	25.00	
48	22.90	

Laboratory	Sample pair AB	Outlier
49	25.50	
51	23.90	
52	23.40	

No of labs, p	42
No of repl, n	2
m	24.5599
s²	0.9989
s	0.9994
Assigned value, µ	24.7
Recovery, %	99.4
t	-0.9086
Sign. level 99.9%	3.5442
Sign. level 99%	2.7012
Sign. level 95%	2.0195

No test statistics were found to be significant

C denotes a Cochran 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	13-15	35.4	33.8	34.6	34.0	35	1.5	4
			41-46	34.0	32.9	33.5				
			62-73	33.7	34.0	33.9				
		B1	13-8	37.5	36.4	37.0	35.5	39		
			29-26	35.8	34.2	35.0				
			59-53	35.0	33.9	34.5				
Total phosphorus	mg/L P	A2	3	0.735	0.735	0.74	0.73	0.71	0.15	0.15
			33	0.729	0.730	0.73				
			66	0.728	0.727	0.73				
		B2	11	0.592	0.592	0.59	0.58	0.56		
			29	0.576	0.576	0.58				
			52	0.583	0.583	0.58				
Chloride	mg/L	A2	3	88.4	88.6	88.5	88.5	128.00	17.3	14
			33	89.7	90.3	90.0				
			66	86.9	87.0	87.0				
		B2	11	71.6	71.4	71.5	71.2	114.00		
			29	70.9	70.8	70.9				
			52	-	-	-				
Sulphate	mg/L	A2	3	116	115	116	117	122	13	20
			33	118	117	118				
			66	118	117	118				
		B2	11	104	103	104	104	102		
			29	105	104	105				
			52	103	103	103				
Total suspended solids	mg/L	A3	11-13	25.05		25.05	24.86	24.70	6.61	6
			35-30	25.36		25.36				
			50-47	24.16		24.16				
		B3	14-5	31.93		31.93	31.47	30.70		
			47-39	30.94		30.94				
			67-66	31.53		31.53				

APPENDIX E   HOMOGENEITY AND STABILITY

PT:	SPIL-1
Parameter:	COD_{Cr}
Unit:	mg/L O_2
Sigma:	10.8

Responsible for tests: DHBP/RQ8G

Approval of controltest: FYE3

Homogeneity test   Date: 2025-02-27

Sample	x(a)	x(b)	average	sd	sd^2
A1-3-4	35	34	34.8	0.566	0.320
10-12	35	34	34.7	0.990	0.98
16-13	36	35	35.4	0.849	0.720
24-23	35	35	35.2	0.071	0.005
30-28	37	35	35.7	1.131	1.280
36-35	35	35	35.1	0.071	0.005
39-43	35	35	34.9	0.212	0.045
45-44	36	34	34.7	1.344	1.805
50-53	35	34	34.7	0.636	0.405
58-59	36	35	35.4	0.283	0.080
64-63	33	34	33.5	0.636	0.405
71-70	35	33	33.7	1.485	2.205

Stability test   Date: 2025-03-13

Sample	x(a)	x(b)
13-15	35.4	33.8
41-46	34	32.9
62-73	33.7	34

For stability

General average (y):	33.96667
/x-y/ =	0.820833

For homogeneity

General average (x)	34.79
Sample average sd (s_x)	0.668
Within-sample sd (s_w):	0.829
Between-samples sd (ss):	0.3208
S_L in the Proficiency Test:	3.3219
S_R in the Proficiency Test:	3.8217

Conclusions

ss = 0.321	0.3*sigma= 3.24
/x-y/ = 0.820833	

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-1
Parameter:	TP
Unit:	mg/L P
Sigma:	0.039

Responsible for tests:	DHBP/RQ8G
Approval of controltest	FYE3

Homogeneity test   Date: 2025-02-25

Sample	x(a)	x(b)	average	sd	sd^2
5	0.73	0.73	0.7	0.001	0.000
11	0.72	0.73	0.7	0.001	0.00
17	0.72	0.72	0.7	0.000	0.000
19	0.73	0.73	0.7	0.001	0.000
26	0.72	0.72	0.7	0.000	0.000
32	0.73	0.72	0.7	0.001	0.000
40	0.71	0.71	0.7	0.000	0.000
45	0.72	0.73	0.7	0.001	0.000
51	0.71	0.71	0.7	0.000	0.000
56	0.73	0.73	0.7	0.000	0.000
64	0.73	0.73	0.7	0.000	0.000
75	0.73	0.73	0.7	0.000	0.000

For homogeneity

General average (x)	0.72
Sample average sd (s_x)	0.007
Within-sample sd (s_w):	0.001
Between-samples sd (ss):	0.0071
S_L in the Proficiency Test:	0.024
S_R in the Proficiency Test:	0.0294

Stability test   Date: 2025-03-13

Sample	x(a)	x(b)
3	0.735	0.735
33	0.729	0.73
66	0.728	0.727

For stability

General average (y):	0.730667
/x-y/ =	0.007833

Conclusions

ss =	0.007	0.3*sigma=	0.01
/x-y/ =	0.007833		

Analytical	Is s_w < 0.15*sigma
quality	**YES**
Homogeneity:	Is ss < 0.3*sigma?
	YES
Stability:	/x-y/ < 0.3*sigma?
	YES

PT:	SPIL-1
Parameter:	TSS
Unit:	mg/L
Sigma:	3.6

Responsible for tests:	DHBP/RQ8G
Approval of controltest:	FYE3

Homogeneity test   Date: 2025-02-25

Sample	x(a)	x(b)	average	sd	sd^2
B3-2-1	32.2		32.2		
9-10	31.9		31.9		
15-15	32.0		32.0		
18-18	32.1		32.1		
26-28	31.5		31.5		
32-31	31.7		31.7		
35-37	31.7		31.7		
46-44	31.7		31.7		
49-52	32.7		32.7		
54-56	32.2		32.2		
63-60	31.7		31.7		
69-70	31.8		31.8		

Stability test   Date: 2025-03-13

Sample	x(a)	x(b)
14-5	31.93	
47-39	30.94	
67-66	31.53	

For stability

General average (y):	31.46667
/x-y/ =	0.466667

For homogeneity

General average (x)	31.9
Sample average sd (s_x)	0.328
Within-sample sd (s_w):	
Between-samples sd (ss):	0.328
S_L in the Proficiency Test:	0.8088
S_R in the Proficiency Test:	1.1592

Conclusions

ss = 0.33	0.3*sigma= 1.08
/x-y/ = 0.466667	

Analytical	Is s_w < 0.15*sigma
quality	**No data**
Homogeneity:	Is ss < 0.3*sigma?
	YES
Stability:	/x-y/ < 0.3*sigma?
	YES