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Magnetic effervescent tablet-assisted ionic liquid-based dispersive liquid-liquid microextraction of polybrominated diphenyl ethers in liquid matrix samples

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ABSTRACT

Herein, a novel method, magnetic effervescent tablet-assisted ionic liquid-based dispersive liquid-liquid microextraction (META-IL-DLLME), was pioneered for extraction and preconcentration of polybrominated diphenyl ethers (PBDEs) in liquid matrix samples. In this proposed method, a magnetic effervescent tablet, containing CO_2 sources, ionic liquids and Fe_3S_4 magnetic nanoparticles (MNPs), combines extractant dispersion and magnetic recovery into one-step. Fe_3S_4 was synthesized, characterized and applied it for the first time to the newly developed method, and its extraction recoveries (ERs) for PBDEs were 20.8–32.0% higher than those of conventional Fe_3O_4 MNPs. The increased ERs of Fe_3S_4 resulted from its larger specific surface area and pore size. Some important parameters were rigorously optimized, such as kinds of magnetic nanoparticles, effervescent agents, extraction solvents and their volumes, elution solvents, extraction temperature and salt addition. Under the optimized conditions, the META-IL-DLLME method combined with HPLC-DAD analysis gave the linear ranges of 0.1–0.5–100 $\mu g\,L^{-1}$ with correlation coefficients of $>$ 0.9990. The ERs ranged from 80.7% to 99.3%, and the limits of detection and quantitation were 0.012–0.078 $\mu g\,L^{-1}$ and 0.04–0.26 $\mu g\,L^{-1}$, respectively. The intra- and inter-day precisions, expressed as relative standard deviations (RSD, n = 6), were 1.32–4.83% and 1.99–4.25%, respectively. To evaluate its matrix effect, the relative recoveries of PBDEs from tap and river water, skim and whole milk, pregnant women and women serum samples at three fortification levels (2.0, 5.0 and 20.0 $\mu g\,L^{-1}$) were in the range of 77.3–106.7%. Overall, the commercial Fe_3O_4 MNPs can only be used for magnetic separation in microextraction procedures, while Fe_3S_4 MNPs gave the higher adsorption and extraction efficiency for organic analytes besides the convenient magnetic separation. Therefore, the results obtained in this study provide a superior alternative for the conventional magnetic separation and adsorbent material. Also, this newly developed method has a great potential in routine monitoring of liquid matrix samples.

1. Introduction

Due to their high performance and cost-effectiveness, polybrominated diphenyl ethers (PBDEs) have been used for many years as flame retardants in various commercial products, such as furniture, textiles, plastics, paints, and electronic appliances [1]. As added flame retardants, PBDEs can easily enter the environment during production processes or when the products are in use. Currently, they have become ubiquitous contaminants because of their persistence, bioaccumulation, and toxicity [2]. Based on these characteristics, PBDEs have been considered as persistent organic pollutants (POPs) over the last few decades [3]. In the recent decade, PBDEs were frequently detected with rapidly increasing levels in the global environment, humans, and other biota. Several epidemiological studies have shown PBDEs to pose health

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risks, such as endocrine disruption, adverse neurobehavioral effects, to act as reproductive toxicants, and probably as carcinogens [4,5]. Owing to their ubiquity and toxicity, PBDE congeners have become an increasing concern.

As a member of POPs, different environmental monitoring programs have been proposed to detect trace PBDEs. Known methods for the detection of PBDEs in different matrices include microwave-assisted extraction (MAE) [6], solid-phase microextraction (SPME) [7], stir bar sorptive extraction (SBSE) [8], matrix solid-phase dispersion (MSPD) [9], and dispersive liquid-liquid microextraction (DLLME) [10]. Among the above methods, DLLME is a novel microextraction technique, which has advantages such as simplicity of operation, rapidity, low time and cost, high recovery and enrichment factor. Therefore, DLLME has been successfully used for determination of polycyclic aromatic hydrocarbons (PAHs) [11], polychlorinated biphenyl (PCBs) [12], organophosphorus pesticides (OPPs) [13], and chlorobenzenes (CBs) [14] in water samples. Our research group also successfully applied DLLME to detect PBDEs in water and food samples [15–17], methomyl in natural waters [18], triazophos and carbaryl pesticides in water and fruit juice samples [19], four aromatic amines in water samples [20], polychlorinated biphenyls in soils [21] and fish [22], estrone and 17β-estradiol in water samples [23], and so on. In these previously reported literatures [15–23], chlorinated solvents were preferred as extraction solvents. Even though these conventional solvents give good recoveries, they are volatile, toxic and flammable. To overcome weaknesses of the previous methods, ionic liquids (ILs) have been recently introduced as extraction solvents in DLLME procedures [24,25]. They are simple molten salts, consisting of cations and anions, and possess high thermal stability, negligible vapor pressure, tunable viscosity and miscibility with water and organic solvents, making them attractive alternatives to environmentally unfriendly solvents [26].

In IL-DLLME, the dispersion of solvent is usually assisted by an external organic solvent or by an additional energy such as shaking [27], vortexing [28], ultrasound [29], or heating [30]. The dispersive solvents, such as methanol or acetonitrile, usually in the mL range to create a cloudy solution of the extraction solvent. The dispersive solvent may participate in the partition of analytes since it increases their solubility in the aqueous phase and therefore it can reduce the potential efficacy of the technique. In recent years, several novel dispersive-solvent-free techniques, such as effervescence-assisted microextraction (EALLME), which operates on the basis of effervescent reaction, was first introduced by Lasarte-Aragones et al. in 2014 [31]. The extraction solvent was dispersed into water through the carbon dioxide produced by an added glacial acetic acid solution and the sodium carbonate contained in the samples.

Collection of the extraction solvent is usually accomplished by centrifugation, which is considered to be the most time-consuming step in the IL-DLLME technique [32]. Zhang et al. (2012) used magnetic nanoparticles (MNPs) to retrieve an IL extractant and decreased the sample preparation time in IL-DLLME [33]. A distinct advantage of MNPs is their superparamagnetism, i.e., MNPs can be easily isolated from a sample solution using an external magnetic field, and they retain no residual magnetism after the field is removed [34]. In addition, MNPs have a large surface area, which means that equilibrium can be reached more rapidly because of the larger interfacial area between the extractant and the sample, to contribute to a faster mass transfer. As a result, MNPs such as Fe_3O_4 have been widely used in chemical and biological analyses [31,35]. As an analogue of magnetite with ferromagnetic, Fe_3S_4, designated as greigite, was first proposed as a mineral by Skinner et al. [36]. Greigite was identified in many natural environments of up to a few million years old [37]. Meanwhile, the natural Fe_3S_4 sample presents a core-shell structure of crystallized greigite surrounded by an amorphous iron oxide phase [38]. Nanoscale Fe_3S_4 shows excellent magnetic property and more environmentally friendly nature as its counterpart oxide (Fe_3O_4) [39]. It was reported that Fe_3S_4 exhibited great potential applications in cancer hyperthermia and magnetic guided delivery of drugs owing to its non-toxicity and abundance [40]. However, to the best of our knowledge, there is a paucity of data regarding the use of Fe_3S_4 MNPs coupled with ILs in DLLME procedure. In this investigation, Fe_3S_4 played dual functions, i.e., adsorbent and magnetic separation, in the newly developed microextraction procedures.

The aim of this research was to synthetize and characterize a novel MNPs, Fe_3S_4, and introduced it into an analytical method, denoted as magnetic effervescent tablet-assisted ionic liquid-based dispersive liquid-liquid microextraction (META-IL-DLLME), for the trace-level determination of PBDEs in water/milk/serum samples by high performance liquid chromatography with diode array detector (HPLC-DAD). Several experimental parameters were optimized in detail. Using the optimized conditions, the proposed method was successfully applied for analyzing the real-world liquid matrix samples.

