



Proficiency test SPIL-3 (2023)

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

Proficiency test SPIL-3 (2023) Quality Documentation

November 2023

Eurofins Miljø A/S
Smedeskovvej 38
DK-8464 Galten
Denmark

Tlf. : +45 7022 4266
e-mail: proficiency@eurofins.com
Web: www.eurofins.dk

Client	Client's representative
Environmental laboratories	

Project	Project No
Proficiency test SPIL-3 (2023)	20405-33

Authors	Date
Rikke Mikkelsen	2023-11-29
	Approved by
	Peter Rerup

	Quality Documentation Report	FYE3	DPRE	2023-11-29
--	------------------------------	------	------	------------

Revision	Description	By	Approved	Date
----------	-------------	----	----------	------

Key words	Classification
Analytical quality, assigned value, precision, trueness, homogeneity, stability, COD, BOD ₅ (w. ATU), BOD ₇ (w. ATU), NVOC/TOC, total phosphorus, chloride, sulphate, suspended solids, wastewater	☒ Open ☐ Internal ☐ Proprietary

Distribution	
Available online:	www.eurofins.dk
Eurofins:	Rikke Mikkelsen, Peter Rerup

CONTENTS

1	INTRODUCTION	1
2	FEATURES OF THE PROFICIENCY TEST	2
2.1	Sample preparation	2
2.2	Statistical analysis of participants' data.....	2
2.3	Assigned and spike value	2
2.3.1	Assigned and spike values	3
2.3.2	Test of spike values	3
2.3.3	Test of assigned values	3
3	HOMOGENEITY AND STABILITY OF SAMPLES	5
4	CONCLUSION.....	6
5	REFERENCES	7
ANNEX A	SAMPLE PREPARATION.....	9
ANNEX B	CONTROL OF SPIKE VALUES.....	11
	COD _{Cr} , mg/L O ₂	11
	BOD ₅ w. ATU, mg/L O ₂	12
	BOD ₇ w. ATU, mg/L O ₂	13
	NVOC/TOC, mg/L C	14
	Total phosphorus, mg/L P	15
	Chloride, mg/L	16
	Sulphate, mg/L	17
	Total suspended solids, mg/L	18
ANNEX C	CONTROL OF RECOVERY	19
	COD _{Cr} , mg/L O ₂	19
	BOD ₅ w. ATU, mg/L O ₂	20
	BOD ₇ w. ATU, mg/L O ₂	21
	NVOC/TOC, mg/L C	22
	Total phosphorus, mg/L P	23
	Chloride, mg/L	24
	Sulphate, mg/L	25
	Total suspended solids, mg/L	26
ANNEX D	CONCENTRATION LEVEL	27
ANNEX E	HOMOGENEITY AND STABILITY.....	28

1 INTRODUCTION

A proficiency test on the analysis of organic matter, phosphorus, chloride, sulphate and suspended solids in wastewater was conducted on 14 September 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 17 October 2023.

2 FEATURES OF THE PROFICIENCY TEST

Participants in the proficiency test were a total of 49 laboratories from Brazil, Denmark, Finland, Germany, Japan, The Netherlands, Norway, Singapore, Slovakia and Sweden.

The closing date for submission of results was 29 September 2023. All participants except laboratory no. 5, 12, 39 and 41 submitted their results.

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 wastewater, effluent. Sample preparation is described in Appendix B.

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/ 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 synthetic wastewater, 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	47	0.96	12
5 day biochemical oxygen demand (w. ATU)	BOD ₅ w. ATU	mg/L O ₂	2-6	3.4	0.64	0.8
7 day biochemical oxygen demand (w. ATU)	BOD ₇ w. ATU	mg/L O ₂	2-6	4.3	0.87	0.8
Non-volatile/Total organic carbon	NVOC/TOC	mg/L C	2-30	18.7	0.38	4.6
Total phosphorus	TP	mg/L P	0.2-2	1.01	0.012	0.15
Chloride	Cl	mg/L	50-700	40.4	0.26	5.9
Sulphate	SO ₄	mg/L	20-200	105	1.2	16
Total Suspended Solids	TSS	mg/L	20-500	29.9	1.8	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. 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, see Appendix C. The test showed no significant difference between the two values 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.

