

CERTIFICATE FOR**QC WW4A****CHEMICAL OXYGEN DEMAND WITH POTASSIUM DICHROMATE (COD_{Cr}) AND
TOTAL ORGANIC CARBON (TOC/NVOC)****BATCH:** VKI-23-3-0114**INSTRUCTIONS FOR USE OF THE REFERENCE MATERIAL****Description**

This reference material consists of an ampoule with concentrate for preparation of reference samples for quality control after dilution with water. The certificate includes documentation for the analytical parameters chemical oxygen demand with potassium dichromate (COD_{Cr}) and total organic carbon (TOC/NVOC).

Quantity and Preservation

QC WW4A consists of ampoules with minimum 10 mL concentrate in each. 1 litre reference sample is prepared by dilution of 10 mL QC WW4A. The concentrate has been 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 samples. 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 ampoule at room temperature (approx. 20°C). Break the ampoule neck open at the mark, so that contamination of the concentrate from particles is avoided. Withdraw the appropriate amount of concentrate with a pipette and dilute 1:100 with water without a significant content of COD_{Cr} and TOC (NVOC). For example, 2.0 mL concentrate is diluted up to 200 mL. This dilution gives the approximate concentrations 50 mg/L O₂ for COD_{Cr} and 20 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 2031** provided the material is stored under the recommended conditions.

After preparation, the reference material has an expected storage time of up to 24 hours.

This certificate is prepared in accordance with the international ISO guidelines for certification of reference materials /1/ and /2/.

PRODUCTION OF THE REFERENCE MATERIAL AND DOCUMENTATION

Production

This reference material is produced in accordance with the quality management procedures of Eurofins, with the aim to obtain 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 TOC (NVOC) in randomly selected ampoules of QC WW4A. 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 ampoule (F-test, 95%). In addition, homogeneity testing in accordance with ISO 33405 /1/ was included in the external control. Homogeneity was confirmed for COD_{Cr} and not confirmed for TOC (NVOC) in the external control. For TOC (NVOC) 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, 20°C and 37°C, and no indications of instability were 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 May 2014. 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 WW4A: 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 33405 /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 33405, section A.2.4.

$s(y)$ standard deviation between the laboratories, calculated in accordance with ISO 33405, 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:

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

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 10% 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

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
		y_{char}	$s(y)$	$y_{char} \pm t_{0,025}(v) \cdot \frac{s(y)}{p}$ Lower Upper		(p)	
COD _{Cr}	mg/L O ₂	50.0	1.6	49.4	50.7	1/G	13
						3/H	
						3/I	
						5/K	
						2/L	
						1/O	
						9/X	
TOC (NVOC)	mg/L C	20.3	0.51	20.0	20.6	9/A	15
						1/C	
						8/E	
						2/X	

Methods

COD_{Cr}

- G: Nanocolor COD 60, 5 - 60 mg/L O₂. (Macherey-Nagel 985 022)
H: Lange 5 – 60 mg/L. (Lange LCK 414)
I: Lange 15 – 150 mg/L. (Lange LCK 314)
K: Lange 0 – 150 mg/L. (ISO COD). (Lange LCI 500)
L: Hach 3 – 150 mg/L. (Hach method 8000)
O: Merck 15 – 300 mg/L. (Merck 1.14895)
X: Other method

TOC (NVOC)

- A: Purge CO₂ from the acidified sample. Oxidise organic compounds in the sample catalytically at $\geq 680^{\circ}\text{C}$ to CO₂. Quantify by IR-spectrophotometry. (SM 19-20th ed. method 5310 A + B, EN 1484)
- C: Purge CO₂ from the acidified sample. Oxidise organic compounds in the sample by K₂S₂O₈ at approx. 100°C to CO₂. Quantify by IR-spectrophotometry. (SM 19-20th ed. method 5310 A + D, EN 1484)
- E: Lange 3 – 30 mg/L. (Lange LCK 385)
- X: Other method

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:

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

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

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

Metrological traceability

This Certified Reference Material (CRM) has been collaboratively determined to be traceable through a documented metrological traceability chain involving multiple participating laboratories. The metrological traceability of the certified value is established in compliance with the stated requirements of DS/EN ISO/EIC 17025:2017.

The certified value is obtained by combining different measurement procedures and laboratories accredited according to DS/EN ISO/EIC 17025:2017 or operating under a Quality Management System with comparable requirements. The individual values contributing to the certified value are considered independently metrological traceable.

Eurofins Miljø A/S is accredited according to ISO 17034:2016 by DANAK under accreditation number 535, and the scope of accreditation includes the collaborative certification of reference materials.

