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Proficiency test SPIL-4 (2015)

Nitrogen parameters in 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 12 November 2015. 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 14 December 2015.

2 FEATURES OF THE PROFICIENCY TEST

Participants in the proficiency test were a total of 63 laboratories from Denmark, Norway and Sweden. A list of participants is shown in Appendix A.

The closing date for submission of results was 27 November 2015. All participants except laboratory no. 40 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 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+NO_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 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	4.0	0.10	0.8
Ammonium	NH_4	mg/L N	0.1-2	0.567	0.0097	0.130
Nitrite+nitrate	NO_{2+3}	mg/L N	1-5	2.07	0.043	0.57
Nitrate	NO_3	mg/L N	1-5	2.13	0.038	0.57
Conductivity	γ_{25}	mS/m	50-300	54.2	0.39	0.4
pH	pH		6-9	7.24	0.051	0.00

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 adjusted 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, 5 and 7. A list of method identification numbers is found in the report to participants /1/. Assigned values for NH_4, NO_{2+3}, NO_3, conductivity and pH are consensus values for all laboratories based on the median. The assigned value for NO_3 (2.13 mg/L N) is higher than the assigned value for NO_{2+3} (2.07 mg/L N). This is due to differences in results obtained from standard methods and test kit 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 of the parameters. The test revealed a significant difference between the two for pH. 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 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	Homogeneity 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.

5 REFERENCES

/1/ Eurofins A/S, *Proficiency test SPIL-4 (2015)*, Report to participants, December 2015.

/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**
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
FORCE Technology	Holstebro	Denmark
Frederikssund Forsyning	Frederikssund	Denmark
Greve Solrød Forsyning	Greve	Denmark
Halsnæs Spildevand A/S	Liseleje	Denmark
Hedensted Spildevand A/S	Daugård	Denmark
Hillerød Forsyning Spildevand A/S	Hillerød	Denmark
Holbæk Forsyning	Holbæk	Denmark
Holstebro Centralrenseanlæg, Vestforsyning A/S	Holstebro	Denmark
Højmarklaboratoriet	Lem St.	Denmark
Kerteminde Forsyning - Spildevand A/S	Kerteminde	Denmark
Kolding Spildevand A/S	Bjert	Denmark
Køge-Egnens Renseanlæg	Køge	Denmark
Middelfart Spildevand A/S	Middelfart	Denmark
Mølleåværkets Driftslaboratorium	Lyngby	Denmark
NK-Spildevand Lab	Næstved	Denmark
Nyborg Renseanlæg	Nyborg	Denmark
Provas Haderslev Forsyningsservice A/S	Haderslev	Denmark
Randers Spildevand A/S	Randers SØ	Denmark
Rønne Renseanlæg	Rønne	Denmark
SK Forsyning, Slagelse Renseanlæg	Slagelse	Denmark
Svendborg Centralrenseanlæg	Skårup Fyn	Denmark
Tårnby Forsyning	Kastrup	Denmark
Vandrens - Stigsnæs Industripark A/S	Skælskør	Denmark
Vejen Renseanlæg	Vejen	Denmark
Vejle Spildevand A/S	Vejle	Denmark
NGI Miljølaboratorium	Oslo	Norway

Laboratory	Town	Country
Ernemar Laboratorium	Oskarshamn	Sweden
Eurofins Environment Testing Sweden AB	Lidköping	Sweden
GRYAAB AB	Göteborg	Sweden
Holmen Paper AB Bravikens Pappersbruk	Norrköping	Sweden
Kalmar Vatten AB, VA-lab	Kalmar	Sweden
Kristianstad Kommun	Kristianstad	Sweden
Käppalaverket	Lidingö	Sweden
Mjölby Kommun	Mjölby	Sweden
Motala Kommun	Motala	Sweden
NSVA/Öresundsverket	Helsingborg	Sweden
Preem AB Göteborg	Göteborg	Sweden
Preemraff Lysekil	Lysekil	Sweden
Reningsverket Aggerud	Karlskoga	Sweden
Smurfit Kappa Kraftliner	Piteå	Sweden
St1 Refinery AB	Göteborg	Sweden
Stora Enso Paper	Hyltebruk	Sweden
Södra Cell AB Mönsterås	Mönsterås	Sweden
Tekniska förvaltningen, Verksamhetsstöd VA, Laboratoriet	Örebro	Sweden
Uppsala Vatten o. Avfall AB, Vattenlaboratoriet	Uppsala	Sweden
Vallviks Bruk AB	Vallvik	Sweden
VIVAB	Falkenberg	Sweden
Västerviks Miljö & Energi AB, Vattenlaboratoriet	Västervik	Sweden
Yara AB	Köping	Sweden

