# Proficiency test SPIL-2 (2015)

## Nitrogen parameters in wastewater (untreated sewage)

**Quality Documentation**
**July 2015**

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| Eurofins: | Maj-Britt Fruekilde, Stine Kjær Ottsen |

## *CONTENTS*

# *1 INTRODUCTION*

A proficiency test on the analysis of nitrogen parameters in wastewater was conducted on 7 May 2015. The proficiency test was organised by Eurofins Miljø A/S.

The present report contains Eurofins' documentation for the quality of the proficiency test. Results of the proficiency test including data from participating laboratories and statistical analysis of these data were issued in a report to all participants /1/ on 8 June 2015.

# 2 FEATURES OF THE PROFICIENCY TEST

Participants in the proficiency test were a total of 64 laboratories from Denmark, Norway and Sweden. A list of participants is shown in Appendix A.

The closing date for submission of results was 22 May 2015. All participants except laboratory no. 7, 16, 17 and 22 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 untreated sewage. Sample preparation is described in Appendix B.

*Table 1 Samples in the proficiency test*

| Sample name | Parameters |
|---|---|
| A1/B1 | TN, $NH_4$, $NO_2$+$NO_3$, $NO_3$, $\gamma_{25}$ |
| 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" (1994) /2/ and as described in detail in Spliid (1992) /3/. A short introduction to the statistics and a list of symbols and abbreviations used is given in Eurofins document "Schedule for a proficiency test", which is available at Eurofins' home page /4/.

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

## 2.3 Assigned and spike value

An overview of the concentrations in the samples (the assigned values) and the difference in concentration between the two samples of a sample pair (spike value) are shown in Table 2 compared to the range of concentrations normally encountered in untreated sewage. 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 | 30-80 | 34 | 1.1 | 4 |
| Ammonium | $NH_4$ | mg/L N | 20-50 | 29.0 | 0.31 | 3.2 |
| Nitrite+nitrate | $NO_{2+3}$ | mg/L N | < 5 | 0.95 | 0.068 | 0.23 |
| Nitrate | $NO_3$ | mg/L N | < 5 | 1.09 | 0.062 | 0.23 |
| Conductivity | $\gamma_{25}$ | mS/m | 50-2000 | 88.9 | 0.59 | 3.6 |
| pH | pH | | 6-9 | 6.92 | 0.039 | 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, 3, 4, 5. A list of method identification numbers is found in the report to participants /1/. Assigned values for $NH_4$, $NO_{2+3}$, $NO_3$, conductivity and pH are consensus values for all laboratories based on the median. The assigned value for $NO_3$ (1.09 mg/L N) is higher than the assigned value for $NO_{2+3}$ (0.95 mg/L N). This is due to differences in results obtained from standard methods and test kit methods.

### *2.3.2 Test of spike values*

A comparison was made (t-test, 95% confidence level) between the spike value and the difference in concentration between the two samples in the sample pair found from the laboratories' results, see Appendix C. The test showed no significant difference between the two.

### *2.3.3 Test of assigned values*

The assigned value and the average of the results obtained from all laboratories were also compared (t-test, 95% confidence level), see Appendix D. The test showed no significant difference between the two and the control of assigned value at Eurofins confirmed the value (Appendix E).

# 3 HOMOGENEITY AND STABILITY OF SAMPLES

The homogeneity and stability of samples were tested using the following parameters as indicators:

| | |
|---|---|
| $NH_4$ | Homogeneity test |
| $NO_3$ | Combined homogeneity and stability test |
| pH | Homogeneity test |

The results of control measurements are shown in Appendix F. The appendix also gives the results of the statistical evaluation of the control data. The data are analysed by analysis of variance (ANOVA) giving:

1. the standard deviation/variance for replicates (the contribution from analytical variability),

2. the between bottle standard deviation/variance (the contribution from heterogeneity) and

3. the between days concentration difference (the contribution from instability).

Homogeneity is evaluated by comparing the between bottle variance to 0.3 * the standard deviation for evaluation of participants' performance ($0.3 \cdot \hat{\sigma}$) specified by the Danish EPA /5/, whereas the stability is evaluated by comparing the concentration change of the samples to $0.3 \cdot \hat{\sigma}$. This test ensures that heterogeneity and instability will not have negative influence on the evaluation of participant performance /6/.

The appendix also shows the standard deviation within and between laboratories from the proficiency test to allow comparison between tests performed and average quality from participating laboratories.

The tests for stability and homogeneity show that the samples are stable and homogeneous.

# *4 CONCLUSION*

The quality control performed, including test of sample stability and homogeneity as well as test of recovery of spike and assigned values, shows that the samples and their assigned values are suitable for testing the proficiency of the participating laboratories for all parameters. The results are also suitable for estimation of the general quality of analyses among all participating laboratories.

# 5 REFERENCES


/1/ Eurofins A/S, *Proficiency test SPIL-2 (2015)*, Report to participants, June 2015.

/2/ ISO 5725-2, *Accuracy (trueness and precision) of measurement methods and results – Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method*, 1994.

/3/ Spliid, H., *Procedure and analysis of data for proficiency tests and environmental analyses*, Report to Danish Environmental Protection Agency, 1994 (in Danish).

/4/ Eurofins A/S, *Schedule for a proficiency test*, document may be downloaded from www.eurofins.dk/proficiencytest.

/5/ Ministry of Environment regulation no. 231 on *quality criteria for environmental measurements,* 5 March 2014 (in Danish).

/6/ ISO 13528, *Statistical methods for use in proficiency testing by interlaboratory comparison*, 2005.

