

CERTIFICATE FOR
QC RW1
NUTRIENTS IN RECIPIENT WATER

BATCH: VKI-9-5-0112

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 nitrate-nitrogen ($\text{NO}_3\text{-N}$), ammonium-nitrogen ($\text{NH}_4\text{-N}$) and orthophosphate-phosphorus ($\text{PO}_4\text{-P}$).

Quantity and Preservation

QC RW1 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 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 NO₃-N, NH₄-N and PO₄-P in randomly selected ampoules of QC RW1. 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 NO₃-N, NH₄-N and PO₄-P in the reference material was determined by selected laboratories in an external documentation in April-May 2012. 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 RW1: 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 \bar{Y}	BETWEEN LABORATORY STANDARD DEVIATION s_L	95% CONFIDENCE LIMITS OF THE AVERAGE VALUE $\bar{Y} \pm t_{0,025}(v) \cdot \frac{s_L}{\sqrt{p}}$		NUMBER OF DATA SETS IN CALCULATIONS/METHOD (p)	EXCLUDED DATA SETS C: Cochran outlier G: Grubbs outlier
				Lower	Upper		
Nitrate-N (NO ₃ -N)	µg/L N	99	2.6	97	100	2/A 8/C 2/X	4C
Ammonium-N (NH ₄ -N)	µg/L N	101	3.4	99	102	9/A 2/B 1/C 8/D 2/H 1/X	3C
Orthophosphate-P (PO ₄ -P)	µg/L P	100	2.8	98	101	6/A 7/B 1/D 1/E 1/F	6C

Methods

Nitrate-N:

- A Reduction on a Cd-Hg- or Cd-Cu-column to NO₂. Formation of a diazonium salt with sulfanilamid, coupling with N-(1-naphtyl)-ethylendiamin and spectrophotometric measurement of azo dye. (DS 223; SFS 3030; NS 4745; SS 28133)
- C Reduction on a Cd-Hg- or Cd-Cu-column to NO₂. Formation of a diazonium salt with sulfanilamid, coupling with N-(1-naphtyl)-ethylendiamin and spectrophotometric measurement of azo dye. Determination using CFA or FIA. (EN ISO 13395)
- X Other methods

Ammonium-N:

- A Reaction with the hypochlorite/phenol in an alcalic environment to form an indo phenol blue compound and spectrophotometric measurement. (DS 224; SFS 3032; NS 4746; SS 28134)
- B Reaction with the hypochlorite ions and salicylat in an alcalic environment to form an indo phenol blue compound in the presence of sodium nitroprussid and spectrophotometric measurement. (ISO 7150-1)
- C Gas diffusion. (The 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)
- H Lange (hypochlorite/salicylat method). 0.015 – 2.0 mg/L NH₄-N. (Lange LCK 304)
- 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)
- D Reaction with ammonium molybdate and reduction with tin(II)chloride to molybdenum blue. Determination using FIA. (EN ISO 15681-1)
- E Reaction with molybdate and antimony ions and reduction with ascorbic acid to molybdenum blue. Determination using CFA. (EN ISO 15681-2)
- F Lange (molybdate/ascorbic acid method) 0.05-1.5 mg/L PO₄-P. (Lange LCK 349)

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 31:2000 Reference materials - Contents of certificates and labels.

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Certificate revision history: June 2016 (expiry date extended); December 2013 (expiry date added); July 2012 (original certificate date)

ANNEX TO CERTIFICATE QC RW1

Laboratory Measurements

Nitrate-N					
Y _i µg/L N	s _{ri} µg/L N	n _{ri}	s _{Li} µg/L N	n _{Li}	Method
93.76	2.25	4	1.29	2	C
96.85	1.75	4	2.32	3	C
98.79	0.44	4	0.96	3	C
97.23	0.59	4	1.05	3	C
99.18	0.73	4	1.76	3	C
99.88	2.79	4	1.85	3	A
98.55	1.23	4	2.60	3	C
96.92	2.08	4	1.40	3	C
100.00	0.58	4	0.87	3	A
101.67	2.08	4	1.44	3	X
98.55	0.65	4	2.19	3	C
103.83	1.23	4	3.47	3	X

Ammonium-N					
Y _i µg/L N	s _{ri} µg/L N	n _{ri}	s _{Li} µg/L N	n _{Li}	Method
100.38	1.93	4	0.80	3	A
98.05	2.76	4	4.73	3	D
101.18	0.90	4	2.64	3	D
98.15	2.17	4	1.42	3	D
102.33	2.94	4	9.02	3	B
100.81	1.20	4	1.57	3	A
101.67	5.32	4	6.91	3	D
103.33	2.45	4	4.62	3	X
104.50	0.96	4	4.26	3	C
104.62	6.61	4	3.46	3	D
105.78	1.28	4	1.68	3	A
106.08	2.82	4	2.56	3	D
100.50	1.29	4	0.50	3	A
97.83	3.97	4	7.07	3	H
94.67	1.13	4	2.63	3	D
101.62	2.56	3	8.88	2	A
102.40	0.82	4	4.91	3	D
98.50	2.63	4	2.05	3	H
99.67	0.33	4	1.70	3	A
91.67	3.92	4	4.62	3	A
101.50	1.50	4	3.27	3	A
100.00	0.96	4	2.02	3	B
99.63	3.57	4	3.31	3	A

Orthophosphate-P					
Y_i µg/L P	s_{ri} µg/L P	n_{ri}	s_{Li} µg/L P	n_{Li}	Method
99.37	0.41	4	0.94	3	A
99.25	1.76	4	0.90	3	A
95.95	0.82	4	2.06	3	D
98.20	1.74	4	2.68	3	B
102.33	1.26	4	0.88	3	F
97.17	0.00	4	0.58	3	E
102.67	2.16	4	1.15	3	B
96.58	0.25	4	0.66	3	B
99.45	0.86	4	1.04	3	B
104.50	0.60	4	1.99	3	B
96.67	0.58	4	0.29	3	B
98.98	0.84	4	0.86	3	A
100.00	1.26	4	0.66	3	A
99.33	2.75	4	1.51	3	A
100.00	0.96	4	2.02	3	B
105.90	2.43	4	1.52	3	A

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 3-4

ANNEX TO CERTIFICATE QC RW1

Certifying Laboratories

Denmark

AnalyTech Miljølaboratorium A/S, Nørresundby,
Højvang Miljølaboratorium, Dianalund
LabVest, Holstebro
Milana A/S, Humlebæk
Århus Universitet, Silkeborg

Finland

Kainuun Elintarvike- ja ympäristölaboratorion, Kajaani
Maintpartner Oy, Laboratorio, Kokkola
MetropoliLab Oy, Helsinki
Novalab Oy, Karkkila
Ramboll Analytics, Lahti
Water and Environment Research of South-West Finland, Turku

Germany

LUFA-ITL GmbH, Kiel

Norway

Eurofins Environment Testing Norway AS, Bergen
Eurofins Environment Testing Norway AS, Moss
Hardanger Miljøsender AS, Odda
Labora, Bodø
Nedre Romerike Vannverk IKS, avd. NorAnalyse, Strømmen

Sweden

ALcontrol AB, Linköping
ALcontrol AB, Umeå
Eurofins Environment Testing Sweden AB, Lidköping
Ineos Sverige AB, Stenungsund
Jönköpings Kommun, VA-lab, Jönköping
Nyköping Vatten, Vattenlaboratoriet, Nyköping
St1 Refinery AB, Göteborg
Örtofta Sockerbruk, Eslöv

Åland

Ålands Miljö- och hälsoskyddsmyndighet Laboratoriet, Jomala-Åland