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Proficiency test SPIL-2 (2019)

Nitrogen parameters in wastewater (untreated sewage)

Quality Documentation
August 2019

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Project	Project No
Proficiency test SPIL-2 (2019)	20404-92
Authors Rikke Mikkelsen	Date 2019-08-08
	Approved by Peter Rerup

Revision	Description	By	Checked	Approved	Date
	Quality Documentation Report	FYE3	PRE	PRE	2019-08-09

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

Distribution	
DANAK	
Eurofins:	Rikke Mikkelsen, Peter Rerup

CONTENTS

1 INTRODUCTION

A proficiency test on the analysis of nitrogen parameters in wastewater was conducted on 16 May 2019. 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 25 June 2019.

2 FEATURES OF THE PROFICIENCY TEST

Participants in the proficiency test were a total of 56 laboratories from Denmark, Norway and Sweden. A list of participants is shown in Appendix A.

The closing date for submission of results was 7 June 2019. All participants except laboratory no. 1, 12 and 39 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" (1994) /2/ and as described in detail in Spliid (1992) /3/. A short introduction to the statistics and a list of symbols and abbreviations used is given in Eurofins document "Schedule for a proficiency test", which is available at Eurofins' home page /4/.

The statistical model used is based on the assumption that the variances for the two samples in a sample pair are identical. The assumption was tested (F-test, 95% confidence level) and the result was that the two variances may be assumed to be identical for all parameters.

2.3 Assigned and spike value

An overview of the concentrations in the samples (the assigned values) and the difference in concentration between the two samples of a sample pair (spike value) are shown in Table 2 compared to the range of concentrations normally encountered in 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	63.64	0.024	8.17
Ammonium	NH_4	mg/L N	20 – 50	45.498	0.0066	4.614
Nitrite+nitrate	NO_{2+3}	mg/L N	< 5	0.36	0.020	0.19
Nitrate	NO_3	mg/L N	< 5	0.78	0.020	0.19
Conductivity	γ_{25}	mS/m	50 – 2000	154	1.7	4
pH	pH	-	6 – 9	7.54	0.063	-

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. 2. 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 (0.78 mg/L N) is higher than the assigned value for NO_{2+3} (0.36 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 C. The test showed no significant difference between the two for most parameters. The test revealed a significant difference between the two for pH.

The difference for pH is numerically small and has insignificant influence on the general quality of analysis 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 for most parameters showed no significant difference between the two and the control of assigned value at Eurofins confirmed the value (Appendix E).

The test revealed a significant difference between the two for TN. Average recovery was 104.8 %. 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. 6, 9, 71, 71B, 73, 73A and 73B 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 no significant difference between the two for NO_3. Most laboratories using other methods than no. 71 or 71A deviated significant and was excluded as outliers. The assigned value is therefore the consensus value found using method no. 71 and 71A and is not necessary the true value. For that reason it was named an indicative value on the individual reports.

3 HOMOGENEITY AND STABILITY OF SAMPLES

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

NH_4	Homogeneity test
NO_2	Combined homogeneity and stability test
NO_3	Combined homogeneity and stability test
pH	Homogeneity 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 * 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 pH 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 TN the participants did not recover the assigned value. 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 NO_3 the assigned value is based on consensus values for method no. 71 and 71A. The assigned value can be viewed as indicative and not is necessary true. It is therefore recommended to evaluate deviations from the assigned value with caution.

5 REFERENCES

/1/ Eurofins A/S, *Proficiency test SPIL-2 (2019)*, Report to participants, June 2019.

/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*, 1994.

/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. 523 on *quality criteria for environmental measurements,* 1 May 2019 (in Danish).

/6/ ISO 13528, *Statistical methods for use in proficiency testing by interlaboratory comparison*, 2005.

