Proficiency test SPIL-2 (2023)

Nitrogen parameters in wastewater (untreated sewage)

Quality Documentation
July 2023

Proficiency test SPIL-2 (2023)
Quality Documentation

July 2023

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

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

Client	Client's representative
Environmental laboratories	

Project	Project No
Proficiency test SPIL-2 (2023)	20405-32
Authors: Peter Rerup	Date: 2023-07-30
	Approved by: Rikke Mikkelsen

Revision	Description	By	Approved	Date
	Quality Documentation Report	DPRE	FYE3	2023

Key words	Classification
Analytical quality, assigned value, precision, trueness, homogeneity, stability, total nitrogen, ammonium, nitrite+nitrate, conductivity, pH, wastewater	☒ Open ☐ Internal ☐ Proprietary

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

CONTENTS

1 INTRODUCTION

A proficiency test on the analysis of nitrogen parameters in wastewater was conducted on 4 May 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 6 June 2023.

2 FEATURES OF THE PROFICIENCY TEST

Participants in the proficiency test were a total of 59 laboratories from Denmark, Norway and Sweden.

The closing date for submission of results was 17 May 2023. All participants except laboratory no. 19 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.

Four 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	TN, NH_4, NO_{2+3}, NO_3, γ_{25}
A2/B2	pH

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
Total nitrogen	TN	mg/L N	30 – 80	52	2.27	7
Ammonium	NH_4	mg/L N	20 – 50	24.0	0.24	2.6
Nitrite+nitrate	NO_{2+3}	mg/L N	< 5	0.89	0.061	0.29
Nitrate	NO_3	mg/L N	< 5	1.11	0.051	0.29
Conductivity	γ_{25}	mS/m	50 – 2000	63.3	0.51	4.9
pH	pH	-	6 – 9	6.32	0.097	-

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 except for γ_{25} where the spike value is the difference between median values for the two samples in the sample pair.

The assigned value for TN is operationally defined and is a consensus value based upon the median for method no. 1, 2, 3, 4 and 5 (methods prescribed by the Danish EPA). A list of method identification numbers is found in the report to participants /1/. Assigned values for NH_4, NO_{2+3}, NO_3, γ_{25} and pH are consensus values for all laboratories based on the median. The assigned value for NO_3 (1.11 mg/L N) is higher than the assigned value for NO_{2+3} (0.89 mg/L N). This is due to differences in results obtained from different methods.

2.3.2 Test of spike values

A comparison was made (t-test, 95% confidence level) between the spike value and the difference in concentration between the two samples in the sample pair found from the laboratories' results, see Appendix B. The test showed no significant difference between the two for TN, NH_4, γ_{25} and pH. The test revealed a significant difference between the two for NO_{2+3} and NO_3. 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 C. The test for most parameters showed no significant difference between the two and the control of assigned value at Eurofins confirmed the value (Appendix D).

The test revealed a significant difference between the two for TN. Average recover was 97.4 %. The difference could be attributed to influence from laboratories using methods other than those prescribed by the Danish EPA. The test was repeated after exclusion of the results for method no. other than 1, 2 and 3 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.

3 HOMOGENEITY AND STABILITY OF SAMPLES

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

NH_4	Combined homogeneity and stability test
NO_3	Combined homogeneity and stability test
pH	Combined homogeneity and stability test

The results of control measurements are shown in Appendix E. The appendix also gives the results of the statistical evaluation of the control data. The data are analysed by analysis of variance (ANOVA) giving:

1. the standard deviation/variance for replicates (the contribution from analytical variability),

2. the between bottle standard deviation/variance (the contribution from heterogeneity) and

3. the between days concentration difference (the contribution from instability).

Homogeneity is evaluated by comparing the between bottle variance to 0.3 * the standard deviation for evaluation of participants' performance ($0.3 \cdot \hat{\sigma}$) specified by the Danish EPA /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. However, the pH is not stable. It is therefore recommended to assess deviations from the assigned value for this component with caution.

