

Use of hydroxylapatite composite membranes for analysis of bisphenol A

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Abstract This study evaluates solid-phase micro-extraction (SPME) coupled with gas chromatography–mass spectrometry (GC–MS) to determine trace levels of bisphenol A in water and leached from plastic containers. In our study, we used very thin composite membranes prepared in the laboratory. The extraction using headspace post-derivatization with bis(trimethylsilyl) trifluoroacetamide (BSTFA), containing 1 % trimethylchlorosilane (TMCS) vapor, following SPME was compared with extraction without derivatization. The SPME experimental procedures to extract bis-phenol A in water were optimized with a relatively polar polyacrylate (PA)-coated fiber, an extraction time of 50 min, and desorption at 300 °C for 2 min. Headspace derivatization following SPME was performed using 7 μL of BSTFA with 1 % TMCS at 65 °C for 30 s. The precision was 5.2 % without derivatization and 9.0 % headspace derivatization. The detection limit was determined to be at the nanogram per liter level. When SPME was used following headspace derivatization, the detection limit was one order of magnitude better than that achieved without derivatization. The results of this study reveal the adequacy of the SPME–GC–MS method for analyzing bisphenol A leached from plastic containers. The concentrations of bisphenol A leached from plastic containers into water ranged from 0.7 to 78.5 $\mu\text{g L}^{-1}$.

Keywords Composite · Hydroxylapatite · TFME · Bisphenol A · Adsorption · Derivatization · GC/MS/SIM

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Introduction

Thin film micro-extraction (TFME) made from polymers such as PLA, PCL and hydroxylapatite (HAp) has been tested as adsorption films [1]. These TFME can enhance the efficacy of adsorption of organic compound (bisphenol A), and they can also play a role to evaluate the relative difference between different homogenized stationary phases [2]. Because of their polymeric nature, these small films (diameter 100 μm) are able to adsorb a wide variety of drugs in a stable and reproducible way [3], and can be used in order to improve mass transfer from the aqueous sample [4]. The evaluation and monitoring of trace level of the contaminant in various matrices of children and baby food samples is an important objective.

Bisphenol A (BPA) is an endocrine-disrupting organic compound used in the industrial manufacture of polycarbonate plastic bottles, and is known to be toxic or carcinogenic; its metabolism is well known [5, 6]. For the study of the influence degradation of this organic compound, it was necessary to control the quantity of BPA released from the plastics. GC–MS and HPLC–UV after and without derivatization, have been used for determination of BPA in baby food matrices [7, 8]. TFME–GC–MS could be a good alternative method, because it can be used not only for the control of BPA but also for identification of metabolites and degradation products.

The technology employed for the extraction of BPA from aqueous samples includes solid phase micro-extraction (SPME) [9], liquid–liquid extraction (LLE) [10] and solid-phase extraction (SPE) [11].

News stories about contamination with BPA, and the situation has since, have become an international health scare. In this work, a novel analytical method based on enrichment and pretreatment of analytes in the water sample, HAP/PLA/PCL sorptive extraction and gas chromatography–mass spectrometry SIM mode have been developed for the rapid analysis of BPA in water. The obtained results demonstrated that HAP/PLA/PCL combined with GC–MS is a simple, rapid and solvent-free method for the analysis of BPA in water.

The aim of this work was then to choose the best stationary phase (TFME) and best chromatographic method for the quantification of BPA in samples of baby food matrices, which could be used for routine controls.

Materials and methods

Reagents

Hydroxyapatite (HAp) was synthesised in our laboratory, PLA, PCL, DMF, acetone and absolute ethanol, all of analytical grade, trimethylsilyl trifluoroacetamide (BSTFA + 1 % TMCS), purity >98 %, and BPA (bisphenol A purity >99 %) were purchased from Somaprol (Casablanca, Morocco). High purity distilled water was used throughout the whole experiment.

Synthesis thin film PLA/PCL/HAp

Poly- ϵ -caprolactone (PCL) and poly-(lactic acid) (PLA) polymers were dissolved in DMF at 40 °C under stirring to form solution A. Solution B was hydroxylapatite (HAp) dispersed in DMF at room temperature and added to solution A. The solution turned to opaque milky white after about half an hour. Thin films were obtained by during the procedure with careful temperature control to 120 °C at the temperature rate of 2 °C min⁻¹ and maintained for 2 h, and then cleaned in absolute ethanol to remove any possible impurities in the film.

