Comunicaciones

IV REUNIÓN NACIONAL DE DIOXINAS, FURANOS Y COMPUESTOS ORGÁNICOS PERSISTENTES RELACIONADOS

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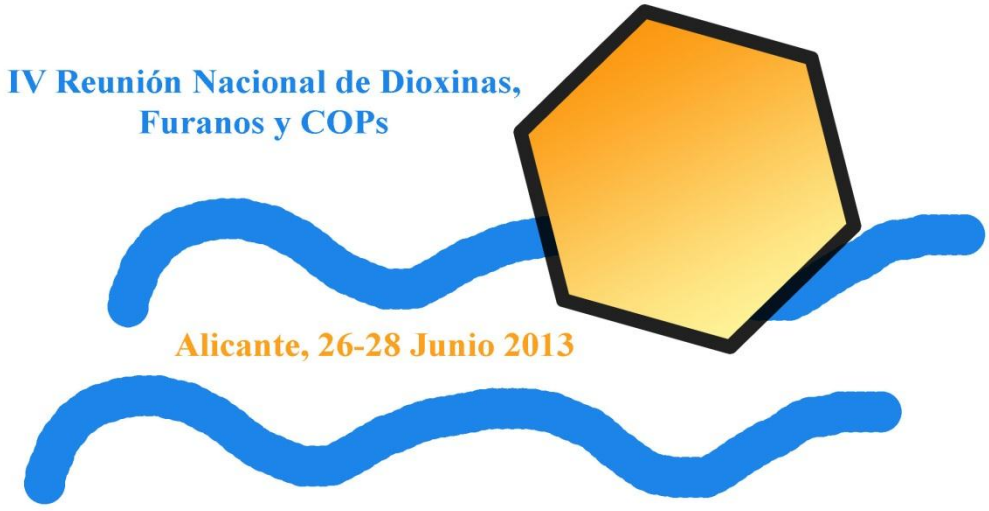

IV REUNIÓN NACIONAL DE DIOXINAS, FURANOS Y COMPUESTOS ORGÁNICOS PERSISTENTES RELACIONADOS

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DETERMINATION OF PERSISTENT HALOGEN HYDROCARBONS IN EUROPEAN EEL (ANGUILLA ANGUILLA) BY GAS CHROMATOGRAPHY COUPLED TO MASS SPECTROMETRY

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Introduction

Persistent halogenated hydrocarbons (PHHs) such as polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs) and polybrominated diphenyl ethers (PBDEs) are lipophilic and ubiquitous persistent organic pollutants (POPs).[1,2] They can accumulate in sediments, biota and food and they are reported to be toxic and bioaccumulative, and thus potentially pose a major health risk to the consumer of seafood.[3] Therefore, the levels of these type of contaminants should be monitored in edible tissues in order to evaluate human exposure.[4] In this sense, eels have several ecological and physiological characteristics that make them susceptible to accumulate contaminants, such as relatively high lipid content, long life expectancy, diverse dietary habits, and the ability to inhabit a variety of aquatic environments.[5] Therefore, PHHs can accumulate to a significant extent in the fat tissue of eels.[6] For this purpose, reliable analytical methods should be developed in order to provide suitable tools for routine analysis of these type of contaminants. Thus, gas chromatography (GC) coupled to mass spectrometry (MS) analysers, such as triple quadrupole (QqQ) or ion trap (IT) can be used, considering that good selectivity, low limits of detection (LODs) and reliable confirmation can be obtained.

Materials and Methods

Chemicals and Materials

PBDEs analytical standards were purchased from Cambridge Isotope Laboratories, Inc (Andover, Ma, USA). PCBs and OCPs were obtained from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Isotopically labelled PCB 28F and p,p'-DDE-d_8, obtained from Dr. Ehrenstorfer GmbH, were used as internal standards. Dichloromethane, *n*-hexane, ethyl acetate and sulphuric acid were purchased from Fluka (Steinheim, Germany). All of them were analytical grade. Anhydrous magnesium sulphate was obtained from Panreac (Barcelona, Spain).

Samples

Samples were obtained at several river systems throughout Spain and from commercial fishermen. Collected eels were stored in aluminium foil at -20 °C until analysis.

Extraction procedure

A Soxhlet extraction procedure was used for the simultaneous extraction of PHHs from eels. Briefly, approximately 5 g of sample were homogenized with anhydrous magnesium sulphate (5 g). The samples were extracted in a Soxhlet apparatus for 12 hours using a mixture of dichloromethane:*n*-hexane (1:1 v/v, 150 mL). Then, the solvent was evaporated to dryness and 2 mL of *n*-hexane was added. Then, 5 mL of sulphuric acid was added and the mixture was shaken end-over-end for 10 min in a rotary agitator. The tube was centrifuged (10 min, 4500 rpm, 2264 x *g*) and the acid solution was discarded. Finally, evaporate the organic solvent and add 2 mL of *n*-hexane to the residue.