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.

However, the tests for stability shows that pH are not stable and there is greater deviation and uncertainty in the laboratory results for pH than usual. It is therefore recommended to assess deviations from the assigned pH value with caution.

5 REFERENCES

/1/ Eurofins A/S, *Proficiency test SPIL-2 (2023)*, Report to participants, June 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. 2362 on *quality criteria for environmental measurements,* 16 November 2021 (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
Stock TN	60.000 g Disodium edetate, $2H_2O$ milli-Q water up to 1000.0 g	TN: 4516 mg/kg N
Stock NH_4	30.000 g Ammonium chloride (NH_4Cl) milli-Q water up to 1000.0 g	NH_4: 7858 mg/kg N
Stock NO_3	2.500 g Potassium nitrate (KNO_3) milli-Q water up to 1000.2 g	NO_3: 346.4 mg/kg N

Sample	Sample prepared from	TN mg/kg N	NH_4 mg/kg N	NO_3 mg/kg N	Conductivity mS/m
A1	350.0 g stock TN 100.0 g stock NH_4 150.0 g stock NO_3 Filtered water from Gørding sewage treatment plant up to 60.00 kg	a+40.31	b+13.10	c+0.866	d
B1	25.0 g stock TN 10.0 g stock NH_4 25.0 g stock NO_3 Sample A1 up to 30.00 kg	0.998· (a+40.31) +6.67	0.998· (b+13.10) +2.62	0.998· (c+0.866) +0.289	e

Sample	Sample prepared from	pH
A2/B2	Filtered untreated wastewater from Gørding sewage treatment plant.	f

ANNEX B CONTROL OF SPIKE VALUES

Total Nitrogen, mg/l N
Control of differences within sample pairs

Laboratory	Difference AB	
1	-1.90	
2	1.20	
3	3.80	
4	1.05	
5	1.30	
6	-1.40	
7	-2.90	
8	-	
9	0.75	
10	0.05	
11	0.70	
12	1.20	
13	1.10	
14	-0.03	
15	-3.50	
16	0.71	
17	1.20	
18	-2.60	
19	-	
20	0.20	
21	0.66	
22	1.30	
23	-	
24	-	
25	2.60	
26	53.40	UC
27	23.40	UC
28	-0.30	
29	-0.90	
30	0.57	
31	-1.50	
32	-1.60	
33	-0.23	
34	-0.10	
35	1.00	
36	0.90	
37	1.13	
38	1.50	
39	-	
40	0.30	
41	2.50	
42	-1.20	
43	0.00	
44	-2.90	
45	1.90	
No of labs., p	38	
No of repl., n	2	
d	0.17	
s^2	2.60	
s	1.61	
$t = \sqrt{p} \cdot (d/s)$	0.6595	
Sign. level, p(t)	0.5137	

No test statistics were found to be significant
UC denotes a Cochran outlier

Ammonium, mg/l N
Control of differences within sample pairs

Laboratory	Difference AB	
1	0.40	
2	-	
3	-1.20	
4	-	
5	-0.20	
6	-0.54	
7	-0.20	
8	-	
9	0.00	
10	-0.30	
11	0.60	
12	0.60	
13	-	
14	-0.30	
15	-0.20	
16	0.71	
17	-0.30	
18	0.30	
19	-	
20	-0.27	
21	0.70	
22	0.70	
23	0.20	
24	-0.35	
25	-0.40	
26	-0.40	
27	0.90	UG
28	-	
29	-0.40	
30	-1.27	
31	-	
32	-0.01	
33	-0.30	
34	0.10	
35	-0.20	
36	0.50	
37	0.10	
38	0.00	
39	0.50	
40	-0.30	
41	0.30	
42	0.50	
43	0.60	
44	-1.10	
45	-0.20	
No of labs., p	37	
No of repl., n	2	
d	-0.04	
s^2	0.26	
s	0.51	
$t = \sqrt{p} \cdot (d/s)$	-0.5206	
Sign. level, p(t)	0.6058	

