

## **Proficiency test SPIL-4 (2021)**

**Nitrogen parameters in wastewater (effluent)**

# Proficiency test SPIL-4 (2021) Quality Documentation

January 2022

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|                            |                         |
|----------------------------|-------------------------|
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| Environmental laboratories |                         |

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|----------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------|
| Project                                                                                                                                                  | Project No                               |
| Proficiency test SPIL-4 (2021)                                                                                                                           | 20405-14                                 |
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|                                                                                                                                                          |                                          |
|                                                                                                                                                          |                                          |
| 1                                                                                                                                                        | Quality Documentation Report             |
|                                                                                                                                                          | DPRE                                     |
|                                                                                                                                                          | FYE3                                     |
|                                                                                                                                                          | 2022-01-17                               |
| Revision                                                                                                                                                 | Description                              |
|                                                                                                                                                          | By                                       |
|                                                                                                                                                          | Approved                                 |
|                                                                                                                                                          | Date                                     |
| Key words                                                                                                                                                | Classification                           |
| Analytical quality, assigned value, precision, trueness, homogeneity, stability, total nitrogen, ammonium, nitrite+nitrate, conductivity, pH, wastewater | <input checked="" type="checkbox"/> Open |
|                                                                                                                                                          | <input type="checkbox"/> Internal        |
|                                                                                                                                                          | <input type="checkbox"/> Proprietary     |

|                                                                        |
|------------------------------------------------------------------------|
| Distribution                                                           |
| Available online: <a href="http://www.eurofins.dk">www.eurofins.dk</a> |
| Eurofins: Rikke Mikkelsen, Peter Rerup                                 |

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## **1 INTRODUCTION**

A proficiency test on the analysis of nitrogen parameters in wastewater was conducted on 18 November 2021. 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 2021.

## 2 FEATURES OF THE PROFICIENCY TEST

Participants in the proficiency test were a total of 51 laboratories from Denmark, Norway, Sweden, Germany and Singapore. A list of participants is shown in Appendix A.

The closing date for submission of results was 3 December. All participants 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 <sub>4</sub> , NO <sub>2+3</sub> , NO <sub>3</sub> and $\gamma_{25}$ |
| A2/B2       | pH                                                                          |

### 2.2 Statistical analysis of participants' data

A split-level design was used. The data analysis was performed in accordance with ISO 5725: "Accuracy (trueness and precision) of measurement methods and results" (2019) /2/ and as described in detail in Spliid (1992) /3/. A short introduction to the statistics and a list of symbols and abbreviations used is given in Eurofins document "Schedule for a proficiency test", which is available at Eurofins' home page /4/.

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

### 2.3 Assigned and spike value

An overview of the concentrations in the samples (the assigned values) and the difference in concentration between the two samples of a sample pair (spike value) are shown in Table 2 compared to the range of concentrations normally encountered in 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          | 3.5            | 0.18                          | 0.6         |
| Ammonium        | NH <sub>4</sub>   | mg/L N | 0.1-2         | 0.312          | 0.0057                        | 0.260       |
| Nitrite+nitrate | NO <sub>2+3</sub> | mg/L N | 1-5           | 2.31           | 0.044                         | 0.19        |
| Nitrate         | NO <sub>3</sub>   | mg/L N | 1-5           | 2.33           | 0.035                         | 0.19        |
| Conductivity    | $\gamma_{25}$     | mS/m   | 50-300        | 181            | 2.2                           | 1           |
| pH              | pH                | -      | 6-9           | 7.59           | 0.031                         | 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  $\gamma_{25}$  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 and 3 (TN). A list of method identification numbers is found in the report to participants /1/. Assigned values for  $\text{NH}_4$ ,  $\text{NO}_3$  and pH are consensus values for all laboratories based on the median.

Assigned values for  $\text{NO}_{2+3}$  are consensus values for all laboratories based on the median, however, except for values that clearly only include  $\text{NO}_2$ . These values are less than 1% of the expected value and are therefore excluded before the data processing after a professional assessment. This applies to labs 4, 16, 30, 36 and 49.

Assigned values for conductivity are consensus values for all laboratories based on the median, however, except for values that clearly deviate greatly from the expected value, partly because they are given with an incorrect unit. These values are therefore excluded before the data processing after a professional assessment. This applies to labs 2, 13, 16, 27A, 27B, 30, 36, 45 and 49.

### **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 was/were tested using the following parameters as indicators:

|                 |                                         |
|-----------------|-----------------------------------------|
| NH <sub>4</sub> | Combined homogeneity and stability test |
| NO <sub>3</sub> | 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  $0.3 \cdot \hat{\sigma}$  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 stable.

## **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.

## 5 REFERENCES

- /1/ Eurofins A/S, *Proficiency test SPIL-4 (2021)*, Report to participants, December 2021.
- /2/ ISO 5725-2, *Accuracy (trueness and precision) of measurement methods and results – Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method*, 2019.
- /3/ Spliid, H., *Procedure and analysis of data for proficiency tests and environmental analyses*, Report to Danish Environmental Protection Agency, 1994 (in Danish).
- /4/ Eurofins A/S, *Schedule for a proficiency test*, document may be downloaded from [www.eurofins.dk/proficiencytest](http://www.eurofins.dk/proficiencytest).
- /5/ Ministry of Environment regulation no. 1770 on *quality criteria for environmental measurements*, 28 October 2020 (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**

