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Proficiency test SPIL-1 (2023)

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

**Quality Documentation
May 2023**

Proficiency test SPIL-1 (2023) 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 16 March 2023. The proficiency test was organised by Eurofins Miljø A/S.

The present report contains Eurofins' documentation for the quality of the proficiency test. Results of the proficiency test including data from participating laboratories and statistical analysis of these data were issued in a report to all participants /1/ on 21 April 2023 and an edited version was issued 31 May 2023.

2 FEATURES OF THE PROFICIENCY TEST

Participants in the proficiency test were a total of 61 laboratories from Denmark, Finland, Germany, Japan, The Netherlands, Norway, Slovakia and Sweden. A list of participants is shown in Appendix A.

The closing date for submission of results was 31 March 2023. Two participants did not submit results for the proficiency test.

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 B.

Table 1 Samples in the proficiency test

Sample name	Parameters
A1/B1 BOD	BOD ₅ w. ATU, BOD ₇ w. ATU
A1/B1 COD/NVOC	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" (1994) /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	24	2.5	2
Five day biochemical oxygen demand w. ATU	BOD ₅ w. ATU	mg/l O ₂	2-6	2.0	0.43	0.4
Seven day biochemical oxygen demand w. ATU	BOD ₇ w. ATU	mg/l O ₂	2-6	2.5	0.16	0.4
Non-volatile organic carbon	NVOC/TOC	mg/l C	2-30	10.1	0.37	0.9
Total phosphorus	TP	mg/l P	0.2-2	0.913	0.013	0.220
Chloride	Cl	mg/l	50-700	222	3.3	55
Sulphate	SO ₄	mg/l	20-200	58	0.98	12
Total suspended matter	TSS	mg/l	20-100	43.7	1.9	7.4

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 Cl and SO₄ are operationally defined and are consensus values based upon the median for method no. 76, 77, 92 (COD_{Cr}), method no. 1 (NVOC), method no. 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 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 Appendix C. The test showed no significant difference between the two for most parameters. The test revealed a significant difference between the two for Cl. 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.

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 D. The test showed no significant difference between the two and the control of assigned value at Eurofins confirmed the value (Appendix E).

3 HOMOGENEITY AND STABILITY OF SAMPLES

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

COD	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 F. The appendix also gives the results of the statistical evaluation of the control data. The data are analysed by analysis of variance (ANOVA) giving:

1. the standard deviation/variance for replicates (the contribution from analytical variability),
2. the between bottle standard deviation/variance (the contribution from heterogeneity) and
3. the between days concentration difference (the contribution from instability).

Homogeneity is evaluated by comparing the between bottle variance to $0.3 \cdot \hat{\sigma}$ 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 $0.3 \cdot \hat{\sigma}$. 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 CI 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.

