

CERTIFICATE FOR
QC METAL HL1
METALS

BATCH: VKI-14-3-0899

INSTRUCTIONS FOR THE USE OF THE REFERENCE MATERIAL

Description

This reference material consists of an ampoule with concentrate containing the elements aluminium, lead, iron, manganese, molybdenum, tin and zinc for preparation of a reference sample for quality control after dilution with water.

Quantity and preservation

QC METAL HL1 consists of an ampoule with a minimum of 15 ml concentrate. 10 ml concentrate gives 250 ml reference sample. The concentrate is preserved with suprapur nitric acid, 5% (v/v), and suprapur hydrochloric acid, 5% (v/v).

Use

The reference sample is intended for use in quality control, i.e. measurement and control of the trueness and precision of analyses. The reference sample is typically intended for analyses of metals in water. The sample may also be used in the quality control of other sample types and for the implementation and optimisation of analytical instruments and methods. For these purposes, other dilutions 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 at room temperature. Break the ampoule neck open at the mark in a way so that contamination of the concentrate with glass particles is avoided. Withdraw the concentrate with a pipette, dilute with water and preserve with hydrochloric acid and nitric acid. For example, dilute 10.0 ml concentrate with water to a final volume of 250 ml, including additions of 3.5 ml hydrochloric acid and 3.5 ml nitric acid.

The dilution rate between the concentrate QC METAL HL1 and the water can be altered as appropriate for the intended use.

Note: The reference material must not be poured 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.

Analyses

For quality control analyse the reference sample 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 2021** provided the material is stored under the recommended conditions.

PRODUCTION OF THE REFERENCE MATERIAL AND DOCUMENTATION

Production

This reference material has been produced in accordance with the quality management procedures of Eurofins Miljø A/S, 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 Swedish, Finnish and Dutch interlaboratory comparisons and certification of the BCR reference materials CRM 398 and 399 /2/.

Homogeneity:

The homogeneity has been analysed for all parameters in the reference material QC METAL HL1 by measurement of 3 metals (Al, Pb and Sn) in 12-15 randomly selected ampoules. The test for homogeneity has been performed by testing the standard deviation between the reference samples against Eurofins' standard deviation of internal quality control samples within the analytical series and also against the standard deviation of double determinations of the reference material (F-test, 95%). Further, homogeneity has been tested for all parameters in accordance with ISO Guide 35 as part of the external control. No sign of inhomogeneity was observed.

Stability:

The stability of the reference material is being followed by regular check measurements of Pb and Sn in ampoules stored at 20°C and 37°C. No sign of instability was observed at the date of this certificate where control analyses were conducted in the Autumn 1999.

External Control

The external laboratory documentation was performed by laboratories who were interested in taking part, where Danish laboratories had participated in the Danish interlaboratory comparisons PP 1994:3 /5/ and PP 1997:4 /6/, where Norwegian laboratories had participated in the Norwegian interlaboratory comparison Ringtest 9818 /7/ and where Finnish laboratories had been selected by the Finnish reference laboratory. The laboratories were requested to analyse two ampoules of QC METAL HL1 in the same analytical series, where one was analysed in duplicate, and to analyse the reference material in two additional analytical series.

The external control values have been calculated by using the statistical procedures of the international standard ISO Guide 35 /1/. The following calculations have been made on the basis of the analytical results submitted by the laboratories:

\bar{Y} : average calculated in accordance with ISO Guide 35, 10.5.2

S_L : standard deviation between the laboratories calculated in accordance with ISO Guide 35, 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

v : $p-1$, degrees of freedom

$t_{0,025}(v)$: t-value of 0,025 level at v degrees of freedom.

Results are excluded from the certification, if the laboratory results are Grubbs' outliers (Gr), or if both the results from analysis within the same analytical series and the results between analytical series are Cochran outliers (Co). Results are also excluded if the results of one or both control samples are outside the nominal value ± 2 times the standard deviation (Ex). Finally, laboratories with insufficient routine are excluded from the certification.

