

POLYCHLORINATED DIBENZODIOXINS AND DIBENZOFURANS
IN SAMPLES OF SUSPENDED DUST FROM LUBLIN

ANETA DUDA¹, JACEK CZERWIŃSKI²

¹Lublin University of Technology, Department of Fundamentals of Technology, Faculty of Management and Fundamentals of Technology ul. Nadbystrzycka 38, 20-618 Lublin, Poland

²Lublin University of Technology, Institute of Environmental Protection Engineering, Faculty of Environmental Engineering ul. Nadbystrzycka 40B, 20-618 Lublin, Poland

Keywords: polychlorinated dibenzodioxins, polychlorinated dibenzofurans, fine dust.

WYSTĘPOWANIE POLICHLOROWANYCH DIBENZODIOKSYN
I DIBENZOFURANÓW W PRÓBKACH PYŁU ZAWIESZONEGO
W POWIETRZU ATMOSFERYCZNYM LUBLINA

Polichlorowane dibenzodioxyny i dibenzofurany (PCDD/Fs) są obecne w powietrzu atmosferycznym zarówno w postaci zaadsorbowanej na cząstkach pyłów jak i, w znacznie mniejszej części, w postaci gazowej. Dioksyny są znane jako związki posiadające własności mutagenne i kancerogenne. W niniejszej pracy próbki pyłów atmosferycznych były zbierane w Lublinie przez okres 12 miesięcy i analizowane na zawartość PCDD/Fs. Do analizy próbek wykorzystano ekstrakcję w aparacie Soxhleta, dwustopniowe oczyszczanie ekstraktów w oparciu o chromatografię wykluczania i chromatografię oddziaływań elektronów π - π i analizę końcową z wykorzystaniem systemu GC-MS.

Summary

Polychlorinated dibenzodioxins and dibenzofurans (PCDD/Fs) are present in the air either adsorbed on particulate matter or as vapor (minor part). They are known to be effective carcinogenic and mutagenic agents. In this study dust samples from Lublin were collected for twelve months and analyzed for PCDD/Fs content. For the analysis of these samples classical extraction with a Soxhlet apparatus, double step clean-up based on SEC and charge-transfer interactions chromatography, and final analysis with GC-MS were applied.

INTRODUCTION

Dioxins have been known to be among the most spectacular environmental pollutants for over 30 years. More than 10 billion dollars (according to the Dioxin'2003 conference held in Boston) was spent on investigating them.

Dioxins (polychlorinated dibenzodioxins and dibenzofurans) and/or coplanar polychlorinated biphenyls (c-PCB) harm living organisms by disfunctioning their endocrine system, e.g. production of steroid and thyroid hormones and cause procreation problems. Carcinogenic, mutagenic and teratogenic activities have, as yet, not been proved though there are currently considerable discussions on this topic. Paradoxically, it has even been observed that, during examination of development of cancer tissue promoters,

dioxins stopped development of some cancers. Anyhow, they are still classified by the IARC under the carcinogenic substances group A [1, 7, 8].

One of the main sources of human contact with dioxins is atmospheric air and fine dusts; for this reason we tried to determine this group of compounds in dust taken from filters situated in the town of Lublin (Botanical Garden). Up to the present in Poland such determinations have only been conducted for the City of Krakow, which is known to have a higher emission concentration [4, 5]. Pollution in Lublin is mainly connected with traffic but also with coal-based heating systems.

MATERIALS AND METHODS

Materials and equipment:

- solvents: toluene, hexane and dichloromethane – “for residue analysis” (JT Baker, Germany);
- anhydrous sodium sulphate(VI) *puriss* (POCh, Gliwice, Poland);
- standard solutions of 17 congeners of PCDD/Fs according to EN-1949, native and labeled (CIL, Germany);
- Soxhlet apparatus, 200 cm³ capacity with reflexive/check cooling system and heating neck for 250 cm³ flasks;
- rotary evaporator – (Büchi, Germany);
- vacuum pump with dephlegmator and vacuum control (Büchi, Germany);
- needle evaporator (Supelco – USA);
- reaction vessels – 3 cm³ and 40 cm³ capacity (Supelco, USA).