5 REFERENCES

- /1/ Eurofins A/S, *Proficiency test SPIL-1 (2023)*, Report to participants, April 2023.
- /2/ ISO 5725-2, *Accuracy (trueness and precision) of measurement methods and results – Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method*, 2019.
- /3/ Spliid, H., *Procedure and analysis of data for proficiency tests and environmental analyses*, Report to Danish Environmental Protection Agency, 1994 (in Danish).
- /4/ Eurofins A/S, *Schedule for a proficiency test*, document may be downloaded from www.eurofins.dk/proficiencytest.
- /5/ Ministry of Environment regulation no. 1146 on *quality criteria for environmental measurements*, 24 October 2017 (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	0.925g 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: 1.295 g/kg
Concentrate B1	1.154 g D-glucose 1.154 g 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	1.501 g Na-B.glycerophosphate milli-Q water up to 1000.0 g	TP: 151.9 mg/kg
Stock Cl	25.003 g Sodium chloride (NaCl) milli-Q water up to 1000.0 g	Cl: 15.168 g/kg
Stock SO ₄	5.003 g Sodium sulphate (Na ₂ SO ₄) milli-Q water up to 1000.0 g	SO ₄ : 3.383 g/kg
Stock TSS	15.000 g Microcrystalline cellulose milli-Q water up to 1000.0 g	TSS: 15.000 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 1.00 mL of concentrate A1 is diluted up to 200.0 mL with filtered water from Gørding sewage treatment plant	a + 9.46	b + 3.74					
B1-COD/NVOC	At the laboratory 1.00 mL of concentrate B1 is diluted up to 200.0 mL with filtered water from Gørding sewage treatment plant	a + 11.8	b + 4.66					
A1-BOD	At the laboratory 2.50 mL of concentrate A1 is diluted up to 2000.0 mL with filtered water from Gørding sewage treatment plant			c + 1.6				
B1-BOD	At the laboratory 2.50 mL of concentrate B1 is diluted up to 2000.0 mL with filtered water from Gørding sewage treatment plant			c + 2.0				
A2	60.0 g stock TP 150.0 g stock Cl 150.0 g stock SO ₄ Sample B2 up to 40.0 kg				0.991 · (d+0.868) + 0.228	0.991 · (e+152) + 56.9	0.991 · (f+12.1) + 12.7	
B2	400.0 g stock TP 700.0 g stock Cl 250.0 g stock SO ₄ filtered water from Gørding sewage treatment plant up to 70.0 kg				d + 0.868	e + 152	f + 12.1	
A3	At the laboratory 1000.0 mL of filtered water from Gørding sewage treatment plant is added to 3.0 mL stock TSS							g + 44.9
B3	At the laboratory 1000.0 mL of filtered water from Gørding sewage treatment plant is added to 3.5 mL stock TSS							g + 52.3

ANNEX B CONTROL OF SPIKE VALUES

COD_{Cr}, mg/l O₂

Control of differences within sample pairs

Laboratory	Difference AB	Outlier
1	-0.30	
4	-6.44	
5	-1.80	
6	-1.00	
7	2.80	
10	-2.30	
11	-8.90	UC
12	-1.70	
13	-1.50	
14	1.10	
15	-2.10	
16	0.00	
17	-0.70	
21	-0.70	
23	1.80	
24	-2.30	
25	-2.50	
26	-0.80	
27	2.22	UG
28	-1.33	
29	-0.10	
30	-1.30	
32	3.50	
37	-0.20	
38	-2.70	
40	0.20	
41	-	

Laboratory	Difference AB	Outlier
43	0.50	
44	-0.10	
45	-2.70	
48	-0.40	
50	-0.20	
53	0.80	
54	-0.60	
56	0.70	
57	3.00	
58	0.00	
60	-0.60	
No of labs	p	35
No of repl	n	2
d	-0.57	
s ²	3.42	
s	1.85	
t	-1.8244	
Sign. level 99.9%	3.6007	
Sign. level 99%	2.7284	
Sign. level 95%	2.0322	

No test statistics were found to be significant

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
4	-0.190	
6	-0.130	
13	-	
16	-0.600	
23	1.550	
26	-0.300	
28	0.500	
29	0.860	
38	0.000	
44	0.060	
48	-0.070	
53	0.160	
54	-	
59	-1.900	
60	-0.900	
No of labs	p	13
No of repl	n	2
d	-0.074	
s ²	0.690	
s	0.831	
t	-0.3206	
Sign. level 99.9%	4.3178	
Sign. level 99%	3.0545	
Sign. level 95%	2.1788	

No test statistics were found to be significant

BOD₇ w. ATU, mg/l O₂

Control of differences within sample pairs

Laboratory	Difference AB	Outlier
4	0.220	
6	-0.170	
7	0.400	
14	0.000	
16	0.800	
17	-0.100	
28	0.540	
33	0.240	
35	0.030	
41	0.290	
42	-0.100	
43	-0.050	
44	-0.130	
46	0.100	
48	-0.110	
49	0.120	
58	0.000	
61	-0.100	
No of labs	p	17
No of repl	n	2
d	0.116	
s ²	0.073	
s	0.270	
t	1.7783	
Sign. level 99.9%	4.0150	
Sign. level 99%	2.9208	
Sign. level 95%	2.1199	