REFERENCES

- /1/ ISO 33405:2024. Reference materials – Approaches for characterization and assessment of homogeneity and stability.
- /2/ ISO 33401:2024. Reference materials – Contents of certificates, labels and accompanying documentation.

Date of issue: April 2025

RESPONSIBLE SCIENTIST



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Certificate revision history: April 2025 (expiry date extended; Update to newest ISO standard); May 2020 (expiry date extended); June 2018 (expiry date extended); July 2015 (original certificate date)
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ANNEX TO CERTIFICATE QC WW4A

Laboratory Measurements

COD _{Cr}						TOC (NVOC)					
y _i mg/L O ₂	s _{ri} mg/L O ₂	n _{ri}	s _{Li} mg/L O ₂	n _{Li}	Method	y _i mg/L C	s _{ri} mg/L C	n _{ri}	s _{Li} mg/L C	n _{Li}	Method
51.83	0.62	4	0.43	3	X	19.72	0.21	4	0.08	3	A
47.67	0.82	4	1.53	3	L	19.73	0.19	4	0.28	3	A
50.85	0.24	4	1.10	3	I	20.55	0.17	4	0.32	3	E
49.65	0.64	4	0.91	3	X	21.03	0.15	4	0.24	3	E
46.55	1.56	4	1.44	3	X	21.23	0.17	4	0.08	3	A
51.97	1.47	4	1.35	3	K	20.56	0.29	4	0.17	3	E
50.12	0.68	4	0.46	3	X	20.42	0.43	4	0.40	3	A
51.95	0.47	4	0.52	3	X	19.53	0.13	4	0.29	3	X
50.02	2.35	4	1.21	3	I	20.45	0.25	4	0.16	3	E
50.00	1.94	4	1.09	3	X	20.05	0.22	4	0.24	3	E
49.28	0.38	4	0.65	3	K	20.53	0.33	4	0.09	3	E
52.50	1.61	4	0.79	3	H	20.75	0.34	4	0.15	3	A
50.45	1.06	4	2.85	3	I	20.00	0.18	4	0.26	3	A
52.05	0.55	4	0.95	3	X	20.03	0.12	4	0.23	3	E
50.73	0.52	4	1.08	3	K	20.59	0.14	4	0.24	3	A
49.50	1.73	4	0.50	3	L	21.00	0.10	4	0.07	3	X
50.67	0.82	4	2.31	3	G	20.14	0.02	4	0.31	3	A
52.00	0.40	4	0.60	3	H	19.39	0.46	4	0.35	3	E
49.50	0.54	4	0.64	3	H	19.93	0.10	4	0.24	3	A
49.33	0.90	4	0.58	3	K	20.27	0.34	4	0.46	3	C
50.00	1.63	4	3.00	3	X						
47.00	2.06	4	1.39	3	O						
49.50	0.48	4	1.22	3	K						
47.98	0.49	4	1.41	3	X						

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 WW4A

Certifying Laboratories

Denmark

Analytech Miljølaboratorium A/S, Nørre Sundby
BIOFOS, København K
CP Kelco, Lille Skensved
Eurofins Miljø A/S, Vejen
Faxe Spildevand, Faxø
Force LabVest, Holstebro
Greve Solrød Forsyning, Greve
Kerteminde Forsyning-Spildevand A/S, Kerteminde
NORDs Laboratorium, Nyborg
Randers Spildevand A/S, Randers SØ
Ringsted Forsyning, Ringsted

Finland

Eurofins Scientific Finland Oy, Kokkola Laboratory and Environmental Service unit, Kokkola
Finnish Environment Institute SYKE, Joensuu
Metropolilab Oy, Helsinki
Ramboll Analytics, Lahti

Norway

Eurofins Environment Testing Norway A/S, Moss
Hardanger Miljøscenter A/S, Odda
Nedre Romerike Vannverk IKS, Avd. Noranalyse, Strømmen

Sweden

Ahlstrom Ställdalen AB, Ställdalen
Akzo Nobel Functional Chemicals AB, Domsjö
Eurofins Environment Testing Sweden A/S, Lidköping
GRYAAB, Göteborg
Gästrike Vatten AB, Skutskär
Hammargårds Avloppsreningsverk, Kungsbacka
Holmen Paper Braviken, Norrköping
Ineos Sverige AB, Stenungsund
Komlab, Örnsköldsviks kommun, Själevad
Ljungby Kommun, Avloppsreningsverk, Ljungby
Motala Kommun, Tekniska förvaltningen Vatten & Avfall, Motala
Nynäshamns Kommun, VA-avdelingen, Nynäshamn
Piteå Renhållning & Vatten AB, Hortlax
Uddebo laboratorium, Luleå
VIVAB, Varberg