No test statistics were found to be significant
UG denotes a Grubbs outlier

Nitrite + nitrate, mg/l N
Control of differences within sample pairs

Laboratory	Difference AB	
1	-0.680	UG
2	-	
3	-	
4	-	
5	-	
6	-	
7	-	
8	-	
9	-	
10	0.060	
11	-	
12	-	
13	-	
14	-	
15	-	
16	0.062	
17	-	
18	-	
19	-	
20	-	
21	0.010	
22	-	
23	0.388	UG
24	0.022	
25	-	
26	-	
27	-	
28	-	
29	-	
30	0.046	
31	-	
32	-	
33	-	
34	-	
35	-	
36	-	
37	0.100	
38	-	
39	-	
40	-	
41	-	
42	-	
43	-	
44	-	
45	-	
No of labs., p	6	
No of repl., n	2	
d	0.050	
s^2	0.001	
s	0.032	
$t = \sqrt{p} \cdot (d/s)$	3.8184	
Sign. level, p(t)	0.0124	*

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

** denotes that there is a significant difference (t-test, 1%-level)
*** denotes that there is a significant difference (t-test, 0.1%-level)
UG denotes a Grubbs outlier

Difference for sample pair AB is significantly different from 0,
and data should be corrected with the difference (in spike value),
during execution of Cochran's test.

Nitrate, mg/l N
Control of differences within sample pairs

Laboratory	Difference AB	
1	-0.410	UC
2	-	
3	-0.030	
4	-	
5	-	
6	-0.030	
7	0.000	
8	-	
9	0.090	
10	0.060	
11	-	
12	-0.370	UC
13	-	
14	-	
15	-0.130	
16	-	
17	0.030	
18	-0.050	
19	-	
20	-	
21	-	
22	-	
23	-	
24	0.020	
25	0.060	
26	0.000	
27	0.020	
28	-	
29	0.050	
30	-	
31	-	
32	-	
33	0.010	
34	0.010	
35	-	
36	0.050	
37	0.100	
38	0.060	
39	-0.030	
40	0.070	
41	0.029	
42	0.030	
43	0.050	
44	0.050	
45	-	
No of labs., p	24	
No of repl., n	2	
d	0.022	
s^2	0.003	
s	0.050	
$t = \sqrt{p} \cdot (d/s)$	2.1039	
Sign. level, p(t)	0.0465	*

* denotes that there is a significant difference (t-test, 5%-level)
** denotes that there is a significant difference (t-test, 1%-level)
*** denotes that there is a significant difference (t-test, 0.1%-level)
UC denotes a Cochran outlier

Difference for sample pair AB is significantly different from 0,
and data should be corrected with the difference (in spike value),
during execution of Cochran's test.

Conductivity, mS/m
Control of differences within sample pairs

Laboratory	Difference AB	
1	-35.10	UG
2	-0.02	
3	-	
4	-42.60	UG
5	-0.20	
6	-	
7	-	
8	0.00	
9	-0.90	
10	0.10	
11	-	
12	0.00	
13	0.00	
14	-	
15	-	
16	0.05	
17	0.00	
18	-	
19	-	
20	-0.20	
21	-	
22	-	
23	-	
24	14.80	UG
25	0.10	
26	-	
27	-1.20	UG
28	0.20	
29	-46.10	UG
30	-0.40	
31	-	
32	-	
33	1.70	
34	-	
35	0.10	
36	-0.10	
37	0.45	UG
38	-4895.10	UC
39	-	
40	0.20	
41	-	
42	0.60	
43	-	
44	-	
45	-	
No of labs., p	18	
No of repl., n	2	
d	0.07	
s^2	0.26	
s	0.51	
$t = \sqrt{p} \cdot (d/s)$	0.5739	
Sign. level, p(t)	0.5736	

