Eurofins Miljø A/S
Smedeskovvej 38
DK-8464 Galten

DANAK
RM Reg. nr. 535

VKI
REFERENCE MATERIALS

CERTIFICATE FOR

QC METAL LL3A

MERCURY

BATCH: VKI-28-1-0400

INSTRUCTIONS FOR USE OF THE REFERENCE MATERIAL

Description
This reference material consists of an ampoule with concentrate containing mercury for preparation of a reference sample for quality control after dilution with water.

Quantity
QC METAL LL3A is an ampoule with approx 12 mL concentrate. 1 L reference sample is produced by diluting 10 mL of the concentrate. The concentrate is preserved with nitric acid, 5%, and sodium chloride, 0,5%.

Use
The reference sample is intended for quality control, i.e. measurement and control of the trueness and precision of analytical methods. The reference sample is typically intended for analyses of mercury 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 the certificate are identical.

Preparation for use
Stabilise the ampoule at room temperature (approx. 20°C). Break the ampoule neck open at the mark, in such a way that contamination of the concentrate with particles is avoided. Withdraw the concentrate with a pipette and preserve according to the procedure normally used in the laboratory with reagents that have no measurable content of mercury. Then dilute 1:100 with water without a measurable content of mercury. For example, 5.0 mL concentrate is diluted with water to a final volume of 500 mL.

It is recommended to use an air-tight container of e.g. borosilicate glass for preparation and storage to prevent the Hg from evaporating. Ensure by a suitable pre-treatment of the container, that the mercury is not adsorbed/desorbed to the container surface during storage. In addition the diluted reference material shall be preserved in such a way that mercury is ionised. For this purpose add an oxidising acid and also if deemed necessary an oxidising agent. The diluted sample is stable for up to 24 hours after the ampoule has been opened. However, if the laboratory has a documented preservation procedure the sample may be stable for a longer period.

A number of recommendations are given in the literature regarding preservation and the choice can depend on the analytical method used. A couple of examples of preservation are as follows:

- Addition of 50 mg $K_2Cr_2O_7$ and 5,0 mL concentrated HNO_3 per litre sample for mercury determination by atomic absorption spectroscopy (AAS) after reduction with tin(II)chloride or sodium boron hydride (EN 1483:1997, EN 12338:1998, ISO/FDIS 5666:1999)
- Addition of 1 mL concentrated HNO_3 and 1 g NaCl per 100 mL sample (NIVA – Norsk Institut for Vannforskning).

This certificate is prepared in accordance with the international ISO guidelines for certification of reference materials /1/ and /2/.

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

Analysis
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 2020** 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 of obtaining the intended quality of the material.

Documentation of Content

Internal control
The analytical quality of Eurofins Miljø A/Shas been documented and found satisfactory by regular participation in international interlaboratory comparisons.

Homogeneity:
The homogeneity has been investigated by measurements of mercury in randomly selected ampoules of QC METAL LL3A. 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 testings were followed up in accordance with ISO Guide 35 /1/ as a part og the external control (see below). No signs of inhomogeneity were found.

Stability:
The stability of the reference material is being followed by regular Hg analyses of reference materials stored at 20°C and 37°C. No signs of instability were observed at the date of this certificate.

External control
The external laboratory documentation was performed by Nordic laboratories in 2000. The laboratories were requested to analyse two ampoules in the same analytical series, one as a duplicate determination and the other as a single determination, and to analyse two ampoules in 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:

$\overline{Y}$: 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):

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

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 from Denmark, Norway and Sweden were that the laboratories perform the analyses on a routine basis. Furthermore the laboratories were selected on the basis of their results in the proficiency test “Mercury in Water 1996” from NIVA /3/ or on the basis of their participation in the certification of the QC METAL LL3 in 1996. The criteria for selection of laboratories were as follows:

- the laboratory results for mercury in the above-mentioned proficiency tests diverged less than 20% from the nominal value, or
- the laboratory results were selected for certification of QC METAL LL3, Batch VKI-22-1-0996.

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

In addition, the criteria are:

- the laboratory has less than two result sets that are Cochran or Grubbs outliers, and
- the laboratory result for the control sample in the certification deviated less than 20% from the nominal value, and
- the laboratory results in the certification are 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 is based on a follow-up questionnaire sent to the laboratories with deviating results.

