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Simultaneous microwave-assisted extraction of polycyclic aromatic hydrocarbons, polychlorinated biphenyls, phthalate esters and nonylphenols in sediments

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Abstract

A new method was developed for the simultaneous extraction of polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), phthalate esters (PEs), nonylphenols (NPs) and nonylphenol mono- and diethoxylates (NP1EOs and NP2EOs, respectively) in sediment samples by means of a closed microwave system. The extractions were carried out at 21 psi and 80% of microwave power and 15 ml of acetone were used as the common extraction solvent. The filtered extract was further fractionated in two groups using Florisil® cartridges: PAHs and PCBs were eluted with *n*-hexane:toluene (4:1) and the PEs, NPs and ethoxylates were eluted with ethyl acetate. All the compounds were analysed by gas chromatography–mass spectrometry (GC–MS). In case of PAHs and PCBs, the developed method was validated by comparison of the results obtained for the certified reference material NIST 1944 with the certified values. In the absence of a reference material for phthalate esters and nonylphenols, one sediment sample was extracted twice under the optimal conditions in order to check than an exhaustive extraction of the analytes occurred. This method is currently used in the study of the distribution of those organic contaminants in the estuaries of the Bay of Biscay (Spain).

Keywords: Microwave-assisted extraction; Sediment samples; Polycylic aromatic hydrocarbons; Polychlorinated biphenyls; Nonylphenols; Nonylphenol ethoxylates; Phthalate esters

1. Introduction

The environmental monitoring of anthropogenic pollutants is required to understand the impact of these compounds in the ecosystems and to prevent or minimise their adverse effects [1]. Two of the most critical steps in analytical procedures are extraction and clean-up, due to the uncontrolled losses and non-quantitative recoveries that often occur in those steps. Thus, the optimisation and the control of these steps is necessary [2].

Microwave-assisted extraction (MAE) has been widely used in the literature for the extraction of organic pollutants from solid samples [3–7]. However, most methods found in the literature were developed only for an specific family of analytes [8–10] or for different families with similar polarities [4,11]. Therefore, in our group MAE procedures have been developed for the extraction of polychlorinated biphenyls (PCBs) [12,13], polycyclic aromatic hydrocarbons (PAHs) [14], phthalate esters (PEs) [15] and nonylphenols (NPs) mono- and diethoxylates (NP1EOs and NP2EOs, respectively) [15]. Since the various analyte classes were studied separately in earlier papers, different solvents or solvent mixtures were obtained as optimum, acetone:*n*-hexane mixtures for PAHs [14] and PCBs [12,13] and methanol for PEs and NPs [15]. Similar results were observed in the literature and while different acetone:*n*-hexane mixtures have been widely used for PAHs [16,17], PCBs [18,19] and PEs [20,21]

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more polar solvents (methanol [22–25], hexane:2-propanol [26], ethyl acetate [27], for instance) have been applied in the extraction of NPs.

As a consequence, the need of different extraction procedures for the extraction of different families of analytes increases the amount of work to be done in monitoring programs where different families of organic pollutants are studied in a high number of samples. Thus, it was thought it would be interesting to develop a simultaneous MAE procedure for the four families of analytes mentioned above.

As well as a simultaneous extraction method, it was also thought that the development of a simple clean-up step was necessary. In this sense, a simple solid phase extraction (SPE) with Florisil® cartridges was developed with two aims: (i) the elimination of interferences and (ii) the fractionation of the analytes in two groups, PAHs and PCBs in one extract and PEs, NPs and NP1EOs + NP2EOs in another. The separation of the four families of analytes in two groups was not performed due to problems in the final chromatographic separation but due to the extremely different concentrations in which the two groups of analytes were found in some of the sediments monitored.

The whole analytical procedure was validated using the certified reference material NIST 1944 in case of PCBs and PAHs. Since no certified reference sediment was available for PEs and NPs, one sediment sample was extracted twice under the optimal conditions in order to check than an exhaustive extraction of the analytes had occurred.