No test statistics were found to be significant
UC denotes a Cochran outlier
UG denotes a Grubbs outlier

pH,
Control of differences within sample pairs

Laboratory	Difference AB	
1	0.000	
2	-0.050	
3	-0.150	
4	-0.200	
5	0.030	
6	-0.060	
7	-	
8	0.060	
9	0.010	
10	0.400	UC
11	0.130	
12	-0.060	
13	0.150	
14	-0.020	
15	-0.180	
16	0.040	
17	0.000	
18	0.060	
19	-	
20	0.040	
21	0.020	
22	-0.030	
23	0.040	
24	0.000	
25	0.047	
26	0.000	
27	-0.030	
28	-0.050	
29	-0.840	UC
30	0.200	
31	0.040	
32	0.020	
33	0.150	
34	0.030	
35	-0.020	
36	0.070	
37	0.040	
38	0.070	
39	-0.010	
40	0.020	
41	0.105	
42	0.067	
43	0.080	
44	-0.940	UC
45	-0.120	
No of labs., p	40	
No of repl., n	2	
d	0.013	
s^2	0.007	
s	0.083	
$t = \sqrt{p} \cdot (d/s)$	1.0223	
Sign. level, p(t)	0.3130	

No test statistics were found to be significant
UC denotes a Cochran outlier

ANNEX C CONTROL OF RECOVERY

Total Nitrogen, mg/l N
Control of recovery, average of results

Laboratory	Sample pair AB	
1	55.45	
2	50.50	
3	54.80	
4	49.02	
5	50.45	
6	49.79	
7	54.15	
8	-	
9	50.42	
10	50.70	
11	50.75	
12	51.10	
13	49.35	
14	44.06	
15	55.35	
16	53.19	
17	50.80	
18	53.10	
19	-	
20	50.90	
21	50.80	
22	51.25	
23	-	
24	-	
25	48.10	
26	25.70	UC
27	64.20	UC
28	50.85	
29	47.05	
30	50.25	
31	47.65	
32	51.20	
33	52.95	
34	49.05	
35	54.00	
36	50.55	
37	51.95	
38	54.75	
39	-	
40	48.85	
41	43.45	
42	43.40	
43	55.30	
44	53.65	
45	46.65	
No of labs., p	38	
No of repl., n	2	
m	50.67	
s^2	9.65	
s	3.11	
Assigned value, μ	52	

Recovery, %	97.4	
$t = \sqrt{p} \cdot (m-\mu)/s$	-2.6318	
Sign. level, p(t)	0.0123	*

* denotes that there is a significant difference (t-test, 5%-level)
** denotes that there is a significant difference (t-test, 1%-level)
*** denotes that there is a significant difference (t-test, 0.1%-level)
UC denotes a Cochran outlier

Ammonium, mg/l N
Control of recovery, average of results

Laboratory	Sample pair AB	
1	24.00	
2	-	
3	22.70	
4	-	
5	24.00	
6	23.57	
7	24.10	
8	-	
9	24.10	
10	24.80	
11	23.70	
12	23.20	
13	-	
14	24.25	
15	24.10	
16	22.95	
17	24.75	
18	23.75	
19	-	
20	24.12	
21	24.22	
22	24.55	
23	23.54	
24	24.44	
25	23.50	
26	23.70	
27	15.15	UG
28	-	
29	20.50	
30	25.09	
31	-	
32	24.56	
33	25.73	
34	23.75	
35	24.00	
36	23.85	
37	23.90	
38	25.50	
39	24.25	
40	21.75	
41	24.15	
42	20.85	
43	22.90	
44	25.05	
45	22.70	
No of labs., p	37	
No of repl., n	2	
m	23.80	
s^2	1.19	
s	1.09	
Assigned value, μ	24.0	
Recovery, %	99.2	
$t = \sqrt{p} \cdot (m-\mu)/s$	-1.1171	
Sign. level, p(t)	0.2713	