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

## *ANNEX A LIST OF PARTICIPANTS*

| Laboratory | Town | Country |
|---|---|---|
| Analyseenheden, Institut for Agroøkologi | Tjele | Denmark |
| AquaDjurs - Fornæs Renseanlæg | Grenaa | Denmark |
| Bjergmarken R/A, Roskilde Forsyning | Roskilde | Denmark |
| Biofos A/S | København K | Denmark |
| CP Kelco ApS, Spildevandslaboratoriet | Ll. Skensved | Denmark |
| Esbjerg Forsyning Spildevandslaboratorium | Esbjerg | Denmark |
| Esbjerg Forsyning Spildevandslaboratorium | Esbjerg | Denmark |
| Eurofins Miljø A/S | Vejen | Denmark |
| Faxe Forsyning | Faxe | Denmark |
| Faxe Forsyning | Faxe | Denmark |
| FORCE Technology | Holstebro | Denmark |
| Greve Solrød Forsyning | Greve | Denmark |
| Halsnæs Kommunale Forsyning A/S | Liseleje | Denmark |
| Hedensted Spildevand A/S | Daugård | Denmark |
| Hedensted Spildevand A/S | Daugård | Denmark |
| Hillerød Forsyning Spildevand A/S | Hillerød | Denmark |
| Holbæk Forsyning | Holbæk | Denmark |
| Holstebro Centralrenseanlæg, Vestforsyning A/S | Holstebro | Denmark |
| Kerteminde Forsyning - Spildevand A/S | Kerteminde | Denmark |
| Kolding Spildevand A/S | Bjert | Denmark |
| Middelfart Spildevand A/S | Middelfart | Denmark |
| Mølleåværkets Driftslaboratorium | Lyngby | Denmark |
| Nyborg Renseanlæg | Nyborg | Denmark |
| NK-Spildevand Lab | Næstved | Denmark |
| Provas Haderslev Forsyningsservice A/S | Haderslev | Denmark |
| Randers Spildevand A/S | Randers SØ | Denmark |
| Rønne Renseanlæg | Rønne | Denmark |
| SK Forsyning, Slagelse Renseanlæg | Slagelse | Denmark |
| SK Forsyning, Slagelse Renseanlæg | Slagelse | Denmark |
| SK Forsyning, Slagelse Renseanlæg | Slagelse | Denmark |
| SK Forsyning, Slagelse Renseanlæg | Slagelse | Denmark |
| SK Forsyning, Slagelse Renseanlæg | Slagelse | Denmark |
| Svendborg Centralrenseanlæg | Skårup Fyn | Denmark |
| Vejen Renseanlæg | Vejen | Denmark |

| | | |
|---|---|---|
| Vejle Spildevand A/S | Vejle | Denmark |
| AlControl Hamar | Hamar | Norway |
| Eurofins Environment Testing Norway AS | Moss | Norway |
| NGI Miljølaboratorium | Oslo | Norway |
| Ernemar Laboratorium | Oskarshamn | Sweden |
| Eurofins Environment Testing Sweden AB | Lidköping | Sweden |
| GRYAAB AB | Göteborg | Sweden |
| Hallsta Pappersbruk | Hallstavik | Sweden |
| Holmen Paper AB, Bravikens Pappersbruk | Norrköping | Sweden |
| Kalmar Vatten AB, VA-lab | Kalmar | Sweden |
| Klippans Reningsverk | Klippan | Sweden |
| Käppalaverket | Lidingö | Sweden |
| Laboratoriet vid Smedjeholms avolppsreningsverk | Falkenberg | Sweden |
| Mjölby Kommun | Mjölby | Sweden |
| Motala Kommun | Motala | Sweden |
| Nordic Sugar, Örtofta Sockerbruk | Eslöv | Sweden |
| NSVA/Öresundsverket | Helsingborg | Sweden |
| Nynäshamn Kommun, VA-avdelningen | Nynäshamn | Sweden |
| Preem AB Göteborg | Göteborg | Sweden |
| Reningsverket Aggerud | Karlskoga | Sweden |
| Smurfit Kappa Kraftliner | Piteå | Sweden |
| St1 Refinery AB | Göteborg | Sweden |
| Södra Cell Mörrum | Mörrum | Sweden |
| Tekniska förvaltningen, Verksamhetsstöd VA, Laboratoriet | Örebro | Sweden |
| Uddebo Laboratorium | Luleå | Sweden |
| Uppsala Vatten o. Avfall AB, Vattenlaboratoriet | Uppsala | Sweden |
| VIVAB | Falkenberg | Sweden |
| Västerviks Miljö & Energi AB, Vattenlaboratoriet | Västervik | Sweden |
| Vallviks Bruk AB | Vallvik | Sweden |
| Yara AB | Köping | Sweden |

# *ANNEX B SAMPLE PREPARATION*

| **Stock solution** | **Prepared from** | **Concentration** |
|---|---|---|
| Stock TN | 25.018 g Disodium edetate, $2H_2O$<br>milli-Q water up to 1000.0 g | TN: 1882 mg/kg N |
| Stock $NH_4$ | 10.012 g Ammonium chloride ($NH_4Cl$)<br>milli-Q water up to 1000.0 g | $NH_4$: 2619 mg/kg N |
| Stock $NO_3$ | 2.502 g Potassium nitrate ($KNO_3$)<br>milli-Q water up to 1000.0 g | $NO_3$: 346.4 mg/kg N |

| **Sample** | **Sample prepared from** | **TN mg/L N** | **$NH_4$ mg/L N** | **$NO_3$ mg/L N** | **Conductivity mS/m** |
|---|---|---|---|---|---|
| A1 | 75.01 g stock $NH_4$<br>40.00 g stock $NO_3$<br>25.00 g stock TN<br>Sample B1 up to 59.99 kg | 0.998 · (c+3.14) + 0.785 | 0.998 · a + 3.279 | 0.998 · (b+0.867) + 0.231 | e |
| B1 | 0 g stock $NH_4$<br>300.02 g stock $NO_3$<br>200.00 g stock TN<br>Filtered untreated wastewater from Varde sewage treatment plant up to 120.00 kg | c+3.14 | a | b+0.867 | d |

| **Sample** | **Sample prepared from** | **pH** |
|---|---|---|
| A2/B2 | Filtered untreated wastewater from Varde sewage treatment plant. | f |

