



Proficiency test SPIL-2 (2024)

**Nitrogen parameters in wastewater
(synthetic wastewater, effluent)**



Proficiency test SPIL-2 (2024) Quality Documentation

July 2024

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

Phone: +45 7022 4266

E-mail:

proficiencytest@etn.eurofins.com

Web: www.eurofins.dk

Client		Client's representative		
Environmental laboratories				

Project		Project No		
Proficiency test SPIL-2 (2024)		20405-42		
Authors		Date		
		2024-07-11		
Peter Rerup		Approved by		
		Rikke Mikkelsen		

1	Quality Documentation Report	DPRE	FYE3	2024-07-11

Revision	Description	By	Checked	Approved

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

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

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.....	4
4	CONCLUSION	5
5	REFERENCES	6
ANNEX A	SAMPLE PREPARATION	8
ANNEX B	CONTROL OF SPIKE VALUES	9
ANNEX C	CONTROL OF RECOVERY.....	15
ANNEX D	CONCENTRATION LEVEL.....	21
ANNEX E	HOMOGENEITY AND STABILITY	22

1 INTRODUCTION

A proficiency test on the analysis of nitrogen parameters in synthetic wastewater, effluent was conducted on 2 May 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 3 June 2024.

2 **FEATURES OF THE PROFICIENCY TEST**

Participants in the proficiency test were a total of 41 laboratories from Brazil, Denmark, Faroe Islands, Spain and Sweden.

The closing date for submission of results was 17 May 2024. All participants 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 synthetic wastewater, effluent. Sample preparation is described in Appendix A.

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 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
Total nitrogen	TN	mg/L N	2-10	4.5	0.052	0.9
Ammonium	NH ₄	mg/L N	0.1-2	0.52	0.006	0.11
Nitrite+nitrate	NO ₂₊₃	mg/L N	1-5	2.08	0.024	0.45
Nitrate	NO ₃	mg/L N	1-5	2.08	0.024	0.45
Conductivity	γ_{25}	mS/m	50-300	84.8	0.56	16.8
pH	pH		6-9	7.23	0.015	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 content of each parameter in each sample is given an assigned value for the sample with the lower content and a spike value, the spike value being the difference in concentration between the two samples of the sample pair. The assigned values and split values for TN, NH₄-N, NO₂₊₃-N, NO₃-N and pH are calculated from sample preparation. Assigned and split value for conductivity is calculated on the basis of the participants' median value.

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.

The test showed no significant difference between the two for NH₄, NO₂₊₃, NO₃, conductivity and pH, but the test revealed a significant difference between the two for TN. Depending on the complexity of organic compounds used for TN, we do not always see 100 % recovery, as complete oxidation does not occur. This is stated in Annex B of ISO 11905-1:1997 (*Water quality-Determination of nitrogen - Part 1: Method using oxidative digestion with peroxodisulfate*) where the recovery rate for EDTA Disodium salt is stated to be 87-98%. It was therefore decided to keep the calculated values from sample preparation.

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

3 **HOMOGENEITY AND STABILITY OF SAMPLES**

The homogeneity and stability of samples was 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 multiplied with the standard deviation for evaluation of participants' performance ($0.3 * \hat{\sigma}$) specified by the Danish EPA /5/, whereas the stability is evaluated by comparing the concentration change of the samples to $0.3 * \hat{\sigma}$ or $0.3 * \hat{\sigma} + 2 \sqrt{u_x^2 + u_y^2}$ where the precision of the measurement method contribute to the inability to meet the criterion. This test ensures that heterogeneity and instability will not have negative influence on the evaluation of participant performance /6/.

The annex also shows the standard deviation within and between laboratories from the proficiency test to allow comparison between tests performed and average quality from participating laboratories.

The tests for stability and homogeneity show that the samples are stable and homogeneous.

4 CONCLUSION

The quality control performed, including test of sample stability and homogeneity as well as test of recovery of spike and assigned values, shows that the samples and their assigned values are suitable for testing the proficiency of the participating laboratories for all parameters. The results are also suitable for estimation of the general quality of analyses among all participating laboratories.

For TN the participants could not recover the spike value. No error in preparation could be found. Depending on the complexity of organic compounds used for TN, we do not always see 100 % recovery, as complete oxidation does not occur. This is stated in Annex B of ISO 11905-1:1997 /7/ where the recovery rate for EDTA Disodium salt is stated to be 87-98 %. The possibility of low recovery of EDTA in combination with rounding of the assigned value and split can explain the significant difference between the assigned split and the difference in participants results. It was therefore decided to keep the calculated values from sample preparation.

