

DETERMINATIONS OF TIME WEIGHTED AVERAGE CONCENTRATION OF PCBs AND PCBs DIOXIN-LIKE IN RIVER WATER BY MEANS OF CONTINUOUS FLOW INTEGRATIVE SAMPLER (CFIS).

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Introduction

Polychlorinated biphenyls (PCBs) and specially dioxine-like PCBs, have toxic effects on living organisms, including human beings [6]. In aquatic environments, PCBs are principally adsorbed on particulate matter due to their hydrophobicity ($\log K_{OW} > 4.5$). Their concentration in the dissolved phase is therefore very low, typically in the ng/L to pg/L range and the analysis on particulate matter is also important. Aquatic monitoring programs are generally based on collection of discrete samples of the water phase and analyzed in the laboratory but it only will provide a snapshot of the concentration in the environment at the particular time.

Since two decades, several integrative sampling devices have been developed for the monitoring of organic contaminants in aquatic environments (8). These samplers enable the improvement of limits of quantification (LOQ) by accumulation and concentration of contaminants over long-term exposure.

Since the introduction of passive sampling in water, which dates back to 1980, when Byrne and Aylott [1] patented a simple device for the passive sampling of organic contaminants, a multitude of new devices and set-ups have been developed, and their main advantages and disadvantages have been discussed in publications [2-5]. However, the range of possibilities for the development of new devices is relatively restricted by the theoretical principles governing passive sampling. The variation in the uptake values which result from the variations in turbulence can generate important problems in determining accurately time weighted average concentrations obtained from sampling rates calculated from tests under laboratory conditions. In samplers which are based on sorbents, the problem has been partially resolved by using performance reference compounds (PRCs). These are compounds added at a known concentration to the sorbent, and which are then released in a way which is proportional to the turbulence. Nevertheless, the problems of turbulence vs. sampling rate are still the main sticking point of passive samplers of polar compounds in general, with sorbents governed by adsorption principles.

Another important limitation of passive sampling techniques resides in the fact that only the dissolved fraction (bio available fraction) is sampled. The suspended solid and colloid fraction information is not given as required in different legislations.

A new device for the time weighted average monitoring of water quality has been developed and patented . The new device [7] , Continuous Flow Integrative Sample (CFIS) is a fully immersible “autosampler” based on the principles of passive sampling devices, allowing the time weighted average monitoring (up to 20 days sampling period) of organic pollutants with limits of detection in the range of pg/L levels. The small fully immersible device allows the sampling of dissolved fraction (bio available fraction) as well as the particulate fraction with sampling rates independent from the “in situ” turbulences.

In this presentation, the calibration, validation and also analysis in real samples for PCBs using a final industrial version of CFIS device will be showed to the audience. Limits of detection are in the range from 1 to 50 pg/L with a precision below 20%. An in field evaluation of the CFIS with PCBs and PCBs-dioxin like compounds in waste water treatment plant (WWTP) and rivers will be also showed. The new CFIS device allows the sampling of the bio available fraction together with the suspended solid fraction.

Materials and methods

Continuous Flow Integrative Sampler (CFIS) [7]. The fully immersible device (Figure 1) consists of a small peristaltic pump (WPX1-P3/32M2-WM4-B, Welco, Japan) powered by 3 lithium batteries (ER34615, 3.6V, 14.5Ah., Guangzhou Markyn Battery Co., Guangzhou, China) connected in parallel, which produces a constant flow through a glass cell. An ad hoc electronic circuit board was designed in order to supply a constant voltage to the pump during the 21 days autonomy of the system independently from the battery charge level, thus allowing a constant flow during the deployment time. The energy consumption of the system is 0.5 W (0.1 A x 5 V). A 2.4 mm I.D. and 1.6 mm wall thickness pharmed tube (ISMATEC S.A., Glatbrugg, Switzerland) was selected for the peristaltic pump due to the excellent mechanical resistance which is also a critical aspect to take into account to get a constant flow during the deployment period. As can be seen in Figure 2 the peristaltic tube is installed down stream from the glass cell to avoid adsorptions of the analytes in the polymeric tube. All the elements upstream of the glass cell are made from glass or stainless steel to avoid any adsorption before the PDMS sorbent. Once immersed in the sampling point the water flows downwards inside the glass cell avoiding accumulation of suspended solids. Furthermore a 40 mesh cylindrical stainless steel filter (FEVAL FILTROS, Barcelona, Spain) covered by a glass sleeve allows its application for long sampling periods even in raw waters from waste water treatment plants.

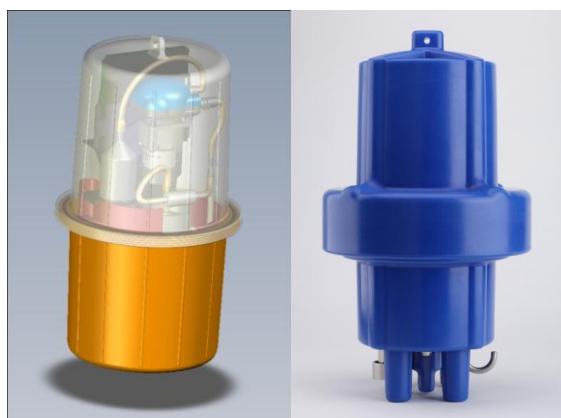


Figure 1. CFIS.

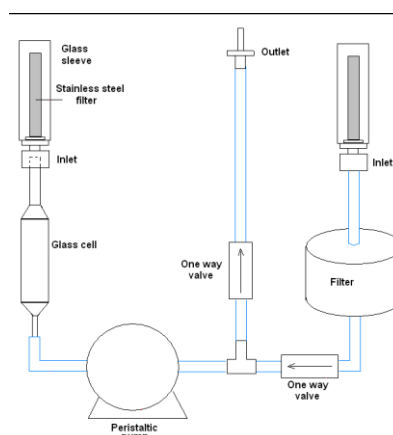


Figure 2. CFIS diagram.

