

## APPLICATION OF GC-MS/MS TECHNIQUE FOR DETERMINATION OF DIOXINS IN AIR SAMPLES COLLECTED FROM DIFFERENT TYPES OF COMBUSTION PROCESSES.

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### Abstract

One of the alternative solutions concerning the analysis of dioxins is a possibility of using the gas chromatograph coupled with a mass spectrometer using the operating principles of quadruple mass spectrometer or an ion trap. GC-MS/MS systems in the optimal working conditions, have a similar selectivity and the detection limit to the high resolution magnetic GC-MS systems. Results of the qualitative and quantitative analysis in solid and gas samples collected from waste incinerators by GC tandem MS, are presented in this paper.

The measurements of dioxin and furans emission from a hospital waste incinerator was carried out in ash samples by GC-MS/MS and compared to HRGC/HRMS results. Identification of PCDD/Fs was also performed in ash samples collected during domestic garbage burning processes. The automatic Power Prep system and the multi-column purification system with the acid-alkaline and silica columns were used for the preparation of samples.

### Introduction

With regard to the specificity of the medical wastes and, first of all, the danger of a microbial infection, thermal methods of waste utilization are the safest and the most environment friendly, providing that the technological and law requirements, as well as the proper technology of exhaust fumes purification are maintained.

Utilization through the combustion, successfully overcomes microorganisms contained in such wastes and what is more, it leads to the decrease of waste products taken out to the landfill.

The European Union researches indicate that 62% of total dioxin and furans emission is the emission to the air.

In Poland, according to the data from a year 2000, the emission of dioxins and furans to the air was estimated for about 505 g TEQ, where the main source of it are the combustion processes in municipal and housing sectors, with 36% of total dioxin emission to the air. The second source of the dioxin and furan pollution is a waste management including medical waste incineration, estimated at 30 %, where the emission associated with the utilization of medical waste products in installations without any air protective solutions is about 7%<sup>1</sup>.

In medical waste products, the main source of chlorine are chlorinated plastic products, mainly the polyvinyl chloride, which is mostly used in a colorful and colorless form, elastic or hardened, used for example to produce different types of disposable containers and boxes for chemicals. Moreover, infected medical wastes contain large amounts of chlorinated paper-pulp and may contain trace amounts of PCDDs and PCDFs<sup>2</sup>. The presence of chlorine and paper in medical waste products, impairs thermal conditions during utilization and unfulfills technological requirements for such an installation, what clearly explains why those wastes are one of the most serious sources of dioxin emission.

### Materials and Methods

Solvents like hexane, dichloromethane, toluene, ethyl acetate, methanol, cyclohexane and acetone of „Ultra Resin” purity, anhydrous sodium sulphate and sulphuric acid were purchased from J.T.Baker (Deventer, The Netherlands).

Isotopically labelled <sup>13</sup>C-PCDDs and <sup>13</sup>C-PCDFs standard and native (not labelled PCDDs and PCDFs) solutions were purchased from Wellington Laboratories, Guelph, Ontario, Canada.

Native standards: EPA-1613 PAR, Internal standard (IS): EPA-1613 LCS, Recovery standard (RS): EPA-1613CSS <sup>37</sup>Cl<sub>4</sub>-2,3,7,8-TCDD. Injection standard: EPA-1613 ISS.

Alumina basic, activity I and Alumina acidic activity I, Silica gel 60 from Merck (Darmstadt, Germany)

### GC-MS/MS system

ThermoQuest GCQplus GC-MS/MS systems were used for the analysis. Mass selective detectors were adjusted in double fragmentation MS/MS mode. The secondary ion signals were recorded separately for PCDDs and PCDFs.

DB-5MS (60m x 0.25 mm x 0,25 mm) columns. The injection port of the gas chromatograph was operated at 280°C and the detector temperature - 250°C. The oven temperature was maintained at 120°C for 3 min., then programmed at 20° min<sup>-1</sup> to 200°C, then at 2° min<sup>-1</sup> to 260°C, and finally at 3° min<sup>-1</sup> to 300°C, which was held for 10 min. The carrier gas - helium, flow rate 1.2 mL min<sup>-1</sup>

The automatic Power Prep system and the multi-column purification system with the acid-alkaline and silica columns were used for the preparation of samples.