The laboratories selected for certification and the data included in this certification are listed in the annexes of this certificate.

Certified Values

Parameter	Unit	Average	Standard deviation between laboratories	95% Confidence limits of the average		Method/Number of laboratories (p)	Excluded laboratories Ex: Manually excluded laboratories Co: Cochran outliers Gr: Grubbs outliers
				Lower	Upper		
		\bar{Y}	S_L	$\bar{Y} \pm t_{0,025}(v) \cdot \frac{S_L}{\sqrt{p}}$			
Aluminium	mg/l Al	2,07	0,14	2,00	2,14	B/3 C/12 D/1 H/2	Ex:4
Iron	mg/l Fe	3,03	0,061	3,00	3,05	A/9 C/10 F/1 H/2	Ex:5 Gr:2
Manganese	mg/l Mn	1,98	0,051	1,96	2,00	A/9 C/11 D/2 H/1	Ex:5 Co:1
Molybdenum	mg/l Mo	9,96	0,38	9,74	10,19	B/1 C/8 D/3 H/1	Ex:3
Lead	mg/l Pb	10,02	0,34	9,88	10,16	A/9 C/12 D/2 E/1 H/1	Ex:3 Gr:1
Tin	mg/l Sn	10,33	0,43	10,08	10,58	B/1 C/10 D/2 E/1	Ex:3
Zinc	mg/l Zn	0,492	0,022	0,482	0,502	A/9 C/12 D/1 H/1	Ex:5

Methods

- A: Atomic absorption spectrometry with air-acetylene flame (FAAS)
- B: Atomic absorption spectrometry with nitrous oxide-acetylene flame (FAAS)
- C: Inductive coupled plasma atomic emission spectrometry (ICP-AES)
- D: Inductive coupled plasma mass spectrometry (ICP-MS)
- E: Atomic absorption spectrometry with graphite furnace technique (ETAAS)
- F: Danish Standard DS 219, Finnish Standard SFS 3028, Norwegian Standard 4741
- G: Danish Standard DS 220, Finnish Standard SFS 3033, Norwegian Standard 4742
- H: Others

Use of External Control 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:

For single determinations, analytical results will, with a probability of 95%, lie within the interval:

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

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/ BCR project RM 297 (CRM 398 and CRM 399). Reference materials for the analysis of fresh water (Al, Ca, Cl, Fe, Mg, Mn, P, K, Na and S).
- /4/ ISO/DIS 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.
- /5/ Proficiency Test 1994:3, Nordic Proficiency Test Scheme on Chemical Drinking Water Analyses, Metals, VKI
- /6/ Proficiency Test 1997:4, Metals in Waste Water and Leachate, VKI (in Danish)
- /7/ Ringtest 9818, NIVA, Rapport LNR 4015-99, Ringtest – Industrial Wastewater.

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Certificate revision history: October 2018 (expiry date extended); December 2013 (expiry date added); November 1999 (original certificate date)

ANNEX TO CERTIFICATE QC METAL HL1

Laboratory Measurements

Aluminium					
m_i	s_i	n_i	s_{Li}	n_{Li}	Method
2,36	0,01	3	0,09	3	C
2,11	0,04	3			B
2,13	0,02	3	0,05	3	C
1,89	0,07	3	0,01	3	B
2,03	0,01	3	0,01	3	C
2,15	0,04	3	0,03	3	C
2,19	0,01	3	0,02	3	C
1,98	0,04	3	0,07	3	C
2,12	0,01	3	0,11	3	C
2,06	0,01	3	0,01	3	B
2,29	0,02	3	0,07	3	C
1,84	0,01	3	0,02	3	C
2,00	0,05	3	0,07	3	C
2,03	0,00	3	0,04	3	C
2,16	0,03	3	0,19	3	C
1,88	0,01	3	0,07	3	H
1,93	0,01	3	0,05	3	D
2,15	0,00	2			H

