Eurofins Miljø A/S
Smedeskovvej 38
DK-8464 Galten

DANAK
RM Reg. nr. 535

VKI
REFERENCE MATERIALS

CERTIFICATE FOR

QC RW2

TOTAL NITROGEN AND TOTAL PHOSPHORUS IN RECIPIENT WATER

BATCH: VKI-10-5-0816

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 RW2 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 recipient 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 box, and at room temperature or in a refrigerator. The certificate is valid until **1st of April 2027** provided 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 Miljø A/S, with the aim of obtaining the intended quality of the material.

Documentation of Content
Internal control
The analytical quality of Eurofins Miljø 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 RW2. 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%), homogeneity was confirmed for TN and TP. In addition, homogeneity testing in accordance with ISO Guide 35 /1/ was included in the external control. Homogeneity was confirmed for TN and not confirmed for TP in the external control. For TP the between bottle standard deviation was taken into account in the uncertainty of the certified values.

Stability:
The stability of the reference material is being followed at 5°C, 20°C and 37°C.

External control
The concentration of TN and TP in the reference material was determined by selected laboratories in an external documentation in October-November 2016. 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 RW2: three samples in the same analytical series, one as a duplicate determination and the others as a single determination, and in addition 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:

$\overline{Y}$: average, calculated in accordance with ISO Guide 35 (section 10.5.2):

s_L : standard deviation between the laboratories, calculated in accordance with ISO Guide 35 (section 10.5.2):

$$\frac{1}{p-1}\sqrt{\sum\left(Y_i - \overline{Y}\right)^2}$$

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

$$\overline{Y} \pm t_{0,025}(\nu).\frac{s_L}{\sqrt{p}}$$

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 $\overline{Y} \pm t_{0,025}(\nu).\frac{s_L}{\sqrt{p}}$		NUMBER OF DATA SETS IN CALCULATIONS/ METHOD	EXCLUDED DATA SETS C: Cochran outlier G: Grubbs outlier
		$\overline{Y}$	s_L	Lower	Upper	(p)	
Total nitrogen	µg/L N	258	14.7	247	268	5/B 2/E 3/X	3C
Total phosphorus	µg/L P	200	6.3	194	206	2/A 6/B 1/D 1/E 3/F 7/G 2/X	1C

Methods

Total nitrogen:

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

E In-line digestion with peroxodisulphate under UV-irradiation and determination of the produced nitrate using the cadmium reduction method (ISO 29441).

X Other methods

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)

D Digestion by peroxodisulphate according to EN ISO 6878 and automated determination of orthophosphate by molybdenum blue method (flow-injection analysis, FIA).(EN ISO 15681-1).

E Manual digestion by peroxodisulphate according to EN ISO 6878 and automated determination of orthophosphate by molybdenum blue method (continuous flow analysis, CFA) (EN ISO 15681-2)

F Automated (in-line) digestion by peroxodisulphate and determination of orthophosphate by molybdenum blue method (continuous flow analysis, CFA) (EN ISO 15681-2)

G Lange (persulphate digestion and molybdate/ascorbic acid method) 0.05 – 1.5 mg/L P. (Lange LCK 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:

$$\overline{Y} \pm t_{0,025}(\nu).s_L$$

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

$$\overline{Y} \pm t_{0,025}(\nu).\frac{s_L}{\sqrt{2}}$$

REFERENCES

/1/ ISO Guide 35:2006. Certification of reference materials - General and statistical principles for certification.

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

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DIRECTOR

Brian Vangsgaard
Eurofins Miljø A/S
DK-8464 Galten

RESPONSIBLE SCIENTIST

Maj-Britt Fruekilde, PhD
Eurofins Miljø A/S
DK-8464 Galten

QUALITY DIRECTOR

Jette Groth
Eurofins Miljø A/S
DK-6600 Vejen

Certificate revision history: April 2017 (original certificate date)

ANNEX TO CERTIFICATE QC RW2

Laboratory Measurements

Total nitrogen					
Y_i µg/L N	s_{ri} µg/L N	n_{ri}	s_{Li} µg/L N	n_{Li}	Metode
245.2	13.49	4	7.83	3	B
236.8	5.66	4	4.04	3	X
245.6	6.37	4	15.46	3	E
240.5	4.11	4	4.76	3	B
280.0	14.93	4	5.95	3	B
266.5	7.20	4	2.19	3	B
267.2	2.94	4	3.51	3	X
270.0	8.04	4	4.00	3	B
268.0	12.34	4	4.44	3	X
258.3	1.73	4	16.31	3	E

Total phosphorus					
Y_i µg/L P	s_{ri} µg/L P	n_{ri}	s_{Li} µg/L P	n_{Li}	Metode
198.6	2.54	4	1.38	3	A
207.5	3.20	4	2.95	3	G
200.5	1.71	4	0.43	3	G
202.8	2.45	4	0.58	3	G
201.5	1.71	4	7.63	3	A
197.3	3.95	4	1.81	3	G
196.3	1.26	4	2.40	3	F
190.7	1.41	4	6.51	3	X
203.7	1.07	4	1.06	3	F
204.5	1.71	4	4.92	3	B
219.5	0.96	4	1.09	3	B
200.2	0.82	4	3.51	3	G
202.5	0.96	4	2.17	3	D
197.5	2.45	4	2.65	3	G
207.5	0.82	4	2.31	3	B
200.7	2.16	4	8.02	3	E
199.2	0.94	4	0.81	3	B
198.2	3.20	4	3.54	3	X
198.0	1.15	4	1.00	3	B
193.0	0.50	4	4.68	3	F
192.2	1.63	4	2.52	3	G
191.8	2.38	4	2.75	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_{ri}
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

ANNEX TO CERTIFICATE QC RW2

Certifying Laboratories

Denmark
AnalyTech Miljølaboratorium A/S, Nørresundby
Ekokem A/S, Nyborg
Eurofins Miljø A/S, Vejen
R/A Bjergmarken, Roskilde
Randers Spildevand, Randers SØ

Finland
Water and Environment Research of South-West Finland, Turku

Norway
Eurofins Environment Testing Norway AS, Moss
Fjellab, Rjukan
Hardanger Miljøsenter AS, Odda

Sweden
ALcontrol AB, Karlstad
AK Lab AB, Borås
Holmen Paper Braviken, Norrköping
Inovyn Sverige AB, Stenungsund
IVL-Svenska Miljöinstitutet AB, Göteborg
Laboratoriet vid Smedjeholms Avloppsreningsverk, Falkenberg
Nyköpings Kommun, Vattenlaboratoriet, Nyköping
Processlab, Gävle
Reningsverket Aggerud, Karlskoga
Södra Cell Mönsterås, Mönsterås
Tekniska Verken i Linköping AB, Linköping
VA-avdelingen, Laboratoriet, Nynäshamns Kommun, Nynäshamn
Vimmerby Energi o Miljö AB, Vattenlab, Vimmerby

Åland
ÅMHM Laboratoriet, Jomala