

Proficiency test SPIL-3 (2024)

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

Proficiency test SPIL-3 (2024) Quality Documentation

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

Tel: +45 7022 4266
proficiencytest@etn.eurofins.com
Web: www.eurofins.dk

November 2024

Client		Client's representative		
Environmental laboratories				

Project		Project No		
Proficiency test SPIL-3 (2024)		20405-43		
Authors		Date		
		2024-11-27		
Rikke Mikkelsen		Approved by		
		Peter Rerup		
	Quality Documentation Report	FYE3	DPRE	2024-11-2029
Revision	Description	By	Approved	Date
Key words		Classification		
Analytical quality, assigned value, precision, trueness, homogeneity, stability, COD _{Cr} , BOD ₅ (w. ATU), BOD ₇ (w. ATU), NVOC/TOC, total phosphorus, chloride, sulphate, total suspended solids, wastewater		☒ Open		
		☐ Internal		
		☐ Proprietary		

Distribution	
Available online:	www.eurofins.dk
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.....	4
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 phosphorous, 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 phosphorous, mg/L P	23
	Chloride, mg/L.....	24
	Sulphate, mg/L.....	25
	Total suspended solids, mg/L.....	26
ANNEX E	CONCENTRATION LEVEL	27
ANNEX F	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 12 September 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 11 October 2024 and an edited version were issued later on the same date to correct a calculation error of the Z-score for NVOC/TOC.

2 FEATURES OF THE PROFICIENCY TEST

Signed up participants in the proficiency test were a total of 59 laboratories from Brazil, Croatia, Denmark, Finland, Germany, Greece, Japan, Netherlands, Norway, Singapore, Spain and Sweden.

The closing date for submission of results was 27 September 2024. All participants except laboratory no. 7, 8, 9, 14, 31, 45, 52 and 55 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 untreated sewage. 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 untreated sewage. 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	COD _{Cr}	mg/L O ₂	100-800	205	14	15
5 day biochemical oxygen demand (w. ATU)*	BOD ₅ w. ATU	mg/L O ₂	50-500	90	4.0	10
7 day biochemical oxygen demand (w. ATU)	BOD ₇ w. ATU	mg/L O ₂	50-500	107	4.1	11
Non-volatile/Total organic carbon	NVOC/TOC	mg/L C	50-800	70	2.2	6
Total phosphorus	TP	mg/L P	5-10	7.79	0.085	1.04
Chloride	Cl	mg/L	50-700	84	1.4	12
Sulphate	SO ₄	mg/L	20-200	76	1.9	12
Total suspended solids	TSS	mg/L	100-500	273	11	40

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 (Equation 1). The spike values for COD_{Cr}, BOD, NVOC/TOC and TSS are calculated from sample preparation. The assigned values for TP, Cl and SO₄ are the consensus values of the median and the spike value for the two samples in the sample pair.

$$\text{Assigned value} = \frac{\text{median}(A) + \text{median}(B) - \text{split value}}{2}$$

Equation 1

The assigned values for all parameters except NVOC, Cl and SO₄ are operationally defined and are consensus values based upon the median for method no. 3, 5, 65, 76, 77, 91, 97 (COD_{Cr}), method no. 1, 2 and comparative international methods (TP), method no. 1, 2 (TSS) or ISO 5815-1 (BOD₅), which are the methods required by the Danish EPA /5/. Assigned values for BOD₇ are based upon standardised methods (method no. 1 – 4 and 9 with approved standard). 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 samples for most parameters. However, the test revealed a significant difference between the spike value and the difference in concentration between the sample pair found from the laboratories' results. for TTS. 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).

The test revealed a recovery which significantly differed from 100 % for TP, this could be attributed to influence from laboratories using methods other than those prescribed by the Danish EPA. The test was repeated with only method 1, 2 and similar international methods and now showed no significant difference. Furthermore, the results of control measurements at Eurofins confirmed the assigned value (Appendix E). The assigned value is therefore kept unchanged.

The test revealed a recovery which significantly differed from 100 % for CI, this could be attributed to influence from one laboratory. The test was repeated after exclusion of the results from laboratory no. 12 and now showed no significant difference between the recovery and 100 %.

