Food Chemistry 261 (2018) 96–102

Contents lists available at ScienceDirect

Food Chemistry

journal homepage: www.elsevier.com/locate/foodchem

Analytical Methods

Ferrofluid-based liquid-phase microextraction: Analysis of four phenolic compounds in milks and fruit juices

Dezhi Yang[a], Guixiang Li[b], Lan Wu[c], Yaling Yang[a,*]

[a] Faculty of Environmental Science and Engineering, Kunming University of Science and Technology, Yunnan Province 650500, China
[b] Yunnan Qujing Medical University, Yunnan Province 655000, China
[c] Kunming Energy-saving Supervision Detachment, Kunming 650021, China

ARTICLE INFO

Chemical compounds studied in this article:
Bisphenol-A (PubChem CID: 6623)
Bisphenol-AF (PubChem CID: 73864)
Tetrabromobisphenol-A (PubChem CID: 6618)
4-Tert-octylphenol (PubChem CID: 8814)
1-Heptanol (PubChem CID: 8129)
Oleic acid (PubChem CID: 445639)

Keywords:
Bisphenol
Ferrofluid
1-Heptanol
Liquid-phase microextraction

ABSTRACT

A novel liquid-phase microextraction based on the ferrofluid was successfully applied for the extraction and determination of four phenolic compounds (bisphenol-A, bisphenol-AF, tetrabromobisphenol-A and 4-tert-octylphenol) in milks and fruit juices. In this study, a range of alkyl (C_4–C_{10}) alcohols as the carrier liquid were used for the preparation of ferrofluids. The study showed that an appropriate chain length of alkyl alcohol may improve the extraction efficiency and maintain the integrity of ferrofluids during extraction, so 1-heptanol (C_7) was selected as the optimal carrier liquid. Specifically, the effects of various parameters on the extraction of phenolic compounds were investigated and optimized. Under the optimized conditions, the limits of detection were between 0.35 and 0.66 $\mu g\,L^{-1}$. The intra-day and inter-day precision (RSD %) for the analytes at 10 and 50 $\mu g\,L^{-1}$ were in the range of 3.2–6.7 % and 2.9–7.1%, respectively.

1. Introduction

Endocrine disrupting compounds (EDCs), such as bisphenol-A (BPA), bisphenol-AF (BPAF), tetrabromobisphenol-A (TBBPA) and 4-tert-octylphenol (4-TOP), have attracted worldwide attention during decades because of its potential risk for human and wildlife health. These phenolic compounds as the additive are widely used in the production of commercial and industry to improve materials' properties (i.e. flexibility and resistance) (Liao & Kannan, 2013; Salgueiro-González, Muniategui-Lorenzo, López-Mahía, & Prada-Rodríguez, 2017; Sun et al., 2014). Taking plastics as an example, residues of bisphenols (BPs) and 4-tert-octylphenol (4-TOP) in beverage and food packages can easily migrate into foods, milks and drinking water during prolonged storage and at elevated temperatures (Sakhi et al., 2014; Sungur, Köroğlu, & Özkan, 2014; Wang, Zhang, Xu, & Zhang, 2016). The leakage of additives from the packages have been demonstrated (Cacho, Campillo, Vinas, & Hernández-Córdoba, 2012; Fasano, Cirillo, Esposito, & Lacorte, 2015), and can cause a decreased sperm count, increased incidence of breast, testicular and ovarian cancers (Auriol, Filali-Meknassi, Tyagi, Adams, & Surampalli, 2006; Fowler et al., 2012; Kim, Cho, Kim, Vanderford, & Snyder, 2007).

Due to the complexity of the matrix and the low concentration of phenolic compounds in aqueous samples, a sensitive, simple and reliable method for the determination of these phenolic compounds from the packing materials is of great importance. For the analysis of phenolic compounds in milk and juice samples by HPLC, an effective sample treatment technique is required to separate and pre-concentrate the analytes prior to analysis. Liquid-liquid extraction (LLE) and solid phase extraction (SPE) are the most common techniques for analyzing phenolic compounds in liquid samples (Ballesteros-Gómez, Rubio, Pérez-Bendito, 2009; Sun et al., 2014; Wu et al., 2014). According to Green Chemistry principles, the most of these methods are very time- and reagent consumption. A clear trend in sample preparation is miniaturization of the volume of organic solvent and extraction time. Liquid-phase microextraction (LPME), as an alternative to traditional preparation methods, has been increasingly applied to extract trace level organic compounds in complex samples and used to overcome many of the disadvantages of traditional methods (García-López, Rodriguez, & Cela, 2007; Melwanki & Huang, 2006; Yu, Liu, Lan, & Hu, 2008). Several extracting solvent such as supramolecular solvents, ionic liquids, supercritical fluids and ferrofluids have been used to meeting these goals (Farahani, Shemirani, & Gharehbaghi, 2013; Moral, Caballo, Sicilia, & Rubio, 2012; Naeeni, Yamini, & Rezaee, 2011; Zhang, Wang, Su, & Yang, 2013; Zohrabi, Shamsipur, Hashemi, & Hashemi,

