



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; Tl; 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, May 22<sup>nd</sup> 2023 Our ref. No.: PW/41/05/23

# Report No PW/41/05/23

on concentration measurements of dioxins and furans 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:

inż. Dariusz Guja

Verified by:

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

Purpose of executed measurements was to determine the concentration and emission of dioxins and furans 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 No MX27936LTKLJ21 dated May 07<sup>th</sup> 2021, our reference number PP/01/05/21.

## 3. MEASUREMENT TEAM

The measurements taken on April 25<sup>th</sup> 2023 were executed by the following team:

Grzegorz Bortel specialist- measurement team leader,

Bartłomiej Glik specialist,

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	0,0014
Emission limits	PCDDF	ng/m3	0,1
Transgerssion	PCDDF	ng/m3	- 1

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 O<sub>2</sub> content

The concentration of O2 was determined using gas analyzer HORIBA PG-350E-EU

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<sub>2</sub> - Reference method - Paramagnetism". Measurement is accredited.

Accreditation range: O<sub>2</sub> content: 3-21%

Measurement CO<sub>2</sub> content

The concentration of CO<sub>2</sub> was determined using gas analyzer HORIBA PG-350E-EU

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: CO<sub>2</sub> 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>

## PCDD+PCDF 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".

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

### Stage I - sampling

For the determination of mass concentration of PCDD/DF 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 sampling system conformed to European Standard PN-EN 1948-1:2006.

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

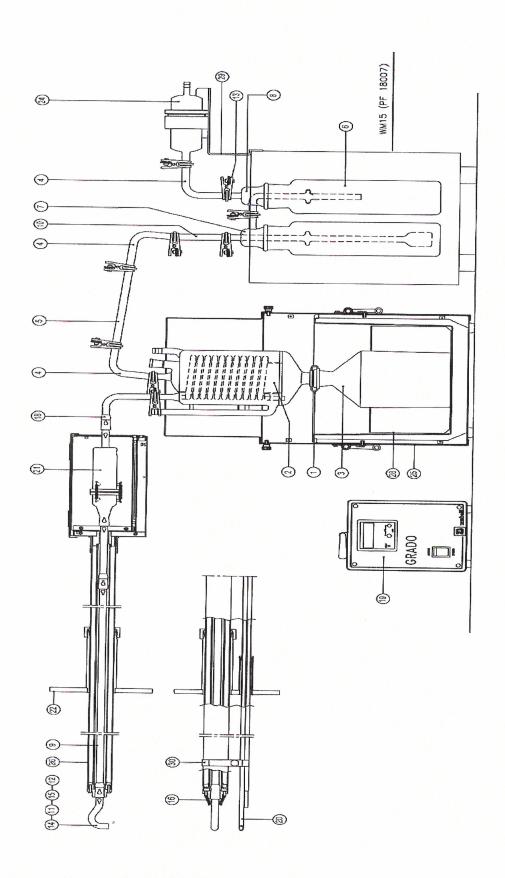
## Stage II - laboratory analysis

The samples were analysed at the ALS Czech Republic, s.r.o accredited laboratory following the CSN EN 1948-2,3 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 concentration as well as comparison to the standards in force.



11,12,14,15. – aspiration endings 19. temperature controller 24. gas dryer 29.30. support

4,18. aspiration path - elbows 9. aspiration path - probe tube 17. aspiration controller 22. yoke 28. cooler coil

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

2. cooler 5,10. aspiration path - tubes 13. clamp 20. Pitot tube "S" - type 25. cooler casina

Opis:

1. ferrule

**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: ~85,0 MW¹)
- 4) Fuel type or material mass flow in process: 40% municipal waste, 60% industrial waste: 27,3 t/h1)
- 5) Location of sampling and measurements: in duct, after flue gases cleaning unit

