Proficiency test SPIL-2 (2014)

Nitrogen parameters in wastewater (synthetic wastewater, effluent)

Quality Documentation
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CONTENTS

1 INTRODUCTION

A proficiency test on the analysis of nitrogen parameters in wastewater was conducted on 15 May 2014. 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 16 June 2014.

2 FEATURES OF THE PROFICIENCY TEST

Participants in the proficiency test were a total of 65 laboratories from Denmark, Norway and Sweden. A list of participants is shown in Appendix A.

The closing date for submission of results was 2 June 2014. All participants except laboratory no. 28 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.

Two samples were dispatched for the proficiency test. The samples were sample pairs covering the parameters as described in Table 1. The matrix of the samples represented wastewater, in this case synthetic wastewater, effluent. Sample preparation is described in Appendix B.

Table 1 Samples in the proficiency test

Sample name	Parameters
A1/B1	TN, NH_4, NO_{2+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 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	2.97	0.027	0.39
Ammonium	NH_4	mg/L N	0.1 – 2	0.409	0.0046	0.046
Nitrite+nitrate	NO_{2+3}	mg/L N	1 – 5	1.87	0.024	0.21
Conductivity	γ_{25}	mS/m	50 – 300	93.3	0.47	11.4
pH	pH		6 – 9	7.20	0.011	0.05

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 and spike values are both calculated from sample preparation except for conductivity and pH where the assigned values are a consensus value for all laboratories based on the median and the spike value the difference between median values for the two samples in the sample pair.

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.

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).

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 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.

5 REFERENCES

/1/ Eurofins A/S, *Proficiency test SPIL-2 (2014)*, Report to participants, June 2014.

/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. 231 on *quality criteria for environmental measurements,* 5 March 2014 (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 Agroøkologi	Tjele	Denmark
AquaDjurs - Fornæs Renseanlæg	Grenaa	Denmark
Biofos A/S	København K	Denmark
Bjergmarken R/A, Roskilde Forsyning	Roskilde	Denmark
CP Kelco ApS, Spildevandslaboratoriet	Ll. Skensved	Denmark
Esbjerg Forsyning Spildevandslaboratorium	Esbjerg	Denmark
Eurofins Miljø A/S	Vejen	Denmark
Faxe Forsyning	Faxe	Denmark
Faxe Forsyning	Faxe	Denmark
FORCE LabVest	Holstebro	Denmark
Greve Solrød Forsyning	Greve	Denmark
Halsnæs Kommunale Forsyning A/S	Liseleje	Denmark
Hedensted Spildevand A/S	Daugård	Denmark
Hedensted Spildevand A/S	Daugård	Denmark
Hillerød Forsyning Spildevand A/S	Hillerød	Denmark
Holstebro Centralrenseanlæg, Vestforsyning A/S	Holstebro	Denmark
Kerteminde Forsyning - Spildevand A/S	Kerteminde	Denmark
Kolding Spildevand A/S	Bjert	Denmark
Mølleåværkets Driftslaboratorium	Lyngby	Denmark
Nyborg Renseanlæg	Nyborg	Denmark
Næstved Centralrenseanlæg	Næstved	Denmark
Provas Haderslev Forsyningsservice A/S	Haderslev	Denmark
Randers Spildevand A/S	Randers SØ	Denmark
Ringkøbing-Skjern Forsyning A/S, Spildevand	Skjern	Denmark
Ringsted Renseanlæg	Ringsted	Denmark
Rønne Renseanlæg	Rønne	Denmark
SK Forsyning, Slagelse Renseanlæg	Slagelse	Denmark
SK Forsyning, Slagelse Renseanlæg	Slagelse	Denmark
SK Forsyning, Slagelse Renseanlæg	Slagelse	Denmark
SK Forsyning, Slagelse Renseanlæg	Slagelse	Denmark
SK Forsyning, Slagelse Renseanlæg	Slagelse	Denmark
Svendborg Centralrenseanlæg	Skårup Fyn	Denmark
Sønderborg Forsyning	Sønderborg	Denmark
Vejen Renseanlæg	Vejen	Denmark

