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Determination of bisphenol-A, 2,4-dichlorophenol, bisphenol-AF and tetrabromobisphenol-A in liquid foods and their packaging materials by vortex-assisted supramolecular solvent microextraction/high-performance liquid chromatography

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A new and fast microextraction technique termed vortex-assisted supramolecular solvent microextraction (VASUSME) has been developed. The method was based on the microextraction of endocrine disrupting compounds (EDCs), including bisphenol-A (BPA), 2,4-dichlorophenol (2,4-DCP), bisphenol-AF (BPAF) and tetrabromobisphenol-A (TBBPA) in 10 mL sample with 500 μL of a supramolecular solvent (SUPRASs), and then detection by high-performance liquid chromatography (HPLC). In the VASUSME procedure, dispersion of microvolumes of a low density extraction solvent into the aqueous sample is achieved by vortex mixing, a mild emulsification procedure. Under the optimum conditions, the repeatability of the proposed method was found to be good. The relative standard deviations (RSD, $n = 5$) were 3.98–5.64%. The limits of detection (LOD) were in the range of 0.14–0.32 ng mL^{-1} and the limits of quantification (LOQ) were in the range of 0.41–1.02 ng mL^{-1}. All correlation coefficients of the calibration curves were higher than 0.998. Recoveries of the EDCs spiked into samples of liquid foods and their packaging materials were in the range of 91% to 105.1%. The VASSUSME method was successfully applied to the analysis of BPA, 2,4-DCP, BPAF and TBBPA in samples of liquid foods and their packaging materials. Moreover, the method is simple, sensitive and environmentally-friendly and consumes much less solvent than traditional methods.

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Introduction

Bisphenol-A (BPA), 2,4-dichlorophenol (2,4-DCP), bisphenol-AF (BPAF) and tetrabromobisphenol-A (TBBPA) are four phenol chemicals which are extensively used in consumer products.[1–4] BPA is a major industry product widely used in the production of resins and polycarbonate plastics.[5] As a cross-linking and curing agent, BPAF is mainly used in the synthesis of speciality elastomers to improve their chemical and thermal properties.[6] TBBPA is the most important individual brominated flame retardant (BFR) used in industry.[7] These compounds all belong to the family of synthetic endocrine disrupting compounds (EDCs), and several studies have shown that these compounds have potential risk to the health of humans and animals.[2,4,8,9]

Different chromatographic techniques such as gas chromatography (GC), high performance liquid chromatography (HPLC), and capillary electrophoresis (CE) with different detectors have found extensive application for the simultaneous determination of various EDCs in liquid samples.[10–12]

Sample preparation prior to the chromatographic analysis is one of the most crucial steps in the whole analytical procedure to obtain accurate and sensitive results.[13–16] Solid-phase extraction (SPE), liquid-phase microextraction (LPME) and liquid–liquid microextraction (LLME) have appeared as new attractive alternatives for sample preparation, which leads to the saving of time, labor, and solvent consumption, and can improve the analytical performance of the procedure. Lately, several different types of LLME have been developed, including single drop microextraction (SDME),[17,18] hollow fiber LPME,[19–22] and dispersive liquid–liquid microextraction (DLLME).[23,24]

The application of SUPRASs based on non-ionic surfactant micelles aggregates (*e.g.* cloud point technique) was first introduced by Watanabe *et al.* in 1978.[25,26] In 2009, new SUPRASs produced from vesicles[27] or reverse micelles[28] of alkyl carboxylic acids were described. These solvents constitute an advantageous alternative for the extraction of organic compounds in a wide polarity range from both liquid[29,30] and solid samples.[31–34]

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The extraction of bisphenols was achieved with the tetrabutylammonium-induced liquid–liquid phase separation in vesicular solutions of alkyl carboxylic acids.[35]

Alkyl alcohols are similar to alkyl carboxylic acids in their physical and chemical characteristics (*e.g.* long chain alkyl group, hydroxyl group, and lone pair of electrons). So, in our study, the new SUPRAS consisting of octyl alcohol and THF was used as the extractant to extract EDCs from samples of liquid foods and their packaging materials, which is safe, simple and has a high enrichment factor and recovery in a short time. The parameters affecting recovery were also studied and optimized. Below the most salient results of this study are described and discussed.

Materials and methods

Samples of liquid foods and their packaging materials

Samples of fruits and vegetables, lactic acid milk drinks, carbonated drinks, milk and their packaging materials were purchased from local supermarkets in Kunming (China).

