

CERTIFICATE FOR

QC ORGANIC COMPONENTS IN MUNICIPAL SLUDGE

ORGANIC MATERIAL

BATCH: VKI-27-1-0297

INSTRUCTION FOR USE OF THE REFERENCE MATERIAL

Description, quantity and preservation

This reference material consists of dried and homogenised sludge in containers of approx. 100 g each. The reference material is certified for:

PAH (16 components)	(Polycyclic aromatic hydrocarbons)
DEHP	(di(2-ethyl hexyl)phtalate)
NPE	(4-nonylphenol and 4-nonylphenol mono- and diethoxylates)
C ₁₀ ⁻ , C ₁₁ ⁻ , C ₁₂ ⁻ , og C ₁₃ -LAS	(linear alkyl benzene sulphonates)

The certified values are calculated both for individual components and for the sums of components in accordance with the Order on the Use of Waste for Agricultural Purposes of the Danish Ministry of Environment and Energy /3/. The reference material is preserved by drying and homogenisation. If kept dry, the content of dry matter is at least 97%.

Use

The reference sample is intended for quality control, i.e. measurement and control of the trueness and precision of analyses. The reference is typically intended for analyses of the above-mentioned organic parameters in sludge, including analyses of sludge intended for agricultural use /3/. It is important that the batch numbers of the reference material and on the certificate are identical.

Analysis

For quality control the reference sample is analysed at the same time and in the same manner as other samples.

Storage and durability

Store the reference material in the sample container, tightly sealed. The certificate is valid until **1st of October 2019** provided the material is stored under the recommended conditions.

After opening, the sample may be affected by microbial pollution and humidity.

PRODUCTION OF THE REFERENCE MATERIAL AND DOCUMENTATION

Production

The reference material is municipal sludge from Køge Egnens Rensningsanlæg and has been dried in a sludge drying plant where the sludge is heated to a temperature of approx. 80°C. It has been homogenised to a particle size of 63 µm and filled in metal containers. The material has been produced in accordance with the quality

management procedures of VKI (now: Eurofins Miljø A/S), with the aim to obtain the intended quality of the material.

Documentation of content

Internal control

The analytical quality of VKI has been documented and found satisfactory by regular participations in proficiency tests conducted by NERI/4, 5/, Denmark.

Homogeneity:

The homogeneity of the reference material has been investigated as part of two interlaboratory comparisons. The test for homogeneity has been performed by testing the standard deviation between container units and this certification against the standard deviation of duplicate determinations of individual containers (F-test, 95%). The samples were found homogenous.

Stability:

The stability is being followed by regular analyses of all individual certified components stored at 5°C, room temperature and 37°C. No signs of instability were observed at the date of this certificate.

External documentation

The external laboratory documentation was performed by Danish laboratories. The laboratories were requested to analyse the reference material in two containers in the same analytical series, where one was analysed in duplicate. For control of the analytical quality of the laboratory, the laboratories were requested to analyse two control samples consisting of a known amount of DEHP, NPE, PAH and LAS. 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 included in the calculations

v: p-1, degrees of freedom

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

Selection of results for certification is based on the following:

- the laboratory being experienced, i.e. having analysed minimum five analytical series using the analytical methods applied in this certification
- the results of the laboratory from its participation in one or both proficiency test(s) for these components in sludge conducted by NERI in 1997 and 1998 /4, 5/. The requirements for each individual parameter are that the laboratory's results do not deviate by more than ± 1 times the standard deviation or $\pm 40\%$ from the median value
- the recovery of the results of the analyses of the above-mentioned control samples lies within $\pm 40\%$ of the nominal value.

Finally, results are excluded if they are Grubbs or Cochran outliers /6/, or if a discussion with the laboratory indicates that the analytical quality is not optimal. The statistical parameters are listed in the table below.

