Eurofins Miljø A/S
Smedeskovvej 38
DK-8464 Galten

DANAK
RM Reg. nr. 535

VKI
REFERENCE MATERIALS

CERTIFICATE FOR

QC DWB

MAJOR COMPONENTS IN DRINKING WATER

BATCH: VKI-16-10-0117 and VKI-16-11-0117

INSTRUCTIONS FOR USE OF THE REFERENCE MATERIAL

Description
This reference material consists of two different ampoules with concentrates for preparation of one reference sample for quality control after dilution with water. The certificate includes documentation for the analytical parameters sodium, potassium, calcium, magnesium, chloride, fluoride, sulphate, hydrogen carbonate, conductivity, pH and total dissolved solids.

Quantity and Preservation
For practical reasons, QC DWB consists of 2 types of ampoules packed separately: QC DW1B and QC DW2B. 1 L reference sample is produced by dilution of 10 ml of each of the two concentrates. 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 major components in drinking water. 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 of DW1B and DW2B open at the mark, withdraw the concentrate with a pipette, and dilute as follows:

Distilled water (or water of equivalent purity)	500	ml
QC DW1B	10,0	ml
QC DW2B	10,0	ml
Distilled water (or water of equivalent purity) up to	1000	ml

The reference material is only certified for sample preparation using both ampoule concentrates.

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, 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 as described above.

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 sodium, potassium, calcium, magnesium, chloride, fluoride, sulphate, hydrogen carbonate and pH in randomly selected ampoules of QC DWB. 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 in the external control. Homogeneity was confirmed for all parameters except chloride and hydrogen carbonate in the external control. For chloride and hydrogen carbonate 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.

External control
The concentration of major components in the reference material was determined by selected laboratories in an external documentation in August-September 2017. 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-DWB: 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 (appendix A.2.4):

s_L : standard deviation between the laboratories, calculated in accordance with ISO Guide 35 (appendix A.2.5):

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

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 10% (0.2 pH-units) 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 $\bar{Y}$	BETWEEN LABORATORY STANDARD DEVIATION s_L	95% CONFIDENCE LIMITS OF THE AVERAGE VALUE $\bar{Y} \pm t_{0,025}(\nu).\frac{s_L}{\sqrt{p}}$ Lower	Upper	NUMBER OF DATA SETS IN CALCULATIONS/ METHOD (p)	EXCLUDED DATA SETS C: Cochran outlier G: Grubbs outlier
Sodium	mg/L	50.9	1.29	50.2	51.6	2/A 5/B 1/C 6/D 2/X	
Potassium	mg/L	4.98	0.159	4.89	5.07	6/B 1/C 5/D 2/X	1C
Calcium	mg/L	25.3	0.68	24.9	25.7	1/A 8/B 1/C 4/D	1C
Magnesium	mg/L	4.94	0.115	4.88	5.00	2/A 8/B 1/C 5/D 1/X	
Chloride	mg/L	60	2.1	59	62	1/A 10/B 2/C 1/X	1C
Fluoride	mg/L	1.00	0.032	0.98	1.03	2/A 6/B 3/X	2C
Sulphate	mg/L	61	2.9	59	63	11/B 2/C	
Hydrogen carbonate (HCO_3)	mg/L mmol/L*	65 1.07	2.9 0.048	63 1.03	67 1.10	3/B 4/C 1/D 2/X	1C
Conductivity (κ_{25})	mS/m	44.7	0.87	44.3	45.2	17/A	5C

DETERMINAND	UNIT	AVERAGE	BETWEEN LABORATORY STANDARD DEVIATION	95% CONFIDENCE LIMITS OF THE AVERAGE VALUE $\overline{Y} \pm t_{0,025}(\nu).\frac{s_L}{\sqrt{p}}$		NUMBER OF DATA SETS IN CALCULATIONS/ METHOD	EXCLUDED DATA SETS C: Cochran outlier G: Grubbs outlier
		$\overline{Y}$	s_L	Lower	Upper	(p)	
pH (25°C)		9.13	0.047	9.11	9.16	6/A 13/B	1C
Total dissolved solids	mg/L	246	9.9	237	256	7/A	

* : The results are measured in mg/L; the concentrations in mmol/L are calculated on this basis.