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 values for BOD, NVOC/TOC and Cl. The control of assigned value at Eurofins confirmed the value (Appendix E).

The test revealed a significant difference between the two values for COD_{Cr} and the control measurements at Eurofins confirmed the difference (Appendix D). Average recovery was 94.3 %. However, scrutiny of documentation from the sample preparation showed no indications of mistakes in sample preparation. Furthermore, the difference between the assigned value and the average of the results obtained from all laboratories were for NVOC/TOC found to be 100.4 % which confirmed the correctness of the sample preparations. The assigned value is therefore kept unchanged.

The test revealed a significant difference between the two values for TP. Average recovery was 98.4 %. However, the results of control measurements at Eurofins confirmed the assigned value (Appendix D), and scrutiny of documentation from the sample preparation showed no indications of mistakes in sample preparation. The assigned value is therefore kept unchanged.

The test revealed a significant difference between the two values for SO_4 and the control measurements at Eurofins confirmed the difference (Appendix D). However, scrutiny of documentation from the sample preparation showed no indications of mistakes in sample preparation. The assigned value is kept unchanged.

The test revealed a significant difference between the two values for TSS. Average recovery was 97.9 % and the numerical difference between mean and nominal was 0.63 mg/L. The control measurements at Eurofins confirmed the difference (Appendix D). However, the results of stability measurements at Eurofins confirmed the assigned value (Appendix E), and scrutiny of documentation from the sample preparation showed no indications of mistakes in sample preparation.

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 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 multiplied 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 TP the participants could not recover the spike value or the assigned 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. 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.

For COD_{Cr}, SO₄ and TSS the participants did not recover the assigned value and Eurofins' control measurements confirmed the difference. No error in preparation could be found and therefore the assigned value is kept unchanged and it is recommended as the basis for evaluation of participating laboratories.

5 REFERENCES

- /1/ Eurofins A/S, *Proficiency test SPIL-3 (2023)*, Report to participants, October 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. 529 on *quality criteria for environmental measurements*, 14 May 2023 (in Danish).
- /6/ DS/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	1.153 g D-glucose 1.153 g L-glutamic acid milli-Q water up to 1000 g	COD _{Cr} : 2.360 g/kg NVOC: 0.932 g/kg BOD: 1.523 g/kg
Concentrate B1	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: 1.221 g/kg
Stock TP	1.499 g Na-B.glycerophosphate milli-Q water up to 1000.0 g	TP: 151.7 mg/kg
Stock Cl	9.999 g Sodium chloride (NaCl) milli-Q water up to 1000.0 g	Cl: 6.066 g/kg
Stock SO ₄	9.999 g Sodium sulphate (Na ₂ SO ₄) milli-Q water up to 1000.0 g	SO ₄ : 6.762 g/kg
Stock TSS	15.003 g Microcrystalline cellulose milli-Q water up to 1000.0 g	TSS: 15.003 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 5.00 mL of concentrate A1 is diluted up to 200.0 mL with pure water	59.0	23.3					
B1-COD/NVOC	At the laboratory 5.00 mL of concentrate B1 is diluted up to 200.0 mL with pure water	47.3	18.7					
A1-BOD	At the laboratory 5.00 mL of concentrate A1 is diluted up to 2000.0 mL with filtered water from Gørding sewage treatment plant			a + 3.8				
B1-BOD	At the laboratory 5.00 mL of concentrate B1 is diluted up to 2000.0 mL with filtered water from Gørding sewage treatment plant			a + 3.1				
A2	300.0 g stock TP 300.0 g stock Cl 700.0 g stock SO ₄ Pure water up to 45.0 kg				1.01	40.4	105	
B2	20.01 g stock TP 20.02 g stock Cl 50.00 g stock SO ₄ Sample A2 up to 20.0 kg				0.995 · 1.01 + 0.152	0.995 · 40.4 + 6.07	0.995 · 105 + 16.9	
A3	At the laboratory 1000.0 mL of pure water is added to 2.0 mL stock TSS							29.9
B3	At the laboratory 1000.0 mL of pure water is added to 2.4 mL stock TSS							35.9