2. Experimental section

2.1. Reagents and materials

EPA phthalate ester mix (six PEs at 2000 μg ml^{-1} each), SS TCL PAH mix (16 PAHs at 2000 μg ml^{-1} each), CB congener mix (CBs 10, 28, 52, 138, 153 and 180 at 10 μg ml^{-1} each) and 525 fortification solution A (acenaphthene-d_{10}, chrysene-d_{12} and phenanthrene-d_{10} at 2000 μg ml^{-1} each) were purchased from Supelco (Walton-on-Thames, UK). The PCB nomenclature used was the one proposed by Ballschmiter and Zell [28]. The mixture of dibenzyl phthalate (DBeP), diphenyl isophthalate (DPiP) and diphenyl phthalate (DPP) (500 μg ml^{-1} each) ISM-390 was purchased from ULTRAScientific (North Kingston, RI, USA). Nonylphenol technical mixture (Pestanal®) was obtained from Riedel-de-Haën (Seelze, Germany) and Igepal® from Aldrich (Milwaukee, WI, USA). Stock standard solutions of approximately 2000 μg ml^{-1} of nonylphenol, nonylphenol mono- and diethoxylates were prepared in methanol. Intermediate dilutions of the above mentioned stock solution were prepared in order to build the calibration curves.

Acetone, dichloromethane (DCM), ethyl acetate (EtOAc), toluene and *iso*-octane were purchased from LabScan (Dublin, Ireland) and *n*-hexane from Merck (Darmstadt, Germany). One gram Florisil® cartridges was purchased from Supelco.

The certified reference material (CRM) 1944 was supplied by NIST (Gaitherburg, ND, USA).

Sediment samples were collected in four different sampling points (A, Kanala; B, Arteaga; D, Gernika; and E, Murueta) in the Urdaibai estuary (Gernika, Bay of Biscay) in March 2003. Urdaibai is a protected estuarine area located in a rural environment that in 1984 was declared reserve of the biosphere by the United Nations for the Education, Science and Culture Organisation (UNESCO). It exists nowadays, however, a noticeable industrial activity in the surroundings of Gernika, a medium-size town (a population of ∼20000 inhabitants) in the upper part of the estuary.

Once in the laboratory, the sediment samples were frozen and lyophilised at low temperatures (−46/−52 °C) and pressures (0.17/0.22 mbar) in a Cryodos-50 freeze-drier (Telstar, Spain). The dried samples were ground in a ball grinder (Fristch Pulverisette 6, Germany), sieved (250 μm), stored in glass vials and kept in the fridge at 4 °C until analysis.

2.2. Optimisation of the clean-up and fractionation step

For the optimisation of the clean-up and fractionation steps, standard solutions containing all PAHs, PCBs, PEs, NPs and NP1EOs + NP2EOs at a concentration of ca. ∼17 μg ml^{-1} were prepared in *n*-hexane. The *n*-hexane solutions were loaded onto 1 g Florisil® cartridges that had been previously conditioned with 5 ml of *n*-hexane. Three elution procedures were assayed in order to obtain the clean-up and fractionation of the analytes in two groups: PAHs and PCBs, and PEs and NPs, NP1EOs and NP2EOs. The procedures were as follows:

(i) 5 ml of *n*-hexane (fraction i1), 10 ml of DCM (fraction i2) and 10 ml of EtAcO (fraction i3);
(ii) 5 ml (2×) of toluene (fractions ii1 and ii2) and 10 ml of EtAcO (fraction ii3);
(iii) 5 ml (2×) of (4:1) *n*-hexane:toluene (fractions iii1 and iii2) and 5 ml of EtAcO (fractions iii3 and iii4).

All the fractions were evaporated to dryness using a gentle stream of nitrogen in the Turbovap LV Evaporator (Zymark, Hopkinton, MA, USA) and re-dissolved in 500 μl of *iso*-octane for GC–MS analysis.

In order to estimate the recoveries obtained in each experiment, the peak areas of each analyte obtained in the different fractions were compared to those obtained for a standard solution of the same concentration, which had not been submitted to the clean-up and fractionation process.

