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Proficiency test SPIL-4 (2019)

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 14 November 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 17 December 2019.

2 FEATURES OF THE PROFICIENCY TEST

Participants in the proficiency test were a total of 50 laboratories from Denmark, Norway and Sweden. A list of participants is shown in Appendix A.

The closing date for submission of results was 28 November 2019. All participants except laboratory no. 40 and 50 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+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	6.9	0.16	0.9
Ammonium	NH_4	mg/L N	0.1-2	0.679	0.0094	0.191
Nitrite+nitrate	NO_{2+3}	mg/L N	1-5	4.24	0.068	0.60
Nitrate	NO_3	mg/L N	1-5	4.31	0.050	0.60
Conductivity	γ_{25}	mS/m	50-300	64.3	0.94	1.0
pH	pH	-	6-9	7.44	0.057	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.

In order to ensure optimal use of the data, the assigned value is calculated as the average of the median for both samples in the sample pair after subtraction of the spike value. The spike values are calculated from sample preparation except for γ_{25} where the spike value is the difference between median values for the two samples in the sample pair.

The assigned value for TN is operationally defined and is a consensus value based upon the median for method no. 1, 2, 3, 4 and 5 prescribed by the Danish EPA. A list of method identification numbers is found in the report to participants /1/. Assigned values for NH_4, NO_{2+3}, NO_3, conductivity and pH are consensus values for all laboratories based on the median.

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 three of the parameters.

The test revealed a significant difference between the two for pH and NH_4. 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.

The test revealed a significant difference for TN. 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 other methods than no. 1, 2, 3, 4 and 5 and now showed no significant difference. Furthermore, the results of control measurements at Eurofins confirmed the assigned value.

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 homogeneity show that the samples are homogeneous.

The tests for stability show that the samples are not stable from the date of production to the day of analysis. This is seen for all tested parameters. Since the recoveries for the proficiency test were not significant different from 100 % and the proficiency should be performed on a specific date. The instability should not affect the validity of the proficiency test. The analytical quality is compared to the analytical quality in previous proficiency test and is not found to be worse than normal.

4 CONCLUSION

The quality control performed, including test of sample 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.

The tests for stability show that the samples are not stable from the date of production to the date of analysis. The instability can give different results for laboratories analysing on other dates than the one set by the proficiency test.

5 REFERENCES

/1/ Eurofins A/S, *Proficiency test SPIL-4 (2019)*, Report to participants, December 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. 1071 on *quality criteria for environmental measurements,* 28 November 2019 (in Danish).

/6/ ISO 13528, *Statistical methods for use in proficiency testing by interlaboratory comparison*, 2015.

A N N E X E S

ANNEX A LIST OF PARTICIPANTS

Laboratory	**Town**	**Country**
Spildevandslaboratoriet (2 participants)	Esbjerg	Danmark
Faxe Forsyning	Faxe	Danmark
AquaDjurs A/S	Grenaa	Danmark
Provas	Haderslev	Danmark
Hillerød Forsyning, Spildevand	Hillerød	Danmark
Fors Spildevand Holbæk	Holbæk	Danmark
Holstebro Centralrenseanlæg, Vestforsyning Spildevand	Holstebro	Danmark
Kerteminde Forsyning - Spildevand A/S	Kerteminde	Danmark
BlueKolding A/S	Kolding	Danmark
Biofos A/S	København K	Danmark
Klarforsyning, Køge-Egnens Renseanlæg	Køge	Danmark
Melby Renseanlæg	Liseleje	Danmark
CP Kelco, Spildevandslaboratoriet	Ll. Skensved	Danmark
NK-Spildevand A/S	Næstved	Danmark
Vandmiljø Randers A/S	Randers SØ	Danmark
Bjergmarken R/A, Fors Spildevand Roskilde	Roskilde	Danmark
Rønne Renseanlæg	Rønne	Danmark
Ringkøbing-Skjern Forsyning A/S	Skjern	Danmark
RGS Nordic A/S	Skælskør	Danmark
SK Spildevand, Slagelse Renseanlæg (5 participants)	Slagelse	Danmark
Eurofins Miljø A/S	Vejen	Danmark
Vejle Spildevand	Vejle	Danmark
Aalborg Forsyning, Renseanlæg Øst	Aalborg Øst	Danmark
SYNLAB AS (Hamar)	Hamar	Norge
Laboratoriet på Vatten och Avloppsavdelningen, SBF, Enköpings Kommun	Enköping	Sverige
Laboratoriet vid Smedjeholms avloppsreningsverk	Falkenberg	Sverige
Preem AB Göteborg	Göteborg	Sverige
St1 Refinery AB	Göteborg	Sverige
GRYAAB AB	Göteborg	Sverige
Hallsta Pappersbruk	Hallstavik	Sverige
Kalmar Vatten AB, VA-lab	Kalmar	Sverige

