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Analysis of tetrabromobisphenol A and other phenolic compounds in water samples by non-aqueous capillary electrophoresis coupled to photodiode array ultraviolet detection

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Abstract

Non-aqueous capillary electrophoresis (NACE) with large-volume sample stacking injection using the electroosmotic flow pump (LVSEP) has been developed for the determination of tetrabromobisphenol A (TBBPA) and other phenolic compounds in environmental matrices. Methanol has been used as run buffer solvent to reduce the electroosmotic flow (EOF). Identification and quantification of the analytes was performed by photodiode array ultraviolet detection. LVSEP–NACE improved sensitivity of the peak height by 90–300-fold. The method developed was applied to the analysis of TBBPA in river water and wastewater samples, using solid-phase extraction (SPE) as sample pretreatment process. The average recoveries of the analytes were in the range of 96–106% and 73–103% for 1 L of river water and 0.5 L of wastewater samples, respectively. When the method was based on off line SPE–LVSEP–NACE, sensitivity was improved by 3300–4500-fold and 1600–2200-fold for river water and wastewater samples, respectively.

Keywords: Brominated flame retardants; Bromophenols; Tetrabromobisphenol A; Tetrachlorobisphenol A; Solid-phase extraction; Non-aqueous capillary electrophoresis; Large-volume sample stacking; Water analysis

1. Introduction

Some organic halogenated compounds are widely used by industry as flame retardant additives in different polymeric materials, like plastics, electronic applications, . . ., to protect products from catching fire. Halogenated flame retardants represent about 45% of the world-wide production [1], and within this group, tetrabromobisphenol A (TBBPA) is the most commonly used, as well as some brominated phenolic compounds, such as 2,4,6-tribromophenol (2,4,6-TriBP) and pentabromophenol (PeBP).

These chemicals can be released to the environment during industrial processes, during the entire life-time of the flame-retarded product and after disposal [2]. Recently, they have been received attention from chemists and biologists because they are both lipophilic and persistent, some of them are either known or suspected endocrine disruptors, and have the ability to bioaccumulate in the food chain, being a potential environmental and human health problem [3].

Chromatographic techniques have been employed for the analysis of polymer additives, being gas chromatography preferred [4,5]. Due to the low concentrations as additives present in a large variety of environmental matrices, different sample pretreatment processes, like extraction and preconcentration, are needed before its separation, detection and quantification.

Capillary electrophoresis (CE) has been proven to be an efficient technique for the separation of charged species. The application of organic solvents in CE as an alternative to aqueous solutions has been constantly increasing [6,7]. This analytical technique usually permits the use of simpler sample

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pretreatments than others, although CE applications are often limited by sensitivity. To overcome this problem, some authors use CE with sample concentration directly on the capillary (on-column stacking). These techniques include field-amplified methods that are based on conductivity differences between the sample and the electrophoretic medium, such as large-volume sample stacking injection using the EOF pump (LVSEP) [6,8,9]. This on-column concentration could stack trace amounts of negatively charged species without polarity switching, and enhanced the sensitivity in comparison with hydrodynamic injection. The electrophoretic mobility of the sample ions must be greater than and opposite to the EOF during both sample stacking and subsequent separation processes, so that they can proceed consecutively under the same voltage [8].

In this work, a new method for the determination of TBBPA and other phenolic compounds in environmental matrices by non-aqueous capillary electrophoresis (NACE) coupled to photodiode array ultraviolet detection has been developed. It has been used LVSEP, with methanol as the run buffer solvent to reduce the EOF. Finally, to test the applicability of the developed method, river water and wastewater samples extracted by SPE were analysed.

