

## DETERMINATION OF POLYCHLORINATED DIBENZO-P-DIOXINS AND DIBENZOFURANES IN THE FLY ASHES FROM THE HOVAL TYPE MEDICAL WASTE INCINERATORS

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### Introduction

Utilization of the hazardous waste in Poland is generally based on incineration and combustion techniques. For this they are applied different kind of incinerators working at many different conditions. Medical waste is one of the most dangerous kinds of waste. Utilization of it is based on 32 currently working medical waste incinerators (MWI). Only fourteen from them are regularly checked on pollutants emission – especially on polychlorinated dibenzo-p-dioxins, dibenzofurans and also other dioxin like compounds.

These incinerators are also the source of ashes which, due to high concentration of hazardous elements and chemical compounds, must be stored in special dangerous waste stores.

During this research it was made an effort to determined polychlorinated dibenzo-p-dioxins and dibenzofurans in bottom and fly ashes from one of the Hoval-type medical waste incinerators, working in the Eastern part of Poland.

### Materials and methods

In analytical procedures following solvents: toluene, hexane, dichloromethane chromatographic grade (JT. Baker, Germany) were used. Standard solutions: EDF-4947 EN-1948 – calibration solution, EDF-4138 – sampling standard solution, EDF-4139 – extraction standard solution and EDF-4140 – syringe standard solution were purchased from Cambridge Isotope Laboratories. Adsorbents for the clean-up of obtained extracts (silica gel and aluminium oxide) and other chemicals were obtained from Merck.

The samples of bottom (from hearth) and fly ashes and (absorbed in filter sacks) were taken in about 5 kilogram quantities to provide proper representativity of the taken sample. Next, metal parts and fragments of melted glass were removed from the hearth ashes and ground in the agate mill to get properly disintegrated material. Then, just before the extraction processes it was given recovery standards. Toluene extraction was executed in Soxhlet apparatus during 48 hours. Next, the solvent was changed into hexane to prevent from sulfonation of it during initial purification of the extracts by concentrated sulphuric acid.

Finally the extracts were purified with – first, acidic and then neutral silica gel and also aluminium oxide. After evaporation and addition of syringe standards extracts were injected into GC-MS – system. GC-MS conditions are given in the table 1.

**Table 1.** GC-MS conditions

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Gas chromatographic conditions  
AS 200 Autosampler

2µl sandwich type injection

# FORMATION AND SOURCES

Split-splitless injector	operated in splitless mode, valve opening time: 150s
Temperature of injection port	250 °C
Precolumn:	2 m x 0.25 mm I.D., deactivated
Analytical column:	DB-5ms 60m x 0.25 mm I.D. coated with 0.25 µm stationary phase (J&W)
Temperature program:	50 °C 1 min. hold, 20 °C/min till 180 °C, 4 °C/min till 320 °C, 1min. hold
Carrier gas:	He @ 40 cm/min
GC-MS Finnigan GCQ conditions:	
Ionization mode:	Electron impact, 70 eV
Full scan mode:	for determination of compounds "windows"
Selected ion monitoring	for quantitative determination of dioxins

## Results and discussion

The examples of results of determination of polychlorinated dibenzo-p-dioxins and dibenzofurans in fly and bottom ashes are given in a table 2

CONGENER	WHO-TEF	CONCENTRATION [ng/g]	WHO-TEQ	CONCENTRA-TEQ	WHO-TEQ	DETECTION LIMIT [pg/g]
			[ng/g]	[ng/g]	[ng/g]	
			BOTTOM ASH		FLY ASH	
<i>2,3,7,8-TCDD</i>	1	0,01	0,01	0,01	0,01	1
<i>1,2,3,7,8-PeCDD</i>	1	0,05	0,05	0,01	0,01	0,7
<i>1,2,3,4,7,8-HxCDD</i>	0,1	0,02	0,002	0,00		0,6
<i>1,2,3,6,7,8-HxCDD</i>	0,1	0,02	0,002	0,00		0,6
<i>1,2,3,7,8,9-HxCDD</i>	0,1			0,00		0,6
<i>1,2,3,4,6,7,8,-HpCDD</i>	0,01	1,08	0,0108	0,28	0,0028	1,5
<i>OCDD</i>	0,0001	0,06	0,001	0,06	0,00006	0,7
Total PCDDs:	<b>1,24</b>	<b>0,0758</b>	0,36	<b>0,02286</b>		
<i>2,3,7,8-TCDF</i>	0,1	0,5	0,05	0,00		5
<i>1,2,3,7,8-PeCDF</i>	0,05			0,00		5
<i>2,3,4,7,8-PeCDF</i>	0,5	0,3	0,015			5
<i>1,2,3,4,7,8-HxCDF</i>	0,1					5
<i>1,2,3,6,7,8-HxCDF</i>	0,1	1,35	0,135	0,38	0,038	5
<i>2,3,4,6,7,8-HxCDF</i>	0,1					5
<i>1,2,3,7,8,9-HxCDF</i>	0,1					5
<i>1,2,3,4,6,7,8,-HpCDF</i>	0,01	0,63	0,0063	0,21	0,0021	2
<i>1,2,3,4,7,8,9-HpCDF</i>	0,01					2
OCDF	0,0001	0,58	0,00058	0,33	0,00033	2
Total PCDFs:	<b>2,26</b>	<b>0,20688</b>	<b>0,92</b>	<b>0,04043</b>		
TOTAL PCDD/Fs		<b>3,5</b>	<b>0,28268</b>	<b>1,28</b>	<b>0,06329</b>	

Method is suitable for the determination of polychlorinated dibenzo-p-dioxins and dibenzofurans.

## FORMATION AND SOURCES

Obtained results suggested mechanics of dibenzo(p)dioxins and dibenzofurans synthesis, based on assumption that the mayor role in polymerisation of  $C_2H_2$ ,  $C_2$  radicals and dehydrobenzene. This, explain that mechanics of creating dibenzo(p)dioxins and dibenzofurans can be a part of a wider theory for combustion processes, which can include entirely all the processes of creating (in conditions of “*de novo*” synthesis) polyaromatic hydrocarbons, fullerenes and the soot.

Domination of dibenzofurans over dibenzo(p)dioxins can be interpreted as a difference in adsorption dioxins on the dust particles, but analogous profiles are observed in engines with any differences, for example in mineral additives.

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### References:

1. “Persistent organic contaminants in Poland”, Polish Society for Utilization of Wastes “3R”, Krakow, Poland, 2001,
2. EN-PN 1948 Norma
3. A. Grochowalski, *Chemosphere*, 37 (1998) 2297 – 2309
4. Z. Kozak, J. Czerwiński, On the possible role of dehydrobenzene in formation of dibenzodioxins and dibenzofurans in high temperature flue gases, in print,

