



**AB 994** 

Research laboratory accredited by PCA, Nr AB 994

#### Scopes of accreditation:

- concentration and mass measurements of flow of fine particles
- measurements of concentration and mass flow of SO<sub>2</sub>, NO<sub>x</sub>, CO
- concentration measurements of CO<sub>2</sub>, O<sub>2</sub>
- concentration and mass flow measurements of OWO
- sampling for mass concentration determination of PCDD/PDF and dioxin type PCB
- sampling for concentration determination of (As; Cd; Cr; Co; Cu; Mn; Ni; Pb; Sb; Ti; V)
- sampling for concentration determination of Hg
- sampling and determination of concentration and mass flow of HCI
- sampling and determination of concentration and mass flow of HF
- sampling for determining the concentration of individual gaseous organic compounds
- calibration of Automated Monitoring systems,
- QAL2 procedure
- annual performance test of Automated Monitoring Systems, AST procedure
- noise measurement from machinery, installations and industrial plants

Chorzów, October 31<sup>st</sup> 2024 Our ref. No.: PW/81/10/24

## Report No PW/81/10/24

on concentration measurements of PCDDs/PCDFs emitted into environment from flue gas channel located at UAB GREN KLAIPEDA, Kretainio g. 3 LT-94103, Klaipeda, Lithuania.

Client name and address:

**UAB "GREN KLAIPEDA"** 

Kretainio g. 3, LT-94103 Klaipeda

Developed by:

mgr Grzegorz Bortel

Calculation and data transfer checked by:

inz. Dariusz Guja

Verified by:

inż. Dariusz Guja

Copy number: .1/.3..

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#### 1. PURPOSE AND SCOPE OF THE REPORT

Purpose of executed measurements was to determine the concentration and emission of *PCDDs/PCDFs and dioxins-like PCBs* emitted to environment from flue gas channel located at UAB GREN KLAIPEDA, Kretainio g. 3 LT-94103, Klaipeda, Lithuania *Measurements range:* 

PCDD/DF emission and concentration,

The measurements were carried out in accordance with the sampling plan and the described sampling methods.

Operating parameters of the technological installation was obtained from the customer's representative.

#### 2. BASIS OF MEASUREMENTS EXECUTION

The measurements were taken according to the Purchase Order dated June 06<sup>th</sup> 2024, our reference number PP/28/06/24.

#### 3. MEASUREMENT TEAM

The measurements taken on October 1st 2024 were executed by the following team:

Grzegorz Bortel

specialist- measurement team leader,

Grzegorz Kurzeja

specialist,

#### 4. MEASUREMENT RESULTS SUMMARY

Below are presented measurement results summary, full measurement results are presented in chapter no 6, at page 8.

Concentration of the substance in the gas in the reference conditions O2 ref. 11%	PCDDF	ng/m3	0,0045
Emission limits	PCDDF	ng/m3	0,06

## 5. DESCRIPTION OF THE MEASUREMENT METHOD

## Measurement of the gas volumetric flow

The flow rate was determined according to ISO Standard PN-EN ISO 16911-1:2013 "Stationary source emissions - Manual and automatic determination of velocity and volume flow rate in ducts - Part 1: Manual reference method". Gravimetric dust monitor type Megasystem APIS X-1 and type "S" Pitot tube were used for the measurements. Measurement is accredited.

Accreditation range: differential pressure: > 5 Pa

## Measurement O2 content

The concentration of  $O_2$  was determined using gas analyzer HORIBA PG-350E-HR equipped with testing probe 1750 mm long. The measurements were taken according to the procedure described in measurement unit as well as to Polish Standard PN-EN 14789:2017 "Stationary source emissions - Determination of volume concentration of oxygen  $O_2$  - Reference method - Paramagnetism". Measurement is accredited.

Accreditation range: O2 content: 3-21%

#### Measurement CO<sub>2</sub> content

The concentration of  $CO_2$  was determined using gas analyzer HORIBA PG-350E-HR equipped with testing probe 1750 mm long. The measurements were taken according to the procedure described in measurement unit as well as to Polish Standard PN-ISO 10396:2001 "Stationary Source Emissions - Sampling For The Automated Determination Of Gas Concentrations". Measurement is accredited.