Reagents and solutions

BPA, TBBPA, BPAF and 2,4-DCP (analytical standard) were all purchased from Aladdin (Shanghai, China). The stock solutions of BPA, TBBPA, BPAF and 2,4-DCP with a concentration of 0.2 mg mL^{-1} were prepared in ethanol/ultra-pure water (1/48, v/v) and then stored at 4 °C in the refrigerator until analysis. The chemical structures of these compounds are depicted in Fig. 1. HPLC grade acetonitrile was obtained from Merck (Darmstadt, Germany). Pure analysis methanol was purchased from Aladdin (Shanghai, China). Caproic acid, heptanoic acid, octylic acid, pelargonic acid, decanoic acid, butyl alcohol, octyl alcohol and tetrahydrofuran (98%) were purchased from Aladdin (Shanghai, China). Hydrochloric acid (analytical reagent) was purchased from ZhiYuan (Tianjin, China). A stock solution of hydrochloric acid with a concentration of 2 M was prepared in distilled water. All the other solvents were of analytical reagent grade unless stated.

Instrumentation

Reverse-phase high-performance liquid chromatography system, consisting of a vacuum degasser, an auto sampler, a towpump, and a diode-array detector (Agilent 1200 Series, Agilent Technologies, CA, U.S.A.) equipped with a reverse phase C18 analytical column (particle size 5 μm) of 150 mm × 4.6 mm were used for the analysis and separation. An ultrasonic cleaner with temperature control (Shanghai, China) was used for ultrasonic extraction. A centrifuge (Shanghai, China) was used for complete phase separation. A vortex agitator (Jiangsu, China) was used for vortex extraction. A water-bathing constant temperature vibrator (Jintan, China) crystal glass was used to treat the samples of packaging materials.

The preparation of the supramolecular solvent

Supramolecular solvent was prepared by mixing 2 mL of octyl alcohol and 10 mL of THF in 38 mL distilled water and 10 μL HCl (2 M). A mixture was made by vortex-shaking for 2 minutes.

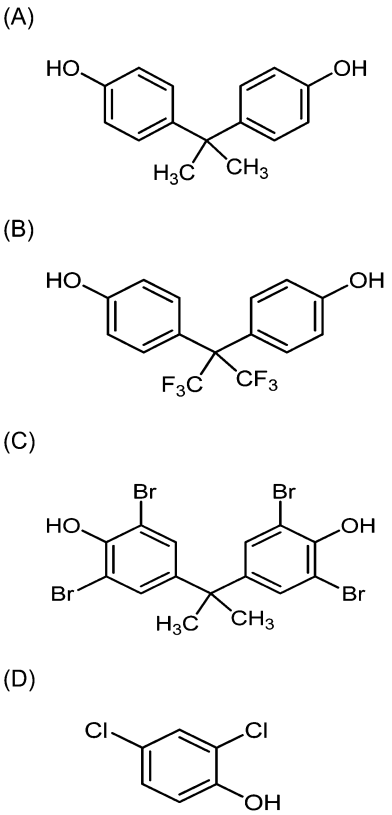

Fig. 1 Chemical structures of phenol compounds (A) BPA, (B) BPAF, (C) TBBPA and (D) 2,4-DCP.

Next, phase separation was achieved by centrifugation at 3500 rpm for 5 min. Finally, SUPRAS, which is less dense than water and consequently remains at the top of the solution, and was transferred into a centrifuge tube. The preparation process is shown in Fig. 2.

VASUSME procedure

Packaging materials sample preparation and VASUSME procedure. A sample of crushed packaging material (1 g) and

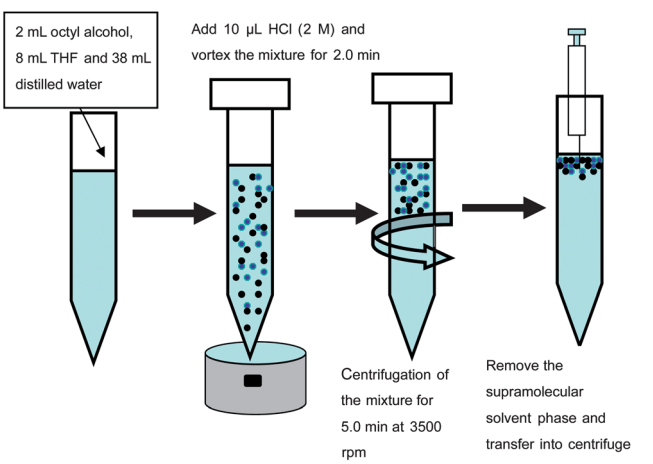

Fig. 2 Diagram of the preparation of the supramolecular solvent used in this study.

