CERAMIC TOXIMETER AS A PASSIVE SAMPLER FOR OF DIOXIN-CONTAMINATED WATER ANALYSIS USING THE CALUX BIOASSAY

Amr Addeck[1], Kim Croes[1], Kersten Van Langenhove[1], Tara Vandermarken[1], Michael Denison[2], Willy Baeyens[1]

1. Vrije Universiteit Brussel (VUB), Department of Analytical and Environmental Chemistry, Pleinlaan 2, 1050-Brussels, Belgium
2. Department of Environmental Toxicology, University of California, Davis, CA 95616, USA

Introduction

Passive sampling is a new trend in environmental monitoring and analysis. Several Passive samplers are being developed to overcome the drawbacks of the conventional snapshot sampling approach. The idea relies on the uptake of contaminants into an appropriate sampling device along a diffusion gradient without using pumps or bailers. Once the diffusion gradient between the medium and the sampler's interior is steady, the contaminants can be continuously sampled over an extended period allowing for the calculation of a time-weighted average (TWA) concentration[1].
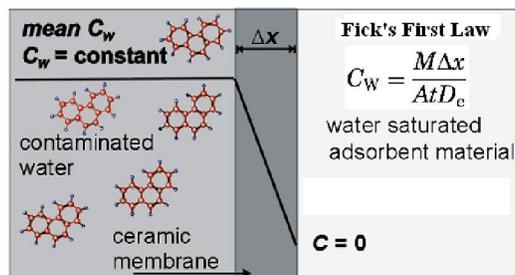

Figure 1. Concentration profile in the ceramic toximeter.

Where C_w: the concentration of the chemicals in water, M: the mass of adsorbed chemicals on the receiving material, Δx: the thickness of the diffusion membrane, A: the area of the exposed ceramic surface, t: the exposure time and D_e: the effective diffusion coefficient of the chemicals in porous membrane compared to water.

In this research, we aim to develop and evaluate the ceramic toximeter as a passive sampler for monitoring dioxin-contaminated water.

Materials and methods

The purely diffusion-controlled sampling device is based on a porous ceramic membrane in the shape of a cylinder of alumina (α-Al$_2$O$_3$) internally lined with a 5 μm layer of titania (TiO$_2$). The cylinder has a length of 5 cm length, a wall thickness of 2 mm, an external diameter of 1 cm, and a porosity of 30%. About 0.62 g of conditioned X-CARB (XDS,USA) were packed in each cylinder and small plugs of pre-cleaned glass-wool were inserted in both ends. Two caps of PTFE were used to tightly close both ends of each cylinder. The toximeters were immersed in deionized Milli-Q water under vacuum to assure a complete saturation of the toximeters with water. An aqueous saturated solution of 2,3,7,8 tetrachlorodibenzo-ρ-dioxin (TCDD) was prepared by using a modified design of generator column. This stock solution is to be used as an in-vitro testing medium for the ceramic samplers. The CALUX (Chemically Activated LUciferase gene eXpression) bio-assay technique (H1L7.5c1 mouse hepatoma cell line)[2,3] was utilized to quantitatively analyze the amounts of dioxin trapped by the toximeters[4].

Results and discussion:

The concentration of the prepared TCDD saturated solution was $6.70×10^{-5}$ mg/L which is within the saturation levels previously reported in literature[5]. After four months, the concentration decreased to 2.5 times of starting value, probably due to the sorbtion of TCDD on the glass walls of the reservoir. From that point on, the concentration remained almost constant probably due to reaching an equilibrium state between sorbed and free TCDD molecules. A working concentration of 0.00135 ng/mL was obtained by diluting this saturated solution. Ceamic toximeters were immersed in this working solution and extracted at different times (24, 48, 72, 96, 120, and 168 hours) during several cycles[4]. A standard dose-response curve was obtained by plotting the CALUX response (%RLU, Relative Light Units) of 10 standard TCDD solutions (in DMSO) against their concentrations (Figure 2).
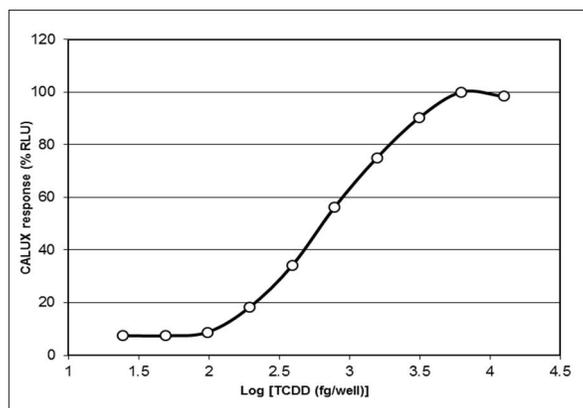