Vejle Spildevand A/S	Vejle	Denmark
Aalborg Renseanlæg Vest	Ålborg	Denmark
LabNett Hamar	Hamar	Norway
Norways Geotekniske Institutt	Oslo	Norway
Statoil ASA, Kollsnes gassanlegg	Rong	Norway
Eurofins Environment Testing Sweden AB	Lidköping	Sweden
GRYAAB AB	Göteborg	Sweden
Gästrike Vatten AB	Skutskär	Sweden
Holmen Paper	Norrköping	Sweden
Holmen Paper AB	Hallstavik	Sweden
Ineos Sweden AB	Stenungsund	Sweden
Kalmar Vatten AB, VA-lab, Avloppsreningsverket	Kalmar	Sweden
Klippans Reningsverk	Klippan	Sweden
Laboratoriet vid Smedjeholms avolppsreningsverk	Falkenberg	Sweden
Mjölby Kommun	Mjölby	Sweden
Motala Kommun	Motala	Sweden
Nordic Sugar	Eslöv	Sweden
Perstorp Oxo AB	Stenungsund	Sweden
Preem AB Göteborg	Göteborg	Sweden
Reningsverket Aggerud	Karlskoga	Sweden
Rottneros Bruk AB	Rottneros	Sweden
Smurfit Kappa Kraftliner	Piteå	Sweden
St1 Refinery AB	Göteborg	Sweden
Södra Cell AB Mönsterås	Mönsterås	Sweden
Södra Cell AB, Värö	Väröbacka	Sweden
Uddebo Laboratorium	Luleå	Sweden
Vallviks Bruk AB	Vallvik	Sweden
VA-verkets lab. Vänersborg	Vänersborg	Sweden
VIVAB	Varberg	Sweden
Västerviks Miljö & Energi AB, Vattenlaboratoriet	Västervik	Sweden
Yara AB	Köping	Sweden

ANNEX B SAMPLE PREPARATION

Stock solution	**Prepared from**	**Concentration**
Stock TN	3.0024 g Disodium edetate, $2H_2O$ milli-Q water up to 1000.0 g	TN: 226.0 mg/kg N
Stock NH_4	1.0023 g Ammonium chloride (NH_4Cl) milli-Q water up to 1000.0 g	NH_4: 262.5 mg/kg N
Stock NO_3	2.5007 g Potassium nitrate (KNO_3) milli-Q water up to 1000.0 g	NO_3: 346.5 mg/kg N
Stock NaCl	50.000 g Sodium chloride (NaCl) milli-Q water up to 1000.0 g	conductivity: c. 10668 mS/m

Sample	**Sample prepared from**	**TN mg/L N**	**NH_4 mg/L N**	**NO_3 mg/L N**	**Conductivity mS/m**
A1	101.24 g stock NH_4 350.52 g stock NO_3 200.44 g stock TN 599.2 g stock NaCl Milli-Q water up to 65.00 kg	2.97	0.409	1.87	c. 93.3
B1	6.07 g stock NH_4 21.26 g stock NO_3 20.02 g stock TN 40.85 g stock NaCl Sample A1 up to 34.00 kg	0.997· 2.97 + 0.39	0.997· 0.409 + 0.046	0.997· 1.87 + 0.21	0.997· c. 93.3 + c. 11.4

Sample	**Sample prepared from**	**pH**
A2/B2	25.52 g Potassium dihydrogen phosphate (KH_2PO_4) 77.86 g Disodium hydrogen phosphate, $2H_2O$ (Na_2HPO_4, $2H_2O$) milli-Q water up to 12.50 kg	7.2