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

Certified values
Individual components

PARAMETER	UNIT	AVERAGE	STANDARD DEVIATION BETWEEN LABORATORIES	95% CONFIDENCE LIMITS OF THE AVERAGE		NUMBER OF LABORATORIES INCLUDED IN THE CALCULATION	EXCLUDED LABORATORIES
				$\bar{Y} \pm t_{0,025}(v) \cdot \frac{s_L}{\sqrt{p}}$			
		\bar{Y}	s_L	Lower	Upper	(p)	
acenaphthane *	mg/kg	(0,112)	(0,049)	(0,051)	(0,172)	5	2
acenaphthylene *	mg/kg	(0,064)	(0,030)	(0,016)	(0,112)	4	2
anthracene *	mg/kg	(0,569)	(0,033)	(0,516)	(0,622)	4	2
benzo(a)anthracene *	mg/kg	(0,52)	(0,16)	(0,32)	(0,72)	5	1
benzo(a)pyrene *	mg/kg	(0,40)	(0,16)	(0,20)	(0,59)	5	0
benzo(ghi)perylene *	mg/kg	(0,23)	(0,11)	(0,096)	(0,36)	5	2
benzo(b+j+k)fluoranthenes	mg/kg	0,83	0,39	0,47	1,19	7	0
chrysene *	mg/kg	(0,60)	(0,19)	(0,37)	(0,83)	5	1
dibenzo(a,h)anthracene**	mg/kg	< ca. 0,1					
fluoranthene	mg/kg	1,11	0,26	0,83	1,38	6	1
fluorene	mg/kg	0,29	0,19	0,09	0,50	6	1
indeno(1,2,3-cd)pyrene *	mg/kg	(0,34)	(0,13)	(0,14)	(0,55)	4	3
phenanthrene	mg/kg	1,01	0,34	0,66	1,36	6	1
pyrene	mg/kg	0,92	0,36	0,58	1,26	7	0
di(2-ethyl hexyl) phthalate (DEHP)	mg/kg	26,7	5,78	20,7	32,8	6	1
4-nonylphenol	mg/kg	78	27	49	106	6	1
4-nonylphenol-monoethoxylate *	mg/kg	(5,5)	(2,1)	(3,2)	(8,4)	5	1
4-nonylphenol-diethoxylate *	mg/kg	(2,4)	(0,71)	(1,5)	(3,3)	5	1
C ₁₀ -LAS	mg/kg	72	38	32	112	6	3
C ₁₁ -LAS *	mg/kg	(520)	(67)	(440)	(600)	5	4
C ₁₂ -LAS	mg/kg	850	100	740	960	6	3
C ₁₃ -LAS	mg/kg	700	90	600	790	6	3

*: As fewer than 6 sets of results are included in this certification the data are stated in brackets.

** : Results of only 2 of the 6 participating laboratories exceed the analytical detection limit.

The sum of components in accordance with the Order of the Danish Ministry of the Environment /3/

PARAMETER	UNIT	AVERAGE	STANDARD DEVIATION BETWEEN LABORATORIES	95% CONFIDENCE LIMITS OF THE AVERAGE		NUMBER OF LABORATORIES INCLUDED IN THE CALCULATION	EXCLUDED LABORATORIES
				Lower	Upper		
		\bar{Y}	s_L	$\bar{Y} \pm t_{0,025}(v) \cdot \frac{s_L}{\sqrt{p}}$			
LAS ²	mg/kg	2150	160	1960	2430	5-6	3-4
ΣPAH ³	mg/kg	5,24	0,747	4,38	6,10	5-7	0-2
NPE ⁴	mg/kg	86	27,7	53	119	5-6	1
DEHP	mg/kg	26,7	5,78	20,7	32,8	6	1

- 1 Calculated on the basis of the results of the individual components listed in the table above.
 2 The sum of C₁₀, C₁₁, C₁₂, and C₁₃-LAS
 3 ΣPAH= Σacenaphtene, phenanthrene, fluorene, fluoranthene, pyrene, benzfluoranthenes (b+j+k), benzo(a)pyrene, benz(ghi)perylene, indeno(1,2,3-cd)pyrene
 4 The sum of 4-nonylphenol and 4-nonylphenol mono- and diethoxylates

Methods

PAH, NPE, DEHP: Extraction by dichlormethane and analysis by GC-MS with SIM (single ion monitoring)
 LAS: Extraction by alkaline methanol and analysis by reverse-phase HPLC with UV-detection in accordance with "Determination of organic pollutants in sludge - PAH, DEHP, NPE and LAS", The Danish Environmental Protection Agency 1997/7/

Use of the certified values

For laboratories with an analytical quality comparable with that of 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%, 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 31:2000. Reference materials - Contents of certificates and labels.
 /3/ Order No. 1650 on the Use of Waste for Agricultural Purposes, 2006, The Ministry of the Environment (In Danish).
 /4/ Organic Pollutants in Sludge. Proficiency Test, NERI (National Environmental Research Institute) October 1997 (In Danish).
 /5/ PAH, PCB, plastisizers, alkylphenols and LAS in sludge. Proficiency Test, November 1998.
 /6/ 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.
 /7/ Determination of organic pollutants in sludge - PAH, DEHP, NPE and LAS, The Danish Environmental Protection Agency 1997 (In Danish).

