



## **Proficiency test SPIL-2 (2026)**

**Nitrogen parameters in wastewater  
(synthetic wastewater, effluent)**

**Quality Documentation  
July 2026**

# Proficiency test SPIL-2 (2026) Quality Documentation

July 2026

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|                                                                                                                                                          |                              |                                          |          |            |  |
|----------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------|------------------------------------------|----------|------------|--|
| Project                                                                                                                                                  |                              | Project No                               |          |            |  |
| Proficiency test SPIL-2 (2026)                                                                                                                           |                              | 20405-62                                 |          |            |  |
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|                                                                                                                                                          |                              | 2026-07-16                               |          |            |  |
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|                                                                                                                                                          |                              |                                          |          |            |  |
|                                                                                                                                                          |                              |                                          |          |            |  |
|                                                                                                                                                          | Quality Documentation Report | HT5M                                     | FYE3     | 2026-07-16 |  |
| 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: Anette Ørnskov Rønsch, Rikke Mikkelsen                       |

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## **1 INTRODUCTION**

A proficiency test on the analysis of nitrogen parameters in wastewater was conducted on 30 April, 2026. 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 2 June, 2026.

## 2 FEATURES OF THE PROFICIENCY TEST

Participants in the proficiency test were a total of 27 laboratories from Denmark, Spain and Sweden.

The closing date for submission of results was 18 May, 2026. All participants had submitted their results before the deadline.

### 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 synthetic wastewater, effluent. Sample preparation is described in Appendix A.

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> , γ <sub>25</sub> |
| 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/, ISO 13528:2022 /3/ and as described in detail in Spliid (1992) /4/. 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 /5/.

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

### 2.3 Assigned and spike value

An overview of the concentrations in the samples (the assigned values) and the difference in concentration between the two samples of a sample pair (spike value) are shown in Table 2 compared to the range of concentrations normally encountered in synthetic wastewater, effluent. The table also gives the expanded uncertainty of the assigned values. Assigned values, spike values and uncertainty of the assigned values were calculated in accordance with ISO 13528:2022 /3/. The Uncertainty of the assigned values are the expanded uncertainty with coverage factor,  $k = 2$ .

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        | 6.0            | 0.07                          | 1.3         |
| Ammonium        | NH <sub>4</sub>   | mg/L N | 0.1 – 2       | 1.01           | 0.012                         | 0.23        |
| Nitrite+nitrate | NO <sub>2+3</sub> | mg/L N | 1 – 5         | 2.7            | 0.031                         | 0.7         |
| Nitrate         | NO <sub>3</sub>   | mg/l N | 1 – 5         | 2.66           | 0.031                         | 0.65        |
| Conductivity    | γ <sub>25</sub>   | mS/m   | 50 – 300      | 121            | 2.2                           | 23          |
| pH              |                   |        | 6 - 9         | 7.47           | 0.015                         | 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.

The content of each parameter in each sample is given an assigned value for the sample with the lower content and a spike value, the spike value being the difference in concentration between the two samples of the sample pair. The assigned and spike values are both calculated from sample preparation except for conductivity and pH where the assigned value is a consensus value for all laboratories based on the median and the spike value for the two samples in the sample pair.

### 2.3.2 Test of spike values

A comparison was made (t-test, 95% confidence level) between the spike value and the difference in concentration between the two samples in the sample pair found from the laboratories' results, see Appendix B. 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 C. The test showed no significant difference between the two for NH<sub>4</sub>, NO<sub>2+3</sub>, NO<sub>3</sub>, γ<sub>25</sub> and pH and the control of assigned value at Eurofins confirmed the value (Appendix D).

The test revealed a significant difference between the two for TN. Average recovery was 95.7%. However, the results of control measurements at Eurofins confirmed the assigned value (Appendix D), and scrutiny of documentation from the sample preparation showed no indications of mistakes in sample preparation. Furthermore, recovery was close to 100%. The assigned value is therefore kept unchanged.

### 3 **HOMOGENEITY AND STABILITY OF SAMPLES**

The homogeneity and stability of samples 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              | Combined homogeneity and stability test |

The results of control measurements are shown in Appendix E. 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  $0.3 \cdot \hat{\sigma}$  specified by the Danish EPA /6/, whereas the stability is evaluated by comparing the concentration change of the samples to  $0.3 \cdot \hat{\sigma}$  or  $0.3 \cdot \hat{\sigma} + 2\sqrt{u_x^2 + u_y^2}$  where the precision of the measurement method contribute to the inability to meet the criterion. This test ensures that heterogeneity and instability will not have negative influence on the evaluation of participant performance /3/.

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 TN the participants did not recover the assigned value. Eurofins' scrutiny of the combined evidence gave the conclusion that the assigned value is correct. The assigned value is therefore kept unchanged and it is recommended as the basis for evaluation of participating laboratories.