5) Location of sampling and		in duct, after f	lue gases cl	eaning unit		
Measurement reference	number		1440,5	25-04-01		
Date of measurement				25.04.2023	$\square$ $\times$	$\rightarrow$
Measurement time range				10:1916:20		
Scope of test		Unit	Results	Uncertainty +/-	Method	
diodiological	Atmospheric p	ressure	hPa	1000,0		
conditions	Air temperature		оС	14		
Maggurament plans	Diameter		m	2,20		
Measurement plane	Area		m2	3,7994		
	Temperature		оС	53		PN-Z-04030-7:1994
	Static pressure		Pa	-46		
	Differential press	sure	Pa	178		
	Gas moistness g	grade X	kg/kg	0,098		
	Average velocity	( =	m/s	14,0	0,9	
Stack gas parameters	Chemical	02	%	8,3	0,2	PN-EN 14789:2017
	composition	CO2	%	11,2	0,4	PN-ISO 10396:2001
	Wet gas density during testing		kg/m3	1,050		PN-EN 14790:2017
	Gas density in normal conditions		kg/m3 N	1,269		PN-EN 14790:2017
	Gas density in conventional conditions		kg/m3 U	1,345		PN-EN 14790:2017
Concentration in the gas at measurement conditions	PCDDF*		ng/m3	0,0014	0,0004	PN-EN 1948:2006
Concentration in the gas at normal conditions	PCDDF*		ng/m3 N	0,0015	0,0005	PN-EN 1948:2006
Concentration of the substance in the gas in the standard conditions	ne gas in PCDDF*		ng/m3 U	0,0018	0,0006	PN-EN 1948:2006
Concentration of the substance in the gas in the reference conditions O2 ref. 11%	PCDDF*		ng/m3 U	0,0014	0,0004	PN-EN 1948:2006
	measurement conditions		m3/h	191353	24062	
0	normal conditions		m3N/h	158362	19927	
Gas volume flow	conventional c	onditions	m3U/h	135978	17914	PN-EN ISO 16911-1:2013
	conventional c	onditions O2	m3U/h	172693	23110	
The emission obtained by measuring			ng/h	244,76	82,96	PN-EN 1948:2006
1.0	PCDDF*		ng/m3 U	0,1		
		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/203/04/23, P/204/04/23

Date of delivery to the laboratory:

27.04.2023

Date of analysis:

28.04 - 15.05.2023

#### 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/204/04/23	PCDD/DF	0,01	< 0,0012	+

#### Work parameters of measurement system:

#### PCDD/DF (PN-EN 1948:2006):

sampling method:

condensation - adsorption method

filter paramethers:

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

sampling train:

2 measurement axis

oxygen reference:

nozzle diameter:

11 %

8

time of dioxins and furans measerument:

10:19 - 16:20 (360,1 min) mm

probe temperature: scrubbers temperature 118 ٥С ٥С 4

aspired gas volume average sampling flow

11,7  $m^3$ 32,5 I/min

izokinetic ratio:

99,5 %

leak test:

+/+

gas meter temperature gas meter pressure

٥С 18 0 bar

spiking pattern:

filter surface

absorption solution:

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

recovery:

56 % <sup>13</sup>C<sub>12</sub>-1,2,3,7,8-PECDF, />50%/

64 %

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

/>50%/

100 %

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

/>50%/

TEQ sample mass:

0,02

# 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: PT-01

cartridge:

moisture measurement set

number of samplings:

1

sampling time:

30 min

sampling volume:

2,0 I/min

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

6,5 g

absrobtion efficiency:

98,5 %

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

Range:

0-5% []

0 – 10 % [X]

0 – 25 % [ ]

Calibration gas:

 $O_2 - 9,012\%$ 

[X] R/07/W

 $O_2 - 20,018\%$ 

[]

R/12/W

 $N_2 - 99,99\%$ 

[X]