Laboratory	Town	Country
Reningsverket Aggerud	Karlskoga	Sverige
Kristianstad Kommun	Kristianstad	Sverige
Yara AB	Köping	Sverige
Käppalaverket	Lidingö	Sverige
Tekniska Verken i Linköping AB (publ), Laboratoriet Avloppsreningsverket	Linköping	Sverige
Preemraff Lysekil	Lysekil	Sverige
Mjölby Kommun	Mjölby	Sverige
Motala Kommun, Tekniska Förvaltningen, Vatten & Avfall	Motala	Sverige
Arctic Paper Munkedals AB	Munkedal	Sverige
Södra Cell Mörrum	Mörrum	Sverige
Fiskeby Board AB	Norrköping	Sverige
Holmen Paper AB, Bravikens Pappersbruk Bravikens Pappersbruk	Norrköping	Sverige
Vatten och Avloppslaboratoriet VAL AB	Norrtälje	Sverige
Ernemar Laboratorium	Oskarshamn	Sverige
Rottneros Bruk AB	Rottneros	Sverige
Vallviks Bruk AB	Vallvik	Sverige
Kretslopp & Vattens laboratorium , Vänersborgs kommun	Vänersborg	Sverige
Västervik Miljö & Energi AB, Vattenlaboratoriet	Västervik	Sverige
Perstorp Oxo AB	Ödsmål	Sverige

ANNEX B SAMPLE PREPARATION

Stock solution	**Prepared from**	**Concentration**
Stock TN	2.9999 g Disodium edetate, $2H_2O$ milli-Q water up to 1000.1 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	2.5000 g Potassium nitrate (KNO_3) milli-Q water up to 1000.0 g	NO_3: 346.4 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	10.00 g stock TN 25.00 g stock NH_4 60.00 g stock NO_3 Sample B1 up to 34.00 kg	0.997 · (a+4.66) + 0.870	0.997 · (b+0.604) + 0.193	0.997 · (c+2.66) + 0.611	c
B1	400.00 g stock TN 150.01 g stock NH_4 500.00 g stock NO_3 Filtered water from Holsted sewage treatment plant up to 65.00 kg	a+4.66	b+0.604	c+2.66	d

Sample	**Sample prepared from**	**pH**
A2/B2	Filtered water 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	
1	-0.550	
2	-0.050	
3	-0.110	
4	-0.030	
5	-0.060	
6	-0.760	
7	0.020	
8	-0.160	
9	-0.100	
10	0.090	
11	-	
12	0.031	
13	-0.080	
14	0.020	
15A	-0.450	
15B	-0.480	
16	0.130	
17	-0.250	
18	0.040	
19	-0.140	
20	-0.130	
21	-0.010	
22	-0.070	
23	0.294	
24	0.120	
25	-0.050	
26	0.070	
27	-0.080	
28	-0.840	
29	-0.090	
30	0.030	
31	0.020	
32	-0.060	
33	-	
34	-0.180	
35	-0.970	
36	-0.070	
37	-0.100	
38	0.090	
39	0.190	
41	0.050	
42	-0.280	
43	0.010	
44	-1.170	UG
45	-0.010	
46	-0.450	
48	0.010	
49	0.120	
51	-0.040	
52	0.330	
53	-0.050	
54	-0.040	
55	-0.950	
56	0.080	
No of labs., p	51	
No of repl., n	2	
d	-0.117	
s^2	0.080	
s	0.283	
$t = \sqrt{p} \cdot (d/s)$	-2.9430	
Sign. level, p(t)	0.0049	**

