

## CERTIFICATE FOR

## QC SW3.1B

## NUTRIENTS IN NATURAL COASTAL/ESTUARINE WATER

**BATCH:** VKI-32-3-0910

### INSTRUCTIONS FOR USE OF THE REFERENCE MATERIAL

#### Description

This reference material consists of a glass bottle with a natural reference sample for quality control. The certificate includes documentation for the analytical parameters Ammonium (NH<sub>4</sub>), Nitrite (NO<sub>2</sub>), Nitrite+Nitrate (NO<sub>2+3</sub>, or TOxN) and Total Nitrogen (TN). The salinity of the sample is approximately 11 (PSS 78).

#### Quantity and Preservation

QC SW3.1B contains bottles with approximately 100 mL sample, ready for use. The sample has been preserved by filtration and 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 NH<sub>4</sub>, NO<sub>2</sub>, NO<sub>2+3</sub> and TN in coastal water and marine estuaries. It may also be used in the quality control of other types of saline 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 bottle at room temperature (approx. 20°C). Open the bottle and withdraw the sample with a pipette. Treat the reference material in the same way as an ordinary sample. If, e.g., filtration or other pre-treatment is normally used, this should be applied to the reference material as well. 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 bottles protected from sunlight, e.g. in the box, and in a refrigerator. The certificate is valid until **1<sup>st</sup> of April 2020** provided the material is stored under the recommended conditions.

After opening the bottle, the reference material should be preserved or used on the same day.

## 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

#### *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 NH<sub>4</sub>, NO<sub>2+3</sub> and TN in randomly selected bottles of QC SW3.1B. 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 bottle (F-test, 95%). In addition, homogeneity testing was included for all parameters in the external control. No indication of heterogeneity was found.

#### Stability:

The stability of the reference material is being followed at 5°C and 20°C, and no indication of instability was observed at the date of this certificate.

#### *External control*

The external laboratory documentation was performed by selected laboratories. The laboratories were requested to analyse 5 bottles: three bottles in the same analytical series, one as duplicate determination, and two bottles in two different analytical series as single determinations. In addition, the laboratories were requested to analyse in duplicate a control sample sent together with the reference material. 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 that the laboratories perform the analyses on a routine basis. Furthermore, laboratories were selected based on their performance for control samples included in the certification study.

The criterion for pre-selection of laboratories is:

- the laboratory analyses more than 20 analytical series each year or holds accreditation for the parameter.

In addition, the criteria are:

- the laboratory average for the control sample in the certification study deviated less than 25% from the nominal value, and
- the laboratory results in the certification study are not Cochran outliers or Grubbs outliers.

The data included in the certification 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 (p)	EXCLUDED DATA SETS C: Cochran outlier G: Grubbs outlier
				Lower	Upper		
Ammonium (NH <sub>4</sub> )	μM	2.03	0.265	1.81	2.25	8	1C
Nitrite (NO <sub>2</sub> )	μM	0.86	0.028	0.84	0.89	7	4C
Nitrite+nitrate (NO <sub>2+3</sub> )	μM	11.5	0.289	11.2	11.8	7	3C
Total Nitrogen (TN)	μM	14.9	0.985	13.9	16.0	6	1C

### Methods

The laboratories have used spectrophotometric measurements according to the principles for seawater analysis laid out in Grasshoff et al., Methods of Seawater Analysis, 2<sup>nd</sup> edition, 2000. Most laboratories have adapted the methods to automated analysis.

### 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.

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**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

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## ANNEX TO CERTIFICATE QC SW3.1B

### Laboratory Measurements

Ammonium				
$Y_i$ $\mu\text{M}$	$S_{ri}$ $\mu\text{M}$	$n_{ri}$	$S_{Li}$ $\mu\text{M}$	$n_{Li}$
1.71	0.006	4	0.018	3
2.53	0.023	3		
1.83	0.105	4	0.109	3
2.28	0.075	4	0.070	3
2.08	0.011	4	0.162	3
1.90	0.000	4	0.061	3
2.01	0.020	4	0.111	3
1.90	0.034	4	0.023	3

Nitrite+nitrate				
$Y_i$ $\mu\text{M}$	$S_{ri}$ $\mu\text{M}$	$n_{ri}$	$S_{Li}$ $\mu\text{M}$	$n_{Li}$
11.4	0.070	4	0.093	3
11.5	0.053	4	0.157	3
11.3	0.084	4	0.159	3
11.8	0.068	4	0.206	3
11.1	0.139	4	0.150	3
11.9	0.243	4	0.312	3
11.4	0.321	4	0.297	3

Nitrite				
$Y_i$ $\mu\text{M}$	$S_{ri}$ $\mu\text{M}$	$n_{ri}$	$S_{Li}$ $\mu\text{M}$	$n_{Li}$
0.91	0.003	4	0.007	3
0.89	0.006	3		
0.85	0.006	4	0.011	3
0.84	0.010	4	0.001	3
0.86	0.003	4	0.010	3
0.87	0.004	4	0.017	3
0.83	0.005	4	0.007	3

Total nitrogen				
$Y_i$ $\mu\text{M}$	$S_{ri}$ $\mu\text{M}$	$n_{ri}$	$S_{Li}$ $\mu\text{M}$	$n_{Li}$
15.8	0.11	4	0.25	3
15.4	0.10	4	0.22	3
15.9	0.25	4	0.35	3
13.5	0.19	4	0.47	3
14.9	0.19	4	0.81	3
14.0	0.31	4	0.83	3

#### 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  $S_{Li}$

## **ANNEX TO CERTIFICATE QC SW3.1B**

### **Certifying Laboratories**

MARCHEM, Oostende, BELGIUM

Danmarks Miljøundersøgelser, Århus Universitet, Roskilde, DENMARK

Eurofins Miljø A/S, Vejen, DENMARK

Finnish Environment Institute SYKE, Helsinki, FINLAND

RWS - Waterdienst, Lelystad, HOLLAND

Israel Oceanographic and Limnological Research , Haifa, ISRAEL

ENEA, Centro Ricerche Ambiente Marino - S. Teresa, La Spezia, ITALY

Instituto Hidrografico, Lisboa, PORTUGAL

Scottish Environment Protection Agency, East Kilbride, SCOTLAND

CEFAS, Suffolk, UNITED KINGDOM