Figure 2. Example of a 10-point standard TCDD calibration curve

The amounts of dioxin extracted from the dosimeters and testing solutions were obtained by fitting their measured CALUX response on the calibration curve. A single point estimate is better not to be used since this can bias the results[6]. The best way to determine the BEQ-concentration of 2,3,7,8-TCDD trapped in the ceramic toximeter is by establishing a (full dose) dilution curve of the sample with the CALUX bioassay. Therefore, one dilution point was measured to determine the amount of trapped material. Depending on the % RLU induction, choice of further dilutions was decided.
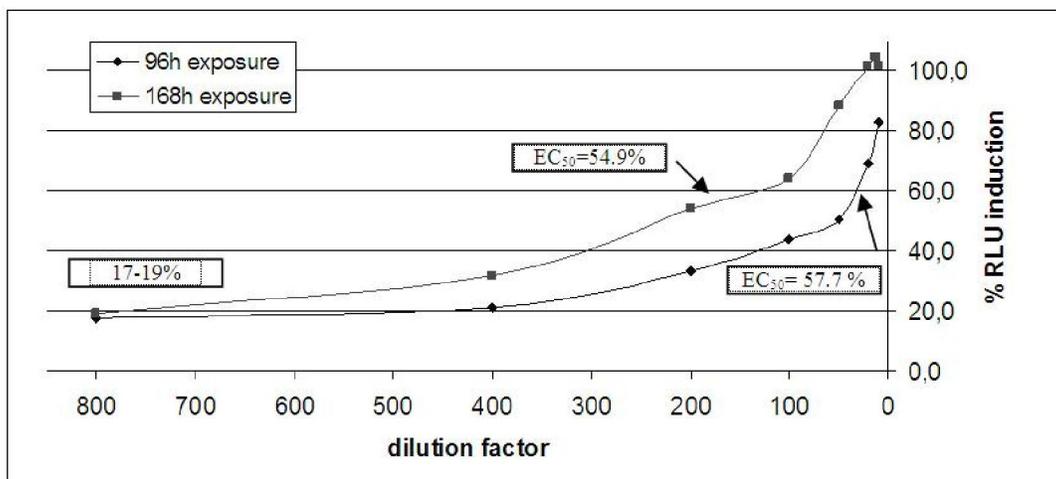

Figure 3. An overview of the dilution curves for two ceramic dosimeters with exposure times of 96 and 168 h

Figure 3 gives an overview of the full dose dilution curves for two ceramic dosimeters after an exposure to the saturated TCDD working solution of respectively 96 and 168 h. For the ceramic tube that was in the TCDD solution for 168 h, a maximum around 100% induction was found, while at dilution factor (df) of 800, the full dose curve was leveling off to a minimum level (DMSO). For the dosimeter at time 96 h, the maximum was not yet reached at df 10, but since the slope of the curve is still steep, it can be expected that the maximum will also be around the theoretical maximum of 100% RLU induction. The amounts of dioxin trapped by the toximeter was increasing with time, which is helpful to obtain the time-weighed average concentration required for the field application of this toximeter in monitoring the dioxin-contaminated waters (Figure 4).
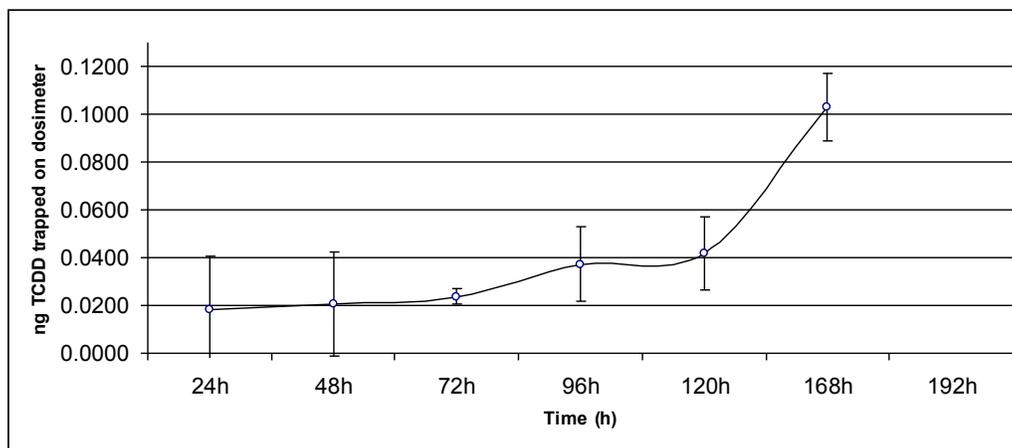