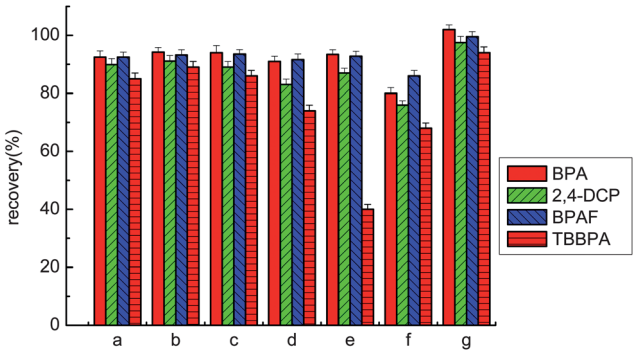

Fig. 3 Effect of different compositions of supramolecular solvent. Extraction conditions: sample volume, 10.0 mL spiked with 10 ng mL^{-1} of each EDC; extractant solvent volume, 500 μL; sample pH, 7.0; vortex time, 2 min; centrifuging time, 5 min. (a) caproic acid, (b) heptanoic acid, (c) octylic acid, (d) pelargonic acid, (e) decanoic acid, (f) butyl alcohol, (g) octyl alcohol.

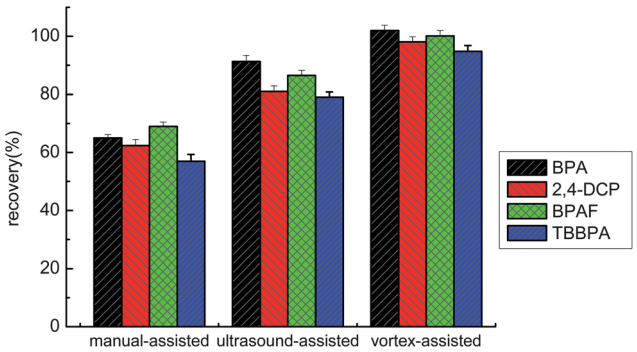

Fig. 4 Effect of extraction method. Extraction conditions: sample volume, 10.0 mL spiked with 10 ng mL^{-1} of each EDC; extraction solvent volume, 500 μL; sample pH, 7.0; vortex time, 2 min; manual time, 2 min; ultrasound time, 2 min; centrifuging time, 5 min.

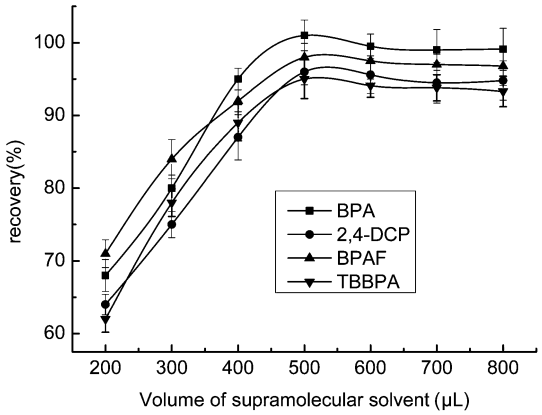

Fig. 6 Effect of extractant solvent volume. Extraction conditions: sample volume, 10.0 mL spiked with 10 ng mL^{-1} of each EDC; sample pH, 7.0; vortex time, 2 min; centrifuging time, 5 min.

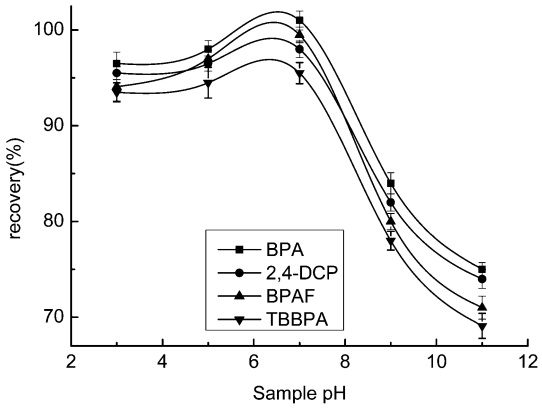

Fig. 7 Effect of sample pH. Extraction conditions: sample volume, 10.0 mL spiked with 10 ng mL^{-1} of each EDC; extractant solvent volume, 500 μL; vortex time, 2 min; centrifuging time, 5 min.

distilled water (15 mL) were placed in centrifuge tube. Then the centrifuge tube was left in a thermostatically controlled bath at 75 °C for 24 h. A portion of the liquid phase was transferred into a centrifuge tube through a paper filter. 500 μL supramolecular solvent was added into 10 mL filtrate. The mixture solution was vortex-mixed for 2.0 min to form a homogeneous cloudy solution. The phase separation was performed by a rapid centrifugation at 3500 rpm for 5.0 min. The aqueous phase was removed and the coacervate was deposited at the bottom of the tube. Then the coacervate was diluted to 1.0 mL with acetonitrile, and 10.0 μL of the solution was injected into the HPLC system for analysis.