2. Experimental

2.1. Reagents and materials

The representative species of PBDE congeners were purchased from Accustandard (New Haven, CT, USA), were selected as follows: 2,4,4′-tribromodiphenyl ether (BDE-28), 2,2′,4,4′-tetrabromo diphenyl ether (BDE-47), 2,2′4,4′,5-pentabromodiphenyl ether (BDE-99), 2,2′4,4′,6-pentabromodiphenyl ether (BDE-100), 2,2′4,4′,5,5′-hexabromodiphenyl ether (BDE-153) and 2,2′4,4′,5,6′-hexabromodiphenyl ether (BDE-154). All of the above standards for PBDEs (50 μg mL^{-1}) were dissolved in isooctane.

Three ILs, 1-butyl-3-methylimidazolium hexafluorophosphate ([C_4MIM][PF_6]), 1-hexyl-3- methylimidazolium hexafluorophosphate ([C_6MIM][PF_6]), 1-octyl-3-methylimidazolium hexa- fluorophosphate ([C_8MIM][PF_6]), were purchased from Shanghai Chengjie Chemical Co., Ltd. (Shanghai, China). The HPLC-grade acetonitrile and methanol were obtained from Merck Company (Darmstadt, Germany). Ethanol, glycol, carbon disulfide and tetrahydrofuran were all of analytical grade and redistilled prior to use. Analytical grade reagents of sodium bicarbonate ($NaHCO_3$), sodium carbonate (Na_2CO_3), sodium dihydrogen phosphate dihydrate (NaH_2PO_4) were acquired from Sinopharm Chemical Reagent Company (Beijing, China). Iron (III) chloride hexahydrate ($FeCl_3{\cdot}6H_2O$) and thiourea were used for the synthesis of the magnetic nanoparticles (Fe_3S_4). All these reagents were supplied by Sigma-Aldrich (St. Louis, MO, USA). Deionized water was purified with a Millipore Mill-Q Plus System (Bedford, MA, USA).

2.2. Standard solutions and real samples

Due to the limited solubility of isooctane in water, acetonitrile was selected as intermediate solvent. Firstly, 1 mL of each PBDE congener was mixed and evaporated under a gentle nitrogen flow to remove isooctane. Then, the residue was dissolved in 10 mL HPLC-grade acetonitrile to prepare stock solution (5 μg mL^{-1} for each PBDE congener). Working standard solution was prepared by dilution of the above stock solution in acetonitrile, and stored in a refrigerator at 4 °C.

Tap water was sampled from our environmental chemistry laboratory (Wenzhou Medical University, Wenzhou, China). River water was collected from the Wen-Rui Tang River (Wenzhou, Zhejiang). They were filtered through a 0.45-μm membrane filter (Scharlau, Barcelona, Spain) to remove any particulate matters and maintained in the dark at 4 °C until analysis.

Dairy milk samples were purchased from Wenzhou Haoyouduo Supermarket (Wenzhou, China): skim milk (zero fat content; Yili brand, Inner Mongolia, China) and whole milk (high calcium milk; Yili brand, Inner Mongolia, China). Aliquots of milk (3 mL, pH = 6.81) were mixed with 200 μL of 20% acetic acid aqueous solution in a 15 mL centrifuge tube, followed by the addition of 2.8 mL water. The sample was ultrasonically shaken for 1 min and stored in a refrigerator at 4 °C for

15 min. Finally, each sample was centrifuged for 15 min at 3000 rpm and filtered with a 0.22-μm PTFE membrane filter [41]. After the above procedures, the pretreated milk samples were kept in buffer at 4 °C for further use.

Blood samples (pregnant women's blood and women's blood) were collected in the Clinical Laboratory, the first Affiliated Hospital of Wenzhou Medical University (Wenzhou, China). The plasma samples were taken intravenously in the presence of EDTA-2Na as an anticoagulant and centrifuged at 12,000 rpm for 10 min at 4 °C. Then, the supernatant (serum) was immediately transferred into an individual 2.0-mL Eppendorf tube after filtration by 0.22-μm filter membrane and stored at − 80 °C. Prior to the META-IL-DLLME procedures, the serums were thawed at ambient temperature, an aliquot of serum (1.0 mL) was extracted with 4.0 mL cold methanol for precipitating proteins, the sample were followed by centrifugation at 12,000 rpm 10 min at 4 °C. Under a gentle N_2 flow, the resulting supernatant was evaporated to 1.0 mL for further use. Ethical approval for this study was obtained from the Ethics Committee.

2.3. Apparatus

A HITACHI Chromaster 5000 HPLC system equipped with a 5430 diode array detector (DAD) was used for PBDEs quantification. Separations were obtained on a LaChrom C_{18} column (150 mm × 4.6 mm I.D., 5 μm, HITACHI Corporation, Japan) at 30 °C. The injections were carried out through a 5210 automatic sample injector. The operating conditions were as follows: mobile phase, acetonitrile-water, 85:15 (v/v); flow rate, 1.0 mL min^{-1}; injection volume, 20.0 μL; column temperature, 30 °C, and the wavelength of DAD, 226 nm.

A XH-D vortex mixer (Shanghai Zhengqiao Scientific Instrument Corporation, Shanghai, China) was used for mixing solutions. Ultrasound mixing was carried out by a model SB-5200D ultrasound cleaner (Ningbo Scientific Biology Corporation, Ningbo, China). Screw-cap centrifuge tube (15 mL) with conical bottoms (used as extraction vessels) were heated at 60 °C in an electric heating drum air temperature drying oven (Shanghai Yiheng Scientific Instrument Corporation, shanghai, China) to remove organic interferences. A T5 Single Punch Press (Shanghai Pharmaceutical Equipment Corporation, Shanghai, China) was used for preparation effervescent tablet. The materials were dried in a Senxin Vacuum Oven (DZG-6021, Shanghai, China).

The morphologies of MNPs were observed using a Zeiss Merlin Sigma 300 (Carl Zeiss SMT AG, Germany) scanning electron microscope (SEM). The identification of the crystalline phase was tested using X-ray diffraction (XRD) measurements with a Cu Kα radiation (D8 Advance, Bruker, Germany). Fourier transform infrared (FTIR) spectra were recorded on a Nicolet iN 10 instrument (Thermo Fisher Scientific, USA) with the KBr method. The magnetic property of the prepared MNPs was analyzed at 300 K with a vibrating sample magnetometer (MPMS SQUID VSM, Quantum Design, San Diego, CA, USA). The Brunauer-Emmett-Teller (BET) surface areas were determined from the N_2 adsorption at 77 K using a Quadrasorb SI system (USA). Zeta potential was measured by using Zeta potential analyzer (Malvern, UK).

2.4. Synthesis of Fe_3S_4 magnetic nanoparticles

In a typical synthesis, $FeCl_3 \cdot 6H_2O$ (3.0 mmol) and thiourea (6.0 mmol) were dissolved in 60 mL of glycol in a 100 mL Teflon-lined stainless-steel autoclave [42]. The mixture was vigorously stirred for 30 min at ambient conditions and then heated at 180 °C for 12 h (see Fig. 1A). After that, the autoclave was naturally cooled down to room temperature. The solid product was sequentially rinsed by distilled water, carbon disulfide, and ethanol several times with the separation of magnet. Finally, the obtained product was dried in a vacuum oven at 60 °C for 12 h for further characterization.

2.5. Preparation of the magnetic effervescent tablets

The effervescent precursor was prepared by mixing NaH_2PO_4 (0.24 g) and anhydrous Na_2CO_3 (0.212 g). Initially, two inorganic salts, previously dried at 90 °C for 3 h in an oven, were mixed at a molar ratio of 1:1. Then, 10 μL of the selected IL and 0.01 g of magnetic Fe_3S_4 nanoparticles were added into an aliquot (0.452 g) of the effervescence precursor mixture and then grounded in an agate mortar. Subsequently, the mixed homogeneous powder was compressed into a compact magnetic effervescent tablet (8-mm diameter × 2-mm thickness) using a T5 Single Punch Press (see Fig. 1B). Among the various types of effervescent tablets, the effervescent tablets containing IL were significantly easier to grind and shape, possibly due to the viscosity and lubricity of the IL. Then, the tablets were stored in a sealed bag in a desiccator at room temperature.