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 $0.3 \cdot \hat{\sigma}$ 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 $0.3 \cdot \hat{\sigma}$ or $0.3 \cdot \hat{\sigma} + 2 \sqrt{u_x^2 + u_y^2}$ 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 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 sample pair 2 (TP, Cl, SO₄) and sample pair 3 (TSS) are stable and homogeneous.

The test for homogeneity of sample pair 1 (COD_{Cr}, BOD w. ATU, NVOC/TOC) shows that the samples are homogeneous. Stability test for sample pair 1 indicated instability. The measurement found a decrease in COD_{Cr} for sample A1. The assigned values for COD_{Cr}, BOD w. ATU and NVOC/TOC are found using consensus median values and the assigned COD_{Cr} value also reflects the decrease. The total variation coefficients (CV_t) for the COD_{Cr}, BOD₅ w. ATU and NVOC/TOC results in SPIL-3 2024 are within the normal range from our proficiency tests provided by Eurofins Environment Denmark. CV_t for BOD₇ w. ATU is larger than normal, but since CV_t for BOD₅ w. ATU is within normal range the larger CV_t for BOD₇ w. ATU is considered to originate from other factors than the instability.

Therefore, it is concluded that the found instability has insignificant influence on the evaluation of the participants performance.

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 TSS 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.

For TP and Cl the participants did not recover the assigned values. Eurofins' scrutiny of the combined evidence gave the conclusion that the assigned values are correct. The assigned values are therefore kept unchanged and they are recommended as the basis for evaluation of participating laboratories.

The tests for stability and homogeneity show that sample pair 2 (TP, Cl, SO₄) and sample pair 3 (TSS) are stable and homogeneous. The test for homogeneity of sample pair 1 (COD_{Cr}, BOD w. ATU, NVOC/TOC) shows that the samples are homogeneous. Stability test for sample pair 1 indicates instability. Eurofins Environment Testing Denmark's scrutiny of the combined evidence gave the conclusion that the instability has insignificant influence on the evaluation of the participants' performance.

5 REFERENCES

- /1/ Eurofins A/S, *Proficiency test SPIL-3 (2024)*, Report to participants, October 2024 and Eurofins A/S, *Proficiency test SPIL-3 (2024)*, Report to participants v.2, October 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 and Equality regulation no. 811 on *quality criteria for environmental measurements*, 19 June 2024 (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	0.738 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: 1.034 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: 1.295 g/kg
Stock TP	4.000 g Na-B.glycerophosphate milli-Q water up to 1000.0 g	TP: 404.7 mg/kg
Stock Cl	10.000 g Sodium chloride (NaCl) milli-Q water up to 1000.0 g	Cl: 6.067 g/kg
Stock SO ₄	5.000 g Sodium sulphate (Na ₂ SO ₄) milli-Q water up to 1000.0 g	SO ₄ : 3.381 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	At the laboratory 20.00 mL of concentrate A1 is diluted up to 500.0 mL with filtered water from Holsted sewage treatment plant	a + 60.4	b + 23.9	c + 41.4				
B1	At the laboratory 20.00 mL of concentrate B1 is diluted up to 500.0 mL with filtered water from Holsted sewage treatment plant	a + 75.7	b + 29.9	c + 51.8				
A2	850 g stock TP 200 g stock Cl 600 g stock SO ₄ Filtered water from Holsted sewage treatment plant up to 60* kg				d + 5.73	e + 20.2	f + 33.8	
B2	80.0 g stock TP 60.0 g stock Cl 100 g stock SO ₄ Sample A2 up to 30* kg				0.992* · (d+5.73) + 1.08	0.992* · (e+20.2) + 12.1	0.992* · (f+33.8) + 11.3	
A3	At the laboratory 250.0 mL of filtered water from Holsted sewage treatment plant is added to 4.4 mL stock TSS							g + 259
B3	At the laboratory 250.0 mL of filtered water from Holsted sewage treatment plant is added to 5.1 mL stock TSS							g + 300

*Malfunctional weight - number is approximate and is not used directly for assigning values in proficiency test.