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

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

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

Laboratory	Difference AB	
1	0.0030	UG
2	-0.0180	
3	-0.0110	
4	0.0120	
5	-0.0160	
6	-0.0070	
7	-0.0040	
8	0.0000	
9	-0.0010	
10	0.0240	
11	-0.0110	
12	-0.0080	
13	0.0000	
14	-0.0030	
15A	0.0010	
15B	-0.0060	
16	0.0050	
17	-	
18	0.3690	UC
19	-0.0020	
20	-0.0030	
21	-0.0070	
22	-0.0110	
23	-0.0260	
24	0.0030	
25	0.0370	UG
26	-0.0280	
27	0.0090	
28	-	
29	-0.0270	
30	-	
31	0.0190	
32	-	
33	-0.0190	
34	0.0090	
35	0.0290	
36	-	
37	-0.0060	
38	-	
39	-0.0010	
41	0.1240	UC
42	-0.0080	
43	-0.0090	
44	-	
45	0.0060	
46	0.0000	
48	0.0010	
49	-0.0140	
51	-0.0110	
52	-	
53	-0.0130	
54	-0.0010	
55	-0.0140	
56	-0.0000	
No of labs., p	42	
No of repl., n	2	

Laboratory	Difference AB	
d	-0.0040	
s^2	0.0001	
s	0.0122	
$t = \sqrt{p} \cdot (d/s)$	-2.1149	
Sign. level, p(t)	0.0406	*

* 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.

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

Laboratory	Difference AB
1	-
2	-
3	-
4	-
5	-
6	-
7	-
8	-
9	-
10	0.080
11	0.050
12	-0.009
13	-
14	-
15A	-
15B	-
16	-
17	-
18	-0.030
19	-
20	-
21	-
22	-0.060
23	-
24	-
25	-
26	-
27	-
28	-
29	-
30	-
31	-
32	-
33	-0.001
34	0.050
35	-
36	-
37	0.020
38	-
39	-
41	0.030
42	-
43	-
44	-
45	-
46	-
48	-
49	-
51	-
52	0.010
53	-
54	-
55	-
56	-0.018
No of labs., p	11
No of repl., n	2

Laboratory	Difference AB
d	0.011
s^2	0.002
s	0.040
$t = \sqrt{p} \cdot (d/s)$	0.9096
Sign. level, p(t)	0.3844

No test statistics were found to be significant

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

Laboratory	Difference AB	
1	-	
2	-0.010	
3	-0.020	
4	-0.070	
5	-	
6	0.030	
7	0.030	
8	-0.090	
9	0.020	
10	-	
11	0.050	
12	-0.009	
13	0.070	
14	0.040	
15A	-0.030	
15B	-0.040	
16	-0.020	
17	-	
18	-0.030	
19	-0.100	
20	0.060	
21	-0.050	
22	-	
23	-0.416	UC
24	0.000	
25	-0.190	
26	0.040	
27	0.040	
28	-	
29	0.120	
30	-	
31	-	
32	-	
33	-	
34	-	
35	0.120	
36	-	
37	-	
38	-	
39	0.000	
41	-	
42	-	
43	-0.040	
44	-	
45	0.000	
46	-0.604	UC
48	0.050	
49	-0.030	
51	0.140	UG
52	-	
53	-	
54	-0.160	
55	0.000	
56	-	
No of labs., p	31	
No of repl., n	2	

Laboratory	Difference AB
d	-0.007
s^2	0.005
s	0.069
$t = \sqrt{p} \cdot (d/s)$	-0.5720
Sign. level, p(t)	0.5716