ANNEX B CONTROL OF SPIKE VALUES

COD_{Cr} , mg/L O_2

Control of differences within sample pairs

Laboratory	Difference AB	Outlier
1	-7.80	
2	0.00	
3	-6.90	UG
4	-4.40	
6	-2.90	
7	-0.20	
8	-2.00	
9	2.00	
10	1.10	
14	-2.10	
15	-1.20	
16	-1.30	
17	-1.40	
18	1.00	
19	-16.50	UC
21	-0.80	
22	0.40	
23	-26.20	UC
24	-0.90	
27	7.00	
28	2.80	
29	-2.00	
31	-1.10	
33	-1.40	
34	-27.50	UC

Laboratory	Difference AB	Outlier
35	0.40	
37	-4.00	
40	-0.87	
42	-6.30	
43	-0.80	
44	1.90	
45	0.00	
46	-1.50	
47	-1.00	
48	-	-
No of labs	p	30
No of repl	n	2
d	-0.91	
s ²	7.35	
s	2.71	
t	-1.8433	
Sign. level 99.9%	3.6594	
Sign. level 99%	2.7564	
Sign. level 95%	2.0452	

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
3	-0.17	
4	0.47	
14	0.10	
17	-0.28	
18	-0.14	
19	-0.80	
25	-0.11	
27	0.23	
28	0.00	
29	0.09	
35	-1.07	
40	-0.08	
43	-2.20	UC
45	-0.21	
46	0.30	
No of labs	p	14
No of repl	n	2
d	-0.12	
s ²	0.17	
s	0.41	
t	-1.0937	
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

BOD₇ w. ATU, mg/L O₂

Control of differences within sample pairs

Laboratory	Difference AB	Outlier
1	-0.400	
4	0.280	
7	-1.920	UC
13	0.120	
18	0.010	
24	0.280	
29	-0.050	
30	0.200	
32	-0.350	
35	-0.550	
38	0.200	
40	-0.001	
No of labs	p	11
No of repl	n	2
d	-0.024	
s ²	0.083	
s	0.289	
t	-0.2727	
Sign. level 99.9%	4.5869	
Sign. level 99%	3.1693	
Sign. level 95%	2.2281	

No test statistics were found to be significant

UC denotes a Cochran outlier

NVOC/TOC, mg/L C

Control of differences within sample pairs

Laboratory	Difference AB	Outlier
4	0.29	
9	-0.36	
11	0.30	
13	-0.70	
14	0.20	
18	0.00	
21	0.30	
26	-0.61	
27	-0.15	
28	-0.38	
29	-0.20	
32	-0.40	
34	0.40	
35	-0.48	
36	0.00	
37	-0.60	
38	-0.20	
40	-0.24	
43	0.10	
45	0.04	
47	0.20	
49	-0.60	
No of labs	p	22
No of repl	n	2
d	-0.14	
s ²	0.12	
s	0.34	
t	-1.9123	
Sign. level 99.9%	3.8193	
Sign. level 99%	2.8314	
Sign. level 95%	2.0796	

No test statistics were found to be significant

Total phosphorus, mg/L P

Control of differences within sample pairs

Laboratory	Difference AB	Outlier
1	0.030	
2	-0.010	
3	0.000	
4	0.005	
6	0.020	
7	-0.010	
8	0.010	
9	0.017	
10	0.010	
11	0.032	
13	0.008	
14	0.040	
15	0.010	
16	0.011	
17	-0.010	
18	0.040	
19	0.042	
20	-0.009	
21	0.020	
22	0.010	
23	0.010	
24	0.058	
26	-0.006	
27	-0.005	
28	0.020	
29	0.004	
30	0.019	
31	0.010	
32	0.000	

Laboratory	Difference AB	Outlier
33	0.000	
34	0.050	
35	0.124	UC
37	-0.030	
38	0.020	
40	0.020	
42	-0.008	
43	0.060	
44	0.030	
45	0.012	
46	0.005	
47	0.010	
48	-0.010	UG
49	0.032	
No of labs	p	41
No of repl	n	2
d	0.014	
s ²	0.000	
s	0.020	
t	4.6074	***
Sign. level 99.9%	3.5510	
Sign. level 99%	2.7045	
Sign. level 95%	2.0211	