Liquid foods sample preparation and VASUSME procedure. In the extraction procedure, 10 mL of liquid food sample mixed

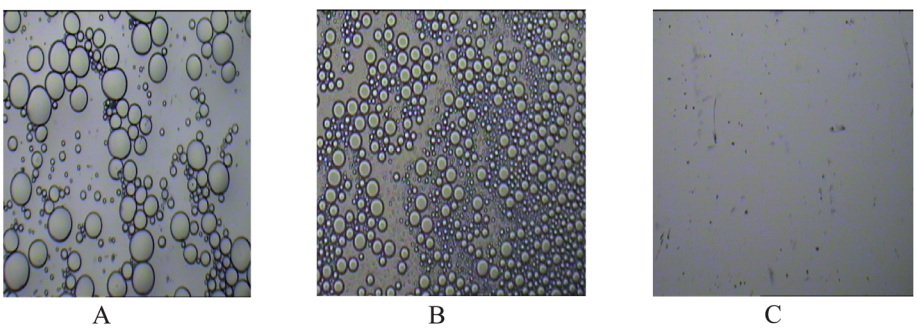

Fig. 5 Optical microscope diagrams: (A) manual-assisted extraction; (B) vortex-assisted extraction; (C) ultrasound-assisted extraction.

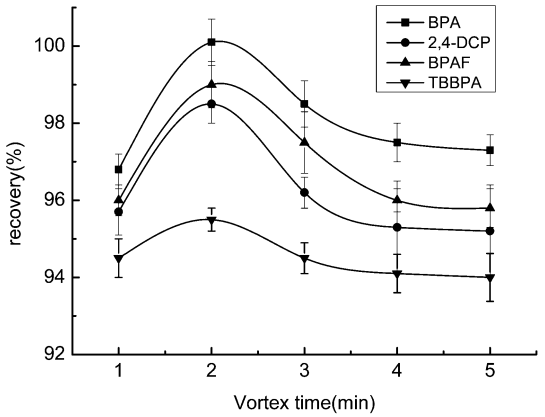

Fig. 8 Effect of vortex time. Extraction conditions: sample volume, 10.0 mL spiked with 10 ng mL^{-1} of each EDC; sample pH, 7.0; extractant solvent volume, 500 μL; centrifuging time, 5 min.

with 26 mg $MgSO_4$ was centrifuged at 12 000 rpm for 4 min. The supernatant was removed to a centrifuge tube by a syringe. Afterwards 500 μL of the supramolecular solvent was added. The mixture was vortex-shaken immediately for 2.0 min and then centrifuged at 3500 rpm for 5.0 min to accelerate the separation of the supramolecular solvent from the bulk solution. The aqueous phase was removed and the coacervate was deposited at the bottom of the tube. Then the coacervate was diluted to 1.0 mL with acetonitrile, and 10.0 μL of the solution was injected into the HPLC system for analysis.

HPLC conditions. The HPLC separation was performed on a reverse-phase system with gradient elution using acetonitrile and water. The gradient elution was performed as follows: 42% acetonitrile (0–8.0 min), ramped to 85% acetonitrile (8.0–16.0 min). Next, the system was allowed to stabilize for 1.0 to 2.0 min under the initial conditions. The prepared mobile phase was filtered and degassed using ultrasonic agitation. The flow rate was set at 1 mL min^{-1}. The column temperature was maintained at 30 °C and the injection volume was set to 10.0 μL. BPA, TBBPA, BPAF and 2, 4-DCP were recorded at the wavelength of 240 nm.

Results and discussion

Optimization

The extraction efficiency was investigated in our experiments using the recovery from the spiked samples of EDCs at a concentration of 10 ng mL^{-1} in a liquid food sample. The optimization procedure was performed as described for vortex-assisted supramolecular solvent extraction. Different composition of supramolecular solvent and extraction method, volume of extractant, pH and time required to reach equilibrium conditions to obtain free particle extracts were investigated.

Effect of different compositions of supramolecular solvent

Different solvents or mixtures of them were tested to provide the best recoveries, because the nature of the solvent is the most important parameter in the extraction process. Caproic acid, heptanoic acid, octylic acid, pelargonic acid, decanoic acid, butyl alcohol and octyl alcohol matched with THF were studied. From Fig. 3, it was found that the SUPRAS consisting of octyl alcohol and THF gave the best recoveries (recovery 102% for BPA, 97.5% for 2,4-DCP, 99.5% for BPAF and 94% for TBBPA, respectively).

