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

VKI
REFERENCE MATERIALS

CERTIFICATE FOR

QC WW5

BIOCHEMICAL OXYGEN DEMAND (BOD)

BATCH: VKI-21-5-0115

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 BOD_5 and BOD_7.

Quantity and Preservation
QC WW5 consists of ampoules with a minimum of 25 mL concentrate in each. 250 mL reference sample is produced by dilution of 25 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 biochemical oxygen demand after 5 days (BOD_5) or after 7 days (BOD_7) in wastewater. 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 1:10 with water without a detectable content of BOD, e.g. 10,00 mL concentrate up to 100 mL with water. The approximate concentrations are 200 mg/L O_2. 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 April 2023** 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 Miljø A/S, 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 1:10.

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 COD_{Cr} in randomly selected ampoules of QC WW5. 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 for BOD_5 and BOD_7 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 BOD_5 and BOD_7 in the reference material was determined by selected laboratories in an external documentation in April-May 2015. 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-WW5: 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:

$\overline{Y}$: 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):

$$\frac{1}{p-1}\sqrt{\sum\left(Y_i - \overline{Y}\right)^2}$$

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

$$\overline{Y} \pm t_{0,025}(\nu).\frac{s_L}{\sqrt{p}}$$

where

p: number of laboratories included in calculations

ν: p-1, degrees of freedom

$t_{0,025}(\nu)$: t value of 0,025 level at ν 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 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 $\overline{Y}$	BETWEEN LABORATORY STANDARD DEVIATION s_L	95% CONFIDENCE LIMITS OF THE AVERAGE VALUE $\overline{Y} \pm t_{0,025}(\nu).\frac{s_L}{\sqrt{p}}$ Lower	Upper	NUMBER OF DATA SETS IN CALCULATIONS/ METHOD (p)	EXCLUDED DATA SETS
BOD_5	mg/L O_2	(200)*	(8.6)	(190)	(210)	3/A 1/B2 1/C	5
BOD_7	mg/L O_2	208	11.1	201	215	12/A	5

*: Values in brackets are indicative.

Methods

BOD_5, BOD_7:
A Dilution method: EN 1899-1
B2 Dilution method: DS 254/R with addition of A.T.U. (allylthiouric acid).
Addition of A.T.U.: 1.2 mg/L
C For undiluted samples: EN 1899-2

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:

$$\overline{Y} \pm t_{0,025}(\nu).s_L$$

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

$$\overline{Y} \pm t_{0,025}(\nu).\frac{s_L}{\sqrt{2}}$$

REFERENCES

/1/ ISO guide 35:2006. Certification of reference materials - General and statistical principles for certification.

/2/ ISO guide 31:2000 Reference materials - Contents of certificates and labels.

Date of issue: April 2019

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Certificate revision history: April 2019 (expiry date extended); January 2016 (original certificate date)

ANNEX TO CERTIFICATE QC WW5

Laboratory Measurements

BOD_5					
Y_i mg/L O_2	s_{ri} mg/L O_2	n_{ri}	s_{Li} mg/L O_2	n_{Li}	Metode
200	3.4	4	9.4	3	B2
199	4.8	4	6.3	3	A
186	1.4	4	6.2	3	A
204	2.8	4	3.8	3	C
209	6.6	4	9.3	3	A

BOD_7					
Y_i mg/L O_2	s_{ri} mg/L O_2	n_{ri}	s_{Li} mg/L O_2	n_{Li}	Metode
194	3.8	4	9.8	3	A
209.2	2.1	4	6.4	3	A
206.0	3.1	4	6.5	3	A
224.7	4.7	4	7.7	3	A
199.2	4.2	4	14.5	3	A
203.3	2.1	4	3.6	3	A
221.1	9.3	4	6.1	3	A
219.7	6.1	4	6.4	3	A
203.7	3.1	4	5.5	3	A
218.7	2.2	4	11.5	3	A
189.5	15.0	4	5.5	3	A
206	7.3	4	6.2	3	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 WW5

Certifying Laboratories

Denmark
ALS Denmark, Humlebæk
AnalyTech Miljølaboratorium, Nørresundby
Eurofins Miljø A/S, Vejen
FORCE Technology, Holstebro

Finland
Nab Labs Ltd / Ambiotica, Jyväskylä
Water and Environment Research of South-West Finland, Turku

Sweden
Alcontrol AB, Umeå
ALcontrol Linköping AB, Linköping
Eurofins Environment Testing Sweden AS, Lidköping
Karlskrona Kommuns Laboratorium, Lyckeby
Laboratoriet vid Smedjeholms Arv, Falkenberg
Nynäshamns kommun, VA-avdelingen, Nynäshamn
Piteå Renhållning & Vatten AB, Öjebyn
Tekniska Förvaltningen, Verksamhetsstöd VA, Laboratoriet, Örebro
Trollhättan Energi AB, Arvidstorps Laboratorium, Trollhättan
VA SYD, Malmö