5 REFERENCES

- /1/ Eurofins A/S, *Proficiency test SPIL-2 (2024)*, Report to participants, June 2024.
- /2/ ISO 5725-2, *Accuracy (trueness and precision) of measurement methods and results – Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method*, 2019.
- /3/ Spliid, H., *Procedure and analysis of data for proficiency tests and environmental analyses*, Report to Danish Environmental Protection Agency, 1994 (in Danish).
- /4/ Eurofins A/S, *Schedule for a proficiency test*, document may be downloaded from www.eurofins.dk/proficiencytest.
- /5/ Ministry of Environment, *Regulation no. 529 on quality criteria for environmental measurements*, 14 May 2023 (in Danish).
- /6/ ISO 13528, *Statistical methods for use in proficiency testing by interlaboratory comparison*, 2022.
- /7/ ISO 11905-1, *Water quality - Determination of nitrogen - Part 1: Method using oxidative digestion with peroxodisulfate*, 1997.

A N N E X E S

ANNEX A SAMPLE PREPARATION

Stock solution	Prepared from	Concentration
Stock TN	25.00 g Disodium edetate, 2H ₂ O milli-Q water up to 1000.3 g	TN: 188.1 mg/kg N
Stock NH ₄	5.000 g Ammonium chloride (NH ₄ Cl) milli-Q water up to 2000.0 g	NH ₄ : 655.0 mg/kg N
Stock NO ₃	2.500 g Potassium nitrate (KNO ₃) milli-Q water up to 1000.0 g	NO ₃ : 346.4 mg/kg N
Stock NaCl	50.000 g Sodium chloride (NaCl) milli-Q water up to 1000.0 g	conductivity: c. 10679 mS/m

Sample	Sample prepared from	TN mg/L N	NH ₄ mg/L N	NO ₃ mg/L N	Conductivity mS/m
A1	49.99 g stock TN 40.00 g stock NH ₄ 300.00 g stock NO ₃ 400.0 g stock NaCl milli-Q water up to 50.00 kg	4.48	0.524	2.08	85.43
B1	5.00 g stock TN 5.00 g stock NH ₄ 40.00 g stock NO ₃ 50.0 g stock NaCl Sample A1 up to 30.00 kg	0.997 · 4.48 + 0.87	0.997 · 0.524 + 0.107	0.997 · 2.08 + 0.45	0.997 · 85.43 + 17.8

Sample	Sample prepared from	pH
A2/B2	25.50 g Potassium dihydrogen phosphate (KH ₂ PO ₄) 77.88 g Disodium hydrogen phosphate, 2H ₂ O (Na ₂ HPO ₄ , 2H ₂ O) milli-Q water up to 12500 g	c. 7.20

ANNEX B CONTROL OF SPIKE VALUES

Total Nitrogen, mg/L N

Control of differences within sample pairs

Laboratory	Difference AB	Method	Outlier
1	0.05	71A	
3	0.06	71	
4	0.22	71A	
5	0.23	9	
7	0.30	6	
8	0.21	6	
9	0.38	71B	
10	0.56	72	
11	-0.91	71A	C
13	-0.06	71A	
14	0.08	71	
15	0.05	9	
16	0.20	2	
17	0.20	1	
18	0.06	51	
19	0.10	61	
20	0.12	6	
21	0.00	71	
22	-0.43	71A	
23	-0.15	71	
24	0.06	72	
25	0.15	71	
26	1.55	71B	C
27	0.26	6	
28	0.11	71B	
29	-3.34	71A	C
30	0.02	3	
31	0.36	71A	
32	0.13	71	
33	0.13	9	
34	0.23	6	
35	0.02	71	
36	0.10	51	
37	0.01	71	
38	0.03	6	
40	0.12	71B	
41	0.12	71	

No of labs, p	34
No of repl, n	2
d	0.1187
s ²	0.0277
s	0.1664
t	4.1595 ***
Sign. level 99.9%	3.6109
Sign. level 99%	2.7333
Sign. level 95%	2.0345