Methods – a schematic diagram of the analysis pathway is presented in Figure 1.

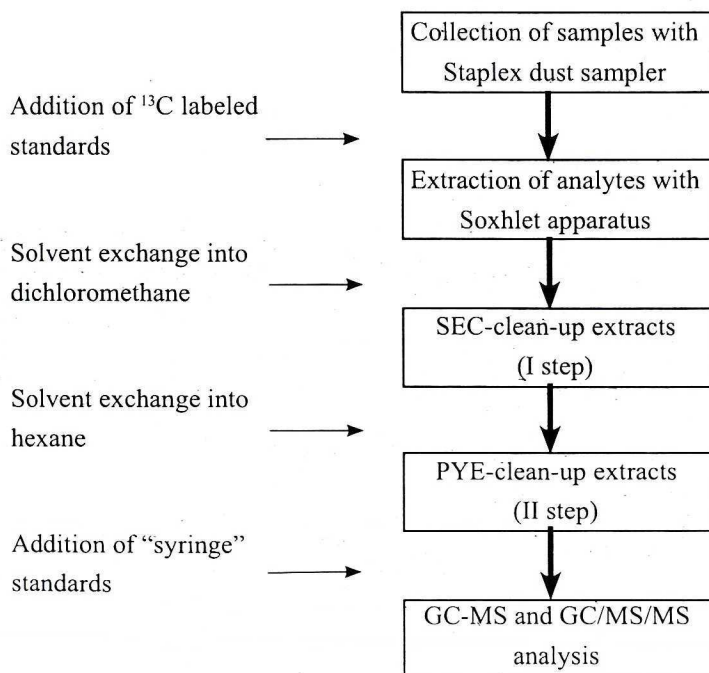


Fig. 1. Scheme of steps in the analysis of dust samples

Dust samples were collected over 12 months (from January 2004 till December 2004) on quartz fiber filters in the Botanical Garden of Lublin. The site lies in the vicinity of the most important route from Warsaw to the border areas of Poland and the residential district Slawinek.

Filters were extracted in a Soxhlet apparatus with 200 cm³ of dichloromethane and toluene mixture (80/20 v/v) for 16 hours, providing at least four flows of solvent per hour.

The extract obtained was evaporated in a vacuum evaporator (< 36°C) to a volume of ca. 3 cm³ and then quantitatively transferred to reaction vessels (3 cm³), where it was evaporated to the volume of 2.5 cm³ (including additional extracts from flask and Soxhlet apparatus flushing).

Purification of the extract was done with high-resolution elimination chromatography (HR-SEC) using a Breeze 1525 liquid chromatograph (Waters – USA) consisting of the following elements:

- binary gradient pump – Waters 1525,
 - injector – Rheodyne with 2000·10⁻⁶ dm³ sample loop,
 - columns: Envirogel GPC cleanup 19 x 150 mm and Envirogel GPC cleanup 19 x 300 mm,
 - two-wave, tunable detector UV-VIS Waters M2487,
 - fraction Collector – Waters FC III,
 - data acquisition and system control – Breeze 3.30SPA software,
 - chromatographic syringes with nonstick pistons – 2500·10⁻⁶ dm³ (Hamilton).
- The system was standardized for a standard solution containing:
- corn oil – lipid and waxes fraction marker,
 - bis(ethylcyclohexyl) phthalate – Phthalate fraction marker,
 - methoxychlor – PCDD/Fs fraction marker,
 - perylene – PAH fraction marker,
 - elementary sulphur – low-particle compounds fraction marker, all compounds in dichloromethane.

Mobile phase (dichloromethane) flow rate – 5 cm³/min and wave length during chromatograms collection – $\lambda = 254$ nm.

Examples of chromatograms of the standard mixture and sample extract are presented in Figure 2.

To provide the wide PAHs fraction spectrum and also PCDD/Fs determination from the same extract the eluate was collected from 14 to 21 minutes. This “time window” also allowed the collection of interesting compounds under column overloading conditions. The results of such PAHs determination were previously described in Duda and Czerwiński [3].