Preparation of standards and sample solution

The standard stock solution was prepared by accurately weighing 100 mg of BPA into a 1-L (S₀) volumetric flask and dissolving them in distilled water. The stock solution was diluted with distilled water to obtain solutions S₁ and S₂, at 10 and 1 mg L⁻¹, respectively.

Prior to use, the thin films were washed with deionised water and absolute ethanol and dried in the oven at 120 °C for 1 h in order to remove impurities and any possible residual analytes (interferences). Extraction and desorption were carried out as follows: thin films were immersed in 50 mL of S₂ in a glass vial under stirring (contact 20 min), after extraction, the thin films were taken out from the water, gently dried with a filter paper and put in an oven to dry at 40 °C for 40 min. Finally, the thin films were directly placed in a centrifuge tube (1.5 ml) to desorb and derive target analyte BPA with BSTFA 1 % TMCS (200 μ L) under sonication and heating at 70 °C for 30 min. Of the final 0.2 mL derivative solution, 1 μ L was directly injected into the Shimadzu GC/MS system for analysis. In each experiment, the analyte concentration was the same and each solution were analyzed in triplicate.

Conditions of BPA analysis

For the GC/MS system, a Shimadzu GCMS-QP2010 (Shimadzu, Japan) with GCMS solution 2.5 software was used. The chromatographic conditions involved GC analysis performed on a Shimadzu QP 2010 system with a fused silica capillary column (30 m, 0.25 mm i.d. and film thickness of 0.25 mm with chemically bonded phase DB-5). The oven temperature was held at 60 °C for 1 min and programmed to rise by 10 °C min⁻¹ to 280 °C and held for 5 min. A sample volume of 0.1–1 μ L was injected in splitless mode (high pressure). The injector and interface temperature was kept at 250 °C. Helium was used as the carrier gas. The spectrometric conditions involved the following mass spectrometric parameters: the electron impact ionization energy was 70 eV, the detector voltage 1.7 kV, the ion source temperature was 200 °C, and the solvent delay time was 3 min. An MS detector was used in multiple ion monitoring mode (ions characteristic of BPA in SIM mode were: $m/z = 357$ and 372). The infrared absorption spectra were obtained using a spectrophotometer, Shimadzu FTIR-8400S, in wave number 400–4,000 cm⁻¹.

