Eurofins Miljø A/S
Smedeskovvej 38
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DANAK
RM Reg. nr. 535

VKI
REFERENCE MATERIALS

CERTIFICATE FOR

QC SW4.1B

NUTRIENTS IN NATURAL SEAWATER

BATCH: VKI-33-7-0422

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_4), Nitrite (NO_2), Nitrite+nitrate (NO_{2+3} or TOxN) and Total Nitrogen (TN). The salinity of the sample is approximately 33 (PSS 78).

Quantity and Preservation
QC SW4.1B consists of bottles with a minimum of 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_4, NO_2, NO_{2+3} and TN in seawater. 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 bottles 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 ampoules protected from sunlight, e.g. in the box, and in a refrigerator. The certificate is valid until **1st of April 2026** 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_4, NO_{2+3} and TN in randomly selected bottles of QC SW4.1B. 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 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 all parameters except TN in the external control. Uncertainty from heterogeneity is emitted in the uncertainty of the reference material.

Stability:
The stability of the reference material is being followed at 5°C and 20°C.

External control
The concentration of major components in the reference material was determined by selected laboratories in an external documentation in December 2022-February 2023. The participating laboratories are skilled and have documented good analytical quality by analysis of a control sample in the certification. The laboratories were requested to analyse five bottles: 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):

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

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 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 25% from the nominal value, and
- the laboratory results in the certification study are not 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 y_{char}	BETWEEN LABORATORY STANDARD DEVIATION s(*y*)	EXPANDED UNCERTAINTY ON CERTIFIED VALUE U_{CRM}	NUMBER OF DATA SETS IN CALCULATIONS/ METHOD (p)	EXCLUDED DATA SETS G: Grubbs outlier
Ammonium (NH_4)	µM	2.7	0.24	0.20	5/A 1/X	-
Nitrite (NO_2)	µM	0.20	0.013	0.0094	6/A 2/X	-
Nitrite+nitrate (NO_{2+3})	µM	12.9	0.96	0.62	8/A 2/X	-
Total Nitrogen (TN)	µM	19	0.96	1.8	5/A 1/X	-

Methods

A Spectrophotometric measurement according to the principles for seawater analysis laid out in Grasshoff et al., Methods of Seawater Analysis, 2nd edition, 2000.

X Other methods

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: March 2023

RESPONSIBLE SCIENTIST

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ANNEX TO CERTIFICATE QC SW4.1B

Laboratory Measurements

Ammonium					
y_i µM	s_{ri} µM	n_{ri}	s_{Li} µM	n_{Li}	Metode
3.05	0.12	4	0.12	3	A
2.45	0.12	4	0.06	3	A
2.99	0.02	4	0.09	3	A
2.63	0.14	4	0.22	3	X
2.77	0.12	4	0.56	3	A
2.54	0.04	2			A

Nitrite					
y_i µM	s_{ri} µM	n_{ri}	s_{Li} µM	n_{Li}	Metode
0.203	0.0029	4	0.0017	3	A
0.208	0.0032	4	0.0042	3	A
0.219	0.0034	4	0.0045	3	X
0.183	0.0058	4	0.0026	3	A
0.194	0.0067	4			A
0.215	0.0113	4	0.0222	3	A
0.185	0.0383	4	0.0361	3	X
0.195	0.0071	2			A

Nitrite+nitrate					
y_i µM	s_{ri} µM	n_{ri}	s_{Li} µM	n_{Li}	Metode
11.58	0.040	6	0.196	2	A
13.18	0.025	4	0.016	3	A
12.93	0.073	4	0.028	3	A
13.80	0.000	4	0.200	3	X
12.31	0.077	4	0.103	3	A
13.35	0.051	4	0.130	3	A
13.32	0.135	4	0.235	3	A
11.02	0.411	4	0.388	3	X
14.07	0.776	4	0.376	3	A
13.10	0.085	2			A

Total nitrogen					
y_i µM	s_{ri} µM	n_{ri}	s_{Li} µM	n_{Li}	Metode
19.2	1.12	3	1.10	3	A
19.6	0.22	4	0.17	3	A
21.1	0.43	4	0.36	3	A
22.3	0.06	4	0.49	3	X
17.9	0.44	4	1.42	3	A
16.5	0.15	2			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

ANNEX TO CERTIFICATE QC SW4.1B

Certifying Laboratories

DOCEAN-UFPE, Recife, BRAZIL
ALS Denmark A/S, Humlebæk, DENMARK
Bundessamt für Seeschiffahrt und Hydrographie, Hamburg, GERMANY
Marine Institute, Co. Galway, IRLAND
Israel Oceanographic & Limnological Reasearch, National Institute of Oceanography, Haifa, ISRAEL
Eurofins Environment Testing Norway AS, Moss, NORWAY
Instituto Hidrográfico, Lisboa, PORTUGAL
Marine Scotland Science, Aberdeen, SCOTLAND
Eurofins Environment Testing Sweden AB, Lidköping, SWEDEN
Rijkswaterstaat Laboratory, Lelystad, THE NETHERLANDS