*** denotes that there is a significant difference (t-test, 0.01 %-level)

C denotes a Cochran outlier

Ammonium, mg/L N

Control of differences within sample pairs

Laboratory	Difference AB	Method	Outlier
1	0.013	62A	
4	-0.002	62A	
5	-0.001	62	
6	-0.005	9	
7	-0.001	9	
8	0.006	7	
9	0.013	62	
10	0.003	62	
11	0.041	62A	G
13	0.014	62A	
14	-0.007	5	
15	0.010	9	
16	0.021	63	
18	0.000	82	
19	-0.009	62	
20	-0.001	62	
21	0.000	62	
22	0.007	62A	
23	-0.011	62	
24	0.000	63	
26	-0.010	62	
27	-0.003	51	
28	-0.120	2	C
29	0.010	62A	
30	-0.004	62	
31	0.001	62A	
32	-0.010	62	
33	0.043	4	G
35	0.046	62	
36	0.006	83	
39	0.003	7	
40	0.002	62	

No of labs, p	29
No of repl, n	2
d	0.0031
s ²	0.0001
s	0.0114
t	1.4802
Sign. level 99.9%	3.6739
Sign. level 99%	2.7633
Sign. level 95%	2.0484

No test statistics were found to be significant

C denotes a Cochran outlier

G denotes a Grubbs outlier

Nitrite+Nitrate, mg/L N

Control of differences within sample pairs

Laboratory	Difference AB	Method	Outlier
6	-0.107	9	
14	0.000	9	
15	0.010	9	
28	0.030	7A	
39	0.102	7A	

No of labs, p	5
No of repl, n	2
d	0.0071
s ²	0.0057
s	0.0753
t	0.2102
Sign. level 99.9%	8.6103
Sign. level 99%	4.6041
Sign. level 95%	2.7764

No test statistics were found to be significant

Nitrate, mg/L N

Control of differences within sample pairs

Laboratory	Difference AB	Method	Outlier
1	-0.045	71A	
2	0.030	71	
4	0.010	71A	
5	-0.030	9	
9	0.090	71	
10	-0.010	71	
11	0.170	71A	
13	-0.050	71A	
16	0.020	9	
18	-0.080	9	
19	0.050	71	
20	-0.050	71	
22	0.060	71A	
23	0.010	71	
24	0.010	71	
25	0.020	71	
26	0.080	71	
27	-0.010	9	
28	0.030	7B	
29	-0.050	71A	
30	-0.030	9	
31	0.000	71A	
33	0.027	9	
35	0.040	71	
37	0.020	71	
40	-0.020	71	

No of labs, p	26
No of repl, n	2
d	0.0112
s ²	0.0028
s	0.0530
t	1.0809
Sign. level 99.9%	3.7251
Sign. level 99%	2.7874
Sign. level 95%	2.0595

No test statistics were found to be significant

Conductivity, mS/m

Control of differences within sample pairs

Laboratory	Difference AB	Method	Outlier
5	0.70	1	
6	0.30	1	
9	0.60	2	
10	0.00	1	
11	*)	1	U
12	-0.30	1	
14	-0.01	1	
16	0.20	1	
17	0.00	1	
20	-0.05	1	
21	-0.20	1	
22	-0.30	1	G
25	1.88	1	
26	0.50	2	
27	-0.18	1	
29	*)	1	U
30	-0.20	1	
31	-0.20	1	
32	-0.60	1	
33	0.83	9	
34	-0.40	1	
37	0.84	1	
41	-1.90	1	

No of labs, p	20
No of repl, n	2
d	0.0905
s ²	0.5458
s	0.7388
t	0.5478
Sign. level 99.9%	3.8834
Sign. level 99%	2.8609
Sign. level 95%	2.0930

No test statistics were found to be significant

U denote a manual selected outlier

G denotes a Grubbs outlier

*) Not calculated as the result is excluded

pH

Control of differences within sample pairs

Laboratory	Difference AB	Method	Outlier
2	-0.010	1	
3	0.020	1	
4	0.006	1	
6	0.000	1	
7	0.000	1	
8	0.000	1	
9	-0.015	1	
10	-0.020	1	
11	-0.010	1	
12	-0.013	1	
13	0.000	1	
14	-0.020	1	
15	-0.010	1	
16	-0.010	1	
17	-0.020	1	
18	-0.010	1	
19	-0.040	1	
20	0.000	1	
21	-0.010	1	
22	0.012	1	
23	-0.010	1	
24	0.000	1	
25	0.000	1	
26	0.010	1	
27	0.000	1	
28	0.020	1	
29	0.000	1	
30	0.000	1	
31	0.008	1	
32	0.000	1	
34	0.000	1	
35	0.000	1	
36	-0.020	1	
37	0.020	1	
39	0.000	1	
40	-0.020	1	
41	0.030	1	

