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

VKI
REFERENCE MATERIALS

CERTIFICATE FOR

QC METAL LL2

TRACE ELEMENTS/METALS

BATCH: VKI-13-3-0304

INSTRUCTIONS FOR USE OF THE REFERENCE MATERIAL

Description
This reference material consists of ampoules with a concentrate containing the trace elements/metals Ag, Ba, Cd, Co, Fe, Mn, Pb, Sb, Se and Sr for preparation of reference samples for quality control after dilution with water.

Quantity
QC METAL LL2 consists of ampoules with a minimum of 15 mL concentrate in each. 1 litre reference sample is prepared by dilution of 10 mL QC METAL LL2. The concentrate has been preserved with nitric acid, 5% (V/V).

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 determination of trace trace in water. It may also be used in the quality control of other sample types and for the implementation and optimisation of analytical instruments and analytical methods. For these purposes other dilutions than intended for quality control of water may be appropriate. It is important that the batch numbers of the reference material and on the certificate are identical.

Preparation for Use
Stabilise the ampoule QC METAL LL2 at room temperature (approx. 20°C). Break the ampoule neck open at the mark, withdraw the concentrate with a pipette, and dilute with water without a detectable content of trace elements/metals and preserve with nitric acid, e.g. 10.00 mL concentrate and 3 mL concentrated nitric acid is diluted up to 1000 mL with water. The certified concentrations are given in the table on page 3 of this certificate.

The dilution rate between the concentrate QC METAL LL2 and water can be altered as appropriate for the intended use.

Please observe. Do not pour the concentrate out of the ampoule. It is important to ensure sufficient purity of the water and acid used for preparation. Use for example an analytical quality, ultrapure or quartz distilled quality.

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, 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.

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
The production of this reference material is in accordance with the quality management procedures of Eurofins, with the aim to obtain the intended quality of the material.

Documentation of Content

Internal Control
The analytical quality of Eurofins has been documented and found satisfactory by regular participation in international interlaboratory comparisons.

Homogeneity:
The homogeneity of all parameters has been investigated by measurements of Ag, Ba, Cd, Co, Fe, Mn, Pb, Se and Sr in randomly selected ampoules of the reference material QC METAL LL2. Tests for homogeneity have been performed by comparing the standard deviation between the ampoules with the within batch standard deviation obtained from duplicate measurements of the reference material in the same ampoule (F-test, 95%). No signs of inhomogeneity were found.

Stability:
The stability of the reference material is being followed by regular check measurements of the reference material as part of Eurofins' normal laboratory routine. No signs of instability were observed at the date of this certificate.

External Control
Danish, Finnish, Norwegian and Swedish laboratories performed the external laboratory documentation. The laboratories were requested to analyse two ampoules in the same analytical series, one as a duplicate determination, the other as a single determination and also to analyse one ampoule 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 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)

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

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

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

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 first criterion for selection of certifying Danish, Norwegian and Swedish laboratories was that the laboratories perform the analyses on a routine basis, i.e. more than approximately 20 samples each year.

Furthermore, the laboratories were selected on the basis of their results in recent proficiency tests, the criterion being that the laboratory results in those proficiency tests diverged less than 2 standard deviations from the nominal value.

For Finnish laboratories the Finnish Reference Laboratory has identified the laboratories as qualified.

The criteria for selection of laboratory results in this certification were:
- the laboratory result for the control sample deviated less than 15% from the nominal value and
- the laboratory results were not Cochran outliers, Grubbs outliers or deemed to be an outlier on the basis of a scientific evaluation.

Final decision regarding exclusion of deviating results was based on feed-back from the laboratories with deviating results. The statistical parameters, the applied laboratory methods and number of laboratories using each method are given in the following table.

The data included in the external control and names of the participating laboratories are listed in an annex to this certificate.