No test statistics were found to be significant

NVOC, mg/l C

Control of differences within sample pairs

Laboratory	Difference AB	Outlier
3	0.140	
4	-0.420	
6	0.000	
8	-0.290	
9	-0.062	
12	-0.230	
15	-0.667	
16	-0.100	
17	-0.140	
20	-0.255	
21	0.200	
22	0.100	
24	-2.140	UC
26	-0.010	
28	-0.043	
29	0.040	
33	-0.180	
35	-0.100	
36	0.000	
37	0.500	
38	0.390	
39	-0.260	
43	0.420	
44	0.100	

Laboratory	Difference AB	Outlier
45	0.100	
46	-0.800	
47	0.060	
48	0.200	
49	-0.100	
51	0.060	
55	0.410	
59	0.325	
61	-0.100	
No of labs	p	32
No of repl	n	2
d	-0.022	
s ²	0.084	
s	0.290	
t	-0.4343	
Sign. level 99.9%	3.6335	
Sign. level 99%	2.7440	
Sign. level 95%	2.0395	

No test statistics were found to be significant

UC denotes a Cochran outlier

UG denotes a Grubbs outlie

TP, mg/l P

Control of differences within sample pairs

Laboratory	Difference AB	Outlier
1	-0.016	
3	-0.004	
4	0.005	
5	0.014	
6	-0.007	
7	0.010	
8	0.000	U
9	0.001	
10	0.009	
11	0.013	
12	-0.003	
13	0.000	
14	0.006	
15	-0.012	
16	0.080	UG
17	0.001	
19	0.012	
20	-0.006	
21	0.010	
22	-0.012	
23	0.012	
24	0.005	
25	0.050	
26	0.010	
27	-2.220	UC
28	0.076	
29	0.019	
30	-0.040	
31	-0.140	UC
32	0.014	
33	0.048	
34	-0.001	
35	-0.015	
37	0.007	

Laboratory	Difference AB	Outlier
38	-0.048	
39	-0.008	
40	0.021	
41	0.003	
43	-0.002	
44	-0.024	
45	-0.003	
46	0.000	
48	-0.014	
49	-0.023	
50	0.002	
52	-0.036	
53	-0.010	
54	-0.047	
55	-1.078	UC
56	-0.007	
57	-0.003	
59	0.005	
60	0.186	UC
61	-0.001	
No of labs	p	48
No of repl	n	2
d	0.000	
s ²	0.000	
s	0.022	
t	0.0685	
Sign. level 99.9%	3.5099	
Sign. level 99%	2.6846	
Sign. level 95%	2.0117	

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	2.00	UG
4	-7.70	
6	-7.00	
10	-6.40	
11	-4.00	
13	-30.50	UC
15	-8.92	
16	5.00	
23	1.00	
25	-4.00	
26	-5.00	
27	-6.00	
28	-5.30	
29	-3.00	
32	-5.00	
38	-5.10	
44	-7.90	
47	-11.00	
48	-6.60	
49	-8.50	
50	-9.00	

Laboratory	Difference AB	Outlier
53	-8.49	
55	-2.79	
57	-14.00	UG
59	-12.00	
60	-10.00	
No of labs	p	23
No of repl	n	2
d	-5.99	
s ²	14.34	
s	3.79	
t	-7.5808	***
Sign. level 99.9%	3.7921	
Sign. level 99%	2.8188	
Sign. level 95%	2.0739	

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

UC denotes a Cochran outlier

UG denotes a Grubbs outlier

SO₄, mg/l

Control of differences within sample pairs

Laboratory	Difference AB	Outlier
1	0.50	
4	-0.10	
6	0.00	
16	-4.20	
26	-0.30	
27	6.60	UG
28	-0.55	
29	-0.50	
37	0.40	
38	2.80	
44	-0.20	
47	0.70	
48	-0.20	
53	0.10	
55	0.25	UG
60	-4.20	
No of labs	p	14
No of repl	n	2
d	-0.41	
s ²	3.26	
s	1.81	
t	-0.8509	
Sign. level 99.9%	4.2208	
Sign. level 99%	3.0123	
Sign. level 95%	2.1604	