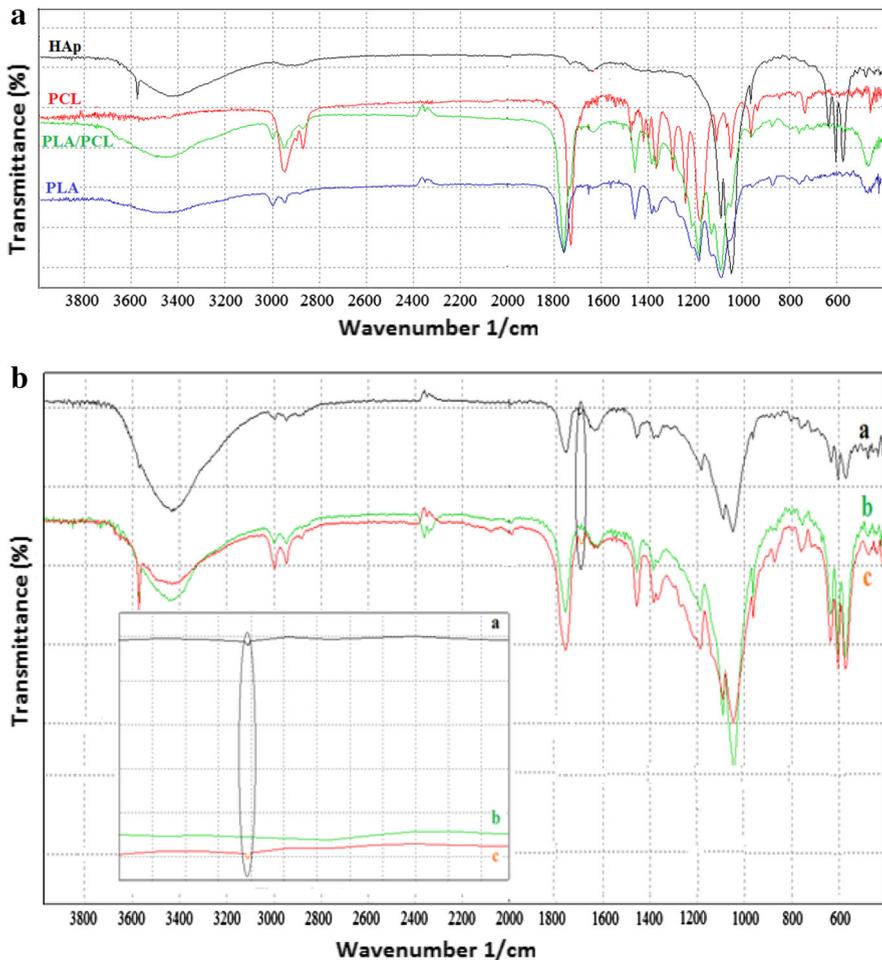


Fig. 1 a FTIR spectra of PLA, PCL, PLA/PCL and pure HAp. b FTIR spectra of the PLA/HAp composite, with molar ratios: a = 50/50, b = 40/60 and c = 30/70

Results and discussion

Thin films were characterized by IR and MEB and are presented in Figs. 1, 2, 3, and 4. The five thin films were tested and compared with florisol (60–100 mesh). All thin film extractions were examined using BPA standard in water as the testing substance. The obtained data (Fig. 5) were compared with those for commercial florisol (Fig. 6). Various extraction times of TFME-BPA extraction were taken into consideration, but 15 min (under stirring and sonication) was sufficient time for reproducible results. The comparison of extraction recoveries determined by extraction mass of BPA for the tested thin films and florisol shows the efficiency of extraction for BPA after extraction of standard solution S2 with various thin films. The most efficient extraction (adsorption on the thin film) is for the composite 2:

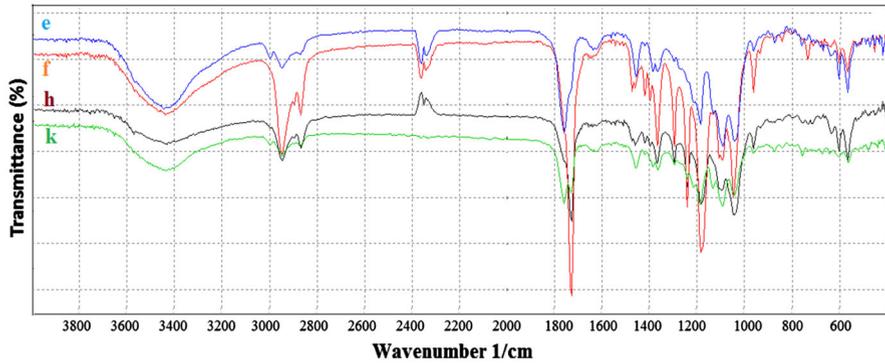


Fig. 2 FTIR spectra of the composite membrane PLA/PCL/HAp, with molar ratios $e = 50/30/20$, $f = 50/10/40$, $h = 50/20/30$ and $k = 50/40/10$

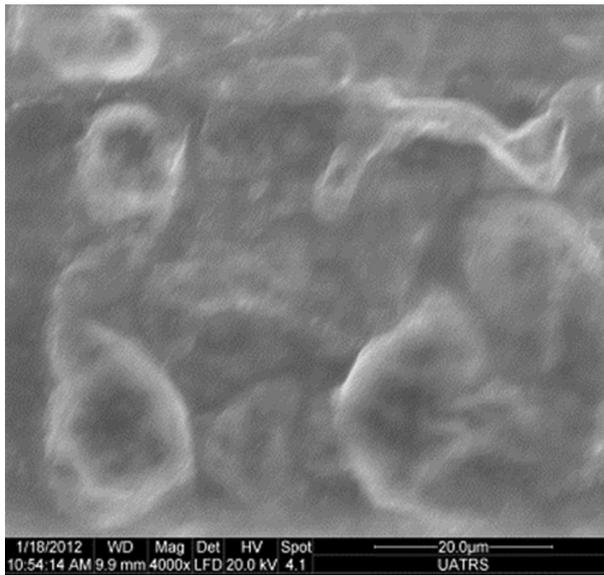


Fig. 3 SEM micrograph of the PLA/HAp film surface with a report 50/50

50 % HAp and 50 % polymer (30 % PLA-20 % PCL). On the other hand, low recoveries were obtained in the cases of $b > c > d > e$. Another interesting result is that higher sorption level was observed in the case of composite 1 : 20 % HAp and 80 % polymer (100 % PLA-0 % PCL).