---

* Corresponding author.
E-mail addresses: 960722979@qq.com, yilyil8@163.com (Y. Yang).

https://doi.org/10.1016/j.foodchem.2018.04.038
Received 8 August 2017; Received in revised form 21 March 2018; Accepted 12 April 2018

2016).

Recently, ferrofluid, as a unique magnetic colloidal systems, has quickly gained popularity because of its significant advantages including simplicity of operation, rapidity and minimum requirements for organic solvents (Farahani et al., 2013; Zohrabi et al., 2016). In typically, ferrofluids are suspensions of magnetic nanoparticles suspended in a carrier liquid. The magnetic particles are usually coated with a layer of the surfactant such as oleic acid, stearic acid and alkenyl succinic anhydride (Borin et al., 2016). The magnetic particles have uniformly distributed particle size (about 10–20 nm) and nearly spherical shape (Borin et al., 2016), which guarantee the stability of the ferrofluid. The magnetic nanoparticles can be stabilized in carrier liquid through some types of interactions (e.g. Van der Waals forces, dipolar attractive interactions, magnetostatic interactions, etc) (Hong et al., 2006; Lin, Lee, & Chiu, 2005; Zhao, Zhuang, Shen, Zhang, & Shao, 2009). Up to now, the magnetic and fluid properties of the ferrofluid have lead to attractive applications in different fields (Baltag, Costandache, & Salceanu, 2000; Hou et al., 2013; Lobato, de Mello Ferreira, & Mansur, 2016; Zaghouane-Boudiaf, Boutahala, & Arab, 2012). And the different mode of LPME based on ferrofluid have been reported in microextraction (Farahani et al., 2013; Shi, Zhang, & Lee, 2010; Zohrabi et al., 2016).

In the present report, a novel, rapid and effective LPME technique based on the ferrofluid was developed to analyze BPs and 4-TOP in fruit juice and milk samples. The prepared ferrofluids were composed of oleic acid-coated magnetic nanoparticles and alkyl alcohol. In comparison with previous methods, the proposed LPME technique can be used to omit the centrifugation step, simplify the extraction step and save operation time. The effect of alkyl alcohol chain length on the extraction of BPs and 4-TOP was systematically studied. Various factors affecting the extraction efficiency were also investigated. In addition, the proposed method was successfully applied for the determination of BPs and 4-TOP in real samples.

2. Experimental

2.1. Chemicals and reagents

All chemicals used were of analytical-reagent grade. Bisphenol-A (BPA, 99%), bisphenol-AF (BPAF, 98%), tetrabromobisphenol-A (TBBPA, 99.8%), 4-tert-octylphenol (4-TOP, 99.9%), n-butanol (C_4), 1-pentanol (C_5), 1-hexanol (C_6), 1-heptanol (C_7), n-octanol (C_8), 1-nonanol (C_9) and n-decyl alcohol (C_{10}) were purchased from Aladdin Industrial Corporation (Shanghai, China). Iron (III) chloride hexahydrate ($FeCl_3·6H_2O$, 98%), ammonium iron (II) sulfate hexahydrate ($(NH_4)_2Fe(SO_4)_2·6H_2O$, 97%), and oleic acid (OA, 97%) were obtained from J&K Chemical Corporation (Beijing, China). Ammonia solution ($NH_3·H_2O$) (25% w/w), sodium chloride (NaCl), sodium acetate (NaAc), magnesium sulfate ($MgSO_4$), sodium hydroxide (NaOH), acetonitrile (ACN), methanol (MeOH), were brought from Tianjin chemical reagent Technology Co., Ltd. (Tianjin, China). Standards stock solutions of BPs and 4-TOP (200 μg mL^{-1}) were prepared in methanol and stored in the refrigerator at 4–8 °C. More diluted working solutions were prepared daily by appropriate dilution of the stock solutions with methanol. HPLC-grade acetonitrile and methanol were obtained from Merck (Darmstadt, Germany).