2. Experimental

2.1. Reagents and materials

Methanol (HPLC gradient grade), ethyl acetate (for liquid chromatography), acetone (for gas chromatography), hexane (for organic trace analysis), and acetic acid glacial were obtained from Merck (Darmstadt, Germany), dimethyl sulfoxide (DMSO) (HPLC gradient grade) from Aldrich (Madrid, Spain), and hydrochloric acid from Prolabo (Fontenay-Sous-Bois, France). 2,4,6-Tribromophenol (99%), pentabromophenol (96%), tetrabromobisphenol A (97%) and tetrachlorobisphenol A (TCBPA, 98%) were obtained from Aldrich. 2,6-Dibromophenol (2,6-DiBP, 97%) was from Fluka (Buchs, Switzerland). Sodium tetraborate decahydrate and sodium hydroxide were supplied by Merck (Darmstadt, Germany). Ultrapure water was obtained from a Milli-Q system purchased from Millipore (Bedford, MA, USA).

Stock solutions of each phenol derivative were prepared at 4000 μg/mL in methanol. Chemical mixture standards for calibrations were dissolved in methanol to appropriate concentration levels. All solutions were refrigerated at 4 °C and protected against daylight. These solutions were used to make daily working standards solutions by appropriate dilution.

Cellulose ester membrane filters (SMWP, 47 mm, 5 μm; HAWP, 47 mm, 0.45 μm), Durapore membrane filters (GVHP, 47 mm, 0.22 μm), and Durapore Millex syringe filters (SLHV, 25 mm, 0.45 μm) were supplied from Millipore. Oasis SPE cartridges (HLB, 60 mg, 3 mL) were obtained from Waters (Milford, MA, USA).

2.2. CE analysis

Capillary electrophoresis was performed using a HP^{3D} system (Hewlett-Packard, Waldbronn, Germany) equipped with an on-column diode array detection (DAD) system. Absorbances at 210 and 230 nm (direct UV detection) were monitored for the detection of the analytes. The migration order was determined by injecting the individual solution of each compound and by the spectral comparison of each peak in electropherograms with an UV spectra library.

Uncoated narrow-bore silica capillary (supplied by Composite Metal Services, UK) with an effective/total length of 61.5/70 cm and 75 μm i.d. was used. The capillary was thermostated to 25.0 °C. A Chrompack RTE-110B external water bath was used for thermostating the samples to 25 °C.

Standards and samples were injected hydrodynamically by applying a pressure of 50 mbar for 2 s and 300 s, depending on the experiment, and the applied voltage for separation was −30 kV, unless otherwise stated.

New capillaries were rinsed with 1 M sodium hydroxide for 20 min. Before injections, capillaries were conditioned by washing them with 0.1 M sodium hydroxide for 5 min, Milli-Q water for 5 min, and 15 min with the separation electrolyte. After each run (once the electrophoretic separation has finished) the capillary was flushed with organic solvent corresponding to the electrophoretic medium for 5 min and with Milli-Q water for 5 min. The inlet and outlet of the capillary were kept overnight in Milli-Q water.

Methanol was assayed as solvent for non-aqueous background electrolyte preparation. Sodium tetraborate, being readily soluble in methanol, was used as electrolytic salt. The apparent pH (pH_{app}) [10] of the solution was 9.4, adjusted by addition of a sodium hydroxide solution, and measured using a Metrohm 654 pH-meter (Herisau, Switzerland) calibrated with aqueous standard buffer solutions. This solution was prepared freshly each two days, sonicated in a P-Selecta ultrasonic bath (Barcelona, Spain) for at least 4 min and filtered through a membrane of 0.22 μm pore size. Every day all remaining solutions were filtered through a 0.45 μm syringe filter before use.

Data acquisition was done by means of HP^{3D} ChemStation Software (Rev. A.06.01[403]) (Hewlett-Packard, Waldbronn, Germany). Statistical analysis of the response variables were supported by the statistical graphics software system Statgraphics Plus 3.3 (STSC, Rockville, MD, USA).

Oasis SPE cartridges were dried using a Turbo-Vap II Nitrogen Evaporator supplied by Zymark (Hopkinton, MA, USA).

2.3. Sample preparation

An off-line solid-phase extraction (SPE) step was used to cleanup and preconcentrate the samples before analysis. Environmental water samples were collected in a river and a wastewater-treatment plant near Santiago de Compostela (NW Spain).