Accreditation range: CO₂ content: 0,1-20%

### Measurement moisture content

Moisture content was determined using condensation-absorption method. The measurements were taken according to Polish Standard PN-EN 14790:2017. Measurement is accredited.

Accreditation range: H<sub>2</sub>O content: 29-250 g/m<sup>3</sup>

### PCDDs/PCDFs and dioxins-like PCBs sampling and determination

PCDD/DF samples were taken according to the requirements of Polish Standard PN-EN 1948–1:2006 "Stationary source emissions - Determination of mass concentration of PCDDs/PCDFs and dioxin-type PCBs - Part 1: Sampling of PCDDs/PCDFs".

PCB samples were taken according to the requirements of Polish Standard PN-EN 1948–4:2014-03 " Stationary source emissions - Determination of mass concentration of PCDDs/PCDFs and dioxin-type PCBs - Part 4: Sampling and analysis dioxin-like PCBs".

The three stages of PCDD/DF and PCBs concentration and emission determination:

### Stage I - sampling

For the determination of mass concentration of PCDD/DF and PCBs proper sampling plays important role that affects following stages of the testing. The sampling were performed by means of the filtration and condensation method using PCDD/DF and PCBs sampling system conformed to European Standard PN-EN 1948-1:2006 and PN-EN 1948-4:2014-03.

The following page shows the schematic diagram of the sampling system.

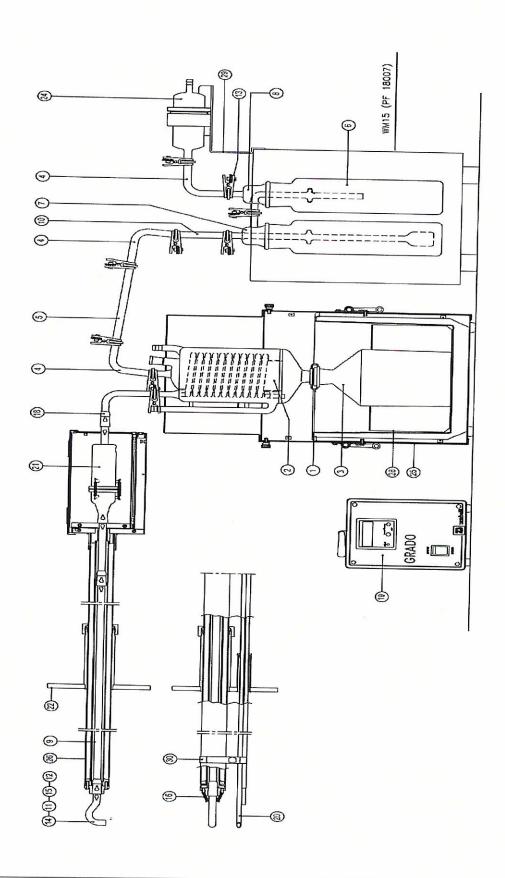
#### Stage II - laboratory analysis

The samples were analysed at the ALS Czech Republic, s.r.o accredited laboratory following the CSN EN 1948-2,3,4 methodology: The determination of polychlorinated dibenzo-p-dioxine, dibenzofurans in emission samples with the method of isotop dillution using HRGC/HRMS.

The dioxin and furans analyses were conducted at the ALS Czech Republic, s.r.o. Laboratory, specifically accredited for the test by the Českŷ Institut Pro Akreditaci, o.p.s., Nr L 1163.

## Stage III - development and the results and discussion

The last stage includes results collection from the previous stages, emission calculation and PCDD/DF and PCBs concentration as well as comparison to the standards in force.



