

**DANAK**
RM Reg.no. 535
Member EA MLA**CERTIFICATE FOR****QC RW1****NUTRIENTS IN RECIPIENT WATER****BATCH:** VKI-9-6-0123**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 September 2028** 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 June-July 2023. 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:

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):

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

where

y_i : average for laboratory i

p: number of laboratories included in calculations

U_{CRM} : Expanded uncertainty of the certified reference material, calculated in accordance with ISO Guide 35 (section 10.2) with coverage factor $k = 2$.

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	EXPANDED UNCERTAINTY ON CERTIFIED VALUE	NUMBER OF DATA SETS IN CALCULATIONS/ METHOD	EXCLUDED DATA SETS C: Cochran outlier G: Grubbs outlier
		y_{char}	$s(y)$	U_{CRM}	(p)	
Nitrate-N (NO ₃ -N)	mg/L N	99	3.7	10	2/A1 7/A2 2/A3 3/B	2C
Ammonium-N (NH ₄ -N)	mg/L N	101	3.2	7.9	1/B1 7/B2 1/E	4C 1G (Straggler)
Orthophosphate-P (PO ₄ -P)	mg/L P	99	5.0	5.8	4/A1 6/A2 5/A3 1/B	1C

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.
A1 Manual, NS 4745
A2 CFA or FIA, EN ISO 13395, DS 223 Scalar
A3 Discrete analysis systems, ISO 15923-1, EPA-126-C
- B Determination by liquid chromatography of ions, EN ISO 10304-1

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)
A1 Manual,
A2 CFA or FIA, SM 17, 4500-NH₃-H, DS 224 Scalar
A3 Discrete analysis systems, EPA-150-C
- 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.
B1 Manual, ISO 7150-1
B2 CFA or FIA, ISO 11732 (CFA)
B3 Discrete analysis systems, ISO 15923-1
- D Determination by liquid chromatography of ions, EN ISO 14911
- H Lange (hypochlorite/salicylat method). 0.015 – 2.0 mg/L NH₄-N. (Lange LCK 304)

Orthophosphate-P:

- A Reaction with ammonium molybdate and reduction with ascorbic acid to molybdenum blue.
A1 Manual, NS 4724, EN ISO 6878, part 4
A2 CFA or FIA, EN ISO 15681-2, DS 291 Scalar
A3 Discrete analysis systems, ISO 15923-1, EPA-118-C
- B Determination by liquid chromatography of ions, EN ISO 10304-1

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: August 2023

RESPONSIBLE SCIENTIST



Rikke Mikkelsen, MSc
Eurofins Miljø A/S
DK-8464 Galten

E-mail: refmat@eurofins.dk

Website: www.eurofins.dk/refmat

Certificate revision history: August 2023 (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}	Methods
99.3	1.65	4	3.81	3	A2
99.9	0.41	4	1.83	3	A1
95.9	0.95	4	4.69	3	A2
99.9	2.71	4	5.80	3	B
103.8	4.39	4	7.51	3	B
107.1	3.24	4	5.80	3	A2
98.5	0.19	4	1.89	3	A2
95.4	0.26	4	4.74	3	B
100.2	8.50	4	4.47	3	A3
94.1	2.10	4	4.51	3	A1
103.3	5.77	4	2.89	3	A2
98.6	1.08	4	1.10	3	A2
94.3	1.29	3	2.05	3	A2
98.3	5.97	4	5.86	3	A3

Ammonium-N					
y_i µg/L N	s_{ri} µg/L N	n_{ri}	s_{Li} µg/L N	n_{Li}	Methods
107.0	2.43	4	2.38	3	B2
101.1	1.28	4	0.31	3	B2
102.4	0.42	4	3.61	3	B2
97.1	5.68	4	0.74	3	B1
99.1	0.57	4	1.15	3	B2
100.5	0.96	4	2.05	3	E
100.0	0.97	4	2.25	3	B2
97.6	1.31	3	2.94	3	B2
104.6	4.16	4	1.87	3	B2

Orthophosphate-P					
y_i µg/L P	s_{ri} µg/L P	n_{ri}	s_{Li} µg/L P	n_{Li}	Methods
103.4	2.56	4	1.80	3	A3
104.1	3.08	4	2.86	3	A2
98.5	0.63	4	0.51	3	A2
97.5	0.10	4	1.48	3	A3
88.9	1.98	4	4.03	3	A3
102.0	1.17	4	1.85	3	A2
95.5	0.40	4	3.42	3	A3
99.1	1.52	4	5.84	3	A2
101.9	0.68	4	1.19	3	A2
110.8	2.16	4	5.13	3	A1
92.8	0.95	4	4.70	3	B
101.0	1.26	4	0.66	3	A3
97.0	2.08	4	4.44	3	A1
99.0	0.65	4	0.90	3	A2
102.4	0.61	3	1.80	3	A1
97.2	0.78	4	1.83	3	A1

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 RW1

Certifying Laboratories

Danmark

Aarhus Universitet, Ecoscience, Roskilde
BIOFOS Spildevand og driftslab, Avedøre
Eurofins Miljø A/S, Vejen
Højvang Laboratorier A/S, Dianalund
Højvang Laboratorier A/S, Holstebro

Norge

Eurofins Environment Testing Norway AS, Moss
FJELLAB, Rjukan
Labora AS, Bodø
Norsk Institutt for vannforskning (NIVA), Oslo
SGS Analytics Norway AS, Hamar
Vann- og avløpsetaten, Oslo kommune, Oslo
VestfoldLAB AS, Sem

Sverige

DGE Mark & Miljö AB, Västra Frölunda
Eurofins Water Testing Sweden AB, Lidköping
GRYAAB AB, Göteborg
Karlskrona kommuns laboratorium, Lyckeby
Norrvattens Laboratorium, Järfälla

Finland

ÅMHM Laboratoriet, Jomala Åland