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Decanoic acid reverse micelle-based coacervates for the microextraction of bisphenol A from canned vegetables and fruits

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ABSTRACT

Decanoic acid reverse micelle-based coacervates were proposed for the extraction of bisphenol A (BPA) from canned vegetables and fruits prior to its determination by liquid chromatography and fluorescence detection at $\lambda_{exc} = 276$ nm and $\lambda_{em} = 306$ nm. The procedure involved the extraction of minute quantities (300–700 mg) of homogenized food sample with an aqueous solution containing 10% of THF and 0.5% of decanoic acid, conditions under which the coacervate (around 340 μL) formed *in situ* and instantaneously. The overall sample treatment, which included extraction and centrifugation, took about 25–30 min, and several samples could be simultaneously treated using conventional lab equipment. No clean-up or solvent evaporation were required. Extraction efficiencies mainly depended on the decanoic acid and THF concentration in the aqueous solution and were not affected by the pH or the temperature in the ranges studied (1–4 and 20–60 °C, respectively). Recoveries in samples ranged between about 81 and 96%. The precision of the method, expressed as relative standard deviation, was about 3% and the quantitation limit was around 9 ng g^{-1}, which was far below the current specific migration limit (SML) set for BPA by the EU Commission (600 ng g^{-1}). The method was successfully applied to the determination of BPA in the solid content of canned fruit salad, peaches in syrup, mango slices, red peppers, sweetcorn, green beans and peas. BPA was present at concentrations in the range from 7.8 to 24.4 ng g^{-1} in canned fruits and from 55 to 103 ng g^{-1} in canned vegetables.

1. Introduction

Epoxy resins are widely used as internal coatings in canned food thus preventing the metal from the can corroding and migrating into the can contents. Bisphenol A (BPA) is a major component of epoxy resins [1]. The residual non-polymerized BPA easily migrates into the food during the thermal treatment required for its sterilization [2]. Because of the estrogenic character of BPA [3–5], a specific migration limit (SML) of 600 ng g^{-1} was set by the EU Commission in 2004 [6] in order to ensure consumer health protection.

The consumption of fruits and vegetables plays a vital role in providing a diversified and nutritious diet [7]. Canned vegetables are a convenient staple for evening meals and make up about 10% of total vegetable human consumption [8]. Canned fruits accounts for about 7% of total fruit intake [9]. According to the results obtained by different researchers, the migration of BPA into this type of foods causes their contamination at

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concentration levels around 20–100 ng g^{-1} [10–18]. Although these values are below the SML for BPA, the low-dose reproductive and developmental effects of this contaminant is currently the focus of a strong debate in the scientific community, the conclusions going from no risk to human health [11] to the need for a new risk assessment [4]. So, the determination of BPA in food is required for both the control of the compliance of current legislation and the assessment of human exposure.

Quantification of BPA in canned foods has frequently been performed by gas chromatography/mass spectrometry (GC/MS) [2,12,19] however, the need for derivatisation has fostered the use of liquid chromatography (LC) coupled to fluorimetry [15,17,20–22] or mass spectrometry (MS) [14,23]. Sample treatment is always the bottleneck of these methods since tedious, solvent-consuming and rather impracticable procedures are used.

Three main strategies have been proposed for the extraction of BPA from canned vegetables and fruits so far. The first one involves the use of repetitive extractions with high volumes of organic solvents (e.g. 270 mL of methanol [17] or 40 mL of acetonitrile [11,18]), subsequent evaporation to dryness and redissolution with a low-volume, chromatographically compatible, solvent. In the second strategy, the organic solvent extraction, which still involves large solvent volumes (e.g. 100 mL of acetonitrile for treatment of 5 g of sample [14,15]) is followed by two clean-up steps consisting in the rinse of the acetonitrile phase with 75 mL of *n*-hexane and subsequent solid phase extraction (SPE) in Oasis HLB (hydrophilic–lipophilic balance) cartridges [14,15]. The use of MS for BPA detection simplifies this procedure (e.g. 25 mL of acetonitrile are used and the rinse with *n*-hexane becomes unnecessary [24]). Recently, sol–gel immunoaffinity columns made up of BPA antibodies immobilized in a silica matrix have been proposed for the clean-up of the acetonitrile extracts (2 mL) obtained after duplicate extraction of 1 g of canned vegetables and fruits [13,25]. Sol–gel pre-columns have to be used to prevent the clogging of the immunoaffinitty columns from small particles originating in the sample extracts. This strategy reduces drastically the volume of organic solvent required for sample treatment, but the need to prepare the columns makes it rather time consuming and complicated for routine analysis. Because of the strong demand for environmentally friendly methods that permit high sample throughput, this research assesses the use of reverse micelle-based coacervates for the extraction of BPA from canned vegetables and fruits.