4,18. aspiration path - elbows11,12,14,15. - aspiration endings9. aspiration path - probe tube11,12,14,15. - aspiration endings17. aspiration controller19. temperature controller22. yoke24. gas dryer28. cooler coil29.30. support

3. condensation pot 6-8. scrubbers 16. holding springs 21. filter casing 26. heated probe

9. con 6-8. s 16. hc 5" - type 21. fill

ferrule
 cooler
 s,10. aspiration path - tubes
 clamp
 Pitot tube "S" - type
 cooler casina

Opis:

6. MEASUREMENT RESULTS

- 1) Plant or unit name: Combined Heat and Power Plant<sup>1)</sup>
- 2) Flue gases cleaning unit: ALSTOM NID flue gas cleaning solution (bag filters, activate carbon, ammonia solution, hydrated lime)<sup>1)</sup>
- 3) Emission source load during measurements: 89 MW
- 4) Fuel type or material mass flow in process: 40% municipal waste, 60% industrial waste; 33 t/h
- 5) Location of sampling and measurements: in duct, after flue gases cleaning unit

Measurement reference number				01-10-02 0185			
Date of measurement				01.10.2024	$\neg$ $\times$		
Measurement time range				10:32-16:33			
Scope of test		Unit	Results	Uncertainty +/-	Method		
Meteorological	Atmospheric pressure		hPa	1016,5			
conditions	Air temperature		оС	8			
Measurement plane	Diameter		m	2,20			
Measurement plane	Area		m2	3,7994			
	Temperature		оС	55		PN-Z-04030-7:1994	
1100	Static pressure		Pa	10			
	Differential pressu	ire	Pa	127			
	Gas moistness gr	ade X	kg/kg	0,131			
	Average velocity		m/s	12,3	0,8		
Stack gas parameters	Chemical	O2	%	8,2	0,2	PN-EN 14789:2017	
	composition	CO2	%	11,7	0,5	PN-ISO 10396:2001	
	Wet gas density d	uring testing	kg/m3	1,043		PN-EN 14790:2017	
	Gas density in normal conditions Gas density in conventional conditions		kg/m3 N	1,250		PN-EN 14790:2017	
			kg/m3 U	1,348		PN-EN 14790:2017	
Concentration in the gas at measurement conditions	PCDDF*		ng/m3	0,0045	0,0014	PN-EN 1948:2006	
Concentration in the gas at normal conditions	PCDDF*		ng/m3 N	0,0057	0,0018	PN-EN 1948:2006	
Concentration of the substance in the gas in the standard conditions	PCDDF*		ng/m3 U	0,0058	0,0018	PN-EN 1948:2006	
Concentration of the substance in the gas in the reference conditions O2 ref. 11%	s in popper		ng/m3 U	0,0045	0,0014	PN-EN 1948:2006	
	measurement c	onditions	m3/h	168785	21224		
Coo valum a fi	normal conditions		m3N/h	140854	17712		
Gas volume flow	conventional co	nditions	m3U/h	115482	14522	PN-EN ISO 16911-1:201	
	conventional co ref. 11%	nditions O2	m3U/h	147817	18904		
The emission obtained by measuring	PCDDF*		ng/h	669,80	225,49	PN-EN 1948:2006	
	PCDDF*		ng/m3 U	0,06			
Transgerssion	PCDDF*		ng/m3 U				

<sup>\*-</sup> the results obtained from the subcontractor ( accredited )

<sup>1)-</sup>information obtained from the client

#### Notes:

Normal conditions designate the temperature of 273 K and pressure of 101,3kPa, defining normal cubic meter m³N. The conventional conditions designate the temperature of 273K, pressure of 101,3 kPa and dry gases (steam contents less than 5 g/kg of flue gas), defining conventional cubic meter, m3U

The specified expanded uncertainty comes from standard uncertainty multiplied by expansion coefficient k = 2, which provides 95% level of confidence for normal distribution. Uncertainty takes into account the sampling and analysis.

Registry of samples delivered to the laboratory:

P/55/10/24, P/56/10/24

Date of delivery to the laboratory:

03.10.2024

Date of analysis:

03.10 - 24.10.2024

#### Field blanks:

ID/ number of sample	Type of substance	The criterion of the blank [ng/m³] 11%O <sub>2</sub>	The value of the blank [ng/m³] 11% O <sub>2</sub>	Result [+/-]
P/56/10/24	PCDD/DF	0,006	< 0,0013	+

#### Work parameters of measurement system:

#### PCDD/DF (PN-EN 1948:2006) and PCB (PN-EN 1948-4+A1:2013)::

sampling method:

condensation - adsorption method

filter paramethers:

