



Proficiency test SPIL-1 (2024)

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

**Quality Documentation
May 2024**

Proficiency test SPIL-1 (2024) Quality Documentation

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1 INTRODUCTION

A proficiency test on the analysis of organic matter, phosphorus, chloride, sulphate and suspended matter in wastewater was conducted on 14 March 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 23 April 2024.

2 FEATURES OF THE PROFICIENCY TEST

Participants in the proficiency test were a total of 58 laboratories from Brazil, Croatia, Denmark, Faroe Islands, Finland, Germany, Greece, Japan, Netherlands, Norway, Spain and Sweden.

The closing date for submission of results was 5 April 2024. All participants except laboratory no 3 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.

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 Annex A.

Table 1 Samples in the proficiency test

Sample name	Parameters
A1/B1 BOD	BOD ₅ (w. ATU), BOD ₇ (w. ATU)
A1/B1 COD	COD _{Cr} , NVOC/TOC
A2/B2	TP, Cl, 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/ 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
Chemical oxygen demand – dichromate method	COD _{Cr}	mg/L O ₂	5-75	29	1.8	4
Five day biochemical oxygen demand (w. ATU)	BOD ₅ (w. ATU)	mg/L O ₂	2-6	3.2	0.41	0.7
Seven day biochemical oxygen demand (w. ATU)	BOD ₇ (w. ATU)	mg/L O ₂	2-6	3.5	0.21	0.7
Non-volatile/Total organic carbon	NVOC/TOC	mg/L C	2-30	11.6	0.34	1.5
Total phosphorus	TP	mg/L P	0.2-2	1.59	0.028	0.26
Chloride	Cl	mg/L	50-700	345	7.2	59
Sulphate	SO ₄	mg/L	20-200	88	1.4	11
Total suspended matter	TSS	mg/L	20-100	57.8	2.5	10.0

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 values for all parameters except NVOC/TOC, Cl and SO₄ are operationally defined and are consensus values based upon the median for method no. 76, 77, 77A, 91 and 92 (COD_{Cr}), method no. 1, 2 and 5 (TP), or method no. 1 and 2 (TSS), which are the methods required by the Danish EPA /5/. Assigned values for BOD are based upon standardised methods (method no. 1 - 4). A list of method identification numbers is found in the report to participants /1/. Assigned values for NVOC/TOC, Cl and SO₄ 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 Annex C. The test showed no significant difference between the spike value and the difference in concentration between the two samples for most parameters. The test showed a significant difference for the COD_{Cr} sample pair. However, the difference is small compared to the rounding of the calculated spike and assigned value. The test of spike value for the BOD₅ (w. ATU) sample pair showed a difference, but since the test for BOD₇ (w. ATU) did not confirm this, the difference is accepted and the calculated spike value 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 Annex D. The test showed no significant difference between the two and the control of assigned value at Eurofins confirmed the value (Annex E).

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 Annex F. The annex 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 ($0.3 * \hat{\sigma}$) specified by the Danish EPA /5/, whereas the stability is evaluated by comparing the concentration change of the samples to $0.3 * \hat{\sigma}$ 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 /6/.

