



CERTIFICATE FOR
QC METAL LL1
TRACE ELEMENTS/METALS

BATCH: VKI-12-5-0908

INSTRUCTIONS FOR USE OF THE REFERENCE MATERIAL

Description

This reference material consists of an ampoule with concentrate for preparation of a reference sample for quality control after dilution with water. The certificate includes documentation for the analytical parameters Al, As, Cr, Cu, Mo, Ni, Sn, V, and Zn.

Quantity and Preservation

QC METAL LL1 is an ampoule with approx. 15 mL concentrate. 1000 mL of reference sample is produced by dilution of 10 mL concentrate. The concentrate is preserved with nitric acid, 5 %, and hydrochloric acid, 5 %.

Use

The reference material is intended for quality control, i.e. measurement and control of the trueness and precision of analyses. It is typically intended for analyses of trace elements/metals in water. It may also be used in the quality control of other sample types and for the qualification and validation 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 preserve with acids that have no measurable content of trace elements/metals. Then dilute 1:100 with water without a measurable content of trace elements/metals. For example 10.0 mL concentrate and 3.0 mL concentrated nitric acid is diluted up to 1000 mL with water. For analysis for Sn, for example 10.0 mL concentrate and 10.0 mL concentrated hydrochloric acid is diluted up to 1000 mL with water. The certified concentrations are given in the table on page 3 of this certificate.

The reference material must not be poured out of the ampoule. It is important to ensure sufficient purity of the water and acids used for preparation. Use for example an analytical, ultrapure or quartz distilled quality.

The dilution ratio between the concentrate QC METAL LL1 and water can be altered as appropriate for the intended use. However, please note that the certified value and the confidence limits are only valid for the prescribed dilution ratio 1:100.

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 2030** provided the material is stored under the recommended conditions.

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

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 all certified trace elements in randomly selected ampoules of QC METAL LL1. 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 was followed up in accordance with ISO Guide 35 /1/ for all parameters as a part of the external control. No indication of heterogeneity was found.

Stability:

The stability of the reference material is being followed by regular analyses of Cu and Zn in reference materials stored at 20 °C and 37 °C, and no indication of instability was observed at the date of this certificate.

External documentation

The external laboratory documentation was performed by selected Nordic and German laboratories. The laboratories were requested to analyse 4 ampoules: two ampoules as duplicate determinations in the same analytical series, followed by one ampoule in each of two different analytical series as single determinations. In addition, the laboratories were requested to analyse a control sample sent together with the reference material. 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):

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

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

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 that the laboratories perform the analyses on a routine basis. Furthermore, the laboratories were selected on the basis of their results in proficiency tests and earlier certifications.

The criteria for selection of laboratories from Denmark, Germany, Norway and Sweden were as follows:

- the laboratory results in the proficiency tests gave z-scores below 2 (absolute values), and
- the laboratory analyses more than 20 analytical series each year or holds accreditation for the parameter.

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

The criteria for selection of laboratory results for the certification were:

- the laboratory result for the control sample in the certification deviated less than 15 % from the nominal value, and
- the laboratory results in the certification are not Cochran or Grubbs outliers.

The data included in the external documentation 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 y_{char}	BETWEEN LABORATORY STANDARD DEVIATION $s(y)$	95 % CONFIDENCE LIMITS OF THE AVERAGE VALUE $y_{char} \pm t_{0,025}(v) \cdot \frac{s(y)}{\sqrt{p}}$		NUMBER OF DATA SETS IN CALCULATIONS/ METHOD (p)	EXCLUDED DATA SETS C: Cochran outlier G: Grubbs outlier
				Lower	Upper		
Aluminium	µg/L Al	204	10.4	197	212	3/D and 7/E	1C
Arsenic	µg/L As	29.1	0.85	28.5	29.6	1/A and 12/E	1C
Chromium	µg/L Cr	19.5	0.45	19.2	19.9	3/D and 8/E	2C, 1G
Copper	µg/L Cu	19.6	0.71	19.1	20.0	11/E	1C
Molybdenum	µg/L Mo	19.3	0.95	18.6	19.9	1/D and 10/E	2C
Nickel	µg/L Ni	19.8	0.83	19.2	20.4	1/D and 10/E	4C
Tin	µg/L Sn	19.5	0.69	18.9	20.0	1/D and 8/E	
Vanadium	µg/L V	19.7	0.61	19.3	20.1	11/E	1C
Zinc	µg/L Zn	49.9	1.72	48.8	51.0	1/D and 11/E	2C