Milli-Q water and real water samples, non-spiked or spiked with the appropriate standard, were acidified when needed at different pH values between 2.5 and 6.8 with hydrochloric acid. They were filtered through 0.45 μm cellulose ester membrane filters before the SPE to eliminate particulate matter (in some cases, for influent wastewater samples with high content of particulate matter, samples were prefiltered through 5 μm membrane filters). We used Oasis SPE cartridge columns from Waters packed with 60 mg of polystyrene–divinylbenzene (PS–DVB) sorbent. Three organic solvents were assayed as eluents: methanol, ethyl acetate and acidified hexane (containing 2% acetic acid). The SPE Oasis cartridges were conditioned by passing 4 mL of organic solvent, 4 mL of acetone (in the case of solvent incompatibility with water) and 4 mL of Milli-Q water at adequate pH. After that the water sample was loaded trough the cartridge, then the cartridge was washed with 10 mL of Milli-Q water at the corresponding pH, and then dried under nitrogen stream for 45 min at a pressure of 12 psi (1 psi = 6894.76 Pa). The analytes trapped on the column were eluted with organic solvent.

In all cases, in order to determine the optimum elution volume, eluent was subdivided in 1 mL fractions that were subsequently subjected to CE analysis.

2.4. LVSEP

All analytes were dissolved in methanol and introduced hydrodynamically into the capillary with a pressure of 50 mbar for 300 s, unless otherwise stated. After sample injection, a negative voltage of −30 kV was applied for both sample stacking and subsequent separation. Fresh electrolyte and sample solutions were always used for each injection. The compounds, which are present in the anionic form at the pH_{app} of the background electrolyte (9.4), migrate to the detection window by their own electrophoretic mobility while the EOF moves in the opposite direction because they were injected on the cathodic side.

3. Results and discussion

3.1. Separation by non-aqueous capillary electrophoresis

In NACE, the nature and properties of the organic solvent have the strongest influence on the separation efficiency and resolution [11]. Methanol is the most commonly used organic solvent in CE [12]. It has favourable properties, such as dielectric constant, viscosity, and a useful UV range for detection [13], it is an appropriate solvent for common electrolyte salts, and allows LVSEP as field-amplified technique of on-line concentration in NACE (see the next section). Moreover, is a usual solvent used as extractant in many sample pretreatment processes, like SPE, allowing the direct injection of the extracts in the NACE system. For these reasons, it was chosen as the run buffer solvent.

Some parameters affecting the electrophoretic separation were studied with a test mixture of the studied compounds, being salt concentration, electrolyte pH_{app}, and capillary and solutions temperatures the most important.

All of the compounds under investigation have weakly acid hydroxyl groups, so capillary zone electrophoresis (CZE) at high or moderate pH might be suitable for their determination. The pK_a values in water of the bromophenols and halogenated bisphenols considered range from 4.4 and 8.5 [14–19], which means that at a pH value over 8.5 they are expected to be all at least partially dissociated, present in their anionic forms and therefore ready for CE analysis. But this only gave us an idea for choosing the starting experimental conditions, because the solute K_a may change for organic solvents by some orders of magnitude, and their values are unknown. So, optimum electrolyte pH_{app} was determined by testing values in the range of 8.6 and 9.6, obtaining better results at 9.4. Working at lower pH_{app} values the analysis time was too long, and at higher pH_{app} values the separation was incomplete, and some compounds coeluted.

Electrolyte concentration depends on separation requirements. In earlier investigations, three levels of molarity of the running buffer were assayed: 20, 30 and 40 mM sodium tetraborate in methanol. As could be expected, the resolution was improved with the decrease in the ionic strength because of the EOF increasing and the apparent solute mobility decreasing, at the expense of higher analysis time. Best results were reached by using a concentration electrolyte salt of 20 mM, with an analysis time lower than 30 min. So, a 20 mM solution of sodium tetraborate in methanol adjusted at pH_{app} 9.4 was finally chosen as running buffer.