Iron					
m_i	s_i	n_i	s_{Li}	n_{Li}	Method
3,01	0,02	3	0,03	3	A
3,04	0,02	3	0,06	3	C
2,97	0,05	3	0,01	3	A
3,06	0,03	3	0,07	3	A
3,14	0,02	3	0,26	3	A
2,98	0,01	3	0,01	3	H
2,99	0,02	3	0,02	3	C
3,07	0,09	3	0,06	3	A
2,94	0,02	3	0,04	3	C
3,09	0,03	3	0,09	3	A
2,99	0,01	3	0,01	3	C
2,92	0,07	3	0,21	3	C
3,02	0,01	3	0,02	3	C
3,02	0,01	3	0,00	3	A
2,99	0,03	3	0,05	3	F
3,10	0,03	3	0,03	3	C
3,11	0,01	3	0,01	3	C
2,97	0,06	3	0,02	3	C
3,04	0,01	3	0,05	3	C
3,07	0,06	3	0,02	2	A
3,09	0,05	3	0,07	3	A
2,95	0,00	2			H

- m_i : average for laboratory i
 s_i : standard deviation for laboratory i within an analytical series
 n_i : number of results for determination of s_i
 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

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Laboratory Measurements

Manganese					
m_i	s_i	n_i	s_{Li}	n_{Li}	Method
1,99	0,01	3	0,14	3	A
1,86	0,02	3	0,06	3	C
1,99	0,01	3	0,02	3	A
2,01	0,01	3	0,01	3	C
2,00	0,02	3	0,04	3	A
2,00	0,02	3	0,09	3	A
1,98	0,01	3	0,02	2	A
2,00	0,01	3	0,01	3	C
1,85	0,03	3	0,03	3	D
1,92	0,01	3	0,02	3	C
1,96	0,01	3	0,02	3	A
1,99	0,01	3	0,01	3	C
1,93	0,05	3	0,13	3	C
1,99	0,02	3	0,03	3	D
2,03	0,00	3	0,03	3	C
2,00	0,01	3	0,00	3	A
2,02	0,02	3	0,01	3	C
2,09	0,01	3	0,00	3	C
1,97	0,01	3			A
1,98	0,02	3	0,02	3	C
2,00	0,00	3	0,02	3	C
1,95	0,02	3	0,05	2	A
2,02	0,00	2			H

Molybdenum					
m_i	s_i	n_i	s_{Li}	n_{Li}	Method
10,50	0,06	3	0,07	3	C
9,83	0,07	3	0,22	3	C
9,26	0,21	3	0,31	3	D
9,94	0,04	3	0,04	3	C
9,92	0,29	3	0,50	3	C
10,44	0,15	3	0,27	3	D
10,15	0,03	3	0,32	3	C
9,49	0,05	3	0,05	3	B
10,47	0,03	3	0,02	3	C
9,87	0,27	3	0,22	3	C
9,99	0,04	3	0,11	3	C
9,60	0,08	3	0,26	3	D
10,08	0,00	2			H

m_i : average for laboratory i
 s_i : standard deviation for laboratory i within an analytical series
 n_i : number of results for determination of s_i
 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

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Laboratory Measurements

Lead					
m_i	s_i	n_i	s_{Li}	n_{Li}	Method
9,72	0,09	3	0,04	3	A
9,97	0,08	3	0,74	3	C
10,03	0,08	3	0,02	3	A
9,93	0,06	3	0,05	3	C
10,44	0,06	3	0,34	3	E
10,09	0,15	3	0,53	3	A
9,89	0,05	3	0,12	2	A
9,74	0,06	3	0,04	3	C
9,16	0,04	3	0,43	3	D
10,14	0,04	3	0,01	3	A
9,79	0,03	3	0,04	3	C
9,82	0,26	3	0,63	3	C
10,74	0,06	3	0,15	3	A
10,51	0,04	3	0,23	3	C
10,10	0,05	3	0,20	3	C
10,11	0,08	3	0,05	3	A
10,00	0,07	3	0,10	3	C
10,57	0,01	3	0,02	3	C
9,92	0,17	3			A
10,23	0,07	3	0,32	3	C
10,10	0,05	3	0,06	3	C
10,04	0,27	3			C
9,69	0,06	3	0,50	2	A
9,46	0,17	3	0,02	3	D
10,30	0,00	2			H

