

CERTIFICATE FOR

QC WW4

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

BATCH: VKI-8-6-0115

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 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

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 1:100 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 O₂ 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 2025** 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 1:100.

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 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 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 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:

\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,

- 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	95% CONFIDENCE LIMITS OF THE AVERAGE VALUE		NUMBER OF DATA SETS IN CALCULATIONS/METHOD	EXCLUDED DATA SETS
				$\bar{Y} \pm t_{0,025}(v) \cdot \frac{s_L}{\sqrt{p}}$			
		\bar{Y}	s_L	Lower	Upper	(p)	
COD _{Cr}	mg/L O ₂	507	7.9	504	510	7/G 4/H 1/HB 5/I 1/IA 1/L 4/O 4/X	4
TOC/NVOC	mg/L C	202	4.2	200	203	18/A 9/F	7

Methods

COD_{Cr}:

- G Lange 150 - 1000 mg/L. (Lange LCK 114)
H Lange 100 - 2000 mg/L. (Lange LCK 514)
HB Lange 100 - 2000 mg/L, oxidation at 170°C for 15 min. (Lange LCK 514, HT)
I Lange 0 - 1000 mg/L (ISO COD). (Lange LCI 400)
IA Lange 0 - 1000 mg/L (ISO COD), robot version. (Lange APC 400)
L Merck 50 - 500 mg/L. (Merck 1.14690)
O Merck 25 - 1500 mg/L. (Merck 1.14541)
X Other method

TOC/NVOC:

- A Purge CO₂ from the acidified sample. Oxidise organic compounds in the sample catalytically at ≥ 680°C to CO₂. 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)

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:

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

- 2) 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

- /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.

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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}	Method
509.2	0.5	4	1.0	3	I
498.5	11.2	4	3.0	3	G
507.3	3.7	4	1.2	3	G
499.8	3.4	4	1.0	3	I
512.2	4.1	4	8.2	3	IA
509.8	2.2	4	2.1	3	I
509.8	3.2	4	3.2	3	H
502	4.8	4	3.6	3	I
502.3	2.6	4	3.0	3	G
504.2	3.9	4	2.9	3	G
506.7	1.2	4	3.1	3	G
494.2	4.7	4	0.8	3	L
531.8	2.6	4	8.2	3	H
516	1.9	4	0.7	3	X
495	2.3	4	7.2	3	O
508.2	5.5	4	3.5	3	O
502.7	1.4	4	3.1	3	X
506.5	7.0	4	3.0	3	O
500	3.7	4	0.7	3	HB
516.2	2.8	4	1.6	3	G
511.3	2.6	4	8.3	3	X
497.7	4.7	4	2.3	3	I
508.3	2.5	4	1.7	3	G
504.3	5.4	4	3.0	3	H
516.2	2.1	4	2.9	3	H
512	3.1	4	4.0	3	X
502	9.7	4	3.5	3	O

TOC/NVOC					
Y _i mg/L C	s _{ri} mg/L C	n _{ri}	s _{Li} mg/L C	n _{Li}	Method
200.0	0.8	4	0.6	3	F
204.5	1.3	4	0.5	3	A
205.3	1.3	4	1.2	3	F
201.0	0.9	4	0.8	3	A
205.8	3.2	4	1.9	3	F
204.2	3.8	4	1.4	3	F
199.7	6.3	4	3.3	3	A
199.7	1.5	4	3.1	3	A
201.1	1.7	4	1.2	3	A
210.2	5.4	4	3.2	3	A
197.9	1.6	4	0.9	3	A
196.3	1.3	4	1.5	3	A
197.2	4.0	4	2.6	3	F
203.8	0.5	4	7.0	3	A
198.2	1.0	4	1.7	3	F
205.7	0.8	4	1.2	3	A
196.5	2.2	4	2.0	3	F
200.4	1.2	4	2.7	3	A
199.2	1.0	4	1.0	3	A
196.7	1.7	4	0.9	3	F
211.7	1.5	4	0.2	3	A
199	0.8	4	2.0	3	A
206.7	3.9	4	7.0	3	A
197.2	2.1	4	2.9	3	A
204	1.3	4	1.4	3	F
199.8	1.1	4	3.4	3	A
199.1	1.6	4	1.8	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

ALS Denmark, Humlebæk
AnalyTech Miljølaboratorium, Nørresundby
BIOFOS A/S, København K
Eurofins Miljø A/S, Vejen
FORCE Technology, Holstebro
Kerteminde Forsyning - Spildevand A/S, Kerteminde
Kolding Spildevand A/S, Kolding
Provas, Haderslev Forsyningservice, Haderslev
Randers Spildevand A/S, Randers SØ
Svendborg Spildevand A/S, Svendborg Centralrenseanlæg, Skårup Fyn

Finland

KVVY, Tampere
Nab Labs Ltd / Ambiotica, Jyväskylä
Ramboll Analytics, Lahti
Water and Environment Research of South-West Finland, Turku

Norway

Toslab A/S, Tromsø
Vestfoldlab A/S, Sem

Sweden

Ahlstrom Ställdalen AB, Ställdalen
AkzoNobel Functional Chemicals AB, Örnsköldsvik
Alcontrol AB Umeå, Umeå
ALcontrol Linköping AB, Linköping
Ernemar Laboratorium, Oskarshamn
Eurofins Environment Testing Sweden AS, Lidköping
Hammargårds Arv. Kungsbacka Kommun, Kungsbacka
Holmen Paper Braviken, Norrköping
Iggesund Paperboard AB, Cell o. Miljölab, Iggesund
INEOS Sverige AB, Stenungsund
Karlskrona Kommuns Laboratorium, Lyckeby
Laboratoriet vid Smedjeholms Arv, Falkenberg
Norrköping Vatten och Avfall AB, Laboratoriet Slottshagen Reningsverk, Norrköping
Nynäshamns kommun, VA-avdelingen, Nynäshamn
Piteå Renhållning & Vatten AB, Öjebyn
Preemraff Lysekil, Lysekil
St1 Refinery AB, Göteborg
Stora Enso Hylte AB, Hyltebruk
Södra Cell Värö, Väröbacka
Tekn. Förv., Verksamhetsstöd VA, Laboratoriet, Örebro
Trollhättan Energi AB, Arvidstorps Laboratorium, Trollhättan
VA SYD, Malmö
VIVAB, Varberg