## *ANNEX C CONTROL OF SPIKE VALUES*

Total nitrogen, mg/L N

Control of differences within sample pairs

| Laboratory | Difference AB | |
|---|---|---|
| 1 | -1.80 | |
| 2 | 0.70 | |
| 3 | -1.90 | |
| 4A | -0.70 | |
| 4B | -2.50 | |
| 5 | 0.70 | |
| 6 | 1.40 | |
| 8 | -0.53 | |
| 9 | 0.19 | |
| 10 | 0.30 | |
| 11 | 0.10 | |
| 12 | -0.20 | |
| 13 | 1.20 | |
| 14 | -1.40 | |
| 15 | -0.90 | |
| 18 | -0.50 | |
| 19 | -0.81 | |
| 20A | -0.50 | |
| 20B | 1.20 | |
| 21 | - | |
| 23 | -0.20 | |
| 24 | 0.10 | |
| 25 | 0.40 | |
| 26 | 0.80 | |
| 27 | 1.10 | |
| 28 | -1.70 | |
| 29 | -0.50 | |
| 30 | -2.00 | |
| 31 | 0.10 | |
| 32 | -0.10 | |
| 33 | 0.00 | |
| 34 | -0.25 | |
| 35 | 0.90 | |
| 36 | -0.24 | |
| 37 | -0.74 | |
| 38 | 0.90 | |
| 39 | 0.90 | |
| 40 | -3.00 | |
| 41 | 0.00 | |
| 42A | -1.00 | |
| 42B | -0.90 | |
| 43 | 0.90 | |
| 44 | -0.20 | |
| 45 | 0.80 | |
| 46 | 0.16 | |
| 47 | -2.80 | |
| 48 | -0.40 | |
| 49 | -3.20 | |
| 50A | 1.00 | |
| 50B | 5.10 | UC |
| 51 | 1.53 | |
| 52 | 0.40 | |
| 53 | 0.20 | |
| 54 | 1.90 | |
| 55 | -0.10 | |
| 56 | 0.28 | |
| 57 | -3.50 | |
| 58 | -2.20 | UG |
| 59 | 0.30 | |
| 60 | -1.10 | |
| 61 | 0.75 | |
| 62 | -1.00 | |
| 63 | - | |
| 64 | -0.20 | |
| No of labs., p | 60 | |
| No of repl., n | 2 | |
| d | -0.26 | |
| $s^2$ | 1.44 | |
| s | 1.20 | |
| $t = \sqrt{p} \cdot (d/s)$ | -1.6845 | |
| Sign. level, p(t) | 0.0974 | |

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 AB | |
|---|---|---|
| 1 | 1.10 | |
| 2 | -5.49 | UC |
| 3 | -0.70 | |
| 4A | 0.10 | |
| 4B | 0.20 | |
| 5 | -1.10 | |
| 6 | -0.00 | |
| 8 | -0.10 | UG |
| 9 | -1.80 | |
| 10 | -0.70 | |
| 11 | 0.10 | |
| 12 | - | |
| 13 | 0.50 | |
| 14 | 0.50 | |
| 15 | -0.90 | |
| 18 | 0.30 | |
| 19 | - | |
| 20A | -1.50 | |
| 20B | -0.50 | |
| 21 | - | |
| 23 | -0.70 | |
| 24 | 1.00 | |
| 25 | 0.50 | |
| 26 | -0.23 | |
| 27 | 0.20 | |
| 28 | -0.60 | |
| 29 | 0.20 | |
| 30 | 0.20 | |
| 31 | -1.60 | |
| 32 | - | |
| 33 | -0.10 | |
| 34 | 1.20 | |
| 35 | 0.70 | |
| 36 | 0.70 | |
| 37 | 0.00 | |
| 38 | - | |
| 39 | -0.70 | |
| 40 | -0.20 | |
| 41 | 0.20 | |
| 42A | 0.10 | |
| 42B | - | |
| 43 | 0.10 | |
| 44 | 0.00 | |
| 45 | -0.40 | |
| 46 | -1.33 | |
| 47 | 0.70 | |
| 48 | - | |
| 49 | -2.75 | |
| 50A | -0.20 | |
| 50B | 1.40 | |
| 51 | - | |
| 52 | -2.30 | |
| 53 | -1.40 | |
| 54 | 0.50 | |
| 55 | -0.20 | |
| 56 | 0.08 | |
| 57 | -0.20 | |
| 58 | 0.10 | |
| 59 | 0.10 | |
| 60 | -0.10 | |
| 61 | -0.22 | |
| 62 | -0.85 | |
| 63 | 0.24 | |
| 64 | -0.90 | |
| No of labs., p | 54 | |
| No of repl., n | 2 | |
| d | -0.21 | |
| $s^2$ | 0.71 | |
| s | 0.84 | |
| $t = \sqrt{p} \cdot (d/s)$ | -1.8085 | |
| Sign. level, p(t) | 0.0762 | |

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

Nitrite+nitrate, mg/L N

Control of differences within sample pairs

| Laboratory | Difference AB | |
|---|---|---|
| 1 | -0.010 | |
| 2 | - | |
| 3 | -0.090 | |
| 4A | -0.030 | |
| 4B | 0.001 | |
| 5 | -0.022 | |
| 6 | - | |
| 8 | 0.010 | |
| 9 | - | |
| 10 | 0.000 | |
| 11 | 0.180 | |
| 12 | - | |
| 13 | - | |
| 14 | - | |
| 15 | - | |
| 18 | - | |
| 19 | - | |
| 20A | - | |
| 20B | - | |
| 21 | - | |
| 23 | - | |
| 24 | - | |
| 25 | 0.020 | |
| 26 | 0.000 | |
| 27 | - | |
| 28 | - | |
| 29 | - | |
| 30 | 0.027 | |
| 31 | - | |
| 32 | - | |
| 33 | - | |
| 34 | - | |
| 35 | - | |
| 36 | - | |
| 37 | 0.010 | |
| 38 | 0.020 | |
| 39 | 0.000 | |
| 40 | -0.130 | |
| 41 | -0.094 | |
| 42A | 0.049 | |
| 42B | - | |
| 43 | - | |
| 44 | - | |
| 45 | - | |
| 46 | 0.019 | |
| 47 | - | |
| 48 | - | |
| 49 | 0.010 | |
| 50A | -0.031 | |
| 50B | -0.090 | |
| 51 | - | |
| 52 | - | |
| 53 | - | |
| 54 | 0.010 | |
| 55 | - | |
| 56 | 0.047 | |
| 57 | - | |
| 58 | - | |
| 59 | -0.005 | |
| 60 | -0.010 | |
| 61 | 0.039 | |
| 62 | 0.110 | UG |
| 63 | 0.013 | |
| 64 | - | |
| No of labs., p | 27 | |
| No of repl., n | 2 | |
| d | -0.002 | |
| $s^2$ | 0.003 | |
| s | 0.057 | |
| $t = \sqrt{p} \cdot (d/s)$ | -0.1914 | |
| Sign. level, p(t) | 0.8497 | |