Analytical method.

Water analysis:

The concentration of the water samples from laboratory exposure tank and the real samples tested campaign were determined using the stir bar sorptive extraction (SBSE) method, and analysis [9].

For water analysis the first step is an extraction with a PDMS stir bar (twister) of the PCBs. The SBSE extraction was carried out as following: 200 ml of water sample, 10% of methanol and 20 hour of extraction time.

After the exposure time, the Twisters™ were removed either from the water sample or the CFIS, gently dried with a paper tissue and finally introduced in glass desorption tubes. Desorption was carried out at 280°C during 6 minutes under a helium flow of 75 mL•min⁻¹ in the splitless mode while maintaining a cryofocussing temperature of 20°C in the PTV injector of the GC-MS/MS system. The programmable temperature vaporisation system (PTV) was ramped to a final temperature of 280°C and the analytes were transferred to the GC column. A SRM acquisition method was created in the QqQ mass spectrometer. Two transitions were monitored for each analyte, the first for quantification and the second for confirmation.

PDMS CFIS analysis:

The quantification of the analytes accumulated in the CFIS sorbent (PDMS) in the different were analyzed by means of the same chromatographic method (thermal desorption on line with GC-MS/MS) [9].

Infield campaigns to determine PCBs in real river samples..

The CFIS device will be tested in river water. The results of TWA obtained by CFIS in different sampling periods were compared with the analysis of spot samples.

Results and discussion

Calibration and validation of CFIS device. Sampling rate (Rs)

The experimentally determined accumulated time profiles were fitted by linear regression analysis using the equation.

$$C_w = \frac{N_i}{R_{S,i} t}$$

Where N_i is a mass of compound in ng, C_w aqueous analyte concentration during exposure and t is the sampling time in days.

The obtains R_s of each PCB compound different experiments at different times will be carried out and represented as N_i to t . The adjustable parameters were the intercept (M_0) and the slope ($C_w R_s$) of the linear uptake curve $M_s = f(t)$. The sampling rates of the device, R_s values, for individual test compounds were calculated by dividing the slope of the linear uptake curve by the mean aqueous analyte concentration during exposure.

For CFIS, the determination of TWA concentrations of contaminants in water only requires predetermined R_s . Indeed, sampling rates are not influenced by water velocity and R_s estimated from laboratory calibration to different temperatures can be used for field sampling.

The Table 1 shows the sampling rates obtained for each PCB compound. In this Table other parameters as LOQ, RSD and linearity were also shown.

Table 1. Validation data.

PCB-Congener	PCB sampling rates for 100 cm ² (L/day/100cm ²)	LOQ (pg/L)	RSD (%)	PCB-Congener	PCB sampling rates for 100 cm ² (L/day/100cm ²)	LOQ (pg/L)	RSD (%)
PCB 18	6.1	2.26	15	PCB 105	7.0	1.42	15
PCB 28	6.1	1.63	14	PCB 114	7.0	3.57	18
PCB 52	7.2	1.19	16	PCB 118	7.0	0.93	22
PCB 101	7.1	0.65	18	PCB 123	7.0	1.05	21
PCB 118	6.9	1.93	19	PCB 126	7.0	1.55	21
PCB 138	7.0	2.18	21	PCB 156	6.8	1.59	20
PCB 153	6.6	1.74	18	PCB 157	6.8	1.3	21
PCB 180	5.5	2.26	15	PCB 167	6.8	1.44	19
PCB 77	7.2	2.65	14	PCB 169	6.8	2.48	22
PCB 81	7.2	1.67	19	PCB 189	5.5	0.64	21

Infield campaigns.

The CFIS were tested in a real river water and some of the result obtained are shown in the Table 2. Concentration of PCBs near to ppt.

Table 2. Field campagne. Results of PCBs in a river water.

	Cw CFIS 1 (ng/L)	Cw CFIS 2 (ng/L)	Cw CFIS 3(ng/L)		Cw CFIS 1 (ng/L)	Cw CFIS 2 (ng/L)	Cw 3 (ng/L)
PCB 18	0.0693	0.0872	0.0737	PCB 105	0.2923	0.0651	0.0742
PCB 28	0.0495	0.0281	0.114	PCB 114	0.0335	0.0092	0.0347
PCB 52	0.4693	0.1908	0.2646	PCB 118	0.0827	0.1563	0.1034
PCB 101	0.5602	0.2051	0.5288	PCB 123	0.0282	0.0886	0.1093
PCB 118	0.0827	0.1563	0.1034	PCB 126	3.0985	3.6424	5.1176
PCB 138	0.1322	0.1908	0.2304	PCB 156	< 0.0030	< 0.0030	< 0.0030
PCB 153	0.0442	0.1181	0.144	PCB 157	< 0.0030	< 0.0030	< 0.0030
PCB 180	0.0384	0.0572	0.0313	PCB 167	0.0286	< 0.0030	0.1082
PCB 77	0.0068	0.0401	0.0666	PCB 169	< 0.0030	< 0.0030	< 0.0030
PCB 81	0.0221	0.0104	0.0125	PCB 189	0.0207	0.0033	0.0088

Conclusions:

A new device to analyse PCBs and PCBs dioxine-like have been developed. The device permits obtain TWAC and determine very low concentrations. The result indicates that low concentrations of PCBs have be found in the Rodane river and that CFIS is a powerful tool to control the environmental contamination of this compounds.

Acknowledgements

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