| <b>Laboratory</b>                                           | <b>Town</b>  | <b>Country</b> |
|-------------------------------------------------------------|--------------|----------------|
| Rensningsanlæg Øst, Spildevandslaboratoriet                 | Esbjerg      | Denmark        |
| AquaDjurs A/S                                               | Grenaa       | Denmark        |
| Provas - Haderslev Forsyningservice A/S                     | Haderslev    | Denmark        |
| Cheminova A/S                                               | Harboøre     | Denmark        |
| Hillerød Spildevand                                         | Hillerød     | Denmark        |
| Holbæk RA, Fors Spildevand Holbæk                           | Holbæk       | Denmark        |
| Holstebro Renseanlæg, Vestforsyning Spildevand              | Holstebro    | Denmark        |
| Kerteminde Forsyning - Spildevand A/S                       | Kerteminde   | Denmark        |
| BlueKolding A/S                                             | Kolding      | Denmark        |
| Biofos A/S                                                  | København K  | Denmark        |
| Klarforsyning, Køge-Egnens Renseanlæg                       | Køge         | Denmark        |
| CP Kelco, QC Analyselab.                                    | Ll. Skensved | Denmark        |
| NK-Forsyning A/S                                            | Næstved      | Denmark        |
| Vandmiljø Randers A/S                                       | Randers SØ   | Denmark        |
| Bjergmarken RA, Fors Spildevand Roskilde                    | Roskilde     | Denmark        |
| Bornholms Spildevand A/S                                    | Rønne        | Denmark        |
| Ringkøbing-Skjern Forsyning A/S                             | Skjern       | Denmark        |
| RGS Nordic A/S                                              | Skælskør     | Denmark        |
| Svendborg Spildevand A/S,<br>Svenborg Centralrenseanlæg     | Skårup Fyn   | Denmark        |
| Eurofins Miljø A/S (2 participants)                         | Vejle        | Denmark        |
| Vejle Spildevand                                            | Vejle        | Denmark        |
| Arla Foods Nr. Vium (4 participants)                        | Videbæk      | Denmark        |
| Aalborg Renseanlæg Vest                                     | Ålborg       | Denmark        |
| Eurofins Umwelt West GmbH                                   | Wesseling    | Germany        |
| SGS Analytics Norway AS (Hamar)                             | Hamar        | Norway         |
| EUROFINS MECHEM PTE. LTD.                                   | Singapore    | Singapore      |
| Preemraff AB Göteborg                                       | Göteborg     | Sweden         |
| St1 Refinery AB                                             | Göteborg     | Sweden         |
| GRYAAB AB                                                   | Göteborg     | Sweden         |
| Hallsta Pappersbruk                                         | Hallstavik   | Sweden         |
| AB Lennart Månsson International                            | Helsingborg  | Sweden         |
| Kalmar Vatten AB, VA-lab                                    | Kalmar       | Sweden         |
| Kristianstad Kommun                                         | Kristianstad | Sweden         |
| Yara AB                                                     | Köping       | Sweden         |
| Käppalaverket                                               | Lidingö      | Sweden         |
| Preemraff Lysekil                                           | Lysekil      | Sweden         |
| Mjölby Kommun                                               | Mjölby       | Sweden         |
| Motala Kommun, Tekniska Förvaltningen,<br>Vatten och Avfall | Motala       | Sweden         |
| Fiskeby Board AB                                            | Norrköping   | Sweden         |
| Holmen Paper AB, Bravikens Pappersbruk                      | Norrköping   | Sweden         |
| Ernemar Laboratorium                                        | Oskarshamn   | Sweden         |

| <b>Laboratory</b>                                | <b>Town</b> | <b>Country</b> |
|--------------------------------------------------|-------------|----------------|
| Smurfit Kappa Piteå                              | Piteå       | Sweden         |
| Uppsala Vatten och Avfall AB, Vattenlaboratoriet | Uppsala     | Sweden         |
| Vallviks Bruk AB                                 | Vallvik     | Sweden         |
| Södra Cell AB, Värö                              | Väröbacka   | Sweden         |
| Västervik Miljö & Energi AB, Vattenlaboratoriet  | Västervik   | Sweden         |
| Roslagsvatten AB                                 | Åkersberga  | Sweden         |

## ANNEX B    SAMPLE PREPARATION

| Stock solution        | Prepared from                                                                  | Concentration                   |
|-----------------------|--------------------------------------------------------------------------------|---------------------------------|
| Stock TN              | 3.000 g Disodium edetate, 2H <sub>2</sub> O<br>milli-Q water up to 1000.0 g    | TN: 225.8 mg/kg N               |
| Stock NH <sub>4</sub> | 1.000 g Ammonium chloride (NH <sub>4</sub> Cl)<br>milli-Q water up to 1000.0 g | NH <sub>4</sub> : 261.9 mg/kg N |
| Stock NO <sub>3</sub> | 2.500 g Potassium nitrate (KNO <sub>3</sub> )<br>milli-Q water up to 1000.0 g  | NO <sub>3</sub> : 346.4 mg/kg N |

| Sample | Sample prepared from                                                                                                                                   | TN<br>mg/L N                       | NH <sub>4</sub><br>mg/L N          | NO <sub>3</sub><br>mg/L N         | γ <sub>25</sub><br>mS/m |
|--------|--------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------|------------------------------------|-----------------------------------|-------------------------|
| A1     | 20.00 g stock TN<br>35.00 g stock NH <sub>4</sub><br>20.00 g stock NO <sub>3</sub><br>Sample B1 up to 34.00 kg                                         | 0.997 ·<br>(a+1.39)<br>+<br>0.0664 | 0.997 ·<br>(b+0.605)<br>+<br>0.193 | 0.997 ·<br>(c+2.66)<br>+<br>0.611 | d                       |
| B1     | 70.0 g stock TN<br>50.0 g stock NH <sub>4</sub><br>100.0 g stock NO <sub>3</sub><br>filtered water from Brørup sewage<br>treatment plant up to 65.0 kg | a+1.39                             | b+0.605                            | c+2.66                            | e                       |

| Sample | Sample prepared from                                  | pH |
|--------|-------------------------------------------------------|----|
| A2/B2  | Filtered water from Brørup sewage<br>treatment plant. | f  |

## ANNEX C CONTROL OF SPIKE VALUES

Total Nitrogen, mg/L N

Control of differences within sample pairs

| Laboratory | Difference<br>AB |
|------------|------------------|
| 1          | -0.140           |
| 2          | 0.050            |
| 3          | -                |
| 4          | -0.100           |
| 5          | -0.010           |
| 6          | 0.090            |
| 7          | 0.000            |
| 8          | -0.120           |
| 9          | 0.010            |
| 10         | -0.030           |
| 11         | -0.130           |
| 12         | 0.060            |
| 13         | 0.460 UG         |
| 14         | -0.059           |
| 15         | -0.020           |
| 16         | -0.020           |
| 17         | -0.091           |
| 18         | -0.410           |
| 19         | 0.010            |
| 20         | 0.010            |
| 21         | -0.166           |
| 22         | -0.040           |
| 23         | -0.100           |
| 24         | -0.130           |
| 25         | 0.010            |
| 26         | 0.200            |
| 27A        | -0.090           |
| 27B        | -0.040           |
| 28         | 0.080            |
| 29         | 0.070            |
| 30         | 0.080            |
| 31         | 0.620 UC         |
| 32         | -0.140           |
| 33         | -0.030           |
| 34         | -                |
| 35         | -0.000           |
| 36         | 0.200            |
| 37         | 0.050            |
| 38         | 0.350            |
| 39         | 0.000            |
| 40         | -0.040           |
| 41         | 0.020            |
| 42         | -0.410           |
| 43         | -0.028           |
| 44         | -0.070           |
| 45         | -0.140           |
| 46         | 0.250            |
| 47         | 0.023            |
| 48         | 0.020            |
| 49         | -0.100           |
| 50         | -0.100           |
| 51         | -0.040           |