No test statistics were found to be significant

UG denotes a Grubbs outlier

Nitrate, mg/L N

Control of differences within sample pairs

| Laboratory | Difference AB | |
|---|---|---|
| 1 | - | |
| 2 | -0.430 | UC |
| 3 | 0.035 | |
| 4A | - | |
| 4B | - | |
| 5 | 0.000 | |
| 6 | -0.010 | |
| 8 | 0.020 | |
| 9 | - | |
| 10 | 0.000 | |
| 11 | - | |
| 12 | - | |
| 13 | -0.098 | |
| 14 | - | |
| 15 | -0.010 | |
| 18 | 0.000 | |
| 19 | - | |
| 20A | -0.320 | UC |
| 20B | -0.930 | UC |
| 21 | - | |
| 23 | -0.030 | |
| 24 | -0.100 | |
| 25 | - | |
| 26 | - | |
| 27 | 0.000 | |
| 28 | 0.020 | |
| 29 | 0.000 | |
| 30 | - | |
| 31 | -0.030 | |
| 32 | - | |
| 33 | -0.040 | |
| 34 | -0.090 | |
| 35 | 0.010 | |
| 36 | -0.110 | |
| 37 | - | |
| 38 | 0.030 | |
| 39 | - | |
| 40 | - | |
| 41 | -0.088 | |
| 42A | 0.062 | |
| 42B | - | |
| 43 | 0.020 | |
| 44 | 0.010 | |
| 45 | -0.030 | |
| 46 | - | |
| 47 | 0.020 | |
| 48 | - | |
| 49 | - | |
| 50A | - | |
| 50B | - | |
| 51 | - | |
| 52 | 0.634 | UC |
| 53 | 0.030 | |
| 54 | - | |
| 55 | -0.110 | |
| 56 | - | |
| 57 | 0.020 | |
| 58 | - | |
| 59 | -0.001 | |
| 60 | 0.000 | |
| 61 | 0.041 | |
| 62 | - | |
| 63 | - | |
| 64 | 0.060 | |
| No of labs., p | 32 | |
| No of repl., n | 2 | |
| d | -0.012 | |
| $s^2$ | 0.002 | |
| s | 0.049 | |
| $t = \sqrt{p} \cdot (d/s)$ | -1.3329 | |
| Sign. level, p(t) | 0.1923 | |

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

Conductivity, mS/m

Control of differences within sample pairs

| Laboratory | Difference AB | |
|---|---|---|
| 1 | -0.80 | |
| 2 | - | |
| 3 | - | |
| 4A | 28.40 | U |
| 4B | - | |
| 5 | - | |
| 6 | - | |
| 8 | -1.71 | |
| 9 | - | |
| 10 | - | |
| 11 | 0.00 | |
| 12 | -1.30 | UG |
| 13 | -0.20 | |
| 14 | 0.20 | |
| 15 | - | |
| 18 | - | |
| 19 | - | |
| 20A | 36.40 | U |
| 20B | 46.40 | U |
| 21 | -0.10 | |
| 23 | - | |
| 24 | - | |
| 25 | 30.40 | U |
| 26 | - | |
| 27 | -0.30 | |
| 28 | - | |
| 29 | - | |
| 30 | - | |
| 31 | - | |
| 32 | - | |
| 33 | -0.20 | |
| 34 | - | |
| 35 | -1.10 | |
| 36 | -0.30 | |
| 37 | - | |
| 38 | - | |
| 39 | 31.40 | U |
| 40 | - | |
| 41 | 1.00 | |
| 42A | 0.10 | |
| 42B | - | |
| 43 | -0.10 | |
| 44 | -0.10 | |
| 45 | 30.40 | U |
| 46 | - | |
| 47 | - | |
| 48 | - | |
| 49 | - | |
| 50A | - | |
| 50B | - | |
| 51 | -0.20 | |
| 52 | - | |
| 53 | 1.80 | |
| 54 | - | |
| 55 | -0.50 | |
| 56 | -0.28 | |
| 57 | - | |
| 58 | - | |
| 59 | 0.00 | |
| 60 | 0.50 | |
| 61 | -0.80 | UG |
| 62 | - | |
| 63 | 0.40 | |
| 64 | -3.30 | UC |
| No of labs., p | 21 | |
| No of repl., n | 2 | |
| d | -0.09 | |
| $s^2$ | 0.50 | |
| s | 0.71 | |
| $t = \sqrt{p} \cdot (d/s)$ | -0.5844 | |
| Sign. level, p(t) | 0.5655 | |

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 AB |
|---|---|
| 1 | -0.050 |
| 2 | -0.079 |
| 3 | -0.040 |
| 4A | -0.070 |
| 4B | - |
| 5 | -0.020 |
| 6 | 0.300 |
| 8 | -0.100 |
| 9 | -0.060 |
| 10 | -0.110 |
| 11 | -0.040 |
| 12 | -0.030 |
| 13 | -0.010 |
| 14 | -0.030 |
| 15 | 0.290 |
| 18 | 0.050 |
| 19 | -0.080 |
| 20A | 0.370 |
| 20B | 0.220 |
| 21 | 0.020 |
| 23 | -0.200 |
| 24 | -0.070 |
| 25 | -0.390 |
| 26 | -0.060 |
| 27 | -0.070 |
| 28 | -0.210 |
| 29 | -0.020 |
| 30 | 0.000 |
| 31 | 0.040 |
| 32 | - |
| 33 | 0.000 |
| 34 | 0.010 |
| 35 | -0.180 |
| 36 | -0.040 |
| 37 | -0.020 |
| 38 | -0.010 |
| 39 | 0.000 |
| 40 | -0.080 |
| 41 | -0.030 |
| 42A | -0.080 |
| 42B | - |
| 43 | -0.030 |
| 44 | -0.040 |
| 45 | 0.000 |
| 46 | -0.170 |
| 47 | -0.220 |
| 48 | -0.100 |
| 49 | -0.200 |
| 50A | - |
| 50B | 0.040 |
| 51 | - |
| 52 | -0.310 |
| 53 | 0.030 |
| 54 | 0.040 |
| 55 | 0.010 |
| 56 | -0.010 |
| 57 | -0.150 |
| 58 | 0.000 |
| 59 | 0.130 |
| 60 | 0.040 |
| 61 | -0.040 |
| 62 | - |
| 63 | -0.030 |
| 64 | 0.010 |
| No of labs., p | 58 |
| No of repl., n | 2 |
| d | -0.032 |
| $s^2$ | 0.016 |
| s | 0.127 |
| $t = \sqrt{p} \cdot (d/s)$ | -1.9353 |
| Sign. level, p(t) | 0.0579 |