ANNEX B CONTROL OF SPIKE VALUES

COD_{Cr} , mg/L O_2

Control of differences within sample pairs

Laboratory	Difference AB	Outlier
4	5.0	
6	-1.0	
10	-72.0	C
11	-4.4	
12	5.0	
13	-7.0	
15	1.0	
16	3.0	
17	-6.0	
18	-3.0	
19	-1.0	
21	3.0	
23	-10.0	
25	4.0	
26	-1.0	
27	0.0	
29	7.0	
30	4.0	
32	1.6	
33	-6.0	
34	4.0	
35	0.0	
36	0.0	
38	7.0	
40	3.0	
41	2.0	

Laboratory	Difference AB	Outlier
43	-3.0	
44	3.0	
46	9.0	G
47	-6.0	
48	-15.0	
51	0.3	
56	0.7	
57	8.0	
58	0.0	
59	-5.0	

No of labs	33
No of repl	2
d	-0.2061
s ²	26.6
s	5.2
t	-0.2297
Sign. level 99.9%	3.6218
Sign. level 99%	2.7385
Sign. level 95%	2.0369

No test statistics were found to be significant

U denote a manual selected outlier

C denotes a Cochran outlier

G denotes a Grubbs outlier

BOD₅ w. ATU, mg/L O₂

Control of differences within sample pairs

Laboratory	Difference AB	Outlier
4	2.9	
6	5.3	
10	-212.0	C
16	-10.0	
17	6.0	
18	-12.7	
19	-1.0	
23	-16.0	
25	-1.1	
29	4.4	
32	-5.5	
36	-24.0	G
43	-5.5	
44	5.0	
46	13.2	
51	14.0	
59	-1.7	

No of labs	15
No of repl	2
d	-0.1813
s ²	76.4204
s	8.7419
t	-0.0803
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

C denotes a Cochran outlier

G denotes a Grubbs outlier

BOD₇ w. ATU, mg/L O₂

Control of differences within sample pairs

Laboratory	Difference AB	Outlier
1	-4.0	
5	5.0	
6	6.7	
20	-7.4	
22	16.6	
26	3.0	
28	8.2	
32	0.9	
40	-0.5	
42	4.7	
43	-4.8	
46	4.0	
51	5.4	
53	-3.0	
54	0.9	

No of labs	15
No of repl	2
d	2.3780
s ²	36.3381
s	6.0281
t	1.5278
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

C denotes a Cochran outlier

G denotes a Grubbs outlier

NVOC/TOC, mg/L C

Control of differences within sample pairs

Laboratory	Difference AB	Outlier
1	-1.7	
2	-0.6	
4	2.0	
5	2.0	
6	-0.4	
15	1.0	
16	-4.0	
17	-1.0	
18	-2.8	
19	-0.9	
20	3.0	
22	-0.5	
23	-1.2	
24	1.2	
25	0.2	
28	-0.8	
29	-0.7	G
32	-1.2	
34	0.1	
37	1.4	
38	2.5	
39	1.4	
40	0.6	
42	1.7	
43	3.7	

Laboratory	Difference AB	Outlier
44	2.9	G
46	0.6	
48	-0.6	
49	27.4	C
51	1.5	
53	-0.3	
56	0.8	
58	1.0	
59	0.8	

No of labs	31
No of repl	2
d	0.3135
s ²	2.7313
s	1.6527
t	1.0562
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

C denotes a Cochran outlier

G denotes a Grubbs outlier

Total phosphorous, mg/L P

Control of differences within sample pairs

Laboratory	Difference AB	Outlier
1	0.090	
2	0.050	
3	0.100	
4	-0.180	
5	0.180	
6	0.000	
10	-2.260	C
11	-0.110	
12	-0.160	
13	0.410	
15	0.060	
16	-0.130	
17	0.040	
18	-0.060	
19	-0.200	
20	-0.080	
21	-0.060	
22	0.190	
23	-0.040	
25	0.210	
26	-0.040	
27	-0.060	
28	-0.010	
29	-0.032	
30	0.010	
32	0.128	
33	-0.180	
34	0.395	
35	-0.010	
36	-0.170	
37	0.080	
38	-0.140	
39	-0.060	

Laboratory	Difference AB	Outlier
40	-0.072	
41	-0.020	
42	-0.020	
43	-0.060	
44	-2.960	C
46	0.120	
47	0.010	
48	0.140	
49	0.090	
50	0.010	
51	-0.060	
53	-0.080	
54	-0.450	
56	-0.360	
57	-0.250	
58	-0.320	
59	-0.040	

No of labs	48
No of repl	2
d	-0.0238
s ²	0.0266
s	0.1632
t	-1.0092
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