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DIREKTØR

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ANNEX TO CERTIFICATE QC ORGANIC COMPONENTS IN MUNICIPAL SLUDGE

LABORATORY MEASUREMENTS

Acenaphthene		
m_i mg/kg	S_{ri} mg/kg	n_{ri}
0,09	0,00	3
0,18	0,00	3
0,07	0,00	3
0,08	0,01	3
0,14	0,00	3

Acenaphthylene		
m_i mg/kg	S_{ri} mg/kg	n_{ri}
0,04	0,00	3
0,05	0,00	3
0,11	0,00	3
0,06	0,01	3

Anthracene		
m_i mg/kg	S_{ri} mg/kg	n_{ri}
0,61	0,02	3
0,55	0,01	3
0,58	0,01	3
0,54	0,01	3

Benzo(a)anthracene		
m_i mg/kg	S_{ri} mg/kg	n_{ri}
0,42	0,01	3
0,37	0,01	3
0,61	0,00	3
0,76	0,06	3
0,44	0,06	3

Benzo(a)pyrene		
m_i mg/kg	S_{ri} mg/kg	n_{ri}
0,27	0,01	3
0,64	0,02	3
0,26	0,02	3
0,36	0,02	3
0,45	0,00	3

Benzo(ghi)perylene		
m_i mg/kg	S_{ri} mg/kg	n_{ri}
0,09	0,01	3
0,21	0,01	3
0,21	0,01	3
0,25	0,04	3
0,38	0,04	3

Benzo(b+j+k)fluor-anthenes		
m_i mg/kg	S_{ri} mg/kg	n_{ri}
0,21	0,01	3
0,67	0,00	3
1,02	0,03	3
0,53	0,04	3
1,06	0,02	3
1,38	0,04	3
0,95	0,01	3

Chrysene		
m_i mg/kg	S_{ri} mg/kg	n_{ri}
0,51	0,01	3
0,48	0,04	3
0,56	0,03	3
0,93	0,03	3
0,52	0,07	3

Dibenzo(a,h)anthracene		
m_i mg/kg	S_{ri} mg/kg	n_{ri}
<0,01		
<0,02		
0,04	0,01	3
<0,20		
<0,02		
0,12	0,02	3

Flouranthene		
m _i mg/kg	S _{ri} mg/kg	n _{ri}
0,68	0,02	3
1,24	0,07	3
1,45	0,05	3
0,97	0,01	3
1,11	0,07	3
1,19	0,01	3

Flourene		
m _i mg/kg	S _{ri} mg/kg	n _{ri}
0,18	0,00	3
0,68	0,02	3
0,19	0,01	3
0,18	0,01	3
0,24	0,02	3
0,28	0,01	3

Indeno(1,2,3-cd)pyrene		
m _i mg/kg	S _{ri} mg/kg	n _{ri}
0,28	0,01	3
0,21	0,02	3
0,38	0,02	3
0,51	0,05	3

Phenanthrene		
m _i mg/kg	S _{ri} mg/kg	n _{ri}
0,52	0,01	3
1,24	0,01	3
1,01	0,04	3
0,71	0,03	3
1,18	0,02	3
1,40	0,05	3

Pyrene		
m _i mg/kg	S _{ri} mg/kg	n _{ri}
0,48	0,02	3
0,98	0,05	3
1,25	0,05	3
0,72	0,04	3
0,57	0,01	3
0,98	0,07	3
1,48	0,03	3

DEHP		
m _i mg/kg	S _{ri} mg/kg	n _{ri}
18,6	0,6	3
25,0	0,6	3
23,5	0,7	3
32,2	2,0	3
26,6	1,5	3
34,3	0,7	3

Nonylphenol		
m _i mg/kg	S _{ri} mg/kg	n _{ri}
73	1,7	3
110	2,4	3
46	0,7	3
76	0,8	3
53	0,9	3
108	3,2	3

Nonylphenol-monoethoxylat		
m _i mg/kg	S _{ri} mg/kg	n _{ri}
5,11	0,09	3
4,86	0,26	3
5,01	0,24	3
4,53	0,19	3
9,57	0,33	3

Nonylphenol-diethoxylat		
m _i mg/kg	S _{ri} mg/kg	n _{ri}
1,68	0,03	3
1,61	0,19	3
2,90	0,44	3
2,85	0,04	3
3,05	0,33	3

C ₁₀ -LAS		
m _i mg/kg	s _{ri} mg/kg	n _{ri}
42	4	3
46	5	3
99	14	3
104	14	3
27	2	2
116	6	3

C ₁₁ -LAS		
m _i mg/kg	s _{ri} mg/kg	n _{ri}
595	30	3
449	7	3
544	17	3
570	15	2
454	2	3

C ₁₂ -LAS		
m _i mg/kg	s _{ri} mg/kg	n _{ri}
905	33	3
988	18	3
717	22	3
862	16	3
890	7	2
745	9	3

C ₁₃ -LAS		
m _i mg/kg	s _{ri} mg/kg	n _{ri}
745	31	3
793	65	3
562	28	3
733	5	3
737		1
605	10	3

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}

ANNEX TO CERTIFICATE QC ORGANIC COMPONENTS IN MUNICIPAL SLUDGE

CERTIFYING LABORATORIES

A/S Analycen, Fredericia
Levnedsmiddelkontrollen, Skovlunde
Miljø- og Levnedsmiddelcentret, Holbæk
Miljø-Kemi, Viborg
MLK-Fyn I/S, Odense
MLK Vestjylland I/S, Holstebro
MLK Østjylland I/S, Silkeborg
Steins Laboratorium, Brørup
VKI, Hørsholm