No test statistics were found to be significant

UC denotes a Cochran outlier

TSS, mg/l

Control of differences within sample pairs

Laboratory	Difference AB	Outlier
3	0.40	
4	0.70	
5	-1.20	
6	-0.20	
7	1.00	
10	0.10	
12	0.40	
13	-0.40	
14	-1.60	
15	-0.10	
16	15.40	UC
17	0.90	
19	0.10	
20	13.10	UC
21	-0.40	
22	0.50	
23	0.30	
24	-0.50	
26	-1.40	
28	-5.48	UC
29	0.00	
30	7.40	UC
31	0.40	
33	-2.63	
34	-0.50	
35	0.60	
36	-0.60	
37	-0.20	
38	1.20	

Laboratory	Difference AB	Outlier
39	0.10	
41	0.20	
42	0.00	
44	-0.40	
45	-0.60	
46	-0.90	
48	0.20	
49	-0.30	
50	0.10	
52	-0.20	
53	-2.03	
54	3.20	
55	1.10	
58	-0.20	
60	22.60	UC
61	-0.40	
No of labs	p	40
No of repl	n	2
d	-0.08	
s ²	0.93	
s	0.96	
t	-0.5354	
Sign. level 99.9%	3.5581	
Sign. level 99%	2.7079	
Sign. level 95%	2.0227	

No test statistics were found to be significant

UC denotes a Cochran outlier

ANNEX C CONTROL OF RECOVERY

COD_{Cr} , mg/l O_2

Control of recovery, average of results

Laboratory	Sample pair AB	Outlier
1	24.75	
4	24.95	
5	34.50	
6	28.50	
7	24.20	
10	24.25	
11	27.65	UC
12	27.55	
13	25.55	
14	25.25	
15	31.95	
16	24.00	
17	24.65	
21	28.75	
23	14.00	
24	28.25	
25	25.45	
26	27.10	
27	0.03	UG
28	24.21	
29	22.85	
30	26.75	
32	21.45	
37	28.40	
38	24.05	
40	23.30	
41	-	

Laboratory	Sample pair AB	Outlier
43	24.65	
44	24.65	
45	18.65	
48	26.20	
50	22.80	
53	25.50	
54	24.30	
56	27.35	
57	23.00	
58	23.00	
60	22.20	
No of labs	p	35
No of repl	n	2
m	25.06	
s ²	12.22	
s	3.50	
Assigned value	μ	24
Recovery	%	104.4
t	1.7871	
Sign. level 99.9%	3.6007	
Sign. level 99%	2.7284	
Sign. level 95%	2.0322	

No test statistics were found to be significant

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
4	2.295	
6	2.575	
13	0.850	U
16	3.300	
23	1.895	
26	1.850	
28	2.490	
29	2.210	
38	1.820	
44	1.890	
48	1.775	
53	1.950	
54	1.900	U
59	2.850	
60	2.150	
No of labs	p	13
No of repl	n	2
m	2.235	
s ²	0.213	
s	0.461	
Assigned value	μ	2.0
Recovery	%	111.7
t	1.8342	
Sign. level 99.9%	4.3178	
Sign. level 99%	3.0545	
Sign. level 95%	2.1788	

No test statistics were found to be significant

U denote a manual selected outlier

BOD₇ w. ATU, mg/l O₂

Control of recovery, average of results

Laboratory	Sample pair AB	Outlier
4	2.750	
6	2.755	
7	2.200	
14	2.540	
16	3.700	
17	2.150	
28	2.700	
33	2.420	
35	2.315	
41	3.175	
42	2.550	
43	2.535	
44	1.895	
46	2.450	
48	2.345	
49	1.840	
58	-	
61	2.350	
No of labs	p	17
No of repl	n	2
m	2.510	
s ²	0.198	
s	0.445	
Assigned value	μ	2.5
Recovery	%	100.4
t	0.0926	
Sign. level 99.9%	4.0150	
Sign. level 99%	2.9208	
Sign. level 95%	2.1199	