In first runs, capillary and sample tray temperatures in the range of 18.5 and 25.0 °C were tested. Although at 18.5 °C somewhat better results as for resolution for the pair 1 and 2 (for peak assignation see Fig. 1) were obtained, in general, it is not easy to consistently maintain this temperature under usual laboratory conditions so 25.0 °C was the temperature finally chosen.

Fig. 1(A) shows the separation of the standard mixture in the optimised conditions. As it can be seen, all the analytes were baseline separated. Electroosmotic mobility (μ_{eo}) and effective electrophoretic mobilities (μ_{ef}) of the analytes were evaluated. μ_{eo} was measured using DMSO as EOF marker and in positive polarity. Negative values of μ_{ef} were in the range of -2.72×10^{-4} for 2,4,6-TriBP and -2.16×10^{-4} cm^2 V^{-1} s^{-1} for TCBPA, and were higher (absolute values) than μ_{eo} of methanol run buffer (1.27×10^{-4} cm^2 V^{-1} s^{-1}). So, under these conditions, these anionic compounds could reach the detector placed on the anodic side of the capillary.

Linearity, precision, and detection and quantification limits (LODs and LOQs) were evaluated in order to assess the

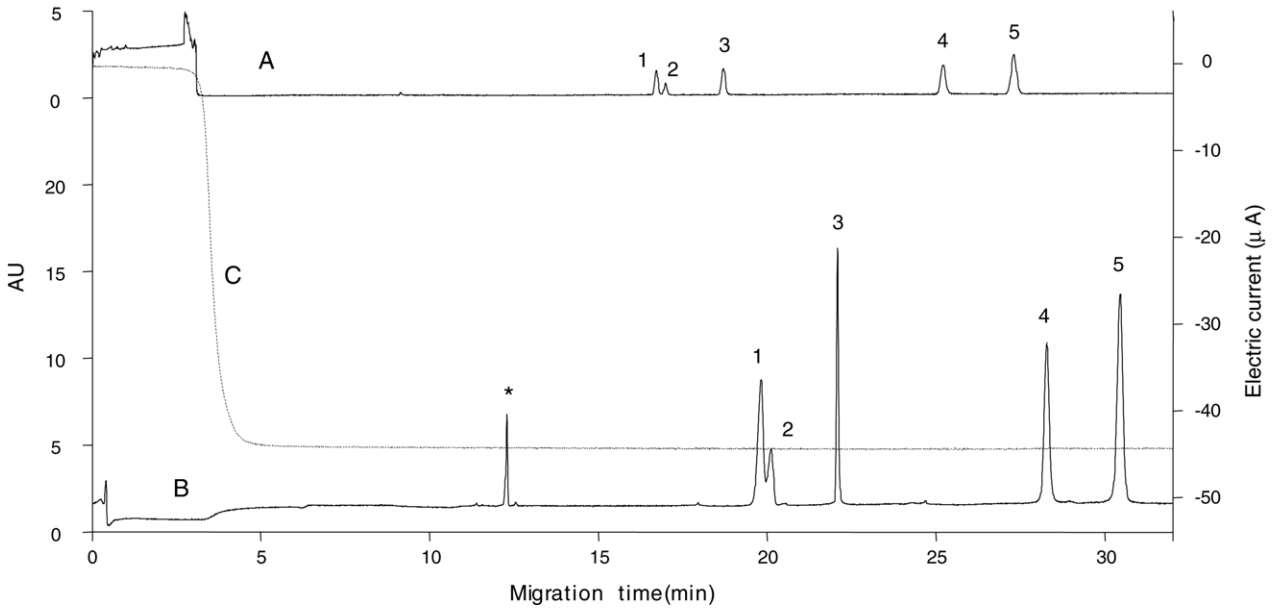

Fig. 1. Electropherograms of standard solutions in methanol of the five compounds in study in concentration of (A) 2 μg/mL and (B) 0.1 μg/mL. (C) Electric current during the LVSEP process. Running buffer: 20 mM sodium tetraborate at apparent pH 9.4; capillary: 70 cm × 75 μm i.d.; applied voltage: −30 kV; detection: 210 nm; capillary and sample tray temperature: 25 °C; hydrodynamic injection: (A) 50 mbar by 2 s, (B) 50 mbar by 300 s. Peak designation: (1) 2,4,6-TriBP, (2) PeBP, (3) 2,6-DiBP, (4) TBBPA, and (5) TCBPA.