No test statistics were found to be significant

## *ANNEX D CONTROL OF RECOVERY*

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

| Laboratory | Sample pair AB | |
|---|---|---|
| 1 | 32.60 | |
| 2 | 35.85 | |
| 3 | 36.85 | |
| 4A | 36.45 | |
| 4B | 35.25 | |
| 5 | 34.95 | |
| 6 | 34.80 | |
| 8 | 35.51 | |
| 9 | 34.61 | |
| 10 | 40.65 | |
| 11 | 32.75 | |
| 12 | 32.70 | |
| 13 | 33.10 | |
| 14 | 29.40 | |
| 15 | 37.45 | |
| 18 | 34.45 | |
| 19 | 32.25 | |
| 20A | 34.95 | |
| 20B | 33.50 | |
| 21 | - | |
| 23 | 34.10 | |
| 24 | 32.15 | |
| 25 | 33.60 | |
| 26 | 36.10 | |
| 27 | 30.35 | |
| 28 | 30.55 | |
| 29 | 31.75 | |
| 30 | 30.80 | |
| 31 | 32.45 | |
| 32 | 35.80 | |
| 33 | 31.50 | |
| 34 | 35.17 | |
| 35 | 35.35 | |
| 36 | 34.97 | |
| 37 | 35.70 | |
| 38 | 37.05 | |
| 39 | 33.05 | |
| 40 | 33.70 | |
| 41 | 34.60 | |
| 42A | 32.50 | |
| 42B | 32.85 | |
| 43 | 36.65 | |
| 44 | 38.30 | |
| 45 | 34.20 | |
| 46 | 35.55 | |
| 47 | 33.80 | |
| 48 | 32.00 | |
| 49 | 36.15 | |
| 50A | 26.70 | |
| 50B | 33.05 | UC |
| 51 | 38.88 | |
| 52 | 33.20 | |
| 53 | 35.80 | |
| 54 | 32.35 | |
| 55 | 33.35 | |
| 56 | 36.85 | |
| 57 | 32.75 | |
| 58 | 22.30 | UG |
| 59 | 33.08 | |
| 60 | 33.65 | |
| 61 | 35.23 | |
| 62 | 30.52 | |
| 63 | - | |
| 64 | 34.65 | |
| No of labs., p | 60 | |
| No of repl., n | 2 | |
| m | 34.10 | |
| $s^2$ | 5.72 | |
| s | 2.39 | |
| Assigned value, μ | 34 | |
| Recovery, % | 100.3 | |
| $t = \sqrt{p} \cdot (m-\mu)/s$ | 0.3146 | |
| Sign. level, p(t) | 0.7541 | |

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 AB | |
|---|---|---|
| 1 | 30.15 | |
| 2 | 31.05 | UC |
| 3 | 28.25 | |
| 4A | 29.05 | |
| 4B | 26.50 | |
| 5 | 28.45 | |
| 6 | 30.10 | |
| 8 | 35.85 | UG |
| 9 | 27.82 | |
| 10 | 28.79 | |
| 11 | 28.05 | |
| 12 | - | |
| 13 | 29.65 | |
| 14 | 28.45 | |
| 15 | 29.85 | |
| 18 | 29.25 | |
| 19 | - | |
| 20A | 27.35 | |
| 20B | 27.05 | |
| 21 | - | |
| 23 | 29.45 | |
| 24 | 29.70 | |
| 25 | 30.15 | |
| 26 | 28.16 | |
| 27 | 28.10 | |
| 28 | 29.30 | |
| 29 | 30.50 | |
| 30 | 30.10 | |
| 31 | 30.00 | |
| 32 | - | |
| 33 | 29.45 | |
| 34 | 30.50 | |
| 35 | 28.65 | |
| 36 | 31.38 | |
| 37 | 28.39 | |
| 38 | - | |
| 39 | 28.75 | |
| 40 | 29.30 | |
| 41 | 28.50 | |
| 42A | 28.95 | |
| 42B | - | |
| 43 | 31.05 | |
| 44 | 29.00 | |
| 45 | 29.10 | |
| 46 | 28.59 | |
| 47 | 29.45 | |
| 48 | - | |
| 49 | 30.18 | |
| 50A | 27.10 | |
| 50B | 29.20 | |
| 51 | - | |
| 52 | 29.75 | |
| 53 | 27.60 | |
| 54 | 27.95 | |
| 55 | 28.90 | |
| 56 | 29.56 | |
| 57 | 25.90 | |
| 58 | 28.45 | |
| 59 | 29.02 | |
| 60 | 30.85 | |
| 61 | 28.30 | |
| 62 | 31.23 | |
| 63 | 28.27 | |
| 64 | 28.10 | |
| No of labs., p | 54 | |
| No of repl., n | 2 | |
| m | 28.99 | |
| $s^2$ | 1.34 | |
| s | 1.16 | |
| Assigned value, μ | 29.0 | |
| Recovery, % | 100.0 | |
| $t = \sqrt{p} \cdot (m-\mu)/s$ | -0.0417 | |
| Sign. level, p(t) | 0.9669 | |