Tin					
m_i	s_i	n_i	s_{Li}	n_{Li}	Method
11,06	0,06	3	0,40	3	C
10,61	0,12	3			C
9,63	0,05	3	1,24	3	C
10,35	0,07	3	0,11	3	C
10,57	0,31	3	0,81	3	C
10,42	0,45	3	0,23	3	E
10,88	0,15	3	0,80	3	D
10,33	0,04	3	0,27	3	C
10,41	0,07	3	0,08	3	B
10,45	0,04	3	0,03	3	C
10,22	0,21	3	0,35	3	C
10,34	0,08	3	0,09	3	C
9,53	0,08	3	0,25	3	C
9,81	0,08	3	0,15	3	D

m_i : average for laboratory i
 s_i : standard deviation for laboratory i within an analytical series
 n_i : number of results for determination of s_i
 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

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Laboratory Measurements

Zink					
m_i	s_i	n_i	s_{Li}	n_{Li}	Method
0,50	0,01	3	0,00	3	A
0,51	0,00	3	0,04	3	C
0,48	0,00	3	0,01	3	A
0,50	0,00	3	0,01	3	C
0,50	0,01	3	0,00	3	A
0,54	0,01	3	0,01	3	A
0,47	0,00	3	0,01	3	C
0,50	0,00	3	0,01	3	C
0,50	0,01	3	0,01	3	A
0,47	0,00	3	0,00	3	C
0,45	0,01	3	0,03	3	C
0,50	0,00	3	0,01	3	A
0,49	0,00	3	0,01	3	C
0,49	0,00	3	0,00	3	A
0,48	0,01	3	0,00	3	C
0,51	0,00	3	0,00	3	C
0,49	0,00	3			A
0,49	0,00	3	0,01	3	C
0,48	0,00	3	0,00	3	C
0,43	0,01	3	0,01	3	C
0,50	0,00	3	0,00	2	A
0,51	0,05	3	0,01	3	D
0,50	0,00	2			H

m_i : average for laboratory i
 s_i : standard deviation for laboratory i within an analytical series
 n_i : number of results for determination of s_i
 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

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Certifying Laboratories

Denmark

AnalyCen A/S, Fredericia
Dansk Chemex, Kalundborg
Fælleskommunal Levnedsmiddelkontrol, Glostrup
Hygiejnelaboratoriet A/S, Tønder
Institut for Geologi & Geoteknik DTU, Lyngby
Miljø- og LevnedsmiddelCentret, Holbæk
Miljøcentret I/S, Næstved
Miljølaboratoriet Østjylland A/S, Vejle
MLK Fyn I/S, Odense SØ
MLK Vestjylland I/S, Holstebro
MLK Østjylland I/S, Silkeborg
R. Dons, Nærum
SH Energi, Åbenrå
Steins Laboratoruim, Brørup

Norway

AnalyCen A/S, Moss
Hydro Aluminium Karmøy, Håvik
Hydro Magnesium Norway Laboratorium, Porsgrunn
Jordforsk. Lab, Ås
KM Lab A/S, Grimstad
Molab A/S, Mo i Rana
Norcem A/S, Brevik
Næringsmiddeltilsynet for Sogn, Sogndal
Næringsmiddeltilsynet i Tønsberg
Oslo Kommune, Oslo
RF Miljølab, Stavanger
Vest-Lab Services A/S, Tananger

Finland

Kokemäenjoen vesisstön vesiensuojeluyhdistys ry, Tampere
Lahden Tutkimuslaboratorio, Lahti
Metsäntutkimuslaitos (METLA), Vantaa
Tampereen Vesilaitos Viemärlaitoksen laboratorio, Tampere