Coacervates are water immiscible liquids that separate from colloidal solutions under the action of a desolvating agent, mainly changes in the temperature or the pH of the colloidal solution or the addition of electrolytes or a non-solvent for the macromolecule [26,27]. Their application to analytical extractions was proposed by Watanabe and Tanaka [28] and Watanabe et al. [29] a long time ago, and for many years it focused on the use of non-ionic micelle-based coacervates for the extraction of hydrophobic compounds from environmental waters [30–32]. In recent years, the development of coacervates made up of zwitterionic [33], anionic [34] and cationic [35] aqueous micelles, and reverse micelles [36] and vesicles [37] have extended significantly the scope of these extractants with regard to both the polarity range of compounds that can be extracted [36,37] and the samples that may be analysed (e.g. soil and sediment [38], sludge [39,40], etc.).

Coacervates have intrinsic properties that greatly benefit extractions. Thus, because of the special structure of the supramolecular assemblies making them up, they are multifunctional solvents with the ability to establish multiple bonds with solutes, which results in very high extraction efficiencies. Also, the high concentration of surfactant in some coacervates (e.g. around 0.7–1 mg μL^{-1} in the reverse micelle- and vesicle-based coacervates) [36,37] permits good solute recovery using minute coacervate volumes, which results in low detection limits without the need to evaporate extracts. On the other hand, the basis and procedures of coacervative extraction are similar to those of conventional solvent-based extraction, and like the latter, it uses conventional lab equipment, which makes their implantation easy. All these properties make that coacervative extraction has a great potential to simplify sample treatment in food analysis.

This paper focus on the use of decanoic acid reverse micelle-based coacervates for the extraction of BPA from canned vegetables and fruits using minute amounts of food sample and coacervate. The aim was to develop a simple, rapid and low cost method suitable for the routine control of this contaminant. The research included the study of the parameters affecting the extraction efficiency of BPA, the study of the quantitative performance of the method using LC–FL and its application to the determination of BPA in several samples of canned vegetables and fruits purchased in local supermarkets.

2. Experimental

2.1. Chemicals

All chemicals were of analytical reagent-grade and were used as supplied. Bisphenol A (BPA) [$(CH_3)_2C(C_6H_4OH)$] and decanoic acid [$CH_3(CH_2)_8COOH$] were obtained from Fluka (Madrid, Spain). Tetrahydrofuran, hydrochloric acid and HPLC-grade acetronitrile were purchased from Panreac (Barcelona, Spain). Stock solutions of BPA (0.5 g L^{-1}) were prepared in acetonitrile and stored under dark conditions at 4 °C not more than three months. Working solutions were made by appropriate dilution of the stock solution with acetonitrile. Ultra-high-quality water was obtained from a Milli-Q water purification system (Millipore, Madrid, Spain).

2.2. Apparatus

The liquid chromatographic system used (Spectra System SCM1000, ThermoQuest, San Jose, CA, USA) consisted of a P4000 quaternary pump, a UV6000LP diode-array detector and a FL3000 fluorescence detector. In all experiments, a Rheodyne 7125 NS injection valve, with a 20 μL sample loop, was used. The stationary-phase column was a Hypersil ODS C_{18} column (5 μm, 4.6 mm × 150 mm) from Análisis Vinicos (Tomelloso, Spain). A Mixtasel Selecta centrifuge (Barcelona, Spain) was used for sample preparation.

