



DANAK
RM Reg.no. 535
Member EA MLA

CERTIFICATE FOR
QC LOAM SOIL B
TRACE ELEMENTS/METALS IN SOIL

BATCH: VKI-20-3-0109

INSTRUCTIONS FOR USE OF THE REFERENCE MATERIAL

Description

This reference material consists of dried soil. The certificate includes documentation for the analytical parameters As, Cd, Cr, Cu, Hg, Ni, Pb Zn, K and loss on ignition.

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 and loss on ignition in soil. It may also be used for the validation of analytical methods. It is important that the batch numbers of the reference material and on the certificate are identical.

Preparation for Use

Digest samples for determination of trace elements/metals. The material is hygroscopic. It is therefore recommended to determine the content of dry matter at regular intervals.

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 reference material protected from sunlight at room temperature in the original brown glass container. Keep the container tightly closed. The certificate is valid until **1st of September 2027** provided the material is stored under the recommended conditions.

PRODUCTION OF THE REFERENCE MATERIAL AND DOCUMENTATION

Production

The reference material is contaminated soil. Stones and plant material was removed. The soil was dried at approximately 100 °C, crushed and sieved to < 90 µm, and homogenised again. The material was sterilised by γ-irradiation. 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

Documentation of the reference material's content of trace elements/metals is based on measurements in digested samples. The measured concentrations are calculated on the basis of dry matter.

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/metals in randomly selected containers of QC Loam Soil B. Tests for homogeneity have been performed by comparing the standard deviation between the reference material units with the within batch standard deviation obtained from triplicate measurements of the reference material in the same container (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 except for Pb in the external control. The difference may be attributed to variation between laboratories and not between samples.

Stability:

The stability of the reference material is being followed by regular analyses of As and Hg in reference materials stored at 20 °C and 4 °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 two containers of QC Loam Soil B: both containers as duplicate determinations in the same analytical series, followed by analysis of the containers in two different analytical series as single determinations. In addition, the laboratories were requested to analyse a control sample (soil) 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:

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

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 certification for trace elements/metals is based on measurements for samples digested with 7 N nitric acid in microwave oven or autoclave. All methods are included in the certified value for loss on ignition.

Digestion in autoclave or microwave oven gives no significant difference for Cd, Cu, Hg, Pb and K. Certified values are therefore based on the combined results for both procedures.

For As, Cr, Ni and Zn the results after digestion in autoclave or microwave oven were significantly different. The number of laboratories using digestion in microwave oven was too small to allow estimation of a certified value, but for Cr, Ni and Zn an indicative value is given. Only three non-excluded laboratories used digestion in microwave oven for As and the certificate therefore has no information for this procedure.

The certified values are based on results from selected laboratories. 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 25 % 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

Formed Values							
DETERMINAND	UNIT	AVERAGE	BETWEEN LABORATORY STANDARD DEVIATION	95 % CONFIDENCE LIMITS OF THE AVERAGE VALUE		NUMBER OF DATA SETS IN CALCULATIONS/ METHOD	EXCLUDED DATA SETS
		y_{char}	$s(y)$	$y_{char} \pm t_{0,025}(\nu) \cdot \frac{s(y)}{\sqrt{p}}$			C: Cochran outlier G: Grubbs outlier
				Lower	Upper	(p)	
Arsenic (autoclave digestion)	mg/kg DM	3,49	0,290	3,22	3,76	5/D 2/E	2C
Cadmium	mg/kg DM	0,279	0,0350	0,258	0,300	1/A 7/D 5/E	1C
Chromium (autoclave digestion)	mg/kg DM	46,8	4,06	43,9	49,7	9/D 1/E	1C
Chromium * (microwave digestion)	mg/kg DM	(65)	(16)	(45)	(86)	1/B 1/D 3/E	
Copper	mg/kg DM	23,3	1,74	22,4	24,2	1/B 11/D 4/E	
Mercury	mg/kg DM	0,094	0,0077	0,088	0,099	3/C 4/D 2/E 1/F	1C
Nickel (autoclave digestion)	mg/kg DM	13,2	1,27	12,3	14,1	9/D 1/E	1C
Nickel * (microwave digestion)	mg/kg DM	(15)	(1,4)	(13)	(18)	1/D 3/E	1C
Lead	mg/kg DM	115	10,8	109	122	9/D 5/E	2C
Zinc (autoclave digestion)	mg/kg DM	73,7	6,49	69,0	78,4	9/D 1/E	1C
Zinc * (microwave digestion)	mg/kg DM	(78)	(4,0)	(71)	(84)	1/B 1/D 2/E	1C

Potassium	g/kg DM	1,43	0,122	1,35	1,52	9/D 1/E	3C
Loss on ignition	g/kg DM	26,4	3,11	24,5	28,3	13	1C

*: Values in brackets are indicative.