No of labs, p	37
No of repl, n	2
d	-0.0030
s ²	0.0002
s	0.0137
t	-1.3398
Sign. level 99.9%	3.5821
Sign. level 99%	2.7195
Sign. level 95%	2.0281

No test statistics were found to be significant

ANNEX C CONTROL OF RECOVERY

Total Nitrogen, mg/L N

Control of recovery, average of results

Laboratory	Sample pair AB	Method	Outlier
1	4.14	71A	
3	4.39	71	
4	5.04	71A	
5	5.00	9	
7	3.72	6	
8	3.76	6	
9	4.01	71B	
10	4.99	72	
11	3.82	71A	C
13	4.63	71A	
14	4.34	71	
15	4.56	9	
16	4.48	2	
17	3.98	1	
18	4.44	51	
19	4.55	61	
20	4.10	6	
21	4.50	71	
22	4.95	71A	
23	5.36	71	
24	4.36	72	
25	4.63	71	
26	4.88	71B	C
27	4.19	6	
28	4.35	71B	
29	7.15	71A	C
30	4.36	3	
31	4.27	71A	
32	4.32	71	
33	3.68	9	
34	3.94	6	
35	4.64	71	
36	4.14	51	
37	4.51	71	
38	3.79	6	
40	4.32	71B	
41	4.39	71	

No of labs, p	34
No of repl, n	2
m	4.3763
s ²	0.1566
s	0.3957
Assigned value, μ	4.5
Recovery, %	97.3
t	-1.8234
Sign. level 99.9%	3.6109
Sign. level 99%	2.7333
Sign. level 95%	2.0345

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

Ammonium, mg/L N

Control of recovery, average of results

Laboratory	Sample pair AB	Method	Outlier
1	0.477	62A	
4	0.502	62A	
5	0.534	62	
6	0.491	9	
7	0.547	9	
8	0.513	7	
9	0.510	62	
10	0.512	62	
11	0.219	62A	G
13	0.516	62A	
14	0.579	5	
15	0.522	9	
16	0.484	63	
18	0.480	82	
19	0.560	62	
20	0.535	62	
21	0.540	62	
22	0.487	62A	
23	0.560	62	
24	0.540	63	
26	0.539	62	
27	0.565	51	
28	0.760	2	C
29	0.514	62A	
30	0.521	62	
31	0.511	62A	
32	0.526	62	
33	0.354	4	G
35	0.545	62	
36	0.465	83	
39	0.511	7	
40	0.528	62	

No of labs, p	29
No of repl, n	2
m	0.5209
s ²	0.0008
s	0.0281
Assigned value, μ	0.52
Recovery, %	100.2
t	0.1808
Sign. level 99.9%	3.6739
Sign. level 99%	2.7633
Sign. level 95%	2.0484

No test statistics were found to be significant

C denotes a Cochran outlier

G denotes a Grubbs outlier

Nitrite+Nitrate, mg/L N

Control of recovery, average of results

Laboratory	Sample pair AB	Method	Outlier
6	1.959	9	
14	2.120	9	
15	2.015	9	
28	1.945	7A	
39	1.987	7A	

No of labs, p	5
No of repl, n	2
m	2.0052
s ²	0.0048
s	0.0695
Assigned value, μ	2.08
Recovery, %	96.4
t	-2.4048
Sign. level 99.9%	8.6103
Sign. level 99%	4.6041
Sign. level 95%	2.7764

No test statistics were found to be significant

Nitrate, mg/L N

Control of recovery, average of results

Laboratory	Sample pair AB	Method	Outlier
1	1.987	71A	
2	2.055	71	
4	1.895	71A	
5	2.115	9	
9	1.645	71	
10	2.095	71	
11	2.045	71A	
13	2.045	71A	
16	2.240	9	
18	2.060	9	
19	1.965	71	
20	2.095	71	
22	1.900	71A	
23	1.985	71	
24	2.095	71	
25	2.020	71	
26	2.010	71	
27	2.445	9	
28	1.945	7B	
29	1.905	71A	
30	2.145	9	
31	1.970	71A	
33	1.819	9	
35	1.960	71	
37	2.030	71	
40	1.990	71	

No of labs, p	26
No of repl, n	2
m	2.0177
s ²	0.0207
s	0.1438
Assigned value, μ	2.08
Recovery, %	97.0
t	-2.2076
Sign. level 99.9%	3.7251
Sign. level 99%	2.7874
Sign. level 95%	2.0595