ANNEX C CONTROL OF SPIKE VALUES

Total nitrogen, mg/L N

Control of differences within sample pairs

Laboratory	Difference AB	
1	-0.080	
2	-0.080	
3	-0.050	
4	0.010	
5A	0.280	
5B	0.120	
6	0.170	
7	0.080	
8	-0.340	
9	0.030	
10	-0.150	
11	0.230	
12	-0.120	
13	0.000	
14	-0.130	
15	-0.010	
16	0.050	
17	0.000	
18	0.020	
19	0.050	
20	-0.010	
21	-0.040	
22	0.100	
23	-0.020	
24	0.090	
25	0.000	
26	0.370	
27	0.050	
29	0.070	
30	0.070	
31	-0.050	
32	0.090	
33	0.110	
34	0.080	
35	-	
36	0.120	
37	-	
38	-0.080	
39	0.530	
40	-0.080	
41	-	
42	0.100	
43	-	
44	0.140	
45	-0.020	
46	0.230	UG
47A	0.030	
47B	0.090	
48	0.330	
49	-0.335	
50A	-	
50B	-	
51	0.076	
52	-0.040	
53	0.000	
54	-0.360	
55	0.069	
56	0.010	
57	0.080	
58	0.012	
59	0.090	
60	-0.030	
61	0.084	
62	-0.120	
63	-0.100	
64	-0.020	
65	0.180	
No of labs., p	60	
No of repl., n	2	
d	0.029	
s^2	0.022	
s	0.149	
$t = \sqrt{p} \cdot (d/s)$	1.5129	
Sign. level, p(t)	0.1357	

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

Ammonium, mg/L N

Control of differences within sample pairs

Laboratory	Difference AB	
1	-0.0050	
2	-0.0040	
3	-0.0140	
4	-	
5A	0.0030	
5B	0.0070	
6	0.0020	
7	0.0010	
8	0.0060	
9	-0.0010	
10	0.0010	
11	0.0020	
12	-0.0040	
13	0.0060	
14	-0.0140	
15	0.0040	
16	0.0040	
17	-0.0040	
18	0.0100	
19	0.0160	
20	-0.0040	
21	-	
22	0.0000	
23	-	
24	0.0080	
25	0.0000	
26	-0.0040	
27	-0.0000	
29	-0.0000	
30	-0.0010	
31	0.0010	
32	0.0160	
33	-0.0010	
34	-0.0950	UC
35	-0.0040	
36	-	
37	-	
38	-0.0000	
39	-0.0040	
40	-0.0070	
41	-0.0030	
42	-	
43	0.0010	
44	-	
45	-0.0030	
46	0.0030	
47A	-0.0000	
47B	0.0030	
48	0.0060	
49	-0.0050	
50A	-	
50B	-	
51	0.0670	UC
52	-0.0070	
53	-0.0000	
54	0.0040	
55	-	
56	0.0060	
57	0.0020	
58	-	
59	-0.0010	
60	0.0010	
61	0.0060	
62	0.0080	
63	-0.0050	
64	-0.0030	
65	0.0080	
No of labs., p	54	
No of repl., n	2	
d	0.0007	
s^2	0.0000	
s	0.0058	
$t = \sqrt{p} \cdot (d/s)$	0.8622	
Sign. level, p(t)	0.3925	

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

Nitrite+nitrate, mg/L N

Control of differences within sample pairs

Laboratory	Difference AB
1	-0.010
2	-0.040
3	0.050
4	-
5A	0.040
5B	-0.040
6	0.050
7	0.120
8	0.010
9	-
10	-
11	0.030
12	0.030
13	0.000
14	-0.010
15	0.050
16	-
17	0.000
18	-
19	0.050
20	-
21	-
22	0.020
23	-
24	-0.010
25	-0.090
26	-0.010
27	0.030
29	-0.070
30	-0.040
31	0.050
32	-0.000
33	0.020
34	-0.020
35	-0.010
36	-0.070
37	-
38	0.050
39	0.010
40	0.010
41	-
42	-
43	0.060
44	-
45	0.070
46	-0.050
47A	0.040
47B	-0.030
48	-0.060
49	-0.070
50A	-
50B	-
51	-0.007
52	0.010
53	-0.000
54	-
55	-
56	0.010
57	-0.060
58	-
59	-0.020
60	0.010
61	0.000
62	0.040
63	0.050
64	-
65	0.120
No of labs., p	49
No of repl., n	2
d	0.006
s^2	0.002
s	0.046
$t = \sqrt{p} \cdot (d/s)$	0.9736
Sign. level, p(t)	0.3351