|                            |         |
|----------------------------|---------|
| No of labs., p             | 48      |
| No of repl., n             | 2       |
| d                          | -0.025  |
| s <sup>2</sup>             | 0.017   |
| s                          | 0.132   |
| $t = \sqrt{p} \cdot (d/s)$ | -1.3266 |
| Sign. level, p(t)          | 0.1911  |

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<br>AB |    |
|------------|------------------|----|
| 1          | 0.0060           |    |
| 2          | 0.0870           |    |
| 3          | -0.0020          |    |
| 4          | -0.0100          |    |
| 5          | -0.0800          |    |
| 6          | -0.0130          |    |
| 7          | -                |    |
| 8          | -0.0040          |    |
| 9          | -0.0000          |    |
| 10         | 0.0160           |    |
| 11         | 0.0240           |    |
| 12         | 0.0073           |    |
| 13         | -0.0100          |    |
| 14         | -0.0080          |    |
| 15         | 0.0600           |    |
| 16         | -0.0040          |    |
| 17         | -0.0240          |    |
| 18         | 0.0100           |    |
| 19         | 0.0120           |    |
| 20         | -                |    |
| 21         | -0.0380          | UG |
| 22         | -                |    |
| 23         | 0.0000           |    |
| 24         | 0.0180           |    |
| 25         | 0.0040           |    |
| 26         | -0.0140          |    |
| 27A        | -0.0100          |    |
| 27B        | -0.0310          |    |
| 28         | 0.0060           |    |
| 29         | -                |    |
| 30         | 0.0030           |    |
| 31         | -0.0170          |    |
| 32         | -0.0000          |    |
| 33         | 0.0100           |    |
| 34         | -                |    |
| 35         | 0.0000           |    |
| 36         | 0.0050           |    |
| 37         | 0.0120           |    |
| 38         | 0.0010           |    |
| 39         | -0.0200          |    |
| 40         | 0.0300           | UG |
| 41         | -0.0000          |    |
| 42         | 0.0010           |    |
| 43         | -0.0678          |    |
| 44         | 0.0000           |    |
| 45         | -                |    |
| 46         | -0.0140          |    |
| 47         | 0.0080           |    |
| 48         | 0.0070           |    |
| 49         | 0.0030           |    |
| 50         | 0.0000           |    |
| 51         | 0.0200           |    |

|                            |         |
|----------------------------|---------|
| No of labs., p             | 44      |
| No of repl., n             | 2       |
| d                          | -0.0002 |
| s <sup>2</sup>             | 0.0006  |
| s                          | 0.0254  |
| $t = \sqrt{p} \cdot (d/s)$ | -0.0505 |
| Sign. level, p(t)          | 0.9600  |

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

Nitrite+Nitrate, mg/L N

Control of differences within sample pairs

| Laboratory | Difference<br>AB |    |
|------------|------------------|----|
| 1          | -0.0100          |    |
| 2          | 0.6570           | UC |
| 3          | 0.0640           |    |
| 4          | -                | U  |
| 5          | -                |    |
| 6          | -                |    |
| 7          | -                |    |
| 8          | -                |    |
| 9          | -                |    |
| 10         | -0.0300          |    |
| 11         | 0.0900           |    |
| 12         | -0.0520          |    |
| 13         | -                |    |
| 14         | 0.0190           |    |
| 15         | -0.0300          |    |
| 16         | -                | U  |
| 17         | -                |    |
| 18         | -0.0400          |    |
| 19         | -                |    |
| 20         | -                |    |
| 21         | -0.0610          |    |
| 22         | -                |    |
| 23         | 0.0100           |    |
| 24         | 0.0200           |    |
| 25         | -                |    |
| 26         | -                |    |
| 27A        | 0.0900           |    |
| 27B        | -                |    |
| 28         | -                |    |
| 29         | -                |    |
| 30         | -                | U  |
| 31         | 0.0100           |    |
| 32         | 0.0300           |    |
| 33         | -                |    |
| 34         | -                |    |
| 35         | -                |    |
| 36         | -                | U  |
| 37         | -                |    |
| 38         | -                |    |
| 39         | -                |    |
| 40         | -                |    |
| 41         | -                |    |
| 42         | -                |    |
| 43         | -0.0575          |    |
| 44         | -                |    |
| 45         | -                |    |
| 46         | -                |    |
| 47         | -                |    |
| 48         | -                |    |
| 49         | -                | U  |
| 50         | -                |    |
| 51         | 0.0300           |    |

|                            |        |
|----------------------------|--------|
| No of labs., p             | 16     |
| No of repl., n             | 2      |
| d                          | 0.0052 |
| s <sup>2</sup>             | 0.0024 |
| s                          | 0.0489 |
| $t = \sqrt{p} \cdot (d/s)$ | 0.4218 |
| Sign. level, p(t)          | 0.6791 |