No test statistics were found to be significant
UG denotes a Grubbs outlier

Nitrite + nitrate, mg/l N
Control of recovery, average of results

Laboratory	Sample pair AB	
1	3.270	UG
2	-	
3	-	
4	-	
5	-	
6	-	
7	-	
8	-	
9	-	
10	0.860	
11	-	
12	-	
13	-	
14	-	
15	-	
16	0.881	
17	-	
18	-	
19	-	
20	-	
21	0.845	
22	-	
23	0.102	UG
24	0.901	
25	-	
26	-	
27	-	
28	-	
29	-	
30	0.923	
31	-	
32	-	
33	-	
34	-	
35	-	
36	-	
37	1.010	
38	-	
39	-	
40	-	
41	-	
42	-	
43	-	
44	-	
45	-	
No of labs., p	6	
No of repl., n	2	
m	0.903	
s^2	0.004	
s	0.059	
Assigned value, μ	0.89	
Recovery, %	101.5	
$t = \sqrt{p} \cdot (m-\mu)/s$	0.5513	
Sign. level, p(t)	0.6052	

No test statistics were found to be significant
UG denotes a Grubbs outlier

Nitrate, mg/l N
Control of recovery, average of results

Laboratory	Sample pair AB	
1	2.105	UC
2	-	
3	1.125	
4	-	
5	-	
6	1.085	
7	1.110	
8	-	
9	1.205	
10	0.850	
11	-	
12	1.855	UC
13	-	
14	-	
15	1.195	
16	-	
17	0.685	
18	1.065	
19	-	
20	-	
21	-	
22	-	
23	-	
24	0.880	
25	1.210	
26	1.110	
27	1.200	
28	-	
29	0.985	
30	-	
31	-	
32	-	
33	1.115	
34	1.065	
35	-	
36	1.135	
37	1.000	
38	1.350	
39	1.055	
40	0.975	
41	0.894	
42	0.995	
43	1.135	
44	1.115	
45	-	
No of labs., p	24	
No of repl., n	2	
m	1.064	
s^2	0.020	
s	0.141	
Assigned value, μ	1.11	
Recovery, %	95.9	
$t = \sqrt{p} \cdot (m-\mu)/s$	-1.5929	
Sign. level, p(t)	0.1248	

No test statistics were found to be significant
UC denotes a Cochran outlier

Conductivity, mS/m
Control of recovery, average of results

Laboratory	Sample pair AB	
1	643.55	UG
2	61.93	
3	-	
4	591.40	UG
5	63.50	
6	-	
7	-	
8	65.10	
9	64.55	
10	62.65	
11	-	
12	63.40	
13	63.10	
14	-	
15	-	
16	64.89	
17	63.40	
18	-	
19	-	
20	63.40	
21	-	
22	-	
23	-	
24	56.20	UG
25	64.45	
26	-	
27	58.80	UG
28	62.80	
29	666.05	UG
30	64.36	
31	-	
32	-	
33	62.35	
34	-	
35	62.85	
36	63.85	
37	65.22	UG
38	66347.55	UC
39	-	
40	63.90	
41	-	
42	62.60	
43	-	
44	-	
45	-	
No of labs., p	18	
No of repl., n	2	
m	63.50	
s^2	0.82	
s	0.91	
Assigned value, μ	63.6	
Recovery, %	99.9	
$t = \sqrt{p} \cdot (m-\mu)/s$	-0.4462	
Sign. level, p(t)	0.6611	

