

**Determination of PCDFs/PCDDs in stack gas from
GG14 HOVAL/ŐSCO
Hospital Waste Incineration Plant in Gorzów Wlkp, Poland**

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1. Introduction

Many hospital wastes, including hazardous wastes, are burned as hazardous waste fuel in incinerators for the purpose of hospital waste destruction. Combustion of hospital wastes has been shown to produce chlorinated dibenzofurans and dibenzoparadiioxins (PCDFs/PCDDs). The modern incinerator plant must be equipped with flue gas purification system, reducing the levels of chlorinated furans and dioxins down to the 0.1 ng/Nm^3 (2,3,7,8 Toxic Equivalent), to comply with the actual European regulations. The first Pyrolysis Unit of Hoval GG 14 hospital wastes incinerator was installed and is operated in Gorzów Wielkopolski (Nord - West part of Poland). The GG 14 Incinerator operates on-line with ŐSKO wastewater-free treatment of flue gas stream. Furans and dioxins removal is performed with dry sorption process, when Sorbalit (a mixture of high purity hydraulic lime Ca(OH)_2 with brown-coal coke) is added at a prescribed ratio to the stream of flue gas. Afterwards the flue gas is filtering on a special filter which is upstream of the lye scrubber. The filter is equipped with a special teflon-coated filtering material. Daily capacity of GG 14 incinerator is 2700 kg of hospital wastes.

2. Sampling procedure

Samples for determination of polychlorinated dioxins and polychlorinated furans in flue gas were taken on 30 of April 1994 and 1 of May 1994 from the installation for incineration of hospital wastes at Wojewódzki Szpital Zespólny w Gorzowie Wielkopolskim (Hospital serves for Gorzów Voivodship). Sampling methodology was determined by the complexity of PCDFs and PCDDs formation in flue gas. First of all, large volumes of flue gas were taken (several dozens of m^3 before flue gas purification unit and over 160 m^3 after the unit) because it was assumed that concentrations of PCDFs and PCDDs would be at ng / Nm^3 or even pg / Nm^3 level. As PCDFs and PCDDs condense on particulates of fly ash in the zone of flue gas cooled below 200°C , samples of fly ash were taken using glass fibre filters of pore size of $0.2 \text{ }\mu\text{m}$. PCDDs and PCDFs present in vapour form in cool flue gas were adsorbed using sorbent XAD-2 placed between

layers of polyurethane foam. In addition, at high humidity of flue gas, samples of water condensate containing dissolved PCDFs and PCDDs and other organic compounds were also taken. Sampling of PCDFs and PCDDs in flue gas was carried out isokinetically.

Sampling line consisted of heated filter holder with glass fibre filter, gas cooler, container with XAD-2 sorbent and condenser for water condensate. Temperature and flow rate of sampled gas were continuously measured.

Samples of fly ash collected on glass fibre filters, sorbents and water condensate were transported to our laboratory and extracted with organic solvents, according to procedures recommended by EPA (EPA-1613), C. Rappe, H. R. Buser, B. Dodet and I. K. O'Neill ¹⁾ and Warren Spring Lab. (LR 778) and also described by P.T. Williams ²⁾ and others. The procedure of sampling and determination of PCDDs and PCDFs had been introduced and adapted to Polish Laboratory Standards in our Laboratory at Cracow University of Technology. This procedure guarantees 95% collection efficiency of PCDFs and PCDDs from flue gas and determination limit of PCDFs/PCDDs at 0.001 ng/Nm³ in gas sample as expressed as Toxic Equivalent (TEq) parameter.

Samples were taken during two different periods of operation of the installation for incineration:

- I period (sample I) - incineration of unseparated solid wastes from all departments of Gorzow Wielkopolski Hospital, together with used mineral light oil from Plastic Works "Stilon" in Gorzow Wielkopolski.
- II period (sample II) - incineration of unseparated solid wastes from all departments of Gorzow Wielkopolski Hospital.

In both periods of operation samples were taken from two points: before flue gas purification unit (inlet) and after the unit (outlet). Flue gas was sampled through inlets mounted in standardized R64 holes. Temperature of sampled gas was 150 and 50°C, respectively. Sampling of flue gas was carried out isokinetically. Volume of samples taken at the inlet of the gas purification unit was 25 Nm³ and volume of samples taken at the outlet of the gas purification unit was 160 Nm³.

This sampling scheme made it possible to determine efficiency of the purification of flue gas from PCDDs and PCDFs.

Samples were protected from sunlight, transported to our laboratory and immediately treated following the analytical procedure described below.

3. Analytical procedures

Glass fibre filters collected particulates of fly ash separated from flue gas stream (practically not visible), polyurethane foam plugs and XAD-2 sorbent cartridges were spiked with the 2,3,7,8-C¹³ PCDFs/PCDDs internal standard mixture (Cambridge Isotope Laboratories, Woburn (MA) - Promochem Warsaw), for the recovery evaluation. After Soxhlet extraction with toluene (J.T.Baker 9336-03) within 24 hours, extracts were concentrated in Kuderna-Danish concentrators to dryness, and residues were dissolved in 10 ml of hexane (J.T.Baker 9262-03). Aqueous flue gas condensate samples were extracted on solid phases with J.T.Baker Empore C-18 Extraction Discs, accordingly to the previously published procedure ³⁾.

Dichloromethane extracts after solvent exchange to hexane were combined with the Soxhlet, hexane extracts.