Chromatographic analysis

Chromatographic analyses were carried in a Scion GC system(Bruker Corporation, Freemont, CA, USA) equipped with an autosampler from the same company for the analysis of PCBs and OCPs and a GC system Varian 3800 (Varian Instruments, Sunnyvale, CA, USA) for the analysis of PBDEs. The column used were a BR-1ms (15 m x 0.25 mm, 0.25 µm particle size) from Bruker for the analysis of PBDEs and VF-5 ms (30 m x 0.25mm, 0.25 µm particle size) from

Agilent (Santa Clara, CA, USA) for the separation of PCBs y OCPs. A fused silica untreated capillary column (2m x 0.25mm) from Supelco (Bellefonte, PA, USA) was used as a guard column. Mass spectrometric detection was carried out using a Scion QqQ-MS/MS (Bruker) operating in positive electron ionization mode (PEI) for the detection of PCBs and OCPs, and an ion trap (Saturn 2200) from Varian, applying negative chemical ionization (NCI) for PBDEs.

Results and Discussion

A conventional Soxhlet extraction was used for the simultaneous extraction of OCPs, PCBs and PBDEs from eels. Solvent extraction and extraction time were optimized, obtained suitable recoveries when a mixture of dichloromethane:n-hexane was used during 12 h. Besides, a clean-up step, based on the use of sulphuric acid was needed in order to remove matrix interferents.

Then, the chromatographic conditions were evaluated and two methods were performed. The first one based on GC-QqQ-MS/MS, applying selected reaction monitoring (SRM) was used for the simultaneous analysis of OCPs and PCBs, whereas PBDs were determined using the ion trap analyser. Running time was lower than 20 min per injection.

The optimized method was validated in terms of linearity, matrix effect, trueness, precision (intra and inter-day precision) and lower limits (LODs and limits of quantification (LOQs)), showing in Table 1 an overview of the obtained results, observing that LOQs were equal or lower than 1 µg/kg, recovery ranged from 89 to 105 % and inter-day precision were lower than 11 %.

Table 1.- Overview of the validation parameters obtained for the analysed compounds

Compound	LOQ (µg/kg)	R (%)[a]		Compound	LOQ (µg/kg)	R (%)[a]
p,p'-DDT	1.0	92 (10)		p,p'-DDE	1.0	100 (9)
p,p'-TDE	1.0	92 (8)		PCB 28	1.0	98 (4)
PCB 52	1.0	91 (11)		PCB 77	1.0	98 (7)
PCB 81	1.0	99 (5)		PCB 101	1.0	93 (3)
PCB 105	1.0	91 (12)		PCB 114	1.0	95 (8)
PCB 118	1.0	101 (7)		PCB 123	1.0	105 (7)
PCB 126	1.0	98 (8)		PCB 138	1.0	105 (8)
PCB 153	1.0	102 (3)		PCB 156	1.0	95 (3)
PCB 157	1.0	90 (3)		PCB 167	1.0	105 (4)
PCB 169	1.0	92 (3)		PCB 170	1.0	89 (6)
PCB 180	1.0	102 (5)		PCB 189	1.0	103 (3)
PBDE 17	0.1	99 (12)		PBDE 28	0.1	98 (5)
PBDE 47	0.1	97 (11)		PBDE 66	0.1	96 (5)
PBDE 85	0.1	99 (8)		PBDE 99	0.1	90 (4)
PBDE 100	0.1	104 (5)		PBDE 153	0.1	94 (11)
PBDE 154	0.1	89 (9)		PBDE 183	0.1	89 (8)
PBDE 184	0.1	93 (11)		PBDE 191	0.1	96 (8)
PBDE 196	0.1	94 (5)		PBDE 197	0.1	94 (7)
PBDE 209	0.1	92 (10)				

[a] Recovery values obtained when blank eels were spiked at 1.2 µg/kg (0.12 µg/kg for PBDEs) . Inter-day precision was provided in brackets (n = 5).

Finally the method was applied to samples and PCBs and p,p'-DDT and p,p'-DDD were the compounds most frequently detected in the analysed samples.

Conclusions

Two methods for the determination of PHHs in eels have been optimized and validated. The extraction procedure was based in a Soxhlet extraction, allowing the simultaneous extraction of OCPs, PCBs and PBDEs. A clean-up step was needed in order to eliminate some interferents. GC-QqQ-MS/MS and GC-IT-MS were used for the separation and detection of the target compounds. Good results were obtained during the validation of the proposed procedures.

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References

1. Qiu Y, Strid A, Bignert A, Zhu Z, Zhao J, Athanasiadou M, Athanassiadis I, Bergman A. *Chemosphere*, 2012; 89:458-466.
2. http://chm.pops.int
3. Montie EW, Letcher RJ, Reddy CM, Moore MJ, Rubinstein B, Hahn ME. *Marine Pollution Bulletin*, 2010; 60:1160-1169.
4. McHugh B, Poole R, Corcoran J, Anninou P, Boyle B, Joyce E, Foley MB, McGovern E. *Chemosphere*, 2010; 79:305-313.
5. Byer JD, Lebeuf M, Alaee M, Stephen BR, Trottier S, Backus S, Keir M, Couillard CM, Casselman J, Hodson PV. *Chemosphere*, 2013; 90:1719-1728.
6. Szlinder-Richert J, Usydus Z, Pelczarski W. *Chemosphere*, 2010; 80:93-99.