2.6. META-IL-DLLME procedures

The schematic illustration on the META-IL-DLLME procedures is depicted in Fig. 1C. It includes the following steps: (1) First of all, a 15-mL centrifuge tube containing 7.0 mL of the pretreated aqueous sample was placed in water bath at 30 °C; (2) Next, magnetic effervescent tablet was placed into the tube and then a large quantity of bubbles (CO_2) formed and rose from down to the top due to the effervescence reaction; the effervescent tablets were disintegrated within 1 min, and the extractant ($[C_nMIM][PF_6]$) and the magnetic nanoparticles (Fe_3S_4) are homogeneously distributed into aqueous sample; (3) After that, an Nd magnet was held at the bottom of the tube to achieve the separation of the $[C_nMIM][PF_6]$-coated MNPs enriched with the analytes; (4) The supernatant was decanted and discarded, and the sedimented particles are gently eluted three times with 500, 300, 200 μL of acetonitrile for analytes. The particles are again separated from the acetonitrile by means of the Nd magnet and the acetonitrile phase containing the eluted analytes were passed through a 0.22-μm PTFE membrane filter to remove potential particles; and (5) The collected eluate was concentrated with a gentle stream of nitrogen at room temperature, then the residue was redissolved in 60 μL of acetonitrile and transferred into an autosampler vial, and 20-μL was injected into the HPLC-DAD system for further analysis.

2.7. Calculation formula

In order to find the appropriate parameters to preconcentrate the selected PBDEs, the effects of some parameters on extraction performance were rigorously investigated such as kinds of magnetic nanoparticles, effervescent agents, extraction solvents and their volumes, elution solvents, extraction temperature and salt addition. In order to assess the above-mentioned parameters, enrichment factor (EFs) and extraction recovery ER (%) were used. Eqs. (1) and (2) were used for calculation of EFs and ER (%):

$$EF = \frac{C_c}{C_0} \tag{1}$$

$$ER\% = \frac{n_c}{n_0} \times 100 = \frac{C_c \times V_c}{C_0 \times V_{aq}} \times 100\% \tag{2}$$

where C_c, C_0, V_c and V_{aq} are the analyte concentration in the finally collected organic phase, the volume of organic phase, the initial analyte concentration in the sample and the volume of sample solution, respectively.

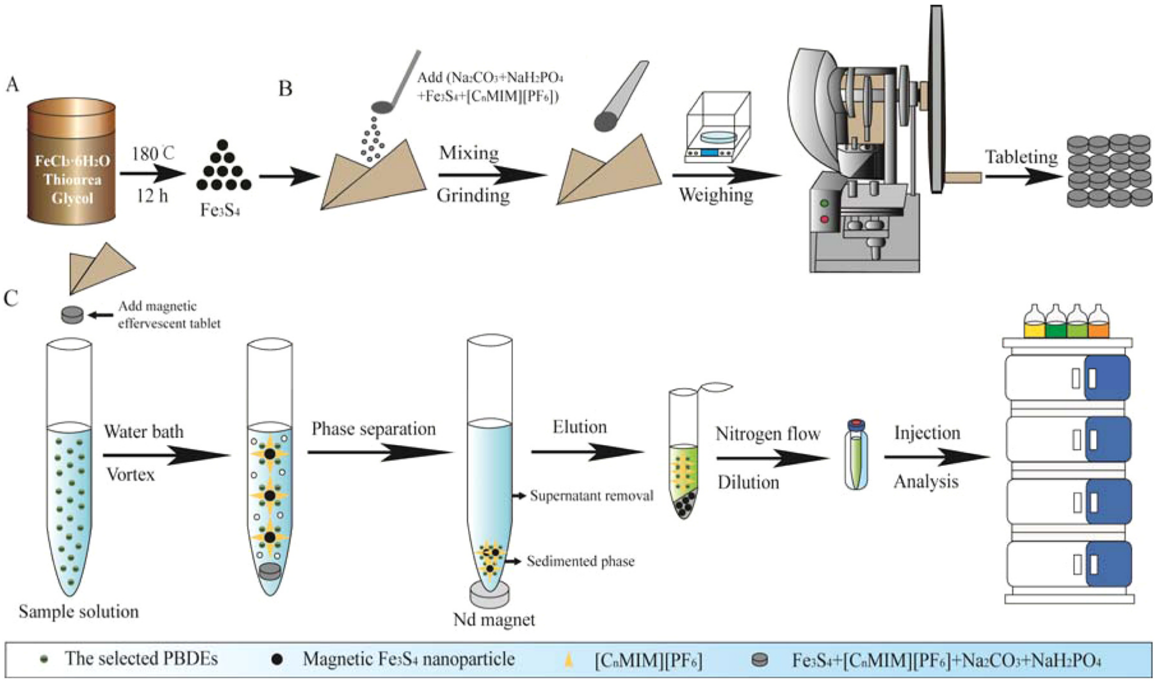


Fig. 1. Schematic illustration on the META-IL-DLLME/HPLC-DAD method. **Note**: (A) synthesis of magnetic Fe_3S_4 nanoparticles; (B) Preparation of the magnetic effervescent tablets; (C) Preconcentration of PBDEs by the developed method.

3. Result and discussion

3.1. Comparison of extraction efficiency between as-synthesized Fe_3S_4 and commercial Fe_3O_4

The extraction efficiency of the as-synthesized Fe_3S_4 and commercial Fe_3O_4 was compared by the ERs for six PBDE congeners. At the fortification amount of 0.01 g, both MNPs were observed to form a similarly homogeneous dispersive solution. As shown in Fig. 2, the commercial Fe_3O_4 has low ERs (almost below 60%) for PBDEs (53.68%, 56.28%, 54.59%, 67.11%, 59.85%, 53.4% for BDE-28, BDE-47, BDE-100, BDE-99, BDE-154, BDE-153, respectively). In contrast to Fe_3O_4, the as-synthesized Fe_3S_4 displayed better extraction capacities for PBDEs with the ERs of more than 80% (85.66%, 86.53%, 86.05%, 92.76%, 80.65%, 83.79% for BDE-28, BDE-47, BDE-100, BDE-99, BDE-154, BDE-153, respectively). The above phenomenon can be explained by the properties of the test MNPs in terms of XRD, SEM, magnetic property, FI-TR, zeta potential and N_2 adsorption-desorption isotherms, as described in the following sections. Based on these observations, the Fe_3S_4 MNPs were chosen as the optimal material in the following microextraction procedures.

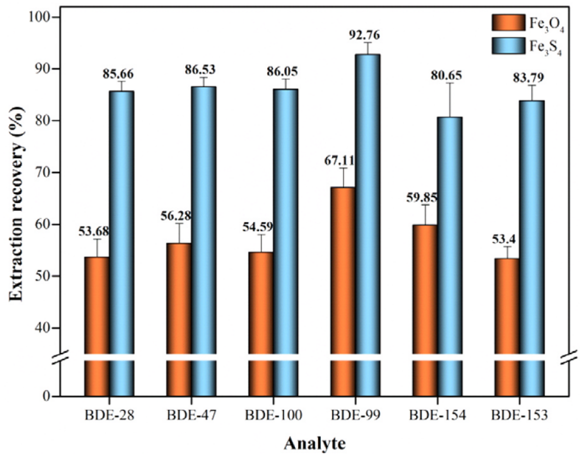


Fig. 2. Comparison in the extraction efficiency between Fe_3S_4 and commercial Fe_3O_4.