C denotes a Cochran outlier

G denotes a Grubbs outlier

Chloride, mg/L

Control of differences within sample pairs

Laboratory	Difference AB	Outlier
3	0.4	
4	-1.4	
6	-0.6	
10	8.0	
11	0.2	
12	-6.0	
13	3.4	
16	0.0	
17	-2.0	
18	1.6	
21	4.9	
23	-0.2	
25	3.9	
29	0.4	
30	8.7	
32	-0.3	
33	-2.0	
34	4.7	
41	-3.0	
43	-1.0	
44	1.3	
46	-1.3	
47	0.2	
49	-13.9	C
50	-1.4	
51	-1.6	
56	-0.6	
59	1.5	

No test statistics were found to be significant

U denote a manual selected outlier

C denotes a Cochran outlier

G denotes a Grubbs outlier

No of labs	27
No of repl	2
d	0.6584
s ²	10.4205
s	3.2281
t	1.0598
Sign. level 99.9%	3.7066
Sign. level 99%	2.7787
Sign. level 95%	2.0555

Sulphate, mg/L

Control of differences within sample pairs

Laboratory	Difference AB	Outlier
3	0.1	
4	1.0	
6	2.3	
15	-2.2	
16	0.0	
17	-3.0	
18	-1.0	
23	1.7	
25	-0.9	
29	-2.4	
32	0.3	
34	5.3	
43	-1.0	
44	4.0	
46	0.1	
47	6.9	
48	-	U
49	-1.3	
51	-2.1	
59	0.1	

No of labs	19
No of repl	2
d	0.4193
s ²	7.0091
s	2.6475
t	0.6904
Sign. level 99.9%	3.9216
Sign. level 99%	2.8784
Sign. level 95%	2.1009

No test statistics were found to be significant

U denote a manual selected outlier

C denotes a Cochran outlier

G denotes a Grubbs outlier

Total suspended solids, mg/L

Control of differences within sample pairs

Laboratory	Difference AB	Outlier
1	-8.0	
2	-0.8	
4	-11.4	
5	-2.0	
6	-5.8	
10	-4.4	
11	-4.0	
12	0.0	
15	2.0	
16	69.0	C
17	-6.0	
18	1.0	
19	-19.3	
20	-12.0	
22	-7.0	
23	0.0	
25	-3.0	
26	8.0	
28	2.6	
29	0.0	
32	-4.0	
34	1.0	
35	11.6	
36	-4.8	
37	-2.0	
40	-10.1	
42	-2.0	
43	0.0	

Laboratory	Difference AB	Outlier
44	-3.0	
46	-3.0	
48	-4.8	
49	-2.9	
51	0.3	
53	0.0	
54	-4.0	
56	3.2	
57	0.0	
58	-5.0	
59	-10.0	

No of labs	38
No of repl	2
d	-2.8871
s ²	30.3955
s	5.5132
t	-3.2281 **
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, 1 %-level)

U denote a manual selected outlier

C denotes a Cochran outlier

G 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
4	219.5	
6	210.5	
10	272.0	C
11	175.0	
12	217.5	
13	238.5	
15	222.5	
16	179.5	
17	201.0	
18	187.5	
19	206.5	
21	232.5	
23	197.0	
25	177.0	
26	212.5	
27	0.0	
29	223.5	
30	188.0	
32	178.8	
33	218.0	
34	219.0	
35	211.0	
36	205.0	
38	202.5	
40	211.5	
41	224.0	
43	187.5	

Laboratory	Sample pair AB	Outlier
44	214.5	
46	102.5	G
47	240.0	
48	221.5	
51	182.4	
56	216.2	
57	204.0	
58	228.0	
59	215.5	

No of labs	33
No of repl	2
m	208.1
s ²	323.1
s	17.9
Assigned value	205
Recovery	101.5
t	0.9955
Sign. level 99.9%	3.6218
Sign. level 99%	2.7385
Sign. level 95%	2.0369

No test statistics were found to be significant

U denote a manual selected outlier

C denotes a Cochran outlier

G denotes a Grubbs outlier

BOD₅ w. ATU, mg/L O₂

Control of recovery, average of results

Laboratory	Sample pair AB	Outlier
4	94.2	
6	89.2	
10	253.0	C
16	95.0	
17	90.0	
18	104.3	
19	82.5	
23	131.0	
25	60.9	
29	97.8	
32	59.8	
36	453.0	G
43	65.3	
44	123.5	
46	71.8	
51	71.5	
59	102.4	
4	94.2	
6	89.2	
10	253.0	
16	95.0	
17	90.0	

