

## CERTIFICATE FOR

## QC METAL HL2

## METALS IN WATER

**BATCH:** VKI-15-3-1203

### INSTRUCTIONS FOR USE OF THE REFERENCE MATERIAL

#### Description

This reference material consists of ampoules with a concentrate containing the elements Ag, Ba, Cd, Co, Cr, Cu, Ni and Sr for preparation of reference samples for quality control after dilution with water.

#### Quantity

QC METAL HL2 consists of ampoules with a minimum of 15 mL concentrate in each. 250 mL reference sample is prepared by dilution of 10 mL QC METAL HL2. 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 internal quality control in connection with determination of metals 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 HL2 at room temperature (approx. 20°C). Break the ampoule neck open at the mark in such a way that contamination of the concentrate from particles is avoided, withdraw the concentrate with a pipette, and dilute with water without a detectable content of metals and preserve with nitric acid, e.g. 10.00 mL concentrate and 750 µL concentrated nitric acid is diluted up to 250 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 HL2 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 of nitric acid.

#### 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 **1<sup>st</sup> of April 2021** 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 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, Cr, Cu, Ni and Sr in randomly selected ampoules of the reference material QC METAL HL2. 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. For control of the analytical quality a control sample was provided to be analysed in the first analytical series. 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 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

DETERMINAND	UNIT	AVERAGE $\bar{Y}$	BETWEEN LABORATORY STANDARD DEVIATION $S_L$	95% CONFIDENCE LIMITS OF THE AVERAGE VALUE $\bar{Y} \pm t_{0,025}(v) \cdot \frac{S_L}{\sqrt{p}}$		NUMBER OF LABORATORIES IN CALCULATIONS/METHOD  (p)	EXCLUDED LABORATORIES  G: Grubbs outlier C: Cochran outlier U: Other excluded
				Lower	Upper		
Silver	mg/L Ag	2.04	0.045	2.01	2.07	1/150, 1/162, 2/520, 2/550, 1/552, 3/562, 1/950	1U
Barium	mg/L Ba	2.04	0.033	2.01	2.07	2/550, 1/552, 3/562, 1/950	1C, 2U
Cadmium	mg/L Cd	1.02	0.025	1.00	1.04	1/150, 1/162, 1/520, 3/550, 1/552, 3/562, 1/950	1U
Cobalt	mg/L Co	0.512	0.011	0.503	0.521	1/150, 1/520, 2/550, 1/552, 3/562, 1/950	2C, 1U
Chromium	mg/L Cr	4.05	0.109	3.98	4.13	1/150, 1/520, 3/550, 1/552, 3/562, 1/950	1C, 1U
Copper	mg/L Cu	4.28	0.051	4.24	4.32	1/150, 3/550, 1/552, 3/562, 1/950	1C, 2G, 1U
Nickel	mg/L Ni	2.04	0.044	2.01	2.07	1/150, 1/520, 3/550, 1/552, 3/562, 1/950	1C, 1U
Strontium	mg/L Sr	5.08	0.21	4.87	5.30	1/150, 2/550, 1/552, 1/562, 1/950	2C, 1U

### Methods

#### Digestion method, first digit of the method number

Method code	Principle
1	Digestion with HNO <sub>3</sub> 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
20	AAS with acetylene-air flame
50	ICP-AES, calibration curve
52	ICP-AES, internal standard and 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:

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

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

$$\bar{Y} \pm t_{0,025}(v) \cdot \frac{s_L}{\sqrt{2}}$$

Parameter	Single determination mg/L	Duplicate determination mg/L
Silver (Ag)	1.94 - 2.14	1.97 – 2.11
Barium (Ba)	1.95 – 2.12	1.98– 2.09
Cadmium (Cd)	0.96 – 1.07	0.98 – 1.06
Cobalt (Co)	0.486 – 0.538	0.494 – 0.531
Chromium (Cr)	3.81 – 4.30	3.88 – 4.23
Copper (Cu)	4.16 – 4.40	4.20 – 4.36
Nickel (Ni)	1.94 – 2.14	1.97 – 2.11
Strontium (Sr)	4.55 – 5.62	4.71 – 5.46

## REFERENCES

- /1/ ISO Guide 35:2006. Certification of reference materials - General and statistical principles for certification.
- /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.