The data included in the external control and names of the participating laboratories are listed in the annex of this certificate. On the basis of the selected results, the following has been calculated:

Certified values

DETERMINAND	UNIT	AVERAGE	BETWEEN LABORATORY STANDARD DEVIATION	95% CONFIDENCE LIMITS OF THE AVERAGE VALUE		NUMBER OF LABORATORIES IN CALCULATIONS/ METHOD	EXCLUDED LABORATO-RIES Co: Cochran outlier Gr: Grubbs outlier Ex: Other excluded
		$\overline{Y}$	s_L	$\overline{Y} \pm t_{0,025}(\nu).\frac{s_L}{\sqrt{p}}$ Lower	Upper	(p)	
Mercury	µg/L Hg	0.354	0.016	0.346	0.363	9/A 1/B 1/D 4/E 2/H	Co: 2 Gr: 1 Ex: 4

Methods

A.	CVAAS/Sn	Atomic absorption with cold vapour technique, reduction by stannochloride
B.	CVAAS/NaBH4	Atomic absorption with cold vapour technique, reduction by sodium tetrahydroborate
D.	CVAAS/NaBH4-Au	Atomic absorption with cold vapour technique, reduction by sodium tetrahydroborate and gold amalgamation
E.	AFS	Atomic fluorescense
H.	Other methods	

Use of the Certified Values
For laboratories with an analytical quality that is comparable with the laboratories who have contributed with the external control data of this certificate, the following applies:

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

$$\overline{Y} \pm t_{0,025}(\nu).s_L$$

REFERENCES

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

/2/ ISO guide 31:2000 Reference materials - Contents of certificates and labels.

/3/ "Kvikksølv i Vann 1996", Norsk Institutt for Vannforskning (NIVA), Norway

/4/ ISO 5725-2, 1994, Accuracy (trueness and precision) of measurement methods and results.

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Certificate revision history: April 2015 (expiry date extended); December 2013 (expiry date added); September 2000 (original certificate date)

ANNEX TO CERTIFICATE QC METAL LL3A

Laboratory Measurements

Mercury					
m_i µg/L	s_{ri} µg/L	n_{ri}	s_{Li} µg/L	n_{Li}	Method
0,342	0,001	3	0,013	3	A
0,326	0,007	3	0,001	3	A
0,346	0,010	3	0,006	3	H
0,370	0,014	2	0,010	3	D
0,360	0,030	3	0,046	3	A
0,376	0,002	3	0,011	2	E
0,338	0,015	3	0,021	3	A
0,355	0,004	3	0,004	3	E
0,344	0,017	3	0,011	3	B
0,356	0,012	3	0,004	3	A
0,337	0,037	3	0,030	3	E
0,379	0,010	3	0,026	3	E
0,340	0,010	3	0,029	3	A
0,347	0,026	3	0,019	3	A
0,380	0,017	3	0,021	3	A
0,368	0,010	3	0,006	3	H
0,365	0,006	3	0,024	2	A

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 page 3

ANNEX TO CERTIFICATE QC METAL LL3A

Certifying Laboratories

Danish laboratories
FORCE Instituttet, Brøndby
ELSAM A/S, Skødstrup
ROVESTA Miljø I/S, Holbæk
MILJØ-KEMI, Dansk Miljø Center A/S, Viborg
Miljøcenter Vestjylland I/S, Holstebro
Steins Laboratorium A/S, Brørup
ELSAM, Åbenrå

Finnish laboratories
Kokemäenjoen vesistön vesiensuojeluyhdistys ry., Tampere
Outokumpu Harjavalta Metals Oy, Harjavalta
EKA Chemicals Oy, Oulu

Norwegian laboratories
Folkehelsa, Oslo
A/S Sentralrenseanlegget RA-2, Strømmen
Norges Geologiske Undersøkelse, Trondheim
RF-Rogalandsforsk., Stavanger
NIVA, Oslo

Swedish laboratories
Akzo Nobel Base Chemicals AB, Skoghall
Vattenlaboratoriet, Uppsala