R/17/

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-EU (130/1/AW/21)		
check operation		unit	result	criterion	result +/-
"0" after adjustment, without sampling train		%	0,05	± 0,1 [%]*	+
	before measurement	%	0,1	± 0,2 [%]**	+
"0" after adjustment, with sampling train	after measurement	%	0,07	± 0,2 [%]**	+
0	before measurement	%	9,0	± 0,2 [%]**	+
"Span" after adjustment with sampling train	after measurement	%	0,05 ± 0,1 [%]* 0,1 ± 0,2 [%]** 0,07 ± 0,2 [%]**	+	
/standard 9,012 % <b>R/07/W</b> analyzer range 25%/	before measurement	%	8,2	> 8,12 [%]	
time T90		sec.	30	< 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 measuring device	HORIBA			
Type of measuring device	HORIBA PG-350E-EU  130/1/AW/21  Laboserwis Sp. z o.o. Katowice			
Certificate Calibration No	130/1/AW/21			
Issued by	Laboserwis Sp. z o.o. Katowice			
Date of issue the certificate of calibration	28.05.2021			
Expiration date of the certificate of calibration	ing a ggaisgeal seed is s			

Name of meas	uring device	Sampler
Type of measu	ring device	PT-01
Certificate Calibration No		R-286/16-186/16 G-354/22-208/22 1189/436/LA/T/2022 786/281/LA/P/2022 ZAP BESTWINKA
Issued by		PLUM SP. Z O.O. KLEOSIN
Date of issue tl	he certificate of calibration	24.08.2016 30.08.2022 06.09.2022 09.09.2022
Expiration date	of the certificate of calibration	rain resident

#### 8. ANALYSIS RESULTS

#### Attachment no. 1 to the Certificate of Analysis for work order PR2344599

Sample:

P/203/04/23

Measurement results Sample:	St. Clark Time Read On Final State Conference of the Party	/04/23	Final extract [µl]:		60	
			and consider [par].			
			Injection volume [	all:	4	
			Acquisition date [d		8.5.23 2:00	
2,3,7,8-PCDD/Fs	Result	Limit of	Limit of	I-TEFs	I-TEQ	
-		Detection	Quantification		Upperbound	
	[ng/sample]	[ng/sample]	[ng/sample]		[ng/sample]	
2,3,7,8-TCDD	< 0.0019	0.0019	0.0037	1	0.0019	
1,2,3,7,8-PeCDD	< 0.0035	0.0035	0.0071	0.5	0.0018	
1,2,3,4,7,8-HxCDD	< 0.0087	0.0087	0.017	0.1	0.00087	
,2,3,6,7,8-HxCDD	< 0.0087	0.0087	0.017	0.1	0.00087	
1,2,3,7,8,9-HxCDD	< 0.0087	0.0087	0.017	0.1	0.00087	
1,2,3,4,6,7,8-HpCDD	< 0.025	0.025	0.049	0.01	0.00025	
OCDD	< 0.031	0.015	0.031	0.001	0.000031	
2,3,7,8-TCDF	< 0.017	0.0085	0.017	0.1	0.0017	
,2,3,7,8-PeCDF	< 0.0062	0.0062	0.012	0.05	0.00031	
2,3,4,7,8-PeCDF	< 0.012	0.0062	0.012	0.5	0.0062	
,2,3,4,7,8-HxCDF	< 0.014	0.0072	0.014	0.1	0.0014	
1,2,3,6,7,8-HxCDF	< 0.0072	0.0072	0.014	0.1	0.00072	
1,2,3,7,8,9-HxCDF	< 0.0072	0.0072	0.014	0.1	0.00072	
2,3,4,6,7,8-HxCDF	< 0.014	0.0072	0.014	0.1	0.0014	
1,2,3,4,6,7,8-HpCDF	< 0.035	0.017	0.035	0.01	0.00035	
1,2,3,4,7,8,9-HpCDF	< 0.017	0.017	0.035	0.01	0.00017	
DCDF	< 0.027	0.014	0.027	0.001	0.000027	
-TEQ from quantified	2,3,7,8-PCDD/Fs	-"Lowerbound"			0	
-TEQ from 2,3,7,8-PC					0.0098	
Maximum possible I-TEQ -"Upperbound"					0.02	
PCDDs	Result [ng/samp	le]	PCDFs Result [ng/samp		aple]	
Tetra-CDDs	< 0.041 Tetra-CDFs		<	0.32		
Penta-CDDs	< 0.05		Penta-CDFs	< 0.17		
Hexa-CDDs	< 0.087		Hexa-CDFs	< 0.12		
Hepta-CDDs	< 0.049		Hepta-CDFs	< 0.07		
DCDD	< 0.031		OCDF	< 0.027		