ANNEX B SAMPLE PREPARATION

Stock solution	**Prepared from**	**Concentration**
Stock TN	2.9997 g Disodium edetate, $2H_2O$ milli-Q water up to 1000.0 g	TN: 225.8 mg/kg N
Stock NH_4	1. 0003 g Ammonium chloride (NH_4Cl) milli-Q water up to 1000.0 g	NH_4: 262.0 mg/kg N
Stock NO_3	2.502 g Potassium nitrate (KNO_3) milli-Q water up to 1000.0 g	NO_3: 346.7 mg/kg N

Sample	**Sample prepared from**	**TN mg/L N**	**NH_4 mg/L N**	**NO_3 mg/L N**	**Conductivity mS/m**
A1	100.00 g stock NH_4 150.00 g stock NO_3 250.00 g stock TN Filtered treated wastewater from Bramming sewage treatment plant up to 55.00 kg	c+2.448	a+0.476	b+0.946	d
B1	15.04 g stock NH_4 50.02 g stock NO_3 10.03 g stock TN Sample A1 up to 30.00 kg	0.998 · (c+2.448) + 0.785	0.998 · (a+0.476) + 0.131	0.998 · (b+0.946) + 0.578	e

Sample	**Sample prepared from**	**pH**
A2/B2	Filtered treated wastewater from Bramming sewage treatment plant.	f

ANNEX C CONTROL OF SPIKE VALUES

Total nitrogen, mg/L N
Control of differences within sample pairs

Laboratory	Difference AB	
1	-0.350	
2	-0.190	
3	0.730	
4	-1.100	
5	-0.010	
6	-	
7	-0.030	
8	-0.040	
9	0.200	
10	0.040	
11	-0.100	
12	-0.310	
13A	-0.234	
14	0.800	
15	0.120	
16	0.080	
17	-0.410	
18	-0.200	
19	0.250	
20	0.110	
21	0.020	
22	-0.030	
23	-0.190	
24	0.390	
25	0.300	
26A	-0.098	
26B	-0.060	
27	-0.110	
28	0.350	
29	0.010	
30	0.160	
31	-0.320	
32	-0.020	
33	-0.070	
34	0.071	
35	0.340	
36	-0.070	
37	-0.170	
38	-0.210	
39	0.200	
41	-0.140	
42	0.260	
43	-0.380	
44	0.140	
45	0.191	
46	-0.370	
47	0.040	
48A	0.032	
48B	1.020	
49A	-0.040	
49B	0.210	
50	0.040	
51	0.290	
52A	-0.050	
52B	0.060	
53	1.060	
54	0.135	
55	0.870	
56	0.220	
57	0.180	
58	-	
59	-0.530	
60	-0.603	UG
61	0.130	
62	0.100	
63	0.050	
13B	-	
No of labs., p	63	
No of repl., n	2	
d	0.053	
s^2	0.122	
s	0.349	
$t = \sqrt{p} \cdot (d/s)$	1.2146	
Sign. level, p(t)	0.2291	

