MONITORING OF PCDDS, PCDFS AND PAHS IN WASTE-WATER WITH USE OF SEMIPERMEABLE MEMBRANE DEVICES (SPMD)

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Introduction

A new semipermeable membrane dialysis (SPMD) method for the determination of polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) in waste water samples from municipal and industrial Waste Water Treatment Plants (WWTP) in Poland, containing lower than 1pg-TEQ/m^3 is described. In this work three WWTPs were selected: Strzelce Opolskie – plant I, Opole – plant II and Zabrze – plant III. Plant III is operated for mixed - municipal and industrial waste waters. The sampling procedure is based on passive sampling based on semi permeable membrane dialysis for preconcentration by selective absorption in triolein. The clean-up method was introduced in laboratory practice for the determination of PCDDs and PCDFs using GC-MS/MS system.

The method is suitable for any other aqueous samples as for example for the determination of dioxins in mineral waters. It was indicated that this method is not suitable for preconcentration of dioxins in input stream in waste water treatment plants due to the high fat content.

The SPMD method for sampling of waste waters was not used in practice so far.

Methods and Materials

Modern analytical methods are more and more expensive because of rising quality criteria of this analysis and the necessity of measuring the concentrations of pollutants at ultra-low levels.

The determination of traces of contaminants in water and waste water needs sampling of high volume of the individual sample, causing problems with delivery and extraction. It is inconvenient and expensive. Nowadays rapid, effective and no expensive analytical methods for direct monitoring of pollutant concentrations in the environment are searched. One of this method is passive sampling technique based on semi permeable membrane devices (SPMD), invented by Huckins et al[1]. The SPMD method is used for the determination of pollutants in aquatic environment, especially to control the concentrations of organic compounds in surface waters. For the determination of trace concentrations of dioxins and furans in this work SPMD method was used.

Experiment were carried out on four waste-water treatment plants. SPMD membranes were used to determinate dioxins, furans and PAHs in waste-water stream. Plants I and II were municipal, in plant III 5 % of waste-water comes from metallurgical, mining and brewing industry. The plant IV was industrial one. To compare results of experiments membranes were exposure in inlet stream (Fig. 1 and 2) after the sand trap and in outlet stream (fig. 3) simultaneously.

In described experiment the membranes consist of thin-walled layflat tubing made from polyethylene were used (size 25x990 mm and 75-90 μm wall thickness). Membranes are filled with 1 g of triolein inside as an absorber. SPMDs were placed in samplers which are made of stainless steel - fig.4. The samplers were cleaned-up by hexane just before exposure.

Membranes were exposure over 14 days period in each case. The temperature of waste-water was 14-16^{0}C.

Figure 1. The exposure point – inlet stream on Plant I.

Figure 2. The exposure point – outlet stream on Plant II.

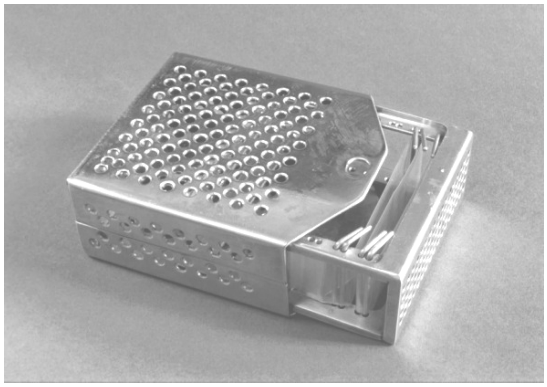

Figure 3. Ready for use sampler of stainless steel containing 1 m of length SPMD membrane

Membranes were exposured in special, perforated cages made of stainless steal (Fig. 3).
After exposure membranes were transported to laboratory and cleaned up by following way:

1. mechanical removing of soil and periphyton from the surfaces of the membrane,
2. rinsing the membrane with hexane for a few second,
3. rinsing the mebrane with tap water,
4. rinsing the mebrane with 1N HCl for a few seconds,
5. rinsing the membrane with tap water,
6. rinsing the membrane with acethone to remove surface water,
7. air drying the SPMD for a few seconds,

Then membranes were extracted in hexane 24 h. The extracts were concentrated to volume of 5 ml and cleaned-up by liquid chromatography methods as described previously [2, 3].
Sample analysis were performed usinga gas chromatography mass spectrometery with multi-fragmentation mode (GC-MS/MS).