No test statistics were found to be significant

Conductivity, mS/m

Control of differences within sample pairs

Laboratory	Difference AB	
1	-	
2	-	
3	0.40	
4	-	
5A	-	
5B	-	
6	-	
7	-104.60	UC
8	-	
9	-	
10	-	
11	-	
12	-2.60	UC
13	0.40	
14	-	
15	-	
16	-0.10	
17	-	
18	0.00	
19	-	
20	-0.10	
21	0.10	
22	0.10	
23	-	
24	-	
25	-0.40	
26	-	
27	-	
29	-	
30	-	
31	-0.60	
32	-	
33	-0.70	
34	-	
35	0.20	
36	0.00	
37	1.10	
38	0.10	
39	-	
40	0.00	
41	-0.10	
42	-	
43	5.20	UC
44	-	
45	-	
46	-	
47A	-	
47B	-	
48	-	
49	-	
50A	-	
50B	-	
51	-0.20	
52	1.20	
53	-	
54	-	
55	0.10	
56	0.50	
57	0.30	
58	0.10	
59	-0.50	
60	-	
61	-0.05	
62	-	
63	-2.10	UC
64	0.10	
65	-	
No of labs., p	25	
No of repl., n	2	
d	0.08	
s^2	0.19	
s	0.44	
$t = \sqrt{p} \cdot (d/s)$	0.8918	
Sign. level, p(t)	0.3814	

No test statistics were found to be significant

UC denotes a Cochran outlier

pH,

Control of differences within sample pairs

Laboratory	Difference AB	
1	0.010	
2	-0.040	UG
3	-0.060	
4	-	
5A	0.040	
5B	-	
6	0.020	
7	-0.010	UG
8	-0.050	
9	-0.010	
10	0.020	
11	-	
12	-0.010	
13	0.100	
14	-0.050	UG
15	0.010	
16	0.000	
17	0.020	
18	-0.040	
19	-	
20	0.000	
21	0.040	
22	-0.020	
23	-	
24	-0.040	
25	0.000	
26	0.000	
27	-0.010	
29	0.000	
30	0.041	
31	-0.050	
32	-0.020	
33	-0.050	
34	0.000	
35	0.000	
36	-0.060	UG
37	-0.030	
38	-0.020	
39	0.010	
40	0.000	
41	-0.010	
42	-	
43	0.010	
44	-	
45	-0.020	
46	-0.010	
47A	0.000	
47B	-	
48	-0.030	
49	-0.020	
50A	-0.020	
50B	-	
51	0.030	
52	-0.010	
53	-0.020	
54	-0.020	
55	-0.020	
56	0.030	
57	-0.030	
58	0.030	
59	-0.050	
60	0.000	
61	-0.031	
62	0.010	
63	0.030	
64	0.000	
65	-0.020	UG
No of labs., p	53	
No of repl., n	2	
d	-0.005	
s^2	0.001	
s	0.029	
$t = \sqrt{p} \cdot (d/s)$	-1.1851	
Sign. level, p(t)	0.2414	

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

ANNEX D CONTROL OF RECOVERY

Total nitrogen, mg/L N
Control of recovery, average of results

Laboratory	Sample pair AB	
1	2.540	
2	2.930	
3	3.305	
4	2.635	
5A	4.090	
5B	2.120	
6	2.905	
7	2.920	
8	3.990	
9	3.085	
10	3.055	
11	2.975	
12	3.200	
13	2.830	
14	2.875	
15	2.905	
16	2.935	
17	3.030	
18	3.000	
19	2.875	
20	2.945	
21	2.900	
22	3.070	
23	3.130	
24	3.255	
25	3.130	
26	2.655	
27	2.965	
29	3.065	
30	3.055	
31	3.155	
32	3.045	
33	2.805	
34	2.730	
35	-	
36	2.750	
37	-	
38	2.770	
39	3.645	
40	2.970	
41	-	
42	3.000	
43	-	
44	2.680	
45	2.920	
46	4.905	UG
47A	2.975	
47B	2.535	
48	2.855	
49	2.893	
50A	2.920	
50B	3.080	
51	2.647	
52	2.950	
53	2.750	
54	3.590	
55	2.755	
56	2.945	
57	3.120	
58	2.699	
59	3.045	
60	3.175	
61	2.734	
62	2.560	
63	2.900	
64	3.080	
65	3.290	
No of labs., p	60	
No of repl., n	2	
m	2.972	
s^2	0.099	
s	0.315	
Assigned value, μ	2.97	
Recovery, %	100.1	
$t = \sqrt{p} \cdot (m-\mu)/s$	0.0561	
Sign. level, p(t)	0.9554	