The annex 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 COD_{Cr} and BOD₅ (w. ATU) the participants did not recover the spiked value. Eurofins' scrutiny of the combined evidence gave the conclusion that the prepared spiked value is correct. The spike values for COD_{Cr} and BOD₅ (w. ATU) are 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 (2024)*, Report to participants, April 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 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
Concentrate A1	0.925 g D-glucose 0.925 g L-glutamic acid milli-Q water up to 1000 g	COD _{Cr} : 1.892 g/kg NVOC: 0.747 g/kg BOD ₅ : 1.295 g/kg
Concentrate B1	0.738 g D-glucose 0.738 g L-glutamic acid milli-Q water up to 1000 g	COD _{Cr} : 1.510 g/kg NVOC: 0.597 g/kg BOD ₅ : 1.034 g/kg
Stock TP	1.500 g Na-B.glycerophosphate milli-Q water up to 1000.0 g	TP: 151.8 mg/kg
Stock Cl	50.000 g Sodium chloride (NaCl) milli-Q water up to 1000.0 g	Cl: 30.333 g/kg
Stock SO ₄	10.000 g Sodium sulphate (Na ₂ SO ₄) milli-Q water up to 1000.0 g	SO ₄ : 6.759 g/kg
Stock TSS	20.000 g Microcrystalline cellulose milli-Q water up to 1000.0 g	TSS: 20.000 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 2.00 mL of concentrate A1 is diluted up to 200.0 mL with filtered water from Holsted sewage treatment plant	a + 18.9	b + 7.47					
B1-COD/NVOC	At the laboratory 2.00 mL of concentrate B1 is diluted up to 200.0 mL with filtered water from Holsted sewage treatment plant	a + 15.1	b + 5.97					
A1-BOD	At the laboratory 5.00 mL of concentrate A1 is diluted up to 2000.0 mL with filtered water from Holsted sewage treatment plant			c + 3.24				
B1-BOD	At the laboratory 5.00 mL of concentrate B1 is diluted up to 2000.0 mL with filtered water from Holsted sewage treatment plant			c + 2.59				
A2	700.0 g stock TP 700.0 g stock Cl 600.0 g stock SO ₄ filtered water from Holsted sewage treatment plant up to 70.0 kg				d + 1.518	e + 303	f + 57.9	
B2	70.00 g stock TP 80.00 g stock Cl 70.00 g stock SO ₄ water from Sample B2 up to 40.0 kg				0.994 · (d + 1.518) + 0.266	0.994 · (e + 303) + 60.7	0.994 · (f + 57.9) + 11.8	
A3	At the laboratory 1000.0 mL of filtered water from Holsted sewage treatment plant is added to 3.0 mL stock TSS							g + 59.8
B3	At the laboratory 1000.0 mL of filtered water from Holsted sewage treatment plant is added to 3.5 mL stock TSS							g + 69.8

ANNEX B CONTROL OF SPIKE VALUES

COD_{Cr} , mg/L O_2

Control of differences within sample pairs

Laboratory	Difference AB	Outlier
1	1,3	
2	3,9	
4	-1,4	
5	0,5	
6	-3,4	
7	-1,2	
8	1,9	UG
9	-0,5	
10	-2,3	
11	0,7	
12	-0,5	
13	-2,9	
14	-0,2	
15	-	
17	1,7	
18	0,4	
19	0,6	
20	-3,8	
21	-1,3	
25	-2	
26	1	
28	-12,7	UC
30	-0,2	
31	2	
33	-	
36	-0,9	
37	-0,6	
38	1	
40	-1,2	

Laboratory	Difference AB	Outlier
43	-1,3	
44	-1,2	
45	-1,9	
47	-2	
49	-1,7	
50	-1,7	
51	-1,7	
52	-6	
53	0	
55	-0,05	
56	3,4	
57	-3,8	
58	-0,45	
No of labs	p	38
No of repl	n	2
d	-0,7	
s ²	3,8	
s	1,9	
t	-2,3063	*
Sign. level 99.9%	3,5737	
Sign. level 99%	2,7154	
Sign. level 95%	2,0262	

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

U denote a manual selected outlier
 UC denotes a Cochran outlier
 UG denotes a Grubbs outlier

BOD₅ (w. ATU), mg/L O₂

Control of differences within sample pairs

Laboratory	Difference AB	Outlier
1	-0,513	UG
5	-	
6	-0,9	
12	-0,67	
17	-0,15	
19	0,12	
21	-0,92	
26	0,35	
31	-0,36	
36	-1,3	
38	-0,4	
44	0,3	
46	-0,4951	
50	0,3	
52	-0,3	
53	-0,9	
57	-	
No of labs	p	14
No of repl	n	2
d	-0,38	
s ²	0,27	
s	0,52	
t	-2,7258	*
Sign. level 99.9%	4,2208	
Sign. level 99%	3,0123	
Sign. level 95%	2,1604	

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

U denote a manual selected outlier

UC denotes a Cochran outlier

UG denotes a Grubbs outlier

BOD₇ (w. ATU), mg/L O₂

Control of differences within sample pairs

Laboratory	Difference AB	Outlier
7	-0,23	
11	-0,2	
13	0,16	UG
14	-0,02	
15	0,12	
16	-0,23	
17	-0,05	
19	-1,06	UC
21	0,05	
26	0,01	
29	0,1	
31	-0,15	
32	-0,23	
33	0,67	
35	0,3	
41	0,2	
43	-0,22	
No of labs	p	15
No of repl	n	2
d	0,01	
s ²	0,06	
s	0,25	
t	0,1238	
Sign. level 99.9%	4,1405	
Sign. level 99%	2,9768	
Sign. level 95%	2,1448	

