

CERTIFICATE FOR

QC WW2.1

NUTRIENTS FOR WASTE WATER ANALYSES

BATCH: VKI-6-6-0113

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 ammonium-nitrogen (NH₄-N) and orthophosphate-phosphorus (PO₄-P).

Quantity and Preservation

QC WW2.1 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 of April 2021** 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.

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 NH₄-N and PO₄-P in randomly selected ampoules of QC WW2.1. 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 in accordance with ISO Guide 35 /1/ 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 NH₄-N and PO₄-P in the reference material was determined by selected laboratories in an external documentation in April-May 2013. 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 WW2.1: 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:

\bar{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):

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

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

$$\bar{Y} \pm t_{0,025}(v) \cdot \frac{s_L}{\sqrt{p}}$$

where

p: number of laboratories included in calculations

v: p-1, degrees of freedom

$t_{0,025}(v)$: t value of 0,025 level at v 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		NUMBER OF DATA SETS IN CALCULATIONS/METHOD	EXCLUDED DATA SETS C: Cochran outlier G: Grubbs outlier
				$\bar{Y} \pm t_{0,025}(v) \cdot \frac{s_L}{\sqrt{p}}$			
		\bar{Y}	s_L	Lower	Upper	(p)	
Ammonium-N (NH ₄ -N)	mg/L N	9.9	0.34	9.8	10.0	4/A 2/B 1/D 7/E 3/I 5/J 1/JA 5/X	3C
Orthophosphate-P (PO ₄ -P)	mg/L P	4.97	0.16	4.90	5.04	4/A 8/B 5/E 2/H 1/HA 1/I 2/X	1C

Methods

Ammonium-N:

- A Reaction with the hypochlorite/phenol in an alkaline environment to form an indophenol blue compound and spectrophotometric measurement. (DS 224; SFS 3032; NS 4746; SS 28134)
- B Reaction with the hypochlorite ions and salicylate in an alkaline environment to form an indophenol blue compound in the presence of sodium nitroprusside and spectrophotometric measurement. (ISO 7150-1)
- D Gas diffusion. (The Tecator method)
- E Reaction with hypochlorite/phenol in an alkaline environment to form an indophenol blue compound, applying flow analysis and spectrophotometric measurement. (EN ISO 11732)
- I Lange (hypochlorite/salicylat method). 1 - 12 mg/L NH₄-N. (Lange LCK 305)
- J Lange 2.0-47 mg/L NH₄-N. (Lange LCK 303)
- JA Lange 2.0-47 mg/L NH₄-N. (Lange APC 303)
- X Other methods

Orthophosphate-P:

- A Reaction with ammonium molybdate and reduction with ascorbic acid to molybdenum blue. (DS 291; SFS 3025; NS 4724; SS 028126)
- B Reaction with molybdate and antimony ions and reduction with ascorbic acid to molybdenum blue. (EN ISO 6878, part 4)
- E Reaction with molybdate and antimony ions and reduction with ascorbic acid to molybdenum blue. Determination using CFA. (EN ISO 15681-2)
- H Lange (ortho/total phosphate) 2.0-20 mg/L PO₄-P. (Lange LCK 350)
- HA Lange (ortho/total phosphate) 2.0-20 mg/L PO₄-P. (Lange APC 350)
- I Lange (ortho/total phosphate) 0.5-25 mg/L PO₄-P. (Lange LCK 348)
- 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:

$$\bar{Y} \pm t_{0,025}(v) \cdot s_L$$

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

$$\bar{Y} \pm t_{0,025}(v) \cdot \frac{s_L}{\sqrt{2}}$$

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.