No test statistics were found to be significant

NVOC, mg/l C

Control of recovery, average of results

Laboratory	Sample pair AB	Outlier
3	9.750	
4	9.950	
6	10.600	
8	10.815	
9	9.759	
12	11.465	
15	10.452	
16	10.050	
17	9.430	
20	9.733	
21	10.300	
22	10.950	
24	11.480	UC
26	9.995	
28	9.489	
29	9.820	
33	8.990	
35	11.050	
36	8.500	
37	10.750	
38	9.635	
39	11.080	
43	9.410	
44	9.340	
45	11.050	

Laboratory	Sample pair AB	Outlier
46	10.700	
47	9.630	
48	10.000	
49	10.010	
51	10.170	
55	10.435	
59	9.653	
61	10.050	
No of labs	p	32
No of repl	n	2
m	10.094	
s ²	0.451	
s	0.672	
Assigned value	μ	10.1
Recovery	%	99.9
t	-0.0503	
Sign. level 99.9%	3.6335	
Sign. level 99%	2.7440	
Sign. level 95%	2.0395	

No test statistics were found to be significant

UC denotes a Cochran outlier

TP, mg/l P

Control of recovery, average of results

Laboratory	Sample pair AB	Outlier
1	0.868	
3	0.936	
4	0.879	
5	0.913	
6	0.884	
7	0.975	
8	0.930	U
9	0.900	
10	0.986	
11	0.934	
12	0.922	
13	0.910	
14	0.927	
15	0.926	
16	1.040	UG
17	0.931	
19	0.924	
20	0.893	
21	0.935	
22	0.896	
23	0.944	
24	0.928	
25	0.905	
26	0.895	
27	26.090	UC
28	0.987	
29	0.970	
30	0.940	
31	1.110	UC
32	0.933	
33	0.926	
34	0.908	
35	0.918	
37	0.907	
38	0.874	
39	0.894	
40	0.960	

Laboratory	Sample pair AB	Outlier
41	0.909	
43	0.910	
44	0.967	
45	0.882	
46	0.915	
48	0.907	
49	0.910	
50	0.899	
52	0.877	
53	0.905	
54	0.904	
55	0.441	UC
56	0.934	
57	0.932	
59	0.943	
60	1.895	UC
61	0.901	
No of labs	p	48
No of repl	n	2
m	0.919	
s ²	0.001	
s	0.028	
Assigned value	μ	0.913
Recovery	%	100.7
t	1.4742	
Sign. level 99.9%	3.5099	
Sign. level 99%	2.6846	
Sign. level 95%	2.0117	

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	265.00	UG
4	218.05	
6	222.50	
10	225.30	
11	233.00	
13	66.25	UC
15	222.50	
16	232.50	
23	207.50	
25	232.00	
26	226.50	
27	222.00	
28	218.15	
29	225.50	
32	222.50	
38	231.15	
44	224.85	
47	218.50	
48	225.80	
49	219.75	
50	221.50	

Laboratory	Sample pair AB	Outlier
53	217.87	
55	210.39	
57	185.00	UG
59	222.00	
60	208.00	
No of labs	p	23
No of repl	n	2
m	222.08	
s ²	49.43	
s	7.03	
Assigned value	μ	222
Recovery	%	100.0
t	0.0536	
Sign. level 99.9%	3.7921	
Sign. level 99%	2.8188	
Sign. level 95%	2.0739	

No test statistics were found to be significant

UC denotes a Cochran outlier

UG denotes a Grubbs outlier

SO₄, mg/l

Control of recovery, average of results

Laboratory	Sample pair AB	Outlier
1	61.35	
4	58.65	
6	58.80	
16	57.40	
26	60.75	
27	48.20	UG
28	56.89	
29	57.15	
37	58.20	
38	58.70	
44	60.60	
47	60.05	
48	57.40	
53	56.86	
55	52.68	UG
60	62.50	
No of labs	p	14
No of repl.	n	2
m	58.95	
s ²	3.30	
s	1.82	
Assigned value	μ	58
Recovery	%	101.6
t	1.9549	
Sign. level 99.9%	4.2208	
Sign. level 99%	3.0123	
Sign. level 95%	2.1604	