No test statistics were found to be significant

Conductivity, mS/m

Control of recovery, average of results

Laboratory	Sample pair AB	Method	Outlier
5	84.65	1	
6	84.85	1	
9	83.80	2	
10	84.80	1	
11	*)	1	U
12	85.65	1	
14	81.91	1	
16	84.70	1	
17	85.30	1	
20	84.83	1	
21	85.70	1	
22	68.45	1	G
25	79.08	1	
26	81.75	2	
27	86.21	1	
29	*)	1	U
30	84.80	1	
31	85.90	1	
32	85.70	1	
33	84.41	9	
34	85.40	1	
37	79.97	1	
41	84.45	1	

No of labs, p	20
No of repl, n	2
m	84.1928
s ²	3.8849
s	1.9710
Assigned value, μ	84.8
Recovery, %	99.3
t	-1.3778
Sign. level 99.9%	3.8834
Sign. level 99%	2.8609
Sign. level 95%	2.0930

No test statistics were found to be significant

U denote a manual selected outlier

C denotes a Cochran outlier

G denotes a Grubbs outlier

*) Not calculated as the result is excluded

pH

Control of recovery, average of results

Laboratory	Sample pair AB	Method	Outlier
2	7.255	1	
3	7.180	1	
4	7.115	1	
6	7.180	1	
7	7.230	1	
8	7.220	1	
9	7.242	1	
10	7.240	1	
11	7.265	1	
12	7.267	1	
13	7.240	1	
14	7.210	1	
15	7.185	1	
16	7.205	1	
17	7.130	1	
18	7.215	1	
19	7.140	1	
20	7.250	1	
21	7.225	1	
22	7.317	1	
23	7.265	1	
24	7.230	1	
25	7.200	1	
26	7.425	1	
27	7.280	1	
28	7.210	1	
29	7.300	1	
30	7.230	1	
31	7.299	1	
32	7.210	1	
34	7.180	1	
35	7.250	1	
36	7.300	1	
37	7.220	1	
39	7.210	1	
40	7.330	1	
41	7.195	1	

No of labs, p	37
No of repl, n	2
m	7.2336
s ²	0.0034
s	0.0585
Assigned value, μ	7.23
Recovery, %	100.1
t	0.3763
Sign. level 99.9%	3.5821
Sign. level 99%	2.7195
Sign. level 95%	2.0281

No test statistics were found to be significant

ANNEX D CONCENTRATION LEVEL

Concentration level SPIL-2 (2024)

Parameter	Unit	Sample	Bottle no.	I	II	Bottle Average	Sample Average	Assigned value	Spike	
									Measured	Assigned
Total nitrogen	mg/L N	A1	3	4.41	4.44	4.43	4.39	4.50	0.82	0.9
			22	4.38	4.38	4.38				
			44	4.35	4.37	4.36				
		B1	5	5.23	5.25	5.24	5.21	5.40		
			39	5.17	5.17	5.17				
			62	5.20	5.23	5.22				
Ammonium	mg/L N	A1	3	0.545	0.546	0.55	0.543	0.520	0.09	0.110
			22	0.555	0.556	0.56				
			44	0.526	0.527	0.53				
		B1	5	0.636	0.637	0.64	0.637	0.630		
			39	0.629	0.629	0.63				
			62	0.646	0.646	0.65				
Nitrite+nitrate / Nitrate	mg/L N	A1	3	2.09	2.09	2.09	2.08	2.08	0.39	0.45
			22	2.08	2.07	2.08				
			44	2.06	2.06	2.06				
		B1	5	2.47	2.47	2.47	2.46	2.53		
			39	2.46	2.46	2.46				
			62	2.46	2.44	2.45				
pH		A2	11	7.35	7.35	7.35	7.35	7.23	0.00	0
			30	7.34	7.34	7.34				
			48	7.36	7.35	7.36				
		B2	14	7.35	7.34	7.35	7.35	7.23		
			37	7.34	7.34	7.34				
			64	7.35	7.35	7.35				

ANNEX E HOMOGENEITY AND STABILITY

PT:SPIL-2

Parameter:NH₄

Unit:mg/L N

Sigma:0.036

Responsible for tests: HBP/S7MS

Homogeneity test Date:2024-04-16

Sample	x(a)	x(b)	average	sd	sd^2
2	0.650	0.651	0.7	0.001	0.000
7	0.648	0.647	0.6	0.001	0.000
12	0.647	0.649	0.6	0.001	0.000
17	0.645	0.646	0.6	0.001	0.000
23	0.645	0.646	0.6	0.001	0.000
30	0.644	0.645	0.6	0.001	0.000
36	0.644	0.645	0.6	0.001	0.000
42	0.643	0.644	0.6	0.001	0.000
48	0.650	0.650	0.7	0.000	0.000
54	0.641	0.641	0.6	0.000	0.000
57	0.642	0.642	0.6	0.000	0.000
63	0.646	0.646	0.6	0.000	0.000