## 5 REFERENCES

- /1/ Eurofins A/S, *Proficiency test SPIL-2 (2026)*, Report to participants, June 2026.
- /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/ ISO 13528, *Statistical methods for use in proficiency testing by interlaboratory comparison*, 2022.
- /4/ Spliid, H., *Procedure and analysis of data for proficiency tests and environmental analyses*, Report to Danish Environmental Protection Agency, 1994 (in Danish).
- /5/ Eurofins A/S, *Schedule for a proficiency test*, document may be downloaded from [www.eurofins.dk/proficiencytest](http://www.eurofins.dk/proficiencytest)
- /6/ Ministry of Environment and Gender Equality regulation no. 1275 on quality criteria for environmental measurements, 31/10-2025 (in Danish).

## ***A N N E X E S***

## APPENDIX A      SAMPLE PREPARATION

| Stock solution        | Prepared from                                                                  | Concentration                   |
|-----------------------|--------------------------------------------------------------------------------|---------------------------------|
| Stock TN              | 25.050 g Disodium edetate, 2H <sub>2</sub> O<br>milli-Q water up to 1000.0 g   | TN: 1886 mg/kg N                |
| Stock NH <sub>4</sub> | 1.010 g Ammonium chloride (NH <sub>4</sub> Cl)<br>milli-Q water up to 1000.0 g | NH <sub>4</sub> : 262.2 mg/kg N |
| Stock NO <sub>3</sub> | 2.500g Potassium nitrate (KNO <sub>3</sub> )<br>milli-Q water up to 1000.0 g   | NO <sub>3</sub> : 346 mg/kg N   |
| Stock NaCl            | 50.06 g Sodium chloride (NaCl)<br>milli-Q water up to 1000.0 g                 | conductivity: c. 10692 mS/m     |

| 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 | Conductivity<br>mS/m       |
|--------|-----------------------------------------------------------------------------------------------------------------------------------------|--------------------------|---------------------------|---------------------------|----------------------------|
| A1     | 80.01 g stock TN<br>25.01 g stock NH <sub>4</sub><br>500.0 g stock NO <sub>3</sub><br>750.6 g stock NaCl<br>Milli-Q water up to 65.0 kg | 5.99                     | 1.01                      | 2.66                      | 123.5                      |
| B1     | 8.02 g stock TN<br>3.01 g stock NH <sub>4</sub><br>65.0 g stock NO <sub>3</sub><br>80.01 g stock NaCl<br>Sample A1 up to 34,0 kg        | 0.995 ·<br>5.99<br>+1.34 | 0.995 ·<br>1.01<br>+0.23  | 0.995 ·<br>2.66<br>+0.66  | 0.995 ·<br>123.5<br>+25.16 |

| Sample | Sample prepared from                                                                                                                                                                                                     | pH      |
|--------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------|
| A2/B2  | 17.0 g Potassium dihydrogen phosphate (KH <sub>2</sub> PO <sub>4</sub> )<br>89.04 g Disodium hydrogen phosphate, 2H <sub>2</sub> O (Na <sub>2</sub> HPO <sub>4</sub> , 2H <sub>2</sub> O)<br>milli-Q water up to 12500 g | ca. 7.4 |

## APPENDIX B CONTROL OF SPIKE VALUES

### Total Nitrogen (TN), mg/L N

Control of differences within sample pairs

| Laboratory | Sample pair AB | Outlier |
|------------|----------------|---------|
| 1          | 0.04           |         |
| 2          | 0.10           |         |
| 3          | 0.20           |         |
| 4          | -5.52          | C       |
| 5          | 0.33           |         |
| 6          | -0.12          |         |
| 7          | 0.12           |         |
| 8          | -0.09          |         |
| 9          | -0.05          |         |
| 10         | 0.06           |         |
| 11         | 0.02           |         |
| 12         | 0.11           |         |
| 13         | -0.33          | G       |

| Laboratory | Sample pair AB | Outlier |
|------------|----------------|---------|
| 14         | 0.07           |         |
| 15         | 0.12           |         |
| 16         | 2.43           | C       |
| 17         | 0.02           |         |
| 18         | -0.55          |         |
| 19         | -0.90          | G       |
| 20         | 0.75           |         |
| 22         | 0.30           |         |
| 23         | 0.11           |         |
| 24         | 0.22           |         |
| 26         | -0.08          |         |
| 27         | 0.09           |         |
|            |                |         |

| Statistical data – Control of spike value |        |                                                                                                                                                                            |
|-------------------------------------------|--------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| No of labs                                | 21     | <b>Notes</b><br><br>No test statistics were found to be significant<br><br>U denote a manual selected outlier<br>C denotes a Cochran outlier<br>G denotes a Grubbs outlier |
| No of repl                                | 2      |                                                                                                                                                                            |
| d                                         | 0.0845 |                                                                                                                                                                            |
| s <sup>2</sup>                            | 0.0558 |                                                                                                                                                                            |
| s                                         | 0.2363 |                                                                                                                                                                            |
| t                                         | 1.6383 |                                                                                                                                                                            |
| Sign. level 99.9%                         | 3.8495 |                                                                                                                                                                            |
| Sign. level 99%                           | 2.8453 |                                                                                                                                                                            |
| Sign. level 95%                           | 2.0860 |                                                                                                                                                                            |