No test statistics were found to be significant
UC denotes a Cochran outlier

pH,
Control of recovery, average of results

Laboratory	Sample pair AB	
1	5.900	
2	6.495	
3	6.235	
4	6.400	
5	6.085	
6	6.310	
7	-	
8	6.550	
9	6.095	
10	5.660	UC
11	6.165	
12	6.680	
13	6.725	
14	6.600	
15	6.200	
16	6.610	
17	6.750	
18	6.640	
19	-	
20	6.310	
21	6.410	
22	6.085	
23	6.050	
24	6.380	
25	6.399	
26	6.000	
27	6.545	
28	6.395	
29	6.980	UC
30	6.300	
31	6.030	
32	6.140	
33	6.465	
34	6.555	
35	6.600	
36	6.315	
37	6.300	
38	6.065	
39	6.205	
40	6.315	
41	5.869	
42	6.054	
43	6.260	
44	6.920	UC
45	6.440	
No of labs., p	40	
No of repl., n	2	
m	6.323	
s^2	0.054	
s	0.233	
Assigned value, μ	6.32	
Recovery, %	100.1	
$t = \sqrt{p} \cdot (m-\mu)/s$	0.0867	
Sign. level, p(t)	0.9314	

No test statistics were found to be significant
UC denotes a Cochran outlier

ANNEX D CONCENTRATION LEVEL

SPIL-2 (2023)

Parameter	Unit	Sample	Bottle no.	I	II	Bottle Average	Sample Average	Assigned value	Spike Measured	Spike Assigned
Total nitrogen	mg/L N	A1	21	50.6	50.4	50.50	50.32	52	6.33	7
			35	50.3	50.4	50.35				
			52	50.1	50.1	50.10				
		B1	6	56.3	56.4	56.35	56.65	59		
			43	57.1	56.8	56.95				
			71	56.5	56.8	56.65				
Ammonium	mg/L N	A1	21	23.3	23.3	23.30	23.22	24.0	2.92	2.6
			35	23.9	24.0	23.95				
			52	22.4	22.4	22.40				
		B1	6	25.9	25.9	25.90	26.13	26.6		
			43	25.7	25.7	25.70				
			71	26.8	26.8	26.80				
Nitrite+nitrate / Nitrate	mg/L N	A1	21	1.13	1.13	1.13	1.11	0.89	0.29	0.29
			35	1.11	1.10	1.11				
			52	1.09	1.10	1.10				
		B1	6	1.39	1.40	1.40	1.40	1.18		
			43	1.41	1.41	1.41				
			71	1.38	1.39	1.39				
pH		A2	6	6.15	6.16	6.16	6.15	6.32	0.00	0.00
			32	6.16	6.13	6.15				
			51	6.16	6.14	6.15				
		B2	12	6.14	6.17	6.16	6.15	6.32		
			39	6.13	6.16	6.15				
			61	6.14	6.14	6.14				

ANNEX E HOMOGENEITY AND STABILITY

PT:	SPIL-2
Parameter:	NH_4
Unit:	mg/L N
Sigma:	1.422

Responsible for tests: HBP/S7MS

Homogeneity test Date: 2023-04-18

Sample	x(a)	x(b)	average	sd	sd^2
B1 5	27.0	27.1	27.1	0.071	0.005
B1 10	25.8	25.9	25.9	0.071	0.005
B1 15	26.5	26.5	26.5	0.000	0.000
B1 19	26.2	26.3	26.3	0.071	0.005
B1 24	26.2	26.2	26.2	0.000	0.000
B1 33	26.1	26.2	26.2	0.071	0.005
B1 38	26.1	26.2	26.2	0.071	0.005
B1 41	26.3	26.3	26.3	0.000	0.000
B1 50	26.2	26.3	26.3	0.071	0.005
B1 56	26.2	26.2	26.2	0.000	0.000
B1 60	26.5	26.5	26.5	0.000	0.000
B1 67	26.7	26.7	26.7	0.000	0.000

For homogeneity

General average (x)	26.3417
Sample average sd (s_x)	0.3096
Within-sample sd (s_w):	0.0500
Between-samples sd (ss):	0.3075
S_L in the Proficiency Test:	1.060
S_R in the Proficiency Test:	1.120