For homogeneity

General average (x)	0.6457
Sample average sd (s _x)	0.0029
Within-sample sd (s _w):	0.0007
Between-samples sd (ss):	0.0029
S _L in the Proficiency Test:	0.027
S _R in the Proficiency Test:	0.029

Stability test Date:2024-05-02

Sample	x(a)	x(b)
B1-5	0.636	0.637
B1-39	0.629	0.629
B1-62	0.646	0.646

For stability

General average (y):	0.6371667
/x-y/ =	0.0085417

Conclusions

ss =0.0029 0.3*sigma=0.0108	
/x-y/ =0.0085417	
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-2
Parameter:NO ₃
Unit:mg/L N
Sigma:0.135

Responsible for tests:

HBP/S7MS

Homogeneity test

Date:2024-04-16

Sample	x(a)	x(b)	average	sd	sd^2
2	2.51	2.54	2.5	0.021	0.000
7	2.49	2.51	2.5	0.014	0.00
12	2.54	2.54	2.5	0.000	0.000
17	2.45	2.44	2.4	0.007	0.000
23	2.54	2.52	2.5	0.014	0.000
30	2.50	2.49	2.5	0.007	0.000
36	2.46	2.48	2.5	0.014	0.000
42	2.49	2.50	2.5	0.007	0.000
48	2.49	2.49	2.5	0.000	0.000
54	2.48	2.50	2.5	0.014	0.000
57	2.50	2.46	2.5	0.028	0.001
63	2.48	2.52	2.5	0.028	0.001

For homogeneity

General average (x)	2.50
Sample average sd (s _x)	0.026
Within-sample sd (s _w):	0.016
Between-samples sd (ss):	0.0237
S _L in the Proficiency Test:	0.141
S _R in the Proficiency Test:	0.146

Stability test

Date:2024-05-02

Sample	x(a)	x(b)
B1-5	2.47	2.47
B1-39	2.46	2.46
B1-62	2.46	2.44

For stability

General average (y): 2.46

/x-y/ = 0.0366667

Conclusions

ss =0.024	0.3*sigma=0.0404
/x-y/ =0.0366667	
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-2
Parameter:	pH
Unit:	
Sigma:	0,1

Responsible for tests: DHBP/S7MS

Homogeneity test Date: 2024-04-16

Sample	x(a)	x(b)	average	sd	sd^2
5	7,29	7,27	7,3	0,014	0,000
10	7,28	7,28	7,3	0,000	0,00
15	7,28	7,28	7,3	0,000	0,000
19	7,28	7,27	7,3	0,007	0,000
24	7,28	7,27	7,3	0,007	0,000
33	7,27	7,28	7,3	0,007	0,000
38	7,26	7,28	7,3	0,014	0,000
41	7,29	7,29	7,3	0,000	0,000
50	7,26	7,26	7,3	0,000	0,000
56	7,27	7,27	7,3	0,000	0,000
60	7,27	7,27	7,3	0,000	0,000
65	7,29	7,28	7,3	0,007	0,000

For homogeneity	
General average (x)	7,28
Sample average sd (s _x)	0,008
Within-sample sd (s _w):	0,007
Between-samples sd (ss):	0,0062
S _L in the Proficiency Test:	0,074
S _R in the Proficiency Test:	0,09

Stability test Date: 2024-05-02

Sample	x(a)	x(b)
B2-14	7,35	7,34
B2-37	7,34	7,34
B2-64	7,35	7,35

For stability	
General average (y):	7,345
x-y =	0,0691667

Conclusions	
ss = 0,006	
x-y = 0,069	
0.3*sigma= 0,022	
$0.3\sigma_{pt} + 2\sqrt{u^2(x) + u^2(y)} = 0,144$	
Analytical quality	Is s _w < 0,15*sigma YES
Homogeneity:	Is ss < 0.3*sigma? YES
Stability:	x-y < 0.3*sigma? NO
Stability:	$ x - y \leq 0,3\sigma_{pt} + 2\sqrt{u^2(x) + u^2(y)}$? YES