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	0.0000	
2	-0.0180	
3	0.0100	
4	-0.0100	
5	0.0120	
6	-	
7	-0.0070	
8	-	
9	0.0100	
10	-	
11	-0.0060	
12	-	
13A	0.0050	
14	-0.0020	
15	-0.0100	
16	0.0400	
17	-0.0130	
18	0.0280	
19	-0.0130	
20	-	
21	0.0000	
22	0.0110	
23	-0.0100	
24	-0.0100	
25	0.0300	
26A	-0.0080	
26B	-	
27	0.0100	
28	-0.0140	
29	0.0000	
30	0.0200	
31	0.0110	
32	0.0070	
33	-0.0200	
34	0.0100	
35	-0.0050	
36	-0.0100	
37	-0.0180	
38	0.1010	UC
39	0.1200	UC
41	0.0000	
42	-0.0040	
43	-0.0200	
44	-0.0120	
45	-	
46	-0.0040	
47	0.0000	
48A	-0.0035	
48B	-	
49A	-0.0090	
49B	0.0010	
50	0.0070	
51	-0.0070	
52A	-0.0250	
52B	-0.0100	
53	0.0100	
54	0.0240	
55	0.0550	
56	-0.0150	
57	0.0140	
58	0.0070	
59	-0.0060	
60	-0.0020	
61	-0.0170	
62	-0.0010	
63	-0.0300	
13B	-0.0027	
No of labs., p	57	
No of repl., n	2	
d	-0.0004	
s^2	0.0002	
s	0.0156	
$t = \sqrt{p} \cdot (d/s)$	-0.1711	
Sign. level, p(t)	0.8648	

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	-	
3	-	
4	-	
5	-	
6	-	
7	0.050	
8	-	
9	-	
10	-	
11	-0.000	
12	-	
13A	-0.032	
14	-	
15	-0.000	
16	-	
17	-	
18	-	
19	-	
20	-	
21	-	
22	-	
23	-	
24	-	
25	-	
26A	-0.053	
26B	-	
27	-	
28	-0.120	
29	-	
30	0.040	
31	0.010	
32	-	
33	0.020	
34	0.002	
35	-	
36	0.060	
37	-	
38	0.150	UG
39	-0.030	
41	-	
42	-	
43	-	
44	-	
45	-	
46	-	
47	0.080	
48A	-0.045	
48B	-	
49A	-	
49B	-	
50	-0.040	
51	-	
52A	-0.010	
52B	0.030	
53	-	
54	1.260	UC
55	-	
56	-	
57	-	
58	-0.020	
59	-	
60	-	
61	-0.010	
62	-	
63	-	
13B	-	
No of labs., p	20	
No of repl., n	2	
d	-0.003	
s^2	0.002	
s	0.045	
$t = \sqrt{p} \cdot (d/s)$	-0.2866	
Sign. level, p(t)	0.7776	

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

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

Laboratory	Difference AB	
1	0.010	
2	0.020	
3	0.000	
4	-0.010	
5	-0.020	
6	-	
7	-	
8	-	
9	-	
10	-	
11	-0.010	
12	-	
13A	-0.032	
14	0.020	
15	-	
16	0.060	
17	-0.010	
18	-0.020	
19	-0.050	
20	-	
21	0.010	
22	-	
23	0.010	
24	0.140	
25	0.070	
26A	-	
26B	-	
27	-0.010	
28	-	
29	-0.030	
30	-	
31	0.010	
32	-0.070	
33	-	
34	-	
35	-0.040	
36	0.060	
37	0.110	
38	0.020	
39	-	
41	-	
42	0.010	
43	0.000	
44	0.100	UG
45	-	
46	-0.010	
47	-	
48A	-	
48B	-	
49A	-0.020	
49B	0.050	
50	-0.040	
51	0.010	
52A	-	
52B	-	
53	0.030	
54	-	
55	0.020	
56	-0.020	
57	0.020	
58	-	
59	0.090	
60	-0.047	
61	-	
62	0.030	
63	-0.020	
13B	-	
No of labs., p	39	
No of repl., n	2	
d	0.009	
s^2	0.002	
s	0.044	
$t = \sqrt{p} \cdot (d/s)$	1.2454	
Sign. level, p(t)	0.2206	

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

Conductivity, mS/m
Control of differences within sample pairs

Laboratory	Difference AB	
1	-	
2	0.40	
3	-2.60	UC
4	-	
5	-0.10	
6	-0.40	
7	0.00	
8	-	
9	-	
10	-0.60	
11	-0.20	
12	-	
13A	-0.15	
14	-	
15	0.34	UG
16	-	
17	-	
18	0.10	
19	-	
20	-	
21	-0.30	
22	-	
23	-	
24	-	
25	1.40	UG
26A	-0.10	
26B	-	
27	-	
28	-	
29	-0.20	
30	-	
31	0.00	
32	-0.70	
33	-	
34	-	
35	0.40	
36	0.90	
37	-	
38	-	
39	0.00	
41	0.10	
42	0.20	
43	-	
44	-0.40	
45	-	
46	-	
47	-	
48A	-	
48B	-	
49A	-	
49B	-	
50	-0.30	
51	-	
52A	-	
52B	-	
53	-	
54	-0.10	
55	0.30	
56	-	
57	-	
58	0.20	
59	0.50	
60	0.50	
61	-	
62	-	
63	-0.10	
13B	-	
No of labs., p	26	
No of repl., n	2	
d	-0.00	
s^2	0.13	
s	0.36	
$t = \sqrt{p} \cdot (d/s)$	-0.0269	
Sign. level, p(t)	0.9787	