Methods

- A Atomic absorption spectrometry with graphite furnace, e.g. ISO 15586
D Inductively coupled plasma atomic emission spectrometry (ICP-AES), e.g. ISO 11885
E Inductively coupled plasma mass spectrometry (ICP-MS), e.g. ISO 17294

Use of the Certified Values

For laboratories with an analytical quality that is comparable with that of the laboratories who have contributed to the external documentation of this certificate, the following applies:

- 1) For single determinations, analytical results will with a probability of 95 % be in the interval:

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

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

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

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 Guide 35:2017. Reference materials – Guidance 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 2024.

RESPONSIBLE SCIENTIST



Rikke Mikkelsen, MSc.
Eurofins Miljø A/S
DK-8464 Galten

Website: www.eurofins.dk/refmat

Certificate revision history: April 2024 (expiry date extended, update to the newest ISO standards); January 2023 (expiry date extended; update according to newest ISO Guide 35); May 2020 (expiry date extended); October 2018 (expiry date extended); December 2013 (expiry date added); August 2009 (original certificate date)

ANNEX TO CERTIFICATE QC METAL LL1

Laboratory Measurements

Aluminium					
y_i µg/L	S_{ri} µg/L	n_{ri}	S_{Li} µg/L	n_{Li}	Method
215	2,08	4	3,33	3	D
195	2,83	4	4,73	3	E
197	1,50	4	3,17	3	E
222	2,05	4	1,11	3	D
199	2,65	4	2,02	3	E
205	3,74	4	8,96	3	E
190	4,69	4	5,69	3	E
199	1,91	4	2,75	3	E
217	4,57	4	11,44	3	D
205	2,67	4	4,50	3	E

Arsenic					
y_i µg/L	S_{ri} µg/L	n_{ri}	S_{Li} µg/L	n_{Li}	Method
28,6	0,10	4	0,44	3	E
28,4	0,66	4	0,73	3	E
28,4	0,17	4	0,22	3	E
30,3	0,29	4	0,62	3	E
29,9	0,06	4	0,09	3	E
29,7	0,20	4	0,45	3	E
28,2	0,24	4	0,14	3	E
29,1	0,26	4	0,38	3	E
28,4	0,65	4	0,67	3	E
28,6	0,31	4	0,39	3	E
28,1	0,34	4			A
30,5	0,48	4	0,16	3	E
29,6	0,25	4	0,60	3	E

Chromium					
y_i µg/L	S_{ri} µg/L	n_{ri}	S_{Li} µg/L	n_{Li}	Method
19,7	0,58	4	0,29	3	D
20,4	0,20	4	0,21	3	E
19,8	0,13	4	0,34	3	E
19,0	0,38	4	0,40	3	E
19,8	0,35	4	0,26	3	E
19,6	0,98	2	0,07	3	D
19,4	0,35	4	0,21	3	E
19,0	0,42	4	0,46	3	E
18,9	0,24	4	0,54	3	E
20,0	1,00	4	0,87	3	D
19,5	0,41	4	0,15	3	E

Copper					
y_i µg/L	S_{ri} µg/L	n_{ri}	S_{Li} µg/L	n_{Li}	Method
21,1	0,71	4	0,74	3	E
20,0	0,59	4	0,70	3	E
20,2	0,25	4	0,42	3	E
19,0	0,15	4	0,48	3	E
19,6	0,26	4	0,25	3	E
19,6	0,14	4	0,10	3	E
19,5	0,34	4	0,41	3	E
18,5	0,56	4	0,28	3	E
18,7	0,22	4	0,16	3	E
19,5	0,42	4	0,21	3	E
19,7	0,49	4	0,26	3	E

