Cod: 2.2002

AN ON-LINE TURBULENT FLOW CHROMATOGRAPHY-LIQUID CHROMATOGRAPHY COUPLED TO TANDEM MASS SPECTROMETRY METHOD FOR THE SIMULTANEOUS ANALYSIS OF 14 ORGANOPHOSPHORUS FLAME RETARDANTS IN ENVIRONMENTAL AND BIOTIC MATRICES

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1. Introduction

Organophosphorus flame retardants (OPFRs) are used as flame retardants (FRs), plasticizers and anti-foaming agents in a wide range of materials due to their excellent physicochemical properties and low cost. After the phase-out of polybrominated diphenyl ethers (PBDEs), OPFRs are increasingly used as alternative FRs.

OPFRs have been found in environmental compartments such as indoor dust, air and soil. However, limited data in sediment have been reported to date, with works in Austria, Spain and China [1,2]. Also, limited information is available in biota samples [3,4].

A variety of extraction and purification techniques are used for OPFR analysis such as pressurized liquid extraction (PLE), shaking and high speed solvent extraction, as well as cleanups such as solid phase extraction (SPE) and filtration. As regards instrumental analysis gas chromatography (GC) coupled to low (LRMS) or high resolution mass spectrometry (HRMS), as well as liquid chromatography (LC) coupled to tandem MS (MS/MS) have been proposed [5,6].

All the extraction and cleanup steps involve time and labor consuming that often constitutes the bottleneck of the analytical method. The aim of this work was to develop an on-line technology based on turbulent flow chromatography (TFC), a robust, fast and high-throughput method, for the determination of OPFRs in environmental and biotic matrices. An on-line cleanup is achieved, minimizing the sample preparation. Recoveries, reproducibility, limits of detection (LODs) and limits of quantification (LOQs) of the developed method will be evaluated and compared with previous off-line methods. Finally, the developed method was applied to sediment and fish samples.

2. Sample extraction

For sediments, extraction was carried out by PLE, using an ASE 350 system (Dionex, CA, USA). One gram of dry weight (dw) was loaded into a 22 mL extraction cell previously filled with copper and hydromatrix, and extracted with hexane:acetone (1:1) at 1500 psi and 100◦C. Extracts were concentrated to incipient dryness and re-dissolved with methanol for a final volume of 500 µL.

Ultrasounds was chosen for fish samples, mainly for being a mild extraction which allows a lower amount of interfering compounds. 0.5 g dw was extracted with 15 mL of hexane:acetone (1:1). The extract was reconstituted in 5 mL of hexane:methanol (1:3). The solution was centrifuged and 200 µL were collected for the instrumental analysis.

Prior to analysis by TFC-LC-MS-MS, labeled compounds, TCEP-d12, TDCPP-d15, TBP-d27, TPHP-d15 and 13C2-TBOEP, were added as internal standards.

3. Instrumental analysis

Online sample purification and analysis was performed by Thermo Scientific TurboFlowTM system consisted of a triple quadrupole (QqQ) MS with an heated-electrospray ionization source (H-ESI), two LC quaternary pumps and three LC columns, two for purification and one for the separation.

Different columns were tested. The best results were obtained for CycloneTM-P (0.5x50mm) and a C18-XL (0.5x50mm). 20 µL of sample were directly injected onto the TurboFlowTM. For the chromatographic separation, Purosphere Star RP-18 (125mmx0.2mm) was selected. Compounds were analyzed in positive ionization and selective reaction monitoring mode was used.

4. Result and discussion

Analytical parameters. The quality parameters are summarized in Table 1.

Recoveries were 48-110% for sediments, and 49-97% for fish, in both cases being the worst compound recovered TPPO. As for the reproducibility, RSD values were lower than 5% for most compounds, and