2.3. Samples

Canned vegetables (red peppers, sweet corn, green beans and peas) and fruits (fruit salad, peaches in syrup and mango slices) were bought in supermarkets in Córdoba (Spain). The unopened cans were stored at room temperature. After the cans were opened, the liquid part was removed by sieving and the solid portion was homogenized using a food mixer. Every sample was analyzed in triplicate using 300 mg aliquots. Samples no immediately analyzed were stored at −20 °C in vinyl bags. The type of the internal coatings of the cans was not investigated.

2.4. Coacervative microextraction of BPA

Decanoic acid (200 mg) was dissolved in THF (4 mL) in a specially designed glass tube with a narrow neck (tube: 25 mm high, 34 mm i.d.; neck; 63 mm high, 8 mm i.d.). Then, 36 mL of 1.3 mM hydrochloric acid aqueous solution were added. Immediately, the coacervate phase separated from the bulk solution. Once the food sample (300 mg) was added to this mixture, it was stirred at 1200 rpm for 15 min to favor BPA extraction and then, centrifuged at 3800 rpm ($2200 \times g$) for 10 min to accelerate phase separation. Next, the volume of the coacervate, which was standing at the narrow neck of the glass tube, was measured with a digital calliper. Finally, 20 μL were withdrawn with a microsyringe and analysed.

2.5. Liquid chromatography/fluorimetry

Quantification of BPA and separation from matrix components was carried out by liquid chromatography–fluorimetry. The mobile phase consisted of water and acetonitrile. The flow-rate was 1 mL min^{-1}. The chromatographic conditions for analysis of canned fruits were: 50:50 (water:acetonitrile). The retention time for BPA was 4.0 min and the corresponding capacity factor (k'), calculated from $k' = (t_R - t_0)/t_0$ where t_0 is the retention time of acetone (hold-up time), was 1.7. The analysis of canned vegetables was carried out using the following elution program: linear gradient from 70:30 to 45:55 (water:acetonitrile) in 13 min and then, isocratic initial conditions (70:30) to clean and stabilize the chromatographic system. BPA eluted to a retention time of 9.3 min. The selected wavelengths were 276 nm (excitation) and 306 nm (emission). Calibration was run by injecting 20 μL of standard solutions in acetonitrile containing between 0.14 and 20 ng. Quantification was performed by measuring peak areas. Correlations between peak areas and BPA amount were in the range 0.9995–0.99990.

3. Results and discussion

3.1. Reverse micelle-based coacervative extraction of bisphenol A

3.1.1. General considerations

Decanoic acid ($pK_a = 4.8 \pm 0.2$) is sparingly soluble in water. It dissolves in THF by forming reverse micelles with different critical aggregation concentrations (e.g. 4.8, 7.6 and 51 mM) according to a sequential-type self-association model [36]. The addition of water to THF solutions containing decanoic acid reverse micelles causes the partial desolvation of the aggregates, which makes easier micelle-micelle interaction and leads to the formation of bigger aggregates. As a result, these aggregates become insoluble in the water:THF solution and separate as an immiscible liquid. The Fig. 1 depicts the region encompassed by the coacervate as a function of THF and decanoic acid concentrations. THF percentages below and above the boundaries of this region caused precipitation and solubilization of decanoic acid, respectively.

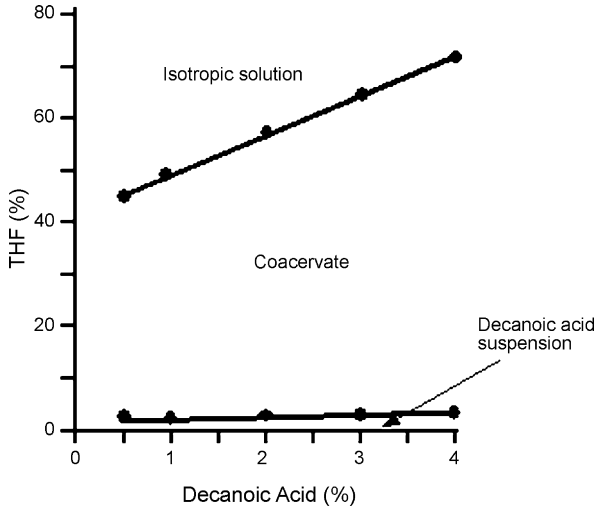

Fig. 1 – Binary diagram of phase boundaries for tetrahydrofuran–decanoic acid–water mixtures at room temperature.