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

UC denotes a Cochran outlier
UG denotes a Grubbs outlier

Chloride, mg/L

Control of differences within sample pairs

Laboratory	Difference AB	Outlier
2	0.10	
3	1.20	
4	-0.15	
6	0.40	
8	0.50	
14	-0.20	
16	0.70	
17	0.10	
18	0.00	
20	0.20	
22	1.10	
23	-1.10	
28	-1.24	
29	-1.10	
31	2.50	
34	3.20	
35	11.70	UC
36	-0.20	
40	-0.02	

Laboratory	Difference AB	Outlier
43	-0.30	
44	-0.90	
46	-0.60	UG
47	0.20	
48	3.90	UG
No of labs	p	21
No of repl	n	2
d	0.24	
s ²	1.20	
s	1.09	
t	0.9958	
Sign. level 99.9%	3.8495	
Sign. level 99%	2.8453	
Sign. level 95%	2.0860	

No test statistics were found to be significant

UC denotes a Cochran outlier

UG denotes a Grubbs outlier

Sulphate, mg/L

Control of differences within sample pairs

Laboratory	Difference AB	Outlier
4	2.80	
14	-0.50	
17	-1.10	
18	-1.00	
20	-0.47	
21	-1.00	
28	-1.45	
29	-2.00	
34	6.00	UC
35	32.30	UC
36	0.00	
37	1.00	
40	-0.20	
43	-1.00	
45	0.99	
48	2.00	
No of labs	p	14
No of repl	n	2
d	-0.14	
s ²	1.88	
s	1.37	
t	-0.3765	
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

Total suspended solids, mg/L

Control of differences within sample pairs

Laboratory	Difference AB	Outlier
1	-0.70	
2	-0.40	
3	0.00	
4	0.07	
7	0.00	
9	0.00	
10	0.40	
11	-0.90	
13	1.00	
14	-0.50	
17	-0.40	
18	1.00	
19	0.50	
21	-0.30	
24	-1.00	UG
26	1.60	
27	-5.20	UG
28	0.46	
29	3.20	
30	0.00	
32	1.20	
35	0.20	
37	1.00	

Laboratory	Difference AB	Outlier
38	-0.70	
40	-0.20	
43	1.00	
45	0.00	UG
46	0.40	
47	0.10	
48	5.00	
No of labs	p	27
No of repl	n	2
d	0.48	
s ²	1.55	
s	1.24	
t	2.0147	
Sign. level 99.9%	3.7066	
Sign. level 99%	2.7787	
Sign. level 95%	2.0555	

No test statistics were found to be significant

UG denotes a Grubbs outlier

ANNEX C CONTROL OF RECOVERY

COD_{Cr} , mg/L O_2

Control of recovery, average of results

Laboratory	Difference AB	Outlier
1	50.10	
2	43.40	
3	10.15	UG
4	43.54	
6	39.85	
7	44.10	
8	37.70	
9	46.70	
10	44.25	
14	44.15	
15	38.20	
16	44.05	
17	43.90	
18	47.50	
19	40.95	UC
21	46.30	
22	48.00	
23	44.00	UC
24	44.45	
27	40.50	
28	43.90	
29	45.30	
31	40.15	
33	44.20	
34	64.25	UC

Laboratory	Difference AB	Outlier
35	49.50	
37	52.00	
40	44.24	
42	37.55	
43	44.00	
44	41.55	
45	49.00	
46	45.95	
47	46.10	
48	-	
No of labs		p 30
No of repl		n 2
m		44.34
s^2		12.76
s		3.57
Assigned value		μ 47
Recovery		% 94.3
$t = \sqrt{p}(m - \mu)/s$		-4.0828 ***
Sign. level 99.9%		3.6594
Sign. level 99%		2.7564
Sign. level 95%		2.0452