No test statistics were found to be significant

UC denotes a Cochran outlier

U denotes data excluded from the data file

Nitrate, mg/L N

Control of differences within sample pairs

| Laboratory | Difference<br>AB |    |
|------------|------------------|----|
| 1          | -                |    |
| 2          | 0.610            | UC |
| 3          | -                |    |
| 4          | -0.010           |    |
| 5          | -0.010           |    |
| 6          | -0.020           |    |
| 7          | -                |    |
| 8          | -0.040           |    |
| 9          | -0.040           |    |
| 10         | -                |    |
| 11         | -                |    |
| 12         | -0.054           |    |
| 13         | 0.010            |    |
| 14         | 0.019            |    |
| 15         | -                |    |
| 16         | -0.110           |    |
| 17         | -0.050           |    |
| 18         | -                |    |
| 19         | 0.000            |    |
| 20         | -                |    |
| 21         | -                |    |
| 22         | -                |    |
| 23         | 0.010            |    |
| 24         | 0.020            |    |
| 25         | 0.040            |    |
| 26         | -0.030           |    |
| 27A        | 0.010            |    |
| 27B        | 0.080            |    |
| 28         | -                |    |
| 29         | -                |    |
| 30         | -0.150           | UG |
| 31         | -                |    |
| 32         | -                |    |
| 33         | 0.210            |    |
| 34         | -                |    |
| 35         | -                |    |
| 36         | 0.000            |    |
| 37         | -0.010           |    |
| 38         | 0.020            |    |
| 39         | -0.030           |    |
| 40         | 0.200            |    |
| 41         | 0.010            |    |
| 42         | -0.020           |    |
| 43         | -                |    |
| 44         | 0.010            |    |
| 45         | -                |    |
| 46         | -0.010           |    |
| 47         | 0.040            |    |
| 48         | -0.050           |    |
| 49         | -0.030           |    |
| 50         | -                |    |
| 51         | -                |    |

|                            |        |
|----------------------------|--------|
| No of labs., p             | 30     |
| No of repl., n             | 2      |
| d                          | 0.006  |
| s <sup>2</sup>             | 0.004  |
| s                          | 0.065  |
| $t = \sqrt{p} \cdot (d/s)$ | 0.4653 |
| Sign. level, p(t)          | 0.6452 |

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<br>AB |    |
|------------|------------------|----|
| 1          | -1.00            |    |
| 2          | -6.00            | UG |
| 3          | -1.30            |    |
| 4          | -                |    |
| 5          | -                |    |
| 6          | -                |    |
| 7          | -                |    |
| 8          | -0.50            |    |
| 9          | -                |    |
| 10         | -1.90            |    |
| 11         | -1.40            |    |
| 12         | -                |    |
| 13         | -                | U  |
| 14         | 0.00             |    |
| 15         | 2.00             |    |
| 16         | -                | U  |
| 17         | -1.00            |    |
| 18         | -                |    |
| 19         | -0.70            |    |
| 20         | -                |    |
| 21         | -0.70            |    |
| 22         | -0.40            |    |
| 23         | -1.20            |    |
| 24         | -0.70            |    |
| 25         | 0.80             |    |
| 26         | -0.40            | UG |
| 27A        | -                | U  |
| 27B        | -                | U  |
| 28         | -                |    |
| 29         | -                |    |
| 30         | -                | U  |
| 31         | -                |    |
| 32         | -                |    |
| 33         | -                |    |
| 34         | -1.10            |    |
| 35         | -                |    |
| 36         | -                | U  |
| 37         | -                |    |
| 38         | -1.48            |    |
| 39         | -1.70            |    |
| 40         | 0.00             |    |
| 41         | -                |    |
| 42         | -                |    |
| 43         | -0.45            |    |
| 44         | 5.80             |    |
| 45         | -24.00           | UC |
| 46         | -                |    |
| 47         | -0.80            |    |
| 48         | -                |    |
| 49         | -                | U  |
| 50         | -                |    |
| 51         | -1.00            |    |

|                            |         |
|----------------------------|---------|
| No of labs., p             | 22      |
| No of repl., n             | 2       |
| d                          | -0.40   |
| s <sup>2</sup>             | 2.64    |
| s                          | 1.63    |
| $t = \sqrt{p} \cdot (d/s)$ | -1.1446 |
| Sign. level, p(t)          | 0.2653  |

No test statistics were found to be significant

UC denotes a Cochran outlier

UG denotes a Grubbs outlier

U denotes data excluded from the data file

pH,  
Control of differences within sample pairs

| Laboratory | Difference<br>AB |    |
|------------|------------------|----|
| 1          | 0.030            |    |
| 2          | 0.020            |    |
| 3          | 0.020            |    |
| 4          | 0.160            |    |
| 5          | -0.080           |    |
| 6          | 0.248            | UC |
| 7          | -                |    |
| 8          | 0.004            |    |
| 9          | -0.010           | UG |
| 10         | 0.000            |    |
| 11         | -0.090           |    |
| 12         | 0.010            |    |
| 13         | 0.100            |    |
| 14         | 0.010            |    |
| 15         | -0.010           |    |
| 16         | -0.060           |    |
| 17         | 0.000            |    |
| 18         | 0.020            |    |
| 19         | -0.050           |    |
| 20         | -0.020           |    |
| 21         | -0.010           |    |
| 22         | -0.030           |    |
| 23         | 0.050            |    |
| 24         | 0.020            |    |
| 25         | -0.070           |    |
| 26         | 0.112            |    |
| 27A        | 0.050            |    |
| 27B        | -                |    |
| 28         | -                |    |
| 29         | -0.020           |    |
| 30         | -0.040           |    |
| 31         | -0.060           | UG |
| 32         | -0.510           | UC |
| 33         | 0.100            |    |
| 34         | 0.003            |    |
| 35         | 0.120            |    |
| 36         | -0.100           |    |
| 37         | -0.040           |    |
| 38         | -0.030           |    |
| 39         | 0.014            |    |
| 40         | -0.060           |    |
| 41         | 0.020            |    |
| 42         | 0.010            |    |
| 43         | -0.001           |    |
| 44         | -0.040           |    |
| 45         | 0.090            |    |
| 46         | -0.010           |    |
| 47         | -0.050           |    |
| 48         | 0.040            |    |
| 49         | -0.050           |    |
| 50         | -0.080           |    |
| 51         | -0.010           |    |

|                            |        |
|----------------------------|--------|
| No of labs., p             | 45     |
| No of repl., n             | 2      |
| d                          | 0.001  |
| s <sup>2</sup>             | 0.003  |
| s                          | 0.058  |
| $t = \sqrt{p} \cdot (d/s)$ | 0.1333 |
| Sign. level, p(t)          | 0.8946 |