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	
1	-1.00	UG
2	-1.00	
3	-	
4	-	
5	-	
6	-	
7	-0.40	
8	-	
9	-	
10	-0.30	
11	-	
12	-0.60	
13	1.10	
14	-0.40	
15A	-	
15B	-	
16	-	
17	-	
18	-0.30	
19	-	
20	-0.10	
21	-	
22	-	
23	1.70	
24	-	
25	-0.50	
26	1.50	
27	-	
28	1.40	
29	12.00	UC
30	-	
31	-	
32	-	
33	-0.30	
34	-	
35	0.90	
36	-0.80	
37	-	
38	-0.80	
39	-	
41	-0.17	
42	-	
43	-	
44	-	
45	-0.50	
46	1.00	UG
48	-0.10	
49	-	
51	-	
52	-0.62	
53	-	
54	-	
55	-1.00	UG
56	-0.50	
No of labs., p	21	
No of repl., n	2	

Laboratory	Difference AB
d	-0.04
s^2	0.68
s	0.82
$t = \sqrt{p} \cdot (d/s)$	-0.2098
Sign. level, p(t)	0.8359

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	0.150
2	0.190
3	-
4	0.160
5	-
6	0.090
7	0.090
8	-
9	0.190
10	0.520
11	0.180
12	0.060
13	0.040
14	-
15A	0.120
15B	-
16	0.090
17	0.000
18	0.330
19	-
20	0.130
21	0.220
22	-0.030
23	0.140
24	0.180
25	0.110
26	0.149
27	0.220
28	0.120
29	0.110
30	0.070
31	0.090
32	-
33	-0.050
34	0.200
35	0.200
36	-0.100
37	-0.030
38	0.130
39	-0.380
41	-0.060
42	-
43	-0.040
44	0.110
45	-0.030
46	0.100
48	0.120 UG
49	0.040
51	0.170
52	-0.080
53	-0.172
54	-
55	-0.040
56	-0.060
No of labs., p	44
No of repl., n	2
d	0.082
s^2	0.020
s	0.142
$t = \sqrt{p} \cdot (d/s)$	3.8399
Sign. level, p(t)	0.0004 ***

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

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

ANNEX D CONTROL OF RECOVERY

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

Laboratory	Sample pair AB	
1	6.565	
2	6.615	
3	6.465	
4	6.955	
5	6.830	
6	7.660	
7	6.500	
8	6.770	
9	7.240	
10	6.895	
11	-	
12	6.524	
13	6.880	
14	6.910	
15A	7.055	
15B	6.890	
16	8.075	
17	7.505	
18	6.710	
19	6.720	
20	5.995	
21	6.735	
22	6.005	
23	7.160	
24	7.020	
25	6.975	
26	6.005	
27	6.700	
28	7.200	
29	6.955	
30	6.175	
31	5.850	
32	5.640	
33	-	
34	6.990	
35	7.265	
36	7.195	
37	7.110	
38	6.214	
39	6.655	
41	6.575	
42	6.500	
43	6.515	
44	9.125	UG
45	6.625	
46	7.465	
48	5.855	
49	7.770	
51	6.640	
52	7.045	
53	7.125	

Laboratory	Sample pair AB
54	5.740
55	6.935
56	6.900
No of labs., p	51
No of repl., n	2
m	6.771
s^2	0.264
s	0.514
Assigned value, μ	6.9
Recovery, %	98.1
$t = \sqrt{p} \cdot (m-\mu)/s$	-1.7981
Sign. level, p(t)	0.0782