Methods

Sodium, potassium:

A F-AAS (DS 258:1985, SFS 3017, NS 4775, SS 02 81 60, SM 19. ed. 3500-Na D / 3500- K D)
B ICP-AES (EN ISO 11885 and others)
C Ion chromatography (EN ISO 14911 and others)
D ICP-MS (EN ISO 17294-2 and others)

Calcium, magnesium:

A F-AAS (DS 238:1985, SFS 3018, NS 4776, SS 02 81 61)
B ICP-AES (EN ISO 11885 and others)
C Ion chromatography (EN ISO 14911 and others)
D ICP-MS (EN ISO 17294-2 and others)

Chloride:

A Potentiometric titration with silver nitrate (DS 239:1984, SFS 3006, NS 4756, SS 02 81 36)
B Ion chromatography (EN ISO 10304-1 and others)
C Flow analysis with photometric or potentiometric detection (EN ISO 15682, SM 17. ed. 4500Cl^- E)

Fluoride:

A Potentiometric measurement with ion selective elektrode (DS 218, SFS 3037, NS 4740, SS 02 81 35)
B Ion chromatography (EN ISO 10304-1 and others)

Sulphate:

B Ion chromatography (EN ISO 10304-1 and others)
C Measurement of turbidity after precipitation with barium (SM 17. ed. 4500 F^- E)

Hydrogen carbonate:

B Potentiometric measurement (EN ISO 9963-1)
C Potentiometric measurement (EN ISO 9963-2)
D Titrimetric measurement (SS 02 81 39)

Conductivity:

A Electrometric measurement (EN 27888, ISO 7888)

pH:

A Potentiometric measurement (DS 287:1978, SFS 3021, NS 4720, SS 02 81 22)
B Potentiometric measurement (EN ISO 10523)

Total dissolved solids:

A Drying of the evaporated sample for > 2 hours at 105°C ± 3 °C (DS 204:1980, SFS 3008, NS 4764, SS 02 81 13)

X Other methods

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 average of two determinations 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 35:2017. 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: April 2021

RESPONSIBLE SCIENTIST

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Certificate revision history: April 2021 (expiry date extended); June 2020 (update of references); May 2018 (original certificate date)

ANNEX TO CERTIFICATE QC DWB

Laboratory Measurements

Sodium					
Y_i mg/L	s_{ri} mg/L	n_{ri}	s_{Li} mg/L	n_{Li}	Method
52.98	0.89	4			D
52.07	0.20	4	0.79	3	X
52.19	0.10	4	0.30	3	B
51.97	0.12	4	0.65	3	D
48.88	1.93	4	0.97	3	A
49.60	0.99	4	1.70	3	D
49.94	0.66	4	1.68	3	B
51.53	0.29	4	0.21	3	B
50.24	0.21	4	0.19	2	D
49.97	0.22	4	0.65	3	D
50.13	0.62	4	1.63	3	X
52.32	0.46	4	0.39	3	D
48.93	1.23	4	0.38	3	B
50.57	0.44	4	0.73	3	B
51.93	0.85	4	1.70	3	A
51.69	0.31	4	0.17	3	C

Potassium					
Y_i mg/L	s_{ri} mg/L	n_{ri}	s_{Li} mg/L	n_{Li}	Method
5.308	0.096	4			D
4.875	0.010	4	0.037	3	X
5.034	0.018	4	0.057	3	B
4.833	0.017	4	0.077	3	D
4.822	0.068	4	0.143	3	D
5.114	0.077	4	0.197	3	B
4.748	0.060	4	0.084	3	B
5.096	0.020	4	0.034	3	B
5.000	0.204	4	0.028	2	D
4.770	0.023	4	0.053	3	D
4.938	0.057	4	0.175	3	X
4.957	0.055	4	0.055	3	B
5.118	0.110	4	0.071	3	B
5.082	0.224	4	0.090	3	C