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

UC denotes a Cochran outlier

UG denotes a Grubbs outlier

BOD₅ w. ATU, mg/L O₂

Control of recovery, average of results

Laboratory	Difference AB	Outlier
3	3.725	
4	3.065	
14	3.450	
17	3.450	
18	4.110	
19	1.600	
25	3.245	
27	3.865	
28	3.500	
29	3.305	
35	4.145	
40	2.172	
43	4.960	UC
45	4.755	
46	3.750	
No of labs	p	14
No of repl	n	2
m	3.438	
s ²	0.633	
s	0.796	
Assigned value	μ	3.4
Recovery	%	101.1
$t = \sqrt{p}(m - \mu)/s$	0.1802	
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

BOD₇ w. ATU, mg/L O₂

Control of recovery, average of results

Laboratory	Difference AB	Outlier
1	4.000	
4	3.680	
7	4.090	UC
13	4.640	
18	4.485	
24	4.440	
29	3.475	
30	4.300	
32	4.385	
35	4.895	
38	5.500	
40	2.915	
No of labs	p	11
No of repl	n	2
m	4.247	
s ²	0.501	
s	0.708	
Assigned value	μ	4.3
Recovery	%	98.8
$t = \sqrt{p}(m - \mu)/s$	-0.2489	
Sign. level 99.9%	4.5869	
Sign. level 99%	3.1693	
Sign. level 95%	2.2281	

No test statistics were found to be significant

UC denotes a Cochran outlier

NVOC/TOC, mg/L C

Control of recovery, average of results

Laboratory	Difference AB	Outlier
4	18.68	
9	19.27	
11	19.15	
13	18.55	
14	19.50	
18	18.60	
21	18.85	
26	18.44	
27	19.23	
28	19.13	
29	18.60	
32	18.90	
34	18.00	
35	17.77	
36	18.60	
37	17.10	
38	18.80	
40	19.78	
43	18.35	
45	20.68	
47	19.20	
49	17.70	
No of labs	p	22
No of repl	n	2
m	18.77	
s ²	0.58	
s	0.76	
Assigned value	μ	18.7
Recovery	%	100.4
$t = \sqrt{p}(m - \mu)/s$	0.4106	
Sign. level 99.9%	3.8193	
Sign. level 99%	2.8314	
Sign. level 95%	2.0796	

No test statistics were found to be significant

Total phosphorus, mg/L P

Control of recovery, average of results

Laboratory	Difference AB	Outlier
1	0.9850	
2	1.0450	
3	1.0200	
4	1.0325	
6	1.0100	
7	1.0250	
8	1.0050	
9	0.9485	
10	0.9950	
11	0.9660	
13	0.9940	
14	1.0100	
15	1.0050	
16	0.9455	
17	1.0250	
18	0.9700	
19	0.9510	
20	0.9895	
21	1.0000	
22	0.9550	
23	0.9950	
24	0.9950	
26	1.0070	
27	0.9955	
28	0.9500	
29	0.9890	
30	0.9765	
31	1.0050	
32	0.9700	
33	1.0000	

Laboratory	Difference AB	Outlier
34	0.9950	
35	0.8660	UC
37	1.0550	
38	0.9700	
40	1.0120	
42	0.9460	
43	0.9900	
44	0.9950	
45	1.0624	
46	0.9925	
47	1.0050	
48	1.2050	UG
49	0.9760	
No of labs		p 41
No of repl		n 2
m		0.9941
s ²		0.0008
s		0.0283
Assigned value		μ 1.01
Recovery		% 98.4
$t = \sqrt{p}(m - \mu)/s$		-3.5976 ***
Sign. level 99.9%		3.5510
Sign. level 99%		2.7045
Sign. level 95%		2.0211

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

UC denotes a Cochran outlier

UG denotes a Grubbs outlier

Chloride, mg/L

Control of recovery, average of results

Laboratory	Difference AB	Outlier
2	40.65	
3	40.70	
4	40.46	
6	42.10	
8	42.75	
14	37.90	
16	38.15	
17	39.85	
18	40.40	
20	39.86	
22	43.05	
23	40.55	
28	41.39	
29	40.25	
31	39.75	
34	34.10	
35	39.35	UC
36	39.50	
40	40.08	
43	41.45	
44	43.05	
46	24.40	UG
47	37.50	
48	27.05	UG
No of labs	p	21
No of repl	n	2
m	40.17	
s ²	4.25	
s	2.06	
Assigned value	μ	40.4
Recovery	%	99.4
$t = \sqrt{p}(m - \mu)/s$	-0.5205	
Sign. level 99.9%	3.8495	
Sign. level 99%	2.8453	
Sign. level 95%	2.0860	