performance of this electrophoretic method under the optimal conditions established. Results have been summarized in Table 1. Calibration curves were linear in the concentration ranges studied (from 500 to 10,000 μg/L), and the correlation factor *r* values were higher than 0.999 for all the compounds. Precision was examined by performing six replicate injections of a mixture of the analytes at a concentration of 2 mg/L for all compounds, in the same day (repeatability) and in different days (reproducibility), and were in the range 3–8% R.S.D. in analyte response. The LODs and LOQs were calculated considering peak height and signal-to-noise ratios (S/N) of 3 and 10, respectively.

3.2. LVSEP in the methanol run buffer

The sensitivity achieved with the NACE developed method previously described can be improved significantly by concentrating the samples directly on the capillary using LVSEP. When methanol was used as the running buffer solvent, appropriate suppression of EOF and an increase in the electrophoretic mobilities of the anionic analytes made LVSEP possible [6].

The capillary was (c.a. 95%) filled with the sample solution in methanol when 300 s were used as hydrodynamic injection time. After injection, the methanol matrix was

Table 1
Regression analysis, LODs and LOQs of NACE methods developed in standard solutions

Method	Compound	Calibration curves	Slope standard error	Intercept standard error	LOD (μg/L)[a]	LOQ (μg/L)[a]
NACE, t_{inj} = 2 s[b]	2,4,6-TriBP	$y = 4.422x + 0.504$	0.028	0.145	125	416
	PeBP	$y = 3.071x + 0.394$	0.025	0.129	135	450
	2,6-DiBP	$y = 5.321x + 0.528$	0.038	0.194	130	433
	TBBPA	$y = 8.262x + 0.535$	0.080	0.403	146	485
	TCBPA	$y = 12.746x + 0.883$	0.118	0.594	84	280
LVSEP–NACE, t_{inj} = 300 s[b]	2,4,6-TriBP	$y = 0.693x + 8.528$	0.016	3.043	1.4	4.6
	PeBP	$y = 0.472x + 6.312$	0.015	3.156	1.7	5.5
	2,6-DiBP	$y = 0.504x + 5.398$	0.011	2.145	0.4	1.3
	TBBPA	$y = 0.882x + 5.295$	0.016	3.261	0.5	1.6
	TCBPA	$y = 1.249x + 24.324$	0.043	9.808	0.4	1.3
LVSEP–NACE, t_{inj} = 30 s[b]	2,4,6-TriBP	$y = 81.157x - 1.553$	0.663	1.830	11.6	38.6
	PeBP	$y = 51.707x + 0.378$	0.329	0.901	13.6	45.4
	2,6-DiBP	$y = 8.624x + 0.934$	0.166	0.400	9.7	32.3
	TBBPA	$y = 12.113x - 0.143$	0.183	0.500	11.9	39.6
	TCBPA	$y = 15.963x + 0.160$	0.177	0.481	7.6	25.2

[a] LOD: S/N = 3; LOQ: S/N = 10; detection at 210 nm, except of PeBP at 230 nm.
[b] t_{inj} = injection time; other CE conditions as in Fig. 1.

removed by the EOF pump while the anions were stacked under the electric field of reverse polarity of −30 kV, because of the differences in conductivity between the sample and the electrophoretic medium. As the capillary was filled with the run buffer of high conductivity, the overall EOF became further reduced due to the increased ionic strength. When the EOF and the electrophoretic velocities of analytes were balanced, the migration direction of the stacked analytes was switched toward the detector, and thus the separation of the highly stacked sample occurs.