Table 1. The concentrations of PCDD/PCDF in waste-water on Plant I, Plant II and Plant III.

Compound	R_S	Plant I		Plant II		Plant III	
		INLET [pg/m^3]	OUTLET [pg/m^3]	INLET [pg/m^3]	OUTLET [pg/m^3]	INLET [pg/m^3]	OUTLET [pg/m^3]
2,3,7,8-TCDD	72,2	0,693	0,495	6,754	5,785	1,088	0,890
1,2,3,7,8-PeCDD	63,8	0,336	2,911	20,995	30,187	0,896	3,919
1,2,3,4,7,8-HxCDD	75,9	0,565	2,635	10,573	7,970	1,457	2,729
1,2,3,6,7,8-HxCDD	59,6	2,517	4,434	25,168	11,773	6,112	19,895
1,2,3,7,8,9-HxCDD	54,4	3,283	0,002	21,900	4,388	7,484	11,029
1,2,3,4,6,7,8-HpCDD	42,1	89,583	5,769	122,137	36,949	218,358	93,485
OCDD	56,9	205,373	91,012	130,508	45,130	532,890	87,246
2,3,7,8-TCDF	69,9	4,803	2,246	20,841	53,045	6,642	8,992
1,2,3,7,8-PeCDF	72,2	2,671	5,540	42,748	293,395	5,046	31,262
2,3,4,7,8-PeCDF	79,4	1,709	6,657	92,515	101,559	5,128	21,860
1,2,3,4,7,8-HxCDF	50,0	11,143	31,714	91,358	82,963	8,571	68,429
1,2,3,6,7,8-HxCDF	54,8	7,821	21,116	86,960	68,074	4,432	198,253
2,3,4,6,7,8-HxCDF	55,5	5,277	18,018	81,192	61,543	6,049	83,398
1,2,3,7,8,9-HxCDF	43,3	0,002	1,092	4,186	0,005	0,002	0,002
1,2,3,4,6,7,8-HpCDF	50,1	39,065	69,718	141,076	63,577	46,051	253,778
1,2,3,4,7,8,9-HpCDF	50,1	11,548	13,830	12,568	4,805	4,847	16,253
OCDF	33,9	51,201	31,816	36,418	7,526	109,566	33,923
SUM pg-TEQ/m^3		7,05	14,70	102,8	116,4	11,76	58,37

Where: Plant I – Strzelce Opolskie, Plant II – Opole, Plant III – Zabrze

The concentration of dioxins were calculated using the formula 1.

$$C_W = \frac{C_{SPMD} \cdot V_{SPMD}}{R_S \cdot t} \qquad (1)$$

where:

C_W - the concentration of a chemical in waste-water in [ng or pg/dm^3],
C_{SPMD} - the concentration of a chemical in the membrane SPMD in[ng],
V_{SPMD} - mass of the trioleine in [g],
t - the time of exposure in [d],
R_S - the effective daily sampling rate of SPMD for particular analyte in [dm^3/d],

R_S are the data obtained from scientific literature [1, 4].

Results and Discussion

The results shown in Table 1 confirm the presence of PCDDs and PCDFs in analyzed waste-water samples.

The membranes exposured in inlet stream absorbed lower quantity of pollutants (7,05 pg-TEQ/m^3 – Plant I; 102,8 pg-TEQ/m^3 – Plant II; 11,76 pg-TEQ/m^3 – Plant III respectively,) than the membranes exposured in outlet stream (14,70 pg-TEQ/m^3 – Plant I; 116,4 pg-TEQ/m^3 – Plant II; 58,37 pg-TEQ/m^3 – Plant III, respectively).

The crude waste-water (Inlet) contain relatively high concentration of fatty particles. Dioxins are hydrophobic and may be absorbed in fat particles presented in the waste-water. Therefore the sampling of PCDDs, PCDFS may be difficult and ineffective in this case. The diffusion of PCDDs and PCDFs from fat to the membrane is significantly low. Therefore, there is no possibilities to obtain reliable analytical result for the determination of PCDDs and PCDFs in crude waste water stream when SPMD is used.

References

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