## Ammonium (NH<sub>4</sub>), mg/L N

Control of differences within sample pairs

| Laboratory | Sample pair AB | Outlier |
|------------|----------------|---------|
| 1          | 0.037          |         |
| 4          | -0.020         |         |
| 5          | -0.010         |         |
| 6          | 0.030          |         |
| 7          | 0.006          |         |
| 8          | 0.040          |         |
| 9          | -0.011         |         |
| 10         | 0.010          |         |
| 11         | 0.004          |         |
| 12         | 0.002          |         |

| Laboratory | Sample pair AB | Outlier |
|------------|----------------|---------|
| 13         | -0.060         |         |
| 14         | -0.010         |         |
| 15         | 0.030          |         |
| 16         | 0.010          |         |
| 17         | 0.033          |         |
| 18         | -0.040         |         |
| 19         | -0.250         | C       |
| 20         | 0.025          |         |
| 21         | -0.074         |         |
| 27         | -0.010         |         |

| Statistical data – Control of spike value |         |                                                                                                                                                                            |
|-------------------------------------------|---------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| No of labs                                | 19      | <b>Notes</b><br><br>No test statistics were found to be significant<br><br>U denote a manual selected outlier<br>C denotes a Cochran outlier<br>G denotes a Grubbs outlier |
| No of repl                                | 2       |                                                                                                                                                                            |
| d                                         | -0.0004 |                                                                                                                                                                            |
| s <sup>2</sup>                            | 0.0010  |                                                                                                                                                                            |
| s                                         | 0.0318  |                                                                                                                                                                            |
| t                                         | -0.0556 |                                                                                                                                                                            |
| Sign. level 99.9%                         | 3.9216  |                                                                                                                                                                            |
| Sign. level 99%                           | 2.8784  |                                                                                                                                                                            |
| Sign. level 95%                           | 2.1009  |                                                                                                                                                                            |

### **Nitrite+nitrate ( $NO_{2+3}$ ), mg/L N**

Control of differences within sample pairs

| Laboratory | Sample pair<br>AB | Outlier |
|------------|-------------------|---------|
| 9          | 0.10              |         |
| 10         | 0.21              |         |
| 13         | 0.03              |         |
| 21         | -0.03             |         |
| 26         | 0.02              |         |

| Statistical data – Control of spike value |        |                                                                                                                                                                            |
|-------------------------------------------|--------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| No of labs                                | 5      | <b>Notes</b><br><br>No test statistics were found to be significant<br><br>U denote a manual selected outlier<br>C denotes a Cochran outlier<br>G denotes a Grubbs outlier |
| No of repl                                | 2      |                                                                                                                                                                            |
| d                                         | 0.0672 |                                                                                                                                                                            |
| s <sup>2</sup>                            | 0.0086 |                                                                                                                                                                            |
| s                                         | 0.0928 |                                                                                                                                                                            |
| t                                         | 1.6198 |                                                                                                                                                                            |
| Sign. level 99.9%                         | 8.6103 |                                                                                                                                                                            |
| Sign. level 99%                           | 4.6041 |                                                                                                                                                                            |
| Sign. level 95%                           | 2.7764 |                                                                                                                                                                            |

## Nitrate (NO<sub>3</sub>), mg/L N

Control of differences within sample pairs

| Laboratory | Sample pair AB | Outlier |
|------------|----------------|---------|
| 1          | -0.055         |         |
| 4          | -0.040         |         |
| 5          | 0.040          |         |
| 6          | 0.030          |         |
| 7          | 0.040          |         |
| 8          | 0.190          |         |
| 10         | 0.160          |         |
| 11         | -0.020         |         |

| Laboratory | Sample pair AB | Outlier |
|------------|----------------|---------|
| 15         | -0.270         | G       |
| 16         | 0.125          |         |
| 17         | -0.010         |         |
| 18         | 0.030          |         |
| 19         | -0.590         | C       |
| 20         | 0.030          |         |
| 27         | 0.050          |         |
|            |                |         |

| Statistical data – Control of spike value |        |                                                                                                                                                                            |
|-------------------------------------------|--------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| No of labs                                | 13     | <b>Notes</b><br><br>No test statistics were found to be significant<br><br>U denote a manual selected outlier<br>C denotes a Cochran outlier<br>G denotes a Grubbs outlier |
| No of repl                                | 2      |                                                                                                                                                                            |
| d                                         | 0.0438 |                                                                                                                                                                            |
| s <sup>2</sup>                            | 0.0055 |                                                                                                                                                                            |
| s                                         | 0.0741 |                                                                                                                                                                            |
| t                                         | 2.1340 |                                                                                                                                                                            |
| Sign. level 99.9%                         | 4.3178 |                                                                                                                                                                            |
| Sign. level 99%                           | 3.0545 |                                                                                                                                                                            |
| Sign. level 95%                           | 2.1788 |                                                                                                                                                                            |