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	0.140	
2	-0.100	
3	-0.060	
4	0.015	
5	-0.110	
6	-0.070	
7	-0.030	
8	-	
9	-0.080	
10	-0.080	
11	0.020	
12	-0.170	
13A	0.000	
14	-0.200	
15	-0.050	UG
16	-0.130	
17	-0.040	
18	0.040	
19	-0.020	
20	-	
21	0.010	
22	0.030	
23	0.050	
24	-0.130	
25	-0.100	
26A	0.020	
26B	-	
27	-0.090	
28	0.000	
29	-0.050	
30	-0.070	
31	-0.090	
32	0.040	
33	0.000	
34	-0.080	
35	0.000	
36	0.060	
37	-0.074	
38	-0.010	
39	0.020	
41	-0.030	
42	-0.030	
43	-0.040	
44	0.000	
45	-	
46	-0.330	UC
47	-0.030	
48A	-0.030	
48B	-0.060	
49A	-0.030	
49B	-	
50	-0.070	
51	-0.070	
52A	-	
52B	0.080	
53	0.010	
54	-0.050	
55	0.000	UG
56	0.010	
57	0.080	
58	-0.210	
59	0.010	
60	0.090	
61	-0.239	
62	-0.020	
63	-0.060	
13B	-	
No of labs., p	57	
No of repl., n	2	
d	-0.036	
s^2	0.005	
s	0.073	
$t = \sqrt{p} \cdot (d/s)$	-3.6568	
Sign. level, p(t)	0.0006	***

* 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

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 differences within sample pairs

Laboratory	Difference AB	
1	-0.350	
2	-0.190	
3	0.730	
4	-1.100	
5	-0.010	
6	-	
7	-0.030	
8	-0.040	
9	0.200	
10	0.040	
11	-0.100	
12	-0.310	
13A	-0.234	
14	0.800	
15	0.120	
16	0.080	
17	-0.410	
18	-0.200	
19	0.250	
20	0.110	
21	0.020	
22	-0.030	
23	-0.190	
24	0.390	
25	0.300	
26A	-0.098	
26B	-0.060	
27	-0.110	
28	0.350	
29	0.010	
30	0.160	
31	-0.320	
32	-0.020	
33	-0.070	
34	0.071	
35	0.340	
36	-0.070	
37	-0.170	
38	-0.210	
39	0.200	
41	-0.140	
42	0.260	
43	-0.380	
44	0.140	
45	0.191	
46	-0.370	
47	0.040	
48A	0.032	
48B	1.020	
49A	-0.040	
49B	0.210	
50	0.040	
51	0.290	
52A	-0.050	
52B	0.060	
53	1.060	
54	0.135	
55	0.870	
56	0.220	
57	0.180	
58	-	
59	-0.530	
60	-0.603	UG
61	0.130	
62	0.100	
63	0.050	
13B	-	
No of labs., p	63	
No of repl., n	2	
d	0.053	
s^2	0.122	
s	0.349	
$t = \sqrt{p} \cdot (d/s)$	1.2146	
Sign. level, p(t)	0.2291	