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	0.4055	UG
2	0.6510	
3	0.6845	
4	0.7000	
5	0.6400	
6	0.6635	
7	0.6990	
8	0.7050	
9	0.6875	
10	0.6690	
11	0.6645	
12	0.6630	
13	0.6630	
14	0.7125	
15A	0.6925	
15B	0.6800	
16	0.6955	
17	-	
18	1.0045	UC
19	0.7070	
20	0.6955	
21	0.6685	
22	0.7785	
23	0.6530	
24	0.5535	
25	0.9105	UG
26	0.6510	
27	0.6945	
28	-	
29	0.6335	
30	-	
31	0.6895	
32	-	
33	0.6695	
34	0.6845	
35	0.5535	
36	-	
37	0.6950	
38	-	
39	0.6295	
41	0.7420	UC
42	0.6750	
43	0.6735	
44	-	
45	0.7000	
46	0.6810	
48	0.6925	
49	0.6970	
51	0.6045	
52	-	
53	0.6765	
54	0.6495	
55	0.6420	
56	0.6780	
No of labs., p	42	

Laboratory	Sample pair AB
No of repl., n	2
m	0.6713
s^2	0.0015
s	0.0389
Assigned value, μ	0.680
Recovery, %	98.7
$t = \sqrt{p} \cdot (m-\mu)/s$	-1.4404
Sign. level, p(t)	0.1574

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

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

Laboratory	Sample pair AB
1	-
2	-
3	-
4	-
5	-
6	-
7	-
8	-
9	-
10	4.280
11	4.445
12	4.178
13	-
14	-
15A	-
15B	-
16	-
17	-
18	4.325
19	-
20	-
21	-
22	4.270
23	-
24	-
25	-
26	-
27	-
28	-
29	-
30	-
31	-
32	-
33	4.240
34	4.345
35	-
36	-
37	4.230
38	-
39	-
41	4.365
42	-
43	-
44	-
45	-
46	-
48	-
49	-
51	-
52	4.165
53	-
54	-
55	-
56	4.205
No of labs., p	11
No of repl., n	2

Laboratory	Sample pair AB
m	4.277
s^2	0.007
s	0.086
Assigned value, μ	4.24
Recovery, %	100.9
$t = \sqrt{p} \cdot (m-\mu)/s$	1.4300
Sign. level, p(t)	0.1832

No test statistics were found to be significant

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

Laboratory	Sample pair AB	
1	-	
2	4.305	
3	4.230	
4	4.485	
5	-	
6	4.445	
7	4.345	
8	4.335	
9	4.340	
10	-	
11	4.445	
12	4.178	
13	4.465	
14	4.450	
15A	4.325	
15B	4.210	
16	4.430	
17	-	
18	4.325	
19	4.350	
20	4.310	
21	4.215	
22	-	
23	4.236	UC
24	4.100	
25	4.285	
26	4.260	
27	4.380	
28	-	
29	4.550	
30	-	
31	-	
32	-	
33	-	
34	-	
35	4.220	
36	-	
37	-	
38	-	
39	4.290	
41	-	
42	-	
43	4.380	
44	-	
45	4.220	
46	-0.211	UC
48	4.255	
49	4.405	
51	3.590	UG
52	-	
53	-	
54	4.200	
55	4.210	
56	-	
No of labs., p	31	
No of repl., n	2	

Laboratory	Sample pair AB
m	4.321
s^2	0.011
s	0.106
Assigned value, μ	4.31
Recovery, %	100.2
$t = \sqrt{p} \cdot (m-\mu)/s$	0.5654
Sign. level, p(t)	0.5760

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	
1	0.13	UG
2	62.50	
3	-	
4	-	
5	-	
6	-	
7	62.00	
8	-	
9	-	
10	65.85	
11	-	
12	63.60	
13	63.65	
14	64.60	
15A	-	
15B	-	
16	-	
17	-	
18	64.45	
19	-	
20	65.25	
21	-	
22	-	
23	64.85	
24	-	
25	62.45	
26	68.35	
27	-	
28	60.00	
29	620.00	UC
30	-	
31	-	
32	-	
33	65.05	
34	-	
35	65.45	
36	59.90	
37	-	
38	64.80	
39	-	
41	63.42	
42	-	
43	-	
44	-	
45	61.65	
46	613.50	UG
48	65.55	
49	-	
51	-	
52	64.33	
53	-	
54	-	
55	51.50	UG
56	67.05	
No of labs., p	21	
No of repl., n	2	