2.3. Optimisation of a simultaneous MAE procedure

MAE experiments were performed with a MDS-2000 closed microwave solvent extraction system (CEM, Matthews, NC, USA) equipped with a 12-sample tray

Table 1
m/z values, surrogate standards, LODs (in ng) and RSDs estimated for each analyte

	m/z	Surrogate	LOD[a] (ng)	RSD
PAHs				
Nap	128, 129	Ace-d_{10}	0.5	3–35
Acy	153, 153	Ace-d_{10}	0.5	2–10
Ace	153, 154	Ace-d_{10}	1.0	5–13
Flu	165, 166	Ace-d_{10}	3	0.3–5
Phe	178, 179	Phe-d_{10}	0.5	2–8
Ant	178, 179	Phe-d_{10}	1	0.5–13
Flr	202, 203	Phe-d_{10}	5	1–11
Pyr	202, 203	Phe-d_{10}	6	1–8
B[a]A	228, 229	Chy-d_{12}	11	1–9
Chy	228, 229	Chy-d_{12}	0.5	0.1–8
B[b]F	252, 253	Chy-d_{12}	6	2–15
B[k]F	252, 253	Chy-d_{12}	5	1–14
B[a]P	252, 253	Chy-d_{12}	6	1–13
Ind	276, 277	Chy-d_{12}	5	0.5–10
D[ah]A	276, 277	Chy-d_{12}	3	1–16
B[ghi]P	276, 277	Chy-d_{12}	2	1–17
PCBs				
CB-10	222, 152	–[b]	1.0	1–10
CB-28	256, 258	–[b]	1	0.2–5
CB-52	220, 292	–[b]	0.7	1–14
CB-138, CB-153	360, 362	–[b]	1, 0.4	1–17
CB-180	394, 396	–[b]	0.8	3–13
PEs				
DMP	77, 163	DBeP, DPiP, DPP	5	33
DEP	149, 177	DBeP, DPiP, DPP	12	2–19
DBP	104, 149	DBeP, DPiP, DPP	4	4–17
BBP	91, 149	DBeP, DPiP, DPP	1	40–44
DEHP	149, 167	DBeP, DPiP, DPP	22	2–6
DOP	149, 279	DBeP, DPiP, DPP	0.5	–[c]
NPs				
NP	149, 135	DBeP, DPiP, DPP	100	30
NP1EO + NP2EO	193[d], 179[d] 223[e], 237[e]	DBeP, DPiP, DPP	100	7

Nap, naphthalene; acy, acenphthylene; ace, acenaphthene; flu, fluorene; phe, phenanthrene; ant, anthracene; flr, fluoranthene; pyr, pyrene; b[a]a, benzo[a]anthracene; chy, chrysene; b[b]f, benzo[b]fuoranthene; b[k]f, benzo[k]fluoranthene; b[a]p, benzo[a]pyrene; d[ah]a, dibenzo[a,h]anthracene; b[ghi]p, benzo[g,h,i]perylene; and ind, indene(1,2,3-cd)pyrene.

[a] LODs calculated as three times the signal of the blank. Blanks obtained from chemicals subjected to whole procedure.

[b] No correction necessary in case of CB congeners.

[c] DOP not quantified in any sample and therefore no RSD calculated.

[d] *m/z* values for NP1EO.

[e] *m/z* values for NP2EO.

and pressure feedback/control. Approximately 1.0 g of the sediment sample (NIST 1944 or naturally polluted sediment) were accurately weighed and quantitatively transferred to the Teflon lined extraction vessel together with 1 g of activated copper [29] (copper was treated with 30% HNO_3, washed with water and with DCM and dried at 50 °C). The activated copper was added to eliminate the possible presence of sulphur in the samples. Twenty-five microlitres of a mixture of acenaphthene-d_{10}, chrysene-d_{12} and phenanthrene-d_{10} at 20 μg ml^{-1} and 25 μl of a mixture of dibenzyl phthalate, diphenyl isophthalate and diphenyl phthalate at 20 μg ml^{-1} in acetone were added in order to correct the possible losses in the procedure. Table 1 summarises which surrogate was used for the correction of losses of each analyte. Fifteen millilitres of acetone were added to the sample and the extraction vessel was closed, after ensuring that a new rupture membrane was used for each experiment. Extraction conditions were programmed in two stages. In the first stage, the system was allowed to reach the required pressure (21 psi ∼ 145 kPa) using full power; in the second stage, the pressure previously reached was kept constant for 15 min at 80% of microwave power. When the irradiation period was completed, samples were removed from the microwave cavity and were allowed to cool to room temperature before opening. The supernatant was filtered through PTFE filters (25 mm, 5 μm, Waters), which had been previously washed with the extraction solvent. The extract was concentrated to ca. 0.5 ml using nitrogen blow-down evaporation after the addition of ca. 1 ml of *iso*-octane. *Iso*-octane was added in order to minimise losses during evaporation [30] and to guarantee that the

concentrated extract was in a non-polar solvent before being loaded onto the polar Florisil® cartridge. The concentrated extract was submitted to the optimal clean-up step.