No test statistics were found to be significant

UC denotes a Cochran outlier

UG denotes a Grubbs outlier

Sulphate, mg/L

Control of recovery, average of results

Laboratory	Difference AB	Outlier
4	103.90	
14	103.15	
17	101.85	
18	104.50	
20	104.01	
21	102.50	
28	103.88	
29	105.00	
34	91.00	UC
35	103.35	UC
36	106.00	
37	105.50	
40	102.70	
43	106.50	
45	101.56	
48	104.00	
No of labs	p	14
No of repl	n	2
m	103.93	
s ²	2.23	
s	1.49	
Assigned value	μ	105
Recovery	%	99.0
$t = \sqrt{p}(m - \mu)/s$	-2.6792	*
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, 5.0%-level)

UC denotes a Cochran outlier

Total suspended solids, mg/L

Control of recovery, average of results

Laboratory	Difference AB	Outlier
1	29.15	
2	29.40	
3	29.20	
4	30.42	
7	30.40	
9	29.40	
10	29.40	
11	27.75	
13	29.00	
14	30.05	
17	26.00	
18	27.50	
19	29.55	
21	29.45	
24	22.50	UG
26	31.20	
27	37.67	UG
28	30.34	
29	29.60	
30	29.80	
32	30.30	
35	29.20	
37	29.50	

Laboratory	Difference AB	Outlier
38	29.75	
40	29.10	
43	29.40	
45	24.00	UG
46	28.90	
47	30.15	
48	26.50	
No of labs	p	27
No of repl	n	2
m	29.27	
s ²	1.34	
s	1.16	
Assigned value	μ	29.9
Recovery	%	97.9
$t = \sqrt{p}(m - \mu)/s$	-2.8094	**
Sign. level 99.9%	3.7066	
Sign. level 99%	2.7787	
Sign. level 95%	2.0555	

** denotes that there is a significant difference (t-test, 1.0%-level)

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 _{Cr}	mg/L O ₂	A1	3	49.20	49.20	49.20	49.00	59	9.22	12
			26	49.30	49.30	49.30				
			58	48.50	48.50	48.50				
		B1	5	39.40	39.40	39.40	39.78	47		
			39	40.20	40.10	40.15				
			69	39.80	39.80	39.80				
Total phosphorus	mg/L P	A2	8	1.01	1.01	1.01	1.01	1.01	0.13	0.15
			33	1.01	1.01	1.01				
			62	1.01	1.01	1.01				
		B2	7	1.12	1.16	1.14	1.14	1.16		
			34	1.15	1.15	1.15				
			53	1.14	1.14	1.14				
Chloride	mg/L	A2	8	41.50	41.40	41.45	41.18	40.4	5.80	5.9
			33	41.30	41.30	41.30				
			62	40.70	40.90	40.80				
		B2	7	46.70	46.80	46.75	46.98	46.3		
			34	46.90	46.80	46.85				
			53	47.30	47.40	47.35				
Sulphate	mg/L	A2	8	100.00	99.60	99.80	98.83	105	20.00	16
			33	97.90	97.50	97.70				
			62	99.20	98.80	99.00				
		B2	7	118.00	118.00	118.00	118.83	121		
			34	120.00	119.00	119.50				
			53	119.00	119.00	119.00				
Total suspended solids	mg/L	A3	19	28.54		28.54	28.94	29.9	6.60	6
			32	29.54		29.54				
			53	28.74		28.74				
		B3	12	35.61		35.61	35.54	35.9		
			36	35.41		35.41				
			47	35.61		35.61				