The vegetable and fruit samples to be extracted were directly added to ternary mixtures made up of decanoic acid (0.25–1%, w/v), THF (5–30%, v/v) and water. Three phases were always observed after the extraction and centrifugation of the food samples; namely a solid phase made up of insoluble matrix components at the bottom, a THF:water solution containing decanoic acid monomers and dissolved matrix components in the middle, and a coacervate phase containing the extracted food components at the top. At equilibrium, BPA distributed among these three phases, although the high solubility of BPA in the coacervate (~500 g L^{-1}) compared to that in THF:water (e.g. ~150 mg L^{-1} for 10% THF) greatly favoured the partition of the analyte to the coacervate phase.

3.1.2. Optimization

The influence of the composition of the coacervate and different operational parameters (e.g. extraction time, stirring rate, temperature, pH, etc.) on both the volume of the coacervate and the recovery of BPA was investigated. The experiments were made by dissolving decanoic acid (100–400 mg) in tetrahydrofuran (5–30%) in a specially designed centrifuge tube that had a narrow neck (7 mm i.d.). Then, water at pH about 3 was added to give a final volume of 40 mL, which caused the immediate separation of the coacervate phase from the bulk solution. Next, a food amount (100–1000 mg) fortified with 50 ng of BPA was added. The mixture was stirred in

Table 1 – Protein, carbohydrate and fat composition of the canned foods selected

Food (100 g)	Protein (g)	Carbohydrate (g)	Fat (g)
Vegetables			
Red peppers	0.6	6	0.2
Sweetcorn	2.9	11.2	0.9
Green beans[a]	1.2	4.2	0.5
Peas	5.5	10.7	0.4
Fruits			
Fruit salad	0.4	14	0
Peaches in syrup[a]	0.5	12.3	0
Mango slices	0.4	19.2	0

[a] Data obtained from Ref. [43].

a range of conditions (600–1500 rpm, 5–30 min, room temperature at 60 °C) and then centrifuged (2200 × *g*, 15 min) to speed up the separation of the two phases. From these results and the instrumental quantification limit (IQL) obtained for BPA (injection of 0.14 ng in the chromatographic system), the corresponding method quantification limits (MQL) were estimated and used as a criterion for the selection of the optimal conditions for extraction. Conditions giving minimal MQL were selected provided that the recovery of BPA was above 70% [41], and the relative standard deviation of the method was below 10% [42].

Canned peas were used as a food sample model for optimisation studies. The selection was based on its higher protein content, compared to the other foods investigated, and its representative content in carbohydrates and fat (Table 1). The information about food composition was extracted from the can label or, as it was not supplied, from the average values provided in food composition tables (e.g. [43]). Independently on the food analysed, a whitish precipitate, which was standing at the bottom of the coacervate as a very thin layer, was extracted. This precipitate was caused by the proteins present in the samples, which were agglutinated by the reverse micelles and extracted by the coacervate, but they did not interfere in the recovery of BPA. Every optimisation experiment was carried out by analysing three non-fortified and three BPA fortified (100–200 ng g^{-1}) pea samples (300 mg) which were prepared according to the procedure specified in Section 2.4.

3.1.2.1. *Influence of the coacervate composition on the extraction of BPA.* Decanoic acid and THF are the major components of the coacervate, so their concentration in the colloidal solution greatly influences both the volume of extractant yielded and the extraction efficiency for BPA. Water is only a minor component of the coacervate on account of its non-solvent character for the decanoic acid reverse micelles.