No test statistics were found to be significant

U denote a manual selected outlier

UC denotes a Cochran outlier

UG denotes a Grubbs outlier

NVOC/TOC, mg/L C

Control of differences with sample pairs

Laboratory	Difference AB	Outlier
2	0,33	
7	0,8	UG
8	-0,19	
11	0,1	
12	0,14	UG
16	-0,1	
17	-1,2	UG
19	0,1	
20	-0,2	
21	-0,34	
22	0,41	
23	-0,04	
24	-0,52	
26	-0,1	
27	-0,1	
29	-1,07	
30	0,04	
31	0	
32	-0,63	
34	0,03	
35	1,3	
36	0,5	
38	0,08	
39	0,16	
40	0,3	

Laboratory	Difference AB	Outlier
41	0,1	
42	-0,49	
44	-0,8	
46	0,12	
48	-0,32	
51	-0,2	
52	-0,1	
54	-1	
57	0,64	
No of labs	p	31
No of repl	n	2
d	-0,064	
s ²	0,225	
s	0,474	
t	-0,7543	
Sign. level 99.9%	3,6460	
Sign. level 99%	2,7500	
Sign. level 95%	2,0423	

No test statistics were found to be significant

U denote a manual selected outlier

UC denotes a Cochran outlier

UG denotes a Grubbs outlier

TP, mg/L P

Control of differences within sample pairs

Laboratory	Difference AB	Outlier
1	0,17	
2	0,14	
4	-0,05	
5	0,00082	
6	-0,02	
7	0,025	
8	0,08	
9	0,01	
10	-0,01	
11	0,107	UG
12	0	
13	0	
14	0	
15	-0,02	
16	-0,02	
17	-0,03	
18	0,03	
19	0,01	
20	0,12	
21	-0,01	
22	-0,01	
23	-0,04	
24	0,022	
25	0,02	
26	0,01	
27	-0,021	
28	0,13	
29	-0,005	
30	-0,01	
31	0	
32	0	
33	0,02	
34	-0,18	
35	0,004	
36	0,07	
37	0,13	

Laboratory	Difference AB	Outlier
38	-0,04	
39	0,06	
40	-0,06	
41	0	
42	-0,002	
43	-0,01	
44	0,26	
45	0,17	
46	-0,081	UG
47	0,004	
48	0,13	
49	0,07	
50	-0,034	
51	0,01	
52	-0,011	
53	-0,02	
54	-0,04	
55	-1,845	UC
56	-0,02	
57	0	
58	-0,04	UG
No of labs	p	53
No of repl	n	2
d	0,019	
s ²	0,005	
s	0,071	
t	2,0007	
Sign. level 99.9%	3,4877	
Sign. level 99%	2,6737	
Sign. level 95%	2,0066	

No test statistics were found to be significant

U denote a manual selected outlier
UC denotes a Cochran outlier
UG denotes a Grubbs outlier

Cl, mg/L

Control of differences within sample pairs

Laboratory	Difference AB	Outlier
1	2	
2	7,22	
4	23	
6	-2	
9	-6	
12	5,28	
17	1	
18	5	
19	3	
21	8,5	
25	-2	
26	-2,5	
27	-2,26	
30	5,07	
31	3	
36	-1	
37	-37	
38	-21,2	
40	1	
44	2,1	
46	-3	
47	-14	

Laboratory	Difference AB	Outlier
49	-10	
50	-8	
51	12	
53	-3	
56	-1,4	
57	0,697	
58	29,8	
No of labs	p	27
No of repl	n	2
d	1,4	
s ²	99,6	
s	10,0	
t	0,7389	
Sign. level 99.9%	3,7066	
Sign. level 99%	2,7787	
Sign. level 95%	2,0555	

No test statistics were found to be significant

U denote a manual selected outlier

UC denotes a Cochran outlier

UG denotes a Grubbs outlier

SO₄, mg/L

Control of differences within sample pairs

Laboratory	Difference AB	Outlier
2	-0,22	
9	4,3	
12	-2,04	
17	0,1	
19	0,7	
20	0,5	
21	1,5	
26	-1	
27	-2,17	
31	-0,1	
36	-1,2	
38	-2,815	
40	0,3	
44	0,1	
50	0,8	
51	-1	
57	3,783	
58	3,1	
No of labs	p	18
No of repl	n	2
d	0,3	
s ²	3,8	
s	2,0	
t	0,5580	
Sign. level 99.9%	3,9651	
Sign. level 99%	2,8982	
Sign. level 95%	2,1098	