2.4. Analysis of the extracts

The extracted compounds were analysed on a 6890N gas chromatograph coupled to a 5973N mass spectrometer with a 7683 autosampler (Agilent Technologies, Avondale, PA, USA). Two microlitres of the sample were injected in the splitless mode (2 min) at 270 °C into a 30 m × 0.25 mm × 0.25 μm HP-5 capillary column. Two different temperature programmes were used: one for the separation of PAHs and PCBs and the other one for PEs, NPs, NP1EOs and NP2EOs. For the separation of PAHs and PCBs the temperature programme was: 60 °C for 2 min, increase at 10 °C min^{-1} to 290 °C with a final hold for 10 min. In case of PEs and NPs the temperature programme was: 80 °C for 2 min, increase at 30 °C min^{-1} to 290 °C with a final hold for 8 min. The carrier gas was helium (C-50) and was kept at a constant flux of 1.5 ml min^{-1} for PAHs and PCBs and 2.0 ml min^{-1} for PEs and NPs. The mass spectrometer was operated in the electron impact ionisation mode at 70 eV. The interface was kept at 300 °C and the ionisation source and the quadrupole at 230 and 150 °C, respectively. Measurements were performed in the SIM mode; the *m*/*z* values for each congener are included in Table 1.

Seven-point internal calibration curves were built in the range of 0.05–16 μg ml^{-1} for PAHs, 25–200 ng ml^{-1} for PCBs, 0.05–100 μg ml^{-1} for PEs, 2.9–26.2 μg ml^{-1} for NPs and 4.0–38.2 μg ml^{-1} nonylphenol ethoxylates (NP1EOs + NP2EOs).

3. Results and discussion

3.1. Optimisation of clean-up and fractionation

In a preliminary assay, the elution and fractionation of the analytes was performed using *n*-hexane, DCM and EtAcO. Since the analytes studied showed different polarities (from the most apolar PCBs to the more polar NPs), solvents with different polarities were chosen for the first step of the optimisation. In this case, PCBs eluted quantitatively (>90%) in the *n*-hexane fraction (fraction i1) but PAHs eluted differently in fractions i1 (*n*-hexane) and i2 (DCM). While the lightest PAHs (acenaphahthene, fluorene, phenanthrene, anthracene and fluoranthene) eluted quantitatively in the *n*-hexane (>90%) (except for naphthalene), the heaviest PAHs eluted in both fractions (i1 and i2) (benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene and benzo[a]pyrene)] or mainly (>90%) in fraction i2 (DCM) (indene[1,2,3-cd]pyrene, dibenzo[a,h]anthracene and benzo[g,h,i]perylene). Moreover, PEs eluted in fraction i2 (DCM). Thus, using this procedure it was impossible to achieve the desired fractionation.

Since both PAHs and PEs showed an affinity towards DCM and *n*-hexane was not able to elute PAHs quantitatively, both solvents were eliminated and toluene was introduced instead.

When toluene was used, the quantitative (>90%) recovery of PAHs was obtained in the first 5 ml of toluene (fraction ii1). The problem using toluene was that PEs were also recovered in this fraction in a percentage of even 20% for DEHP. Besides, the second fraction of toluene (fraction ii2) was not able to elute quantitatively the PEs (<70%), especially the lighter ones (<20%) (dimethyl phthalate, DMP; diethyl phthalate, DEP; and dibutyl phthalate, DBP) and, thus, the addition of EtAcO was necessary. Even if EtAcO is a much stronger solvent than DCM (polarity 4.3 and 3.4, respectively), it was experimentally observed that, when DCM was added, apart from the analytes of interest, all the impurities in the cartridge were also eluted. This fact did not occur when EtAcO was added, and therefore, EtAcO was preferred to DCM.