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

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

| Laboratory | Sample pair AB | |
|---|---|---|
| 1 | 0.805 | |
| 2 | - | |
| 3 | 0.865 | |
| 4A | 1.165 | |
| 4B | 0.980 | |
| 5 | 1.151 | |
| 6 | - | |
| 8 | 1.105 | |
| 9 | - | |
| 10 | 0.840 | |
| 11 | 0.870 | |
| 12 | - | |
| 13 | - | |
| 14 | - | |
| 15 | - | |
| 18 | - | |
| 19 | - | |
| 20A | - | |
| 20B | - | |
| 21 | - | |
| 23 | - | |
| 24 | - | |
| 25 | 1.160 | |
| 26 | 0.880 | |
| 27 | - | |
| 28 | - | |
| 29 | - | |
| 30 | 0.736 | |
| 31 | - | |
| 32 | - | |
| 33 | - | |
| 34 | - | |
| 35 | - | |
| 36 | - | |
| 37 | 0.905 | |
| 38 | 0.970 | |
| 39 | 1.020 | |
| 40 | 0.955 | |
| 41 | 0.498 | |
| 42A | 0.756 | |
| 42B | - | |
| 43 | - | |
| 44 | - | |
| 45 | - | |
| 46 | 0.950 | |
| 47 | - | |
| 48 | - | |
| 49 | 1.205 | |
| 50A | 0.956 | |
| 50B | 1.285 | |
| 51 | - | |
| 52 | - | |
| 53 | - | |
| 54 | 1.095 | |
| 55 | - | |
| 56 | 0.774 | |
| 57 | - | |
| 58 | - | |
| 59 | 0.907 | |
| 60 | 1.095 | |
| 61 | 0.908 | |
| 62 | 1.725 | UG |
| 63 | 0.923 | |
| 64 | - | |
| No of labs., p | 27 | |
| No of repl., n | 2 | |
| m | 0.954 | |
| $s^2$ | 0.029 | |
| s | 0.171 | |
| Assigned value, μ | 0.95 | |
| Recovery, % | 100.4 | |
| $t = \sqrt{p} \cdot (m-\mu)/s$ | 0.1235 | |
| Sign. level, p(t) | 0.9026 | |

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

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

| Laboratory | Sample pair AB | |
|---|---|---|
| 1 | - | |
| 2 | 1.205 | UC |
| 3 | 0.962 | |
| 4A | - | |
| 4B | - | |
| 5 | 1.140 | |
| 6 | 1.095 | |
| 8 | 1.090 | |
| 9 | - | |
| 10 | 0.830 | |
| 11 | - | |
| 12 | - | |
| 13 | 0.929 | |
| 14 | - | |
| 15 | 1.245 | |
| 18 | 1.120 | |
| 19 | - | |
| 20A | 0.050 | UC |
| 20B | 0.365 | UC |
| 21 | - | |
| 23 | 1.085 | |
| 24 | 1.150 | |
| 25 | - | |
| 26 | - | |
| 27 | 1.110 | |
| 28 | 1.170 | |
| 29 | 1.120 | |
| 30 | - | |
| 31 | 1.195 | |
| 32 | - | |
| 33 | 0.800 | |
| 34 | 1.265 | |
| 35 | 1.065 | |
| 36 | 1.465 | |
| 37 | - | |
| 38 | 0.955 | |
| 39 | - | |
| 40 | - | |
| 41 | 0.487 | |
| 42A | 0.749 | |
| 42B | - | |
| 43 | 1.230 | |
| 44 | 1.105 | |
| 45 | 1.085 | |
| 46 | - | |
| 47 | 1.130 | |
| 48 | - | |
| 49 | - | |
| 50A | - | |
| 50B | - | |
| 51 | - | |
| 52 | 0.833 | UC |
| 53 | 0.845 | |
| 54 | - | |
| 55 | 1.465 | |
| 56 | - | |
| 57 | 1.090 | |
| 58 | - | |
| 59 | 0.893 | |
| 60 | 1.080 | |
| 61 | 0.893 | |
| 62 | - | |
| 63 | - | |
| 64 | 1.030 | |
| No of labs., p | 32 | |
| No of repl., n | 2 | |
| m | 1.059 | |
| $s^2$ | 0.038 | |
| s | 0.196 | |
| Assigned value, μ | 1.09 | |
| Recovery, % | 97.1 | |
| $t = \sqrt{p} \cdot (m-\mu)/s$ | -0.9107 | |
| Sign. level, p(t) | 0.3695 | |

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

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

| Laboratory | Sample pair AB | |
|---|---|---|
| 1 | 88.50 | |
| 2 | - | |
| 3 | - | |
| 4A | 913.20 | U |
| 4B | - | |
| 5 | - | |
| 6 | - | |
| 8 | 89.63 | |
| 9 | - | |
| 10 | - | |
| 11 | 89.20 | |
| 12 | 81.55 | UG |
| 13 | 90.80 | |
| 14 | 88.90 | |
| 15 | - | |
| 18 | - | |
| 19 | - | |
| 20A | 878.20 | U |
| 20B | 853.20 | U |
| 21 | 90.85 | |
| 23 | - | |
| 24 | - | |
| 25 | 921.20 | U |
| 26 | - | |
| 27 | 87.45 | |
| 28 | - | |
| 29 | - | |
| 30 | - | |
| 31 | - | |
| 32 | - | |
| 33 | 89.90 | |
| 34 | - | |
| 35 | 87.95 | |
| 36 | 89.35 | |
| 37 | - | |
| 38 | - | |
| 39 | 907.70 | U |
| 40 | - | |
| 41 | 88.40 | |
| 42A | 90.15 | |
| 42B | - | |
| 43 | 86.75 | |
| 44 | 87.65 | |
| 45 | 909.20 | U |
| 46 | - | |
| 47 | - | |
| 48 | - | |
| 49 | - | |
| 50A | - | |
| 50B | - | |
| 51 | 89.70 | |
| 52 | - | |
| 53 | 88.30 | |
| 54 | - | |
| 55 | 89.35 | |
| 56 | 88.97 | |
| 57 | - | |
| 58 | - | |
| 59 | 88.80 | |
| 60 | 89.25 | |
| 61 | 79.10 | UG |
| 62 | - | |
| 63 | 88.50 | |
| 64 | 83.15 | UC |
| No of labs., p | 21 | |
| No of repl., n | 2 | |
| m | 88.97 | |
| $s^2$ | 1.09 | |
| s | 1.04 | |
| Assigned value, μ | 88.9 | |
| Recovery, % | 100.1 | |
| $t = \sqrt{p} \cdot (m-\mu)/s$ | 0.3041 | |
| Sign. level, p(t) | 0.7642 | |