No test statistics were found to be significant  
UC denotes a Cochran outlier  
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          | 3.560          |    |
| 2          | 3.295          |    |
| 3          | -              |    |
| 4          | 3.260          |    |
| 5          | 3.455          |    |
| 6          | 3.275          |    |
| 7          | 3.080          |    |
| 8          | 3.560          |    |
| 9          | 3.585          |    |
| 10         | 3.825          |    |
| 11         | 3.475          |    |
| 12         | 3.679          |    |
| 13         | 4.820          | UG |
| 14         | 3.785          |    |
| 15         | 3.560          |    |
| 16         | 3.320          |    |
| 17         | 2.842          |    |
| 18         | 4.305          |    |
| 19         | 3.575          |    |
| 20         | 3.505          |    |
| 21         | 3.363          |    |
| 22         | 3.149          |    |
| 23         | 3.650          |    |
| 24         | 3.185          |    |
| 25         | 3.565          |    |
| 26         | 3.290          |    |
| 27A        | 3.055          |    |
| 27B        | 3.240          |    |
| 28         | 3.490          |    |
| 29         | 3.385          |    |
| 30         | 3.680          |    |
| 31         | 3.850          | UC |
| 32         | 3.500          |    |
| 33         | 3.575          |    |
| 34         | -              |    |
| 35         | 3.660          |    |
| 36         | 3.680          |    |
| 37         | 3.775          |    |
| 38         | 3.455          |    |
| 39         | 3.290          |    |
| 40         | 2.900          |    |
| 41         | 3.730          |    |
| 42         | 3.645          |    |
| 43         | 3.247          |    |
| 44         | 3.445          |    |
| 45         | 3.670          |    |
| 46         | 4.015          |    |
| 47         | 3.434          |    |
| 48         | 3.540          |    |
| 49         | 3.760          |    |
| 50         | 3.080          |    |
| 51         | 3.790          |    |

|                                    |         |
|------------------------------------|---------|
| No of labs., p                     | 48      |
| No of repl., n                     | 2       |
| m                                  | 3.483   |
| s <sup>2</sup>                     | 0.077   |
| s                                  | 0.277   |
| Assigned value, $\mu$              | 3.5     |
| Recovery, %                        | 99.5    |
| $t = \sqrt{p} \cdot (m - \mu) / s$ | -0.4248 |
| Sign. level, p(t)                  | 0.6729  |

No test statistics were found to be significant

UC denotes a Cochran outlier

UG denotes a Grubbs outlier

Ammonium, mg/L N

Control of recovery, average of results

| Laboratory | Sample pair<br>AB |
|------------|-------------------|
| 1          | 0.3100            |
| 2          | 0.4475            |
| 3          | 0.3120            |
| 4          | 0.2950            |
| 5          | 0.4500            |
| 6          | 0.2835            |
| 7          | -                 |
| 8          | 0.4060            |
| 9          | 0.3150            |
| 10         | 0.3120            |
| 11         | 0.2990            |
| 12         | 0.3047            |
| 13         | 0.3050            |
| 14         | 0.2960            |
| 15         | 0.4450            |
| 16         | 0.3160            |
| 17         | 0.3160            |
| 18         | 0.3150            |
| 19         | 0.3210            |
| 20         | -                 |
| 21         | 0.1000 UG         |
| 22         | -                 |
| 23         | 0.3500            |
| 24         | 0.3150            |
| 25         | 0.3130            |
| 26         | 0.2790            |
| 27A        | 0.2950            |
| 27B        | 0.2765            |
| 28         | 0.3170            |
| 29         | -                 |
| 30         | 0.3175            |
| 31         | 0.2815            |
| 32         | 0.3100            |
| 33         | 0.3350            |
| 34         | -                 |
| 35         | 0.3010            |
| 36         | 0.3105            |
| 37         | 0.3220            |
| 38         | 0.3285            |
| 39         | 0.2800            |
| 40         | 0.6250 UG         |
| 41         | 0.3110            |
| 42         | 0.3135            |
| 43         | 0.1850            |
| 44         | 0.2910            |
| 45         | -                 |
| 46         | 0.2720            |
| 47         | 0.3180            |
| 48         | 0.3155            |
| 49         | 0.3065            |
| 50         | 0.2900            |
| 51         | 0.3300            |

|                                    |        |
|------------------------------------|--------|
| No of labs., p                     | 44     |
| No of repl., n                     | 2      |
| m                                  | 0.3162 |
| s <sup>2</sup>                     | 0.0021 |
| s                                  | 0.0460 |
| Assigned value, $\mu$              | 0.312  |
| Recovery, %                        | 101.3  |
| $t = \sqrt{p} \cdot (m - \mu) / s$ | 0.6051 |
| Sign. level, p(t)                  | 0.5483 |

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

Nitrite+Nitrate, mg/L N

Control of recovery, average of results

| Laboratory | Sample pair<br>AB |    |
|------------|-------------------|----|
| 1          | 2.3350            |    |
| 2          | 9.6055            | UC |
| 3          | 2.3650            |    |
| 4          | -                 | U  |
| 5          | -                 |    |
| 6          | -                 |    |
| 7          | -                 |    |
| 8          | -                 |    |
| 9          | -                 |    |
| 10         | 2.2150            |    |
| 11         | 2.2130            |    |
| 12         | 2.4790            |    |
| 13         | -                 |    |
| 14         | 2.2835            |    |
| 15         | 2.3150            |    |
| 16         | -                 | U  |
| 17         | -                 |    |
| 18         | 2.3500            |    |
| 19         | -                 |    |
| 20         | -                 |    |
| 21         | 2.2795            |    |
| 22         | -                 |    |
| 23         | 2.2950            |    |
| 24         | 2.4000            |    |
| 25         | -                 |    |
| 26         | -                 |    |
| 27A        | 2.2350            |    |
| 27B        | -                 |    |
| 28         | -                 |    |
| 29         | -                 |    |
| 30         | -                 | U  |
| 31         | 2.1850            |    |
| 32         | 2.1350            |    |
| 33         | -                 |    |
| 34         | -                 |    |
| 35         | -                 |    |
| 36         | -                 | U  |
| 37         | -                 |    |
| 38         | -                 |    |
| 39         | -                 |    |
| 40         | -                 |    |
| 41         | -                 |    |
| 42         | -                 |    |
| 43         | 2.2893            |    |
| 44         | -                 |    |
| 45         | -                 |    |
| 46         | -                 |    |
| 47         | -                 |    |
| 48         | -                 |    |
| 49         | -                 | U  |
| 50         | -                 |    |
| 51         | 2.3650            |    |

|                                    |        |
|------------------------------------|--------|
| No of labs., p                     | 16     |
| No of repl., n                     | 2      |
| m                                  | 2.2962 |
| s <sup>2</sup>                     | 0.0076 |
| s                                  | 0.0874 |
| Assigned value, $\mu$              | 2.29   |
| Recovery, %                        | 100.3  |
| $t = \sqrt{p} \cdot (m - \mu) / s$ | 0.2840 |
| Sign. level, p(t)                  | 0.7803 |