From the previous results, it was decided to carry out a third approach where the Florisil® cartridges were eluted with 5 ml (2×) of a (4:1) *n*-hexane:toluene mixture (fractions iii1 and iii2) and 5 ml (2×) of EtAcO (fractions iii3 and iii4). The results are included in Table 2.

The results of Table 2 show that PCBs were quantitatively recovered in the first 5 ml of (4:1) *n*-hexane:toluene and that both PEs and NPs were recovered quantitatively in the first 5 ml of EtAcO. Therefore, it was decided to add only 5 ml of EtAcO.

The heaviest PAHs (indene[1,2,3-cd]pyrene, dibenzo-[a,h]anthracene, benzo[g,h,I]perylene) were not quantitatively recovered even after the addition of the extra 5 ml of (4:1) *n*-hexane:toluene (fraction iii2). In order to quantitatively recover these PAHs, it was decided to add 12 ml of (4:1) *n*-hexane:toluene. This approach was chosen instead of the addition of a mixture richer in toluene for several reasons. On the one hand, a mixture richer in toluene could elute PEs and then it would not be possible to separate PAHs and PCBs from PEs. Besides, since toluene is less volatile than *n*-hexane, longer evaporation periods are required which will increase the risk of losses of the most volatile analytes.

In summary, the elution and fractionation of the analytes of interest was carried out as follows: 12 ml of (4:1) *n*-hexane:toluene (fraction 1) and 5 ml of EtAcO (fraction 2).

3.2. Optimisation of MAE

Since the aim of this work was the simultaneous extraction of the four families of analytes, it was thought that acetone could be the common extraction solvent since its polarity is intermediate between methanol and acetone:*n*-hexane mixtures that had been used previously [12–15]. Besides, acetone is easier to evaporate than methanol or acetone:*n*-hexane mixtures. Acetone was chosen instead of other solvents or solvent mixtures such as DCM or DCM:MeOH in order to avoid the use of chlorinated solvents. In order to test how suit-

Table 2
Analyte recoveries by SPE from 1 g Florisil® cartridge with 5 ml of (4:1) *n*-hexane:toluene (fraction iii1), 5 ml of (4:1) *n*-hexane:toluene (4:1) (fraction iii2) and 5 ml of ethyl acetate (fraction iii3)

	Fraction iii1	Fraction iii2	Fraction iii3
PAHs			
Nap	73	22	6
Acy	100	0.1	0.0
Ace	100	0.0	0.0
Flu	100	0.0	0.0
Phe	100	0.3	0.2
Ant	99	0.7	0.1
Flr	98	2	0.7
Pyr	97	2	0.8
B[a]A	93	5	2
Chy	95	5	0.6
B[b]F	74	24	2
B[k]F	76	21	3
B[a]P	65	31	4
Ind	21	67	12
D[ah]A	21	65	14
B[ghi]P	27	62	11
PCBs			
CB-10	99	0.5	0.5
CB-28	99	0.5	0.9
CB-52	99	0.8	0.4
CB-138, CB-153	98	0.7	1
CB-180	97	0.9	2
PEs			
DMP	0.0	0.0	100
DEP	0.0	0.0	100
DBP	0.0	0.4	99
BBP	0.0	0.0	100
DEHP	3	2	95
DOP	0.0	0.0	100
NPs			
NP	0.0	0.0	100
NP1EO	0.0	0.0	100
NP2EO	0.0	0.0	100

able acetone might be for the simultaneous MAE of PAHs, PCBs, PEs and NPs, two different validations were carried out. In case of PAHs and PCBs, the extraction, clean-up and fractionation was validated by comparison of the results obtained for NIST 1944 marine sediment with the certified reference values. Fig. 1(a) and (b) shows the results (mean value ± two times the standard deviation, 2*s*) obtained for the NIST 1944 marine sediment in case of PAHs and PCBs, respectively.