Calcium					
Y_i mg/L	s_{ri} mg/L	n_{ri}	s_{Li} mg/L	n_{Li}	Method
26.35	0.26	4			D
26.38	0.15	4	0.58	3	A
25.45	0.14	4	0.12	3	B
24.65	0.10	4	0.33	3	D
24.47	0.59	4	0.86	3	B
24.84	0.34	4	0.92	3	B
26.39	0.06	4	0.20	3	B
25.49	1.21	4	0.08	2	D
24.53	0.16	4	0.46	3	D
25.10	0.99	4	0.96	3	B
24.93	0.79	4	0.37	3	B
24.77	0.23	4	0.24	3	B
25.17	0.10	4	0.25	3	B
25.77	0.30	4	0.20	3	C

Magnesium					
Y_i mg/L	s_{ri} mg/L	n_{ri}	s_{Li} mg/L	n_{Li}	Method
5.070	0.020	4			D
4.987	0.025	4	0.043	3	A
4.949	0.035	4	0.045	3	B
5.022	0.030	4	0.024	3	D
4.817	0.026	4	0.219	3	A
4.722	0.042	4	0.080	3	B
5.020	0.052	4	0.162	3	B
5.019	0.021	4	0.049	3	B
4.831	0.177	4	0.049	2	D
4.828	0.013	4	0.129	3	D
4.875	0.071	4	0.232	3	X
4.845	0.111	4	0.084	3	D
4.868	0.217	4	0.159	3	B
4.981	0.097	4	0.190	3	B
4.883	0.031	4	0.003	3	B
5.015	0.015	4	0.071	3	B
5.182	0.061	4	0.096	3	C

Chloride					
Y_i mg/L	s_{ri} mg/L	n_{ri}	s_{Li} mg/L	n_{Li}	Method
59.4	0.2	4	0.3	3	B
57.2	0.4	4	0.4	3	B
58.8	0.1	4	0.1	3	B
60.4	0.3	4	0.1	3	B
65.3	0.3	4	0.03	3	B
57.9	0.3	4	0.7	3	C
63.2	1.0	4	0.3	2	B
60.1	0.2	4	0.4	3	B
58.7	0.2	4	0.7	3	A
61.3	0.6	6	0.6	2	X
60.7	0.2	4	0.4	3	B
60.4	0.2	4	1.0	3	C
59.3	0.3	4	0.1	3	B
60.5	0.2	4	0.4	3	B

Fluoride					
Y_i mg/L	s_{ri} mg/L	n_{ri}	s_{Li} mg/L	n_{Li}	Method
0.989	0.005	4	0.003	3	B
0.971	0.005	4	0.003	3	B
1.028	0.024	4	0.008	3	B
1.011	0.014	4	0.019	3	A
1.008	0.013	4	0.006	3	B
1.033	0.011	6	0.004	2	X
1.073	0.021	4	0.011	3	X
0.960	0.005	4	0.025	3	A
0.996	0.007	4	0.008	3	B
0.984	0.005	4	0.030	2	X
0.983	0.021	4	0.035	3	B

Sulphate					
Y_i mg/L	s_{ri} mg/L	n_{ri}	s_{Li} mg/L	n_{Li}	Method
57.0	0.2	4	1.0	3	B
58.1	0.5	4	0.3	3	B
59.6	0.1	4	0.1	3	B
66.1	0.7	4	0.5	3	B
58.2	0.7	4	1.9	3	C
64.7	0.7	4	0.2	2	B
60.4	0.1	4	0.2	3	B
65.5	0.3	4	0.7	3	B
61.1	0.4	4	0.5	3	B
59.1	0.2	4	1.9	3	C
61.1	1.5	4	0.5	3	B
58.7	0.1	4	0.1	3	B
60.8	0.5	4	0.3	3	B

Hydrogen carbonate					
Y_i mg/L	s_{ri} mg/L	n_{ri}	s_{Li} mg/L	n_{Li}	Method
66.4	0.3	4	0.1	3	D
64.7	0.4	4	0.5	3	X
64.0	1.3	4	0.2	3	B
66.0	0.2	4	0.2	3	C
70.6	0.5	4	1.3	3	C
62.9	1.7	4	0.7	3	B
67.0	0.1	4	0.5	3	C
60.0	0.8	6	0.6	2	B
65.8	1.0	4	0.2	3	C
63.1	0.4	4	0.4	3	X

