Eurofins Miljø A/S
Smedeskovvej 38
DK-8464 Galten

DANAK
RM Reg. nr. 535

VKI
REFERENCE MATERIALS

CERTIFICATE FOR

QC WW2.2

NITRATE FOR WATER ANALYSES

BATCH: VKI-6-6-0698

INSTRUCTIONS FOR USE OF THE REFERENCE MATERIAL

Description
This reference material consists of ampoules with concentrate for preparation of reference samples for quality control after dilution with water.

Quantity
QC WW2.2 consists of ampoules where each ampoule contains a minimum of 10 ml concentrate. 1 litre of reference sample containing nitrate is prepared by dilution of 10 ml QC WW2.2. The concentrate has been preserved by autoclaving.

Use
The reference material is intended for quality control, i.e. measurement and control of the trueness and precision of analyses. It is typically intended for analyses of nitrate in wastewater samples. It may also be used in the quality control of other sample types and for the implementation and optimisation of analytical instruments and analytical methods. For these purposes other dilutions than intended for quality control of wastewater may be appropriate. It is important that the batch numbers of the reference material and on the certificate are identical.

Preparation for Use
Stabilise the ampoule at room temperature (approx. 20°C). Break the ampoule neck open at the mark, so that contamination of the concentrate with particles is avoided. Withdraw the concentrate with a pipette, dilute 1:100 with water without a detectable content of nitrate, e.g. 2,00 ml concentrate up to 200 ml with water. The certified concentration is given in the table on page 3 of this certificate.

If QC WW2.2 is used for other purposes than quality control of wastewater analyses, the dilution ratio between the concentrate and water can be altered.

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, at room temperature or in a refrigerator. The certificate is valid until **1st of April 2028** provided the material is stored under the recommended conditions.

After opening of the ampoule, the concentrate and the dilution of the reference material have 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 to obtain the intended quality of the material.

Documentation of Content
All laboratory documentation of the reference material has been performed after dilution of the ampoule concentrate for use as quality control of wastewater analysis (dilution ratio 1:100).

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

Homogeneity:
The homogeneity has been investigated for nitrate in 12 randomly selected ampoules. Tests for homogeneity have been performed by comparing the standard deviation between the ampoules with the within batch standard deviation obtained from duplicate measurements of the reference material in each ampoule (F-test, 95%). No signs of inhomogeneity were found.

Stability:
The stability of the reference material is being followed at 5°C, 20°C and 37°C, and no signs of instability were observed at the date of this certificate.

External Control
The concentration of NO_3-N in the reference material was determined by selected laboratories during Autumn 1998. The laboratories were requested to analyse nitrate in four ampoules: two ampoules in one analytical series, one as a duplicate determination, the other as a single determination; two ampoules 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 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.):

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

The 95% confidence interval of the true mean value of analytical results is:

$$y_{char} \pm t_{0,025}(\nu).\frac{s(y)}{\sqrt{p}}$$

where
p: number of data sets included in calculations

ν: p-1, degrees of freedom

$t_{0,025}(\nu)$: t value of 0,025 level at ν degrees of freedom.

All the selected laboratories have a good routine in performing the analyses. The Danish and Swedish laboratories selected for certification have documented their analytical quality by taking part in a recent proficiency test where their results deviated not more than 2 x the standard deviation from the median value. The Finnish laboratories in this certification have been selected by the Finnish Reference Laboratory. Further results have been excluded from the final certification based on Grubbs and Cochran outlier criteria /3/ and a following questionnaire to these laboratories regarding their analytical quality. A summarisation of the statistical calculations, the applied laboratory methods and number of laboratories using each method are given in the following table.

Certified values

DETERMINAND	UNIT	AVERAGE	BETWEEN LABORATORY STANDARD DEVIATION	95% CONFIDENCE LIMITS OF THE AVERAGE VALUE		METHOD / NUMBER OF DATA SETS IN CALCULATIONS	EXCLUDED DATA SETS
				$y_{char} \pm t_{0,025}(\nu) \cdot \frac{s(y)}{\sqrt{p}}$			U: Other excluded C: Cochran outlier G: Grubbs outlier
		y_{char}	s(*y*)	Lower	Upper	(p)	
Nitrate-N (NO_3-N)	mg/l N	1.00	0.02	0.99	1.01	A/31 G/2 H/4 I/1	C:5 C+G:1 U:1

Methods

A: Spectrophotometric analysis, reduction with cadmium. Manual method or modified method for automated analysis by FIA, autoanalyzer or TRAACS. Methods: Danish Norm DS 223/ Swedish Norm SS028133/ Finnish Norm SFS 3030 - equivalent to EN/ISO 13395

G: The same principle as method A, Lachat: QuickChem method No. 10-107-04-1-C, No. 10-107-06-3-A, No. 31-107-06-1-A, No. 10-115-01-1-B, No. 31-115-01-3-A.

H: Ion chromatography, EN/ISO 10304-1, AM 3003-3004.

I: Other methods.