The volume of coacervate increased linearly as the amount of decanoic acid did, which indicated that the composition of the surfactant rich-phase kept constant provided that the concentration of the other components remained unchanged. The corresponding equation (100–400 mg decanoic acid and 10% THF) was $y = 22 \pm 22 + 1.5 \pm 0.1x$, where *y* was the volume of coacervate in μL and *x* is the amount of decanoic acid in mg. The correlation coefficient (r^2) was 0.995. The slope of the linear relationship was similar to that obtained in the absence of food sample [44], so although matrix components could be incorporated to the coacervate they did not influence its volume. Recoveries higher than 80% were obtained for BPA at decanoic acid concentrations as low as 0.5% (Table 2), which proved the high solubilization capability of the coacervate for this contaminant. Although lower MQL could be obtained by decreasing the decanoic acid concentration used for extraction (e.g. 0.25% in Table 2) this option was not recommended because of the low recoveries obtained. So, a decanoic acid concentration of 0.5% was selected for further studies.

The relationship between the coacervate volume and the THF percentage was exponential (Table 2), which indicated that progressively more THF was incorporated to the coacervate and consequently the reverse micelles became more and more diluted. The corresponding equation (decanoic acid = 200 mg) was $y = 228 \pm 6\, e^{0.039 \pm 0.001x}$ ($r^2 = 0.995$), where y was the volume of the coacervate in μL and *x* is the percentage of THF. Maximal extraction efficiencies were obtained in the range 10–20% of THF (Table 2). Below this range, only a fraction of the surfactant was incorporated to the coacervate [36] and as a result the recovery decreased. On the other hand, the solubility of BPA in the bulk solution increased as the THF concentration did, which resulted in decreased partition coefficients for THF percentages above 20% and consequently in lower recoveries (Table 2). We selected 10% THF, which gave the highest recoveries and MQL of around 9.3 ng g^{-1}.

3.1.2.2. *Influence of operational parameters on the extraction of BPA.* Food matrix components retain BPA through different types of interactions (e.g. Van der Waals, hydrogen bond, π-cation, etc.) as it migrates from the can coating. So, the optimization of such parameters as extraction time, extraction temperature and stirring rate becomes important to break BPA–matrix interactions and consequently to make BPA extraction faster. None of the operational parameters investigated affected the volume of coacervate yielded because coacervates were formed before extraction and their formation was not influenced by the matrix components of the foods analyzed. So, MQL directly depended on the recoveries obtained for BPA under the different experimental conditions assessed.

The time used for extraction was important for the recoveries obtained for BPA (Table 3). Equilibrium conditions were reached after 15 min of extraction and this time was selected as optimal for further studies. The stirring rate influenced the kinetics of the extraction and consequently more time was required to reach equilibrium conditions at the lowest stirring rates tested (Table 3). A value of 1200 rpm was selected as optimal. The temperature scarcely influenced the extraction kinetics for BPA in the range investigated (20–60 °C, Table 3), so the whole procedure was carried out at room temperature.

The coacervation phenomenon occurs from protonated decanoic acid ($pK_a = 4.8 \pm 0.2$), so extractions must be carried out below pH 4. Recoveries for BPA ($pK_a = 9.46$) were not affected by the pH in the range 1–4. The procedure was carried out at about pH 3.0–3.3 by the addition of hydrochloric acid.

Table 2 – Coacervate volumes, mean recoveries and method quantification limits obtained for BPA as a function of decanoic acid and THF concentrations

Coacervate composition	Coacervate volume (μL)	Mean recovery ± standard deviation[a] (%)	Estimated quantitation limits (ng g^{-1})
Decanoic acid[b] (%)			
0.25	161	55 ± 3	6.8
0.5	342	86 ± 2	9.3
0.75	503	90 ± 3	13.0
1	620	95 ± 4	15.2
Tetrahydrofurane[c] (%)			
5	290	71 ± 3	9.5
7.5	304	77 ± 3	9.2
10	342	86 ± 2	9.3
15	392	87 ± 3	10.5
20	495	86 ± 3	13.4
25	622	78 ± 3	18.5
30	734	70 ± 2	24.4

[a] $n = 3$; 300 mg peas spiked with 60 ng BPA.
[b] THF = 10% (v/v).
[c] Decanoic acid = 0.5% (w/v).