A N N E X E S

ANNEX A LIST OF PARTICIPANTS

Laboratory	Town	Country
Analyseenheden, Institut for Agroøkologi, Aarhus Universitet	Tjele	Danmark
AquaDjurs A/S	Grenaa	Danmark
Biofos A/S	København K	Danmark
Bjergmarken R/A, Fors Spildevand Roskilde	Roskilde	Danmark
BlueKolding A/S	Kolding	Danmark
CP Kelco, Spildevandslaboratoriet	Ll. Skensved	Danmark
Eurofins Miljø A/S (3 participants)	Vejen	Danmark
Faxe Forsyning	Faxe	Danmark
Fors Spildevand Holbæk	Holbæk	Danmark
Hillerød Forsyning, Spildevand	Hillerød	Danmark
Holstebro Centralrenseanlæg, Vestforsyning Spilde-vand	Holstebro	Danmark
Klarforsyning, Køge-Egnens Renseanlæg	Køge	Danmark
Melby Renseanlæg	Liseleje	Danmark
NK-Spildevand A/S	Næstved	Danmark
Nyborg Renseanlæg	Nyborg	Danmark
Provas	Haderslev	Danmark
Ringkøbing-Skjern Forsyning A/S	Skjern	Danmark
Rønne Renseanlæg	Rønne	Danmark
SK Spildevand, Slagelse Renseanlæg (5 participants)	Slagelse	Danmark
Spildevandslaboratoriet (2 participants)	Esbjerg	Danmark
Svendborg Spildevand A/S, Svenborg Centralrense-anlæg	Skårup Fyn	Danmark
Vandmiljø Randers A/S	Randers SØ	Danmark
Vejle Spildevand	Vejle	Danmark
Eurofins Environment Testing Norway AS	Moss	Norge
SYNLAB AS (Hamar)	Hamar	Norge
AB Lennart Månsson International	Helsingborg	Sverige
Campus Roslagen, Utvecklingscentrum för Vatten	Norrtälje	Sverige
Ernemar Laboratorium	Oskarshamn	Sverige
GRYAAB AB	Göteborg	Sverige
Gästrike Vatten AB	Skutskär	Sverige
Hallsta Pappersbruk	Hallstavik	Sverige
Holmen Paper AB, Bravikens Pappersbruk Bravikens Pappersbruk	Norrköping	Sverige
Kalmar Vatten AB, VA-lab	Kalmar	Sverige
Käppalaverket	Lidingö	Sverige
Laboratoriet på Vatten och Avloppsavdelningen, SBF, Enköpings Kommun	Enköping	Sverige
Laboratoriet vid Smedjeholms avolppsreningsverk	Falkenberg	Sverige

Laboratory	Town	Country
Mjölby Kommun	Mjölby	Sverige
Nordic Sugar, Örtofta Sockerbruk	Eslöv	Sverige
Preem AB Göteborg	Göteborg	Sverige
Reningsverket Aggerud	Karlskoga	Sverige
Roslagsvatten AB	Åkersberga	Sverige
Smurfit Kappa Piteå	Piteå	Sverige
St1 Refinery AB	Göteborg	Sverige
Södra Cell AB, Värö	Väröbacka	Sverige
Uddebo Laboratorium	Luleå	Sverige
Vallviks Bruk AB	Vallvik	Sverige
VIVAB	Falkenberg	Sverige
Västervik Miljö & Energi AB, Vattenlaboratoriet	Västervik	Sverige
Yara AB	Köping	Sverige

ANNEX B SAMPLE PREPARATION

Stock solution	**Prepared from**		**Concentration**
Stock TN	25.00 g	Disodium edetate, $2H_2O$ milli-Q water up to 1000.0 g	TN: 1.882 g/kg N
Stock NH_4	20.003 g	Ammonium chloride (NH_4Cl) milli-Q water up to 1000.1 g	NH_4: 5.239 g/kg N
Stock NO_3	2.500 g	Potassium nitrate (KNO_3) milli-Q water up to 999.8 g	NO_3: 0.347 g/kg N

Sample	**Sample prepared from**	**TN mg/kg N**	**NH_4 mg/kg N**	**NO_3 mg/kg N**	**Conductivity mS/m**
A1	850.0 g stock TN 150.0 g stock NH_4 100.0 g stock NO_3 Filtered water from Holsted sewage treatment plant up to 100.0 kg	a+24.20	b+7.859	c+0.3465	d
B1	100.0 g stock TN 50.0 g stock NH_4 30.0 g stock NO_3 Sample A1 up to 55.0 kg	0.997· (a+24.20) + 8.157	0.997· (b+7.859) + 4.614	0.997· (c+0.3465) +0.1824	e

Sample	**Sample prepared from**	**pH**
A2/B2	Filtered untreaded wastewater from Holsted sewage treatment plant.	f

