Eurofins Miljø A/S
Smedeskovvej 38
DK-8464 Galten

DANAK
RM Reg. nr. 535

VKI
REFERENCE MATERIALS

CERTIFICATE FOR

QC WW3

TOTAL NITROGEN AND TOTAL PHOSPHORUS FOR WASTE WATER ANALYSES

BATCH: VKI-7-8-0319

INSTRUCTIONS FOR USE OF THE REFERENCE MATERIAL

Description
This reference material consists of one ampoule with concentrate for preparation of reference sample for quality control after dilution with water. The certificate includes documentation for the analytical parameters total nitrogen (TN) and total phosphorus (TP).

Quantity and Preservation
QC WW3 consists of ampoules with a minimum of 10 mL concentrate in each. 1 L reference sample is produced by dilution of 10 mL concentrate. The concentrates are preserved by autoclaving.

Use
The reference material is intended for quality control, i.e. measurement and control of the accuracy and precision of analyses. It is typically intended for analyses of nutrients in waste water. It may also be used in the quality control of other types of water samples and for the implementation and optimisation of analytical instruments and analytical methods.

It is important that the batch numbers of the reference material and on the certificate are identical.

Preparation for Use
Stabilise the ampoules at room temperature (approx. 20°C). Break the ampoule neck open at the mark, withdraw the concentrate with a pipette, and dilute 1:100 with water without a detectable content of nutrients, e.g. 2.00 mL concentrate up to 200 mL with water. The certified concentrations are given in the table on page 3 of this certificate.

Analysis
For quality control the reference material is analysed at the same time and in the same manner as other samples.

Storage and Durability
Store the ampoules protected from sunlight, e.g. in the ampoule boxes, and at room temperature or in a refrigerator. The certificate is valid until **1st April 2025** provided that the material is stored under the recommended conditions.

After opening of the ampoule and dilution, the reference material has an expected storage time of up to 24 hours.

This certificate is prepared in accordance with the international ISO guidelines for certification of reference materials /1/ and /2/.

PRODUCTION OF THE REFERENCE MATERIAL AND DOCUMENTATION

Production
The production of this reference material is in accordance with the quality management procedures of Eurofins, with the aim of obtaining the intended quality of the material.

Documentation of Content
All documentation for the reference material has been performed after dilution of the ampoule concentrates 1:100.

Internal control
The analytical quality of Eurofins has been documented and found satisfactory by regular participation in international proficiency tests.

Homogeneity:
The homogeneity has been investigated by measurements of both nutrients in randomly selected ampoules of QC WW3. Tests for homogeneity have been performed by comparing the standard deviation between the reference material units with the within batch standard deviation obtained from duplicate measurements of the reference material in the same sample (F-test, 95%). In addition, homogeneity testing was included in the external control. No indication of heterogeneity was found.

Stability:
The stability of the reference material is being followed at 5°C, 20°C and 37°C, and no indication of instability was observed at the date of this certificate.

External control
The concentration of TN and TP in the reference material was determined by selected laboratories in an external documentation in December 2019 and January 2020. The participating laboratories are skilled and have documented good analytical quality by participation in interlaboratory comparisons and by analysis of a control sample in the certification. The laboratories were requested to analyse five samples of QC WW3: three samples in the same analytical series, one by duplicate determination, and two samples in two different analytical series as single determinations. The statistics are in accordance with the international standard: ISO Guide 35 /1/. On the basis of the analytical results submitted by the laboratories the following statistical parameters have been calculated:

y_{char}: average, calculated in accordance with ISO Guide 35 (section A.2.4):

s(y) standard deviation between the laboratories, calculated in accordance with ISO Guide 35 (section A.2.5):

$$\sqrt{\frac{\sum (y_i - y_{char})^2}{\mathrm{p}-1}}$$

The 95% confidence interval of the true mean value of analytical results is:

$$y_{char} \pm \mathrm{t}_{0,025}(\nu).\frac{\mathrm{s}(y)}{\sqrt{\mathrm{p}}}$$

where

p: number of laboratories included in calculations

ν: p-1, degrees of freedom

$t_{0,025}(\nu)$: t value of 0,025 level at ν degrees of freedom.