3.2. *Analytical performance*

Calibration curves were run by injecting 0.14–20 ng of BPA in acetonitrile. No differences in peak areas or retention times were observed for the analyte injected in organic solvent or coacervate. The slope and the intercept of the calibration curve were 5786 ± 80 ng^{-1} and 255 ± 680, respectively. The correlation coefficient was 0.99991. The minimum detectable amount (MDA), corresponding to the amount of BPA injected into the LC system that produced a 3:1 signal-to-noise ratio, was 0.02 ng. Taking into account the amount of sample extracted (300 mg), the volume of coacervate obtained (around 340 μL), the injection volume used (20 μL) and the recovery obtained from spiked samples (around 86%), the detection limit of BPA in canned peas was estimated to be around 1.3 ng g^{-1}. The intra-day precision was estimated by extracting six independent samples of green beans (300 mg) spiked with 60 ng of BPA. The relative standard deviation was 2.8%.

The matrix components extracted into the coacervate were chromatographically separated from BPA. In this respect, vegetable and fruit samples behaved differently; the formers presented much more complex chromatograms that the latter ones (e.g. Figs. 2 and 3). So, simpler chromatographic conditions were used to analyse BPA in canned fruits (e.g. isocratic conditions with 50:50 of water:acetonitrile, retention time for BPA 4.0 min) compared to those used for its analysis in canned vegetables (e.g. linear gradient from 70:30 to 45:55 of water:acetonitrile in 13 min, retention time for BPA 9.3 min). The absence of interference from matrix components that could elute with BPA was checked by comparison of the slopes of the calibration curves ($n = 7$) obtained from standards in distilled water with those obtained from canned peas fortified with known amounts of BPA (20–300 ng) and run using the whole procedure. The difference between both slopes was found to be not statistically significant by applying the two-samples *t*-tests [45]. Therefore, matrix components were not expected to interfere in the determination of BPA.

The amount of sample analyzed did not influence the selectivity or the recoveries for BPA in the range 0.1–1 g. However, the precision of the method greatly decreased for the lowest and highest sample amounts tested (e.g. the standard deviations obtained for BPA recoveries were ±21% and ±11% as 0.1 and 1 g of pea samples were analysed, respectively). Very low sample amounts (e.g. 0.1 g) were not representative of the bulk sample whereas the handling of sample amounts around 1 g became a little more complicated for foods containing high protein levels (e.g. peas) since the protein precipitate standing at the bottom of the coacervate after centrifugation increased as the sample amount did. The precision, expressed as relative standard deviation, kept constant and around 2–4% for sample amounts between 300 and 700 mg. So, any sample amount in this range is recommended for the determination of BPA

Table 3 – Mean recoveries and standard deviations obtained for BPA using different operational conditions

Extraction time (min)	$R^a \pm S^b$ (%)	Stiring rate (rpm)	$R^a \pm S^b$ (%)	Temperature (°C)	$R^a \pm S^b$ (%)
5	44 ± 5	600	54 ± 1	20	86 ± 2
10	70 ± 4	900	81 ± 2	28	85 ± 2
15	86 ± 2	1200	86 ± 2	35	79 ± 3
25	88 ± 3	1500	87 ± 3	44	78 ± 4
30	85 ± 3			60	79 ± 4

[a] Mean recoveries; 300 mg of peas spiked with 60 ng of BPA; decanoic acid = 0.5% (w/v); 10% (v/v) THF.
[b] Standard deviation; $n = 3$.