### Sample preparation

Representative ash and gas samples, in order to determine the PCDDs and PCDFs content in gases emitted from stationary emission sources from the medical waste incineration, were sampled due to the requirements of the EN 1948-1:1996 standard and its polish form PN-EN 1948-1:2002, with the use of a filtration-condensation system called EMIOTEST 2598.

For air sampling, during uncontrolled domestic garbage burning, a sampling device system consisting of a filter and polyurethane foam connected to Leland Legacy pump with a flow rate of 10 l/min was used.

Ash samples were collected from the hospital waste incinerators. They were collected both, from different containers where the ash was stored and different depths to receive a representative sample. Dry and cold ash was stored in plastic bags at room temperature. Before the extraction procedure, a laboratory segregation of collected samples was carried out. In all cases, two types of samples were prepared for extraction. One, where the sample was purified and big, not combusted parts were removed, then subsequently homogenized and sifted through molecular sieves of different diameters with a final diameter of 1mm, which fraction was chosen for further analysis. (This fraction was stored in a borosilicate glass and plastic.) The second type of a research material was a non-sifted and not combusted part of the ash.

### **Results and Discussion**

The results of dioxins analysis were compared regarding to the different methods of sample preparation: automated purification systems and traditional, normalized methods. Dioxin concentrations obtained by HRGC/HRMS and an ion trap GC-MS/MS were similar regardless of the sample preparation technique. However higher concentrations of congeners were determined in ash samples which were homogenized before the main analysis. The highest found concentrations were of 2,3,7,8-TCDF, 2,3,4,7,8-PeCDF, 1,2,3,4,7,8-HxCDF and 2,3,4,6,7,8-HxCDF, while the lowest were determined for OCDD and OCDF, most likely being a result of the fact, that congeners remain in the ash in a combustion chamber, because they have a low vapor pressure and they strongly adsorb to the activated carbon formed in the ash during the pyrolysis reaction. The most toxic congener of 2,3,7,8 TCDD was not found in any of the analyzed samples. When the automatic PowerPrep system was used, the range of discrepancy between minimal and maximal recoveries in samples prepared in a different way of extraction, was significantly lower than the one observed in case of multi-column purification. However, even with the biggest discrepancy the obtained results were still within the acceptable ranges of EPA 1613.

Measurements of the emission of the dioxins and furans present in combustion gases from one of the polish hospital waste incinerators was also carried out within this work. The comparison of collected results with the literature data lets us state that this incinerating plant should be numbered among incinerators of the average dioxin emission. Concentration of the most toxic dioxin congener – 2,3,7,8-TCDD in exhaust fumes from the incinerator was 0,15 ng/m<sup>3</sup>. The total content of PCDDs/Fs congeners in analyzed exhaust fumes amounts to 2,94 ng TEQ/m<sup>3</sup> and in the incinerating plant where the purification systems were applied only to 0,042 ng TEQ/m<sup>3</sup>.

The air samples taken during domestic garbage burning contained only isomers like: hexa- hepta- and octa-dioxins and furans. During combustion of other types of materials, mainly grasses and woods, in the air samples tested no congeners of dioxins and furans were identified.

### Acknowledgments

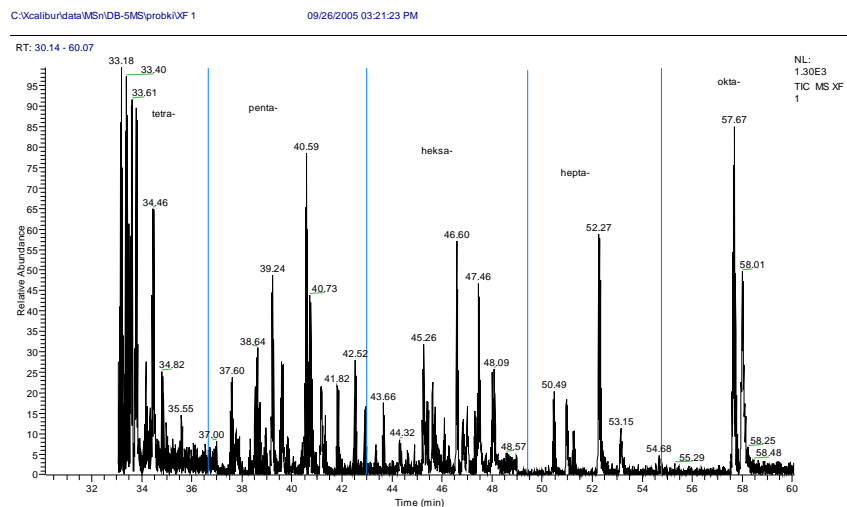
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### References