After analysis for PAH's, the remaining portion of the extract was evaporated to dryness under a gentle flow of nitrogen. The residue was resolved in 550·10⁻⁶ dm³ hexane. A 500·10⁻⁶ dm³ sample was then injected into the previously described HPLC system, equipped with a COSMOSIL PYE column (Phenomenex, Japan), working in the system of normal phases (hexane as the mobile phase α 1 cm³/min – 24 min and the last 5 minutes hexane/CH₂Cl₂ 80/20 v/v) to accelerate elution of the PCDD/Fs mentioned above. The initial 6 cm³ of eluate was rejected because of the non-planar compounds (for example PCB and PCDE) present in this fraction. Figure 2 presents elution fractions of the analyzed compounds obtained from collection of 1 cm³ fractions analyzed on GC-MS.

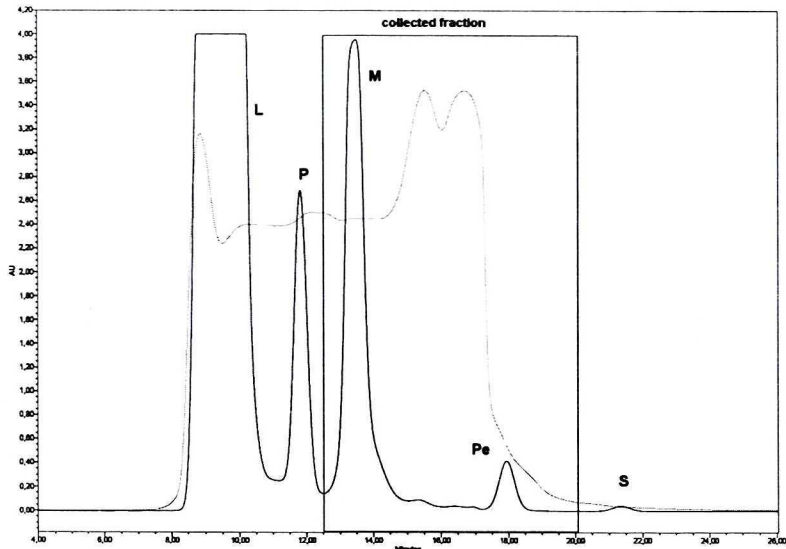


Fig. 2. SEC-chromatograms of calibration standard mixture (thick line) and real sample (thin line); L – corn oil as lipid fraction marker, P – ethylhexylphthalate – phthalate fraction marker, M – methoxychlor – pesticide fraction marker, Pe – perylene – PAHs fraction marker, S – sulfur – low molecular compounds marker

Eluate (25 cm^3) was collected and evaporated to $50 \cdot 10^{-6} \text{ dm}^3$ (in a gentle nitrogen stream). The purified extract was analyzed using the GC-MS/MS system described above. Temperature program parameters and GC-MS/MS parameters have been described previously [2].

Time	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29
Compounds																												
PCB	■	■	■																									
PCDE		■	■	■																								
cp-PCB			■	■	■	■	■																					
TriCDD/F						■	■	■																				
TeCDD/F						■	■	■	■	■																		
PeCDD/F																												
HxCDD/F																												
HpCDD/F																												
OCDD/F																												■
Solvent	100% hexane																						hexane/DCM 80/20					

Fig. 3. Elution fraction from the PYE column (from reconstructed ion chromatograms) working in normal phase mode – utilizing charge-transfer and π - π electron interactions

RESULTS AND DISCUSSION

The results of PCDD/Fs determinations on collected dust samples are presented in Table 1.

Table 1. Concentration of Tri- and Tetra substituted congeners of PCDD/Fs in fine dust