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 AB |
|---|---|
| 1 | 6.945 |
| 2 | 6.833 |
| 3 | 7.030 |
| 4A | 6.775 |
| 4B | - |
| 5 | 6.970 |
| 6 | 7.050 |
| 8 | 7.030 |
| 9 | 6.560 |
| 10 | 6.385 |
| 11 | 6.890 |
| 12 | 6.895 |
| 13 | 6.975 |
| 14 | 6.935 |
| 15 | 6.445 |
| 18 | 6.725 |
| 19 | 6.980 |
| 20A | 6.325 |
| 20B | 6.110 |
| 21 | 6.990 |
| 23 | 6.800 |
| 24 | 6.875 |
| 25 | 7.755 |
| 26 | 6.930 |
| 27 | 6.865 |
| 28 | 7.685 |
| 29 | 7.220 |
| 30 | 7.010 |
| 31 | 7.000 |
| 32 | - |
| 33 | 6.900 |
| 34 | 6.605 |
| 35 | 6.770 |
| 36 | 6.930 |
| 37 | 6.920 |
| 38 | 7.105 |
| 39 | 6.870 |
| 40 | 6.850 |
| 41 | 7.135 |
| 42A | 7.030 |
| 42B | - |
| 43 | 7.025 |
| 44 | 6.900 |
| 45 | 6.900 |
| 46 | 6.775 |
| 47 | 7.250 |
| 48 | 7.750 |
| 49 | 6.700 |
| 50A | - |
| 50B | 6.880 |
| 51 | 7.260 |
| 52 | 7.145 |
| 53 | 6.585 |
| 54 | 6.810 |
| 55 | 7.065 |
| 56 | 7.075 |
| 57 | 6.875 |
| 58 | 6.970 |
| 59 | 6.925 |
| 60 | 7.100 |
| 61 | 7.040 |
| 62 | - |
| 63 | 6.925 |
| 64 | 6.725 |
| No of labs., p | 58 |
| No of repl., n | 2 |
| m | 6.923 |
| $s^2$ | 0.081 |
| s | 0.284 |
| Assigned value, µ | 6.92 |
| Recovery, % | 100.0 |
| $t = \sqrt{p} \cdot (m-\mu)/s$ | 0.0756 |
| Sign. level, p(t) | 0.9400 |

No test statistics were found to be significant

## *ANNEX E CONCENTRATION LEVEL*

| Parameter | Unit | Sample | Bottle no. | I | II | Bottle Average | Sample Average | Assigned value | Spike Measured | Spike Assigned |
|---|---|---|---|---|---|---|---|---|---|---|
| Total nitrogen | mg/L N | A1 | 24 | 38,1 | 37,0 | 37,55 | 37,78 | 38 | 4,37 | 4 |
| | | | 57 | 37,9 | 38,3 | 38,10 | | | | |
| | | | 71 | 37,8 | 37,6 | 37,70 | | | | |
| | | B1 | 26 | 34,1 | 33,0 | 33,55 | 33,42 | 34 | | |
| | | | 49 | 33,6 | 33,3 | 33,45 | | | | |
| | | | 67 | 33,4 | 33,1 | 33,25 | | | | |
| Ammonium | mg/L N | A1 | 24 | 30,0 | 29,3 | 29,65 | 29,88 | 32,2 | 2,52 | 3,2 |
| | | | 57 | 30,3 | 29,8 | 30,05 | | | | |
| | | | 71 | 29,6 | 30,3 | 29,95 | | | | |
| | | B1 | 26 | 27,8 | 26,9 | 27,35 | 27,37 | 29,0 | | |
| | | | 49 | 27,3 | 27,6 | 27,45 | | | | |
| | | | 67 | 27,2 | 27,4 | 27,30 | | | | |
| Nitrite+nitrate | mg/L N | A1 | 24 | 1,29 | 1,31 | 1,30 | 1,32 | 1,18 | 0,21 | 0,23 |
| | | | 57 | 1,33 | 1,33 | 1,33 | | | | |
| | | | 71 | 1,30 | 1,33 | 1,32 | | | | |
| | | B1 | 26 | 1,07 | 1,12 | 1,09 | 1,10 | 0,95 | | |
| | | | 49 | 1,08 | 1,18 | 1,13 | | | | |
| | | | 67 | 1,08 | 1,10 | 1,09 | | | | |
| Nitrate | mg/L N | A1 | 24 | 1,27 | 1,29 | 1,28 | 1,30 | 1,32 | 0,22 | 0,23 |
| | | | 57 | 1,31 | 1,31 | 1,31 | | | | |
| | | | 71 | 1,28 | 1,31 | 1,30 | | | | |
| | | B1 | 26 | 1,04 | 1,09 | 1,07 | 1,08 | 1,09 | | |
| | | | 49 | 1,05 | 1,15 | 1,10 | | | | |
| | | | 67 | 1,05 | 1,07 | 1,06 | | | | |
| pH | | A2 | 8 | 6,79 | 6,80 | 6,80 | 6,74 | 6,92 | 0,05 | 0 |
| | | | 40 | 6,64 | 6,68 | 6,66 | | | | |
| | | | 88 | 6,74 | 6,79 | 6,77 | | | | |
| | | B2 | 28 | 6,60 | 6,62 | 6,61 | 6,69 | 6,92 | | |
| | | | 49 | 6,75 | 6,79 | 6,77 | | | | |
| | | | 50 | 6,67 | 6,72 | 6,70 | | | | |

# *ANNEX F HOMOGENEITY AND STABILITY*

| | | |
|---|---|---|
| **PT:** | SPIL-2 | |
| **Parameter:** | NH4 | |
| **Unit:** | mg/L C | |
| **Sigma:** | 1,9931 | 6,5% of x |