<sup>&</sup>lt;sup>4</sup>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  $S/N \ge 3$ .

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 PR2344599

Sample: P/203/04/23

Standards recovery:	
Sample:	P/203/04/23
	Final extract [µl]:
	Injection volume [µ1]:
	Aconicition data [d m v h·m]:

			injection volume [jii]:			
			Acquisition date	d.m.y h:m]:	8.5.23 2:00	
Extraction standard	Recovery	Acceptable ra	nge [%] Accept. rec. 1		with respect to	
PCDDs	[%]	Basic	Extended.	basic range	extended range	
13C12 - 2,3,7,8-TCDD	86	50 - 130	30 - 150	YES	-	
13C12 - 1,2,3,7,8-PeCDD	55	50 - 130	30 - 150	YES	·	
13C12 - 1,2,3,4,7,8-HxCDD	100	50 - 130	30 - 150	YES	_	
13C12 - 1,2,3,6,7,8-HxCDD	72	50 - 130	30 - 150	YES		
13C12 - 1,2,3,4,6,7,8-HpCDD	99	40 - 130	20 - 150	YES		
13C12 - OCDD	96	40 - 130	20 - 150	YES		
PCDFs						
13C12 - 2,3,7,8-TCDF	92	50 - 130	30 - 150	YES	-	
13C12 - 2,3,4,7,8-PeCDF	60	50 - 130	30 - 150	YES		
13C12 -1,2,3,4,7,8-HxCDF	90	50 - 130	30 - 150	YES	· · · · · ·	
13C12 -1,2,3,6,7,8-HxCDF	120	50 - 130	30 - 150	YES	<u>~</u> .	
13C12 -2,3,4,6,7,8-HxCDF	87	50 - 130	30 - 150	YES		
13C12 -1,2,3,4,6,7,8-HpCDF	77	40 - 130	20 - 150	YES	- 1 - 1	
13C12 - OCDF	56	40 - 130	20 - 150	YES	_	
Sampling standard	Recovery	Acceptable range		Rec. in range?		
	[96]	[%]				
13C12-1,2,3,7,8-PeCDF	56	> 50		YES		
13C12-1,2,3,7,8,9-HxCDF	64	> 50		YES		
13C12-1,2,3,4,7,8,9-HpCDF	100	> 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 meets requirements of the PN-EN ISO/IEC 17025;2018-02 standard

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

Akredytacja pozostaje 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



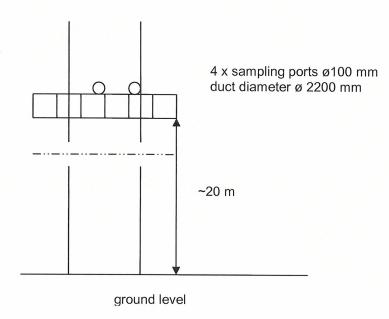


DYREKTOR POLSKIEGO CENTRUM AKREDYTACJI

LUCYNA OLBORSKA

Warszawa, dnia 9 grudnia 2019 roku

# 10. MEASUREMENT PLANE SCHEME



Approved by

DYREKTOR

Dariusz Guja

Name and Signature

**END OF REPORT** 