19 x 90 mm, filter efficiency: 99,998 %

sampling train:

2 measurement axis

oxygen reference:

11 %

6

5

119

time of dioxins and furans measurument:

10:32 - 16:33 (361 min)

nozzle diameter:

mm

probe temperature:

°C

scrubbers temperature

٥С

aspired gas volume

 $m^3$ 

5.225 14,5 l/min

average sampling flow izokinetic ratio:

96,6 %

leak test:

+/+

gas meter temperature

13 °C

gas meter pressure

spiking pattern:

bar filter surface

absorption solution:

100 ml H<sub>2</sub>O dest. + 50 ml 2-etoksyetanol

recovery:

77 % <sup>13</sup>C<sub>12</sub>-1,2,3,7,8-PECDF,

78 %

<sup>13</sup>C<sub>12</sub>-1,2,3,7,8,9-HxCDF,

/>50%/ />50%/

65 %

<sup>13</sup>C<sub>12</sub>-1,2,3,7,8,9 HpCDF.

/>50%/

PCDD/DF TEQ sample mass:

0,029 ng

H<sub>2</sub>O (PN-EN 14790:2017)

sampling train:

2 measurement axis

sampling equipment:

titanium sampling train

heated probe 2,0 m long

sampling pump: SKC

cartridge:

moisture measurement set

number of samplings:

1

sampling time:

30 min

sampling volume:

2,0 l/min

H<sub>2</sub>O maas:

9,4 g

absrobtion efficiency:

98,5 %

O<sub>2</sub> paramagnetic (PN-EN 14789:2017):

Range:

0-5% []

0 - 10 % [ ]

0 – 25 % [X]

Calibration gas:

O<sub>2</sub> - 8,001%

R/07/W

O<sub>2</sub> - 18,85%

D.440

R/12/W

 $N_2 - 99,99\%$ 

R/17/

[]

[X]

[X]

Sampling train:

2 measurement axis

Sampling time/ average time:

360 min / 1 min

O <sub>2</sub> concentration measurement (paramagn	etic):	HORIBA PG-350	E-HR		state and the state of
check operation		unit	result	criterion	result +/-
"0" after adjustment, without sampling train		%	0,04	± 0,1 [%]*	+
"0" after adjustment, with sampling train	before measurement	%	0,10	± 0,1 [%]*  ± 0,2 [%]**  ± 0,2 [%]**  ± 0,2 [%]**	+
,o and adjustment, with sampling train	after measurement	%	0,12	± 0,2 [%]**	+
Cman" often adjustes at 1th 1th	before measurement	%	18,80	± 0,2 [%]** ± 0,2 [%]**	+
"Span" after adjustment with sampling train	after measurement	%	18,95	± 0,2 [%]**	+
standard 18,85 % <b>R/12/W</b> analyzer range 25%/	before measurement	%	17,0	> 17,0 [%]	
	time T90	sec.	12	< 200 sec.	+

## 7. MEASUREMENT DEVICES

Name of measuring	ng device	X1- Apis PLUS
Type of measuring	g device	Isokinetic sampler S/N 0185
Certificate	Calibration No	94/54/LA/P/2023 G-73/23-46/23 65/1/T/23
Issued by		PLUM Sp. z o.o. KLEOSIN ZAP BESTWINKA LABOSERWIS Sp. z o.o. KATOWICE
Date of issue the	certificate of calibration	27.02.2023 r. 23.02.2023 r. 02.03.2023 r.
Expiration date of	the certificate of calibration	-

Name of measi	uring device	HORIBA
Type of measu	ring device	PG-350E-HR
Certificate	Calibration No	69/1/AW/21
Issued by		LABOSERWIS SP. Z O.O. KATOWICE
Date of issue the certificate of calibration 22.03.2021 r.		22.03.2021 r.
Expiration date	date of the certificate of calibration -	

Name of meas	uring device	Sampler
Type of measu	ring device	SKC 224-PCMTX4, 224-44MTX
Certificate	Calibration No	n.d.
Issued by		n.d.
Date of issue the	ne certificate of calibration	n.d.
Expiration date	of the certificate of calibration	-