Molybdenum					
y_i µg/L	S_{ri} µg/L	n_{ri}	S_{Li} µg/L	n_{Li}	Method
18,9	0,38	4	0,44	3	E
19,9	0,38	4	0,30	3	E
18,7	0,42	4	0,54	3	E
19,6	0,13	4	0,17	3	E
18,2	0,28	4	0,65	3	E
21,4	0,68	4	0,60	3	D
19,3	0,30	4	0,21	3	E
18,7	0,33	4	0,16	3	E
18,2	0,37	4	0,22	3	E
19,1	0,14	4	0,10	3	E
20,1	0,37	4	0,12	3	E

Nickel					
y_i µg/L	S_{ri} µg/L	n_{ri}	S_{Li} µg/L	n_{Li}	Method
20,7	0,50	4	0,52	3	D
20,1	0,34	4	0,08	3	E
20,8	0,42	4	0,40	3	E
19,8	0,26	4	0,21	3	E
19,4	0,15	4	0,16	3	E
21,2	0,30	4	0,16	3	E
19,4	0,29	4	0,01	3	E
18,9	0,31	4	0,20	3	E
18,5	0,19	4	0,43	3	E
19,8	0,40	4	0,32	3	E
19,4	0,19	4	0,22	3	E

Tin					
y_i µg/L	S_{ri} µg/L	n_{ri}	S_{Li} µg/L	n_{Li}	Method
19,7	0,13	4	0,44	3	E
19,3	0,21	4	0,28	3	E
20,1	0,19	4	0,16	3	E
20,7	0,64	4	0,66	3	D
18,4	0,13	4	0,12	3	E
19,0	0,50	4	0,26	3	E
19,0	0,27	4	0,53	3	E
19,3	0,21	4	0,17	3	E
19,8	0,24	4	0,63	3	E

Vanadium					
y_i µg/L	S_{ri} µg/L	n_{ri}	S_{Li} µg/L	n_{Li}	Method
20,9	0,22	4	0,51	3	E
19,4	0,48	4	0,29	3	E
20,5	0,50	4	0,51	3	E
19,2	0,38	4	0,44	3	E
19,8	0,17	4	0,10	3	E
19,3	0,33	4	0,11	3	E
20,2	0,31	4	0,68	3	E
19,1	0,26	4	0,26	3	E
19,2	0,33	4	0,36	3	E
19,4	0,39	4	0,17	3	E
19,6	0,22	4	0,35	3	E

Zinc					
y_i µg/L	s_{ri} µg/L	n_{ri}	s_{Li} µg/L	n_{Li}	Method
51,7	1,83	4	1,15	3	D
52,0	0,54	4	2,23	3	E
50,2	0,49	4	0,84	3	E
50,5	0,81	4	1,06	3	E
49,1	0,42	4	0,22	3	E
52,7	0,71	4	0,59	3	E
49,9	0,37	4	1,15	3	E
49,1	1,35	4	0,91	3	E
47,5	0,76	4	0,66	3	E
46,8	0,14	4	1,67	3	E
49,9	0,74	4	0,77	3	E
49,8	0,38	4	1,37	3	E

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 METAL LL1

Certifying Laboratories

Denmark

Eurofins Miljø A/S, Vejle
FORCE Technology, Brøndby
MILANA A/S, Helsingør
Miljøcenter Vestjylland, Holstebro
Miljølaboratoriet I/S, Glostrup

Finland

Finnish Environment Institute, Helsinki
Ramboll Analytics, Lahti

Germany

Agrolab, Saarstedt

Norway

Eurofins Norsk Miljøanalyse, Moss
Hardanger Miljøcenter AS, Odda
NIVA, Oslo

Sweden

Alcontrol AB, Linköping
ALS Scandinavia AB, Luleå
Eurofins Environment Sweden AB, Lidköping