Certified Values

DETERMI-NAND	UNIT	AVERAGE	BETWEEN LABORATORY STANDARD DEVIATION	95% CONFIDENCE LIMITS OF THE AVERAGE VALUE $y_{char} \pm t_{0,025}(\nu) \cdot \frac{s(y)}{\sqrt{p}}$		NUMBER OF LABORATORIES IN CALCULATIONS/METHOD	EXCLUDED LABORA-TORIES G: Grubbs outlier C: Cochran outlier U: Other excluded
		y_{char}	s(y)	Lower	Upper	(p)	
Silver	µg/L Ag	5.02	0.13	4.91	5.12	1/150, 7/562, 1/911	1C
Barium	µg/L Ba	101.5	2.8	99.1	103.8	1/150, 1/550, 5/562, 1/950	1C, 1U
Cadmium	µg/L Cd	1.99	0.033	1.96	2.02	1/510, 1/550, 3/562, 1/911	6U
Cobalt	µg/L Co	51.6	2.5	49.7	53.5	1/150, 1/510, 1/550, 5/562, 1/950	2C, 1U
Iron	µg/L Fe	200	4.7	195	205	5/562, 1/950	3C, 1U
Manganese	µg/L Mn	50.0	1.1	49.2	50.7	1/150, 1/520, 1/550, 6/562, 1/950	1C, 1U
Lead	µg/L Pb	19.8	0.96	19.0	20.6	1/150, 1/510, 6/562	3C, 1U
Antimony	µg/L Sb	49.1	1.2	47.8	50.3	1/550, 4/562, 1/950	4U
Selenium	µg/L Se	99.1	6.8	92.8	105.4	1/550, 5/562, 1/911	1C, 2U
Strontium	µg/L Sr	49.1	0.95	48.3	49.9	1/150, 1/550, 5/562, 1/950	1U

Methods

Digestion method, first digit of the method number

Method code	Principle
1	Digestion with HNO_3 in an autoclave (e.g. DS 259, DS 2210)
5	No digestion
9	Other digestion methods

Analytical methods, second and third digit of the method number

Method code	Principle
10	AAS with graphite furnace, calibration curve
11	AAS with graphite furnace, calibration by standard addition
20	AAS with acetylene-air flame
50	ICP-AES, calibration curve
62	ICP-MS, internal standard and calibration curve

AAS: atomic absorption spectrometry
ICP-AES: inductively coupled plasma – atomic emission spectrometry
ICP-MS: inductively coupled plasma – mass spectrometry

Use of the certified values
For laboratories with an analytical quality that is comparable with the laboratories that have contributed with 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:

$$y_{\text{char}} \pm \text{t}_{0,025}(\nu) \cdot \text{s}(y)$$

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

$$y_{\text{char}} \pm \text{t}_{0,025}(\nu) \cdot \frac{\text{s}(y)}{\sqrt{2}}$$

Parameter	Single determination µg/L	Duplicate determination µg/L
Silver (Ag)	4.71 – 5.32	4.80 – 5.23
Barium (Ba)	94.7 – 108.2	96.7– 106.2
Cadmium (Cd)	1.91 – 2.08	1.93 – 2.05
Cobalt (Co)	45.9 – 57.3	47.6 – 55.7
Iron (Fe)	188 – 212	191 – 208
Manganese (Mn)	47.6 – 52.4	48.3 – 51.7
Lead (Pb)	17.5 – 22.1	18.2 – 21.4
Antimony (Sb)	45.9 – 52.2	46.9 – 51.3
Selenium (Se)	82.4 – 115.7	87.3 – 110.9
Strontium (Sr)	46.9 – 51.4	47.5 – 50.7

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.

/3/ ISO 5725-2, 1994, Accuracy (trueness and precision) of measurement methods and results - Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method.

Date of issue: Januar 2023

RESPONSIBLE SCIENTIST

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Certificate revision history: Januar 2023 (expiry date extended; update according to newest ISO Guide35); May 2020 (expiry date extended); October 2018 (expiry date extended); December 2013 (expiry date added); September 2004 (original certificate date)

ANNEX TO CERTIFICATE QC METAL LL2

Laboratory Measurements

Ag						Ba					
y_i µg/l	s_{ri} µg/l	n_{ri}	s_{Li} µg/l	N_{Li}	Metode	y_i µg/l	s_{ri} µg/l	n_{ri}	s_{Li} µg/l	n_{Li}	Metode
5.08	0.12	3	0.29	3	562	104.0	0.00	3	1.53	3	562
5.18	0.12	3	0.08	3	562	102.0	2.52	3	1.58	3	562
5.01	0.10	3	0.05	3	562	100.7	0.51	3	0.99	3	562
5.10	0.00	3	0.00	3	562	100.5	1.12	3	1.05	3	562
5.03	0.02	3	0.05	3	562	97.1	0.52	3	2.75	3	562
4.89	0.04	3	0.07	3	562	99.7	0.57	3	1.38	3	550
5.00	0.03	3	0.27	3	562	101.1	0.40	3	1.97	3	950
4.74	0.03	3	0.27	3	911	106.6	1.53	3	2.52	3	150
5.12	0.10	3	0.30	3	150						