No test statistics were found to be significant

UC denotes a Cochran outlier

U denotes data excluded from the data file

Nitrate, mg/L N

Control of recovery, average of results

| Laboratory | Sample pair<br>AB |    |
|------------|-------------------|----|
| 1          | -                 |    |
| 2          | 9.605             | UC |
| 3          | -                 |    |
| 4          | 2.355             |    |
| 5          | 2.365             |    |
| 6          | 2.390             |    |
| 7          | -                 |    |
| 8          | 2.520             |    |
| 9          | 2.300             |    |
| 10         | -                 |    |
| 11         | -                 |    |
| 12         | 2.472             |    |
| 13         | 2.385             |    |
| 14         | 2.284             |    |
| 15         | -                 |    |
| 16         | 1.945             |    |
| 17         | 2.265             |    |
| 18         | -                 |    |
| 19         | 2.290             |    |
| 20         | -                 |    |
| 21         | -                 |    |
| 22         | -                 |    |
| 23         | 2.295             |    |
| 24         | 2.400             |    |
| 25         | 2.480             |    |
| 26         | 2.255             |    |
| 27A        | 2.405             |    |
| 27B        | 2.340             |    |
| 28         | -                 |    |
| 29         | -                 |    |
| 30         | 1.705             | UG |
| 31         | -                 |    |
| 32         | -                 |    |
| 33         | 2.385             |    |
| 34         | -                 |    |
| 35         | -                 |    |
| 36         | 2.450             |    |
| 37         | 2.375             |    |
| 38         | 2.330             |    |
| 39         | 1.995             |    |
| 40         | 1.990             |    |
| 41         | 2.255             |    |
| 42         | 2.310             |    |
| 43         | -                 |    |
| 44         | 2.305             |    |
| 45         | -                 |    |
| 46         | 2.415             |    |
| 47         | 2.280             |    |
| 48         | 2.225             |    |
| 49         | 2.425             |    |
| 50         | -                 |    |
| 51         | -                 |    |

|                                    |         |
|------------------------------------|---------|
| No of labs., p                     | 30      |
| No of repl., n                     | 2       |
| m                                  | 2.316   |
| s <sup>2</sup>                     | 0.019   |
| s                                  | 0.136   |
| Assigned value, $\mu$              | 2.33    |
| Recovery, %                        | 99.4    |
| $t = \sqrt{p} \cdot (m - \mu) / s$ | -0.5547 |
| Sign. level, p(t)                  | 0.5834  |

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<br>AB |    |
|------------|-------------------|----|
| 1          | 176.50            |    |
| 2          | 1833.60           | UG |
| 3          | 185.25            |    |
| 4          | -                 |    |
| 5          | -                 |    |
| 6          | -                 |    |
| 7          | -                 |    |
| 8          | 192.65            |    |
| 9          | -                 |    |
| 10         | 184.15            |    |
| 11         | 179.60            |    |
| 12         | -                 |    |
| 13         | -                 | U  |
| 14         | 179.00            |    |
| 15         | 174.40            |    |
| 16         | -                 | U  |
| 17         | 180.50            |    |
| 18         | -                 |    |
| 19         | 177.05            |    |
| 20         | -                 |    |
| 21         | 184.65            |    |
| 22         | 182.90            |    |
| 23         | 183.60            |    |
| 24         | 176.65            |    |
| 25         | 180.70            |    |
| 26         | 159.80            | UG |
| 27A        | -                 | U  |
| 27B        | -                 | U  |
| 28         | -                 |    |
| 29         | -                 |    |
| 30         | -                 | U  |
| 31         | -                 |    |
| 32         | -                 |    |
| 33         | -                 |    |
| 34         | 172.45            |    |
| 35         | -                 |    |
| 36         | -                 | U  |
| 37         | -                 |    |
| 38         | 182.26            |    |
| 39         | 184.55            |    |
| 40         | 180.00            |    |
| 41         | -                 |    |
| 42         | -                 |    |
| 43         | 181.22            |    |
| 44         | 174.90            |    |
| 45         | 1692.00           | UC |
| 46         | -                 |    |
| 47         | 181.60            |    |
| 48         | -                 |    |
| 49         | -                 | U  |
| 50         | -                 |    |
| 51         | 175.40            |    |

|                                    |         |
|------------------------------------|---------|
| No of labs., p                     | 22      |
| No of repl., n                     | 2       |
| m                                  | 180.45  |
| s <sup>2</sup>                     | 21.08   |
| s                                  | 4.59    |
| Assigned value, μ                  | 181     |
| Recovery, %                        | 99.7    |
| $t = \sqrt{p} \cdot (m - \mu) / s$ | -0.5579 |
| Sign. level, p(t)                  | 0.5828  |

No test statistics were found to be significant

UC denotes a Cochran outlier

UG denotes a Grubbs outlier

U denotes data excluded from the data file

pH,  
Control of recovery, average of results

| Laboratory | Sample pair<br>AB |    |
|------------|-------------------|----|
| 1          | 7.525             |    |
| 2          | 7.570             |    |
| 3          | 7.560             |    |
| 4          | 7.750             |    |
| 5          | 7.340             |    |
| 6          | 7.449             | UC |
| 7          | -                 |    |
| 8          | 7.697             |    |
| 9          | 7.085             | UG |
| 10         | 7.680             |    |
| 11         | 7.615             |    |
| 12         | 7.575             |    |
| 13         | 7.950             |    |
| 14         | 7.615             |    |
| 15         | 7.475             |    |
| 16         | 7.530             |    |
| 17         | 7.530             |    |
| 18         | 7.400             |    |
| 19         | 7.355             |    |
| 20         | 7.870             |    |
| 21         | 7.395             |    |
| 22         | 7.625             |    |
| 23         | 7.555             |    |
| 24         | 7.600             |    |
| 25         | 7.505             |    |
| 26         | 7.369             |    |
| 27A        | 7.685             |    |
| 27B        | -                 |    |
| 28         | -                 |    |
| 29         | 7.540             |    |
| 30         | 7.590             |    |
| 31         | 6.960             | UG |
| 32         | 8.205             | UC |
| 33         | 7.450             |    |
| 34         | 7.542             |    |
| 35         | 7.640             |    |
| 36         | 7.540             |    |
| 37         | 7.600             |    |
| 38         | 7.705             |    |
| 39         | 7.631             |    |
| 40         | 7.430             |    |
| 41         | 7.110             |    |
| 42         | 7.615             |    |
| 43         | 7.704             |    |
| 44         | 7.660             |    |
| 45         | 7.695             |    |
| 46         | 7.645             |    |
| 47         | 7.585             |    |
| 48         | 7.610             |    |
| 49         | 7.665             |    |
| 50         | 7.660             |    |
| 51         | 7.535             |    |