Analysis by infrared absorption spectroscopy

The infrared absorption spectra obtained are shown in Figs. 1a, b and 2. The absorption bands of the carbonyl group (CO) are located at 1757 cm^{-1} . In addition,

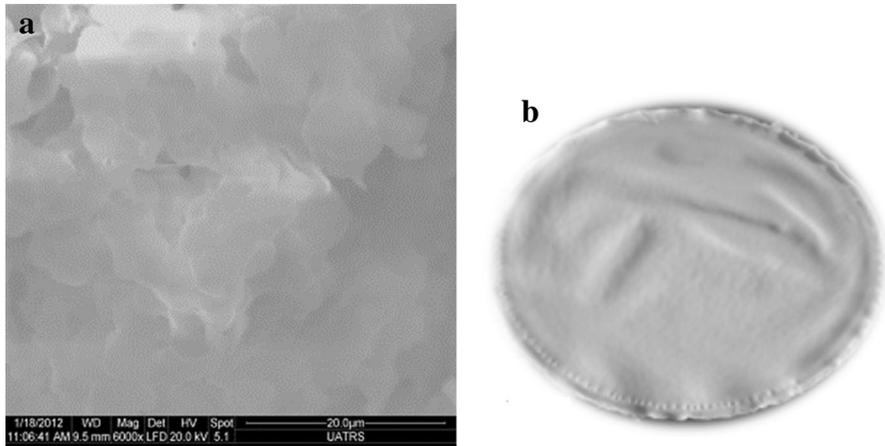


Fig. 4 SEM micrograph of the PLA/PCL/HAP film surface, with a report (20/30)/50 (a). And composite membrane PLA/PCL/HAP (b)

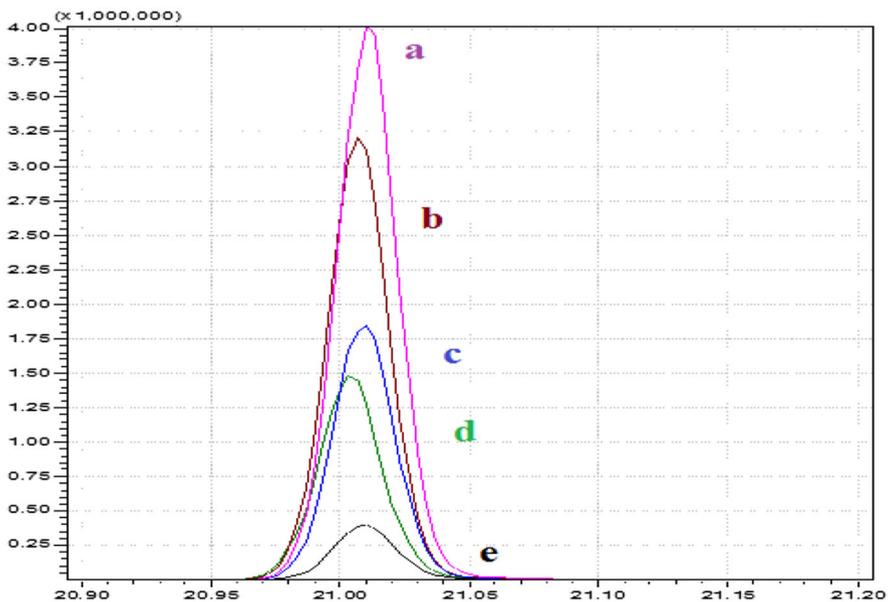


Fig. 5 Chromatogram of BPA desorbed from composites HAP/PLA/PCL, with molar ratios respectively equal to: $a = 50/30/20$, $b = 50/10/40$, $c = 50/20/30$, $d = 50/40/10$ and $e = 20/80/00$

the vibration bands of CH_3 group corresponding to PLA are located at $2,994$ and $2,946 \text{ cm}^{-1}$. The band observed at $3,503 \text{ cm}^{-1}$ could be attributed to hydroxyl groups (OH) of polymer. However, the bands allocated to the hydroxyl ion of hydroxyapatite are found at $3,572$ and 630 cm^{-1} . The bands allocated to groups of PO_4^{3-} are observed at $1,090$, $1,047$, 962 , 602 and 572 cm^{-1} .