Effect of assisted-extraction method

The role of assisted-extraction is to disperse the extraction solvent into the water phase. Vortex-assisted, ultrasound-assisted and manual-assisted extraction were investigated. Fig. 4 shows that the best assisted-extraction method is vortex-assisted extraction; in particular the recoveries were 102% for BPA, 98.1% for 2,4-DCP, 100.1% for BPAF and 94.8% for TBBPA. Ultrasound-assisted extraction showed 91.3% for BPA, 81% for 2,4-DCP, 86.5% for BPAF and 79.4% for TBBPA, while the lowest recoveries were obtained with manual-assisted extraction, which gave values lower than 70% for all compounds.

Fig. 5 shows three micrographs by different assisted-extraction methods. It can be clearly seen from Fig. 5B that the analytes were well dispersed in emulsion. This phenomenon may be explained by the fact that the solution after manual-assisted extraction had not obtained enough force to generate sufficient emulsification (Fig. 5A). Fig. 5C showed that the solution was over-emulsified after ultrasound-assisted supramolecular solvent microextraction, and resulted in incomplete phase separation. Based on these results, vortex-assisted extraction was selected for further experiments.

Effect of extractant volume

In order to evaluate the influence of extractant volume on the extraction recovery and enrichment factor, sample solutions containing different volumes of supramolecular solvent ranging from 200 to 800 μL were examined. As can be seen in Fig. 6,

Table 1 The performance characteristics of the proposed method

Analyte	LR[a] (ng mL^{-1}) equation	Regression	R^2	LOD (ng mL^{-1})	RSD (%) ($n = 5$)	LOQ (ng mL^{-1})
BPA	1.5–300	$y = 32.252x - 2.1125$	0.9992	0.21	4.21	0.66
2,4-DCP	1.5–300	$y = 56.878x + 3.7583$	0.9995	0.17	4.74	0.45
BPAF	1.5–300	$y = 56.975x - 6.7417$	0.9996	0.32	3.98	1.02
TBBPA	1.5–300	$y = 79.295x + 13.204$	0.9988	0.14	5.64	0.41

[a] Linear range.

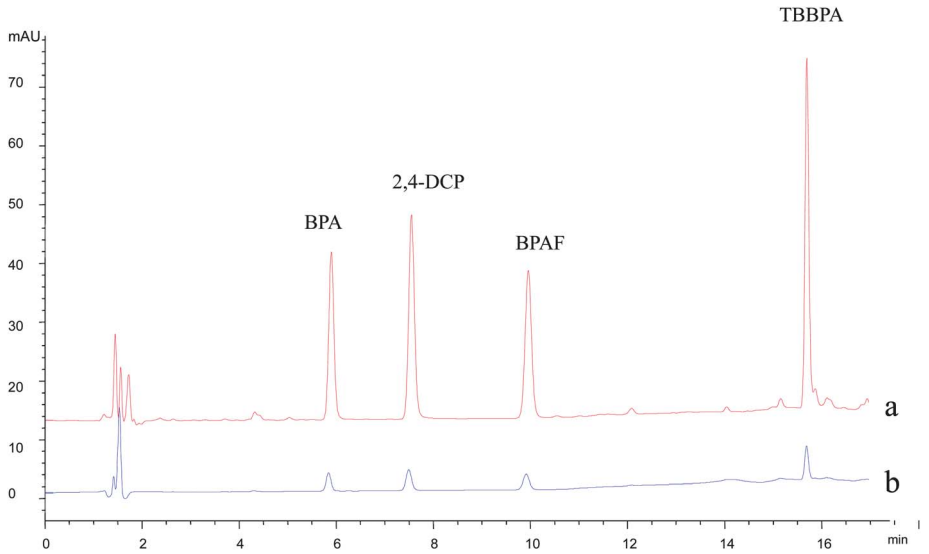

Fig. 9 HPLC-UV chromatograms: (a) distilled water spiked with EDCs (100 ng mL^{-1}) after supramolecular solvent extraction, and (b) distilled water spiked with EDCs (100 ng mL^{-1}) without supramolecular solvent extraction.

recovery gradually increased with an increase in volume of extractant and showed the highest response at 500 μL. Beyond this volume, the response slowly decreased. Based on these results, 500 μL extractant was selected for further experiments.

Effect of sample pH

Sample pH is another important parameter that might affect the extraction efficiency, because the analytes will be present in different forms in different pH environments. A series of experiments were performed to investigate the effect of pH. The sample pH was examined over the pH range 3.0–11.0. The Britton–Robinson buffer solution composed of phosphoric acid, acetic acid and boric acid was used to adjust the sample pH. The data were shown in Fig. 7. It was found that there was no significant effect on the peak areas of BPA, TBBPA, BPAF and 2,4-DCP in the pH range 3.0–7.0, but the peak areas deceased in the pH range 9.0–11.0. These compounds are soluble in alkaline environments, so it is difficult to extract them. Based on this fact, the sample pH was adjusted to be neutral in the subsequent experiments.