Name of meas	suring device	SKC SAMPLER KIT		
Type of measu	uring device	-		
Certificate	Calibration No	T271/PMT/2021 212/1/C/21		
Issued by		CZACH-POMIAR Sp. z o.o. KATOWICE LABOSERWIS Sp. z o.o. KATOWICE		
Date of issue t	the certificate of calibration	21.09.2021 01.09.2021		
Expiration date of the certificate of calibration		( <del>-</del>		

### 8. ANALYSIS RESULTS

Attachment no. 1 to the Certificate of Analysis for work order PR24C3610

Sample:

P/55/10/24

ALS SAMPLE ID:

PR24C3610/ 001

Measurement results PCDD/Fs:

Sample:	P/55/	/10/24	Final extract [µl]: 6		60
~			Injection volume   Acquisition date [		4 20.10.24 1:26
2,3,7,8-PCDD/Fs	Result	Limit of Detection [ng/sample]	Limit of Quantification [ng/sample]	<sup>4</sup> I-TEFs	I-TEQ Upperbound [ng/sample]
2,3,7,8-TCDD	< 0.005	0.005	0.01	1	0.005
1,2,3,7,8-PeCDD	< 0.0067	0.0067	0.013	0.5	0.0034
1,2,3,4,7,8-HxCDD	< 0.0069	0.0069	0.014	0.1	0.00069
1,2,3,6,7,8-HxCDD	0.032	0.0069	0.014	0.1	0.0032
1,2,3,7,8,9-HxCDD	< 0.0069	0.0069	0.014	0.1	0.00069
1,2,3,4,6,7,8-HpCDD	0.4	0.018	0.036	0.01	0.004
OCDD	1.1	0.04	0.08	0.001	0.0011
2,3,7,8-TCDF	0.015	0.0051	0.01	0.1	0.0015
1,2,3,7,8-PeCDF	0.0084	0.0041	0.0083	0.05	0.00042
2,3,4,7,8-PeCDF	0.013	0.0041	0.0083	0.5	0.0063
1,2,3,4,7,8-HxCDF	0.0089	0.00061	0.0012	0.1	0.00089
1,2,3,6,7,8-HxCDF	0.0088	0.00061	0.0012	0.1	0.00088
1,2,3,7,8,9-HxCDF	< 0.00061	0.00061	0.0012	0.1	0.000061
2,3,4,6,7,8-HxCDF	0.009	0.00061	0.0012	0.1	0.0009
1,2,3,4,6,7,8-HpCDF	0.015	0.0071	0.014	0.01	0.00015
1,2,3,4,7,8,9-HpCDF	< 0.0071	0.0071	0.014	0.01	0.000071
OCDF	0.032	0.011	0.023	0.001	0.000032
I-TEQ from quantified :	2,3,7,8-PCDD/Fs -	Lowerbound"			0.019
I-TEQ from 2,3,7,8-PC	DD/Fs -"Mediumbo	nund"			0.024
Maximum possible I-T					0.029
PCDD <sub>2</sub>	Result [ng/samp]	le]	PCDFs	Result [ng/sar	mple]
Tetra-CDDs	< 0.11		Tetra-CDFs	0.55	
Penta-CDDs	0.29		Penta-CDFs	0.43	
Hexa-CDDs	0.43		Hexa-CDF5		0.095
Hepta-CDDs	8.0		Hepta-CDFs		0.049
OCDD	1.1		OCDF		0.032

<sup>&#</sup>x27;I-TEF according to NATO.

Limits of quantification are defined as double of the detection limits.

The limit of detection is defined as the amount of analyte producing a signal with S/N≥3.

The value of the detection limit is mentioned as the actual value at the acquisition date.

Measurement uncertainty is expressed as a double (k=2) relative standard deviation (RSD%), and corresponds to 95% confidence interval.

Estimation of uncertainty of each 2,3,7,8-PCDD/F congener is 30% and total I-TEQ is 20%.

These values were ensured by analyses of certified reference material under conditions of internal reproducibility.

Results marked with "<" are bellow limit of detection or quantification.

<sup>&</sup>quot;Lowerbound" and "Upperbound" are levels defined in Regulation 2017/644 and EN 1948-4.