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

Ammonium, mg/L N

Control of recovery, average of results

Laboratory	Sample pair AB	
1	0.4015	
2	0.4300	
3	0.4170	
4	-	
5A	0.4245	
5B	0.3845	
6	0.4130	
7	0.4225	
8	0.4230	
9	0.4435	
10	0.4025	
11	0.4210	
12	0.4120	
13	0.3870	
14	0.4270	
15	0.3800	
16	0.3860	
17	0.4120	
18	0.3620	
19	0.4120	
20	0.4020	
21	-	
22	0.4280	
23	-	
24	0.4130	
25	0.3860	
26	0.4120	
27	0.4200	
29	0.4100	
30	0.4245	
31	0.4125	
32	0.4520	
33	0.4255	
34	0.5345	UC
35	0.4160	
36	-	
37	-	
38	0.4090	
39	0.4120	
40	0.4005	
41	0.4045	
42	-	
43	0.3945	
44	-	
45	0.4445	
46	0.4325	
47A	0.4120	
47B	0.3935	
48	0.4250	
49	0.4175	
50A	0.4110	
50B	0.4100	
51	0.4995	UC
52	0.3825	
53	0.4170	
54	0.3830	
55	-	
56	0.4270	
57	0.4140	
58	-	
59	0.4425	
60	0.3885	
61	0.4270	
62	0.4190	
63	0.4385	
64	0.4115	
65	0.3970	
No of labs., p	54	
No of repl., n	2	
m	0.4121	
s^2	0.0003	
s	0.0185	
Assigned value, μ	0.409	
Recovery, %	100.8	
$t = \sqrt{p} \cdot (m-\mu)/s$	1.2501	
Sign. level, p(t)	0.2167	

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

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

Laboratory	Sample pair AB
1	1.725
2	1.940
3	1.725
4	-
5A	1.920
5B	1.710
6	1.805
7	1.830
8	1.925
9	-
10	-
11	1.755
12	1.705
13	1.710
14	1.895
15	1.935
16	-
17	1.850
18	-
19	1.835
20	-
21	-
22	1.850
23	-
24	1.775
25	1.955
26	1.895
27	1.955
29	1.955
30	1.970
31	1.835
32	1.890
33	1.860
34	1.950
35	1.905
36	1.775
37	-
38	1.925
39	1.935
40	1.775
41	-
42	-
43	1.790
44	-
45	1.935
46	1.925
47A	1.900
47B	1.825
48	1.910
49	1.785
50A	1.910
50B	1.900
51	1.897
52	1.855
53	1.910
54	-
55	-
56	1.895
57	1.860
58	-
59	1.830
60	1.885
61	1.840
62	1.870
63	1.925
64	-
65	1.740
No of labs., p	49
No of repl., n	2
m	1.858
s^2	0.006
s	0.076
Assigned value, μ	1.87
Recovery, %	99.4
$t = \sqrt{p} \cdot (m-\mu)/s$	-1.0970
Sign. level, p(t)	0.2781

No test statistics were found to be significant

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

Laboratory	Sample pair AB	
1	-	
2	-	
3	90.80	
4	-	
5A	-	
5B	-	
6	-	
7	993.30	UC
8	-	
9	-	
10	-	
11	-	
12	93.30	UC
13	96.80	
14	-	
15	-	
16	91.45	
17	-	
18	92.00	
19	-	
20	93.25	
21	94.45	
22	92.65	
23	-	
24	-	
25	93.50	
26	-	
27	-	
29	-	
30	-	
31	93.70	
32	-	
33	94.15	
34	-	
35	92.20	
36	93.30	
37	93.85	
38	95.85	
39	-	
40	93.50	
41	93.45	
42	-	
43	85.30	UC
44	-	
45	-	
46	-	
47A	-	
47B	-	
48	-	
49	-	
50A	-	
50B	-	
51	92.20	
52	92.00	
53	-	
54	-	
55	93.35	
56	93.65	
57	93.15	
58	94.15	
59	91.95	
60	-	
61	92.88	
62	-	
63	92.85	UC
64	93.05	
65	-	
No of labs., p	25	
No of repl., n	2	
m	93.25	
s^2	1.67	
s	1.29	
Assigned value, μ	93.3	
Recovery, %	99.9	
$t = \sqrt{p} \cdot (m-\mu)/s$	-0.1895	
Sign. level, p(t)	0.8513	

