

CERTIFICATE FOR

QC WW1B

NUTRIENTS FOR WATER ANALYSIS

BATCH: VKI-5-5-0310

INSTRUCTIONS FOR USE OF THE REFERENCE MATERIAL

Description

This reference material consists of an ampoule with concentrate for preparation of a reference sample for quality control after dilution with water. The certificate includes documentation for the analytical parameters nitrate, ammonium and orthophosphate.

Quantity and Preservation

QC WW1B contains ampoules with minimum 10 mL concentrate in each. 1 L reference sample is produced by dilution of 10 mL concentrate. The concentrate has been 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 wastewater. 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. For these purposes other dilutions may be appropriate.

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

Preparation for Use

Stabilise the ampoule at room temperature (approx. 20°C). Break the ampoule neck open at the mark, withdraw the concentrate with a pipette, dilute with nutrient depleted water 1:100, e.g. 2.00 mL concentrate up to 200 mL with distilled water. The certified concentrations are given in the table on page 3 of this certificate.

If QC WW1B is used for other purposes than quality control of wastewater analyses, the dilution ratio between the concentrate and water can be altered. Please note that the certified value and the confidence limits are only valid for the prescribed dilution ratio 1:100.

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 2025** provided the material is stored under the recommended conditions.

After preparation, 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 concentrate (dilution ratio 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 nitrate, ammonium and orthophosphate in randomly selected ampoules of QC WW1B. 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 ampoule (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 nitrate, ammonium and orthophosphate in the reference material was determined by selected laboratories in an external documentation during spring 2011. 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 ampoules: three ampoules in the same analytical series, one by duplicate determination, and two ampoules 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.2.5.3):

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

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

$$y_{char} \pm t_{0,025}(v) \cdot \frac{s(y)}{\sqrt{p}}$$

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 that the laboratories perform the analyses on a routine basis. Furthermore, the laboratories were selected on the basis of their results in proficiency tests and earlier certifications.

The criteria for selection of laboratories from Denmark, Norway and Sweden were as follows:

- the laboratory results in the proficiency tests diverged less than 2 standard deviations from the nominal value, and
- the laboratory analyses more than 20 analytical series each year or holds accreditation for the parameter.

For Finnish laboratories the Finnish Reference Laboratory has identified the laboratory as qualified.

In addition, the criteria are:

- 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

Critical Value							
DETERMINAND	UNIT	AVERAGE	BETWEEN LABORATORY STANDARD DEVIATION	95% CONFIDENCE LIMITS OF THE AVERAGE VALUE		NUMBER OF DATA SETS IN CALCULATIONS/ METHOD	EXCLUDED DATA SETS
				$y_{char} \pm t_{0,025}(v) \cdot \frac{s(y)}{\sqrt{p}}$			C: Cochran outlier G: Grubbs outlier
		y_{char}	$s(y)$	Lower	Upper	(p)	
Nitrate-nitrogen (NO ₃ -N)	mg/L N	4.96	0.127	4.90	5.02	10 / A 6 / E 5 / G	1 C
Ammonium-nitrogen (NH ₄ -N)	mg/L N	1.00	0.0276	0.98	1.01	2 / A 1 / B 1 / C 4 / D 7 / E 1 / G	2 C
Orthophoshate- phosphorus (PO ₄ -P)	mg/L P	0.498	0.0109	0.493	0.504	4 / A 9 / B 4 / E 2 / G	1 C

Methods

NO₃:

- A: Reduction on a Cd-Hg- or Cd-Cu-column to NO₂. Formation of a diazonium salt with sulfanilamide, coupling with N-(1-naphtyl)-ethylenediamine and spectrophotometric measurement of azo dye (Nordic standard methods: DS 223, SFS 3030, NS 4745, SS 28133)
- E: Testkit from Hach-Lange (LCK 339)
- G: Other methods

NH₄:

- A: Reaction with the hypochlorite/phenol in an alkaline environment to form an indophenol blue compound. Spectrophotometric measurement (Nordic standard methods: 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. Spectrophotometric measurement. (ISO 7150-1)
- C: FIA-method, gas diffusion -Tecator method
- D: Reaction with hypochlorite/phenol in an alkaline environment to form an indophenol blue compound, applying flow analysis and spectrophotometric measurement (EN ISO 11732)

E Testkit from Hach-Lange (LCK 304)
G: Other methods

PO₄:

A: Reaction with ammonium molybdate and reduction with ascorbic acid to molybdenum blue (Nordic standard methods: DS 291, SFS 3025, NS 4724, SS 28126)
B: Reaction with ammonium molybdate and reduction with ascorbic acid to molybdenum blue (EN ISO 6878, part 4)
E: Testkit from Hach-Lange (LCK 349)
G: 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:

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

REFERENCES

- /1/ ISO Guide 35:2017. Reference materials – Guidance for characterization and assessment of homogeneity and stability.
/2/ ISO Guide 31:2015. Reference materials - Contents of certificates, labels and accompanying documentation.