ANNEX C CONTROL OF SPIKE VALUES

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

Laboratory	Difference AB	
2	1.37	
3	9.97	UG
4	-6.83	
5	7.41	UG
6	2.27	
8	3.47	
9	-4.58	
10	0.27	
11	1.67	
13	0.77	
14	0.27	
15	-0.03	
16	-4.33	
17	3.47	
18	2.52	
19	6.37	
20	-2.03	
21	2.27	
22	-0.43	
23	0.29	
24	-1.23	
25	-1.43	
26	-1.83	
27A	-	
27B	-	
28	-	
29	3.27	
30	28.77	UC
31	0.08	
32A	-3.33	
32B	-0.63	
33A	-	
33B	-	
34	1.07	
35	0.67	
36	-2.43	
37	0.97	
38	0.77	

Laboratory	Difference AB
40	-1.93
41	-0.59
42	-1.65
43	2.37
44	10.17
45	-0.88
46	-0.36
47	-1.33
48	1.31
49	-1.57
50	1.57
51A	1.77
51B	2.07
52	1.37
53	8.47
54	-0.03
55	0.27
56	2.37
No of labs., p	48
No of repl., n	2
d	0.54
s^2	8.79
s	2.97
$t = \sqrt{p} \cdot (d/s)$	1.2719
Sign. level, p(t)	0.2097

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

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

Laboratory	Difference AB
2	0.01
3	-2.99
4	-2.59
5	1.11
6	-1.99
8	-1.89
9	-
10	-
11	0.21
13	-0.59
14	0.51
15	-
16	0.31
17	-1.09
18	1.71
19	-
20	1.11
21	-0.89
22	-2.51
23	-
24	4.21
25	-0.04
26	-
27A	-
27B	-
28	1.41
29	-1.19
30	-0.19
31	1.98
32A	0.01
32B	5.31
33A	0.61
33B	-1.89
34	3.61
35	2.81
36	-0.19
37	-
38	3.31
40	-2.69
41	-0.79
42	1.02
43	-1.99
44	-5.29
45	-0.76
46	-
47	0.31
48	-
49	-3.49
50	0.91
51A	3.61
51B	0.31
52	0.33
53	4.71
54	0.15
55	-1.09
56	1.81
No of labs., p	45
No of repl., n	2
d	0.16
s^2	5.00
s	2.24
$t = \sqrt{p} \cdot (d/s)$	0.4948
Sign. level, p(t)	0.6232

No test statistics were found to be significant

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

Laboratory	Difference AB	
2	-	
3	-	
4	-	
5	-	
6	-	
8	-	
9	-	
10	-	
11	-	
13	-	
14	-	
15	-	
16	-	
17	-	
18	-	
19	-	
20	0.0300	
21	-	
22	-	
23	-	
24	-	
25	-0.0150	
26	-	
27A	-	
27B	-	
28	0.0100	
29	-	
30	-	
31	0.1290	UC
32A	-	
32B	-	
33A	-	
33B	-	
34	-	
35	-	
36	-	
37	-	
38	-	

Laboratory	Difference AB
40	-
41	-
42	0.0170
43	-
44	-
45	0.0200
46	-
47	-
48	-
49	0.0110
50	-
51A	-
51B	-
52	-0.0280
53	-
54	-
55	0.0250
56	-
No of labs., p	8
No of repl., n	2
d	0.0088
s^2	0.0004
s	0.0201
$t = \sqrt{p} \cdot (d/s)$	1.2305
Sign. level, p(t)	0.2582

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

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

Laboratory	Difference AB	
2	0.0870	
3	0.0470	
4	-	
5	-0.1120	
6	0.3920	
8	0.1860	
9	-0.0230	UG
10	-	
11	-2.6400	UC
13	0.1010	
14	-0.0600	UG
15	-0.0180	
16	-0.0470	
17	0.0000	
18	3.1040	UC
19	-0.0360	
20	-	
21	0.0900	
22	-	
23	-	
24	0.0400	
25	-	
26	-	
27A	-	
27B	-	
28	-	
29	-0.0540	
30	0.2790	
31	0.1290	UG
32A	0.0480	
32B	-0.0370	
33A	-	
33B	-	
34	-0.0760	
35	0.1200	UG
36	-0.1090	
37	-	
38	-0.2700	UG