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	0.5700	
2	0.5770	
3	0.5450	
4	0.5870	
5	0.5290	
6	-	
7	0.5625	
8	-	
9	0.5750	
10	-	
11	0.5410	
12	-	
13A	0.5185	
14	0.5410	
15	0.5870	
16	0.5000	
17	0.5905	
18	0.6230	
19	0.5705	
20	-	
21	0.5460	
22	0.5245	
23	0.5250	
24	0.5690	
25	0.5850	
26A	0.5250	
26B	-	
27	0.5600	
28	0.5820	
29	0.5510	
30	0.6770	
31	0.6285	
32	0.5255	
33	0.5900	
34	0.5920	
35	0.5645	
36	0.5750	
37	0.5850	
38	0.5635	UC
39	0.6400	UC
41	0.5270	
42	0.5700	
43	0.5900	
44	0.5700	
45	-	
46	0.5540	
47	0.5720	
48A	0.6196	
48B	-	
49A	0.5895	
49B	0.5465	
50	0.5465	
51	0.5745	
52A	0.5515	
52B	0.5650	
53	0.5230	
54	0.5240	
55	0.5155	
56	0.5705	
57	0.5070	
58	0.6045	
59	0.5410	
60	0.5120	
61	0.5785	
62	0.5525	
63	0.6510	
13B	0.5213	
No of labs., p	57	
No of repl., n	2	
m	0.5631	
s^2	0.0013	
s	0.0356	
Assigned value, μ	0.567	
Recovery, %	99.3	
$t = \sqrt{p} \cdot (m-\mu)/s$	-0.8179	
Sign. level, p(t)	0.4169	

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	2.125	
2	-	
3	-	
4	-	
5	-	
6	-	
7	1.935	
8	-	
9	-	
10	-	
11	2.050	
12	-	
13A	2.072	
14	-	
15	2.150	
16	-	
17	-	
18	-	
19	-	
20	-	
21	-	
22	-	
23	-	
24	-	
25	-	
26A	2.027	
26B	-	
27	-	
28	2.210	
29	-	
30	2.050	
31	2.165	
32	-	
33	2.240	
34	2.027	
35	-	
36	1.950	
37	-	
38	1.495	UG
39	2.055	
41	-	
42	-	
43	-	
44	-	
45	-	
46	-	
47	2.230	
48A	2.129	
48B	-	
49A	-	
49B	-	
50	2.010	
51	-	
52A	2.065	
52B	2.175	
53	-	
54	2.583	UC
55	-	
56	-	
57	-	
58	2.070	
59	-	
60	-	
61	2.225	
62	-	
63	-	
13B	-	
No of labs., p	20	
No of repl., n	2	
m	2.098	
s^2	0.008	
s	0.091	
Assigned value, μ	2.07	
Recovery, %	101.4	
$t = \sqrt{p} \cdot (m-\mu)/s$	1.3777	
Sign. level, p(t)	0.1843	

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

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

Laboratory	Sample pair AB	
1	2.125	
2	2.010	
3	2.230	
4	2.125	
5	2.030	
6	-	
7	-	
8	-	
9	-	
10	-	
11	2.035	
12	-	
13A	2.071	
14	2.040	
15	-	
16	2.120	
17	2.225	
18	2.280	
19	2.195	
20	-	
21	2.135	
22	-	
23	1.945	
24	2.240	
25	2.165	
26A	-	
26B	-	
27	2.205	
28	-	
29	2.075	
30	-	
31	2.165	
32	2.045	
33	-	
34	-	
35	2.140	
36	1.950	
37	2.085	
38	2.050	
39	-	
41	-	
42	2.165	
43	2.230	
44	2.580	UG
45	-	
46	2.075	
47	-	
48A	-	
48B	-	
49A	2.200	
49B	2.125	
50	2.010	
51	2.215	
52A	-	
52B	-	
53	1.975	
54	-	
55	2.190	
56	2.210	
57	2.160	
58	-	
59	2.045	
60	1.927	
61	-	
62	2.175	
63	1.780	
13B	-	
No of labs., p	39	
No of repl., n	2	
m	2.107	
s^2	0.011	
s	0.106	
Assigned value, μ	2.13	
Recovery, %	98.9	
$t = \sqrt{p} \cdot (m-\mu)/s$	-1.3673	
Sign. level, p(t)	0.1796	