Laboratory	Sample pair AB
m	64.04
s^2	4.42
s	2.10
Assigned value, μ	64.3
Recovery, %	99.6
$t = \sqrt{p} \cdot (m-\mu)/s$	-0.5755
Sign. level, p(t)	0.5714

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	7.225	
2	7.455	
3	-	
4	7.470	
5	-	
6	7.225	
7	7.435	
8	-	
9	7.695	
10	7.610	
11	7.420	
12	7.400	
13	7.400	
14	-	
15A	7.650	
15B	-	
16	7.445	
17	7.100	
18	7.535	
19	-	
20	7.555	
21	7.360	
22	7.595	
23	7.660	
24	7.640	
25	7.395	
26	7.023	
27	7.320	
28	7.470	
29	7.435	
30	8.085	
31	7.455	
32	-	
33	7.265	
34	8.200	
35	7.380	
36	7.250	
37	7.475	
38	7.875	
39	7.380	
41	7.510	
42	-	
43	7.160	
44	7.215	
45	6.895	
46	7.550	
48	6.390	UG
49	7.770	
51	7.305	
52	7.410	
53	7.621	
54	-	
55	7.560	
56	7.530	
No of labs., p	44	
No of repl., n	2	

Laboratory	Sample pair AB
m	7.464
s^2	0.059
s	0.243
Assigned value, μ	7.44
Recovery, %	100.3
$t = \sqrt{p} \cdot (m-\mu)/s$	0.6500
Sign. level, p(t)	0.5192

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

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	13	7,76	7,79	7,78	7,76	7,80	0,85	0,9
			30	7,79	7,80	7,80				
			62	7,70	7,73	7,72				
		B1	19	6,86	6,85	6,86	6,91	6,9		
			30	6,89	6,91	6,90				
			59	6,96	6,99	6,98				
Ammonium	mg/L N	A1	13	0,867	0,869	0,868	0,871	0,871	0,184	0,191
			30	0,875	0,877	0,876				
			62	0,868	0,869	0,869				
		B1	19	0,683	0,682	0,683	0,687	0,680		
			30	0,683	0,684	0,684				
			59	0,694	0,695	0,695				
Nitrate	mg/L N	A1	13	5,02	5,04	5,03	5,03	4,91	0,62	0,60
			30	5,02	5,05	5,04				
			62	5,01	5,02	5,02				
		B1	19	4,41	4,42	4,42	4,41	4,31		
			30	4,37	4,38	4,38				
			59	4,44	4,45	4,45				
pH		A2	9	7,41	7,45	7,43	7,45	7,44	-0,03	0,00
			33	7,43	7,49	7,46				
			56	7,45	7,48	7,47				
		B2	15	7,37	7,36	7,37	7,43	7,44		
			39	7,40	7,44	7,42				
			72	7,50	7,48	7,49				

ANNEX F HOMOGENEITY AND STABILITY

PT:	SPIL-4
Parameter:	NH_4
Unit:	mg/L N
Sigma:	0,050

Responsible for tests: S7MS/HBS

Homogeneity test Date: 2019-10-29

Sample	x(a)	x(b)	average	sd	sd^2
A1-3	0,91	0,91	0,9	0,001	0,000
A1-9	0,91	0,91	0,9	0,001	0,00
A1-21	0,92	0,93	0,9	0,001	0,000
A1-23	0,94	0,94	0,9	0,002	0,000
A1-32	0,93	0,93	0,9	0,001	0,000
A1-38	0,91	0,91	0,9	0,001	0,000
A1-46	0,90	0,91	0,9	0,002	0,000
A1-51	0,92	0,92	0,9	0,001	0,000
A1-60	0,93	0,93	0,9	0,002	0,000
A1-68	0,91	0,91	0,9	0,000	0,000
A1-74	0,92	0,92	0,9	0,001	0,000
A1-81	0,92	0,92	0,9	0,000	0,000