In case of PAHs, there were no significant differences between the results obtained for MAE(acetone)–GC–MS and the certified values. Lower concentrations were obtained for naphthalene. In some cases, half of the certified concentration was obtained for this analyte. This might be due to the fact that this is the most volatile PAH studied in this work and, thus, more susceptible to the evaporation steps carried out in the procedure. For future works, a more suitable surrogate should be found for the correction of the losses that occur in the extraction and clean-up steps for naphthalene, since acenaphthene-d_{10} seems not to correct them properly. The

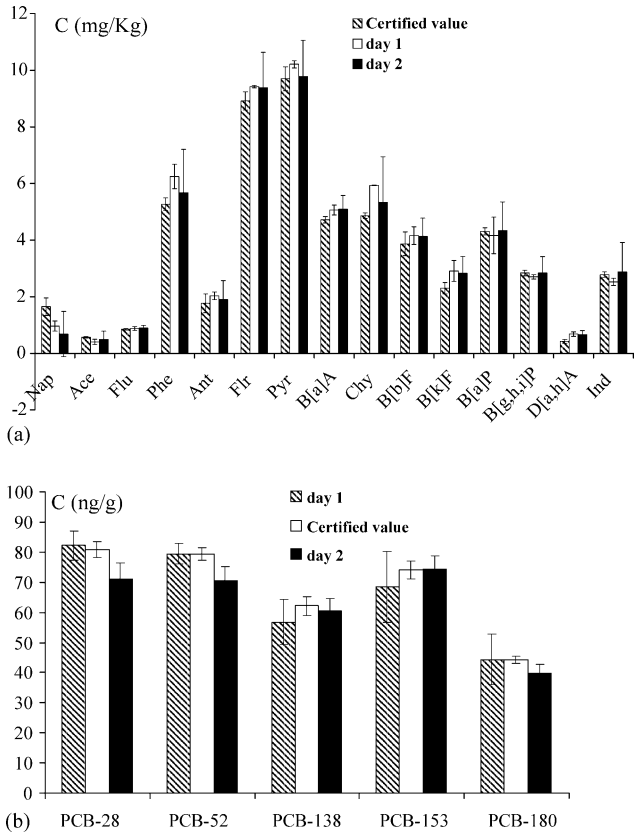

Fig. 1. Comparison of the results (mean value ± 2*s*) obtained for NIST 1944 marine sediment by MAE(acetone)–GC–MS and the certified reference values: (a) PAHs and (b) PCBs.

relative standard deviations obtained in day 2 were higher than those obtained in day 1. In all cases, the relative standard deviations were lower than 20%, except for naphthalene (58%) and acenaphthene (30%) in day 2.

As regards the PCBs, the results agreed with the certified values except for CB-28 and CB-52 in day 2, where slightly lower values were obtained. The relative standard deviations obtained for PCBs in day 1 were higher than those obtained in day 2 but they were always lower than 10%.

In case of PEs and NPs, no certified reference material was available and the validation was not possible in that way. In this case, one sediment sample was extracted twice with the proposed MAE method. The concentrations found in the second extract were 10 times lower than the values obtained for the first extract. No detection of the analytes in the second extraction did not guarantee that an exhaustive extraction had occurred but it proved that the extractable amount of analytes had been effectively extracted.

Thus, it could be concluded that acetone could be an optimum solvent for the simultaneous MAE of PAHs, PCBs, PEs and NPs. From the results shown in Fig. 1a, the clean-up procedure for PAHs was also validated since all extracts had been submitted to the clean-up procedure mentioned above.