## Conductivity ( $\gamma_{25}$ ), mS/m

Control of differences within sample pairs

| Laboratory | Sample pair AB | Outlier |
|------------|----------------|---------|
| 1          | -              | U       |
| 3          | -0.7           |         |
| 5          | -2.1           |         |
| 8          | 0.2            |         |
| 9          | -1.0           |         |
| 11         | 1.2            |         |
| 13         | -0.3           |         |
| 15         | 24.7           | C       |

| Laboratory | Sample pair AB | Outlier |
|------------|----------------|---------|
| 16         | -3.1           |         |
| 17         | 0.0            |         |
| 18         | 4.4            | G       |
| 20         | 1.0            | G       |
| 21         | 0.3            |         |
| 23         | -0.8           |         |
| 25         | -0.3           |         |
| 27         | 0.1            |         |

| Statistical data – Control of spike value |         |                                                                                                                                                                            |
|-------------------------------------------|---------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| No of labs                                | 12      | <b>Notes</b><br><br>No test statistics were found to be significant<br><br>U denote a manual selected outlier<br>C denotes a Cochran outlier<br>G denotes a Grubbs outlier |
| No of repl                                | 2       |                                                                                                                                                                            |
| d                                         | -0.5417 |                                                                                                                                                                            |
| s <sup>2</sup>                            | 1.3081  |                                                                                                                                                                            |
| s                                         | 1.1437  |                                                                                                                                                                            |
| t                                         | -1.6406 |                                                                                                                                                                            |
| Sign. level 99.9%                         | 4.4370  |                                                                                                                                                                            |
| Sign. level 99%                           | 3.1058  |                                                                                                                                                                            |
| Sign. level 95%                           | 2.2010  |                                                                                                                                                                            |

## pH

Control of differences within sample pairs

| Laboratory | Sample pair AB | Outlier |
|------------|----------------|---------|
| 1          | -0.020         |         |
| 2          | 0.000          |         |
| 3          | 0.020          |         |
| 4          | 0.000          |         |
| 5          | 0.000          |         |
| 6          | -0.010         |         |
| 7          | 0.010          |         |
| 8          | -0.003         |         |
| 9          | 0.000          |         |
| 10         | 0.010          |         |
| 11         | -0.010         |         |
| 12         | -0.003         |         |
| 13         | 0.000          |         |

| Laboratory | Sample pair AB | Outlier |
|------------|----------------|---------|
| 15         | 0.007          |         |
| 16         | 0.010          |         |
| 17         | 0.000          |         |
| 18         | 0.044          | C       |
| 19         | -0.010         |         |
| 20         | -0.020         |         |
| 21         | -0.070         | C       |
| 22         | 0.000          |         |
| 23         | 0.000          |         |
| 25         | 0.020          |         |
| 26         | 0.000          |         |
| 27         | 0.010          |         |
|            |                |         |

| Statistical data – Control of spike value |        |                                                                                                                                                                            |
|-------------------------------------------|--------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| No of labs                                | 23     | <b>Notes</b><br><br>No test statistics were found to be significant<br><br>U denote a manual selected outlier<br>C denotes a Cochran outlier<br>G denotes a Grubbs outlier |
| No of repl                                | 2      |                                                                                                                                                                            |
| d                                         | 0.0005 |                                                                                                                                                                            |
| s <sup>2</sup>                            | 0.0001 |                                                                                                                                                                            |
| s                                         | 0.0104 |                                                                                                                                                                            |
| t                                         | 0.2214 |                                                                                                                                                                            |
| Sign. level 99.9%                         | 3.7921 |                                                                                                                                                                            |
| Sign. level 99%                           | 2.8188 |                                                                                                                                                                            |
| Sign. level 95%                           | 2.0739 |                                                                                                                                                                            |

## APPENDIX C CONTROL OF RECOVERY

### Total nitrogen (TN), mg/L N

Control of recovery, average of results

| Laboratory | Sample pair AB | Outlier |
|------------|----------------|---------|
| 1          | 5.90           |         |
| 2          | 4.95           |         |
| 3          | 5.32           |         |
| 4          | 8.84           | C       |
| 5          | 5.12           |         |
| 6          | 6.25           |         |
| 7          | 5.91           |         |
| 8          | 5.70           |         |
| 9          | 5.98           |         |
| 10         | 6.02           |         |
| 11         | 6.14           |         |
| 12         | 5.56           |         |
| 13         | 9.34           | G       |

| Laboratory | Sample pair AB | Outlier |
|------------|----------------|---------|
| 14         | 5.81           |         |
| 15         | 5.46           |         |
| 16         | 6.51           | C       |
| 17         | 6.21           |         |
| 18         | 6.66           |         |
| 19         | 13.45          | G       |
| 20         | 4.96           |         |
| 22         | 5.65           |         |
| 23         | 5.27           |         |
| 24         | 5.51           |         |
| 26         | 6.50           |         |
| 27         | 5.74           |         |
|            |                |         |

| Statistical data – Control of recovery |         |                                                                                                                                                                                                 |
|----------------------------------------|---------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| No of labs                             | 21      | <b>Notes</b><br><br>* denotes that there is a significant difference (t-test, 5 %-level)<br><br>U denote a manual selected outlier<br>C denotes a Cochran outlier<br>G denotes a Grubbs outlier |
| No of repl                             | 2       |                                                                                                                                                                                                 |
| m                                      | 5.7425  |                                                                                                                                                                                                 |
| s <sup>2</sup>                         | 0.2227  |                                                                                                                                                                                                 |
| s                                      | 0.4719  |                                                                                                                                                                                                 |
| Assigned value                         | 6.0     |                                                                                                                                                                                                 |
| Recovery                               | 95.7    |                                                                                                                                                                                                 |
| t                                      | -2.5006 |                                                                                                                                                                                                 |
| Sign. level 99.9%                      | 3.8495  |                                                                                                                                                                                                 |
| Sign. level 99%                        | 2.8453  |                                                                                                                                                                                                 |
| Sign. level 95%                        | 2.0860  |                                                                                                                                                                                                 |