Laboratory	Difference AB	
40	-0.0780	
41	0.1330	
42	-	
43	-	
44	0.1460	
45	-	
46	-	
47	-0.1000	
48	-0.0570	
49	-	
50	0.0130	
51A	0.0570	
51B	0.0700	UG
52	-	
53	0.2020	
54	-	
55	-	
56	0.0200	
No of labs., p	27	
No of repl., n	2	
d	0.0414	
s^2	0.0151	
s	0.1230	
$t = \sqrt{p} \cdot (d/s)$	1.7482	
Sign. level, p(t)	0.0922	

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

Conductivity, mS/m
Control of differences within sample pairs

Laboratory	Difference AB
2	-
3	-
4	-
5	0.00
6	-9.30
8	9.80
9	-
10	-
11	-0.20
13	-
14	-0.40
15	-
16	0.10
17	-
18	0.40
19	-
20	-
21	-
22	-
23	-
24	-
25	-6.00
26	0.20
27A	0.00
27B	-
28	-0.40
29	5.30
30	-
31	0.50
32A	-
32B	-
33A	-
33B	-
34	-
35	-0.10
36	-
37	-
38	-1.50

Laboratory	Difference AB	
40	-	
41	-0.20	
42	-	
43	-	
44	-	
45	-	
46	-0.20	
47	-	
48	-	
49	0.00	
50	-	
51A	-	
51B	-	
52	2.00	UG
53	-	
54	-	
55	-0.20	
56	-27.00	UC
No of labs., p	19	
No of repl., n	2	
d	-0.12	
s^2	13.86	
s	3.72	
$t = \sqrt{p} \cdot (d/s)$	-0.1355	
Sign. level, p(t)	0.8937	

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
2	0.100
3	-0.097
4	0.010
5	-0.130
6	-0.370
8	-0.072
9	0.030
10	-0.020
11	-0.130
13	-
14	-0.040
15	-0.240
16	-0.020
17	-0.080
18	0.140
19	0.380
20	-0.030
21	-0.070
22	-0.290
23	-0.120
24	0.000
25	0.000
26	-0.200
27A	-0.180
27B	-0.250
28	-0.180
29	0.298
30	-0.071
31	-
32A	0.390
32B	-
33A	-
33B	-
34	-0.060
35	-0.110
36	0.040
37	-0.230
38	0.020
40	-0.080
41	-0.490
42	-0.110
43	-0.120
44	-0.070
45	-0.220
46	-0.200
47	0.040
48	-
49	0.000
50	0.120
51A	-0.330
51B	-
52	-0.140
53	0.010
54	-
55	-0.170
56	-0.040
No of labs., p	48
No of repl., n	2
d	-0.070
s^2	0.028
s	0.167
$t = \sqrt{p} \cdot (d/s)$	-2.9151
Sign. level, p(t)	0.0054 **

* 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)

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.

ANNEX D CONTROL OF RECOVERY

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

Laboratory	Sample pair AB	
2	68.81	
3	45.41	UG
4	67.91	
5	2.98	UG
6	71.06	
8	62.16	
9	78.38	
10	67.77	
11	66.06	
13	65.72	
14	66.97	
15	62.33	
16	72.56	
17	67.77	
18	66.64	
19	75.72	
20	63.22	
21	63.77	
22	65.88	
23	65.45	
24	73.81	
25	69.02	
26	63.41	
27A	-	
27B	-	
28	-	
29	68.27	
30	54.21	UC
31	60.79	
32A	70.66	
32B	65.02	
33A	-	
33B	-	
34	66.87	
35	63.66	
36	66.41	
37	68.81	
38	64.02	
40	69.47	
41	70.03	
42	62.08	
43	58.61	
44	58.12	
45	69.79	
46	72.33	
47	66.97	
48	66.19	
49	64.39	
50	66.22	
51A	67.41	
51B	59.46	
52	73.31	
53	60.77	
54	61.77	
55	69.77	
56	65.22	
No of labs., p	48	
No of repl., n	2	
m	66.68	
s^2	18.75	
s	4.33	
Assigned value, μ	63.64	
Recovery, %	104.8	
$t = \sqrt{p} \cdot (m-\mu)/s$	4.8708	
Sign. level, p(t)	0.0000	***

* 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
UG denotes a Grubbs outlier