The criteria for selection of laboratories were as follows:

- the laboratory results in proficiency tests diverged less than 2 standard deviations from the nominal value,
- the laboratory analyses more than 20 analytical series each year or holds accreditation for the parameter,
- the laboratory result for the control sample in the certification study deviated less than 15% from the nominal value, and
- the laboratory results in the certification study are not Cochran outliers or Grubbs outliers or deemed to be an outlier based on a scientific evaluation.

The data included in the external control and names of the participating laboratories are listed in an annex to this certificate. On the basis of the selected results, the following has been calculated:

Certified Values

DETERMINAND	UNIT	AVERAGE	BETWEEN LABORATORY STANDARD DEVIATION	95% CONFIDENCE LIMITS OF THE AVERAGE VALUE $y_{char} \pm t_{0,025}(\nu).\frac{s(y)}{\sqrt{p}}$		NUMBER OF DATA SETS IN CALCULATIONS/ METHOD	EXCLUDED DATA SETS C: Cochran outlier G: Grubbs outlier
		y_{char}	s(*y*)	Lower	Upper	(p)	
Total nitrogen	mg/L N	7.5	0.29	7.3	7.6	3/A 4/B 3/C 3/F 1/G 2/I 1/IA 3/X	3C
Total phosphorus	mg/L P	1.56	0.059	1.53	1.59	1/A 8/B 1/DA 3/E 1/EA 6/X	3C

Methods

Total nitrogen:

A Digestion with peroxodisulphate and determination of the produced nitrate using the cadmium reduction method. (DS 221; SFS 3031; NS 4743; SS 28131)

B Digestion with peroxodisulphate and determination of the produced nitrate using the cadmium reduction method. (ISO 11905-1)

C Digestion with peroxodisulphate and determination of the produced nitrate using UV-spectrophotometry. (DS 221:1975/SFS 3031 + SM[1] 4500 NO3-B 19 ed)

F Oxidation of the sample containing nitrogen by catalytic combustion in an oxygen atmosphere at >700°C, to nitrogen oxides. Quantification of nitrogen concentration by chemiluminescence detection (after reaction with ozone). (EN 12260)

G Merck (Peroxodisulphate digestion and determination of nitrate using reaction with 2.6-dimethylphenol and spectrophotometric measurement). 0.5-15.0 mg/L N. (Merck 1.00613.0001)

I Lange (Peroxodisulphate digestion and determination of nitrate using reaction with 2.6-dimethylphenol and spectrophotometric measurement) 1 - 16 mg/L N (Lange LCK 138)

IA Lange (Peroxodisulphate digestion and determination of nitrate using reaction with 2.6-dimethylphenol and spectrophotometric measurement) 1 - 16 mg/L N, Laboratory robot (Lange APC 138)

X Other methods

1 SM: Standard Methods for the Examination of Water and Wastewater

Total phosphorus:

A Digestion by peroxodisulphate and determination of orthophosphate by molybdenum blue method. (DS 292; SFS 3026; NS 4725; SS 028127)

B Digestion by peroxodisulphate and determination of orthophosphate by molybdenum blue method. (EN ISO 6878, part 7)

DA Lange (persulphate digestion and molybdate/ascorbic acid method) 0,5 - 5 mg/L P. (Lange LCK 348)

E Lange (persulphate digestion and molybdate/ascorbic acid method) 0.05 – 1.5 mg/L P (Lange LCK 349)

EA Lange (persulphate digestion and molybdate/ascorbic acid method) 0.05 - 1,5 mg/L P, Laboratory robot (Lange APC 349)

X Other methods

Use of the Certified Values

For laboratories with an analytical quality that is comparable to that of the laboratories who have contributed to the external control data of this certificate, the following applies:

1) For single determinations, analytical results will with a probability of 95% be in the interval:

$$y_{char} \pm t_{0,025}(\nu) \cdot s(y)$$

2) Analytical results, calculated as the average of two determinations will with a probability of 95% be in the interval:

$$y_{char} \pm t_{0,025}(\nu) . \frac{s(y)}{\sqrt{2}}$$

REFERENCES

/1/ ISO Guide 35:2017. Certification of reference materials - General and statistical principles for certification.