## Ammonium (NH<sub>4</sub>), mg/L N

Control of recovery, average of results

| Laboratory | Sample pair AB | Outlier |
|------------|----------------|---------|
| 1          | 0.938          |         |
| 4          | 1.020          |         |
| 5          | 1.055          |         |
| 6          | 0.905          |         |
| 7          | 0.983          |         |
| 8          | 1.120          |         |
| 9          | 0.998          |         |
| 10         | 1.045          |         |
| 11         | 0.952          |         |
| 12         | 0.971          |         |

| Laboratory | Sample pair AB | Outlier |
|------------|----------------|---------|
| 13         | 1.110          |         |
| 14         | 1.025          |         |
| 15         | 0.955          |         |
| 16         | 1.050          |         |
| 17         | 0.976          |         |
| 18         | 0.960          |         |
| 19         | 2.125          | C       |
| 20         | 0.913          |         |
| 21         | 1.216          |         |
| 27         | 1.045          |         |

| Statistical data – Control of recovery |        |                                                                                                                                                                            |
|----------------------------------------|--------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| No of labs                             | 19     | <b>Notes</b><br><br>No test statistics were found to be significant<br><br>U denote a manual selected outlier<br>C denotes a Cochran outlier<br>G denotes a Grubbs outlier |
| No of repl                             | 2      |                                                                                                                                                                            |
| m                                      | 1.0125 |                                                                                                                                                                            |
| s <sup>2</sup>                         | 0.0061 |                                                                                                                                                                            |
| s                                      | 0.0778 |                                                                                                                                                                            |
| Assigned value                         | 1.01   |                                                                                                                                                                            |
| Recovery                               | 100.2  |                                                                                                                                                                            |
| t                                      | 0.1393 |                                                                                                                                                                            |
| Sign. level 99.9%                      | 3.9216 |                                                                                                                                                                            |
| Sign. level 99%                        | 2.8784 |                                                                                                                                                                            |
| Sign. level 95%                        | 2.1009 |                                                                                                                                                                            |

### **Nitrite+nitrate ( $\text{NO}_{2+3}$ ), mg/L N**

Control of recovery, average of results

| Laboratory | Sample pair<br>AB | Outlier |
|------------|-------------------|---------|
| 9          | 2.60              |         |
| 10         | 2.53              |         |
| 13         | 2.70              |         |
| 21         | 2.96              |         |
| 26         | 2.69              |         |

| Statistical data – Control of recovery |         |                                                                                                                                                                            |
|----------------------------------------|---------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| No of labs                             | 5       | <b>Notes</b><br><br>No test statistics were found to be significant<br><br>U denote a manual selected outlier<br>C denotes a Cochran outlier<br>G denotes a Grubbs outlier |
| No of repl                             | 2       |                                                                                                                                                                            |
| m                                      | 2.6957  |                                                                                                                                                                            |
| s <sup>2</sup>                         | 0.0274  |                                                                                                                                                                            |
| s                                      | 0.1656  |                                                                                                                                                                            |
| Assigned value                         | 2.7     |                                                                                                                                                                            |
| Recovery                               | 99.8    |                                                                                                                                                                            |
| t                                      | -0.0586 |                                                                                                                                                                            |
| Sign. level 99.9%                      | 8.6103  |                                                                                                                                                                            |
| Sign. level 99%                        | 4.6041  |                                                                                                                                                                            |
| Sign. level 95%                        | 2.7764  |                                                                                                                                                                            |

## Nitrate (NO<sub>3</sub>), mg/L N

Control of recovery, average of results

| Laboratory | Sample pair AB | Outlier |
|------------|----------------|---------|
| 1          | 2.742          |         |
| 4          | 2.530          |         |
| 5          | 2.590          |         |
| 6          | 2.565          |         |
| 7          | 2.550          |         |
| 8          | 2.655          |         |
| 10         | 2.550          |         |
| 11         | 2.880          |         |

| Laboratory | Sample pair AB | Outlier |
|------------|----------------|---------|
| 15         | 1.655          | G       |
| 16         | 2.558          |         |
| 17         | 2.805          |         |
| 18         | 3.075          |         |
| 19         | 5.495          | C       |
| 20         | 2.455          |         |
| 27         | 2.585          |         |
|            |                |         |

| Statistical data – Control of recovery |         |                                                                                                                                                                            |
|----------------------------------------|---------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| No of labs                             | 13      | <b>Notes</b><br><br>No test statistics were found to be significant<br><br>U denote a manual selected outlier<br>C denotes a Cochran outlier<br>G denotes a Grubbs outlier |
| No of repl                             | 2       |                                                                                                                                                                            |
| m                                      | 2.6569  |                                                                                                                                                                            |
| s <sup>2</sup>                         | 0.0301  |                                                                                                                                                                            |
| s                                      | 0.1736  |                                                                                                                                                                            |
| Assigned value                         | 2.66    |                                                                                                                                                                            |
| Recovery                               | 99.9    |                                                                                                                                                                            |
| t                                      | -0.0639 |                                                                                                                                                                            |
| Sign. level 99.9%                      | 4.3178  |                                                                                                                                                                            |
| Sign. level 99%                        | 3.0545  |                                                                                                                                                                            |
| Sign. level 95%                        | 2.1788  |                                                                                                                                                                            |

