

CERTIFICATE FOR

QC WW3

TOTAL NITROGEN AND TOTAL PHOSPHORUS FOR WASTE WATER ANALYSES

BATCH: VKI-7-7-0113

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 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 2021** 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.

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 in accordance with ISO Guide 35 /1/ was included in the external control. Homogeneity was confirmed for total nitrogen (TN) and not confirmed for total phosphorus in the external control. For total phosphorus 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, 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 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 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:

\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
				Lower	Upper		
		\bar{Y}	s_L	$\bar{Y} \pm t_{0,025}(v) \cdot \frac{s_L}{\sqrt{p}}$		(p)	C: Cochran outlier G: Grubbs outlier
Total nitrogen	mg/L N	7.5	0.27	7.4	7.6	4/A 9/B 2/C 5/F 4/I 1/IA 5/X	2C
Total phosphorus	mg/L P	1.51	0.046	1.47	1.55	1/A 14/B 10/E 1/EA 3/X	4C

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 + SM¹ 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)
- 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

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

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

- 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:

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

- 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

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

ANNEX TO CERTIFICATE QC WW3

Laboratory Measurements

Total nitrogen					
Y _i µg/L N	s _{ri} µg/L N	n _{ri}	s _{Li} µg/L N	n _{Li}	Method
7.53	0.036	4	0.149	3	F
7.46	0.031	4	0.114	3	B
7.29	0.040	4	0.046	3	C
7.62	0.131	4	0.079	3	B
7.20	0.088	4	0.130	3	B
7.49	0.084	4	0.161	3	F
7.39	0.079	4	0.166	3	F
7.52	0.025	4	0.028	3	B
7.82	0.117	4	0.100	3	A
7.46	0.068	4	0.135	3	B
6.82	0.127	4	0.106	3	IA
7.54	0.052	4	0.166	3	I
7.55	0.077	4	0.103	3	X
7.84	0.065	4	0.154	3	I
7.33	0.040	4	0.138	3	I
7.40	0.045	4	0.136	3	B
8.31	0.104	4	0.170	3	X
7.31	0.172	4	0.151	3	B
7.56	0.076	4	0.014	3	F
7.35	0.090	4	0.125	3	A
7.39	0.033	4	0.125	3	C
7.39	0.054	4	0.217	3	B
7.60	0.022	4	0.140	3	A
7.52	0.163	4	0.266	3	X
7.92	0.175	4	0.107	3	I
7.15	0.041	4	0.068	3	B
7.82	0.087	4	0.060	3	A
7.59	0.040	4	0.066	3	X
7.34	0.037	4	0.022	3	X
7.63	0.031	4	0.054	3	F

Total phosphorus					
Y _i µg/L N	s _{ri} µg/L N	n _{ri}	s _{Li} µg/L N	n _{Li}	Metode
1.49	0.007	4	0.023	3	E
1.45	0.015	4	0.035	3	B
1.56	0.056	4	0.012	3	B
1.60	0.018	4	0.026	3	E
1.48	0.008	4	0.015	3	E
1.53	0.037	4	0.035	3	B
1.53	0.000	4	0.025	3	X
1.57	0.040	3			B
1.51	0.007	4	0.002	3	X
1.43	0.019	4	0.025	3	EA
1.52	0.005	4	0.004	3	E
1.49	0.002	4	0.017	3	B
1.50	0.019	4	0.018	3	E
1.61	0.015	4	0.017	3	B
1.61	0.007	4	0.015	3	X
1.51	0.023	4	0.025	3	B
1.50	0.010	4	0.012	3	E
1.51	0.008	4	0.015	3	B
1.48	0.014	4	0.023	3	B
1.48	0.013	4	0.023	3	A
1.48	0.013	4	0.016	3	B
1.52	0.010	4	0.023	3	E
1.46	0.015	4	0.007	3	E
1.46	0.013	4	0.010	3	B
1.58	0.026	4	0.026	3	B
1.51	0.006	4	0.009	3	B
1.49	0.000	4	0.010	3	B
1.51	0.021	4	0.030	3	E
1.48	0.005	4	0.001	3	E

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

Danmark

AnalyTech Miljølaboratorium A/S, Nørresundby
Eurofins Miljø A/S, Vejen
Højvang Miljølaboratorium, Dianalund
Lynettefællesskabet I/S, København K
R/A Bjergmarken, Roskilde
Randers Spildevand, Randers SØ
Sønderborg Renseanlæg, Sønderborg
Vandsamarbejdet A/S, Holstebro

Finland

Metropolilab OY, Helsinki
Novalab Oy, Karkkila
Ramboll Analytics, Lahti
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

Akzo Nobel Functional Chemicals AB, Stenungsund
ALcontrol AB, Linköping
ALcontrol AB, Umeå
Bravikens Pappersbruk, Norrköping
Eurofins Environment Testing Sweden AB, Lidköping
Iggesund Paperboard AB, Iggesund
Ineos Sverige AB, Stenungsund
Kristianstad Kommun, C4-Teknik, VA-Lab, Kristianstad
Ljungby Kommun, Avloppsreningsverk, Ljungby
Motala Kommun, Tekniska Förvaltningen Vatten, Motala
Norrköping Vatten AB, Laboratoriet Slottshagens Reningsverk, Norrköping
Preemraff Lysekil, Lysekil
Smurfit Kappa Kraftliner, Piteå
St1 Refinery AB, Laboratoriet, Göteborg
Stora Enso Printing and Reading, Hyltebruk
Södra Cell Mönsterås AB, Mönsterås
Södra Cell Värö, Väröbacka
Uddebo Laboratorium, Luleå
VA SYD DON, Malmö
VA-avdelingen, Nynäshamns Kommun, Nynäshamn
VIVAB, Varberg

Åland

Ålands Miljö- och hälsoskyddsmyndighet Laboratoriet, Jomala-Åland