Use of the External Control Values

For laboratories with an analytical quality that is comparable with the laboratories who have contributed with 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:

$$y_{char} \pm t_{0,025}(\nu) \cdot s(y)$$

2) Analytical results, calculated as the average of two determinations will with a probability of 95% be in the interval:

$$y_{char} \pm t_{0,025}(\nu) \cdot \frac{s(y)}{\sqrt{2}}$$

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.

/3/ ISO 5725-2, 1994, Accuracy (trueness and precision) of measurement methods and results. Part 2: A basic method for the determination of repeatability and reproducibility of a standard measurement method.

Date of issue: February 2023

RESPONSIBLE SCIENTIST

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Certificate revision history: February 2023 (expiry date extended; update to newest version of ISO Guide 35); May 2020 (expiry date extended); June 2018 (expiry date extended); December 2013 (expiry date added); April 1999 (original certificate date)

ANNEX FOR CERTIFICATE QC WW2.2

Included Laboratory Measurements

NO_3-N					
m_i mg/l	s_{ri} mg/l	n_{ri}	s_{Li} mg/l	n_{Li}	Method
0,992	0,006	3	0,002	3	A
0,990	0,010	3	0,006	3	A
0,987	0,001	3	0,027	3	G
1,030	0,006	3	0,010	3	A
1,012	0,006	3	0,020	3	H
1,014	0,000	3	0,006	3	A
0,974	0,019	3	0,027	3	A
0,990	0,005	3	0,008	3	A
0,994	0,010	3	0,010	3	A
0,985	0,011	3	0,027	3	A
1,006	0,005	3	0,012	3	A
1,006	0,001	3	0,001	3	I
0,992	0,002	3	0,002	3	A
0,970	0,004	2	0,032	3	A
1,000	0,006	3	0,007	3	A
1,003	0,000	3	0,010	3	A
1,002	0,003	3	0,001	3	A
0,998	0,010	3	0,015	3	A
1,042	0,017	3	0,041	3	H
0,998	0,010	3	0,006	3	A
1,016	0,010	3	0,021	3	A
1,005	0,017	3	0,007	3	A
0,993	0,014	3	0,008	3	A
1,028	0,010	3	0,006	3	A
1,023	0,013	3	0,005	3	A
1,029	0,005	3	0,010	3	H
1,010	0,006	3	0,014	3	A
0,967	0,007	3	0,028	3	G
1,006	0,003	3	0,010	3	A
0,998	0,007	3	0,008	3	A
0,985	0,008	3	0,003	3	A
0,988	0,001	3	0,004	3	A
0,988	0,010	3	0,013	3	A
0,992	0,000	3	0,006	3	A
0,986	0,003	3	0,005	3	H
1,029	0,011	3	0,011	3	A
1,048	0,009	3	0,021	3	A
0,994	0,006	3	0,006	3	A

External Control Values

m_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 page 3.

ANNEX FOR CERTIFICATE QC WW2.2

Certifying Laboratories

Denmark
A/S Analycen, Fredericia
DIFTA, Hirtshals
Hedeselskabets Laboratorium, Viborg
Miljø- og Levnedsmiddelkontrollen, Hjørring
Miljø- og Levnedsmiddelcentret, Holbæk
Miljø- og Levnedsmiddelkontrollen, Ribe
Miljø- og Levnedsmiddelcentret, Slagelse
Miljø- og Levnedsmiddelkontrollen, Lolland Falster og Møn
Miljø- og Levnedsmiddelkontrollen, Hillerød
Levnedsmiddelkontrollen I/S, Frederikssund
Fælleskommunal Levnedsmiddelkontrol, Glostrup
Miljø- og Levnedsmiddelkontrollen, Helsingør
Københavns Miljølaboratorium, København SV
Miljø- og Levnedsmiddelcenter Sjælland Øst I/S, Køge
MLK-Fyn I/S, Odense SØ
Miljø- og Levnedsmiddelkontrollen, Randers
Levnedsmiddelkontrollen I/S, Skovlunde
Hygiejnelaboratoriet A/S, Tønder
MiljøLaboratoriet Østjylland A/S, Vejle
Hygiejnisk Forvaltning, Ålborg
KK-laboratoriet A/S, Nyborg

Sweden
Cenox AB, Lund
Hydro Agri AB, Köping
Klagshamn Avr., Klagshamn
Nordic Synthesis AB, Karlskoga
Svelab Miljölaboratorier AB, Västerås
Tekn. Förvaltningen, Lund
VA-Verket, Mölndal
LV-Lab, Sandarne

Finland
Central Finland Regional Environment Centre, Jyräskylä
North Karelia Regional Environment Centre, Joensuu
University of Jyväskylä, Jyväskylä
Kokemäenjoen visistön vesiensuojeluyhdistys, ry., Tampere
Savo-karjalan Vesien suojeluyhdistys ry., Kuopio
Vasa Stads Miljölaboratorium, Vasa
Helsinki City Environmental Laboratory, Helsinki
PSV-Maaja Vesi Oy, Oulu
Lapin ympäristökeskus, Rovaniemmi
Pohjois-Savon ympäristökeskus, Kuopio