No test statistics were found to be significant

UG denotes a Grubbs outlier

TSS, mg/l

Control of recovery, average of results

Laboratory	Sample pair AB	Outlier
3	43.90	
4	43.35	
5	42.60	
6	43.60	
7	39.90	
10	43.85	
12	43.10	
13	44.00	
14	41.10	
15	44.35	
16	31.30	UC
17	44.55	
19	43.25	
20	37.75	UC
21	45.20	
22	43.55	
23	43.15	
24	44.45	
26	43.90	
28	40.25	UC
29	45.00	
30	40.30	UC
31	42.80	
33	41.18	
34	45.25	
35	43.70	
36	45.10	
37	44.50	
38	45.60	
39	45.25	
41	43.50	

Laboratory	Sample pair AB	Outlier
42	42.20	
44	43.20	
45	43.10	
46	43.45	
48	43.70	
49	43.05	
50	43.55	
52	45.20	
53	50.59	UG
54	45.70	
55	44.30	
58	43.90	
60	31.90	UC
61	43.80	
No of labs	p	39
No of repl	n	2
m	43.71	
s ²	1.51	
s	1.23	
Assigned value	μ	43.7
Recovery	%	100.0
t	0.0683	
Sign. level 99.9%	3.5657	
Sign. level 99%	2.7116	
Sign. level 95%	2.0244	

No test statistics were found to be significant

UC denotes a Cochran outlier

UG denotes a Grubbs outlier

ANNEX D CONCENTRATION LEVEL

Parameter	Unit	Sample	Bottle no.	I	II	Bottle Average	Sample Average	Assigned value	Spike	
									Measured	Assigned
COD	mg/L O2	A1	16-85	21.0	20.7	20.9	21.0	24	1.52	2
			44-47	20.6	20.4	20.5				
			73-19	21.4	21.6	21.5				
		B1	15-10	22.3	22.3	22.3	22.5	26		
			46-32	23.1	23.1	23.1				
			69-50	22.2	21.8	22.0				
Total phosphorus	mg/L P	A2	14	1.16	1.17	1.17	1.15	1.133	0.2	0.220
			37	1.16	1.15	1.16				
			81	1.14	1.14	1.14				
		B2	10	0.912	0.910	0.911	0.917	0.913		
			26	0.917	0.919	0.918				
			48	0.921	0.923	0.922				
Chloride	mg/L	A2	14	261	261	261	260	277	45	55
			37	258	258	258				
			81	259	260	260				
		B2	10	215	216	216	215	222		
			26	218	218	218				
			48	211	211	211				
Sulphate	mg/L	A2	14	67.7	66.4	67.1	68.1	70	17.95	12
			37	71.5	71.2	71.4				
			81	67.2	64.7	66.0				
		B2	10	52.4	52.9	52.7	50.2	58		
			26	50.2	49.6	49.9				
			48	48.1	47.8	48.0				
Total suspended solids	mg/L	A3	14-17	44.27		44.27	44.02	43.7	7.70	7.4
			37-39	43.81		43.81				
			56-60	43.97		43.97				
		B3	14-5	52.12		52.12	51.72	51.1		
			46-44	51.92		51.92				
			75-68	51.12		51.12				

ANNEX E HOMOGENEITY AND STABILITY

PT: SPIL-1
Parameter: COD
Unit: mg/L O ₂
Sigma: 10.8

Responsible for tests: HBP/S7MS

Homogeneity test Date: 2023-03-01

Sample*	x(a)	x(b)	average	sd	sd^2
3-3	22.6	23.2	22.9	0.424	0.180
12-13	23.3	22.5	22.9	0.566	0.32
21-18	22.5	21.9	22.2	0.424	0.180
22-23	22.1	22.3	22.2	0.141	0.020
30-29	22.3	22.3	22.3	0.000	0.000
41-39	22.6	22.1	22.4	0.354	0.125
47-43	22.4	21.8	22.1	0.424	0.180
55-56	22.0	22.7	22.4	0.495	0.245
64-58	23.0	22.6	22.8	0.283	0.080
65-71	22.8	23.2	23.0	0.283	0.080
78-78	22.3	22.7	22.5	0.283	0.080
79-83	22.1	22.3	22.2	0.141	0.020