## Conductivity ( $\gamma_{25}$ ), mS/m

Control of recovery, average of results

| Laboratory | Sample pair AB | Outlier |
|------------|----------------|---------|
| 1          | -              | U       |
| 3          | 122.2          |         |
| 5          | 122.6          |         |
| 8          | 120.3          |         |
| 9          | 124.2          |         |
| 11         | 118.6          |         |
| 13         | 117.4          |         |
| 15         | 55.9           | C       |

| Laboratory | Sample pair AB | Outlier |
|------------|----------------|---------|
| 16         | 112.4          |         |
| 17         | 121.5          |         |
| 18         | 98.4           | G       |
| 20         | 107.5          | G       |
| 21         | 122.1          |         |
| 23         | 125.0          |         |
| 25         | 122.1          |         |
| 27         | 121.4          |         |

| Statistical data – Control of recovery |          |                                                                                                                                                                            |
|----------------------------------------|----------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| No of labs                             | 12       | <b>Notes</b><br><br>No test statistics were found to be significant<br><br>U denote a manual selected outlier<br>C denotes a Cochran outlier<br>G denotes a Grubbs outlier |
| No of repl                             | 2        |                                                                                                                                                                            |
| m                                      | 120.8042 |                                                                                                                                                                            |
| s <sup>2</sup>                         | 11.4616  |                                                                                                                                                                            |
| s                                      | 3.3855   |                                                                                                                                                                            |
| Assigned value                         | 121      |                                                                                                                                                                            |
| Recovery                               | 99.8     |                                                                                                                                                                            |
| t                                      | -0.2004  |                                                                                                                                                                            |
| Sign. level 99.9%                      | 4.4370   |                                                                                                                                                                            |
| Sign. level 99%                        | 3.1058   |                                                                                                                                                                            |
| Sign. level 95%                        | 2.2010   |                                                                                                                                                                            |

## pH

Control of recovery, average of results

| Laboratory | Sample pair AB | Outlier |
|------------|----------------|---------|
| 1          | 7.490          |         |
| 2          | 7.480          |         |
| 3          | 7.390          |         |
| 4          | 7.520          |         |
| 5          | 7.440          |         |
| 6          | 7.495          |         |
| 7          | 7.465          |         |
| 8          | 7.407          |         |
| 9          | 7.440          |         |
| 10         | 7.475          |         |
| 11         | 7.475          |         |
| 12         | 7.518          |         |
| 13         | 7.440          |         |

| Laboratory | Sample pair AB | Outlier |
|------------|----------------|---------|
| 15         | 7.466          |         |
| 16         | 7.525          |         |
| 17         | 7.460          |         |
| 18         | 7.371          | C       |
| 19         | 7.485          |         |
| 20         | 7.520          |         |
| 21         | 7.485          | C       |
| 22         | 7.500          |         |
| 23         | 7.440          |         |
| 25         | 7.460          |         |
| 26         | 7.460          |         |
| 27         | 7.475          |         |
|            |                |         |

| Statistical data – Control of recovery |        |                                                                                                                                                                            |
|----------------------------------------|--------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| No of labs                             | 23     | <b>Notes</b><br><br>No test statistics were found to be significant<br><br>U denote a manual selected outlier<br>C denotes a Cochran outlier<br>G denotes a Grubbs outlier |
| No of repl                             | 2      |                                                                                                                                                                            |
| m                                      | 7.4707 |                                                                                                                                                                            |
| s <sup>2</sup>                         | 0.0012 |                                                                                                                                                                            |
| s                                      | 0.0351 |                                                                                                                                                                            |
| Assigned value                         | 7.47   |                                                                                                                                                                            |
| Recovery                               | 100.0  |                                                                                                                                                                            |
| t                                      | 0.0921 |                                                                                                                                                                            |
| Sign. level 99.9%                      | 3.7921 |                                                                                                                                                                            |
| Sign. level 99%                        | 2.8188 |                                                                                                                                                                            |
| Sign. level 95%                        | 2.0739 |                                                                                                                                                                            |