<sup>&</sup>quot;Mediumbound" is levels defined in Regulation 2017/644.

## Attachment no. 1 to the Certificate of Analysis for work order PR24C3610

Sample:

P/55/10/24

Standards recovery:

Sample:			P/55/10/24		
			Final extract [µl]:		60
			Injection volume		4
			Acquisition date		20.10.24 1:26
Extraction standard	Recovery	Acceptable ra			vith respect to
PCDDs	[%]	Basic	Extended	basic range	extended range
13C12 - 2,3,7,8-TCDD	85	50 - 130	30 - 150	YES	Call
13C12 - 1,2,3,7,8-PeCDD	61	50 - 130	30 - 150	YES	-
13C12 - 1,2,3,4,7,8-HxCDD	81	50 - 130	30 - 150	YES	27
13C12 - 1,2,3,6,7,8-HxCDD	82	50 - 130	30 - 150	YES	
13C12 - 1,2,3,4,6,7,8-HpCDD	87	40 - 130	20 - 150	YES	_
13C12 - OCDD	76	40 - 130	20 - 150	YES	-
PCDFs					
13C12 - 2,3,7,8-TCDF	75	50 - 130	30 - 150	YES	-
13C12 - 2,3,4,7,8-PeCDF	65	50 - 130	30 - 150	YES	-
13C12 -1,2,3,4,7,8-HxCDF	82	50 - 130	30 - 150	YES	-
13C12 -1,2,3,6,7,8-HxCDF	87	50 - 130	30 - 150	YES	-
13C12 -2,3,4,6,7,8-HxCDF	86	50 - 130	30 - 150	YES	-
13C12 -1,2,3,4,6,7,8-HpCDF	79	40 - 130	20 - 150	YES	_
13C12 - OCDF	92	40 - 130	20 - 150	YES	-
Sampling standard	Recovery	Acceptable ra	ange	Rec. in range	?
	[%]	[96]			
13C12-1,2,3,7,8-PeCDF	77	> 50		YES	
13C12-1,2,3,7,8,9-HxCDF	78	> 50		YES	
13C12-1,2,3,4,7,8,9-HpCDF	65	> 50		YES	

### 9. CERTIFICATE OF ACCREDITATION

# POLSKIE CENTRUM AKREDYTACJI

POLISH CENTRE FOR ACCREDITATION



Sygnatariusz EA MLA EA MLA Signatory

# CERTYFIKAT AKREDYTACJI

## LABORATORIUM BADAWCZEGO

ACCREDITATION CERTIFICATE OF TESTING LABORATORY

Nr AB 994

Potwierdza się, że: / This is to confirm that:

"PROFTECH" Sp. z o.o. ul. Kurta Aldera 44, 41-506 Chorzów

spełnia wymagania normy PN-EN ISO/IEC 17025:2018-02 mests requirements of the PN-EN ISO/IEC 17025:2018-02 standard

Akredytowana działalność jest określona w Zakresio Akredytacji Nr AB 994 Accredited activity is defined in the Scope of Accreditation No AB 994

Akredytacja pozostajo w mocy pod warunkiem przestrzegania wymagań jednostki akredytującej określonych w kontrakcie Nr AB 994 This accreditation remains in farce provided the Laboratory observes the requirements of Accreditation Body defined in the Contract No AB 994

> Akredytacji udzielono dnia 30.01.2009 r. Accreditation was granted on 30.01.2009



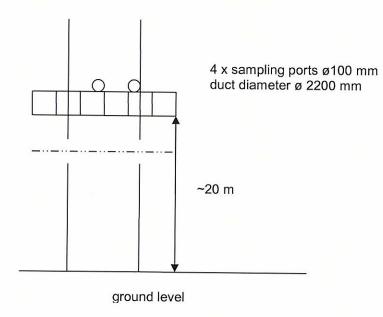


DYREKTOR POLSKIEGO CENTRUM AKREDYTACJI

LUCYNA OLBORSKA

Warszawa, dnia 9 grudnia 2019 roku

### 10. MEASUREMENT PLANE SCHEME



Approved by WREKTOR
Nathe Dand Signature
Signature
Office Signature

**END OF REPORT** 