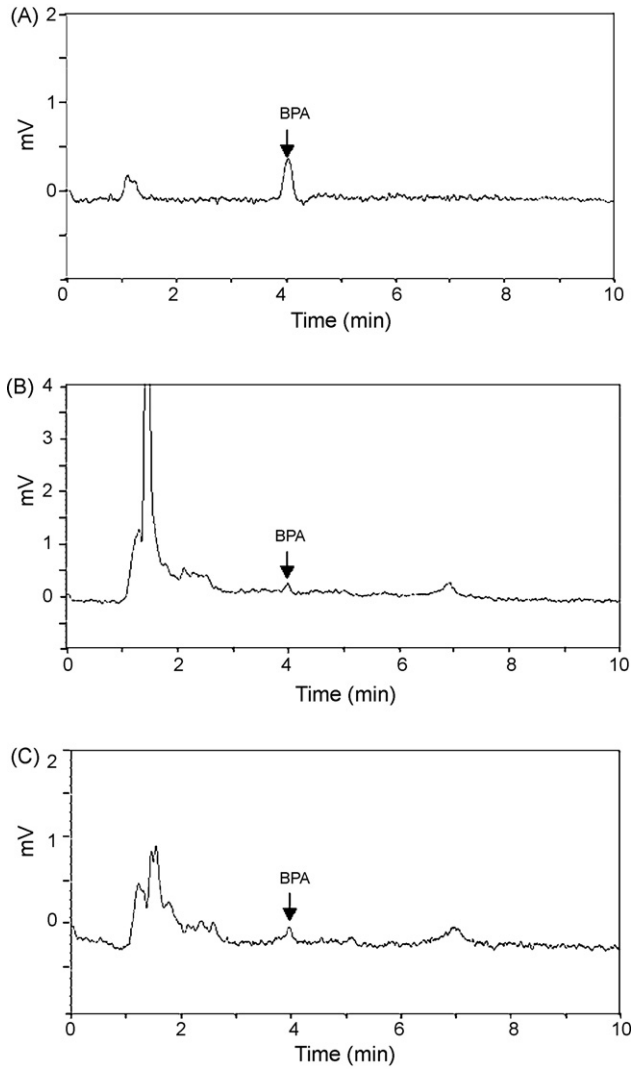

Fig. 2 – LC–fluorescence chromatograms obtained from (A) a standard solution of 50 μg L^{-1} in acetonitrile; (B) 300 mg of peaches in syrup; (C) 300 mg of fruit salad. Chromatographic conditions as specified in Section 2.5 for the analysis of canned fruits.

since the corresponding quantitation limits are low enough for control and risk assessment purposes.

3.3. *Analysis of canned vegetable and fruit samples*

Different canned vegetables and fruits were analyzed using the proposed method in order to prove its suitability for the routine control of BPA. Most of cans were products from Spain. Table 4 shows the concentrations of BPA found as well as the recoveries obtained after spiking the samples with known amounts of this contaminant. Some of the characteristics of the products analysed, as specified in the can labels, were also included. Concentrations of BPA and recoveries were expressed as the mean value of three independent determinations, besides their corresponding standard deviations. Recoveries ranged between 81 and 96% with relative standard deviations varying from 2 to 4%.

Table 4 – Characteristics of the cans, mean recoveries (%) ± standard deviation obtained after spiking the samples and mean concentrations (ng g^{-1}) ± standard deviation found in the canned food analysed

Product	Origin	Lacquer area (cm^2)	Best before date	Net weight (g)	Drained weight (g)	Mean recovery[a] ± S[b] (%)	Mean concentration ± S[b] (ng g^{-1})
Vegetables							
Red peppers	Spain	110	July of 2010	80	60	91 ± 4	72 ± 3
Sweetcorn	Spain	220	July of 2008	150	140	81 ± 2	55 ± 1
Green beans	Spain	300	July of 2010	390	210	95 ± 3	103 ± 3
Peas	Spain	220	July of 2011	200	140	88 ± 2	69 ± 1
Fruits							
Fruit salad	Spain	300	June of 2008	420	240	92 ± 3	7.8 ± 0.2
Peaches in syrup	Spain	300	April of 2008	420	240	96 ± 2	10.3 ± 0.2
Mango slices	Thailand	300	May of 2007	425	230	89 ± 2	24.4 ± 0.7

[a] Spiked sample (100 ng g^{-1}), 10% (v/v) THF, 0.5% (w/v) decanoic acid.
[b] Standard deviation, $n = 3$.