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	7.145	
2	7.040	UG
3	7.130	
4	-	
5A	7.160	
5B	-	
6	7.190	
7	7.395	UG
8	7.185	
9	7.175	
10	7.210	
11	-	
12	7.185	
13	7.180	
14	7.425	UG
15	7.235	
16	7.200	
17	7.180	
18	7.160	
19	-	
20	7.210	
21	7.210	
22	7.250	
23	-	
24	7.220	
25	7.200	
26	7.260	
27	7.145	
29	7.200	
30	7.255	
31	7.255	
32	7.220	
33	7.225	
34	7.150	
35	7.210	
36	7.470	UG
37	7.235	
38	7.240	
39	7.205	
40	7.220	
41	7.155	
42	-	
43	7.255	
44	-	
45	7.200	
46	7.075	
47A	7.230	
47B	-	
48	7.115	
49	7.160	
50A	7.280	
50B	-	
51	7.215	
52	7.195	
53	7.210	
54	7.180	
55	7.270	
56	7.205	
57	7.215	
58	7.195	
59	7.185	
60	7.190	
61	7.191	
62	7.215	
63	7.235	
64	7.190	
65	7.040	UG
No of labs., p	53	
No of repl., n	2	
m	7.200	
s^2	0.002	
s	0.040	
Assigned value, μ	7.20	
Recovery, %	100.0	
$t = \sqrt{p} \cdot (m-\mu)/s$	0.0208	
Sign. level, p(t)	0.9835	

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

ANNEX E CONCENTRATION LEVEL

Concentration level **SPIL-2 (2014)**

Parameter	Unit	Sample	Bottle no.	I	II	Bottle Average	Sample Average	Assigned value	Spike Measured	Spike Assigned
Total nitrogen	mg/L N	A1	3	2,95	2,93	2,94	2,88	2,97	0,37	0,39
			33	2,80	2,89	2,85				
			72	2,86	2,85	2,86				
		B1	18	3,27	3,32	3,30	3,25	3,36		
			51	3,28	3,06	3,17				
			80	3,27	3,29	3,28				
Ammonium	mg/L N	A1	3	0,397	0,401	0,40	0,399	0,409	0,046	0,046
			33	0,398	0,398	0,40				
			72	0,396	0,402	0,40				
		B1	18	0,444	0,446	0,45	0,445	0,456		
			51	0,445	0,444	0,44				
			80	0,444	0,445	0,44				
Nitrite+nitrate	mg/L N	A1	3	1,79	1,78	1,79	1,82	1,87	0,17	0,21
			33	1,78	1,92	1,85				
			72	1,82	1,81	1,82				
		B1	18	1,98	2,02	2,00	1,99	2,08		
			51	1,99	1,95	1,97				
			80	2,02	1,97	2,00				
pH		A2	21	7,23	7,24	7,24	7,22	7,20	-0,01	0,05
			62	7,24	7,24	7,24				
			79	7,18	7,18	7,18				
		B2	3	7,18	7,18	7,18	7,21	7,25		
			35	7,21	7,21	7,21				
			89	7,23	7,23	7,23				

ANNEX F HOMOGENEITY AND STABILITY

PT: SPIL-2
Parameter: NH4
Unit: mg/L N
Sigma: 0,0291 6,5% of x

Responsible for tests: IRL

6,5% level or 1,3*$S_{T\ max}$

Homogeneity test Date: 29.04.2014

Sample	x(a)	x(b)	average	sd	sd^2
B1-2	0,448	0,448	0,448	0,000	0,000
B1-15	0,449	0,450	0,450	0,001	0,00
B1-22	0,449	0,451	0,450	0,001	0,000
B1-29	0,447	0,451	0,449	0,003	0,000
B1-36	0,452	0,455	0,454	0,002	0,000
B1-43	0,449	0,449	0,449	0,000	0,000
B1-56	0,451	0,453	0,452	0,001	0,000
B1-63	0,451	0,454	0,453	0,002	0,000
B1-70	0,444	0,452	0,448	0,006	0,000
B1-77	0,443	0,445	0,444	0,001	0,000
B1-84	0,439	0,442	0,441	0,002	0,000
B1-91	0,432	0,435	0,434	0,002	0,000