Conductivity					
Y_i mS/m	s_{ri} mS/m	n_{ri}	s_{Li} mS/m	n_{Li}	Method
44.83	0.17	4			A
45.02	0.00	4	0.06	3	A
46.60	0.15	4	0.07	3	A
44.50	0.00	4	0.10	3	A
44.93	0.10	4	0.24	3	A
42.60	0.06	4	0.13	3	A
44.62	0.13	4	0.13	3	A
45.65	0.19	4	0.11	3	A
44.32	0.11	6	0.09	2	A
44.72	0.13	4	0.13	3	A
45.62	0.17	4	0.10	3	A
44.61	0.08	4	0.13	3	A
44.00	0.08	4	0.00	3	A
44.24	0.21	4	0.31	3	A
44.34	0.27	4	0.25	3	A
44.36	0.05	4	0.04	3	A
45.73	0.21	4	0.16	3	A

pH					
Y_i	s_{ri}	n_{ri}	s_{Li}	n_{Li}	Method
9.110	0.016	4			B
9.218	0.005	4	0.012	3	A
9.155	0.028	4	0.026	3	A
9.107	0.039	4	0.011	3	B
9.015	0.049	4	0.036	3	A
9.187	0.015	4	0.009	3	B
9.130	0.005	4	0.014	3	A
9.113	0.025	4	0.035	3	B
9.110	0.014	4	0.020	3	B
9.183	0.011	6	0.009	2	A
9.097	0.022	4	0.076	3	B
9.118	0.029	4	0.006	3	B
9.123	0.010	4			B
9.195	0.013	4	0.005	3	B
9.075	0.022	4	0.029	3	B
9.167	0.013	4	0.015	3	B
9.160	0.045	4	0.020	3	A
9.152	0.013	4	0.025	3	B
9.135	0.062	4	0.042	3	B

Total dissolved solids					
Y_i mg/L	s_{ri} mg/L	n_{ri}	s_{Li} mg/L	n_{Li}	Method
228.0	2.8	4	11.3	3	A
240.0	3.8	4	10.0	3	A
256.0	6.9	4	4.6	3	A
246.3	1.0	4			A
252.8	8.4	4	4.1	3	A
254.8	7.4	4	1.5	3	A
247.2	8.7	4	7.2	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 4.

ANNEX TO CERTIFICATE QC DWB

Certifying Laboratories

Denmark
ALS Denmark A/S, Humlebæk
AnalyTech Miljølaboratorium A/S, Nørresundby
Eurofins Miljø A/S, Vejen
Force Technology, Brøndby
Højvang Laboratorier A/S, Dianalund
Højvang Laboratorier A/S, Holstebro
R. Dons' Vandanalytisk Laboratorium A/S, Værløse

Faroe Islands
Heilsufrødiliga Starvsstovan, Tórshavn

Finland
Water and Environment Research of South-West Finland, Turku

Norway
Eurofins Environment Testing Norway AS, Bergen
Eurofins Environment Testing Norway AS, Moss
Eurofins Food & Feed Testing, Alta
Eurofins Food & Feed Testing, Leknes
Eurofins Food & Feed Testing, Sortland
Fjellab, Rjukan
Nedre Romerike Vannverk IKS, avd. NorAnalyse, Strømmen
TosLab A/S, Tromsø
Vestfoldlab A/S, Sem

Sweden
ALcontrol AB, Linköping
ALcontrol AB, Karlstad
ALS Scandinavia, Luleå
Eskilstuna Strängnäs Energi och Miljö AB, Eskilstuna
Eurofins Environment Testing Sweden AB, Lidköping
Karlskrona kommuns Laboratorium, Lyckeby
Tekniska verken i Linköping AB, Linköping
VA Syd, Malmö

Åland Islands
ÅMHM Laboratoriet, Jomala