3.2. Characterization of the MNPs

3.2.1. SEM analysis

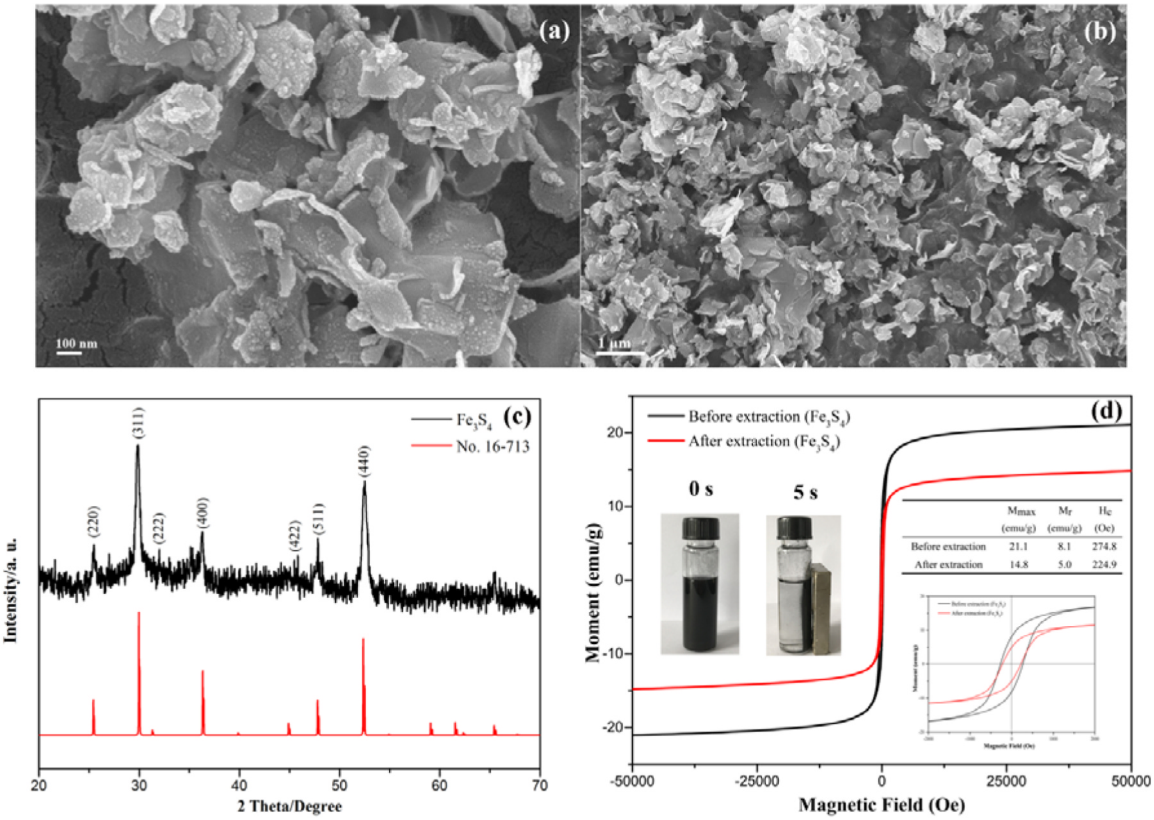
The surface morphology of Fe_3S_4 was observed by SEM. Learning form Fig. 3a and b, many small lamelliforms distribute homogeneously. Under the 50,000-fold magnification, the image clearly shows the Fe_3S_4 crystals without significant particle aggregation, which can help the nanoparticles preferably disperse in the sample solution.

3.2.2. XRD analysis

The XRD pattern of the Fe_3S_4 nanoparticles is shown in Fig. 3c. The determined characteristics at 2θ values of 25.43°, 29.89°, 31.34°, 36.33°, 44.89°, 47.80° and 52.44° can be indexed to the (220), (311), (222), (400), (422), (511) and (440) crystal planes of Fe_3S_4, respectively, when compared with the reference cubic greigite Fe_3S_4 (Joint Committee on Powder Diffraction Standards (JCPDS) No. 16-713). The broad and sharp XRD diffraction peaks are consistent with the small crystallite size and high crystallinity of the Fe_3S_4 phase.

3.2.3. Magnetic property analysis

The magnetic properties of the as-prepared Fe_3S_4 were studied using a vibrating sample magnetometer at room temperature. As shown in Fig. 3d, the saturation magnetization (M_{max}), remnant magnetization (M_r), coercivity field (H_c) with before and after extraction were 21.1 emu/g, 8.1 emu/g, 274.8 Oe and 14.8 emu/g, 5.0 emu/g, 224.9 Oe, respectively, and the curves displayed a small hysteresis loop, respectively. The slight decrease in M_{max} of Fe_3S_4 MNPs after extraction by META-IL-DLLME might result from the adhered nonmagnetic IL. However, the magnetism of the as-prepared Fe_3S_4 is sufficient to meet the requirement for magnetic separation of the solid material from aqueous phase. Very fast isolation within 5 s from the black homogeneous dispersion of Fe_3S_4 powder in water was achieved by a magnet without any remaining residues in the solution, which is of great importance for their practical application.



	Mmax (emu/g)	Mr (emu/g)	Hc (Oe)
Before extraction	21.1	8.1	274.8
After extraction	14.8	5.0	224.9

Fig. 3. Characterization of solvothermal synthesized Fe_3S_4. Note: (a) and (b) SEM; (c) XRD pattern; (d) Magnetic property analysis.

3.2.4. *FT-IR analysis*

Fig. 4A shows the FTIR spectra of the Fe_3S_4 (curve a), $[C_4MIM][PF_6]$ (curve b), the blank water extracted by Fe_3S_4 and $[C_4MIM][PF_6]$ (curve c), and the spiked water extracted by Fe_3S_4 and $[C_4MIM][PF_6]$ (curve d), respectively. In contrast to the curves of Fig. 4A-a, c and d, a peak of 3430 cm^{-1} was assigned to –OH or O-H stretching vibration band on the surface of Fe_3S_4. In the curve of Fig. 4A-b, c and d, the peaks at 1628 cm^{-1}, 1571 cm^{-1}, 1467 cm^{-1} and 1382 cm^{-1} corresponded to the C=C, C=N, $-CH_2$ and $-CH_3$ stretching vibration characteristic absorption of imidazole groups in $[C_4MIM][PF_6]$, respectively. In Fig. 4A-d, the peaks at 1275–1200 cm^{-1}, 1150–1070 cm^{-1} and 910–670 cm^{-1} corresponded to the C-O-C=C, C-O-C, and C-H stretching vibration of the analytes of PBDEs, respectively, which indicated that $[C_4MIM][PF_6]$ and enriched analytes (PBDEs) were successfully adsorbed onto the surface of magnetic Fe_3S_4 nanoparticles. As for Fe_3O_4, the peaks at 3420 cm^{-1} and 560 cm^{-1} can be attributed to -OH and Fe-O stretching vibration of Fe_3O_4, respectively (Fig. 4B-a, c and d). In the curve Fig. 4B-b, the peaks at 1571 cm^{-1} and 1467 cm^{-1} corresponded to the C=N and $-CH_2$ stretching vibration of imidazole groups in $[C_4MIM][PF_6]$, respectively. However, no any stretching vibration absorption of the PBDEs was observed, suggesting that $[C_4MIM][PF_6]$ and PBDEs were little adsorbed onto the surface of Fe_3O_4 MNPs. Consequently, the above FT-IR spectra difference may be used for explaining the differences in ERs between Fe_3S_4 and Fe_3O_4.

3.2.5. *Zeta potential analysis*

In order to further prove the difference of charge on the MNPs surface, the zeta potential of Fe_3S_4 and Fe_3O_4 was individually measured in different pH solutions. Learning from Fig. 4C and D, the values of pH at which the point of zero charge (PZC) occurred were around 5.8 for Fe_3S_4 and 5.6 for Fe_3S_4, respectively. The similar values of PZC indicated that there is almost no difference of charge on the surface of Fe_3S_4 and Fe_3O_4.