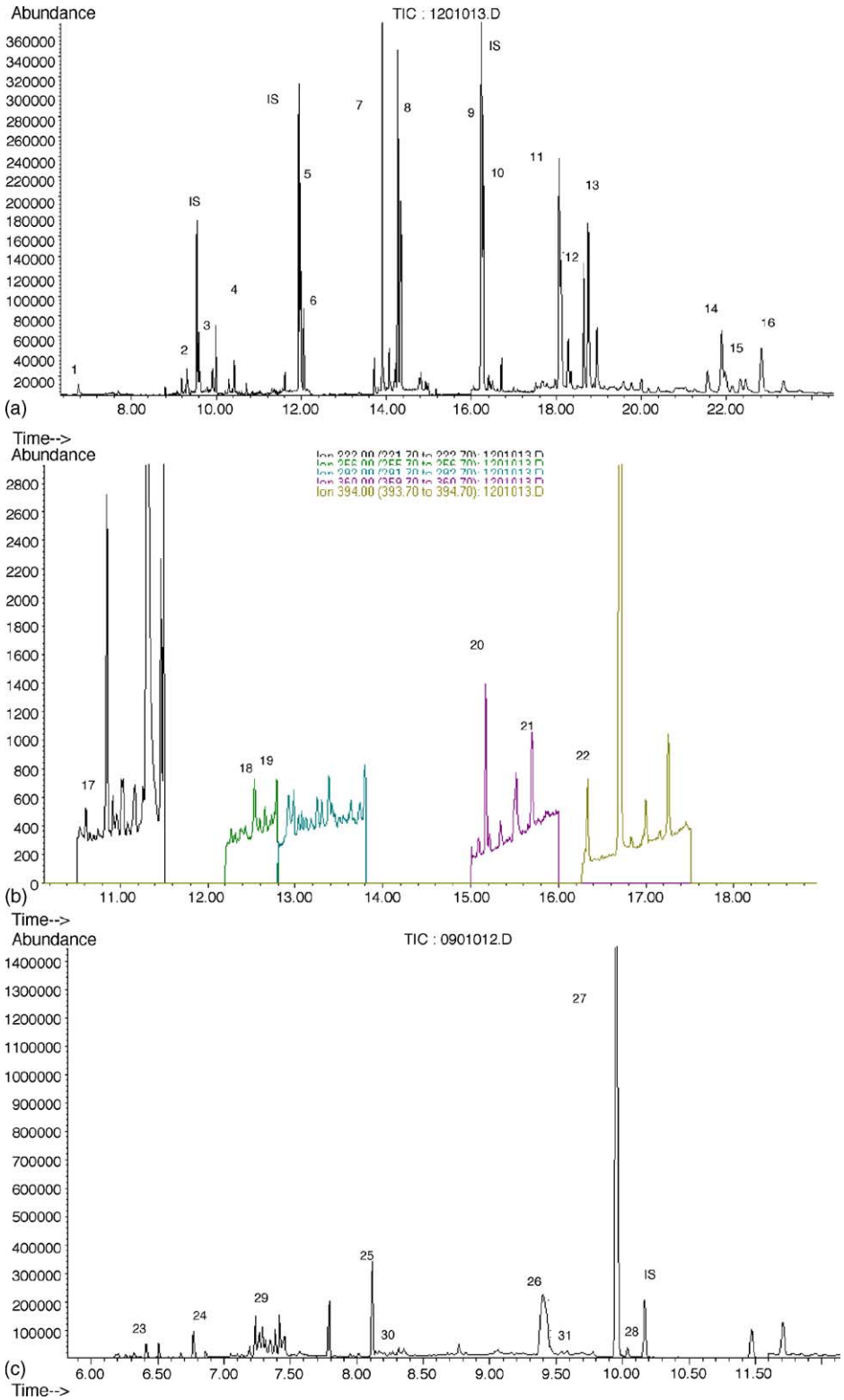

Fig. 2. Chromatograms obtained for a sediment sample from sampling point D. (a) PAHs, (b) PCBs and (c) PEs and NPs. (1) Nap; (2) acy; (3) ace; (4) flu; (5) phe; (6) ant; (7) flr; (8) pyr; (9) b[a]a; (10) chy; (11) b[b]f; (12) b[k]f; (13) b[a]p; (14) d[a,h]a; (15) b[g,h,i]p; (16) ind; (17) CB-10; (18) CB-28; (19) CB-52; (20) CB-138; (21) CB-153; (22) 180; (23) DMP; (24) DEP; (25) DBP; (26) BBP; (27) DEHP; (28) DOP; (29) NPs; (30) NP1EOs; and (30) NP2EOs.