ANNEX E HOMOGENEITY AND STABILITY

PT:	SPIL-3 2023
Parameter:	COD _{Cr}
Unit:	mg/L O ₂
Sigma:	10.8

Responsible for tests: HBP/S7MS

Homogeneity test Date: 2023-08-30

Sample	x(a)	x(b)	average	sd	sd^2
3	38.8	38.6	38.7	0.141	0.020
10	40.1	40.5	40.3	0.283	0.08
13	38.5	38.9	38.7	0.283	0.080
22	39.0	38.9	39.0	0.071	0.005
24	40.0	40.3	40.2	0.212	0.045
35	39.3	39.0	39.2	0.212	0.045
41	39.1	38.5	38.8	0.424	0.180
46	38.8	39.2	39.0	0.283	0.080
54	39.0	39.2	39.1	0.141	0.020
57	38.9	39.4	39.2	0.354	0.125
63	38.7	39.0	38.9	0.212	0.045
70	39.0	39.3	39.2	0.212	0.045

For homogeneity

General average (x)	39.17
Sample average sd (s _x)	0.522
Within-sample sd (s _w):	0.253
Between-samples sd (ss):	0.4907
S _L in the Proficiency Test:	3.30
S _R in the Proficiency Test:	3.82

Stability test Date: 2023-09-14

Sample	x(a)	x(b)
5	39.4	39.4
39	40.2	40.1
69	39.8	39.8

For stability

General average (y):	39.783333
/x-y/ =	0.6166667

Conclusions

ss = 0.491 0.3*sigma= 3.24	
/x-y/ = 0.6166667	
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 2023

Parameter: TP

Unit: mg/L P

Sigma: 0.055

Responsible for tests: HBP/S7MS

Homogeneity test Date: 2023-08-30

Sample	x(a)	x(b)	average	sd	sd^2
1	1.01	1.01	1.0	0.000	0.000
6	1.01	1.01	1.0	0.000	0.00
18	1.02	1.02	1.0	0.000	0.000
20	1.02	1.02	1.0	0.000	0.000
27	1.03	1.03	1.0	0.000	0.000
35	1.03	1.03	1.0	0.000	0.000
40	1.03	1.03	1.0	0.000	0.000
44	1.02	1.02	1.0	0.000	0.000
49	1.03	1.03	1.0	0.000	0.000
60	1.01	1.01	1.0	0.000	0.000
65	1.02	1.01	1.0	0.007	0.000
69	1.02	1.01	1.0	0.007	0.000

For homogeneity

General average (x)	1.02
Sample average sd (s_x)	0.008
Within-sample sd (s_w):	0.003
Between-samples sd (ss):	0.0080
S_L in the Proficiency Test:	0.027
S_R in the Proficiency Test:	0.030

Stability test Date: 2023-09-14

Sample	x(a)	x(b)
A2 - 8	1.01	1.01
A2 - 33	1.01	1.01
A2 - 62	1.01	1.01

For stability

General average (y):	1.01
$ x-y $ =	0.01

Conclusions

ss = 0.008 0.3*sigma= 0.02	
$ x-y $ = 0.01	
Analytical quality	Is $s_w < 0.15 \cdot \sigma$ YES
Homogeneity:	Is ss < 0.3*sigma? YES
Stability:	$ x-y < 0.3 \cdot \sigma$? YES

PT: SPIL-3 2023

Parameter: TSS

Unit: mg/L

Sigma: 3.6

Responsible for tests: HBP/S7MS

Homogeneity test Date: 2023-08-30

Sample	x(a)	x(b)	average	sd	sd^2
4	30.8		30.8		
5	30.4		30.4		
10	30.0		30.0		
18	30.3		30.3		
24	30.5		30.5		
27	30.3		30.3		
34	30.2		30.2		
37	30.3		30.3		
42	30.9		30.9		
50	30.3		30.3		
55	30.2		30.2		
60	30.3		30.3		

For homogeneity

General average (x)	30.4
Sample average sd (s_x)	0.252
Within-sample sd (s_w):	
Between-samples sd (ss):	0.252
S_L in the Proficiency Test:	0.98
S_R in the Proficiency Test:	1.31

Stability test Date: 2023-10-24

Sample	x(a)	x(b)
A3 - 17	30.00	30.18
A3 - 41	27.99	28.04
A3 - 54	30.26	30.42
A3 - 21	30.18	29.1

For stability

General average (y):	29.52125
$/x-y/ =$	0.8929217

Conclusions

ss = 0.25 0.3*sigma= 1.08	
$/x-y/ = 0.8929217$	
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