Effect of vortex time

Vortex time is one of the most important factors in most extraction procedures, especially in microextraction methods. In our study, times from 1.0 to 5.0 min were studied. The results were shown in Fig. 8 and indicated that the extraction efficiency was highest when the vortex time was 2.0 min. However, the recovery decreased when vortex times were greater than 3.0 min. The reason may be that some of the analytes were adsorbed onto the wall of the tube. Based on these results, 2.0 min was selected for further experiments.

Method validation

Table 1 shows some analytical characteristics of the optimized method, including regression equation, linear range, limits of detection, limit of quantification, and reproducibility. The

Table 2 Determination of EDCs in packaging material samples

		Found[a] (μg mL^{-1}) (RSD%)				Recovery (%)			
Packaging material samples	Added (ng mL^{-1})	BPA	2,4-DCP	BPAF	TBBPA	BPA	2,4-DCP	BPAF	TBBPA
Lactic acid milk drinks bottle	0	—	—	—	—	—	—	—	—
	5	5.10 (3.62)	4.71 (4.50)	4.92 (3.94)	4.85 (5.30)	102.2	94.2	98.4	97.0
	10	9.99 (4.14)	9.42 (4.74)	9.87 (2.72)	9.49 (4.91)	99.0	94.2	98.7	94.9
Carbonated drinks bottle	0	2.90 (3.23)	—	—	—	—	—	—	—
	5	7.6 (4.02)	4.76 (3.21)	5.01 (3.27)	4.59 (4.90)	94.4	95.2	100.2	91.8
	10	12.4 (3.91)	9.95 (4.63)	10.0 (2.23)	96.1 (5.51)	95.1	99.5	100.5	96.1
Milk bottle	0	1.6 (3.31)	—	—	—	—	—	—	—
	5	6.31 (2.15)	4.86 (3.90)	5.22 (3.98)	4.78 (5.43)	94.2	97.2	104.0	95.6
	10	11.9 (2.82)	98.6 (2.13)	10.1 (3.20)	97.2 (4.51)	103.0	98.6	101.0	97.0

[a] Data were calculated based on five-replicate experiments.

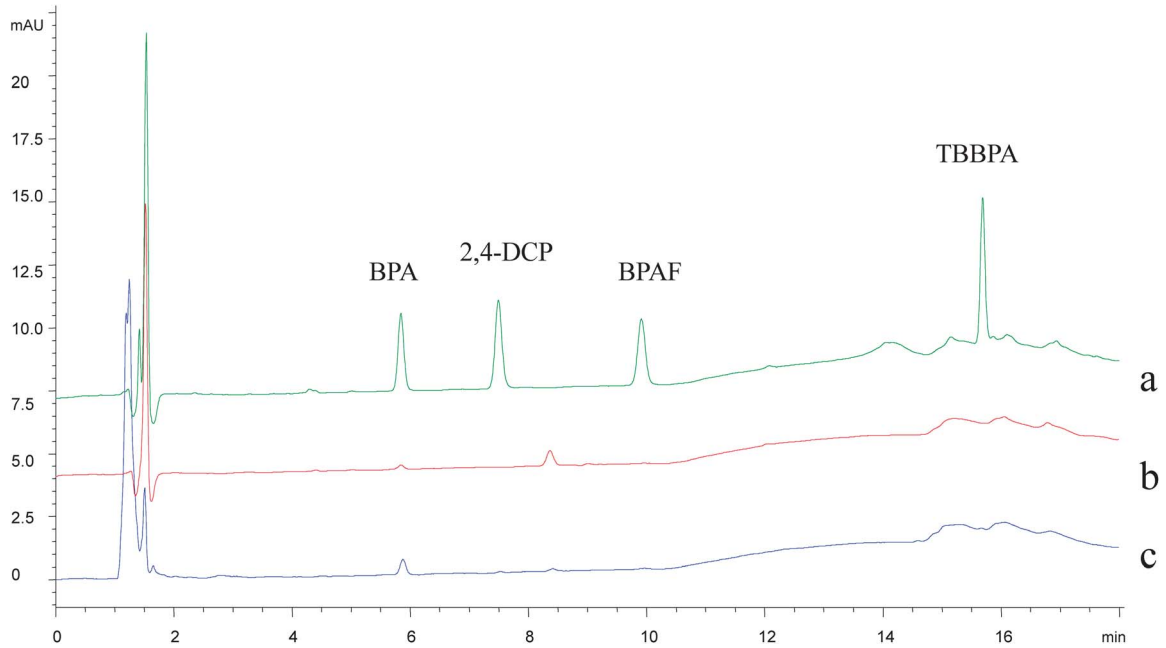

Fig. 10 Typical chromatogram of milk bottle: (a) milk bottle spiked with EDCs (5 ng mL^{-1}) after supramolecular solvent extraction; (b) milk bottle without supramolecular solvent extraction; (c) milk bottle after supramolecular solvent extraction.