2.2. Instrument and characterization

Transmission electron microscopy (TEM) images of the Fe_3O_4@OA NPs were taken on a Tecnai G2 F20 (FEI) electron microscope (200 kV, point-to point resolution 0.24 nm) (FEI, Holland). Fourier transform infrared (FT-IR) spectra of the sorbent (4000–400 cm^{-1}) were recorded on the infrared spectrometer Tensor 27 (Germany, Bruker). X-ray powder diffraction (XRD) measurements were obtained with Cu Kα radiation (γ = 1.5405 A) on a D/Max 2200 diffractometer over an angular range from 5° to 90° (Rigaku, America). A pH-meter Sartorious PB20 was used to detect the pH values (Gttingen, Germany). Vortex agitator (Jintan Guo Wang experimental instrument factory, Jingsu, China), ultrasonic cleaner (KMH1-120W, Shenzhen, China) and vacuum drying oven (BPZ-6011, Shanghai, China) were used in the experiment.

An Agilent 1260 series HPLC system equipped with a UV–vis diode array detector was used for the analysis of BPs and 4-TOP (Agilent Technologies, USA). The chromatographic separation was conducted on an Agilent TC-C18 column (150 mm × 4.6 mm i.d., 5 μm) at column temperature of 25 °C and the injection volume was 20 μL. The mobile phase were water and acetonitrile and performed as follows: 42% acetonitrile (0–8.0 min), 85% acetonitrile (8.0–11.0 min). The flow rate was set as 1.0 mL min^{-1}, and the detection wavelength was set at 280 nm.

2.3. Synthesis of Fe_3O_4@OA NPs

Fe_3O_4@OA NPs were synthesized by a co-precipitation method with minor modifications. Firstly, $FeCl_3·6H_2O$ (4.10 g) and $(NH_4)_2Fe(SO_4)_2·6H_2O$ (2.82 g) were dissolved under N_2 atmosphere in 50 mL of deionized water. Then, 10 mL of $NH_3·H_2O$ was added drop-wise into the solution while the solution was stirred at 80 ± 5 °C. In the next step, 2 mL of OA was added in sequence to the suspension. After the addition of oleic acid, the solution was allowed to stirred at 80 ± 5 °C for 30 min. Finally, the suspension was precipitated with ethanol and the precipitates were magnetically separated and washed twice with deionized water. The as-synthesized NPs were dried in a vacuum oven at 60 °C and then redispersed in water again via sonication. The target concentration of NPs was set to 24.5 mg mL^{-1}. The aqueous NPs products were stored and used for the following experiments.

2.4. Preparation of the ferrofluid

The oleic acid-coated magnetic particles (400 μL) and 1-heptanol (100 μL) were mixed in a vial with sonication for 3 min at room temperature. After that, a magnet at the bottom of the vial was used to collect the prepared ferrofluid and the excess water was discarded. The obtained ferrofluid was stored at 4–8 °C and used within two weeks.

2.5. Extraction procedure

In the extraction procedure, a 20 mL aliquot of sample solution and standard solution containing these phenolic compounds was placed in a screw cap polyethylene centrifuge tube. The solution pH was adjusted to 6.0 with 0.1 mol L^{-1} HCl and NaOH. Then 100 μL of ferrofluid was injected in to the samples by a syringe, and the mixture was vortex-mixed for 3 min at room temperature. After about 8 min, a neodymium magnet was deposited at the outside of the centrifuge tube, and the ferrofluid was separated from the aqueous samples. Thereafter, the separated ferrofluid was dissolved in 1 mL of MeOH containing 1% NaOH, and then the mixture was sonicated for 3 min to elute the 1-heptanol and the phenolic compounds. Finally, when the MNPs were magnetically separated, 20 μL of elution was injected into HPLC instrument for chromatographic analysis. Fig. 1 showed the schematic view of LPME experimental setup.

2.6. Preparation of samples

In this study, two different milk samples and three different commercial fruit juices containing 100% juice (apple, peach and orange) were purchased from local supermarket (Kunming, China) and stored at the same conditions as the mall. In order to avoid any deterioration and contamination, after being opened, these samples were stored at 4 °C and analyzed within two days.

For milk samples, protein precipitation is required to avoid the compromise of phenolic compounds during the extraction. For this