No of labs	15
No of repl	2
m	89.2673
s ²	454.3466
s	21.3154
Assigned value	90
Recovery	99.2
t	-0.1331
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

C denotes a Cochran outlier

G denotes a Grubbs outlier

BOD₇ w. ATU, mg/L O₂

Control of recovery, average of results

Laboratory	Sample pair AB	Outlier
1	108.0	
5	115.5	
6	94.9	
20	104.0	
22	93.7	
26	113.5	
28	104.8	
32	79.4	
40	104.3	
42	106.7	
43	67.0	
46	80.3	
51	74.0	
53	122.5	
54	104.9	

No of labs	15
No of repl	2
m	98.2223
s ²	265.1727
s	16.2841
Assigned value	107
Recovery	91.8
t	-2.0877
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

C denotes a Cochran outlier

G denotes a Grubbs outlier

NVOC/TOC, mg/L C

Control of recovery, average of results

Laboratory	Sample pair AB	Outlier
1	75.9	
2	74.1	
4	67.8	
5	73.8	
6	67.0	
15	67.2	
16	70.0	
17	74.5	
18	57.4	
19	70.9	
20	73.0	
22	69.7	
23	74.5	
24	58.3	
25	66.2	
28	71.6	
29	89.5	G
32	67.2	
34	67.7	
37	69.5	
38	76.6	
39	60.7	
40	72.7	
42	67.1	
43	68.3	
44	30.4	G

Laboratory	Sample pair AB	Outlier
46	62.7	
48	72.5	
49	82.6	C
51	68.2	
53	71.4	
56	73.2	
58	66.9	
59	72.9	

No of labs	31
No of repl	2
m	69.3332
s ²	23.0558
s	4.8016
Assigned value	70
Recovery	99.0
t	-0.7732
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

C denotes a Cochran outlier

G denotes a Grubbs outlier

Total phosphorous, mg/L P

Control of recovery, average of results

Laboratory	Sample pair AB	Outlier
1	7.715	
2	7.985	
3	7.750	
4	7.410	
5	7.700	
6	7.800	
10	25.230	C
11	8.305	
12	7.980	
13	8.215	
15	7.530	
16	8.175	
17	7.980	
18	7.930	
19	7.790	
20	7.790	
21	8.230	
22	7.705	
23	8.300	
25	7.415	
26	8.040	
27	7.710	
28	7.815	
29	8.036	
30	7.905	
32	7.592	
33	7.840	
34	8.493	
35	7.755	
36	7.795	
37	7.860	
38	7.850	
39	8.250	
40	7.963	

Laboratory	Sample pair AB	Outlier
41	8.200	
42	7.930	
43	7.730	
44	9.380	C
46	7.830	
47	8.235	
48	8.030	
49	7.935	
50	8.105	
51	8.270	
53	7.910	
54	8.105	
56	7.920	
57	7.855	
58	7.600	
59	8.280	

No of labs	48
No of repl	2
m	7.9280
s ²	0.0591
s	0.2432
Assigned value	7.79
Recovery	101.8
t	3.9318 ***
Sign. level 99.9%	3.5099
Sign. level 99%	2.6846
Sign. level 95%	2.0117

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

U denote a manual selected outlier

C denotes a Cochran outlier

G denotes a Grubbs outlier

Chloride, mg/L

Control of recovery, average of results

Laboratory	Sample pair AB	Outlier
3	83.4	
4	83.4	
6	86.0	
10	82.6	
11	84.4	
12	72.0	
13	77.1	
16	78.0	
17	85.0	
18	84.2	
21	78.0	
23	87.2	
25	77.0	
29	83.8	
30	83.4	
32	83.1	
33	86.0	
34	78.0	
41	77.5	
43	86.5	
44	83.3	
46	85.4	
47	84.6	
49	92.5	C
50	86.5	
51	81.2	
56	83.6	
59	85.9	

No of labs	27
No of repl	2
m	82.4665
s ²	14.5955
s	3.8204
Assigned value	84
Recovery	98.2
t	-2.0857 *
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, 5%-level)