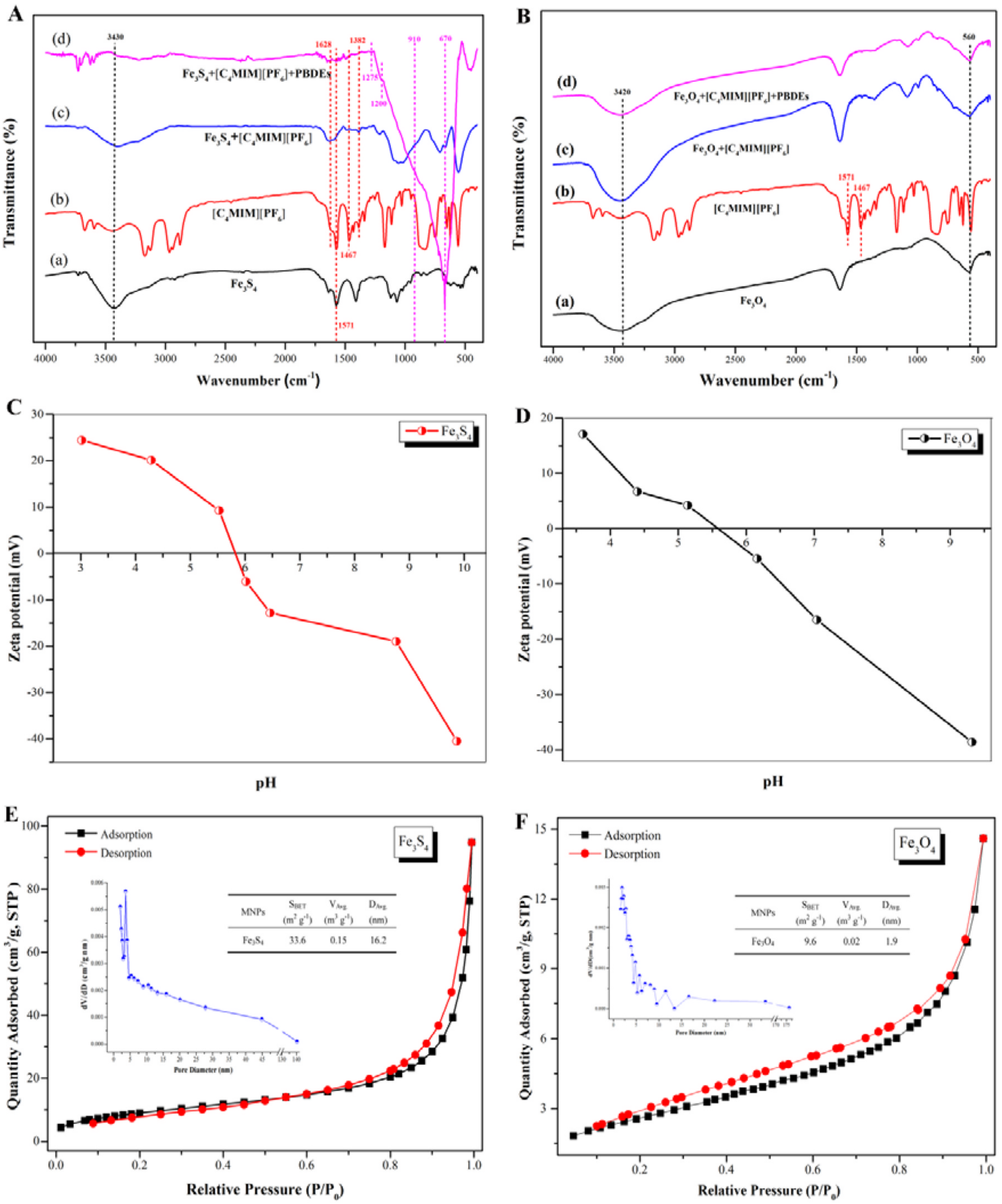
3.2.6. *N_2 adsorption-desorption isotherms*

The N_2 adsorption-desorption isotherms of the Fe_3S_4 were measured to determine the differences between the specific surface areas and the pore structure. As shown in Fig. 4E, the isotherm exhibited a type-IV N_2 adsorption branch associated with a well-defined capillary condensation step at medium relative pressures ($0.1 < P/P_0 < 1$), which indicated the formation of mesopores. The Brunauer-Emmett-Teller (BET) surface area calculated from the N_2 isotherm at 77 K was 33.6 $m^2\ g^{-1}$. The pore volume and pore size distribution of Fe_3S_4 calculated by the Barrett-Joyner-Halenda (BJH) model are shown in the inset of Fig. 4E. The BJH adsorption pore volume and average pore diameter were 0.15 $m^3\ g^{-1}$ and 16.2 nm, respectively. The pore distribution of the Fe_3O_4 was measured at the same time, and the specific surface area, pore volume and average pore diameter were 9.6 $m^2\ g^{-1}$, 0.02 $m^3\ g^{-1}$ and 1.9 nm, respectively (Fig. 4F), which were smaller than those of Fe_3S_4. Furthermore, the higher specific surface area and ultra large pore size of Fe_3S_4 significantly shorten ion diffusion lengths and provide more active sites for organic compound transformation, which might considerably enhance the interactions between analytes and the Fe_3S_4 MNPs. It is generally believed that the high specific surface area and large pore size of MNPs can greatly improve their adsorption efficiency [43].

3.3. *Optimization of META-IL- DLLME procedure*

3.3.1. *Selection of composition and molar ratio of the effervescent tablet*

The effervescent tablet (the mixture of effervescence precursors) served a vital role in this META-IL- DLLME procedure by producing sufficient bubbles during the extraction process to assist dispersion of extraction solvent. The effervescent tablet is composed of two main components, namely, an acid salt and an alkaline salt. $NaHCO_3$, Na_2CO_3 and NaH_2PO_4 were chosen as potential effervescence precursors based on previous report [44]. When $NaHCO_3$ was used in the effervescent



MNPs	S_{BET} ($m^2 g^{-1}$)	$V_{Avg.}$ ($m^3 g^{-1}$)	$D_{Avg.}$ (nm)
Fe_3S_4	33.6	0.15	16.2

MNPs	S_{BET} ($m^2 g^{-1}$)	$V_{Avg.}$ ($m^3 g^{-1}$)	$D_{Avg.}$ (nm)
Fe_3O_4	9.6	0.02	1.9

Fig. 4. Characterization of the synthesized Fe_3S_4 and commercial Fe_3O_4. **Note**: A, C, E and B, D, F were FTIR spectra, zeta potential, N_2 adsorption-desorption isotherm for Fe_3S_4 and Fe_3O_4, respectively.

reaction, the CO_2 was emitted so rapidly that the shorter dispersion time could cause a decrease in the extraction efficiency [45]. Therefore, Na_2CO_3 and NaH_2PO_4 were chosen as the effervescence precursors.

$$2H_2PO_4^{-} + CO_3^{2-} \rightarrow 2HPO_4^{2-} + CO_2 + H_2O \tag{3}$$

$$H_2PO_4^{-} + CO_3^{2-} \rightarrow PO_4^{3-} + CO_2 + H_2O \tag{4}$$

Na_2CO_3 and NaH_2PO_4 react on the basis of the chemical Eqs. (3) and (4); the ratio between two effervescent precursors is an important parameter during extraction. The amount of effervescent precursors also affected the extraction efficiency. Adding more effervescent precursors to an aqueous sample can produce more bubbles, accelerating the dispersion of the extraction solvent but also increasing the ionic strength and viscosity of the solution and possibly decreasing the ERs due to the viscous resistance effect [46]. According to the principle of chemometrics, the molar ratios between Na_2CO_3 and NaH_2PO_4 (1:1 and 1:2) were investigated. It was obvious from Fig. 5A that the ERs for six PBDEs at the ratio of 1:1 were higher than 1:2. However, an excessive amount of the agent may increase the ionic strength and viscosity of the solution, leading to a loss of recovery. Consequently, the effervescent tablet was prepared by using an aliquot (0.452 g) of effervescent agent with a 1:1 M ratio of Na_2CO_3 and NaH_2PO_4.