Season collected sample	Congeners	Concentration in		Congeners	Concentration in	
		Dust	Air		Dust	Air
	Tri-	[ng/g]	[pg/Nm ³]	Tetra-	[ng/g]	[pg/Nm ³]
Spring	2,3,7-CDD	0.7	40.6	2,3,7,8-CDD	0.2	11.6
	2,3,7-CDF	2.2	127.6	2,3,7,8-CDF	0.45	26.1
Summer	2,3,8-CDF	0.9	52.2	2,3,7,9-CDF	14.1	817.8
	2,3,7-CDD	0.4	19.6	2,3,7,8-CDD	0.7	34.3
	2,3,7-CDF	2.7	132.3	2,3,7,8-CDF	1.2	58.8
Autumn	2,3,8-CDF	0.4	19.6	2,3,7,9-CDF	0.9	44.1
	2,3,7-CDD	0.8	40	2,3,7,8-CDD	0.7	35
	2,3,7-CDF	2.1	105	2,3,7,8-CDF	1.2	60
Winter	2,3,8-CDF	0.3	15	2,3,7,9-CDF	0.9	45
	2,3,7-CDD	14.1	888.3	2,3,7,8-CDD	1.6	100.8
	2,3,7-CDF	23.2	1461.6	2,3,7,8-CDF	12.2	768.6
	2,3,8-CDF	14.9	938.7	2,3,7,9-CDF	1.9	119.7

The concentrations of other 2,3,7,8-substituted congeners were below the detection limit of our equipment.

Trichlorosubstituted PCDD/Fs congeners were determined assuming an equimolar response of tri and tetra substituted congeners [9].

FINAL CONCLUSIONS

1. The analysis of trichlorosubstituted congeners is not normally carried out in environmental monitoring – in these samples they may indicate photodegradation caused by exposure to sunlight. This problem was also pointed out by Niu *et al.* [6] in work on the sorption of PCDDs and PAHs on pine needles.
2. The low levels of PCDD/Fs from spring and the higher ones from winter time may also indicate the same problem.
3. The accuracy of the determinations was estimated to be about 30% (based on the low error variance propagation) and is not satisfactory. The reason may be the low PCDD/Fs levels and the sparseness of the available sample, (optimal – 2 g; available *ca.* – 0.2 g).
4. For the same reason, the determination of other 2,3,7,8-substituted congeners was not possible.
5. The temperature program of the GC-MS system used in the separation process is time consuming (> 60 min). However, it allows for the analysis of congeners other than the 17 typically determined according to EN-1949. This could conceivably lead to their use in source apportionment studies.

REFERENCES

- [1] Behnisch P.A., K. Hosoe, S. Sakai: *Bioanalytical screening methods for dioxin and dioxin-like compounds – a review of bioassay/biomarker technology*, Environment Internat., **27**, 413–439 (2001).
- [2] Czerwiński J., M.R. Dudzińska, B. Rut: *GC-MS/MS screening of dioxin-like compounds on example polychlorinated dibenzothiophenes – a thio-analogues of polychlorinated dibenzofurans*, Organohalogen Compounds, **60**, 461–465 (2003).
- [3] Duda A., J. Czerwiński: *Seasonal Changes of PAH Levels in Air Dust Particles taken in Lublin, Poland*, [in:] L. Pawłowski, M. Dudzińska, A. Pawłowski (eds), Environmental Engineering, Taylor & Francis Group, London 2007, 381–385.
- [4] Grochowalski A., R. Chrzęszcz, S. Wybraniec: *Determination of PCDFs/PCDDs in ambient air from Cracow city, Poland*, Organohalogen Compounds, **21**, 321–326 (1995).
- [5] Grochowalski A., R. Chrzęszcz: *PCDDs/Fs in suspended particulate matter in ambient air from Krakow City, Poland*, Organohalogen Compounds, **32**, 76–80 (1997).
- [6] Niu J., J. Chen, B. Henkelmann, X. Quan, F. Yang, H.K. Seidlitz, K-W. Schramm: *The role of UV-B on the degradation of PCDDyFs and PAHs sorbed on surfaces of spruce (Picea abies (L.) Karst.) needles*, Science of the Total Environment, **322**, 231–241 (2004)
- [7] Rappe C., H.R. Buser, B. Dodet, I.K. O'Neill: *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, 1991.
- [8] Schecter A., L. Birnbaum, J.J. Ryanc, J.D. Constable, *Dioxins: An overview*, Environmental Research, **101**, 419–428 (2006).
- [9] Wiedmann T., H. Schimmel, K-H. Ballschmitter: *Ion trap MS/MS of polychlorinated benzo-p-dioxins and dibenzofurans: confirming the concept of the molar response*, Fresenius J. Anal. Chem., **360**, 117–119 (1998).

Received: March 30, 2007; accepted: May 18, 2007.