**Responsible** for tests: SMN / IRL

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

**Homogeneity test** Date: 2015-04-22

| Sample | x(a) | x(b) | average | sd | sd^2 |
|---|---|---|---|---|---|
| A1-4 | 29,8 | 30,7 | 30,3 | 0,636 | 0,405 |
| A1-12 | 30,4 | 30,7 | 30,6 | 0,212 | 0,05 |
| A1-15 | 31,0 | 30,5 | 30,8 | 0,354 | 0,125 |
| A1-29 | 31,1 | 30,8 | 31,0 | 0,212 | 0,045 |
| A1-36 | 30,7 | 30,4 | 30,6 | 0,212 | 0,045 |
| A1-44 | 30,7 | 30,1 | 30,4 | 0,424 | 0,180 |
| A1-54 | 30,6 | 30,6 | 30,6 | 0,000 | 0,000 |
| A1-58 | 30,8 | 30,2 | 30,5 | 0,424 | 0,180 |
| A1-66 | 31,9 | 30,6 | 31,3 | 0,919 | 0,845 |
| A1-76 | 30,7 | 31,1 | 30,9 | 0,283 | 0,080 |
| A1-80 | 30,5 | 31,0 | 30,8 | 0,354 | 0,125 |
| A1-89 | 30,6 | 30,4 | 30,5 | 0,141 | 0,020 |

**For homogeneity**

| | |
|---|---|
| General average (x) | 30,66 |
| Sample average sd ($s_x$) | 0,273 |
| Within-sample sd ($s_w$): | 0,418 |
| Between-samples sd (ss): | 0 |
| $S_L$ in the Proficiency Test: | 1,080 |
| $S_R$ in the Proficiency Test: | 1,230 |

**Conclusions**

| | |
|---|---|
| ss =0 | 0.3*sigma=0,60 |
| /x-y/ =0 | |
| **Analytical quality** | Is $s_w$ < 0,15*sigma **NO** |
| **Homogeneity:** | Is ss < 0.3*sigma? **YES** |

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

**Responsible** for tests: SMN / IRL

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

**Homogeneity test** Date: 2015-04-22

| Sample | x(a) | x(b) | average | sd | sd^2 |
|---|---|---|---|---|---|
| A1-4 | 1,30 | 1,14 | 1,2 | 0,113 | 0,013 |
| A1-12 | 1,26 | 1,25 | 1,3 | 0,007 | 0,000 |
| A1-15 | 1,31 | 1,35 | 1,3 | 0,028 | 0,001 |
| A1-29 | 1,29 | 1,29 | 1,3 | 0,000 | 0,000 |
| A1-36 | 1,42 | 1,3 | 1,4 | 0,085 | 0,007 |
| A1-44 | 1,29 | 1,18 | 1,2 | 0,078 | 0,006 |
| A1-54 | 1,27 | 1,28 | 1,3 | 0,007 | 0,000 |
| A1-58 | 1,20 | 1,39 | 1,3 | 0,134 | 0,018 |
| A1-66 | 1,31 | 1,31 | 1,3 | 0,000 | 0,000 |
| A1-76 | 1,28 | 1,37 | 1,3 | 0,064 | 0,004 |
| A1-80 | 1,30 | 1,31 | 1,3 | 0,007 | 0,000 |
| A1-89 | 1,31 | 1,31 | 1,3 | 0,000 | 0,000 |

**For homogeneity**

| | |
|---|---|
| General average (x) | 1,3 |
| Sample average sd ($s_x$) | 0,041 |
| Within-sample sd ($s_w$): | 0,064 |
| Between-samples sd (ss): | 0 |
| $S_L$ in the Proficiency Test: | 0,194 |
| $S_R$ in the Proficiency Test: | 0,197 |

**Stability test** Date: 2015-05-07

| Sample | x(a) | x(b) |
|---|---|---|
| A1-24 | 1,27 | 1,29 |
| A1-57 | 1,31 | 1,31 |
| A1-71 | 1,28 | 1,31 |
| | | |

**For stability**

| | |
|---|---|
| General average (y): | 1,295 |
| /x-y/ = | 0,0025 |

**Conclusions**

ss = 0 0.3*sigma= 0,03

/x-y/ = 0,0025

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

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

**Stability:** /x-y/ < 0.3*sigma? **YES**

| | | |
|---|---|---|
| **PT:** | SPIL-2 | |
| **Parameter:** | pH | |
| **Unit:** | | |
| | | 1,3*Stma |
| **Sigma:** | 0,065 | x |

**Responsible** for tests: SMN

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

**Homogeneity test** Date: 2015-04-22

| Sample | x(a) | x(b) | average | sd | sd^2 |
|---|---|---|---|---|---|
| A2-3 | 6,98 | 7,02 | 7,0 | 0,028 | 0,001 |
| A2-13 | 6,99 | 7,05 | 7,0 | 0,042 | 0,00 |
| A2-19 | 6,99 | 7,03 | 7,0 | 0,028 | 0,001 |
| A2-23 | 6,99 | 7,04 | 7,0 | 0,035 | 0,001 |
| A2-34 | 7,02 | 7,07 | 7,0 | 0,035 | 0,001 |
| A2-42 | 6,99 | 7,01 | 7,0 | 0,014 | 0,000 |
| A2-45 | 7,04 | 7,08 | 7,1 | 0,028 | 0,001 |
| A2-53 | 7,04 | 7,07 | 7,1 | 0,021 | 0,000 |
| A2-61 | 7,02 | 7,06 | 7,0 | 0,028 | 0,001 |
| A2-70 | 7,02 | 7,04 | 7,0 | 0,014 | 0,000 |
| A2-74 | 7,03 | 7,06 | 7,0 | 0,021 | 0,000 |
| A2-86 | 7,02 | 7,04 | 7,0 | 0,014 | 0,000 |

**For homogeneity**

| | |
|---|---|
| General average (x) | 7,03 |
| Sample average sd ($s_x$) | 0,020 |
| Within-sample sd ($s_w$): | 0,027 |
| Between-samples sd (ss): | 0,0065 |
| $S_L$ in the Proficiency Test: | 0,277 |
| $S_R$ in the Proficiency Test: | 0,291 |

**Conclusions**

| | | |
|---|---|---|
| | | 0.3*sigma |
| ss = | 0,007 | = 0,02 |
| /x-y/ = | 0 | |
| **Analytical quality** | Is $s_w$ < 0,15*sigma | **NO** |
| **Homogeneity:** | Is ss < 0.3*sigma? | **YES** |