No test statistics were found to be significant

U denote a manual selected outlier

UC denotes a Cochran outlier

UG denotes a Grubbs outlier

TSS, mg/L

Control of differences within sample pairs

Laboratory	Difference AB	Outlier
1	-2	
2	10	UG
6	-2	
8	0,3	
10	-1,6	
11	0,4	
12	-1,2	
13	-0,6	
14	0,5	
15	0,4	
16	-0,6	
17	0,8	
19	3,6	
20	-0,6	
21	-0,8	
23	0,1	
26	0,1	
27	-0,55	
28	-0,1	
29	-0,1	
30	-0,4	
31	0	
32	3,3	
33	-0,6	
34	0,1	
35	-6,6	UG
36	-0,3	
38	5	UG
39	1	
41	-7,9	

Laboratory	Difference AB	Outlier
42	-1,2	
43	-0,1	
44	-2,1	
45	-0,7	
48	0,22	
50	1,2	
51	-1,25	
52	9,4	UG
53	-1	
55	1,8	
56	-1,4	
57	0,9	
58	-2,5	
No of labs	p	39
No of repl	n	2
d	-0,38	
s ²	3,16	
s	1,78	
t	-1,3396	
Sign. level 99.9%	3,5657	
Sign. level 99%	2,7116	
Sign. level 95%	2,0244	

No test statistics were found to be significant

U denote a manual selected outlier

UC denotes a Cochran outlier

UG denotes a Grubbs outlier

ANNEX C CONTROL OF RECOVERY

COD_{Cr} , mg/L O_2

Control of recovery, average of results

Laboratory	Sample pair AB	Outlier
1	25,85	
2	32,65	
4	25,5	
5	29,85	
6	33	
7	28,3	
8	42,85	UG
9	29,95	
10	27,35	
11	26,45	
12	28,05	
13	30,25	
14	29,1	
15	-	
17	25,45	
18	27,6	
19	27,1	
20	28,7	
21	25,85	
25	26	
26	29,2	
28	35,35	UC
30	29,9	
31	37	
33	-	
36	29,15	
37	28,6	
38	31,5	
40	30,9	
43	34,65	

Laboratory	Sample pair AB	Outlier
44	29,7	
45	31,35	
47	21,7	
49	30,85	
50	25,95	
51	25,65	
52	31	
53	29	
55	27,625	
56	24,9	
57	29,1	
58	28,925	
No of labs	p	38
No of repl	n	2
m	28,8	
s ²	8,5	
s	2,9	
Assigned value	μ	29
Recovery	%	99,2
t	-0,4654	
Sign. level 99.9%	3,5737	
Sign. level 99%	2,7154	
Sign. level 95%	2,0262	

No test statistics were found to be significant

U denote a manual selected outlier
 UC denotes a Cochran outlier
 UG denotes a Grubbs outlier

BOD₅ (w. ATU), mg/L O₂

Control of recovery, average of results

Laboratory	Sample pair AB	Outlier
1	10,1925	UG
5	-	
6	4,55	
12	2,185	
17	3,445	
19	3,42	
21	3,12	
26	2,935	
31	3,17	
36	2,96	
38	4,62	
44	2,95	
46	3,22995	
50	4,15	
52	2,21	
53	2,85	
57	-	
No of labs	p	14
No of repl	n	2
m	3,27	
s ²	0,55	
s	0,74	
Assigned value	μ	3,2
Recovery	%	102,2
t	0,3596	
Sign. level 99.9%	4,2208	
Sign. level 99%	3,0123	
Sign. level 95%	2,1604	

No test statistics were found to be significant

U denote a manual selected outlier

UC denotes a Cochran outlier

UG denotes a Grubbs outlier

BOD₇ (w. ATU), mg/L O₂

Control of recovery, average of results

Laboratory	Sample pair AB	Outlier
7	3,545	
11	3,2	
13	6,48	
14	3,09	
15	3,53	
16	3,745	
17	3,245	
19	5,14	
21	3,455	
26	3,265	
29	3,65	
31	3,565	
32	3,335	
33	3,845	
35	3,55	
41	3,5	
43	3,26	
No of labs	p	15
No of repl	n	2
m	3,45	
s ²	0,05	
s	0,21	
Assigned value	μ	3,5
Recovery	%	98,6
t	-0,8682	
Sign. level 99.9%	4,1405	
Sign. level 99%	2,9768	
Sign. level 95%	2,1448	

