Eurofins Miljø A/S
Smedeskovvej 38
DK-8464 Galten

DANAK
RM Reg.no. 535

VKI
REFERENCE MATERIALS

CERTIFICATE FOR

QC WW4

CHEMICAL OXYGEN DEMAND WITH DICHROMATE (COD_{Cr}) AND TOTAL ORGANIC CARBON (TOC/NVOC)

BATCH: VKI-8-7-0120

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 chemical oxygen demand with dichromate (COD_{Cr}) and total organic carbon (TOC/NVOC).

Quantity and Preservation
QC WW4 consists of ampoules with a minimum of 10 mL concentrate in each. 1 L reference sample is produced by dilution of 10 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 COD_{Cr} and TOC/NVOC 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
Stabilize the ampoules at room temperature (approx. 20°C). Break the ampoule neck open at the mark, withdraw the concentrate with a pipette, and dilute 1:100 with water without a detectable content of COD_{Cr} and TOC/NVOC, e.g. 2.00 mL concentrate up to 200 mL with water. This dilution gives the approximate concentrations 500 mg/L O_2 for COD_{Cr} and 200 mg/L C for TOC (NVOC). 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 2026** 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, 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 1:100.

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 COD_{Cr} in randomly selected ampoules of QC WW4. 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 both parameters 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 COD_{Cr} and TOC/NVOC in the reference material was determined by selected laboratories in an external documentation in November 2020. 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 WW4: 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):

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

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 results in proficiency tests diverged less than 2 standard deviations from the nominal value,
- 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 20% for COD_{Cr} and 15% for TOC/NVOC 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	BETWEEN LABORATORY STANDARD DEVIATION	EXPANDED UNCERTAINTY ON CERTIFIED VALUE	NUMBER OF DATA SETS IN CALCULATIONS/ METHOD	EXCLUDED DATA SETS C: Cochran outlier G: Grubbs outlier
		y_{char}	$s(y)$	U_{CRM}	(p)	
COD_{Cr}	mg/L O_2	507	9.4	10.1	9/G 2/I 5/O 1/P	2C
TOC/NVOC	mg/L C	201	3.0	7.4	13/A 1/C 5/F	2C 1G

Methods

COD_{Cr}:

G Lange 150 - 1000 mg/L. (Lange LCK 114)
I Lange 0 - 1000 mg/L (ISO COD). (Lange LCI 400)
O Merck 25 - 1500 mg/L. (Merck 1.14541)
P Nanocolor COD 1500, 100 – 1500 mg/L O_2. (Macherey-Nagel 985 029)

TOC/NVOC:

A Purge CO_2 from the acidified sample. Oxidise organic compounds in the sample catalytically at ≥ 680°C to CO_2. Quantify by IR-spectrophotometry. (SM 19-20th ed. method 5310 A + B, EN 1484)
C Purge CO_2 from the acidified sample. Oxidise organic compounds in the sample with $K_2S_2O_8$ at about 100 °C to CO_2. Quantify by IR-spectrophotometry. (SM 19-20th ed. method 5310 A + B, EN 1484)
F Lange 30 - 300 mg/L (photometric method). (Lange LCK 386)

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: July 2023.

RESPONSIBLE SCIENTIST

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Certificate revision history: July 2023 (original certificate date)

ANNEX TO CERTIFICATE QC WW4

Laboratory Measurements

COD_{Cr}					
Y_i mg/L O_2	s_{ri} mg/L O_2	n_{ri}	s_{Li} mg/L O_2	n_{Li}	Metode
513.3	4.1	4	5.2	3	G
500.3	5.6	4	7.7	3	O
520.7	2.9	4	6.6	3	O
512.8	2.1	4	2.7	3	G
497.7	1.9	4	3.6	3	G
505.5	1.7	4	2.3	3	I
501.7	3.3	4	2.0	3	O
494.8	2.4	4	3.2	3	O
527.3	7.7	4	6.7	3	G
492.3	1.2	4	5.9	3	P
511.5	6.4	4	3.0	3	G
515.0	4.8	4	4.9	3	G
496.2	4.3	4	7.4	3	I
503.7	1.7	4	3.7	3	O
507.7	3.1	4	7.7	3	G
507.0	2.9	4	4.4	3	G
507.7	5.4	4	3.6	3	G

TOC/NVOC					
Y_i mg/L C	s_{ri} mg/L C	n_{ri}	s_{Li} mg/L C	n_{Li}	Metode
202.0	1.0	4	1.1	3	A
209.0	1.0	4	1.3	3	F
201.1	2.8	4	1.8	3	F
195.0	3.1	4	8.9	3	C
201.5	7.5	4	4.1	3	A
199.8	1.1	4	2.7	3	A
207.0	2.2	4	4.0	3	A
203.7	0.9	4	1.7	3	A
201.8	4.3	4	0.7	3	A
199.9	0.7	4	7.4	3	A
198.5	0.3	4	4.1	3	A
200.5	5.0	4	1.7	3	F
199.2	0.3	4	2.3	3	A
200.8	2.9	4	3.2	3	A
199.2	1.0	4	2.8	3	A
200.7	1.1	4	3.1	3	F
202.5	2.0	4	1.0	3	F
199.4	1.6	4	1.9	3	A
201.8	0.7	4	0.5	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 WW4

Certifying Laboratories

Denmark
Eurofins Miljø A/S, Vejen
Højvang Laboratorier A/S, Dianalund

Norway
Eurofins Environment Testing Norway AS, Moos
Hardanger Miljøsenter AS, Odda
Labora AS, Bodø
Mjøslab I&S, Gjøvik
Nedre Romerike Vannverk IKS, Strømmen
SINTEF Molab AS, Lokasjon Molde, Molde
SNJ, IVAR IKS, Randaberg
VAV Vann- og avløpsetaten, Oslo
VestfoldLAB AS, Gem

Sweden
ALS Scandinavia AB, Danderyd
Eurofins Water Testing Sweden AB, Lidköping
Gällivare Kommun/Kavahedens Reningsverk, Gällivare
Göteborgs Kemanalys AB, Västra Frölunda
Hallsta Pappersbruk, Hallstavik
Iggesund Paperboard AB , Iggesund
Kristianstads Kommun, VA-laboratoriet, Kristanstad
Käppalaförbundet, Lidingö
Lackarebäcks Laboratorium, Mölndal
Njudung Energi Vetlanda AB, Vattenlaboratoriet, Vetlanda
Nodra AB, Laboratorium Slottshagens Renningsverk, NorrKöping
Nouryon Functional Chemicals AB, Örnsköldsvik
Smedjeholms Avloppsreningsverk, Laboratoriet, VIVAB, Falkenberg
St1 Refinery AB, Gothenburg
Trollhättan Energi AB, Trollhättan
VA SYD, Laboratorieenheten, Malmö
Vallviks Bruk AB, Vallvik