## APPENDIX D 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     | 5          | 5.83 | 5.88 | 5.86           | 5.87           | 6.00           | 1.21           | 1.3            |
|                |        |        | 22         | 5.85 | 5.88 | 5.87           |                |                |                |                |
|                |        |        | 41         | 5.86 | 5.91 | 5.89           |                |                |                |                |
|                |        | B1     | 8          | 7.10 | 7.14 | 7.12           | 7.08           | 7.30           |                |                |
|                |        |        | 31         | 7.07 | 7.11 | 7.09           |                |                |                |                |
|                |        |        | 57         | 7.01 | 7.03 | 7.02           |                |                |                |                |
| Ammonium       | mg/L N | A1     | 5          | 1.04 | 1.05 | 1.05           | 1.032          | 1.010          | 0.223          | 0.230          |
|                |        |        | 22         | 1.02 | 1.03 | 1.03           |                |                |                |                |
|                |        |        | 41         | 1.02 | 1.03 | 1.03           |                |                |                |                |
|                |        | B1     | 8          | 1.25 | 1.25 | 1.25           | 1.255          | 1.24           |                |                |
|                |        |        | 31         | 1.26 | 1.26 | 1.26           |                |                |                |                |
|                |        |        | 57         | 1.25 | 1.26 | 1.26           |                |                |                |                |
| Nitrate        | mg/L N | A1     | 5          | 2.58 | 2.59 | 2.59           | 2.59           | 2.66           | 0.61           | 0.65           |
|                |        |        | 22         | 2.56 | 2.57 | 2.57           |                |                |                |                |
|                |        |        | 41         | 2.60 | 2.61 | 2.61           |                |                |                |                |
|                |        | B1     | 8          | 3.20 | 3.21 | 3.21           | 3.20           | 3.31           |                |                |
|                |        |        | 31         | 3.19 | 3.19 | 3.19           |                |                |                |                |
|                |        |        | 57         | 3.20 | 3.19 | 3.20           |                |                |                |                |
| pH             |        | A2     | 9          | 7.50 | 7.49 | 7.50           | 7.50           | 7.47           | 0.01           | 0              |
|                |        |        | 23         | 7.50 | 7.50 | 7.50           |                |                |                |                |
|                |        |        | 40         | 7.51 | 7.50 | 7.51           |                |                |                |                |
|                |        | B2     | 13         | 7.52 | 7.52 | 7.52           | 7.51           | 7.47           |                |                |
|                |        |        | 33         | 7.52 | 7.51 | 7.52           |                |                |                |                |
|                |        |        | 48         | 7.50 | 7.50 | 7.50           |                |                |                |                |

## APPENDIX E HOMOGENEITY AND STABILITY

PT: SPIL-2  
Parameter: NH4  
Unit: mg/L N  
Sigma  
: 0,1

Responsible for tests: O6HJ DWY9 DHBP S7MS

Approval of control test: ht5m

### Homogeneity test

Date: 2026-04-14

| Sample | x(a) | x(b) | average | sd    | sd^2  |
|--------|------|------|---------|-------|-------|
| 3      | 1,27 | 1,28 | 1,3     | 0,007 | 0,000 |
| 9      | 1,27 | 1,28 | 1,3     | 0,007 | 0,00  |
| 14     | 1,28 | 1,29 | 1,3     | 0,007 | 0,000 |
| 15     | 1,26 | 1,26 | 1,3     | 0,000 | 0,000 |
| 20     | 1,29 | 1,29 | 1,3     | 0,000 | 0,000 |
| 25     | 1,27 | 1,28 | 1,3     | 0,007 | 0,000 |
| 30     | 1,27 | 1,27 | 1,3     | 0,000 | 0,000 |
| 37     | 1,28 | 1,29 | 1,3     | 0,007 | 0,000 |
| 40     | 1,28 | 1,28 | 1,3     | 0,000 | 0,000 |
| 49     | 1,28 | 1,28 | 1,3     | 0,000 | 0,000 |
| 51     | 1,29 | 1,30 | 1,3     | 0,007 | 0,000 |
| 56     | 1,28 | 1,28 | 1,3     | 0,000 | 0,000 |

#### For homogeneity

General average (x) 1,28

Sample average sd (s<sub>x</sub>) 0,009

Within-sample sd (s<sub>w</sub>): 0,005

Between-samples sd (ss): 0,0086

S<sub>L</sub> in the Proficiency Test: 0,0763

S<sub>R</sub> in the Proficiency Test: 0,0793

### Stability test

Date: 2026-04-30

| Sample | x(a) | x(b) |
|--------|------|------|
| 8      | 1,25 | 1,25 |
| 31     | 1,26 | 1,26 |
| 57     | 1,25 | 1,26 |
|        |      |      |