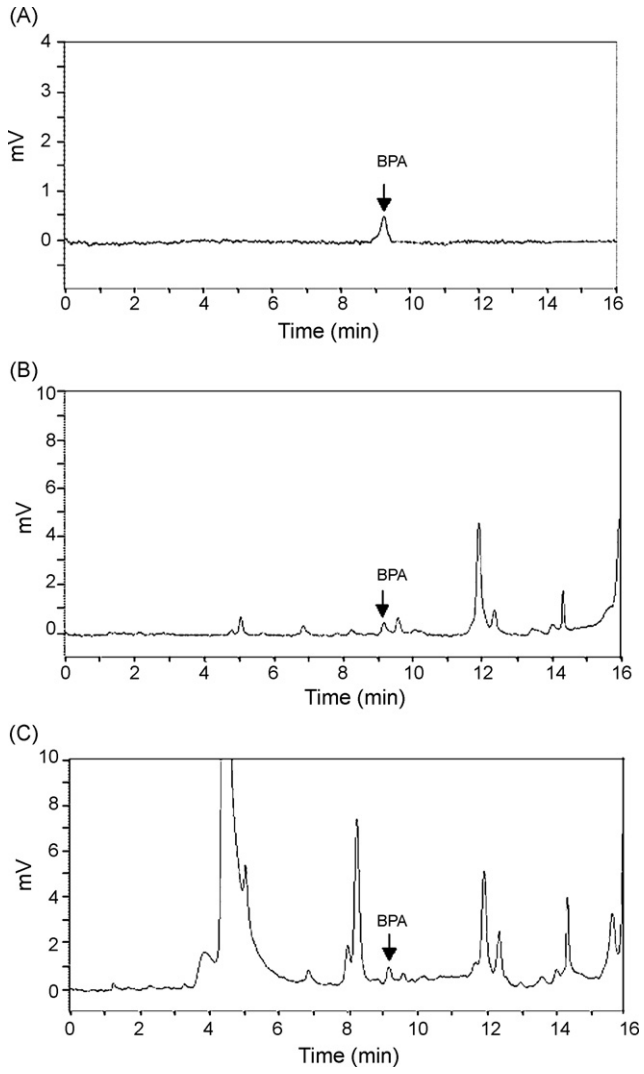

Fig. 3 – LC–fluorescence chromatograms obtained from (A) a standard solution of 50 μg L^{-1} in acetonitrile; (B) 300 mg of red peppers; (C) 300 mg of sweetcorn. Chromatographic conditions as specified in Section 2.5 for the analysis of canned vegetables.

BPA was quantified in all the samples analysed at concentrations in the range 7.8–103 ng g^{-1}. These concentrations were far below the current specific migration limit (SML) of 600 ng g^{-1} set by the EU Commission [6] for BPA and similar to those found by different researchers [10–18]. Fig. 2 compares the chromatograms obtained from a standard solution of BPA (A) with those obtained from the analysis of canned peaches in syrup (B) and fruit salad (C). Despite the low concentration of BPA in fruits, the peak corresponding to BPA could be clearly identified. The chromatograms corresponding to the analysis of vegetable samples were more complex (e.g. Fig. 3B and C) but using the chromatographic conditions proposed in the Section 2.5, BPA was quantified with high precision (Table 4). Identification of BPA in the samples was based on retention times and the UV spectrum obtained from the diode array in line with the fluorescence detector.

4. Conclusions

The combination of reverse micelle-based coacervative extraction and liquid chromatography–fluorimetry constitutes a valuable strategy for the determination of BPA in canned vegetables and fruits. Coacervates surpass the current solvent-based methodologies used for the extraction of BPA in terms of simplicity (sample treatment just requires a single extraction with an aqueous solutions containing 4 mL of THF and 200 mg of decanoic acid, and no clean-up or solvent evaporation is necessary) and rapidity (the whole treatment procedure takes about 30 min and several samples can be simultaneously extracted, so sample throughput is considerable increased). There are additional assets associated to the method developed here; it involves the analysis of minute amounts of sample (300–700 mg), features low cost (the consumption of organic solvent is greatly reduced and the use of SPE columns is avoided), no special equipment is required for sample treatment and it uses fluorimetry for detection, so the method can be applied in routine analysis in labs without extra investment. The quantitation limit of the method is about 9.3 ng g^{-1}, so it can be used for the routine control of BPA in canned vegetables and fruits below the current specific migration limit (SML) of 600 ng g^{-1} set by the EU Commission [6].

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