

## Determination of PCDFs/PCDDs in ambient air from Cracow city, Poland

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### 1. Introduction

Organic toxic air pollutants have been of concern for many years. A great influence of the presence of PCDDs and PCDFs in ambient air are waste incineration and combustion processes. Cracow, the second largest city in Poland is one of high population density. The population in 1994 was estimated to be 950.000. Cracow is located in the south region of Poland at an altitude of 220 meters between hills of mean altitude of 500 m. The surrounding Silesian area from west neighbouring have heavy industry, black coal mines, iron melters. Cracow population traveling by motor vehicles propelled still with leaded petrol and also power generation and household heating facilities are based on black coal burning, all of which contribute to the air quality problems. The aim of this investigations was to evaluate the average mass concentration of dioxins and furans in Cracow ambient air. Cracow has very serious air pollution which has increased with the growth of industry and traffic.

### 2. Sampling procedure

Samples for determination of polychlorinated dibenzodioxins and polychlorinated dibenzofurans in Cracow ambient air were taken from two different places. First of all from the area of heavy traffic crossroad (Mateczny). The second sampling point was positioned at the Market Square in the centre of Cracow. Sampling were performed during the period between 22 March and 27 March 1995. At the time there were dry and no wind in Cracow and average daily temperature was about 0°C.

Large volumes of air were taken (several hundred of cubic meters) because it was assumed that concentrations of PCDFs and PCDDs would be at  $\text{pg} / \text{Nm}^3$  or even  $\text{fg} / \text{Nm}^3$  level. Sampled air was filtered from solid particles on glass fibre filter of pore size of 10  $\mu\text{m}$ . PCDDs and PCDFs present in gas phase were adsorbed on prepurified carbon active sorbent (obtained from Institute for Chemical Processing of Coal, Zabrze, Poland) placed between two layers of silanized glass wool in stainless steel cartridge. Inside diameter of the cartridge was 50 mm.

Sampling line consisted of glass fibre filter holder, cartridge with carbon active sorbent holder and water condenser. Two high volume sampling pumps (Zelmer, Poland) were operated interchangeably with constant flow rate of 2 m<sup>3</sup>/h. Average linear velocity of sampled air passing through the cartridge was 25 cm/s. Temperature and a flow rate of sampled air were measured continuously. Upon completion of sampling period, solid particles collected on glass fibre filters and cartridges with carbon sorbent were delivered to our laboratory. Exposed glass fibre filters and carbon sorbents were spiked with 2,3,7,8-C<sup>13</sup> labelled internal standard mixture (1 ng of each standard). Then they were extracted in soxhlet apparatus with toluene for 24 hours. Afterwards clean-up of toluene extracts was accomplished using H<sub>2</sub>SO<sub>4</sub>/silica gel, basic alumina and activated carbon placed separately in chromatography columns following a standard analytical procedures. Additionally the blank test was performed for evaluation of background level.

Sampling and determination of PCDDs and PCDFs in ambient air had been introduced and adapted to Polish Laboratory Standards at Cracow University of Technology. This procedure guarantees the determination limit of PCDFs/PCDDs at 0.01 pg/m<sup>3</sup> in ambient air sample as expressed for 2,3,7,8-TCDF.

Finally GC-MSD analyses were performed on Hewlett-Packard 5890 capillary gas chromatograph coupled with quadrupole MSD 5971 detector. GC was equipped with DB-5 or SP-2331 (for TCDFs monitoring) capillary columns, 60m, 0.25mm ID, 0.2µm stationary phase film. The system was operated in electron impact with 70eV and SIM mode.

#### 4. Results and discussion

The results presented here indicate that the mass concentration of PCDDs and PCDFs in ambient air in Cracow area is relatively high. In comparison to data presented by Bruckmann et al<sup>1)</sup>, König et al<sup>2)</sup> for German big cities and by Sugita et al<sup>3)</sup> for Japan cities, Cracow ambient air in main crossroad site is average in 100 times more polluted from PCDDs and PCDFs than western cities. For Cracow Center the ambient air in the end of March 1995 was 20 times less contaminated from PCDDs/PCDFs than for crossroad site respectively. Trying to answer the question: what is a reason of such pollution?, we suggest that one of the sources of dioxins and furans in ambient air would be an incineration of domestic wastes in private houses in black coal heat facilities in winter time. However in Poland this is the way of incineration of domestic wastes. The second source seems to be a leaded fuel still being in use in motor cars. The weather during the sampling period was dry and no wind was observed.