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

Laboratory	Sample pair AB
2	46.19
3	42.09
4	49.29
5	42.74
6	43.59
8	43.34
9	-
10	-
11	47.49
13	46.09
14	47.24
15	-
16	47.84
17	44.34
18	43.74
19	46.60
20	44.54
21	44.74
22	44.80
23	-
24	41.49
25	45.51
26	-
27A	-
27B	-
28	45.74
29	46.49
30	45.89
31	46.19
32A	50.99
32B	43.74
33A	46.19
33B	46.74
34	44.89
35	46.29
36	45.49
37	-
38	43.44

Laboratory	Sample pair AB
40	47.04
41	49.79
42	45.81
43	45.99
44	39.44
45	47.21
46	-
47	44.84
48	-
49	40.59
50	46.04
51A	45.19
51B	42.14
52	44.04
53	46.04
54	44.24
55	47.74
56	50.29
No of labs., p	45
No of repl., n	2
m	45.42
s^2	5.65
s	2.38
Assigned value, μ	45.498
Recovery, %	99.8
$t = \sqrt{p} \cdot (m-\mu)/s$	-0.2342
Sign. level, p(t)	0.8159

No test statistics were found to be significant

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

Laboratory	Sample pair AB	
2	-	
3	-	
4	-	
5	-	
6	-	
8	-	
9	-	
10	-	
11	-	
13	-	
14	-	
15	-	
16	-	
17	-	
18	-	
19	-	
20	0.6850	
21	-	
22	-	
23	-	
24	-	
25	0.7765	
26	-	
27A	-	
27B	-	
28	0.3410	
29	-	
30	-	
31	0.0915	UC
32A	-	
32B	-	
33A	-	
33B	-	
34	-	
35	-	
36	-	
37	-	
38	-	

Laboratory	Sample pair AB
40	-
41	-
42	0.3865
43	-
44	-
45	0.3000
46	-
47	-
48	-
49	0.3785
50	-
51A	-
51B	-
52	0.3830
53	-
54	-
55	0.2725
56	-
No of labs., p	8
No of repl., n	2
m	0.4404
s^2	0.0344
s	0.1854
Assigned value, μ	0.36
Recovery, %	122.3
$t = \sqrt{p} \cdot (m-\mu)/s$	1.2262
Sign. level, p(t)	0.2598

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

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

Laboratory	Sample pair AB	
2	0.9435	
3	0.7595	
4	-	
5	0.8340	
6	0.8940	
8	0.3980	
9	0.1465	UG
10	-	
11	10.6000	UC
13	0.8805	
14	3.7600	UG
15	0.9440	
16	0.7215	
17	0.7400	
18	2.3380	UC
19	0.7370	
20	-	
21	0.9350	
22	-	
23	-	
24	0.8500	
25	-	
26	-	
27A	-	
27B	-	
28	-	
29	0.6550	
30	0.8425	
31	0.0915	UG
32A	0.8540	
32B	0.7735	
33A	-	
33B	-	
34	0.7050	
35	3.6000	UG
36	0.8655	
37	-	
38	3.7250	UG

Laboratory	Sample pair AB	
40	0.7910	
41	0.6575	
42	-	
43	-	
44	0.5760	
45	-	
46	-	
47	0.8550	
48	0.7725	
49	-	
50	0.7575	
51A	0.4735	
51B	0.9950	UG
52	-	
53	0.7890	
54	-	
55	-	
56	0.8500	
No of labs., p	27	
No of repl., n	2	
m	0.7724	
s^2	0.0177	
s	0.1330	
Assigned value, μ	0.78	
Recovery, %	99.0	
$t = \sqrt{p} \cdot (m-\mu)/s$	-0.2973	
Sign. level, p(t)	0.7686	

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

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

Laboratory	Sample pair AB
2	-
3	-
4	-
5	158.00
6	130.85
8	137.10
9	-
10	-
11	156.10
13	-
14	154.50
15	-
16	151.85
17	-
18	150.60
19	-
20	-
21	-
22	-
23	-
24	-
25	153.00
26	144.90
27A	156.00
27B	-
28	159.60
29	138.85
30	-
31	150.85
32A	-
32B	-
33A	-
33B	-
34	-
35	155.25
36	-
37	-
38	154.85