U denote a manual selected outlier

C denotes a Cochran outlier

G denotes a Grubbs outlier

Sulphate, mg/L

Control of recovery, average of results

Laboratory	Sample pair AB	Outlier
3	76.1	
4	75.7	
6	71.4	
15	82.7	
16	71.0	
17	75.5	
18	75.7	
23	78.4	
25	82.2	
29	75.9	
32	76.7	
34	69.0	
43	70.5	
44	81.0	
46	75.1	
47	65.9	
48	-	U
49	83.9	
51	78.4	
59	76.9	

No of labs	19
No of repl	2
m	75.8720
s ²	22.8976
s	4.7851
Assigned value	76
Recovery	99.8
t	-0.1166
Sign. level 99.9%	3.9216
Sign. level 99%	2.8784
Sign. level 95%	2.1009

No test statistics were found to be significant

U denote a manual selected outlier

C denotes a Cochran outlier

G denotes a Grubbs outlier

Total suspended solids, mg/L

Control of recovery, average of results

Laboratory	Sample pair AB	Outlier
1	261.0	
2	278.8	
4	273.6	
5	267.0	
6	281.7	
10	259.8	
11	271.2	
12	268.0	
15	275.0	
16	241.5	C
17	281.0	
18	262.5	
19	290.3	
20	273.0	
22	280.5	
23	280.0	
25	276.5	
26	269.0	
28	270.3	
29	273.0	
32	274.0	
34	267.5	
35	265.8	
36	268.0	
37	281.0	
40	273.4	
42	275.1	
43	270.0	

Laboratory	Sample pair AB	Outlier
44	273.5	
46	273.5	
48	286.8	
49	269.7	
51	276.9	
53	275.0	
54	270.0	
56	277.6	
57	270.0	
58	266.5	
59	253.0	

No of labs	38
No of repl	2
m	272.6164
s ²	53.8865
s	7.3407
Assigned value	273
Recovery	99.9
t	-0.3221
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

C denotes a Cochran outlier

G denotes a Grubbs outlier

ANNEX E 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	14-18	200	194	197	196	205	14	15
			41-43	196	193	195				
			61-82	195	198	197				
		B1	5-18	213	211	212	210	220		
			37-43	207	207	207				
			65-82	212	209	211				
Total Phosphorus	mg/L P	A2	8	8.11	8.15	8.13	8.09	7.79	1.05	1.04
			40	8.06	8.10	8.08				
			69	8.05	8.08	8.07				
		B2	13	9.02	9.05	9.04	9.14	8.83		
			51	9.17	9.21	9.19				
			80	9.19	9.21	9.20				
Chloride	mg/L	A2	8	85.40	85.80	85.60	85.20	84.00	14	12
			40	85.20	85.20	85.20				
			69	84.80	84.80	84.80				
		B2	13	99.20	99.20	99.20	98.70	96		
			51	98.40	98.40	98.40				
			80	98.40	98.60	98.50				
Sulphate	mg/L	A2	8	84.80	84.60	84.70	82.20	76	15	12
			40	81.90	81.20	81.55				
			69	80.50	80.20	80.35				
		B2	99.1	99.10	98.30	98.70	96.73	88		
			51	95.20	93.50	94.35				
			80	97.80	96.50	97.15				
Total Suspended Solids	mg/L	A3	16-18	245.28		245.28	245.94	273	47	40
			36-43	254.72		254.72				
			72-82	237.81		237.81				
		B3	9-18	282.24		282.24	293.09	313		
			40-43	298.31		298.31				
			58-82	298.71		298.71				

ANNEX F HOMOGENEITY AND STABILITY

PT: SPIL-3
Parameter: COD _{Cr} A1
Unit: mg/L O ₂
Sigma: 12.2

Responsible for tests: DHBP

Homogeneity test Date: 2024-08-28

Sample	x(a)	x(b)	average	sd	sd^2
3 - 2	222	227	224.5	3.536	12.500
9 - 7	225	231	228.0	4.243	18.00
17 - 15	226	230	228.0	2.828	8.000
25 - 26	223	226	224.5	2.121	4.500
33 - 32	224	230	227.0	4.243	18.000
38 - 36	223	227	225.0	2.828	8.000
48 - 48	226	229	227.5	2.121	4.500
50 - 49	223	228	225.5	3.536	12.500
60 - 57	220	224	222.0	2.828	8.000
68 - 64	223	220	221.5	2.121	4.500
74 - 70	223	227	225.0	2.828	8.000
77 - 78	224	222	223.0	1.414	2.000