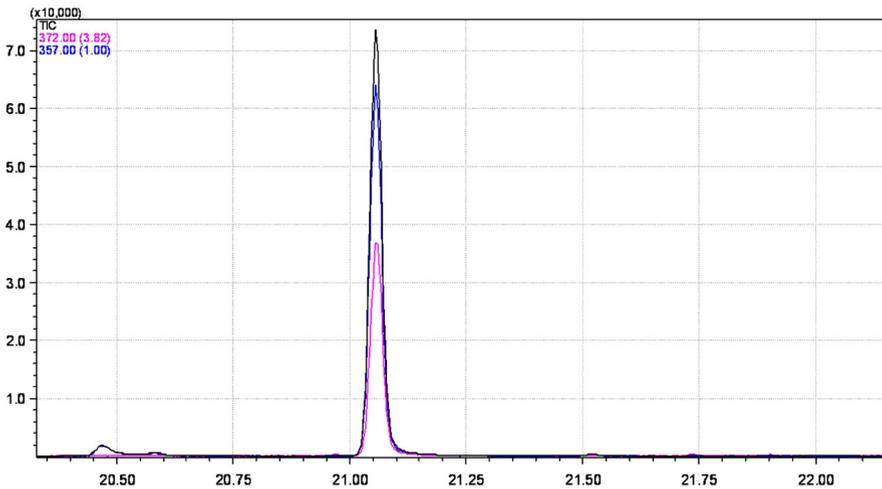


Fig. 6 Chromatogram of BPA desorbed from commercial florisisl

Observing the spectrum corresponding to membrane, there is a new band assigned to COO^- was developed around $1,683\text{ cm}^{-1}$. This band was obtained from the interaction between COOH and calcium ion. Similarly, the band allocated to the hydroxyl ion of polymer is slightly displaced to $3,550\text{ cm}^{-1}$, suggesting a possible interaction between the polymer and hydroxyapatite.

Study by scanning electron microscopy

Figures 3 and 4 show the surface SEM micrograph of PLA/HAp and PLA/PCL/HAp membranes, with a molar ratio between the mineral and the organic portion equal to 50 %. The scanning electron microscopy shows a clear homogeneity of the membranes developed.

The results indicate that the modified particles of hydroxylapatite have relatively small grain size (about $20\text{ }\mu\text{m}$). All membranes used have homogeneous structures, with the exception of a rare agglomerate which are caused by the surface energy of hydroxylapatite.

The thin films made in our laboratory can be used for the qualitative and quantitative analysis of bisphenol A in different and various matrices of children and baby foods.

Conclusion

We have developed very thin membranes that can be used for the extraction of various elements and compounds. The chemical study of these membranes showed

some interaction between the polymers and the inorganic matrix. The Chromatogram of BPA desorbed from composites showed that the polymer alone has the lowest amount adsorbed. The optimum amount of the adsorbate is obtained with the mass ratio HA_p/PLA/PCL is equal to 50/30/20.

References

1. T.M. Lee, C.Y. Yang, E. Chang, R.S. Tsai, *J Biomed Mater Res A* **71**, 652 (2004)
2. C. Auclair-Daigle, M.N. Bureau, J.G. Legoux, L.H. Yahia, *J. Biomed. Mater. Res. A* **73**, 398 (2005)
3. J.M. Gomez-Vega, E. Saiz, A.P. Tomsia, G.W. Marshall, S.J. Marshall, *Biomaterials* **21**(2), 105 (2000)
4. R.Z. LeGeros, *Clin. Orthop. Relat. Res.* **395**, 81 (2005)
5. Y. Ueyama, K. Ishikawa, T. Mano, T. Koyama, H. Nagatsuka, K. Suzuki, K. Ryoke, *Biomaterials* **23**, 2027 (2002)
6. M. Kikuchi, Y. Koyama, K. Takakuda, H. Miyairi, N. Shirahama, J. Tanaka, *J. Biomed. Mater. Res.* **62**, 265 (2002)
7. M. Kikuchi, Y. Koyama, T. Yamada, Y. Imamura, T. Okada, N. Shirahama, K. Akita, K. Takakuda, J. Tanaka, *Biomaterials* **25**, 5979 (2004)
8. F. Chen, Z.C. Wang, C.J. Lin, *Mater. Lett.* **57**, 858 (2002)
9. T. Kasuga, H. Maeda, K. Kato, M. Nogami, K. Hata, M. Ueda, *Biomaterials* **24**, 3247 (2003)
10. X.M. Deng, J.Y. Hao, C.S. Wang, *Biomaterials* **22**, 2867 (2001)
11. B.L. Shafer, P.T. Simonian, *J. Arthrosc. Relat. Surg.* **18**, 189 (2002)