The clean-up of the hexane extracts were performed basically in accordance with recommended procedures by EPA 1613, EPA 8280, Warren Spring Laboratory LR 778 (CA) by A. R. Fernandes, following procedures described by H. R. Buser and C. Rappe¹⁾, P. T. Williams²⁾, not published papers from Rijksinstituut voor Volksgezondheid, Bilthoven, The Netherlands and original, tested in our laboratory analytical procedures. PCDFs/PCDDs were quantitatively analyzed in the fractions of purified samples by coupled capillary gas chromatography / mass spectrometry. GC-MSD analyses were performed on Hewlett-Packard 5890 capillary gas chromatograph coupled with quadrupol MSD 5971 detector and equipped with DB-5, or DB-225 (for TCDFs monitoring) capillary columns, 60m, 0.32mm ID, 0.25 μ m stationary phase film.

The GC-MSD was operated in EI 70eV, SIM mode, in which it can simultaneously monitor 24 ions in selected time windows.

4. Results and discussion

The results presented here indicate that emission of mass concentration of polychlorinated dioxins and furans (calculated as a Toxic Equivalent factor TEq) are less of the threshold value of 0.1 ng (TEq)/Nm³, in accordance with the German 17. BImSchV regulations, or appropriate European and American Standards, however the TEq for inlet stream, before flue gas purification unit was calculated at a level of 13 - 20 ng/Nm³ I-TEq. Results of analysis are presented in table 1.

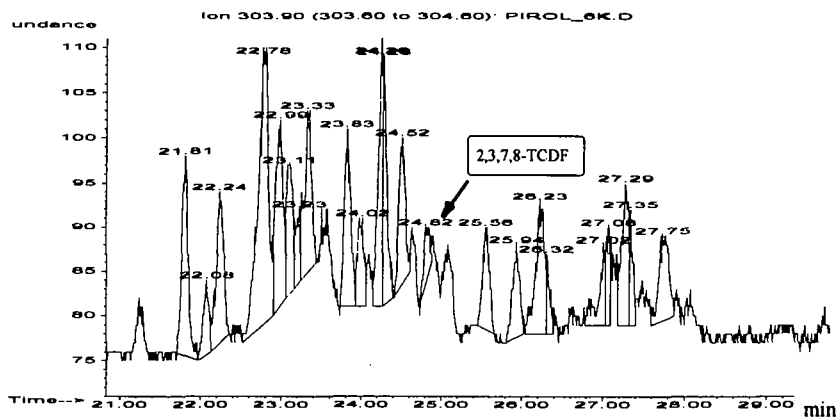
Table 1: Mass concentration of PCDFs/PCDDs in flue gas stream from hospital waste incineration in HOVAL-ŠSKO GG 14 pyrolytic incinerator, before flue gas purification unit (**inlet**) and after the unit (**outlet**). Values of PCDFs/PCDDs concentration are presented as a summarized 2,3,7,8 Toxic Equivalent Factor. The bottom line shows the purification efficiency of the unit.

TEq (NATO/CCMS) in ng/Nm ³			
Inlet Sampling I (Period I)	Outlet Sampling I (Period I)	Inlet Sampling II (Period II)	Outlet Sampling II (Period II)
19.42	0.06	13.29	0.05
Purification efficiency [%]		Purification efficiency [%]	
99.68		99.64	

Tetrachlorodibenzofurans was determined as the most significant group of PCDFs/PCDDs in the flue gas samples for incineration of hospital wastes. Figure 1 shows a chromatogram obtained for TCDFs as a 303.9 m/z ion monitored in selected time window. 2,3,7,8-TCDF was found in all of the investigated flue gas samples on the level of 15 - 18 ng/Nm³ for not purified gas stream and 0.2 to 0.4 ng/Nm³ for stack gas after purification. 2,3,7,8-TCDD mass concentration was calculated at a level of 8 - 9 ng/Nm³ and 0.005 - 0.012 ng/Nm³ respectively.

The recovery of 2,3,7,8-TCDF and 2,3,7,8-TCDD was calculated at 80 - 85% mass concentration based on the introduced 2,3,7,8-TCDF/TCDD-C¹³ isotopically labelled congeners.

Figure 1: GC-MSD single ion chromatogram for 303.9 ion monitored for TCDFs in a mixture of PCDFs/PCDDs isolated from flue gas sample of 160 Nm³ of outlet stream (emission), after purification unit of GG 14 HOVAL-ÖSKO hospital waste incinerator. Separation was carried out on DB-225 capillary column. Retention time for 2,3,7,8-TCDF was recorded as 24.82 min.



5. References

- 1) Rappe C., Buser H.R., Dodet B., O'Neill I.K. (1991) Environmental Carcinogens, Methods of Analysis and Exposure Measurement. Vol.11 - *Polychlorinated dioxins and dibenzofurans*. Int. Agency for Research on Cancer, Lyon, IARC Scientific Publications no: 108.
- 2) Williams P.T. (1992): The Sampling and Analysis of Dioxins and Furans from Combustion Sources: Jour. of the Inst. of Energy 65, 46-54
- 3) Grochowalski A, Wybraniec S., Górski L., Sokołowski M. (1993) : Solid Phase Extraction and Capillary GC-ECD Analysis of PCDFs/PCDDs in Chlorinated Phenols : *Chemia Analityczna* (Warsaw), Vol. 33, 279-283