For homogeneity

General average (x)	225.13
Sample average sd (s _x)	2.217
Within-sample sd (s _w):	3.007
Between-samples sd (ss):	0.6276
S _L in the Proficiency Test:	17.8
S _R in the Proficiency Test:	18.15
Assigned value	205

Stability test Date: 2024-09-12

Sample	x(a)	x(b)
14-18	200	194
41-43	196	193
61-82	195	198

For stability

General average (y):	196
/x-y/ =	29.125

Conclusions

	ss = 0.628
	/x-y/ = 29.125
	0.3*sigma= 3.647
	$0.3\sigma_{pt} + 2\sqrt{u^2(x) + u^2(y)} = 23.944$
Analytical quality	Is s _w < 0.15*sigma NO
Homogeneity:	Is ss < 0.3*sigma? YES
Stability:	/x-y/ < 0.3*sigma? NO
Stability:	$ x - y \leq 0.3\sigma_{pt} + 2\sqrt{u^2(x) + u^2(y)}$? NO

PT: SPIL-3

Parameter: TP B2

Unit: mg/L P

Sigma: 0.500

Responsible for tests: S7MS/DHBP

Homogeneity test

Date: 2024-08-28

Sample	x(a)	x(b)	average	sd	sd^2
5	9.27	9.27	9.3	0.000	0.000
12	9.22	9.26	9.2	0.028	0.00
14	9.20	9.26	9.2	0.042	0.002
26	9.27	9.29	9.3	0.014	0.000
32	9.19	9.19	9.2	0.000	0.000
38	9.22	9.23	9.2	0.007	0.000
47	9.24	9.25	9.2	0.007	0.000
49	9.22	9.23	9.2	0.007	0.000
60	9.21	9.21	9.2	0.000	0.000
68	9.32	9.33	9.3	0.007	0.000
76	9.32	9.31	9.3	0.007	0.000
84	9.25	9.25	9.3	0.000	0.000

For homogeneity

General average (x)

9.25

Sample average sd (s_x)

0.041

Within-sample sd (s_w):

0.016

Between-samples sd (ss):

0.0390

S_L in the Proficiency Test:

0.229

S_R in the Proficiency Test:

0.257

Assigned value

8.83

Stability test

Date: 2024-09-12

Sample	x(a)	x(b)
13	9.02	9.05
51	9.17	9.21
80	9.19	9.21

For stability

General average (y):

9.141667

/x-y/ =

0.10875

Conclusions

ss = 0.039

0.3*sigma= 0.15

/x-y/ = 0.10875

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
Parameter: TSS A3
Unit: mg/L
Sigma: 14.4

Responsible for tests: S7MS/RQ8G

Homogeneity test Date: 2024-08-28

Sample	x(a)	x(b)	average	sd	sd^2
4-2	263.4		263.4		
9-7	266.1		266.1		
12-15	266.1		266.1		
19 - 26	261.4		261.4		
26 - 32	269.3		269.3		
34 - 36	268.5		268.5		
41 - 48	269.3		269.3		
44 - 59	273.2		273.2		
51 - 57	259.8		259.8		
59 - 64	269.7		269.7		
62 - 70	270.8		270.8		
73 - 78	273.2		273.2		

For homogeneity	
General average (x)	267.6
Sample average sd (s _x)	4.314
Within-sample sd (s _w):	
Between-samples sd (ss):	4.314
S _L in the Proficiency Test:	6.664
S _R in the Proficiency Test:	7.961
Assigned value	313

Stability test Date: 2024-09-12

Sample	x(a)	x(b)
9-18	245.28	
40-43	254.71	
58-82	237.81	

For stability	
General average (y):	245.9333
x-y =	21.62432

Conclusions	
	ss = 4.314
	x-y = 21.624
	0.3*sigma= 4.334
	$0.3\sigma_{pt} + 2\sqrt{u^2(x) + u^2(y)}$ = 21.778
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 \leq 0,3\sigma_{pt} + 2\sqrt{u^2(x) + u^2(y)}$? YES