|                                    |         |
|------------------------------------|---------|
| No of labs., p                     | 45      |
| No of repl., n                     | 2       |
| m                                  | 7.576   |
| s <sup>2</sup>                     | 0.020   |
| s                                  | 0.141   |
| Assigned value, $\mu$              | 7.59    |
| Recovery, %                        | 99.8    |
| $t = \sqrt{p} \cdot (m - \mu) / s$ | -0.6627 |
| Sign. level, p(t)                  | 0.5110  |

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

## ANNEX E CONCENTRATION LEVEL

| Parameter      | Unit   | Sample | Bottle no. | I    | II   | Bottle<br>Average | Sample<br>Average | Assigned<br>value | Spike    |          |
|----------------|--------|--------|------------|------|------|-------------------|-------------------|-------------------|----------|----------|
|                |        |        |            |      |      |                   |                   |                   | Measured | Assigned |
| Total nitrogen | mg/L N | A1     | 26         | 3.96 | 3.98 | 3.97              | 4.00              | 4.1               | 0.49     | 0.58     |
|                |        |        | 48         | 4.01 | 4.02 | 4.02              |                   |                   |          |          |
|                |        |        | 65         | 4.01 | 4.01 | 4.01              |                   |                   |          |          |
|                |        | B1     | 16         | 3.45 | 3.48 | 3.47              | 3.51              | 3.5               |          |          |
|                |        |        | 23         | 3.49 | 3.49 | 3.49              |                   |                   |          |          |
|                |        |        | 56         | 3.57 | 3.57 | 3.57              |                   |                   |          |          |
| Ammonium       | mg/L N | A1     | 26         | 0.59 | 0.59 | 0.59              | 0.59              | 0.572             | 0.264    | 0.260    |
|                |        |        | 48         | 0.58 | 0.58 | 0.58              |                   |                   |          |          |
|                |        |        | 65         | 0.58 | 0.59 | 0.59              |                   |                   |          |          |
|                |        | B1     | 16         | 0.32 | 0.32 | 0.32              | 0.32              | 0.312             |          |          |
|                |        |        | 23         | 0.32 | 0.32 | 0.32              |                   |                   |          |          |
|                |        |        | 56         | 0.32 | 0.32 | 0.32              |                   |                   |          |          |
| Nitrate        | mg/L N | A1     | 26         | 2.67 | 2.65 | 2.66              | 2.64              | 2.52              | 0.19     | 0.21     |
|                |        |        | 48         | 2.65 | 2.65 | 2.65              |                   |                   |          |          |
|                |        |        | 65         | 2.59 | 2.62 | 2.61              |                   |                   |          |          |
|                |        | B1     | 16         | 2.46 | 2.48 | 2.47              | 2.45              | 2.33              |          |          |
|                |        |        | 23         | 2.44 | 2.44 | 2.44              |                   |                   |          |          |
|                |        |        | 56         | 2.45 | 2.45 | 2.45              |                   |                   |          |          |
| pH             |        | A2     | 11         | 7.63 | 7.63 | 7.63              | 7.63              | 7.58              | -0.01    | -0.01    |
|                |        |        | 32         | 7.63 | 7.63 | 7.63              |                   |                   |          |          |
|                |        |        | 46         | 7.63 | 7.63 | 7.63              |                   |                   |          |          |
|                |        | B2     | 11         | 7.62 | 7.62 | 7.62              | 7.62              | 7.59              |          |          |
|                |        |        | 31         | 7.62 | 7.62 | 7.62              |                   |                   |          |          |
|                |        |        | 63         | 7.62 | 7.62 | 7.62              |                   |                   |          |          |

## ANNEX F HOMOGENEITY AND STABILITY

|                |
|----------------|
| PT: SPIL-4     |
| Parameter: NH4 |
| Unit: mg/L N   |
| Sigma: 0.036   |

Responsible for tests: HBP/S7MS

### Homogeneity test

Date: 2021-11-02

| Sample | x(a)  | x(b)  | average | sd    | sd^2  |
|--------|-------|-------|---------|-------|-------|
| A1-2   | 0.587 | 0.589 | 0.59    | 0.001 | 0.000 |
| A1-9   | 0.595 | 0.597 | 0.60    | 0.001 | 0.000 |
| A1-17  | 0.587 | 0.587 | 0.59    | 0.000 | 0.000 |
| A1-23  | 0.589 | 0.590 | 0.59    | 0.001 | 0.000 |
| A1-34  | 0.593 | 0.594 | 0.59    | 0.001 | 0.000 |
| A1-37  | 0.593 | 0.594 | 0.59    | 0.001 | 0.000 |
| A1-43  | 0.593 | 0.591 | 0.59    | 0.001 | 0.000 |
| A1-49  | 0.587 | 0.587 | 0.59    | 0.000 | 0.000 |
| A1-55  | 0.596 | 0.598 | 0.60    | 0.001 | 0.000 |
| A1-63  | 0.591 | 0.592 | 0.59    | 0.001 | 0.000 |
| A1-73  | 0.595 | 0.595 | 0.60    | 0.000 | 0.000 |
| A1-77  | 0.593 | 0.593 | 0.59    | 0.000 | 0.000 |

### For homogeneity

|                                         |       |
|-----------------------------------------|-------|
| General average (x)                     | 0.59  |
| Sample average sd (s <sub>x</sub> )     | 0.003 |
| Within-sample sd (s <sub>w</sub> ):     | 0.001 |
| Between-samples sd (ss):                | 0.003 |
| S <sub>L</sub> in the Proficiency Test: | 0.044 |
| S <sub>R</sub> in the Proficiency Test: | 0.048 |