Date of issue: June 2018

DIRECTOR

Jesper Gamst
Eurofins Miljø A/S
DK-8464 Galten

RESPONSIBLE SCIENTIST

Stine Ottsen
Eurofins Miljø A/S
DK-8464 Galten

QUALITY DIRECTOR

Jette Groth
Eurofins Miljø A/S
DK-6600 Vejen

Certificate revision history: June 2018 (expiry date extended); July 2014 (original certificate date)

ANNEX TO CERTIFICATE QC WW2.1

Laboratory Measurements

Ammonium-N					
Y _i mg/L N	S _{ri} mg/L N	n _{ri}	S _{Li} mg/L N	n _{Li}	Method
10.01	0.174	4	0.095	3	J
10.51	0.086	4	0.105	3	E
10.38	0.050	4	0.142	3	I
9.93	0.034	4	0.070	3	E
9.93	0.039	4	0.137	3	E
9.79	0.049	4	0.036	3	B
9.48	0.050	4	0.292	3	E
9.66	0.100	4	0.299	3	J
10.50	0.016	4	0.281	3	X
9.90	0.065	4	0.071	3	E
9.71	0.060	4	0.137	3	JA
9.64	0.024	4	0.066	3	B
9.42	0.058	4	0.346	3	D
9.60	0.050	4	0.126	3	I
10.28	0.096	4	0.245	3	E
9.82	0.096	4	0.056	3	X
9.56	0.042	4	0.140	3	E
9.75	0.106	4	0.090	3	J
9.67	0.050	4	0.032	3	J
10.31	0.000	4	0.242	3	X
10.65	0.358	4	0.158	3	X
9.55	0.082	4	0.014	3	A
9.70	0.237	4	0.161	3	J
9.53	0.187	4	0.106	3	I
10.30	0.058	4	0.087	3	A
9.94	0.052	4	0.011	3	A
9.89	0.156	4	0.195	3	X
9.77	0.149	4	0.355	3	A

Orthophosphat-P					
Y _i mg/L P	S _{ri} mg/L P	n _{ri}	S _{Li} mg/L P	n _{Li}	Method
5.06	0.034	4	0.040	3	A
5.07	0.148	4	0.020	3	H
5.04	0.021	4	0.184	3	B
5.05	0.049	4	0.034	3	B
4.63	0.050	4	0.052	3	E
4.98	0.025	4	0.024	3	H
5.03	0.022	4	0.184	3	E
5.09	0.006	4	0.098	3	X
5.02	0.042	4	0.015	3	B
4.94	0.013	4	0.078	3	HA
5.00	0.059	4	0.069	3	E
4.65	0.024	3			E
4.64	0.051	4	0.196	3	B
4.84	0.005	4	0.005	3	A
5.08	0.082	4	0.058	3	X
4.95	0.142	4	0.132	3	E
4.80	0.043	4	0.131	3	B
5.17	0.010	4	0.012	3	B
5.03	0.026	4	0.024	3	B
5.12	0.025	4	0.060	3	B
5.20	0.104	4	0.104	3	A
4.91	0.020	4	0.006	3	A
5.08	0.030	4	0.045	3	I

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 WW2.1

Certifying Laboratories

Denmark

Analyseenheden, Inst. Agroøkologi, Aarhus Universitet, Tjele
Eurofins Miljø A/S, Vejen
Force Technology, Brøndby
Højvang Miljølaboratorium, Dianalund
Lynettefællesskabet I/S, København K
R/A Bjergmarken, Roskilde
Randers Spildevand, Randers
Sønderborg Renseanlæg, Sønderborg
Vandsamarbejdet A/S, Holstebro

Finland

Boliden Kokkola, Kokkola
Metropolilab, Helsinki
Novalab Oy, Karkkila
Ramboll Analytics, Lahti
University of Jyväskylä, Institute for Environmental Research, Jyväskylä
Water and Environment Research of South-West Finland, Turku

Norway

Eurofins Environment Testing Norway AS, Bergen
Eurofins Environment Testing Norway AS, Moss
TosLab AS, Tromsø

Sweden

ALcontrol AB, Karlstad
ALcontrol AB, Linköping
ALcontrol AB, Umeå
Bravikens Pappersbruk, Norrköping
Eurofins Environment Testing Sweden AB, Lidköping
Kristianstad Kommun, C4-Teknik, VA-Lab, Kristianstad
Ineos Sweden AB, Stenungsund
Ljungby Kommun, Avloppsreningsverk, Ljungby
Motala Kommun, Tekniska Förvaltningen Vatten & Återvinning, Motala
Nyköping kommun, Vattenlaboratoriet, Nyköping
Preemraff, Lysekil
St1 Refinery AB, Göteborg
Uddebo Laboratorium, Luleå
VA-avdelingen, Nynäshamns Kommun, Nynäshamn
VIVAB, Varberg