linearity of each of the four estrogen compounds was in the range 1.5–300 ng mL^{-1}. The LODs were in the range of 0.14–0.32 ng mL^{-1} and LOQs were in the range of 0.41–1.02 ng mL^{-1}. The relative standard deviations were 3.98–5.64%.

Fig. 9 shows the chromatogram of distilled water spiked with standards (BPA, TBBPA, BPAF and 2, 4-DCP). Fig. 9a is the chromatogram of standards (BPA, TBBPA, BPAF and 2,4-DCP) with supramolecular solvent extraction and Fig. 9b is the chromatogram of standards (BPA, TBBPA, BPAF and 2, 4-DCP) without supramolecular solvent extraction. The preconcentration effect of supramolecular solvent extraction is clearly demonstrated in Fig. 9a and b.

To evaluate the effectiveness of the established method in the real samples, it was applied to the analysis of a total of 6 samples of liquid foods and their packaging materials. Sample preparation for the real samples was performed according to the VASUSME procedure.

Three kinds of packaging material samples (lactic acid milk drink, carbonated drink and milk bottle) were analyzed by HPLC-UV after VASUSME. To investigate the accuracy, precision and reproducibility, packaging materials samples spiked at concentrations of 5 ng mL^{-1} and 10 ng mL^{-1} were extracted under the optimized conditions. The results are provided in Table 2. The relative recoveries for the analytes were in the range of 91.8–104.0% and the RSDs ranged from 2.13% to 5.51% in bottle samples.

Typical chromatograms of milk bottles, blank and spiked, at the concentration level 5 ng mL^{-1} of analytes are shown in Fig. 10.

The VASUSME-HPLC method for determination of EDCs was evaluated by analyzing liquid food samples. The results are provided in Table 3. The developed method showed high relative recoveries for different food samples from 91.0 to 101.5%, which ensured the accuracy of the amount of EDCs detected in the liquid foods samples.

Table 3 Determination of EDCs in liquid food samples

		Found[a] (μg mL^{-1}) (RSD%)				Recovery (%)			
Liquid food samples	Added (ng mL^{-1})	BPA	2,4-DCP	BPAF	TBBPA	BPA	2,4-DCP	BPAF	TBBPA
Lactic acid milk drinks	0	—	—	—	—	—	—	—	—
	2	1.92 (4.11)	1.95 (4.42)	2.0 (3.83)	1.84 (5.32)	96.0	97.5	100.0	92.0
	4	3.74 (4.42)	3.68 (2.81)	3.91 (2.98)	3.87 (4.46)	93.5	92.3	97.7	96.5
Carbonated drinks	0	0.1 (3.15)	—	—	—	—	—	—	—
	2	2.10 (3.80)	1.94 (5.70)	1.91 (3.45)	1.82 (3.78)	100.0	97.1	95.5	91.0
	4	4.08 (4.04)	3.82 (3.41)	4.02 (4.91)	3.93 (5.01)	99.5	95.5	101.5	98.3
Milk	0	—	—	—	—	—	—	—	—
	2	1.84 (3.93)	1.85 (4.92)	19.0 (4.22)	1.93 (2.98.)	92.0	92.5	95.1	96.4
	4	3.87 (2.82)	3.75 (3.29)	3.91 (4.08)	3.86 (5.78)	96.8	93.7	97.7	96.7

[a] Data were calculated based on five-replicate experiments.

Conclusions

A new and fast sample preparation method termed VASUSME is presented, having the inherent advantage of achieving equilibrium conditions within only a few minutes. The new SUPRAS consisting of octyl alcohol and THF has proved to be a suitable tool for the extraction of EDCs in liquid foods and their packaging material samples. The method is simple, sensitive, rapid and inexpensive. Analytes are extracted in a single step that takes about 25 min, and several EDCs can be simultaneously extracted.

