

Preliminary validation studies on ACF passive sampler for PCDD/Fs and PCBs in water

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Introduction

Hydrophobic pollutants as polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) have frequently been identified in several matrices of aquatic ecosystems¹⁻³.

The knowledge of the actual concentrations of these pollutants is essential for integrated water quality management. Due to their very low, but toxicologically relevant levels in natural waters, direct determination of their concentrations is difficult with common analytical techniques.

Several passive samplers such as polyoxymethylene strips^{4,5}, silicone rubber^{5,6}, low density polyethylene (LDPE)⁷, and semi-permeable membrane devices (SPMDs)^{8,9} have been commonly used in monitoring of organic compounds in aquatic environment¹⁰.

Nowadays, ACFs are widely used in different sectors for their adsorptive capacity in pollutants abatement systems. Thanks to their large specific surface area (SSA) and porosity evenly distributed on the surface, ACFs have a reversible mass transfer (adsorption/desorption). Moreover, the material is lightweight (low density per m²), it is wrapped in different textiles (easy to handle) and it is fireproof.¹¹

In this paper, preliminary validation studies for a passive sampler based on activated carbon fiber (ACF) for organic chlorinated pollutants in water are presented.

The ACF passive sampler in water is assessed using efficiency required in EPA 1613B and EPA 1668B standard methods.^{12,13}

Materials and methods

Chemicals and reagents

Internal ¹³C₁₂-labeled standards WP-LCS, WP-ISS, EPA-1613LCS, EPA-1613ISS (Wellington Labs) were purchased from Chemical Research 2000. For chemical analysis, acetone, toluene, dichloromethane (DCM) were purchased from Romil.

Water samples were collected from the Rome supply system managed by ACEA with an average conductivity of 546 µS/cm at 20° C and a TOC of 0,6 mg C/L.

Passive sampler

A commercial ACF with a certified SSA > 2000 m²/g and a thickness of 1,5 mm, was used. The BET surface area analysis yield a real SSA of ~2500 m²/g and a microporosity with a pores diameter of ~60 nm.

8x5cm (0.56 ± 0.02 g) square ACF was inserted in a cellulose bag filter, pre-washed in DCM, and a cord of inert material is tied to the bag in order to suspend it in the water sample.

Clean-up and analysis

The clean-up consisted of a multilayer silica column (extract eluted with hexane) and an alumina microcolumn to separate PCDD/Fs from dl-PCBs. The eluted were concentrated and added with ¹³C₁₂-labelled syringe standards (WP-ISS and EPA1613-ISS for PCBs and PCDD/Fs, respectively). The instrumental analysis were performed by a triple quadrupole gas chromatograph/mass spectrometer (Trace 1310 GC/TSQ 8000 Evo, Thermo); the chromatographic separation were performed by a DB-XLB column (60mx0.25mm, 0.25 µm I.D., Agilent J&W).¹⁴

Results and discussion

A suitable amount of WP-LCS and EPA-1613LCS standards are diluted to 5mL of acetone and this standard solution spiked into a glass tank containing 24L of tap water. The sample is shaken and left to stand for 24h before the sampling, as to grant a uniform distribution of standard between water and suspended particulate matter.

An inert magnetic stirrer (40 mm x 5 mm E.D.) is added in the tank, and it is spinned at 300 rpm, in order to simulate a continuous mixing. The sampling lasted 48h, an excess time, with the aim to study, in the future, adsorption kinetics and optimize sampling time. At the end of the sampling, the ACF was Soxhlet extracted with toluene.

Liquid/liquid extraction (LLE) was considered as the “reference” method, so at the same time, 24L water sample is extracted by dichloromethane. Due to the large volume, the sample was L/L extracted in 3L aliquots, in a funnel with three times 300 mL of dichloromethane.

The extracts (both from Soxhlet and from LLE) were then subjected to cleanup procedure and GC/MS analysis, as described in the previous section.

Method performance of the ACF sampler was assessed comparing percentage recoveries of the labeled compounds spiked in the water sample with the corresponding recovery tables in EPA 1613b and 1668b methods.

Figures 1 and 2 show the percentage recoveries of $^{13}\text{C}_{12}$ -labeled compounds WP-LCS and EPA 1613-LCS for both PCBs and PCDD/Fs, respectively, of the two extraction methods.