Fig. 1(B) shows the separation and the enhancement in sensitivity achieved using LVSEP–NACE. The process of removing the methanol plug out of the capillary imposed the differences in migration times between the electropherograms A and B. The mobile anions in the inlet buffer vial, such as borate ions, were also injected hydrodynamically and stacked at the concentration boundary while the methanol plug was being removed [8]. In the electropherogram the peak corresponding to borate is identified by the symbol *.

Fig. 1(C) shows the electric current during the LVSEP process. The intensity of the electric current increased rapidly (in absolute values) for nearly 5 min, while the sample matrix was removed and the ionic strength of the medium in the capillary increased to −44 μA, close to the value registered when the capillary was filled with the run buffer. Then the current stabilised, indicating that most of the methanol sample matrix was replaced with the run buffer, and the analytes were stacked at the beginning of the capillary, reversing their migration direction towards the outlet vial overcoming the reduced EOF [6,8].

The analytical performance of LVSEP–NACE was also evaluated, and the method developed showed good linearity and precision within the concentration range studied (20–400 μg/L), with correlation factor *r* values higher than 0.99 and % R.S.D. between 5 and 9% for all the compounds (see Table 1).

Coupling LVSEP to NACE improved the LODs about two orders of magnitude in comparison with normal hydrodynamic injection. This allows the application of the procedure for samples in the μg/L level using conventional UV absorption detection.

3.3. Analysis of water samples

For the application of the developed procedure to real river water and wastewater samples, the analytes were extracted using SPE Oasis cartridges. Parameters affecting the SPE process (e.g. sample pH, eluent volumes and composition) were studied. Preliminary experiments were conducted on ultrapure (Milli-Q) water samples spiked with all studied compounds at the 0.8 μg/L level. In the view of pK_a values (see Section 3.1) pH of samples was adjusted at 2.5 to enhance the retention of analytes in the polymeric sorbent. Volume of samples was 500–1000 mL. In these experiments recoveries were ranging between 86 and 117% for all analytes. Further experiments, however, evidenced that sample's pH has not significance in the overall efficiency of the SPE process as can be seen in Fig. 2. This means that samples can be processed without pH adjustment. Moreover, since lower pH values favour the adsorption of matrix components in samples (mainly humic and fulvic acids) on the polymeric sorbent, it is advisable to not acidify the samples before extraction [11,20–22].

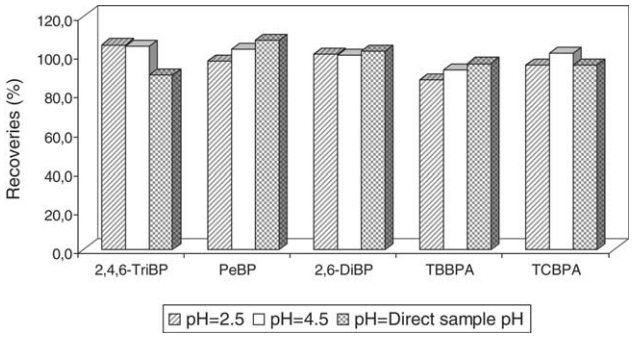

Fig. 2. Effect of the water sample pH on SPE recoveries in the analysis of 1 L of river water samples spiked at a concentration of 6 μg/L for all compounds.

Three solvents of different polarity, methanol, ethyl acetate and hexane acidified with 2% of acetic acid, were assayed as cartridge eluting solvents in the SPE process. Acidified hexane is the less favourable approach because the need of evaporation and solvent exchange due to incompatibility with the solvent background electrolyte. This solvent was soon abandoned in the view of its low efficiency to elute the analytes retained in the cartridge. Ethyl acetate exhibit good behavior as eluting solvent but caused current breakdown in the separation process unless fully exchanged by other compatible solvent. Losses of analytes were registered in the evaporation and solvent exchange processes so the experiences with ethyl acetate were also abandoned. Methanol provided the better performance in removing effectively the analytes from the sorbent and giving an extract fully compatible with the background electrolyte which reduces sample preparation stages and error chances.