#### For stability

General average (y): 1,255

/x-y/ = 0,024167

### Conclusions

ss = 0,009

/x-y/ = 0,024

0.3\*sigma= 0,021

$0.3 * \sigma_{pt} + 2\sqrt{u^2(x) + u^2(y)} = 0,074$

**Analytical quality** Is s<sub>w</sub> < 0,15\*sigma  
**YES**

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

**Stability:** /x-y/ < 0.3\*sigma?  
**NO**

**Stability\*:**  $|x-y| \leq 0,3\sigma_{pt} + 2\sqrt{u^2(x) + u^2(y)}$  ?  
**YES**

PT: SPIL-2  
Parameter: NO3  
Unit: mg/L N  
Sigma: 0,2

Responsible for tests: O6HJ DWY9 DHBP S7MS  
Approval of control test: ht5m

#### Homogeneity test

Date: 2026-04-14

| Sample | x(a) | x(b) | average | sd    | sd^2  |
|--------|------|------|---------|-------|-------|
| 3      | 3,2  | 3,24 | 3,2     | 0,000 | 0,000 |
| 9      | 3,2  | 3,26 | 3,3     | 0,014 | 0,000 |
| 14     | 3,2  | 3,21 | 3,2     | 0,000 | 0,000 |
| 15     | 3,2  | 3,23 | 3,2     | 0,007 | 0,000 |
| 20     | 3,3  | 3,25 | 3,3     | 0,000 | 0,000 |
| 25     | 3,3  | 3,27 | 3,3     | 0,014 | 0,000 |
| 30     | 3,2  | 3,24 | 3,2     | 0,007 | 0,000 |
| 37     | 3,2  | 3,23 | 3,2     | 0,007 | 0,000 |
| 40     | 3,2  | 3,22 | 3,2     | 0,007 | 0,000 |
| 49     | 3,2  | 3,2  | 3,2     | 0,000 | 0,000 |
| 51     | 3,3  | 3,25 | 3,3     | 0,000 | 0,000 |
| 56     | 3,3  | 3,26 | 3,3     | 0,007 | 0,000 |

#### For homogeneity

General average (x) 3,2  
Sample average sd ( $s_x$ ) 0,019  
Within-sample sd ( $s_w$ ): 0,007  
  
Between-samples sd (ss): 0,019  
 $S_L$  in the Proficiency Test: 0,0591  
 $S_R$  in the Proficiency Test: 0,1785

#### Stability test

Date: 2026-04-30

| Sample | x(a) | x(b) |
|--------|------|------|
| 8      | 3,2  | 3,21 |
| 31     | 3,19 | 3,19 |
| 57     | 3,2  | 3,19 |
|        |      |      |

#### For stability

General average (y): 3,196667  
 $|x-y| = 0,03875$

#### Conclusions

ss = 0,02 0.3\*sigma= 0,05  
 $|x-y| = 0,03875$

**Analytical quality** Is  $s_w < 0,15 \cdot \sigma$   
**YES**

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

**Stability:**  $|x-y| < 0.3 \cdot \sigma$ ?  
**YES**

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

Responsible for tests: O6HJ DWY9 DHBP S7MS  
Approval of control test: ht5m

#### Homogeneity test

Date: 2026-04-14

| Sam-<br>ple | x(a) | x(b) | aver-<br>age | sd    | sd^2  |
|-------------|------|------|--------------|-------|-------|
| 1           | 7,48 | 7,49 | 7,5          | 0,007 | 0,000 |
| 5           | 7,49 | 7,48 | 7,5          | 0,007 | 0,00  |
| 11          | 7,50 | 7,48 | 7,5          | 0,014 | 0,000 |
| 18          | 7,50 | 7,48 | 7,5          | 0,014 | 0,000 |
| 20          | 7,50 | 7,49 | 7,5          | 0,007 | 0,000 |
| 29          | 7,51 | 7,49 | 7,5          | 0,014 | 0,000 |
| 31          | 7,56 | 7,48 | 7,5          | 0,057 | 0,003 |
| 38          | 7,50 | 7,49 | 7,5          | 0,007 | 0,000 |
| 43          | 7,49 | 7,48 | 7,5          | 0,007 | 0,000 |
| 46          | 7,49 | 7,48 | 7,5          | 0,007 | 0,000 |
| 52          | 7,48 | 7,48 | 7,5          | 0,000 | 0,000 |
| 57          | 7,48 | 7,49 | 7,5          | 0,007 | 0,000 |

#### For homogeneity

General average (x) 7,49  
Sample average sd (s<sub>x</sub>) 0,011  
  
Within-sample sd (s<sub>w</sub>): 0,019  
Between-samples sd (ss): 0  
S<sub>L</sub> in the Proficiency Test: 8  
S<sub>R</sub> in the Proficiency Test: 0,0354

#### Stability test

Date: 2026-04-30

| Sample | x(a) | x(b) |
|--------|------|------|
| 13     | 7,52 | 7,52 |
| 33     | 7,52 | 7,51 |
| 48     | 7,5  | 7,5  |
|        |      |      |

#### For stability

General average (y): 7,511667  
|x-y| = 0,020417

#### Conclusions

|                           |                                                                                                              |
|---------------------------|--------------------------------------------------------------------------------------------------------------|
|                           | ss = 0<br> x-y  = 0,020<br><br>0.3*sigma= 0,011<br><br>$0.3 * \sigma_{pt} + 2\sqrt{u^2(x) + u^2(y)} = 0,117$ |
| <b>Analytical quality</b> | Is s <sub>w</sub> < 0,15*sigma<br><b>NO</b>                                                                  |
| <b>Homogeneity:</b>       | Is ss < 0.3*sigma?<br><b>YES</b>                                                                             |
| <b>Stability:</b>         | x-y  < 0.3*sigma?<br><b>NO</b>                                                                               |
| <b>Stability*:</b>        | $ x-y  \leq 0,3\sigma_{pt} + 2\sqrt{u^2(x) + u^2(y)}$ ?<br><b>YES</b>                                        |