No test statistics were found to be significant

U denote a manual selected outlier

UC denotes a Cochran outlier

UG denotes a Grubbs outlier

NVOC/TOC, mg/L C

Control of recovery, average of results

Laboratory	Sample pair AB	Outlier
2	12,355	
7	18,1	UG
8	11,285	
11	11,55	
12	15,8	UG
16	10,95	
17	6,1	UG
19	11,2	
20	10,5	
21	11,98	
22	11,105	
23	10,22	
24	11,21	
26	11,65	
27	11,52	
29	11,195	
30	13,95	
31	11,8	
32	11,495	
34	11,885	
35	11,85	
36	11,35	
38	12,28	
39	11,7	
40	13,25	
41	11,35	

Laboratory	Sample pair AB	Outlier
42	11,655	
44	9,7	
46	11,79	
48	11,62	
51	11,5	
52	11,55	
54	14,2	
57	11,58	
No of labs	p	31
No of repl	n	2
m	11,65	
s ²	0,82	
s	0,90	
Assigned value	μ	11,6
Recovery	%	100,5
t	0,3232	
Sign. level 99.9%	3,6460	
Sign. level 99%	2,7500	
Sign. level 95%	2,0423	

No test statistics were found to be significant

U denote a manual selected outlier

UC denotes a Cochran outlier

UG denotes a Grubbs outlier

TP, mg/L P

Control of recovery, average of results

Laboratory	Sample pair AB	Outlier
1	1,525	
2	1,49	
4	1,725	
5	1,6382	
6	1,75	
7	1,5685	
8	1,48	
9	1,535	
10	1,585	
11	0,9565	UG
12	1,5	
13	1,6	
14	1,64	
15	1,53	
16	1,56	
17	1,785	
18	1,605	
19	1,585	
20	1,51	
21	1,625	
22	1,595	
23	1,51	
24	1,557	
25	1,56	
26	1,659	
27	1,6875	
28	1,445	
29	1,5725	
30	1,625	
31	1,56	
32	1,63	
33	1,59	
34	1,57	
35	1,584	
36	1,695	
37	1,515	
38	1,7078	
39	1,62	

Laboratory	Sample pair AB	Outlier
40	1,65	
41	1,574	
42	1,596	
43	1,615	
44	1,77	
45	1,385	
46	2,1095	UG
47	1,642	
48	1,585	
49	1,505	
50	1,607	
51	1,545	
52	1,4225	
53	1,62	
54	1,72	
55	2,5275	UC
56	1,6	
57	1,6	
58	2,22	UG
No of labs	p	53
No of repl	n	2
m	1,592	
s ²	0,007	
s	0,082	
Assigned value	μ	1,59
Recovery	%	100,1
t	0,1432	
Sign. level 99.9%	3,4877	
Sign. level 99%	2,6737	
Sign. level 95%	2,0066	

No test statistics were found to be significant

U denote a manual selected outlier
 UC denotes a Cochran outlier
 UG denotes a Grubbs outlier

Cl, mg/L

Control of recovery, average of results

Laboratory	Sample pair AB	Outlier
1	314	
2	334,45	
4	318,5	
6	310	
9	421	UG
12	346,42	
17	337,5	
18	365,5	
19	332,5	
21	338,85	
25	325	
26	360,15	
27	328,63	
30	353,935	
31	349,5	
36	344,5	
37	642,5	UG
38	382,1	
40	350,5	
44	335,25	
46	349,5	
47	347	
49	372	
50	385	

Laboratory	Sample pair AB	Outlier
51	327	
53	346,5	
56	345,2	
57	337,1645	
58	338,6	
No of labs	p	27
No of repl	n	2
m	343,5	
s ²	342,1	
s	18,5	
Assigned value	μ	345
Recovery	%	99,6
t	-0,4136	
Sign. level 99.9%	3,7066	
Sign. level 99%	2,7787	
Sign. level 95%	2,0555	

No test statistics were found to be significant

U denote a manual selected outlier
UC denotes a Cochran outlier
UG denotes a Grubbs outlier