Optimal elution volume was evaluated as described in Section 2.3 by measuring successive eluting fractions until no signal for analytes can be seen and the sum of signal in the accumulated fractions demonstrated that quantitative recoveries have been attained. A volume of 3 mL of methanol was found to completely elute all the analytes from the cartridges.

At the time of testing these conditions on real river and wastewater samples some added difficulties appeared as expected. Matrix components affects the ionic strength of sample extracts so the removing time of sample plug in the stacking process increased. As a consequence, recoveries were affected because a fraction of the sample kept out the capillary during stacking. Logically, this effect was more noticeable for longer injection times. For samples spiked at 1 μg/L level, losses of 40–50% were observed using injection times of 300 s. Consequently, injection time was reduced to a level enabling quantitative injection of analytes in samples. Using injection times of 30 s recoveries equivalent to those

previously reported were attained. Also good precision (% R.S.D. between 3 and 7% for all the compounds) and linearity (correlation factor *r* values higher than 0.99) within the concentration range studied (100–5000 μg/L for all compounds) were obtained at the logical expense of LODs (Table 1). Fig. 3 shows the electropherograms obtained in the analysis of river water and wastewater extract using the described conditions.

As can be seen in the electropherograms in Fig. 3, non-spiked samples of influent wastewater exhibit several small peaks, some of them in the vicinity of 2,6-DiBP, TBBPA and TCBPA. Experiments using longer injection times and decreasing the tray temperature to enhance separation and to provide more clear spectral information evidenced that these small peaks did not correspond to the analytes studied. In any case, it is advisable to prepare calibration lines based on peak height data to avoid the effect of these small peaks in the tail of analyte peaks.

Table 2 summarized the average recoveries for the studied analytes from four independent 1 L river water samples, four effluent and three influent wastewater samples (500 mL each). These recovery values were checked for consistency in the spiking range 1.2–12 μg/L for all studied compounds. Recoveries in Table 2 are in good agreement with those reported for ultrapure water thus showing that matrix effects in SPE processes were adequately controlled when samples were processed at their natural pH.

Recoveries for river and effluent wastewater samples grant the use of external calibration. However, for influent wastewater samples an evident matrix effect appears, thus making advisable the use of standard additions in the analysis of these samples.

In any case, breakdown volumes must be evaluated in cartridges to confirm that the sample volumes proposed (1 L in the case of river water and 0.5 L for wastewater) can be routinely handled. To verify this point experiences of sample extraction by passing samples through two cartridges connected in tandem were carried out. Both cartridges were eluted independently and extracts analysed. In no case, eluates from the second cartridge evidenced detectable amounts of analytes. Further series of experiments extracting double sample volumes confirm excellent retention of analytes in the cartridges. This means that quantification limits can be decreased by processing up to 2 L of river water samples or 1 L of wastewater samples if needed at the expense of considerably higher processing times.