### Stability test

Date: 2021-11-18

| Sample | x(a)  | x(b)  |
|--------|-------|-------|
| A1     | 0.587 | 0.588 |
| A1     | 0.582 | 0.583 |
| A1     | 0.584 | 0.586 |
|        |       |       |

### For stability

|                      |          |
|----------------------|----------|
| General average (y): | 0.585    |
| /x-y/ =              | 0.006917 |

### Conclusions

|                                |                                              |
|--------------------------------|----------------------------------------------|
| ss = 0.00      0.3*sigma= 0.01 |                                              |
| /x-y/ = 0.006917               |                                              |
| <b>Analytical quality</b>      | Is s <sub>w</sub> < 0,15*sigma<br><b>YES</b> |
| <b>Homogeneity:</b>            | Is ss < 0.3*sigma?<br><b>YES</b>             |
| <b>Stability:</b>              | /x-y/ < 0.3*sigma?<br><b>YES</b>             |

|                   |        |
|-------------------|--------|
| <b>PT:</b>        | SPIL-4 |
| <b>Parameter:</b> | Nitrat |
| <b>Unit:</b>      | mg/L N |
| <b>Sigma:</b>     | 0.141  |

**Responsible for tests:** HBP/S7MS

#### Homogeneity test

Date: 2021-11-02

| Sample | x(a) | x(b) | average | sd    | sd^2  |
|--------|------|------|---------|-------|-------|
| A1-2   | 2.60 | 2.62 | 2.6     | 0.014 | 0.000 |
| A1-9   | 2.59 | 2.59 | 2.6     | 0.000 | 0.00  |
| A1-18  | 2.59 | 2.59 | 2.6     | 0.000 | 0.000 |
| A1-23  | 2.63 | 2.64 | 2.6     | 0.007 | 0.000 |
| A1-34  | 2.61 | 2.62 | 2.6     | 0.007 | 0.000 |
| A1-37  | 2.62 | 2.64 | 2.6     | 0.014 | 0.000 |
| A1-43  | 2.58 | 2.59 | 2.6     | 0.007 | 0.000 |
| A1-49  | 2.59 | 2.61 | 2.6     | 0.014 | 0.000 |
| A1-55  | 2.62 | 2.62 | 2.6     | 0.000 | 0.000 |
| A1-63  | 2.66 | 2.66 | 2.7     | 0.000 | 0.000 |
| A1-73  | 2.65 | 2.63 | 2.6     | 0.014 | 0.000 |
| A1-77  | 2.66 | 2.66 | 2.7     | 0.000 | 0.000 |

#### For homogeneity

|                                         |        |
|-----------------------------------------|--------|
| General average (x)                     | 2.620  |
| Sample average sd (s <sub>x</sub> )     | 0.026  |
| Within-sample sd (s <sub>w</sub> ):     | 0.009  |
| Between-samples sd (ss):                | 0.0253 |
| S <sub>L</sub> in the Proficiency Test: | 0.133  |
| S <sub>R</sub> in the Proficiency Test: | 0.140  |

#### Stability test

Date: 2021-11-18

| Sample | x(a)  | x(b)  |
|--------|-------|-------|
| A1     | 2.670 | 2.650 |
| A1     | 2.650 | 2.650 |
| A1     | 2.590 | 2.620 |
|        |       |       |

#### For stability

|                      |          |
|----------------------|----------|
| General average (y): | 2.638333 |
| /x-y/ =              | 0.01875  |

#### Conclusions

|                                 |                                              |
|---------------------------------|----------------------------------------------|
| ss = 0.025      0.3*sigma= 0.04 |                                              |
| /x-y/ = 0.01875                 |                                              |
| <b>Analytical quality</b>       | Is s <sub>w</sub> < 0,15*sigma<br><b>YES</b> |
| <b>Homogeneity:</b>             | Is ss < 0.3*sigma?<br><b>YES</b>             |
| <b>Stability:</b>               | /x-y/ < 0.3*sigma?<br><b>YES</b>             |

|               |
|---------------|
| PT: SPIL-4    |
| Parameter: pH |
| Unit:         |
| Sigma: 0.072  |

Responsible for tests: HBP/S7MS

**Homogeneity test**

Date: 2021-11-02

| Sample | x(a)  | x(b)  | average | sd    | sd^2  |
|--------|-------|-------|---------|-------|-------|
| B2-1   | 7.514 | 7.513 | 7.5     | 0.001 | 0.000 |
| B2-13  | 7.510 | 7.509 | 7.5     | 0.001 | 0.000 |
| B2-17  | 7.506 | 7.508 | 7.5     | 0.001 | 0.000 |
| B2-23  | 7.514 | 7.517 | 7.5     | 0.002 | 0.000 |
| B2-33  | 7.507 | 7.519 | 7.5     | 0.008 | 0.000 |
| B2-36  | 7.506 | 7.511 | 7.5     | 0.004 | 0.000 |
| B2-42  | 7.510 | 7.513 | 7.5     | 0.002 | 0.000 |
| B2-46  | 7.507 | 7.515 | 7.5     | 0.006 | 0.000 |
| B2-52  | 7.505 | 7.504 | 7.5     | 0.001 | 0.000 |
| B2-54  | 7.509 | 7.525 | 7.5     | 0.011 | 0.000 |
| B2-69  | 7.513 | 7.516 | 7.5     | 0.002 | 0.000 |
| B2-74  | 7.516 | 7.514 | 7.5     | 0.001 | 0.000 |

**For homogeneity**

|                                         |        |
|-----------------------------------------|--------|
| General average (x)                     | 7.51   |
| Sample average sd (s <sub>x</sub> )     | 0.004  |
| Within-sample sd (s <sub>w</sub> ):     | 0.005  |
| Between-samples sd (ss):                | 0.0018 |
| S <sub>L</sub> in the Proficiency Test: | 0.138  |
| S <sub>R</sub> in the Proficiency Test: | 0.144  |

**Conclusions**

|                                 |                                              |
|---------------------------------|----------------------------------------------|
| ss = 0.002      0.3*sigma= 0.02 |                                              |
| /x-y/ = 0.107458                |                                              |
| <b>Analytical quality</b>       | Is s <sub>w</sub> < 0,15*sigma<br><b>YES</b> |
| <b>Homogeneity:</b>             | Is ss < 0.3*sigma?<br><b>YES</b>             |