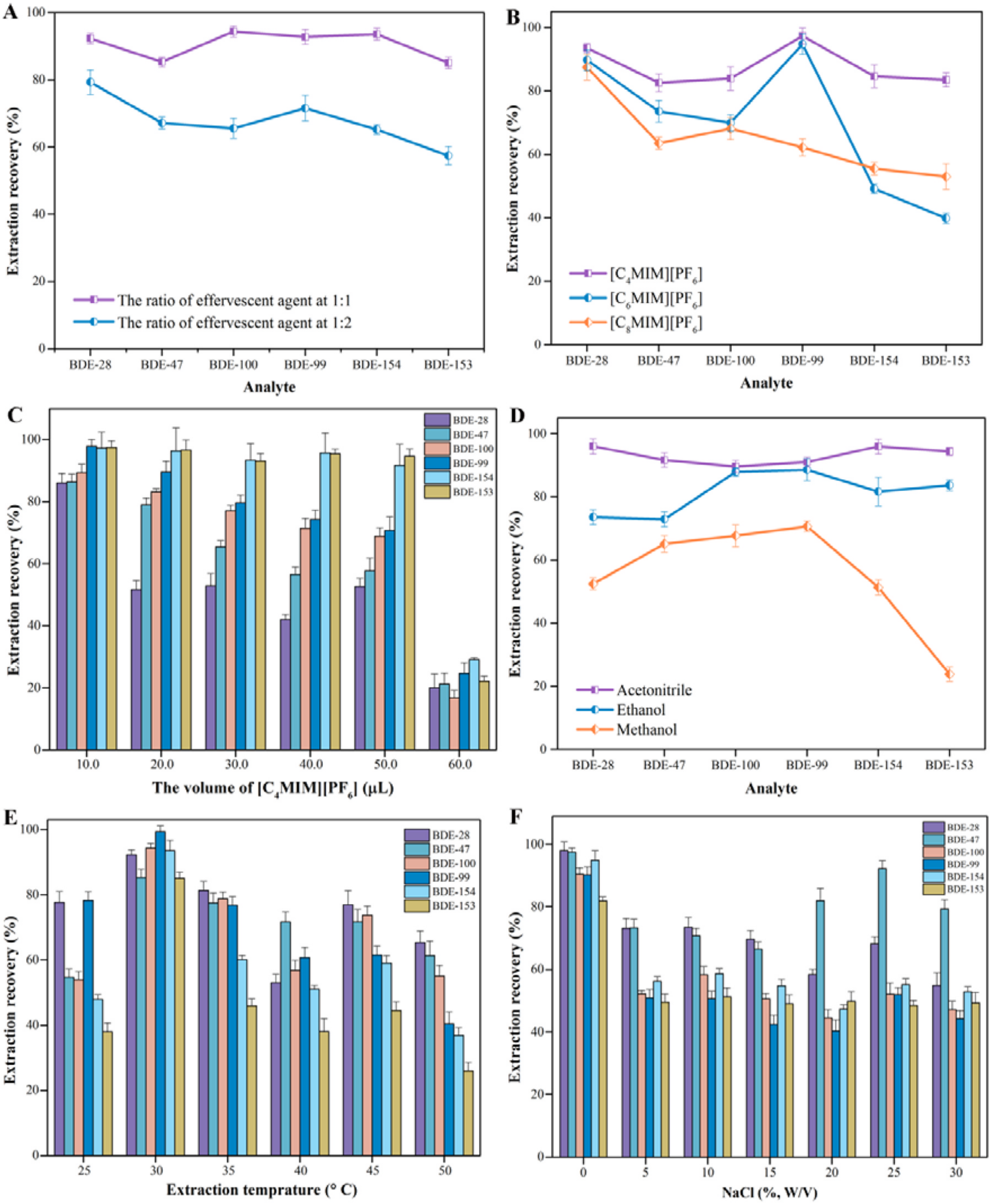


Fig. 5. Effects of the main operational factors on the ERs for PBDEs. *Error bar* shows the standard deviation (n = 3). **Note:** (A) Effect of the molar ratio of the effervescent agent; (B) Type of extraction solvent; (C) Volume of extraction solvent; (D) Type of elution solvent; (E) extraction temperature; (F) Salt effect.

3.3.2. Selection of extraction solvent

To function as an extraction solvent, an IL should posses some advantageous characteristics: (a) low solubility in water, (b) low volatility, (c) high extraction capability and (d) good chromatographic behavior. On the basis of the above considerations, $[C_4MIM][PF_6]$, $[C_6MIM][PF_6]$ and $[C_8MIM][PF_6]$ were selected as potential extraction solvent. As shown in Fig. 5B, $[C_4MIM][PF_6]$ has the highest ERs (82.6–97.3%) among three tested ILs. The higher ERs of $[C_4MIM][PF_6]$ might be explained by that its lower viscosity positively affected the transfer of the target analytes from the sample matrix to the extraction solvent. As a result, $[C_4MIM][PF_6]$ was selected as extraction solvent in subsequent experiments.

3.3.3. Influence of extraction solvent volume

The influence of extraction solvent volume on the preconcentration efficiency was also evaluated. For this purpose, different volumes of $[C_4MIM][PF_6]$ (10.0–60.0 μL) were utilized for the same procedures. According to Fig. 5C, it is clear that by increasing the volume of $[C_4MIM][PF_6]$ from 10.0 to 50.0 μL, the ERs for the most of PBDEs was slightly decreased, however, there was a prominent drop in extraction efficiencies when the volume was 60.0 μL. Due to a certain solubility of $[C_4MIM][PF_6]$ in aqueous phase, the larger volume of $[C_4MIM][PF_6]$ was used, the higher volume loss occurred, thereby resulting in a low extraction efficiency. Additionally, when the adopted volume of $[C_4MIM][PF_6]$ was 60.0 μL, an excess volume easily produced the loss

Table 1

Analytical performance of the proposed method based on META-IL-DLLME combined with HPLC-DAD.

Analyte	Liner range (μg L^{-1})	R^{2}[a]	LODs[b] (μg	LOQs[c] (μg L^{-1})	EFs[d]	RSD[e] (%, n = 6)	
						Intra-day	Inter-day
BDE-28	0.5–100	0.9993	0.075	0.25	114	2.85	2.67
BDE-47	0.5–100	0.9992	0.078	0.26	114	4.24	2.94
BDE-100	0.5–100	0.9994	0.068	0.23	115	4.83	4.07
BDE-99	0.5–100	0.9990	0.067	0.22	116	4.44	2.51
BDE-154	0.1–100	0.9991	0.012	0.04	113	3.81	4.25
BDE-153	0.1–100	0.9994	0.018	0.06	114	1.32	1.99

[a] R^{2}, coefficient of determination.

[b] LODs, limits of detection for S/N = 3.

[c] LOQs, limits of quantitation for S/N = 10.

[d] EFs, enrichment factors.

[e] RSD, relative standard deviation (n = 5).

of IL in the tablet-pressing process. On the contrary, if the volume of $[C_4MIM][PF_6]$ was less than 10.0 μL, it was difficult to be evenly pressed into tablet. Thus, 10.0 μL of $[C_4MIM][PF_6]$ was selected to obtain higher extraction efficiency.

3.3.4. Selection of elution solvent

Because the analytes extracted by the ILs were absorbed by the Fe_3S_4 MNPs and then separated from the aqueous phase, an elution step for the MNPs using an organic solvent was necessary. Herein, four solvents were selected as elution solvents: methanol, ethanol, acetonitrile and carbon disulfide. The Fe_3S_4 MNPs could produce elemental sulfur in the extraction process, which could dissolve in the carbon disulfide to produce interfering effect, and thus carbon disulfide was not appropriate in this experiment. Learning from Fig. 5D, acetonitrile gave the highest ERs of > 90% for PBDEs as compared to ethanol and methanol. A possible reason for the superior performance of acetonitrile is due to its higher solubility for $[C_4MIM][PF_6]$. Ethanol was not a suitable elution solvent because it has a higher volatility. Compared to other alternatives, acetonitrile has a lower toxicity and higher recovery. Therefore, acetonitrile was selected as elution solvent in the following experiments.