For homogeneity

General average (x)	22.48
Sample average sd (s _x)	0.326
Within-sample sd (s _w):	0.355
Between-samples sd (ss):	0.2088
S _L in the Proficiency Test:	3.37
S _R in the Proficiency Test:	3.62

Stability test Date: 2023-03-16

Sample	x(a)	x(b)
15-10	22.3	22.3
46-23	23.1	23.1
69-50	22.2	21.8

For stability

General average (y):	22.46667
/x-y/ =	0.016667

Conclusions

ss = 0.209 0.3*sigma= 3.24	
/x-y/ = 0.016667	
Analytical quality	Is s _w < 0.15*sigma YES
Homogeneity:	Is ss < 0.3*sigma? YES
Stability:	/x-y/ < 0.3*sigma? YES

*Ampoule no. – Matrix bottle no.

PT: SPIL-1
Parameter: TP
Unit: mg/L P
Sigma: 0.062

Responsible for tests: HBP/S7MS

Homogeneity test

Date: 2023-03-01

Sample	x(a)	x(b)	average	sd	sd^2
3	1.15	1.16	1.2	0.007	0.000
12	1.16	1.17	1.2	0.007	0.00
17	1.15	1.16	1.2	0.007	0.000
27	1.15	1.14	1.1	0.007	0.000
34	1.17	1.18	1.2	0.007	0.000
38	1.17	1.16	1.2	0.007	0.000
47	1.16	1.16	1.2	0.000	0.000
53	1.14	1.14	1.1	0.000	0.000
61	1.15	1.16	1.2	0.007	0.000
67	1.15	1.15	1.2	0.000	0.000
74	1.15	1.15	1.2	0.000	0.000
82	1.15	1.15	1.2	0.000	0.000

For homogeneity

General average (x) 1.16
Sample average sd (s_x) 0.010
Within-sample sd (s_w): 0.005

Between-samples sd (ss): 0.0089
 S_L in the Proficiency Test: 0.026
 S_R in the Proficiency Test: 0.03

Stability test

Date: 2023-03-16

Sample	x(a)	x(b)
14	1.16	1.17
37	1.16	1.15
81	1.14	1.14

For stability

General average (y): 1.153333
/x-y/ = 0.002083

Conclusions

ss = 0.009 0.3*sigma= 0.02
/x-y/ = 0.002083

Analytical quality Is $s_w < 0.15 \cdot \sigma$
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: HBP/S7MS

Homogeneity test Date: 2023-03-01

Sample*	x(a)	x(b)	average	sd	sd^2
5-4	52.1		52.1		
9-7	52.4		52.4		
16-14	52.1		52.1		
22-24	52.3		52.3		
31-29	52.3		52.3		
34-33	51.5		51.5		
41-43	51.8		51.8		
49-47	52.2		52.2		
55-55	52.3		52.3		
57-60	52.3		52.3		
69-67	52.2		52.2		
70-74	52.2		52.2		

For homogeneity

General average (x) 52.2
 Sample average sd (s_x) 0.253
 Within-sample sd (s_w):

 Between-samples sd (ss): 0.253
 S_L in the Proficiency Test: 1.14
 S_R in the Proficiency Test: 1.31

Stability test Date: 2023-03-16

Sample	x(a)	x(b)
14-5	52.12	
46-44	51.92	
75-68	51.12	

For stability

General average (y): 51.72
 $|x-y| =$ 0.43911

Conclusions

ss = 0.25 0.3*sigma= 1.08 $ x-y = 0.43911$	
Analytical quality	Is $s_w < 0.15 \cdot \sigma$ No data
Homogeneity:	Is ss < 0.3*sigma? YES
Stability:	$ x-y < 0.3 \cdot \sigma$? YES

* Glass bottle no. – Matrix bottle no.