Laboratory	Sample pair AB	
40	-	
41	153.80	
42	-	
43	-	
44	-	
45	-	
46	154.10	
47	-	
48	-	
49	154.00	
50	-	
51A	-	
51B	-	
52	242.90	UG
53	-	
54	-	
55	152.90	
56	1485.50	UC
No of labs., p	19	
No of repl., n	2	
m	150.90	
s^2	57.66	
s	7.59	
Assigned value, μ	154	
Recovery, %	98.0	
$t = \sqrt{p} \cdot (m-\mu)/s$	-1.7795	
Sign. level, p(t)	0.0921	

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

pH,
Control of recovery, average of results

Laboratory	Sample pair AB
2	7.540
3	7.998
4	7.465
5	7.105
6	7.575
8	7.492
9	7.585
10	7.330
11	7.465
13	-
14	7.540
15	8.080
16	7.720
17	7.540
18	7.440
19	7.670
20	7.795
21	7.235
22	7.565
23	7.530
24	7.450
25	7.360
26	7.500
27A	7.600
27B	7.525
28	7.590
29	7.242
30	7.127
31	-
32A	7.885
32B	-
33A	-
33B	-
34	7.400
35	7.715
36	7.270
37	8.025
38	7.800
40	7.420
41	7.475
42	7.335
43	7.800
44	7.735
45	7.630
46	7.730
47	7.230
48	-
49	7.600
50	7.520
51A	7.475
51B	-
52	7.800
53	7.575
54	-
55	7.885
56	7.460
No of labs., p	48
No of repl., n	2
m	7.559
s^2	0.049
s	0.222
Assigned value, μ	7.54
Recovery, %	100.3
$t = \sqrt{p} \cdot (m-\mu)/s$	0.5919
Sign. level, p(t)	0.5567

No test statistics were found to be significant

ANNEX E CONCENTRATION LEVEL

Parameter	Unit	Sample	Bottle no.	I	II	Bottle Average	Sample Average	Assigned value	Spike Measured	Spike Assigned
Total nitrogen	mg/L N	A1	11	64,80	64,30	64,55	64,23	63,64	8,32	8,17
			42	65,30	65,30	65,30				
			58	62,50	63,20	62,85				
		B1	8	72,60	72,60	72,60	72,55	71,81		
			34	73,80	73,50	73,65				
			62	71,40	71,40	71,40				
Ammonium	mg/L N	A1	11	46,300	46,400	46,35	46,767	45,498	4,833	4,614
			42	47,200	47,200	47,20				
			58	46,700	46,800	46,75				
		B1	8	51,200	51,400	51,30	51,600	50,112		
			34	51,800	51,800	51,80				
			62	51,800	51,600	51,70				
Nitrate	mg/L N	A1	11	0,88	0,89	0,89	0,89	0,78	0,20	0,19
			42	0,91	0,91	0,91				
			58	0,87	0,86	0,86				
		B1	8	1,14	1,14	1,14	1,09	0,97		
			34	1,13	1,12	1,13				
			62	1,01	0,99	1,00				
pH		A2	5	8,12	8,10	8,11	8,11	7,54	-0,01	0,00
			34	8,02	8,08	8,11				
			54	8,11	8,08	8,10				
		B2	18	8,06	8,10	8,08	8,10	7,54		
			48	8,10	8,11	8,11				
			62	8,13	8,07	8,10				

ANNEX F HOMOGENEITY AND STABILITY

PT:	SPIL-2
Parameter:	NH_4
Unit:	mg/l
Sigma:	2,9

Responsible for tests: HBP/S7MS

Homogeneity test Date: 2019-04-30

Sample	x(a)	x(b)	average	sd	sd^2
3	53	54	53,4	0,141	0,020
17	53	53	53,3	0,071	0,00
18	53	53	52,8	0,141	0,020
22	53	53	52,9	0,141	0,020
25	53	54	53,4	0,354	0,125
31	53	53	53,2	0,071	0,005
41	53	53	52,6	0,071	0,005
48	53	53	53,1	0,141	0,020
54	53	53	53,4	0,071	0,005
61	52	52	52,3	0,071	0,005
70	53	53	52,9	0,000	0,000
81	54	54	54,0	0,212	0,045

For homogeneity

General average (x)	53,08
Sample average sd (s_x)	0,442
Within-sample sd (s_w):	0,151
Between-samples sd (ss):	0,4292
S_L in the Proficiency Test:	2,1
S_R in the Proficiency Test:	2,63

Conclusions

ss = 0,429 0.3*sigma= 0,86

/x-y/ = 0

Homogeneity: Is ss < 0.3*sigma?