3.3.5. Effect of extraction temperature

The suitable temperature can make ILs to be better dispersed into aqueous phase, thereby increasing the contact area between aqueous and ILs phases, and thus the analytes can be faster transferred into the ILs phase to improve the extraction efficiency. For this purpose, the water bath temperature was investigated from 25 to 50 °C at 5 °C intervals. There was an obvious increase in the ERs from 25 to 30 °C, while a certain decrease from 30 to 50 ° C (Fig. 5E). The lower temperature can impede production of CO_2, but the higher temperature may enhance the mass transfer due to Brownian motion, leading to the decreased partition coefficients of target analytes into the extraction solvents [35]. Consequently, the optimum temperature was selected at 30 °C for further studies.

3.3.6. Influence of salt addition

The influence of salt concentration on the extraction efficiency was examined in the range of 0–30% (w/v) by adding NaCl into the sample. As can be seen from Fig. 5F, there was a clear decrease in extraction efficiency when salt was added. The possible reason may be that an increase in ionic strength leads to incomplete dispersion of ILs and further to decrease in the extraction efficiency. Therefore, no salt addition was used in this study.

3.4. Method validation

To evaluate the feasibility of the proposed method, the analytical performance parameters including the linear range (LR), coefficient of determination (R^2), repeatability, limits of detection (LODs), limits of quantitation (LOQs), EFs and ERs were rigorously studied under the optimum conditions. As summarized in Table 1, the LRs were in the range of 0.1–0.5–100 μg L^{-1}, and the R^2 varied between 0.9990 and 0.9994 for six PBDEs, respectively. The EFs and ERs values in water and milk samples were in the range of 113–116 and 80.7–99.3%, respectively. The LODs, based on the signal-to-noise ratio of 3, were in the range of 0.012–0.078 μg L^{-1}, while the LOQs, based on the signal-to-noise ratio of 10, were in the range of 0.04–0.26 μg L^{-1}, respectively. The repeatability was evaluated by intra- and inter-day RSDs, which were 1.32–4.83% and 1.99–4.25%, respectively. Overall, the proposed method can meet the requirements for analyses of trace-level PBDEs with relatively low LODs as well as high EFs, ERs and repeatability.

3.5. Real sample analysis

To evaluate the applicability of the proposed method, the collected samples of tap water, river water, skim milk, whole milk, pregnant women serum and women serum were extracted using the META-IL-DLLME method and analyzed by HPLC-DAD. BDE-47, BDE-99 and BDE-154 in blank river water samples were detected at 0.31 ± 4.25, 0.34 ± 3.57 and 0.38 ± 2.62 μg L^{-1}, respectively, (Table 2). To appraise the matrix effect of the proposed method, all the real samples were spiked with target analytes at 2.0, 5.0 and 20.0 μg L^{-1}. The relative recoveries for six PBDEs were in the range of 82.0–106.7%, 82.0–102.8%, 83.7–106.5%, 82.4–94.7%, 75.1–93.5% and 77.3–94.5% for tap water, river water, skim milk, whole milk, pregnant women serum and women serum samples, respectively. The quantitative results are listed in Table 2, and Fig. 6 shows the typical HPLC chromatograms for blank and spiked water/milk/serum samples (20.0 μg L^{-1}). These results demonstrated that the newly developed method is an ideal alternative tool for detecting trace PBDEs in liquid matrix samples.

3.6. Method comparison

Determination of PBDEs in water samples by the META-IL-DLLME/HPLC-DAD method was compared with other ones such as SDME [47] and other classical DLLME [10,15,25,48,49] from the viewpoint of the analytes, sample type, RSD, LODs, extraction time, extraction solvent and its volume, dispersive solvent and its volume, and centrifuge time. As listed in Table 3, this proposed method is superior in the following aspects: (1) ILs replace traditional chlorinated toxic reagents, and also its adopted volume is largely reduced; (2) The reaction of inorganic acid and alkali salts (Na_2CO_3 and NaH_2PO_4.) disperses rapidly the extractant by producing CO_2, which avoids the utilization of traditional organic dispersive solvents (methanol, acetonitrile, acetone and so on); (3) Using Fe_3S_4 MNPs to retrieve $[C_4MIM][PF_6]$ and PBDEs is convenient rather than tedious centrifugation; and (4) The extraction time in this proposed method is very short; the extraction equilibrium (less than

Table 2
Analytical performance of the proposed method for real samples (n = 3).

Analyte	Tap water			River water			Skim milk			Whole milk			Pregnant women serum			Women serum		
	Blank	Spiked level ($\mu g\,L^{-1}$)	R (%) (mean ± SD) (n = 3)	Blank	Spiked level ($\mu g\,L^{-1}$)	R (%) (mean ± SD) (n = 3)	Blank	Spiked level ($\mu g\,L^{-1}$)	R (%) (mean ± SD) (n = 3)	Blank	Spiked level ($\mu g\,L^{-1}$)	R (%) (mean ± SD) (n = 3)	Blank	Spiked level ($\mu g\,L^{-1}$)	R (%) (mean ± SD) (n = 3)	Blank	Spiked level ($\mu g\,L^{-1}$)	R (%) (mean ± SD) (n = 3)
BDE-28	n.d.	2.0	93.95 ± 2.68	n.d.	2.0	92.38 ± 4.40	n.d.	2.0	91.77 ± 2.34	n.d.	2.0	89.21 ± 2.35	n.d.	2.0	85.36 ± 3.49	n.d.	2.0	83.11 ± 3.45
		5.0	98.16 ± 4.94		5.0	90.02 ± 2.66		5.0	88.08 ± 2.28		5.0	86.32 ± 4.75		5.0	82.52 ± 4.21		5.0	85.72 ± 4.26
		20.0	97.57 ± 0.85		20.0	102.58 ± 1.95		20.0	106.45 ± 2.59		20.0	92.63 ± 1.98		20.0	88.46 ± 3.84		20.0	90.69 ± 3.75
BDE-47	n.d.	2.0	91.11 ± 6.19	0.31 ± 4.25	2.0	91.06 ± 0.28	n.d.	2.0	86.53 ± 4.30	n.d.	2.0	91.06 ± 4.87	n.d.	2.0	75.13 ± 3.83	n.d.	2.0	80.49 ± 3.67
		5.0	82.61 ± 1.27		5.0	86.31 ± 1.82		5.0	83.74 ± 1.56		5.0	87.55 ± 3.21		5.0	78.41 ± 4.17		5.0	77.34 ± 3.51
		20.0	82.03 ± 3.70		20.0	83.35 ± 4.22		20.0	85.59 ± 5.05		20.0	82.39 ± 2.68		20.0	81.68 ± 2.83		20.0	85.82 ± 2.95
BDE-100	n.d.	2.0	82.79 ± 3.41	n.d.	2.0	94.28 ± 3.62	n.d.	2.0	97.84 ± 1.73	n.d.	2.0	88.84 ± 4.08	n.d.	2.0	91.56 ± 3.86	n.d.	2.0	87.59 ± 3.95
		5.0	89.06 ± 2.12		5.0	86.35 ± 2.65		5.0	84.38 ± 3.01		5.0	92.23 ± 4.23		5.0	89.47 ± 4.62		5.0	85.34 ± 4.16
		20.0	90.44 ± 3.10		20.0	94.48 ± 4.61		20.0	91.94 ± 4.99		20.0	86.18 ± 1.96		20.0	93.37 ± 2.81		20.0	95.12 ± 4.32
BDE-99	n.d.	2.0	102.63 ± 6.11	0.34 ± 3.57	2.0	87.88 ± 3.08	n.d.	2.0	85.59 ± 5.15	n.d.	2.0	94.22 ± 3.04	n.d.	2.0	84.76 ± 3.69	n.d.	2.0	90.45 ± 2.86
		5.0	99.22 ± 4.80		5.0	93.77 ± 2.09		5.0	88.09 ± 3.59		5.0	86.39 ± 2.24		5.0	85.43 ± 3.43		5.0	87.49 ± 3.09
		20.0	89.01 ± 5.75		20.0	91.55 ± 5.81		20.0	85.79 ± 1.07		20.0	84.73 ± 2.17		20.0	89.50 ± 2.57		20.0	92.87 ± 3.61
BDE-154	n.d.	2.0	86.28 ± 0.78	0.38 ± 2.62	2.0	85.44 ± 4.47	n.d.	2.0	90.19 ± 6.59	n.d.	2.0	87.10 ± 2.64	n.d.	2.0	86.34 ± 3.19	n.d.	2.0	87.69 ± 3.42
		5.0	92.56 ± 3.98		5.0	90.71 ± 6.62		5.0	87.91 ± 4.10		5.0	94.73 ± 2.89		5.0	85.35 ± 3.06		5.0	91.47 ± 2.84
		20.0	91.46 ± 1.50		20.0	86.92 ± 2.68		20.0	85.83 ± 0.20		20.0	83.31 ± 3.55		20.0	88.53 ± 2.14		20.0	92.31 ± 3.58
BDE-153	n.d.	2.0	88.83 ± 4.92	n.d.	2.0	102.76 ± 1.51	n.d.	2.0	84.71 ± 5.86	n.d.	2.0	93.68 ± 2.67	n.d.	2.0	88.64 ± 3.13	n.d.	2.0	92.08 ± 3.39
		5.0	106.68 ± 5.24		5.0	81.97 ± 2.88		5.0	83.77 ± 4.90		5.0	87.76 ± 3.36		5.0	93.48 ± 4.05		5.0	89.49 ± 4.12
		20.0	84.54 ± 2.92		20.0	88.14 ± 4.13		20.0	91.80 ± 3.32		20.0	84.48 ± 4.30		20.0	92.14 ± 2.56		20.0	94.52 ± 3.61