always below 10%. These values are a result of applying an automatic method that minimizes variations that usually occur when using conventional offline methods.
For limits of detection (LODs) and limits of quantification (LOQs), values 0.02-1.25 ng/g dw and 0.05-3.44 ng/g dw, respectively, were obtained for sediments, being the higher levels those for IPPP. In the case of fish, LODs were 0.19-3.44 ng/g lipid weight (lw), except for IPPP which had a LOD of 19.3 ng/g lw. LOQs were 1.03-7.30 ng/g lw, except for IPPP which had a LOQ of 24.8 ng/g lw. In the case of IPPP, the signal is distributed in several isomers and affects their LODs and LOQs.
Comparison with conventional offline methods. Our analytical parameters were compared with a recent study [5] that showed a determination of 16 OPFRs in fish using an ultrasonic extraction followed by SPE and a LC-MS-MS. Recoveries obtained were 46-109%, with RSD up to 25% and LODs 0.34-11.6 ng/g lw, except for IPPP which has LOD of 51.6 ng/g lw. Therefore, our developed online method provides similar recoveries, better reproducibilities and similar or better LODs (Figure 1). As regards sediment methodologies, a recent study [6] reveals that recoveries (74-104%) are similar to those in our study, and LOQs (0.48-11 ng/g dw) are in all cases higher than those in our study.
Application to real samples. The developed method was applied to sediment and fish collected in different river basins. For biota, OPFRs were detected in all the samples at levels 3.29-314 ng/g lw. All analytes included in our method have been detected in at least one of the samples, but TBOEP and TDCPP have been always found at levels below LOQ. The most abundant OPFR in all the fish species was TBP, between 45.2-314 ng/g lw, followed by IDPP (18.2-182 ng/g lw). For sediment samples, OPFRs were also detected in all the samples at concentration levels of 10.5-550 ng/g dw. The most abundant OPFR was EHDP, at concentration levels of 19.2-388 ng/g dw, followed by IDPP with levels between no quantifiable (nq) and 310 ng/g dw.

5. Conclusion

A new analytical methodology based on an on-line clean up using TFC-LC-MS/MS has been developed for the analysis of 14 OPFRs in sediment and fish samples. This method eliminates time-consuming sample preparation steps. The extraction was performed by ultrasound liquid extraction for biota and PLE for sediments. Analytical parameters showed acceptable recoveries with very low relative standard deviations. Moreover, LODs and LOQs are similar or even lower than those reported using off-line methodologies.
Finally, developed methods were applied to real samples, showing the widespread of OPFRs in environmental and biotic samples.

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Table1. Recoveries, relative standard deviations (RSDs), LODs and LOQs of developed TFC-LC-MS-MS method.

Analyte	Sediment				Fish			
	R(%)	RSD(%)	LOD (ng/g dw)	LOQ (ng/g dw)	R(%)	RSD(%)	LOD (ng/g lw)	LOQ (ng/g lw)
TCEP	51	5.0	0.07	0.13	67	8.3	1.21	3.51
TPPO	48	3.1	0.85	2.51	49	4.9	0.35	1.30
TCIPP	67	6.3	0.09	0.26	63	2.7	1.48	4.18
TDCPP	70	8.0	0.05	0.12	55	5.8	0.19	1.03
TPHP	70	1.7	0.08	0.16	53	4.9	1.30	3.45
TBP	83	3.1	0.03	0.08	70	3.8	3.44	7.30
DCP	88	6.3	0.06	0.11	70	7.5	1.63	4.61
TBOEP	73	2.5	0.03	0.05	63	10	0.44	1.44
TMCP	90	4.6	0.09	0.15	77	11	2.55	4.63
EHDP	110	1.7	0.02	0.07	60	9.8	0.53	0.97
IDPP	92	2.1	0.05	0.19	86	5.1	2.96	5.17
IPPP	93	1.9	1.25	3.44	81	10	19.3	24.8
THP	89	4.2	0.06	0.22	80	9.6	0.88	2.11
TEHP	103	4.9	0.11	0.27	97	11	1.95	3.86

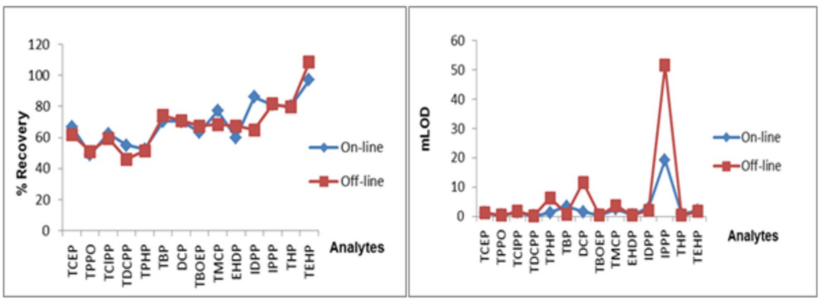

Figure 1. Comparison of (a) recoveries (%) and (b) LODs (ng/g lw) obtained by our developed online method and an off-line methodology (5) in fish matrices.