Stability test Date: 2023-05-04

Sample	x(a)	x(b)
B1 6	25.9	25.9
B1 43	25.70	25.70
B1 71	26.80	26.80

For stability

General average (y):	26.133333
/x-y/ =	0.2083333

Conclusions

ss =	0.3075	0.3*sigma=	0.4267
/x-y/ =	0.2083333		

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

PT:	SPIL-2
Parameter:	NO_3
Unit:	mg/L N
Sigma:	0.360

Responsible for tests: HBP/S7MS

Homogeneity test Date: 2023-04-18

Sample	x(a)	x(b)	average	sd	sd^2
B1 5	1.44	1.44	1.4	0.000	0.000
B1 10	1.41	1.41	1.4	0.000	0.00
B1 15	1.43	1.44	1.4	0.007	0.000
B1 19	1.45	1.46	1.5	0.007	0.000
B1 24	1.45	1.47	1.5	0.014	0.000
B1 33	1.42	1.42	1.4	0.000	0.000
B1 38	1.44	1.46	1.5	0.014	0.000
B1 41	1.41	1.43	1.4	0.014	0.000
B1 50	1.43	1.43	1.4	0.000	0.000
B1 56	1.40	1.40	1.4	0.000	0.000
B1 60	1.35	1.34	1.3	0.007	0.000
B1 67	1.44	1.42	1.4	0.014	0.000

For homogeneity

General average (x)	1.42
Sample average sd (s_x)	0.031
Within-sample sd (s_w):	0.009
Between-samples sd (ss):	0.0301
S_L in the Proficiency Test:	0.139
S_R in the Proficiency Test:	0.143

Stability test Date: 2023-05-04

Sample	x(a)	x(b)
B1 6	1.39	1.40
B1 43	1.41	1.41
B1 71	1.38	1.39

For stability

General average (y):	1.3966667
/x-y/ =	0.0279167

Conclusions

ss =	0.030	0.3*sigma=	0.108 0
/x-y/ =	0.0279167		

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

PT:	SPIL-2
Parameter:	pH
Unit:	
Sigma:	0.1

Responsible for tests: HBP/S7MS

Homogeneity test Date: 2023-04-18

Sample	x(a)	x(b)	average	sd	sd^2
B2 5	7.47	7.43	7.5	0.028	0.001
B2 10	7.40	7.45	7.4	0.035	0.00
B2 15	7.42	7.44	7.4	0.014	0.000
B2 19	7.44	7.48	7.5	0.028	0.001
B2 24	7.46	7.45	7.5	0.007	0.000
B2 33	7.47	7.46	7.5	0.007	0.000
B2 38	7.42	7.46	7.4	0.028	0.001
B2 41	7.39	7.44	7.4	0.035	0.001
B2 50	7.40	7.45	7.4	0.035	0.001
B2 56	7.44	7.44	7.4	0.000	0.000
B2 60	7.45	7.41	7.4	0.028	0.001
B2 67	7.46	7.47	7.5	0.007	0.000

For homogeneity

General average (x)	7.44
Sample average sd (s_x)	0.017
Within-sample sd (s_w):	0.025
Between-samples sd (ss):	0
S_L in the Proficiency Test:	0.229
S_R in the Proficiency Test:	0.236

Stability test Date: 2023-05-04

Sample	x(a)	x(b)
B2 12	6.14	6.17
B2 39	6.13	6.16
B2 61	6.14	6.14

For stability

General average (y):	6.1466667
/x-y/ =	1.295

Conclusions

ss =	0	0.3*sigma= 0.02
/x-y/ =	1.295	
Analytical quality	Is s_w < 0.15*sigma **NO**	
Homogeneity:	Is ss < 0.3*sigma? **YES**	
Stability:	/x-y/ < 0.3*sigma? **NO**	