Table 3
Concentrations of PAHs (mg kg^{-1}), PCBs (μg kg^{-1}), PEs (mg kg^{-1}) and NPs (mg kg^{-1}) observed in four sampling points (A–E) of the Urdaibai estuary in March 2003

	A	B	D	E
PAHs				
Nap	1.5	0.02	0.03	0.91
Acy	1.4	0.04	0.01	1.5
Ace	3.1	0.04	0.03	0.51
Flu	1.7	0.03	0.01	1.3
Phe	11	0.19	0.09	7.0
Ant	4.9	0.07	0.02	3.1
Flr	22	0.50	0.13	14
Pyr	16	0.33	0.10	11
B[a]A	12	0.27	0.07	7.7
Chy	20	0.47	0.12	11
B[b]F	16	0.47	0.23	9.8
B[k]F	6.6	0.19	0.08	3.9
B[a]P	11	0.31	0.17	6.7
Ind	6.7	0.25	0.23	4.1
D[ah]A	3.2	0.15	0.13	2.0
B[ghi]P	3.4	0.22	0.20	3.4
∑PAHs	142	3.5	1.6	88
PCBs				
CB-10	<LOD	<LOD	<LOD	<LOD
CB-28	1.5	1.1	4.4	1.9
CB-52	1.2	<LOD[a]	1.0	1.3
CB-138	2.3	2.4	3.8	5.8
CB-153	1.7	1.7	1.4	5.0
CB-180	1.5	1.3	3.0	4.5
∑PCBs	6.6	6.1	9.3	17
PEs				
DMP	<LOD	<LOD	<LOD	<LOD
DEP	<LOD	<LOD	0.24	0.24
DBP	0.46	0.02	0.31	0.79
BBP	0.50	0.52	0.73	1.0
DEHP	17	10	10	14
DOP	<LOD	<LOD	<LOD	<LOD
NPs				
NP	0.41	0.14	1.1	0.41
NP1EO + NP2EO	0.22	<LOD	1.5	<LOD

[a] <LOD, under the limit of detection (see Table 1).

3.3. Application to sediment samples from the Urdaibai estuary

As an application, sediment samples collected at four different sampling points of the Urdaibai estuary in March 2003 were analysed. Reagent blanks were processed in the same way in order to estimate the detection limits. Some sediment samples were analysed in duplicate to calculate the repeatability (expressed as RSD) of the method. The limits of detection (LODs) and RSDs of each analyte are included in Table 1. Since the RSD deferred for sediment samples collected at various sampling points depending on the concentration level and the complexity of the matrix, the RSD interval obtained for the different duplicates has been included. The RSD value obtained for BBP (butyl, benzyl phthalate) was high (40–44%). We think that this high RSD values were due to an impurity with a similar retention time and which also contained the ion $m/z = 149$. In this sense, before quantification it was always verified that the correct relationship was found for the ions $m/z = 91$ and $m/z = 149$ corresponding to BBP. However, it seems that, even those measures were taken, the interfering compound influenced in the repeatability of BBP. DOP (di-*n*-octyl phthalate) was not quantified in any sample and, therefore, no RSD was calculated.

Fig. 2a–c show the chromatograms obtained in the SIM mode for PAHs, PCBs and PEs and NPs, respectively. Even if PAHs and PCBs were obtained in a single chromatogram, due to the different level of concentration of those families of compounds, a zoom had to be made in the first chromatogram and a second chromatogram had to be included.

The analyte concentrations found are presented in Table 3. In case of PAHs, all sampling points exceeded the AET value (Apparent Threshold value, 1 mg kg^{-1} for total PAHs) established by the US National Oceanic and Atmospheric Administration (NOAA) [31]. In case of PCBs, this AET value was never exceeded (1 mg kg^{-1} for total PCBs) and, in case of DEHP, the concentrations obtained were even ten times higher than the AET value (1.3 mg kg^{-1}), indicating a high pollution of this compound. No AET values have been defined for NPs.

4. Conclusions

A simultaneous extraction procedure was developed using acetone as extraction solvent. The validation of the extraction method proposed was carried out using NIST 1944 certified reference material for PAHs and PCBs and by successive extractions for PEs and NPs. A clean-up and fractionation step was also optimised using Florisil® cartridges and (4:1) *n*-hexane:toluene and ethyl acetate as eluents. The developed method is being successfully applied to the monitoring of PAHs, PCBs, PEs and NPs in sediment samples from different estuaries of the Basque Country (north of Spain). MAE turned out to be a good extraction system for monitoring programmes since the MAE system used in this work can handle up to 12 samples at the same time.

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