

CERTIFICATE FOR

QC SW4.1B

NUTRIENTS IN NATURAL SEAWATER

BATCH: VKI-33-5-0217

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 (NH₄), Nitrite (NO₂), Nitrite+Nitrate (NO₂₊₃, or TOxN) and Total Nitrogen (TN). The salinity of the sample is approximately 30 (PSS 78).

Quantity and Preservation

QC SW4.1B 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 NH₄, NO₂, NO₂₊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 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 **1st 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 Miljø, with the aim of obtaining the intended quality of the material.

Documentation of Content

Internal control

The analytical quality of Eurofins Miljø has been documented and found satisfactory by regular participation in international proficiency tests.

Homogeneity:

The homogeneity has been investigated by measurements of NH₄, NO₂, NO₂₊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 bottle (F-test, 95%). In addition, homogeneity testing in accordance with ISO Guide 35 /1/ was included for all parameters in the external control. Homogeneity was confirmed for all parameters except NO₂ in the external control. For NO₂ the between bottle standard deviation was taken into account in the uncertainty of the certified values.

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 September-November 2017. 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 5 bottles: three bottles in the same analytical series, one as duplicate determination, and two bottles 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, and
- the laboratory analyses more than 20 analytical series each year or holds accreditation for the parameter.
- 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 or deemed to be an outlier based on a scientific evaluation.

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 ₄)	μM	2.4	0.18	2.2	2.5	7	1C
Nitrite (NO ₂)	μM	1.37	0.047	1.32	1.42	10	-
Nitrite+nitrate (NO ₂₊₃)	μM	12.8	0.23	12.6	12.9	10	1C
Total Nitrogen (TN)	μM	18.9	0.46	18.4	19.4	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, 2nd 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:

- For single determinations, analytical results will with a probability of 95% be in the interval:

$$\bar{Y} \pm t_{0,025}(v) \cdot s_L$$

- 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

- ISO guide 35:2006. Certification of reference materials - General and statistical principles for certification.
- ISO Guide 31:2015. Reference materials - Contents of certificates, labels and accompanying documentation.

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Certificate revision history: June 2018 (original certificate date)

ANNEX TO CERTIFICATE QC SW4.1B

Laboratory Measurements

Ammonium				
Y_i μM	s_{ri} μM	n_{ri}	s_{Li} μM	n_{Li}
2.00	0.09	4	0.23	3
2.23	0.06	4	0.08	3
2.47	0.02	6	0.02	2
2.43	0.02	4	0.03	3
2.41	0.10	4	0.25	3
2.52	0.02	4	0.02	3
2.44	0.03	4	0.02	3

Nitrite+nitrate				
Y_i μM	s_{ri} μM	n_{ri}	s_{Li} μM	n_{Li}
12.75	0.10	4	0.39	3
12.93	0.09	4	0.11	3
12.84	0.04	4	0.08	3
12.62	0.06	6	0.23	2
12.61	0.02	4	0.07	3
12.32	0.14	4		
13.18	0.10	4	0.22	3
12.88	0.03	4	0.04	3
12.82	0.11	4	0.16	3
12.79	0.01	4	0.34	3

Nitrite				
Y_i μM	s_{ri} μM	n_{ri}	s_{Li} μM	n_{Li}
1.299	0.011	4	0.070	3
1.307	0.047	4	0.003	3
1.428	0.010	4	0.035	3
1.371	0.008	6	0.003	2
1.362	0	4	0.005	3
1.398	0.017	4		
1.314	0.004	4	0.034	3
1.407	0.008	4	0.012	3
1.396	0.008	4	0.075	3
1.409	0.001	4	0.014	3

Total nitrogen				
Y_i μM	s_{ri} μM	n_{ri}	s_{Li} μM	n_{Li}
18.43	0.56	4	1.14	3
18.32	0.39	4	0.75	3
19.21	0.19	4	0.68	3
18.81	0.07	4	0.35	3
19.40	0.18	4	0.32	3
19.28	0.47	4	0.80	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 SW4.1B

Certifying Laboratories

RBINS - OD NATURE - ECOCHEM, Oostende, BELGIUM

ALS Denmark A/S, Humlebæk, DENMARK

Eurofins Miljø A/S, Vejle, DENMARK

Miljøstyrelsen - Laboratoriet, Odense SØ, DENMARK

IFREMER - DYNECO PELAGOS, Plouzane, FRANCE

BSH Laboratory Sülldorf, Hamburg, GERMANY

Israel Oceanographic and Limnological Research, Marine Chemistry Department, Haifa, ISRAEL

Instituto Hidrográfico, Lisboa, PORTUGAL

Marine Scotland Science, Aberdeen, SCOTLAND

SMHI, Västra Frölunda, SWEDEN

Rijkswaterstaat Water Quality Laboratory, Lelystad, THE NETHERLANDS