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

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

Laboratory	Sample pair AB	
1	-	
2	54.90	
3	56.30	UC
4	-	
5	54.55	
6	54.90	
7	52.40	
8	-	
9	-	
10	55.20	
11	55.00	
12	-	
13A	53.98	
14	-	
15	5.35	UG
16	-	
17	-	
18	51.25	
19	-	
20	-	
21	54.65	
22	-	
23	-	
24	-	
25	549.30	UG
26A	53.95	
26B	-	
27	-	
28	-	
29	54.60	
30	-	
31	53.60	
32	57.55	
33	-	
34	-	
35	49.80	
36	54.75	
37	-	
38	-	
39	54.60	
41	53.45	
42	50.90	
43	-	
44	54.20	
45	-	
46	-	
47	-	
48A	-	
48B	-	
49A	-	
49B	-	
50	54.05	
51	-	
52A	-	
52B	-	
53	-	
54	54.45	
55	50.15	
56	-	
57	-	
58	53.90	
59	53.65	
60	55.25	
61	-	
62	-	
63	53.05	
13B	-	
No of labs., p	26	
No of repl., n	2	
m	53.80	
s^2	2.92	
s	1.71	
Assigned value, μ	54.2	
Recovery, %	99.3	
$t = \sqrt{p} \cdot (m-\mu)/s$	-1.2014	
Sign. level, p(t)	0.2409	

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	
1	7.490	
2	7.050	
3	7.280	
4	7.010	
5	7.245	
6	7.325	
7	7.245	
8	-	
9	7.270	
10	7.160	
11	7.220	
12	7.675	
13A	7.460	
14	6.900	
15	8.135	UG
16	7.425	
17	7.060	
18	7.300	
19	7.050	
20	-	
21	7.325	
22	7.255	
23	7.185	
24	7.155	
25	7.150	
26A	7.360	
26B	-	
27	6.955	
28	7.000	
29	7.545	
30	7.415	
31	7.175	
32	7.360	
33	7.800	
34	7.050	
35	7.130	
36	7.210	
37	7.032	
38	7.335	
39	6.990	
41	7.375	
42	6.945	
43	7.100	
44	7.130	
45	-	
46	6.245	UC
47	6.985	
48A	7.305	
48B	7.290	
49A	7.055	
49B	-	
50	7.285	
51	7.845	
52A	-	
52B	7.560	
53	7.155	
54	7.395	
55	6.300	UG
56	7.165	
57	6.960	
58	7.215	
59	7.285	
60	7.215	
61	7.216	
62	7.300	
63	7.290	
13B	-	
No of labs., p	57	
No of repl., n	2	
m	7.240	
s^2	0.040	
s	0.201	
Assigned value, μ	7.24	
Recovery, %	100.0	
$t = \sqrt{p} \cdot (m-\mu)/s$	-0.0112	
Sign. level, p(t)	0.9911	

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

ANNEX E CONCENTRATION LEVEL

Concentration level **SPIL-4 (2015)**

Parameter	Unit	Sample	Bottle no.	I	II	Bottle Average	Sample Average	Assigned value	Spike Measured	Spike Assigned
Total nitrogen	mg/L N	A1	13	4,08	4,11	4,10	4,08	4,00	-0,73	-0,80
			36	4,15	3,96	4,06				
			63	3,99	4,16	4,08				
		B1	8	4,68	4,81	4,75	4,81	4,8		
			33	5,01	4,79	4,90				
			78	4,77	4,79	4,78				
Ammonium	mg/L N	A1	13	0,53	0,53	0,53	0,53	0,57	-0,13	-0,13
			36	0,53	0,53	0,53				
			63	0,53	0,53	0,53				
		B1	8	0,65	0,66	0,66	0,66	0,70		
			33	0,66	0,66	0,66				
			78	0,66	0,66	0,66				
Nitrate	mg/L N	A1	13	2,08	2,12	2,10	2,11	2,13	-0,55	-0,57
			36	2,13	2,12	2,13				
			63	2,09	2,12	2,11				
		B1	8	2,66	2,66	2,66	2,66	2,7		
			33	2,65	2,65	2,65				
			78	2,69	2,66	2,68				
pH		A2	15	7,26	7,26	7,26	7,25	7,24	0,01	0,00
			23	7,22	7,19	7,21				
			65	7,25	7,30	7,28				
		B2	18	7,24	7,25	7,25	7,24	7,24		
			39	7,22	7,24	7,23				
			79	7,24	7,24	7,24				