For homogeneity

General average (x)	0,447
Sample average sd (s_x)	0,006
Within-sample sd (s_w):	0,002
Between-samples sd (ss):	0,0054
S_L in the Proficiency Test:	0,018
S_R in the Proficiency Test:	0,019

Stability test Date: 15.05.2014

Sample	x(a)	x(b)
B1-18	0,444	0,446
B1-51	0,445	0,446
B1-80	0,444	0,445

For stability

General average (y):	0,445
/x-y/ =	0,002458

Conclusions

ss =0,005 0.3*sigma=0,01
/x-y/ =0,002458

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: NO3
Unit: mg/L N
Sigma: 0,13 6,5% level

6,5% level or 1,3*$S_{T\ max}$

Responsible for tests: IRL

Homogeneity test Date: 29.04.2014

Sample	x(a)	x(b)	average	sd	sd^2
B1-2	2,00	1,99	2,00	0,007	0,000
B1-15	2,07	2,01	2,04	0,042	0,002
B1-22	2,03	2,01	2,02	0,014	0,000
B1-29	2,07	2,03	2,05	0,028	0,001
B1-36	2,04	2,05	2,05	0,007	0,000
B1-43	2,06	1,99	2,03	0,049	0,002
B1-56	2,03	2,03	2,03	0,000	0,000
B1-63	2,07	2,10	2,09	0,021	0,000
B1-70	2,17	2,04	2,11	0,092	0,008
B1-77	2,02	2,05	2,04	0,021	0,000
B1-84	2,04	2,06	2,05	0,014	0,000
B1-91	2,04	2,06	2,05	0,014	0,000

For homogeneity

General average (x)	2,04
Sample average sd (s_x)	0,029
Within-sample sd (s_w):	0,035
Between-samples sd (ss):	0,014
S_L in the Proficiency Test:	0,072
S_R in the Proficiency Test:	0,079

Stability test Date: 02.06.2014

Sample	x(a)	x(b)
B1-10	1,99	2,02
B1-45	1,97	2,06
B1-73	2,02	1,99

For stability

General average (y):	2,008333
/x-y/ =	0,035833

Conclusions

ss =0,01 0.3*sigma=0,04
/x-y/ =0,035833

Analytical quality	Is s_w < 0,15*sigma **NO**
Homogeneity:	Is ss < 0.3*sigma? **YES**
Stability:	/x-y/ < 0.3*sigma? **YES**

PT:	SPIL-2
Parameter:	pH
Unit:	-
Sigma:	0,065

1,3*$S_{T\ max}$

6,5% level or 1,3*$S_{T\ max}$

Responsible for tests: IRL

Homogeneity test Date: 29.04.2014

Sample	x(a)	x(b)	average	sd	sd^2
B2-1	7,24	7,24	7,24	0,000	0,000
B2-19	7,24	7,24	7,24	0,000	0,00
B2-13	7,24	7,24	7,24	0,000	0,000
B2-25	7,24	7,25	7,25	0,007	0,000
B2-43	7,25	7,25	7,25	0,000	0,000
B2-37	7,24	7,24	7,24	0,000	0,000
B2-49	7,24	7,24	7,24	0,000	0,000
B2-61	7,24	7,25	7,25	0,007	0,000
B2-67	7,24	7,24	7,24	0,000	0,000
B2-73	7,24	7,24	7,24	0,000	0,000
B2-85	7,24	7,24	7,24	0,000	0,000
B2-91	7,24	7,24	7,24	0,000	0,000

For homogeneity

General average (x)	7,24
Sample average sd (s_x)	0,003
Within-sample sd (s_w):	0,003
Between-samples sd (ss):	0,0025
S_L in the Proficiency Test:	0,037
S_R in the Proficiency Test:	0,042

Stability test Date: 02.06.2014

Sample	x(a)	x(b)
B2-3	7,23	7,24
B2-35	7,24	7,24
B2-89	7,24	7,24

For stability

General average (y):	7,238333
/x-y/ =	0,003333

Conclusions

ss =0,003 0.3*sigma=0,02

/x-y/ =0,003333

Analytical quality	Is s_w < 0,15*sigma **YES**
Homogeneity:	Is ss < 0.3*sigma? **YES**
Stability:	/x-y/ < 0.3*sigma? **YES**