Methods

- A Atomic absorption spectrometry with graphite furnace (ETAAS), e.g. ISO 11047
- B Atomic absorption spectrometry with flame (FAAS), e.g. ISO 11047
- C Atomic absorption spectrometry with hydride technique (HAAS), e.g. ISO 16772 (Hg), ISO 20280 (As)
- D Inductively coupled plasma atomic emission spectrometry (ICP-AES), e.g. ISO 22036
- E Inductively coupled plasma mass spectrometry (ICP-MS)

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:

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

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

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

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.

Date of issue: January 2024

RESPONSIBLE SCIENTIST



Rikke Mikkelsen
Eurofins Miljø A/S
DK-8464 Galten

Certificate revision history: January 2023 (expiry date extended; update to newest ISO standards); June 2019 (expiry date extended); January 2014 (expiry date added); August 2009 (original certificate date)

ANNEX TO CERTIFICATE QC METAL LOAM SOIL B

Laboratory Measurements

Arsenic (autoclave digestion)					
y_i mg/kg DM	S_{ri} mg/kg DM	n_{ri}	S_{Li} mg/kg DM	n_{Li}	Method
3,65	0,097	4	0,075	3	D
3,65	0,201	4	0,142	3	D
3,40	0,061	4	0,103	3	D
3,61	0,022	4	0,032	3	E
3,79	0,035	4	0,298	3	E
2,91	0,288	4	0,322	3	D
3,40	0,141	4	0,200	3	D

Chromium (autoclave digestion)					
y_i mg/kg DM	S_{ri} mg/kg DM	n_{ri}	S_{Li} mg/kg DM	n_{Li}	Method
45,2	2,31	4	3,30	3	D
44,2	1,04	4	2,55	3	D
43,9	0,93	4	0,46	3	D
43,1	0,71	4	0,44	3	D
49,0	0,36	4	1,01	3	D
49,4	0,53	4	0,35	3	D
56,1	0,83	4	1,81	3	E
44,9	0,69	4	0,70	3	D
43,5	2,36	4	3,47	3	D
48,8	1,26	4	0,83	3	D

Cadmium					
y_i mg/kg DM	S_{ri} mg/kg DM	n_{ri}	S_{Li} mg/kg DM	n_{Li}	Method
0,261	0,0075	4	0,0206	3	D
0,276	0,0103	4	0,0106	3	*E
0,325	0,0026	4	0,0085	3	E
0,277	0,0186	4	0,0109	3	A
0,325	0,0120	4	0,0056	3	*E
0,255	0,0230	4	0,0035	3	D
0,232	0,0039	4	0,0018	3	*D
0,251	0,0101	4	0,0063	3	D
0,309	0,0045	4	0,0078	3	E
0,298	0,0116	4	0,0243	3	E
0,253	0,0154	4	0,0037	3	D
0,235	0,0258	4	0,0153	3	D
0,332	0,0213	4	0,0120	3	D

Chromium (microwave digestion)					
y_i mg/kg DM	S_{ri} mg/kg DM	n_{ri}	S_{Li} mg/kg DM	n_{Li}	Method
65,4	11,3	4	8,4	3	E
76,7	2,4	4	3,6	3	E
39,1	1,4	4	0,2	3	D
63,7	5,7	4	3,0	3	B
81,2	5,9	4	5,9	3	E

*: measurement after digestion in microwave oven. All other measurements are performed after digestion in autoclave

Copper					
y_i mg/kg DM	S_{ri} mg/kg DM	n_{ri}	S_{Li} mg/kg DM	n_{Li}	Method
25,2	0,31	4	1,89	3	D
23,2	0,60	4	0,78	3	*E
22,9	0,58	4	0,20	3	D
19,0	0,99	4	0,61	3	D
23,2	0,40	4	0,42	3	*E
24,0	0,94	4	0,20	3	D
25,0	0,42	4	0,53	3	D
23,1	0,29	4	0,25	3	*D
23,4	0,59	4	0,22	3	D
25,7	0,26	4	0,20	3	E
21,6	0,37	4	1,57	3	D
21,0	0,56	4	1,49	3	D
23,6	0,33	4	0,77	3	D
22,8	0,39	4	0,59	3	D
23,8	0,43	4	0,80	3	*B
25,5	0,56	4	0,57	3	*E

*: measurement after digestion in microwave oven. All other measurements are performed after digestion in autoclave.

Nickel (autoclave digestion)					
y_i mg/kg DM	S_{ri} mg/kg DM	n_{ri}	S_{Li} mg/kg DM	n_{Li}	Method
13,5	0,32	4	0,34	3	D
15,2	0,49	4	0,68	3	D
12,1	0,55	4	0,46	3	D
12,7	0,10	4	0,27	3	D
13,5	0,27	4	0,16	3	D
13,5	0,16	4	0,10	3	D
15,0	0,13	4	0,22	3	E
11,2	0,37	4	0,40	3	D
13,6	0,16	4	0,56	3	D
12,0	0,25	4	0,22	3	D

Mercury					
y_i mg/kg DM	S_{ri} mg/kg DM	n_{ri}	S_{Li} mg/kg DM	n_{Li}	Method
0,094	0,0115	4	0,0053	3	D
0,088	0,0170	4	0,0050	3	*E
0,088	0,0059	4	0,0033	3	D
0,097	0,0198	4	0,0095	3	F
0,089	0,0021	4	0,0028	3	*C
0,109	0,0073	4	0,0126	3	D
0,096	0,0067	4	0,0074	3	E
0,100	0,0058	4	0,0136	3	D
0,096	0,0080	4	0,0040	3	C
0,081	0,0075	4	0,0054	3	C

*: measurement after digestion in microwave oven. All other measurements are performed after digestion in autoclave.