SO₄, mg/L

Control of recovery, average of results

Laboratory	Sample pair AB	Outlier
2	89,87	
9	85,65	
12	93,89	
17	86,85	
19	86,55	
20	83,05	
21	85,75	
26	91,1	
27	81,005	
31	89,95	
36	90,4	
38	87,8575	
40	88,85	
44	87,65	
50	80,1	
51	94,5	
57	88,4965	
58	97,55	
No of labs	p	18
No of repl	n	2
m	88,3	
s ²	20,0	
s	4,5	
Assigned value	μ	88
Recovery	%	100,3
t	0,2670	
Sign. level 99.9%	3,9651	
Sign. level 99%	2,8982	
Sign. level 95%	2,1098	

No test statistics were found to be significant

U denote a manual selected outlier

UC denotes a Cochran outlier

UG denotes a Grubbs outlier

TSS, mg/L

Control of recovery, average of results

Laboratory	Sample pair AB	Outlier
1	56,4	
2	52	UG
6	58,3	
8	57,75	
10	56,4	
11	56,3	
12	59,58	
13	58,7	
14	59,75	
15	58	
16	58,4	
17	55,6	
19	61	
20	59,7	
21	56,9	
23	59,05	
26	59,65	
27	58,525	
28	57,45	
29	57,55	
30	58,7	
31	58	
32	55,65	
33	58,7	
34	57,45	
35	50,9	UG
36	59,75	
38	67,5	UG
39	56,5	
41	54,75	
42	59,9	

Laboratory	Sample pair AB	Outlier
43	57,25	
44	57,75	
45	57,75	
48	59,79	
50	55,5	
51	56,125	
52	63,97	UG
53	56,5	
55	59,9	
56	62,1	
57	57,73	
58	54,25	
No of labs	p	39
No of repl	n	2
m	57,92	
s ²	3,01	
s	1,73	
Assigned value	μ	57,8
Recovery	%	100,2
t	0,4477	
Sign. level 99.9%	3,5657	
Sign. level 99%	2,7116	
Sign. level 95%	2,0244	

No test statistics were found to be significant

U denote a manual selected outlier
UC denotes a Cochran outlier
UG denotes a Grubbs outlier

ANNEX D CONCENTRATION LEVEL

Parameter	Unit	Sample	Bottle no.	Ampul no	I	II	Bottle Average	Sample Average	Assigned value	Spike	
										Measured	Assigned
COD _{Cr}	mg/L O ₂	A1	6	13	30.40	29.70	30.05	29.3	33	4.2	4
			34	34	30.50	28.40	29.45				
			65	66	29.10	27.90	28.50				
		B1	3	15	26.40	24.90	25.65	25.1	29		
			32	32	25.20	24.00	24.60				
			75	63	24.70	25.40	25.05				
Total phosphorus	mg/L P	A2	5		1.59	1.59	1.59	1.59	1.59	0.28	0.26
			35		1.57	1.57	1.57				
			54		1.62	1.62	1.62				
		B2	20		1.87	1.88	1.88	1.88	1.85		
			41		1.88	1.88	1.88				
			77		1.87	1.87	1.87				
Chloride	mg/L	A2	5		367	367	367	358	345	70	59
			35		348	348	348				
			54		357	359	358				
		B2	20		510	409	460	428			
			41		408	408	408				
			77		415	415	415				
Sulphate	mg/L	A2	5		88.20	88.20	88.20	89	88	16	11
			35		91.90	89.90	90.90				
			54		88.20	87.00	87.60				
		B2	20		107.00	106.00	106.50	105	99		
			41		104.00	104.00	104.00				
			77		105.00	104.00	104.50				
Total suspended matter	mg/L	A3	5	1	57.03		57.03	56.8	57.8	8.1	10.0
			35	41	56.13		56.13				
			63	63	57.13		57.13				
		B3	10	4	64.77		64.77	64.9	67.8		
			38	46	65.47		65.47				
			71	74	64.37		64.37				

ANNEX E HOMOGENEITY AND STABILITY

PT: SPIL-1 2024
Parameter: COD_{Cr}
Unit: mg/L O₂
Sigma: 10,8

Responsible for tests: DHBP/S7MS

Homogeneity test

Date: 2024-02-28

Sample	x(a)	x(b)	average	sd	sd^2
B1-5-6#	26,1	25,9	26,0	0,141	0,020
12-8	25,3	26,3	25,8	0,707	0,50
18-14	24,7	27,1	25,9	1,697	2,880
26-24	25,2	24,0	24,6	0,849	0,720
29-29	25,7	25,5	25,6	0,141	0,020
37-40	28,1	25,5	26,8	1,838	3,380
43-43	25,7	25,7	25,7	0,000	0,000
50-51	25,6	26,4	26,0	0,566	0,320
61-56	26,7	25,0	25,9	1,202	1,445
68-62	24,5	25,3	24,9	0,566	0,320
73-74	25,1	25,6	25,4	0,354	0,125
81-80	24,7	25,0	24,9	0,212	0,045