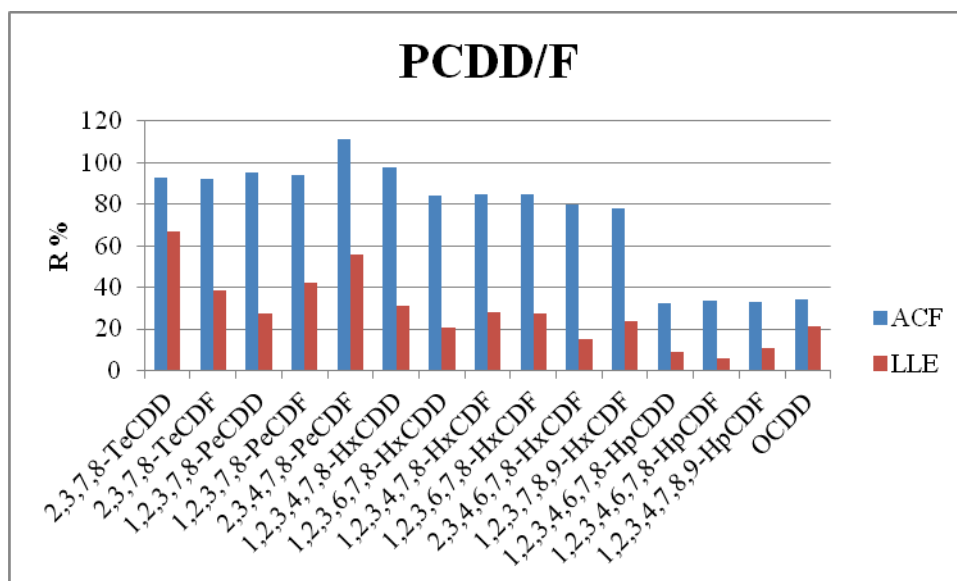


Figure 1 – Comparison of percentage recoveries of $^{13}\text{C}_{12}$ -labeled compounds EPA 1613-LCS

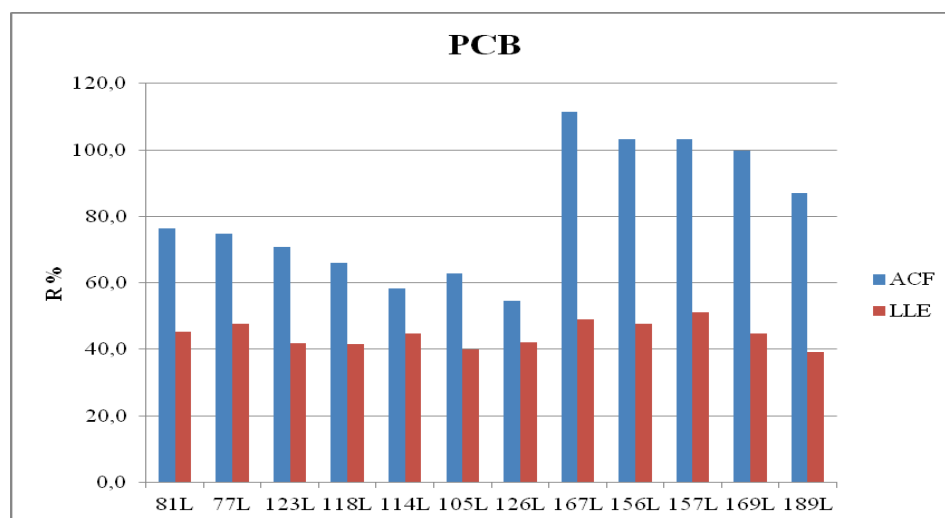


Figure 2 – Comparison of percentage recoveries of $^{13}\text{C}_{12}$ -labeled compounds WP-LCS

As it can be seen from the figures, recoveries are within the limits of EPA methods (25-150%). In general, ACF shows same recoveries or even higher than LLE.

Conclusions

The study showed that ACF responds positively to the range required by the method and shows a higher efficiency compared to the method taken as a reference.

A study of this type opens the door to new tests designed to ascertain what is the breakthrough limit of the material and it is possible to think about the realization of passive samplers in water (eg. rivers) averaged over time. In addition, compared to the method taken as reference (liquid liquid extraction), the enrichment of a passive in ACF and the consequent method of extraction and purification is less laborious and time-consuming.

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Each sample needs to go through the enrichment and purification phases. The ideal is to be able to carry out the two phases simultaneously in order to reduce analysis times and costs. In the future, the aim is to carry out a selective extraction of PCBs and PCDD/Fs or a decrease by oxidation of interfering directly on the trap of enrichment of the analytes.

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