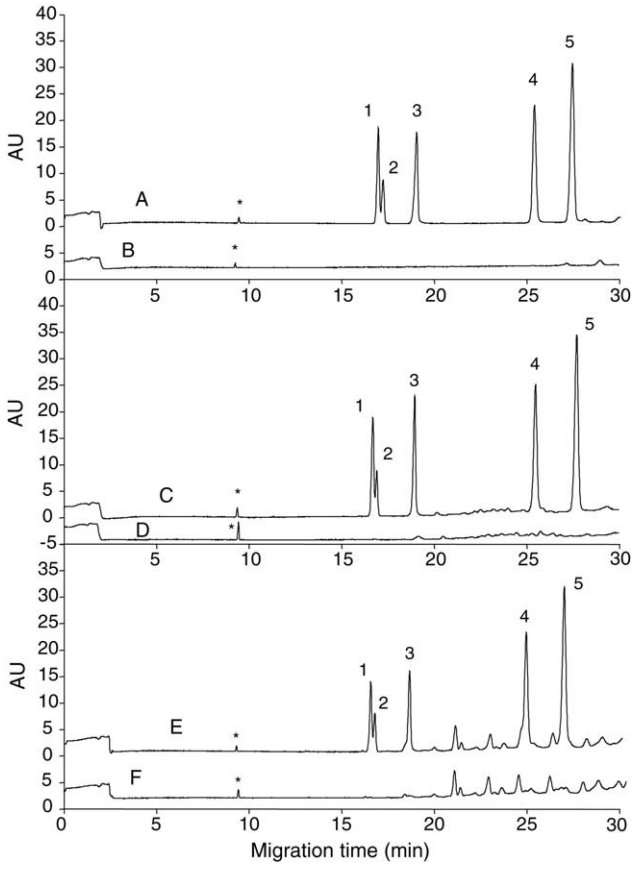

Fig. 3. Electropherograms obtained from SPE extracts of (A) 1 L of river water sample spiked at a concentration of 6 μg/L for all compounds, (B) 1 L of river water non-spiked sample (C) 500 mL of effluent wastewater sample spiked at a concentration of 12 μg/L for all compounds, (D) 500 mL of non-spiked effluent wastewater sample, (E) 500 mL of influent wastewater sample spiked at a concentration of 12 μg/L for all compounds, (F) 500 mL of non-spiked influent wastewater sample; hydrodynamic injection, 50 mbar by 30 s. Other CE conditions and peak assignment as in Fig. 1.

Table 2
Recoveries of compounds on the Oasis cartridge from spiked river water and wastewater samples

Compound	SPE recoveries (%)						SPE–NACE: LOQ (μg/L)[b]		SPE–LVSEP–NACE: LOQ (ng/L)[b]	
	River water	R.S.D. (%)[a]	Effluent	R.S.D. (%)[a]	Influent	R.S.D. (%)[a]	River water[c]	Wastewater[d]	River water[c]	Wastewater[d]
2,4,6-TriBP	101.4	3.4	100.5	1.1	73.0	3.7	1.2	2.4	116	232
PeBP	105.8	3.4	102.6	0.9	82.0	0.2	1.4	2.8	136	272
2,6-DiBP	102.2	3.4	103.4	0.3	88.2	8.3	1.3	2.6	97	194
TBBPA	95.5	1.9	101.2	3.7	93.6	7.5	1.5	3.0	119	238
TCBPA	96.2	2.5	102.3	2.7	94.0	2.2	0.8	1.6	76	151

LOQs of SPE–NACE and SPE–LVSEP–NACE in real water samples.

[a] $n = 4$ for river water and effluent wastewater, and $n = 3$ for influent wastewater.

[b] LOQ: S/N = 10; detection at 210 nm, except of PeBP at 230 nm.

[c] Water volume: 1 L.

[d] Water volume: 0.5 L.

The LOQs including the SPE procedure were considerably improved for both NACE and LVSEP–NACE methods (see Tables 1 and 2). Thus, sensitivity for SPE–LVSEP–NACE method was enhanced between 3300–4500-fold and 1600–2200-fold for river waters and wastewater samples, respectively.

4. Conclusions

This work describes a simple NACE method developed to stack trace amounts of negatively charged halogenated phenolic and bisphenolic compounds without polarity switching using methanol to suppress the EOF flow. Stacking can produce concentration factors that can increase the sensitivity of the method to the low μg/L levels, being about 100 times greater than with usual hydrodynamic injection.

Solid-phase extraction using Oasis cartridges provide excellent recoveries of compounds under study from water samples at neutral pH. Employing the background electrolyte solvent as eluent, the SPE extracts of anionic samples can be directly injected into the NACE system without any dilution or solvent exchange. It allows a good compatibility between extraction and electrophoretic processes.

Using LVSEP, it enhanced the on-line concentration of the analytes studied, giving quantification limits under μg/L levels with conventional UV absorption detection, and consequently SPE–LVSEP–NACE can be successfully applied to the quantitative determination of the compounds studied at trace levels in water samples.

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