For homogeneity

General average (x) 25,61
Sample average sd (s_x) 0,609
Within-sample sd (s_w): 0,903
Between-samples sd (ss): 0
S_L in the Proficiency Test: 2,723
S_R in the Proficiency Test: 3,087

Stability test

Date: 2024-03-14

Sample	x(a)	x(b)
B1-3-15	26,4	24,9
32-32	25,2	24,7
75-36	24,7	25,4

For stability

General average (y): 25,2
/x-y/ = 0,4

Conclusions

ss = 0 0.3*sigma= 3,2
/x-y/ = 0,4

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 2024

Parameter: TP

Unit: mg/L P

Sigma: 0,104

Responsible for tests: DHBP/S7MS

Homogeneity test

Date: 2024-02-28

Sample	x(a)	x(b)	average	sd	sd^2
B2-5	1,89	1,90	1,90	0,007	0,000
7	1,91	1,92	1,92	0,007	0,00
17	1,90	1,91	1,91	0,007	0,000
24	1,92	1,93	1,93	0,007	0,000
34	1,92	1,92	1,92	0,000	0,000
36	1,92	1,93	1,93	0,007	0,000
46	1,91	1,92	1,92	0,007	0,000
49	1,89	1,89	1,89	0,000	0,000
60	1,91	1,91	1,91	0,000	0,000
62	1,94	1,94	1,94	0,000	0,000
69	1,94	1,94	1,94	0,000	0,000
80	1,93	1,93	1,93	0,000	0,000

For homogeneity

General average (x)1,92

Sample average sd (s_x)0,016

Within-sample sd (s_w):0,005

Between-samples sd (ss):0,0155

S_L in the Proficiency Test:0,074

S_R in the Proficiency Test:0,09

Stability test

Date: 2024-03-14

Sample	x(a)	x(b)
B2-20	1,87	1,88
41	1,88	1,88
77	1,87	1,87

For stability

General average (y):1,88

/x-y/ =0,043

Conclusions

ss = 0,015

/x-y/ = 0,043

0.3*sigma= 0,031

0.3σ_{pt} + 2√u²(x) + u²(y)= 0,224

Analytical quality

Is s_w < 0,15*sigma

YES

Homogeneity:

Is ss < 0.3*sigma?

YES

Stability:

/x-y/ < 0.3*sigma?

NO

Stability:

|x - y| ≤ 0,3σ_{pt} + 2√u²(x) + u²(y) ?

YES

PT: SPIL-1 2024

Parameter: TSS

Unit: mg/L

Sigma: 3,7

Responsible for tests: DHBP/S7MS

Homogeneity test

Date: 2024-02-28

Sample	x(a)	x(b)	average	sd	sd^2
B3-5-2#	68,8		68,8		
10-11	69,0		69,0		
18-15	68,9		68,9		
23-25	68,8		68,8		
26-28	68,9		68,9		
35-34	66,7		66,7		
39-40	66,1		66,1		
50-47	69,1		69,1		
53-53	69,0		69,0		
60-59	67,9		67,9		
64-66	68,7		68,7		
75-76	69,4		69,4		

For homogeneity

General average (x)68,4

Sample average sd (s_x)1,020

Within-sample sd (s_w):

Between-samples sd (ss):1,020

S_L in the Proficiency Test:1,484

S_R in the Proficiency Test:1,954

Stability test

Date: 2024-03-14

Sample	x(a)	x(b)
B3-4-10	64,8	
46-38	65,5	
74-41	64,4	

For stability

General average (y):64,9

/x-y/ =3,5

Conclusions

ss = 1,020

/x-y/ = 3,53

0.3*sigma= 1,108

0.3σ_{pt} + 2√u²(x) + u²(y)= 5,633

Analytical quality

Is s_w < 0,15*sigma

No data

Homogeneity:

Is ss < 0.3*sigma?

YES

Stability:

/x-y/ < 0.3*sigma?

NO

Stability:

|x - y| ≤ 0,3σ_{pt} + 2√u²(x) + u²(y) ?

YES

#: Matrix sample - Concentrat