Cd						Co					
y_i µg/l	s_{ri} µg/l	n_{ri}	S_{Li} µg/l	N_{Li}	Metode	y_i µg/l	s_{ri} µg/l	n_{ri}	s_{Li} µg/l	n_{Li}	Metode
2.03	0.036	3	0.021	3	562	52.1	0.30	3	0.21	3	562
1.99	0.012	3	0.031	3	562	54.3	0.21	3	0.60	3	562
2.01	0.021	3	0.008	3	562	51.6	0.24	3	0.60	3	562
1.93	0.066	3	0.136	3	510	51.2	0.36	3	0.39	3	562
1.99	0.038	3	0.049	3	550	52.6	0.20	3	1.02	3	562
2.00	0.029	3	0.094	3	911	45.6	0.60	3	1.50	3	510
						52.1	0.21	3	1.23	3	550
						51.7	0.10	3	1.54	3	950
						53.4	0.76	3	1.29	3	150

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 pages 3 and 4

ANNEX TO CERTIFICATE QC METAL LL2

Laboratory Measurements

Fe						Mn					
y_i µg/l	s_{ri} µg/l	n_{ri}	s_{Li} µg/l	n_{Li}	Metode	y_i µg/l	s_{ri} µg/l	n_{ri}	S_{Li} µg/l	n_{Li}	Metode
202.2	1.5	3	2.6	3	562	49.9	0.32	3	0.93	3	562
198.6	2.0	3	6.4	3	562	49.1	0.95	3	2.04	3	562
200.4	0.7	3	3.0	3	562	52.0	0.36	3	0.15	3	562
193.3	1.3	3	1.7	3	562	49.7	0.26	3	0.46	3	562
207.2	1.2	3	8.7	3	562	49.9	0.38	3	3.40	3	562
197.5	0.6	3	5.4	3	950	50.1	0.29	3	0.86	3	562
						51.2	0.58	3	2.27	3	520
						48.3	0.40	3	0.67	3	550
						49.1	0.10	3	1.34	3	950
						50.5	0.64	3	1.00	3	150

Pb						Sb					
y_i µg/l	s_{ri} µg/l	n_{ri}	s_{Li} µg/l	n_{Li}	Metode	y_i µg/l	s_{ri} µg/l	n_{ri}	S_{Li} µg/l	n_{Li}	Metode
19.9	0.12	3	0.88	3	562	48.8	2.84	3	0.89	3	562
20.2	0.17	3	0.15	3	562	49.3	1.37	3	0.98	3	562
20.1	0.15	3	0.25	3	562	47.3	0.23	3	0.85	3	562
19.8	0.08	3	0.19	3	562	48.6	1.21	3	1.25	3	562
18.7	0.29	3	0.21	3	562	49.4	0.93	3	1.77	3	550
19.9	0.15	3	0.32	3	562	51.0	0.35	3	0.85	3	950
18.4	0.10	3	1.31	3	510						
21.5	0.44	3	0.83	3	150						

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 pages 3 and 4

ANNEX TO CERTIFICATE QC METAL LL2

Laboratory Measurements

Se						Sr					
y_i µg/l	s_{ri} µg/l	n_{ri}	S_{Li} µg/l	n_{Li}	Metode	y_i µg/l	s_{ri} µg/l	n_{ri}	s_{Li} µg/l	n_{Li}	Metode
87.0	0.66	3	8.37	3	562	49.7	0.32	3	0.88	3	562
100.7	1.87	3	0.89	3	562	49.3	0.95	3	1.36	3	562
98.7	0.78	3	0.62	3	562	50.1	0.27	3	0.41	3	562
98.8	0.25	3	0.57	3	562	48.2	0.17	3	1.61	3	562
110.4	0.58	3	4.35	3	562	48.0	0.20	3	0.15	3	562
99.2	1.65	3	2.82	3	550	50.4	0.25	3	0.25	3	550
99.0	0.53	3	2.08	3	911	49.4	0.15	3	1.49	3	950
						47.9	0.78	3	0.86	3	150

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 pages 3 and 4

ANNEX TO CERTIFICATE QC METAL LL2

Certifying laboratories

Denmark

AnalyCen A/S	Fredericia
Elsam Kraft A/S, Enstedværket	Åbenrå
Højvang Miljølaboratorium	Dianalund
Miljølaboratoriet Storkøbenhavn I/S	Glostrup

Finland

Consulting Engineers Paavo Ristola Ltd.	Hollola
Finnish Environment Institute	Helsinki
Helsinki City Environmental Laboratory	Helsingin Kaupunki
University of Jyväskylä, Institute for Environmental Research	Jyväskylä

Norway

NIVA	Oslo

Sweden

Stockholm Vatten AB, Vattenvård	Stockholm
Tekniska Verken i Linköping AB, Avloppsreningsverket, Laboratoriet VPP	Linköping