/2/ ISO Guide 31:2015. Reference materials - Contents of certificates, labels and accompanying documentation.

Date of issue: January 2022

RESPONSIBLE SCIENTIST

Rikke Mikkelsen
Eurofins Miljø A/S
DK-8464 Galten

Certificate revision history: January 2022 (original certificate date)

ANNEX TO CERTIFICATE QC WW3

Laboratory Measurements

Total nitrogen					
y_i mg/L N	s_{ri} mg/L N	n_{ri}	s_{Li} mg/L N	n_{Li}	Method
7.68	0.26	4	0.16	3	IA
7.40	0.04	4	0.10	3	C
7.60	0.06	4	0.03	3	X
7.89	0.07	4	0.17	3	X
7.47	0.08	4	0.06	3	B
7.50	0.06	4	0.04	3	B
7.92	0.06	4	0.14	3	I
7.72	0.11	4	0.06	3	C
7.30	0.02	4	0.22	3	B
6.84	0.08	4	0.07	3	F
6.99	0.09	4	0.09	3	A
7.58	0.14	4	0.18	2	A
7.58	0.06	4	0.05	3	G
7.57	0.04	4	0.19	3	B
7.31	0.04	4	0.15	3	F
7.08	0.20	4	0.17	3	A
7.39	0.05	4	0.04	3	I
7.39	0.16	4	0.18	3	X
7.86	0.14	4	0.05	3	F
7.32	0.07	4	0.11	3	C

Total phosphorus					
y_i mg/L P	s_{ri} mg/L P	n_{ri}	s_{Li} mg/L P	n_{Li}	Method
1.53	0.01	4	0.02	3	B
1.50	0.04	4	0.06	3	X
1.67	0.05	4	0.05	3	DA
1.46	0.02	4	0.05	3	B
1.65	0.02	4	0.07	3	X
1.58	0.01	4	0.01	3	X
1.53	0.01	4	0.04	3	A
1.60	0.04	4	0.04	3	E
1.64	0.01	4	0.02	3	B
1.51	0.01	4	0.02	3	B
1.54	0.03	4	0.03	3	B
1.53	0.02	4	0.02	3	X
1.53	0.01	4	0.01	3	E
1.52	0.01	4	0.01	3	B
1.63	0.02	4	0.00	3	X
1.51	0.01	4	0.02	3	B
1.63	0.01	4	0.05	3	X
1.51	0.01	4	0.01	3	EA
1.60	0.01	4	0.02	3	E
1.55	0.01	4	0.01	3	B

External Control Values

y_i : average for laboratory i

s_{ri} : standard deviation for laboratory i within an analytical series
n_{ri} : number of results for determination of s_r

s_{Li} : standard deviation for laboratory i between analytical series
n_{Li} : number of results for determination of s_{Li}

Methods: See explanation on page 3-4

ANNEX TO CERTIFICATE QC WW3

Certifying Laboratories

Denmark
ALS Denmark A/S, Humlebæk
AnalyTech Miljølaboratorium A/S, Nørresundby
Eurofins Miljø A/S, Vejen
Hillerød Spildevand, Hillerød
Højvang Miljølaboratorium, Dianalund
Klarforsyning, Køge Egnens renseanlæg, Køge
RGS Nordic, Skælskør
Svendborg Spildevand A/S, Skårup Fyn
Vand Miljø Randers, Randers SØ
Vestforsyning, spildevand, Holstebro

Finland
SeiLab Oy, Haapauesi
Sydvästra Finlands vatten- och miljöundersökning Ab, Laboratorium, Åbo

Norway
Eurofins Environment Testing Norway AS, Moss
Labora AS, Bodø
Synlab AS, Hamar
TosLab AS, Tromsø

Sweden
Ernemar laboratorium, Oskarshamn
Gryaab AB, Göteborg
Laboratoriet vid Smedjeholms avloppsreningsverk, Falkenberg
Nordic Sugar AB, Eslöv
St1 Refinery AB, Laboratoriet, Göteborg
Södra Cell Värö, Väröbacka
VIVAB, Varberg

Åland
Ålands Miljö- och hälsoskyddsmyndighet Laboratoriet, Jomala-Åland