Acknowledgements

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References

1 R. J. Kavlock, *Chemosphere*, 1999, **39**, 1227–1236.
2 C. Zheng, J. Zhao, P. Bao, J. Gao and J. He, *J. Chromatogr., A*, 2011, **1218**, 3830–3836.
3 M. Agarwal, K. Rai, R. Shrivastav and S. Dass, *Water, Air, Soil Pollut.*, 2002, **141**, 247–261.
4 S. Kitamura, T. Suzuki and S. Sanoh, *Toxicol. Sci.*, 2005, **84**, 249–259.
5 J. Simal Gándara, S. Paz Abuin, P. Paseiro Losada and J. Simal Lozano, *J. Chromatogr. Sci.*, 1993, **31**, 450.
6 S. K. Khetan and T. J. Collins, *Chem. Rev.*, 2007, **107**, 2319–2364.
7 C. A. de Wit, *Chemosphere*, 2002, **46**, 583–624.
8 X. W. Hu, W. D. Zhang and Y. Q. Liu, *Chinese J. Foods Science*, 2006, **27**, 264–266.
9 A. Tor, *Desalination*, 2006, **201**, 267–276.
10 P. Hoffmann, M. F. Hartmann, T. Remer, K. P. Zimmer and S. A. Wudy, *Steroids*, 2010, **75**, 1067–1074.
11 K. C. Chan, G. M. Muschik, H. J. Issaq and P. K. Siiteri, *J. Chromatogr., A*, 1995, **690**, 149–154.
12 M. J. López de Alda and D. Barceló, *J. Chromatogr., A*, 2001, **911**, 203–210.
13 Y. Picó, M. J. Redondo, G. Font and J. Manes, *J. Chromatogr., A*, 1995, **693**, 339.
14 S. P. Huang and S. D. Huang, *J. Chromatogr., A*, 2007, **1176**, 19.
15 E. Psillakis and N. Kalogerakis, *J. Chromatogr., A*, 2003, **999**, 145.
16 L. M. Zhao, L. Y. Zhu and H. K. Lee, *J. Chromatogr., A*, 2002, **963**, 239.
17 M. A. Jeannot and F. F. Cantwell, *Anal. Chem.*, 1996, **68**, 2236.
18 L. Xia, B. Hu, Z. Jiang, Y. Wu and Y. Liang, *Anal. Chem.*, 2004, **76**, 2910.
19 S. Pedersen-Bjergaard and K. E. Rasmussen, *Anal. Chem.*, 1999, **71**, 2650.
20 E. Psillakis and N. Kalogerakis, *TrAC, Trends Anal. Chem.*, 2003, **22**, 565.
21 K. E. Rasmussen and S. Pedersen-Bjergaard, *TrAC, Trends Anal. Chem.*, 2004, **23**, 1.
22 S. Pedersen-Bjergaard and K. E. Rasmussen, *J. Chromatogr., B: Anal. Technol. Biomed. Life Sci.*, 2005, **817**, 3.
23 M. Rezaee, Y. Assadi, M. R. Milani Hosseini, E. Aghaee, F. Ahmadi and S. Berijani, *J. Chromatogr., A*, 2006, **1116**, 1.
24 E. Zhao, W. Zhao, L. Han, S. Jiang and Z. Zhou, *J. Chromatogr., A*, 2007, **1175**, 137.
25 H. Watanabe and H. Tanaka, *Talanta*, 1978, **25**, 585.
26 H. Watanabe, N. Yamaguchi and H. Tanaka, *Bunseki Kagaku*, 1979, **28**, 366.
27 F. J. Ruiz, S. Rubio and D. Pérez-Bendito, *Anal. Chem.*, 2006, **78**, 7229–7239.
28 F. J. Ruiz, S. Rubio and D. Pérez-Bendito, *Anal. Chem.*, 2007, **79**, 7473–7484.
29 A. M. Ballesteros-Gómez, S. Rubio and M. D. Pérez-Bendito, *Anal. Chim. Acta*, 2007, **603**, 51–59.
30 S. García-Fonseca, A. M. Ballesteros-Gómez, S. Rubio and M. D. Pérez-Bendito, *Anal. Chim. Acta*, 2008, **617**, 3–10.
31 A. García-Prieto, L. Lunar, S. Rubio and D. Pérez-Bendito, *Food Addit. Contam., Part A*, 2009, **26**, 265–274.
32 A. Moral, M. D. Sicilia and S. Rubio, *Anal. Chim. Acta*, 2009, **650**, 207–213.
33 E. M. Costi, M. D. Sicilia and S. Rubio, *J. Chromatogr., A*, 2010, **1217**, 1447–1454.
34 C. Caballo, E. M. Costi, M. D. Sicilia and S. Rubio, *Food Chem.*, 2012, **134**, 1244–1249.
35 F. Ruiz, S. Rubio and D. Pérez-Bendito, *Anal. Chem.*, 2006, **78**, 7229.