Nickel (microwave digestion)					
y_i mg/kg DM	S_{ri} mg/kg DM	n_{ri}	S_{Li} mg/kg DM	n_{Li}	Method
15,1	0,21	4	0,55	3	E
15,4	0,16	4	0,56	3	E
13,8	0,17	4	0,30	3	D
17,2	0,15	4	0,86	3	E

Lead					
y_i mg/kg DM	S_{ri} mg/kg DM	n_{ri}	S_{Li} mg/kg DM	n_{Li}	Method
118	3,6	4	0,0	3	*E
127	5,1	4	2,2	3	D
100	3,5	4	2,8	3	D
108	1,3	4	3,7	3	*E
115	0,8	4	1,4	3	D
115	3,7	4	5,6	3	D
104	1,0	4	1,0	3	*D
114	1,5	4	3,2	3	D
121	0,5	4	1,0	3	E
121	6,0	4	3,3	3	E
99	2,8	4	5,4	3	D
125	4,6	4	6,1	3	D
112	2,0	4	3,8	3	D
138	6,8	4	5,4	3	*E

*: measurement after digestion in microwave oven. All other measurements are performed after digestion in autoclave

Zinc (microwave digestion)					
y_i mg/kg DM	S_{ri} mg/kg DM	n_{ri}	S_{Li} mg/kg DM	n_{Li}	Method
77,4	1,75	4	0,39	3	E
79,8	0,51	4	1,42	3	E
72,0	0,70	4	0,57	3	D
81,0	1,93	4	2,23	3	B

Zinc (autoclave digestion)					
y_i mg/kg DM	S_{ri} mg/kg DM	n_{ri}	S_{Li} mg/kg DM	n_{Li}	Method
79,3	1,50	4	2,04	3	D
70,8	2,39	4	4,72	3	D
63,5	1,18	4	0,74	3	D
73,6	1,36	4	1,09	3	D
82,7	0,50	4	1,06	3	D
82,9	1,38	4	0,49	3	E
69,5	0,88	4	2,87	3	D
70,0	1,91	4	5,29	3	D
76,5	1,67	4	1,80	3	D
68,3	2,23	4	2,42	3	D

Potassium					
y_i g/kg DM	S_{ri} g/kg DM	n_{ri}	S_{Li} mg/kg DM	n_{Li}	Method
1,49	0,028	4	0,047	3	*D
1,30	0,015	4	0,026	3	D
1,39	0,033	4	0,054	3	*D
1,62	0,007	4	0,020	3	D
1,58	0,025	4	0,062	3	E
1,42	0,024	4	0,046	3	D
1,41	0,027	4	0,094	3	D
1,37	0,113	4	0,108	3	D
1,54	0,079	4	0,017	2	D
1,24	0,037	4	0,021	3	D

*: measurement after digestion in microwave oven. All other measurements are performed after digestion in autoclave

Loss on ignition					
y_i g/kg DM	s_{ri} g/kg DM	n_{ri}	s_{Li} g/kg DM	n_{Li}	Method
30,5	0,79	4			A
24,3	0,00	4	1,53	3	A
22,2	1,38	4	1,77	3	A
30,2	1,40	4	0,38	3	-
25,0	0,24	4	0,33	3	A
22,3	1,16	4	0,72	3	A
30,3	0,27	4	0,58	3	A
26,5	0,58	4	0,50	3	A
24,3	1,40	4			A
25,3	0,63	4	0,69	3	A
29,0	2,54	4	0,98	3	A
29,4	1,56	4	1,93	3	A
23,7	1,47	4	0,58	3	A

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 4.

ANNEX TO CERTIFICATE QC METAL LOAM SOIL B

Certifying Laboratories

Denmark

Eurofins Miljø A/S, Vejen
Højvang Miljølaboratorium A/S, Dianalund
MILANA A/S, Helsingør
Miljøcenter Vestjylland, Holstebro
Miljølaboratoriet I/S, Glostrup
VBM Laboratoriet A/S, Fjerritslev

Finland

Finnish Environment Institute, Helsinki
Ramboll Analytics, Lahti
Suomen Ympäristöpalvelu Oy, Oulu

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
Jönköping Kommun, Tekniska Kontoret, VA-lab, Jönköping
VA-lab, Eskilstuna Energi & Miljö, Eskilstuna