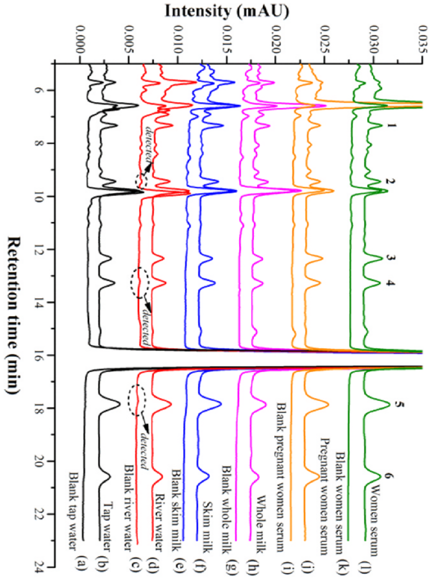


Fig. 6. The HPLC typical chromatograms for blank and spiked water/milk/serum samples (20.0 $\mu g\,L^{-1}$ for selected PBDEs by using the proposed method). **Note:** (A) Blank (a) and spiked tap water (b); Blank (c) and spiked river water (d); Blank (e) and spiked skim milk (f); Blank (g) and spiked whole milk (h); Blank (i) and spiked pregnant women serum (j); Blank (k) and spiked women serum (l). (B) Peak identification: (1) BDE-28, (2) BDE-47, (3) BDE-100, (4) BDE-99, (5) BDE-154, (6) BDE-153.

1 min) is attained very quickly and the low RSDs are probably due to rapid achievement of equilibrium. Expensive instrumentation, hazardous chlorinated extraction solvents, and complicated operations were not involved in this presented method. The green solvent and recyclable MNPs make the method environmentally friendly. Therefore, the proposed method is simple, rapid, inexpensive, easy to use and benign to the environment, which shows a great potential in routine monitoring of PBDEs-like pollutants in complex water/milk/serum samples.

3.7. Recyclability of Fe_3S_4 MNPs

The recyclability of the as-prepared Fe_3S_4 MNPs is of great importance in practical application. To investigate the recycling ability, the used Fe_3S_4 washed by acetonitrile and ultrapure water for three times, respectively. After such washing, no analytes carryover was detected and the Fe_3S_4 MNPs was reused for the further extraction cycle. As shown in Fig. S1 (Supplementary information), the Fe_3S_4 MNPs was repeated for at least six cycles with a loss of less than 15% for ERs, which proved the as-prepared Fe_3S_4 MNPs possessed excellent recyclability.

4. Conclusions

In this article, an attractive method of magnetic effervescent tablet-assisted ionic liquid-based dispersive liquid-liquid microextraction was pioneered and successfully applied for the determination of trace-level PBDEs in liquid matrix samples. As compared to conventional Fe_3O_4, the utilization of Fe_3S_4 in microextraction procedures can not only provide the simple, convenient and quick magnetic separation, but also enhance greatly the extraction efficiency owing to its larger specific surface area and pore size. Therefore, Fe_3S_4 can be used as a promising alternative for conventional magnetic separation and adsorbent material such as Fe_3O_4. The newly developed META-IL-DLLME method, with the assistance of special magnetic effervescent tablets, avoids the utilization of traditional organic dispersive solvents, and the innovative microextraction technique combines extractant dispersion and recovery procedures into one-step, thereby reducing the pretreatment time and making this method more environmental benign. Moreover, it gave high precision with RSDs of 1.32–4.83%, low LODs of 0.012–0.078 $\mu g\,L^{-1}$ and satisfactory recoveries of 77.3–106.7%. Overall, this newly developed method was proved to be simple,

Table 3
Comparison of the newly developed method with other previous ones for determination of PBDEs liquid matrix samples.

Methods	Analytes	Sample type	RSD (%)	LOD (ng L^{-1})	[a] Extraction time (min)	Extraction solvent and its volume (μL)	Dispersive solvent and its volume (mL)	Centrifuge time (min)	References
[b] SDME/HPLC -VWD	BDE-209	Tap/East Lake water	4.4	700	15	Toluene (3.0)	—	—	[47]
DLLME/HPLC -VWD	BDE-209	Tap/river/ lake water	2.1	200	< 1	Tetrachloroethane (22.0)	Tetrahydrofuran (1.0)	2.0	[10]
DLLME/HPLC -VWD	BDE-28/47/ 99/209	Tap/river water/ landfill leachate	3.8–6.3	12.4–55.6	< 1	Tetrachloroethane (20.0)	Acetonitrile (1.0)	5.0	[15]
LLE-SPE-DLLME/GC-MS	BDE-47/ 100/99/85/ 154/153	Milk	2.5–8.5	200–400	< 1	Chlorobenzene (19.0)	Acetonitrile (1.0)	3.0	[48]
LLE-DLLME/ GC-MS	BDE-47/ 100/99/85/ 154/153	Whole milk	1.7–11	12–290	< 1	Tetrachloroethane (22.0)	Acetonitrile (1.0)	10.0	[49]
[c] TA-IL-DLLME /HPLC-VWD	BDE-47/99/ 154/183	Water/urine samples	1.0–5.6	100–400	3	$[C_8MIM][PF_6]$ (40.0)	Methanol (1.0)	8.0	[25]
META-IL-DLLME /HPLC-DAD	BDE-28/47/ 100/99/ 154/153	Water/milk/ serum samples	1.3–4.8	11.8–78.7	< 1	$[C_4MIM][PF_6]$ (10.0)	Na_2CO_3 NaH_2PO_4	0	Represented method

[a] Extraction time: extraction equilibrium time.
[b] SDME: single-drop microextraction.
[c] TA-IL-DLLME: temperature-assisted ionic liquid dispersive liquid-liquid microextraction.

inexpensive, sensitive and environmentally friendly, and thus has a great potential application value in routine water/milk/serum samples monitoring of trace-level PBDEs-like pollutants. Furthermore, the effervescent tablets could be easily prepared in advance and used as needed, which is suitable for on-site detection in the field investigation or developed automation of solvent extraction/ microextraction and is thus a promising method.

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Conflict of interest

The authors declare no conflict of interest.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.talanta.2018.11.106.

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