Figure 4. Amounts of TCDD trapped on the toximeter with time

Assuming that the movement of the TCDD molecules to the inner part of the ceramic dosimeter is based solely on diffusion, the accumulated mass can be described according to Fick's first law of diffusion[7]:

$$M = D_e\, \Delta C\, A\, t/\Delta x \qquad \text{(Equation 1)}$$

Where: . ΔC: the concentration of the chemicals in water (assuming that the concentration on the internal linter of the dosimeter = 0), M: the mass of adsorbed chemicals on the receiving material, Δx: the wall thickness of the cylinder (2 mm), A: the area of the exposed ceramic surface (1257 mm^2), t: the exposure time and D_e: the effective diffusion coefficient of the chemicals in porous membrane compared to water. The effective diffusion coefficient (D_e) refers to alteration in diffusion of analytes (TCDD) in the porous ceramic membrane compared to water according to Archie's law[1]:

$$D_e = D_w\, \varepsilon^m \qquad \text{(Equation 2)}$$

Where D_w is the diffusion coefficient of TCDD in water which has a reported mean value of 5.11×10^{-5} m^2/d at 25 ºC. ε is the porosity of the ceramic membrane (0.30) and m is Archie's law exponent, which ranges from 1.5 to about 2.5 in calibration experiments in the laboratory and the value of 2.0 was determined and applied based on previous calibration experiments of the ceramic dosimeter[7]. The diffusion coefficient (D_e) of TCDD in the ceramic toximeter was 9.062×10^{-6} and 9.928×10^{-6} m^2/d depending on the trapped masses at 96 and 120 h respectively. The difference in D_e might be caused by the decrease of the testing solution concentration with time due to the continueous traping of TCDD by dosimeter. This changing in concentration is one major chalenge during the laboratory evaluation and calibration of the ceramic sampler. In the future field application, temperature would be the only parameter to be determined during the sampling period because of its impact on diffusivity.

The Blank experiments carried out for ceramic cylinders which were used several times with clean-up procedures between every two successive uses, showed contamination of the cylinders starting from the third cycle of use. This means that it is advisable to discard the cylinders at that point.

References:
1. Weiß, H., Schirmer, K., Bopp S. and Grathwohl P. (2007); Elsevier B.V., Ch. 12, vol. 48: 279–293.
2. Denison MS, He G, Baston DS, Tsutsumi T. (2008); Organohalogen Compounds 70: 772-775.
3. He G., Tsutsumi T., Zhao B., Baston DS., Zhao J, Heath-Pagliuso S., Denison MS. (2011); Toxicological Sciences (submitted).
4. XDS Method 4435 (2008).
5. Mackay D., Ying Shiu W., Ma K., Chi Lee S. (2006); CRC Press 2nd ed., vol. II.
6. Elskens M., Baston D.S., Stumpf C., Haedrich J., Keupers I., Croes K., Denison M.S., Baeyens W., Goeyens L. CALUX measurements: statistical inferences for the dose response curve (submitted to Talanta).
7. Martin, H., Patterson, B.M., Davis, G.B., Grathwohl, P., (2003). Environ. Sci. Technol. 37, 1360-1364.
8. Bopp, S., Weißb, H., Schirmer, K., (2005); Journal of Chromatography A, 1072, 137–147.