The recovery rates of 2,3,7,8-TCDF and 2,3,7,8-TCDD were determined at 60% mass concentration calculated by introducing 2,3,7,8-TCDF/TCDD-C<sup>13</sup> isotopically labelled congeners. Standard deviation for single measurement for whole analytical procedure was calculated on 20%. The results of the analysis of ambient air samples are summarized in Table 1. Figure 1 shows the TCDDs area obtained from GC-MSD analysis.

Table 1 Concentration of PCDDs/PCDFs in Cracow ambient air samples

Individual congener 2,3,7,8-substituted	concentration in $\mu\text{g}/\text{m}^3$		
	Blank test	Mateczny crossroad	The Market Square
2,3,7,8-TCDF	n.d.	3.75	0.38
2,3,7,8-TCDD	n.d.	1	0.15
2,3,4,7,8-P <sub>1</sub> CDF	0.01	7.4	0.51
1,2,3,7,8-P <sub>1</sub> CDD	n.d.	1.15	0.18
1,2,3,7,8-P <sub>2</sub> CDF	n.d.	4.25	0.26
1,2,3,4,7,8-H <sub>2</sub> CDD	0.01	2.15	0.21
1,2,3,6,7,8-H <sub>2</sub> CDD	0.01	3	0.2
1,2,3,7,8,9-H <sub>2</sub> CDD	0.01	1.05	0.16
1,2,3,4,7,8-H <sub>2</sub> CDF	0.01	8.8	0.79
1,2,3,7,8,9-H <sub>2</sub> CDF	n.d.	2.65	0.25
1,2,3,6,7,8-H <sub>2</sub> CDF	0.01	7.5	0.6
2,3,4,6,7,8-H <sub>2</sub> CDF	0.01	9.9	0.58
1,2,3,4,6,7,8-H <sub>2</sub> CDD	0.02	55	2.7
1,2,3,4,6,7,8-H <sub>2</sub> CDF	0.02	110	5.55
1,2,3,4,7,8,9-H <sub>2</sub> CDF	n.d.	42	1.35
OCDD	0.05	280	10.4
OCDF	0.02	220	7.5
Total PCDDs/PCDFs	0.5	1060	59.5
TEQ value ( $\mu\text{g}/\text{m}^3$ )	0.02	11.95	0.95

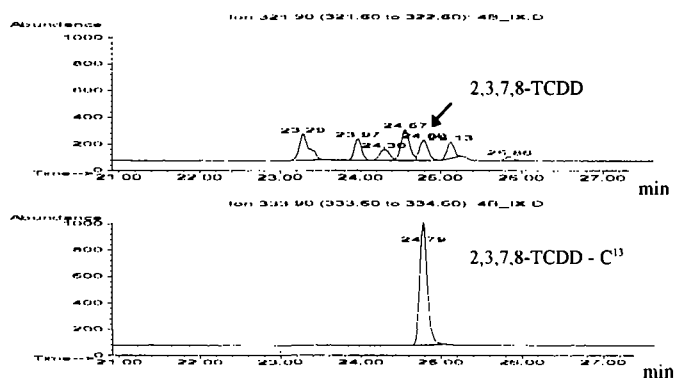


Figure 1: GC-MSD single ion chromatogram for 321.9 ion monitored for TCDDs and for 333.9 ion for 2,3,7,8-C<sup>13</sup> TCDD in a mixture of PCDFs/PCDDs isolated from 100 m<sup>3</sup> of ambient air sample taken from Mateczny crossroad. Separation was carried out on DB-5 capillary column. Retention time for 2,3,7,8-TCDD was recorded as 24.79 min.

## 5. References

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