YES

PT:	SPIL-2
Parameter:	NO_2
Unit:	mg/L
Sigma:	0,036

Responsible for tests: HBP/S7SM

Homogeneity test Date: 2019-04-30

Sample	x(a)	x(b)	average	sd	sd^2
3	0,02	0,02	0,0	0,000	0,000
17	0,03	0,03	0,0	0,000	0,00
18	0,02	0,02	0,0	0,000	0,000
22	0,02	0,03	0,0	0,001	0,000
25	0,02	0,02	0,0	0,000	0,000
31	0,02	0,02	0,0	0,000	0,000
41	0,03	0,03	0,0	0,000	0,000
48	0,03	0,03	0,0	0,000	0,000
54	0,03	0,03	0,0	0,000	0,000
61	0,02	0,02	0,0	0,000	0,000
70	0,02	0,02	0,0	0,000	0,000
79	0,03	0,03	0,0	0,000	0,000

For homogeneity

General average (x)	0,02
Sample average sd (s_x)	0,002
Within-sample sd (s_w):	0,000
Between-samples sd (ss):	0,0020
S_L in the Proficiency Test:	0,1851
S_R in the Proficiency Test:	0,1857

Stability test Date: 2019-05-16

Sample	x(a)	x(b)
8	0,023	0,023
34	0,022	0,022
62	0,021	0,02

For stability

General average (y):	0,0218333
/x-y/ =	0,0022083

Conclusions

ss = 0,002 0.3*sigma= 0,01

/x-y/ = 0,0022083

Homogeneity: Is ss < 0.3*sigma?
YES

Stability: /x-y/ < 0.3*sigma?
YES

PT: SPIL-2
Parameter: NO_3
Unit: mg/L
Sigma: 0,360

Responsible for tests: HBP/S7SM

Homogeneity test Date: 2019-04-30

Sample	x(a)	x(b)	average	sd	sd^2
3	1,13	1,14	1,1	0,007	0,000
17	1,13	1,14	1,1	0,007	0,00
18	1,11	1,12	1,1	0,007	0,000
22	1,13	1,16	1,1	0,021	0,000
25	1,17	1,17	1,2	0,000	0,000
31	1,11	1,14	1,1	0,021	0,000
41	1,15	1,17	1,2	0,014	0,000
48	1,10	1,10	1,1	0,000	0,000
54	1,09	1,08	1,1	0,007	0,000
61	1,16	1,19	1,2	0,021	0,000
70	1,05	1,05	1,1	0,000	0,000
79	1,10	1,08	1,1	0,014	0,000

For homogeneity

General average (x)	1,12
Sample average sd (s_x)	0,038
Within-sample sd (s_w):	0,013
Between-samples sd (ss):	0,0364
S_L in the Proficiency Test:	0,118
S_R in the Proficiency Test:	0,1465

Stability test Date: 2019-05-16

Sample	x(a)	x(b)
8	1,14	1,14
34	1,13	1,12
62	1,01	0,993

For stability

General average (y):	1,0888333
/x-y/ =	0,0349167

Conclusions

ss = 0,036 0.3*sigma= 0,11
/x-y/ = 0,0349167

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: HBP/S7SM

Homogeneity test Date: 2019-04-30

Sample	x(a)	x(b)	average	sd	sd^2
2	7,85	7,83	7,8	0,014	0,000
10	7,86	7,87	7,9	0,007	0,000
25	7,85	7,84	7,8	0,007	0,000
29	7,85	7,84	7,8	0,007	0,000
40	7,80	7,88	7,8	0,057	0,003
43	7,89	7,85	7,9	0,028	0,001
52	7,84	7,90	7,9	0,042	0,002
57	7,85	7,86	7,9	0,007	0,000
65	7,87	7,85	7,9	0,014	0,000
69	7,82	7,90	7,9	0,057	0,003
80	7,85	7,86	7,9	0,007	0,000
67	7,85	7,87	7,9	0,014	0,000

For homoge-neity

General average (x)	7,9
Sample average sd (s_x)	0,011
Within-sample sd (s_w):	0,029
Between-samples sd (ss):	0
S_L in the Proficiency Test:	0,205
S_R in the Proficiency Test:	0,237

Conclusions

ss = 0 0.3*sigma= 0,02

/x-y/ = 0

Homogeneity: Is ss < 0.3*sigma?

YES