ANNEX F HOMOGENEITY AND STABILITY

	SPIL-4
PT:	2015
Parameter:	NH4
Unit:	mg/L N
Sigma:	0,0442 6,5% of x

Responsible for tests: SMN/IRL

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

Homogeneity test Date: 2015-10-28

Sample	x(a)	x(b)	average	sd	sd^2
B1-5	0,673	0,675	0,7	0,001	0,000
B1-10	0,682	0,683	0,7	0,001	0,00
B1-20	0,678	0,685	0,7	0,005	0,000
B1-23	0,688	0,682	0,7	0,004	0,000
B1-34	0,676	0,682	0,7	0,004	0,000
B1-38	0,681	0,675	0,7	0,004	0,000
B1-49	0,673	0,676	0,7	0,002	0,000
B1-52	0,682	0,681	0,7	0,001	0,000
B1-64	0,687	0,679	0,7	0,006	0,000
B1-70	0,678	0,676	0,7	0,001	0,000
B1-75	0,677	0,681	0,7	0,003	0,000
B1-79	0,678	0,682	0,7	0,003	0,000

For homogeneity

General average (x)	0,68
Sample average sd (s_x)	0,003
Within-sample sd (s_w):	0,003
Between-samples sd (ss):	0,0024
S_L in the Proficiency Test:	
S_R in the Proficiency Test:	

Conclusions

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

/x-y/ =0

Analytical quality Is s_w < 0,15*sigma **YES**

Homogeneity: Is ss < 0.3*sigma? **YES**

PT: SPIL-4 2015
Parameter: NO3
Unit: mg/L N
Sigma: 0,2 $1,3*s_{T\ max}$

Responsible for tests: SMN/IRL

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

Homogeneity test Date: 2015-10-28

Sample	x(a)	x(b)	average	sd	sd^2
B1-5	2,65	2,69	2,7	0,028	0,001
B1-10	2,68	2,73	2,7	0,035	0,001
B1-20	2,66	2,7	2,7	0,028	0,001
B1-23	2,70	2,73	2,7	0,021	0,000
B1-34	2,67	2,73	2,7	0,042	0,002
B1-38	2,65	2,67	2,7	0,014	0,000
B1-49	2,70	2,69	2,7	0,007	0,000
B1-52	2,68	2,7	2,7	0,014	0,000
B1-64	2,64	2,65	2,6	0,007	0,000
B1-70	2,67	2,66	2,7	0,007	0,000
B1-75	2,67	2,66	2,7	0,007	0,000
B1-79	2,69	2,64	2,7	0,035	0,001

For homogeneity

General average (x)	2,7
Sample average sd (s_x)	0,021
Within-sample sd (s_w):	0,024
Between-samples sd (ss):	0,013
S_L in the Proficiency Test:	
S_R in the Proficiency Test:	

Stability test Date: 2015-11-12

Sample	x(a)	x(b)
B1-8	2,66	2,66
B1-33	2,65	2,65
B1-78	2,69	2,66

For stability

General average (y):	2,661667
/x-y/ =	0,017917

Conclusions

ss =0,01 0.3*sigma=0,05
/x-y/ =0,017917

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-4 2015
Parameter: pH
Unit:
Sigma: 0,065 6,5% of x

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

Responsible for tests: SMN/IRL

Homogeneity test Date: 2015-10-28

Sample	x(a)	x(b)	average	sd	sd^2
B2-4	7,42	7,49	7,5	0,049	0,002
B2-9	7,41	7,45	7,4	0,028	0,00
B2-19	7,44	7,46	7,5	0,014	0,000
B2-22	7,42	7,51	7,5	0,064	0,004
B2-34	7,44	7,44	7,4	0,000	0,000
B2-43	7,44	7,43	7,4	0,007	0,000
B2-51	7,47	7,47	7,5	0,000	0,000
B2-53	7,47	7,48	7,5	0,007	0,000
B2-57	7,49	7,45	7,5	0,028	0,001
B2-65	7,46	7,45	7,5	0,007	0,000
B2-75	7,45	7,46	7,5	0,007	0,000
B2-80	7,44	7,44	7,4	0,000	0,000

For homogeneity

General average (x)	7,45
Sample average sd (s_x)	0,015
Within-sample sd (s_w):	0,027
Between-samples sd (ss):	0
S_L in the Proficiency Test:	
S_R in the Proficiency Test:	

Conclusions

ss =0 0.3*sigma=0,02
/x-y/ =0

Analytical quality Is s_w < 0,15*sigma **NO**

Homogeneity: Is ss < 0.3*sigma? **YES**