For homogeneity

General average (x)	0,92
Sample average sd (s_x)	0,010
Within-sample sd (s_w):	0,001
Between-samples sd (ss):	0,0102
S_L in the Proficiency Test:	0,039
S_R in the Proficiency Test:	0,039

Stability test Date: 2019-11-14

Sample	x(a)	x(b)
A1-13	0,867	0,869
A1-30	0,875	0,877
A1-62	0,868	0,869

For stability

General average (y):	0,8708333
/x-y/ =	0,0475833

Conclusions

ss =	0,010	0.3*sigma=	0,01
/x-y/ =	0,0475833		

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

PT:	SPIL-4
Parameter:	NO_3
Unit:	mg/L N
Sigma:	0,3

Responsible for tests: S7MS/HBS

Homogeneity test Date: 2019-10-29

Sample	x(a)	x(b)	average	sd	sd^2
A1-3	5,12	5,15	5,1	0,021	0,000
A1-9	5,27	5,27	5,3	0,000	0,000
A1-21	5,21	5,23	5,2	0,014	0,000
A1-23	5,23	5,28	5,3	0,035	0,001
A1-32	5,27	5,26	5,3	0,007	0,000
A1-38	5,29	5,29	5,3	0,000	0,000
A1-46	5,23	5,26	5,2	0,021	0,000
A1-51	5,14	5,12	5,1	0,014	0,000
A1-60	5,25	5,24	5,2	0,007	0,000
A1-68	5,21	5,23	5,2	0,014	0,000
A1-74	5,21	5,23	5,2	0,014	0,000
A1-81	5,20	5,17	5,2	0,021	0,000

For homogeneity

General average (x)	5,22
Sample average sd (s_x)	0,051
Within-sample sd (s_w):	0,017
Between-samples sd (ss):	0,049
S_L in the Proficiency Test:	0,099
S_R in the Proficiency Test:	0,111

Stability test Date: 2019-11-14

Sample	x(a)	x(b)
A1-13	5,02	5,04
A1-30	5,02	5,05
A1-62	5,01	5,02

For stability

General average (y):	5,0266667
/x-y/ =	0,1966667

Conclusions

ss =	0,05	0.3*sigma=	0,08
/x-y/ =	0,1966667		

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

PT:	SPIL-4
Parameter:	pH
Unit:	-
Sigma:	0,1

Responsible for tests: S7MS/HBS

Homogeneity test Date: 2019-10-29

Sample	x(a)	x(b)	average	sd	sd^2
B2-6	7,56	7,59	7,58	0,021	0,000
B2-10	7,57	7,57	7,57	0,000	0,00
B2-21	7,54	7,56	7,55	0,014	0,000
B2-25	7,56	7,56	7,56	0,000	0,000
B2-34	7,54	7,58	7,56	0,028	0,001
B2-37	7,55	7,62	7,59	0,049	0,002
B2-49	7,65	7,60	7,63	0,035	0,001
B2-52	7,58	7,60	7,59	0,014	0,000
B2-61	7,55	7,56	7,56	0,007	0,000
B2-69	7,55	7,56	7,56	0,007	0,000
B2-73	7,57	7,60	7,59	0,021	0,000
B2-80	7,59	7,60	7,60	0,007	0,000

For homogeneity

General average (x)	7,58
Sample average sd (s_x)	0,022
Within-sample sd (s_w):	0,022
Between-samples sd (ss):	0,0151
S_L in the Proficiency Test:	0,233
S_R in the Proficiency Test:	0,253

Stability test Date: 2019-11-14

Sample	x(a)	x(b)
B2-15	7,37	7,36
B2-39	7,40	7,44
B2-72	7,50	7,48

For stability

General average (y):	7,425
/x-y/ =	0,1504167

Conclusions

ss =	0,015	0.3*sigma=	0,02
/x-y/ =	0,1504167		

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