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Certificate revision history: October 2018 (expiry date extended); December 2013 (expiry date added); October 2005 (total volume for preparation of reference material corrected); September 2004 (original certificate date)

## ANNEX FOR CERTIFICATE QC METAL HL2

### Laboratory Measurements

Ag						Ba					
$m_i$ mg/l	$S_{ri}$ mg/L	$n_{ri}$	$S_{Li}$ mg/L	$n_{Li}$	Metode	$m_i$ mg/L	$S_{ri}$ mg/L	$n_{ri}$	$S_{Li}$ mg/L	$n_{Li}$	Metode
2.09	0.017	3	0.025	3	562	2.08	0.020	3	0.072	3	562
1.99	0.015	3			520	2.07	0.020	3	0.009	3	550
2.06	0.031	3	0.023	3	162	2.03	0.020	3	0.010	3	562
2.12	0.021	3	0.029	3	550	2.02	0.010	3	0.017	3	552
2.02	0.005	3	0.008	3	562	2.02	0.006	3	0.030	3	562
2.01	0.011	3	0.001	3	552	1.98	0.012	3	0.028	3	550
2.00	0.006	3	0.046	3	562	2.05	0.011	3	0.016	3	950
1.97	0.012	3	0.005	3	520						
2.07	0.030	3	0.062	3	550						
2.03	0.013	3	0.021	3	950						
2.06	0.006	3	0.027	3	150						

Cd						Co					
$m_i$ mg/L	$S_{ri}$ mg/L	$n_{ri}$	$S_{Li}$ mg/L	$n_{Li}$	Metode	$m_i$ mg/L	$S_{ri}$ mg/L	$n_{ri}$	$S_{Li}$ mg/L	$n_{Li}$	Metode
0.98	0.006	3	0.017	3	562	0.524	0.000	3	0.010	3	562
1.01	0.012	3	0.004	3	550	0.520	0.003	3	0.004	3	550
1.02	0.006	3	0.013	3	162	0.501	0.004	3	0.002	3	562
1.08	0.010	3	0.015	3	550	0.501	0.001	3	0.003	3	552
1.01	0.006	3	0.005	3	562	0.505	0.005	3	0.007	3	562
1.01	0.008	3	0.003	3	552	0.533	0.007	3	0.024	3	520
1.01	0.006	3	0.011	3	562	0.514	0.003	3	0.009	3	550
1.01	0.006	3	0.023	3	520	0.508	0.003	3	0.006	3	950
1.02	0.000	3	0.012	3	550	0.503	0.007	3	0.012	3	150
1.01	0.006	3	0.015	3	950						
1.04	0.000	3	0.017	3	150						

### External Control Values

- $m_i$  : 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 FOR CERTIFICATE QC METAL HL2

### Laboratory Measurements

Cr						Cu					
$m_i$ mg/L	$s_{ri}$ mg/L	$n_{ri}$	$S_{Li}$ mg/L	$n_{Li}$	Metode	$m_i$ mg/L	$s_{ri}$ mg/L	$n_{ri}$	$S_{Li}$ mg/L	$n_{Li}$	Metode
3.87	0.030	3	0.079	3	562	4.28	0.026	3	0.142	3	562
4.14	0.039	3	0.031	3	550	4.24	0.034	3	0.020	3	550
4.21	0.015	3	0.074	3	550	4.26	0.029	3	0.040	3	550
4.01	0.019	3	0.021	3	562	4.20	0.049	3	0.027	3	562
4.01	0.020	3	0.028	3	552	4.28	0.056	3	0.034	3	552
4.13	0.036	3	0.092	3	562	4.27	0.045	3	0.088	3	562
3.92	0.015	3	0.096	3	520	4.31	0.023	3	0.143	3	550
4.02	0.038	3	0.065	3	550	4.38	0.017	3	0.019	3	950
4.07	0.014	3	0.039	3	950	4.30	0.021	3	0.070	3	150
4.15	0.012	3	0.022	3	150						

Ni						Sr					
$m_i$ mg/L	$s_{ri}$ mg/L	$n_{ri}$	$S_{Li}$ mg/L	$n_{Li}$	Metode	$m_i$ mg/L	$s_{ri}$ mg/L	$n_{ri}$	$S_{Li}$ mg/L	$n_{Li}$	Metode
2.00	0.015	3	0.038	3	562	5.08	0.060	3			550
2.09	0.045	3	0.025	3	550	4.92	0.026	3	0.016	3	562
2.10	0.006	3	0.048	3	550	4.96	0.012	3	0.023	3	552
1.99	0.010	3	0.007	3	562	5.49	0.030	3	0.050	3	550
2.03	0.020	3	0.025	3	552	5.02	0.007	3	0.023	3	950
2.05	0.021	3	0.037	3	562	5.04	0.070	3	0.012	3	150
1.98	0.020	3	0.057	3	520						
2.04	0.010	3	0.075	3	550						
2.07	0.009	3	0.029	3	950						
2.08	0.010	3	0.010	3	150						

#### External Control Values

- $m_i$  : 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 FOR CERTIFICATE QC METAL HL2

### 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
University of Jyväskylä, Institute for Environmental Research	Jyväskylä

#### *Norway*

AnalyCen A/S	Moss
NIVA	Oslo

#### *Sweden*

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