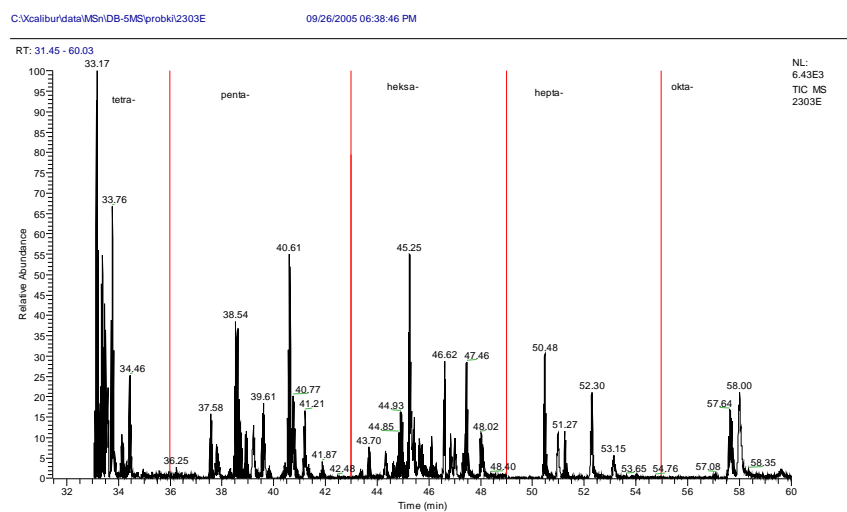
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**Table 1. Concentration range of dioxins and furans in ashes' samples.**

Congener	i-TEF	Power Prep		Multi-column purification	
		Concentration range		Concentration range	
		[i-pg/g]		[i-pg/g]	
		Min	Max	Min	Max
2,3,7,8-TCDF	0,1	11,517	115,473	23,837	474,941
1,2,3,7,8-PeCDF	0,05	1,554	13,999	7,237	14,496
2,3,4,7,8-PeCDF	0,5	39,214	363,773	188,858	400,794
1,2,3,4,7,8-HxCDF	0,1	16,393	184,192	13,248	55,247
1,2,3,6,7,8-HxCDF	0,1	4,520	50,978	18,939	24,101
2,3,4,6,7,8-HxCDF	0,1	6,610	68,177	60,536	96,252
1,2,3,7,9-HxCDF	0,1	1,424	13,969	-	18,038
1,2,3,4,6,7,8-HpCDF	0,01	1,753	18,784	2,922	14,984
1,2,3,4,7,8,9-HpCDF	0,01	0,149	1,478	2,189	2,442
OCDF	0,001	0,056	0,671	0	1,105
2,3,7,8-TCDD	1	-	-	-	-
1,2,3,7,8-PeCDD	0,5	5,893	76,727	38,459	178,040
1,2,3,4,7,8-HxCDD	0,1	0,602	6,783	8,565	11,871
1,2,3,6,7,8-HxCDD	0,1	0,602	14,805	16,072	18,043
1,2,3,7,8,9-HxCDD	0,1	1,623	14,515	3,478	12,779
1,2,3,4,6,7,8-HpCDD	0,01	0,625	7,361	4,047	6,679
OCDD	0,001	0,152	0,808	0,268	1,633



**Figure 1. Exemplary chromatogram of purified sample of exhaust fumes from wastes incineration in the GC-MS/MS (TIC) mode**



**Figure 2. Exemplary chromatogram of an ash sample purified on multi-column system in the GC-MS/MS (TIC) mode.**