Date of issue: April 2021

RESPONSIBLE SCIENTIST

Rikke Mikkelsen
Eurofins Miljø A/S
DK-8464 Galten

Certificate revision history: April 2021 (expiry extended; update of references); September 2019 (expiry date extended); April 2017 (expiry date extended); April 2015 (expiry date extended); December 2013 (expiry date added); December 2011 (error of units corrected); April 2011 (original certificate date)

ANNEX TO CERTIFICATE QC WW1B

Laboratory Measurements

Nitrate					
y _i mg/L N	S _{ri} mg/L N	n _{ri}	S _{Li} mg/L N	n _{Li}	Method
5.00	0.065	4	0.075	3	A
5.06	0.014	4	0.030	3	A
5.02	0.081	4	0.048	3	A
4.87	0.032	3	0.013	3	A
4.89	0.161	4	0.091	3	G
4.85	0.015	4	0.026	3	G
5.08	0.017	4	0.015	3	G
4.90	0.033	4	0.019	3	E
5.12	0.029	4	0.040	3	A
4.86	0.036	4	0.089	3	A
4.93	0.022	4	0.032	3	A
5.24	0.015	4	0.091	3	G
5.15	0.015	4	0.123	3	A
4.98	0.013	4	0.171	3	A
4.85	0.050	4	0.035	3	E
4.79	0.013	4	0.038	3	E
5.09	0.035	4	0.010	3	E
4.91	0.034	4	0.072	3	E
5.00	0.050	4	0.066	3	G
4.76	0.041	4	0.085	3	E
4.86	0.127	4	0.031	3	A

Ammonium					
y _i mg/L N	S _{ri} mg/L N	n _{ri}	S _{Li} mg/L N	n _{Li}	Method
1.02	0.0062	4	0.0067	3	A
0.99	0.0032	3	0.0028	3	D
0.97	0.0034	4	0.0005	3	E
0.97	0.0074	4	0.0030	3	E
1.04	0.0126	4	0.0139	3	D
0.97	0.0051	4	0.0135	3	B
1.00	0.0039	4	0.0188	3	D
1.05	0.0215	4	0.0197	3	G
1.02	0.0050	4	0.0331	3	C
1.00	0.0197	4	0.0115	3	A
0.98	0.0039	4	0.0229	3	E
1.02	0.0096	4	0.0166	3	E
0.96	0.0056	4	0.0105	3	E
0.97	0.0182	4	0.0115	3	E
0.97	0.0226	4	0.0279	3	D
0.98	0.0059	4	0.0086	3	E

Orthophosphate					
y_i mg/L P	s_{ri} mg/L P	n_{ri}	s_{Li} mg/L P	n_{Li}	Method
0.526	0.0123	4	0.0122	3	B
0.509	0.0021	4	0.0014	3	A
0.490	0.0036	3	0.0029	3	B
0.484	0.0176	4	0.0046	3	A
0.497	0.0017	4	0.0028	3	B
0.501	0.0010	4	0.0034	3	G
0.494	0.0029	4	0.0076	3	E
0.481	0.0154	4	0.0111	3	B
0.480	0.0049	4	0.0100	3	B
0.508	0.0049	4	0.0186	3	B
0.504	0.0087	4	0.0075	3	G
0.503	0.0027	4	0.0095	3	A
0.499	0.0035	4	0.0019	3	A
0.497	0.0027	4	0.0029	3	E
0.499	0.0005	4	0.0059	3	B
0.510	0.0041	4	0.0014	3	E
0.500	0.0100	4	0.0020	3	E
0.493	0.0030	4	0.0206	3	B
0.492	0.0066	4	0.0030	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 WW1B

Certifying Laboratories

Denmark

Analytech Miljølaboratorium A/S, Nørresundby
Bjergmarken R/A, Roskilde
Danmarks Miljøundersøgelser, Silkeborg
Eurofins Miljø A/S, Vejle
LabVest I/S, Holstebro
Lynettefællesskabet I/S, København K
Randers Spildevand, Randers
Vand og Affald, Svendborg

Finland

Lounais-Suomen vesi- ja ympäristötutkimus Oy, Turku
Metropolilab, Helsinki

Norway

LabNett, Skien
Mjøslab IKS, Gjøvik
Nedre Romerike Vannverk IKS avd. NorAnalyse, Strømmen

Sweden

ALcontrol AB, Karlstad
ALcontrol AB, Linköping
Ernemar Laboratorium, Oskarshamn
Klippans reningsverk, Klippan
Motala Kommun Tekniska förvaltningen Vatten, Motala
Nynäshamns kommun VA-avdelningen Laboratoriet, Nynäshamn
Shell Raffinaderi AB, Göteborg
VIVAB, Varberg
Örtofta Sockerbruk, Eslöv