



## Rapid magnetic solid phase extraction with in situ derivatization of methylmercury in seawater by Fe<sub>3</sub>O<sub>4</sub>/polyaniline nanoparticle

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### ABSTRACT

A new Fe<sub>3</sub>O<sub>4</sub>/polyaniline nanoparticle (PANI) material has been successfully developed as magnetic solid-phase extraction sorbent in dispersion mode for the determination of methylmercury (MeHg) in aqueous samples, via quantification by gas chromatography/mass spectrometry (GC–MS). The resultant core–shell magnetic solid-phase extraction nanoparticle (MSPE-NP) sorbent was characterized by scanning electron microscopy (SEM), energy dispersive X-ray spectrometry (EDS) and Fourier transform-infrared (FTIR) spectroscopy. Fe<sub>3</sub>O<sub>4</sub>/PANI composites showed fibrous structure with diameters between 50 and 100 nm for fibers. The MSPE-NP process involved the dispersion of the Fe<sub>3</sub>O<sub>4</sub>/PANI nanoparticles in water samples with sonication, followed by magnetic aided retrieval of the sorbent and then, solvent (hexane) desorption of extracted MeHg for GC–MS analysis. The extraction, derivatization and adsorption conditions were optimized by selecting the appropriate extraction parameters including the amount of sorbent, extraction time, derivatizing reagent volume and extraction solvent. The calibration graph was linear in the concentration range of 0.5–300 ng mL<sup>-1</sup> ( $R^2 > 0.993$ ) with detection limit of 0.1 ng mL<sup>-1</sup> ( $n = 3$ ), while the repeatability was 4.1% ( $n = 5$ ). Enrichment factor was obtained as 91. Seawater sample was analyzed as real sample and good recoveries (>98%) were obtained at different spiked values.

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### 1. Introduction

Mercury (Hg) is a well-known environmental pollutant that exists in three major forms: elemental Hg, a common form in air, inorganic Hg (II) and organic Hg, especially methylmercury (MeHg) [1]. Some microbes can convert inorganic forms of mercury into organic forms that can be accumulated by aquatic life. It has been reported that MeHg is a high toxic compound to human [2]. To evaluate the potential risks of various Hg species, they must be determined with highly sensitive and reliable methods.

To measure trace level contaminants in environmental water samples, pre-concentration is usually necessary before instrumental analysis. Some extraction methods, for example, liquid–liquid extraction [3], cloud point extraction [4], and solid-phase extraction (SPE) [5], have been employed to extract organic pollutants. For this purpose, SPE is one of the most effective trace element pre-concentration methods because of its simplicity, rapidity and ability to attain a high concentration factor [6].

Recently many research groups have used nanomaterials for analyte extraction in biological and chemical analysis [7–10].

Compared with traditional SPE sorbents, nanomaterials possess large surface area and short diffusion route, which may result in high extraction efficiency and rapid extraction dynamics. However, there are some unavoidable difficulties when nanomaterials are applied to extract target compounds from large volumes of water samples. If column dynamic extraction mode is used, it consumes plenty of time for water samples passing through nanoparticle packed SPE columns due to the high back-pressure. When static batch mode is used, centrifugal separation is inapplicable for large volumes of samples, and filtration will encounter the same problem as column dynamic extraction mode. In order to overcome these disadvantages, various magnetic nanoparticle (MNP) SPE sorbents have been developed in recent years. Because of the importance and very wide application of MNPs, some researcher groups recently published good reviews about their synthesis methods and applications in various scientific fields [11–13]. Magnetic carrier technology was first reported by Robinson et al. in 1973 [14], the synthesis of nano (or micro) magnetic carriers has been attracting intense interest due to their wide promising applications such as protein and enzyme immobilization, immunoassay, RNA and DNA purification, cell isolation, and target drug [15–18]. A distinct advantage of this technology is that magnetic materials can be readily isolated from sample solutions by the application of an external magnetic field. This

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property makes them particularly suitable for sample preparation because no centrifugation or filtration of sample is needed after extraction. MNPs such as  $\text{Fe}_3\text{O}_4$  is good candidate for magnetic carrier technology by considering the main advantages: (1) magnetic nanoparticles can be produced in large quantity using a simple method; (2) it can be expected that their adsorption capacity is high by considering their large surface area; (3) they have strong magnetic properties and low toxicity [19–22]; and (4) these particles are superparamagnetic, that means metal-loaded sorbent can be easily separated from the treated water via an external magnetic field. Magnetic nanoparticles have been successfully applied to separate some proteins, organic compounds and metal ions [23,24]. Recently, some research groups have developed applicability of modified  $\text{Fe}_3\text{O}_4$  nanoparticle for extraction and determination of trace amounts of organic and inorganic compounds from aqueous solutions [25–27]. Cai et al. [28–30,26,31] employed  $\text{Fe}_3\text{O}_4@\text{C}_{18}$  MNPs as sorbents for the removal and recovery of polycyclic aromatic hydrocarbons and phthalate esters from environmental water samples. The adsorption capacity was found to be very high.  $\text{Fe}_3\text{O}_4$  modified by mercaptopropyltrimethoxysilane was explored for preconcentration of some heavy metal ions and tellurium [32–38].  $\text{Al}(\text{OH})_3$  was used to prepare magnetic doped microcapsules for fluoride adsorption [39], and poly(1-vinylimidazole)-grafted magnetic nanosorbent was also synthesized and used to separate copper ions [40].

It was shown that polyaniline (PANI) is quite efficient in SPE and has many advantages over some commercial sorbents [41,42]. This polymer is promising for extraction applications because of its good environmental stability, facile synthesis, extraction capability of polar compounds and relatively low cost. The use of aniline-based polymer as SPE sorbents has been demonstrated [43–47]. PANI capable extracts acidic, basic, and neutral compounds. It can increase the retention of polar analytes due to the both polymeric skeleton (reversed-phase mechanism and  $\pi$ – $\pi$  interaction) and having the functional groups [48,49].

Shielding of magnetic nanoparticles with intrinsic conducting polymers can exhibit both conducting and magnetic properties for the fabricated nanocomposites. The aim of this study was to develop a novel magnetic solid-phase extraction nanoparticle sorbent for preconcentration and determination of trace amounts of MeHg from environmental water sample after *in situ* phenyl derivatization.

## 2. Experimental

### 2.1. Chemicals and materials

Aniline (reagent grade), iron (II) chloride tetrahydrate, iron (III) chloride hexahydrate, sodium hydroxide, hydrochloric acid, ammonium peroxydisulfate, hexane, ethanol and methanol (analytical grade) were purchased from Merck. All experiments were carried out with Milli-Q purified water. Methylmercury (II) chloride standard was purchased from Alfa Aesar. Sodium tetraphenylborate,  $\text{NaBPh}_4$ , was purchased from Merck.  $100\text{ mg L}^{-1}$  stock solution of MeHg was prepared by dissolving its salt in methanol (HPLC grade, Merck). All stock solutions were stored in glass vials protected against light at  $4^\circ\text{C}$ . Working standard solutions were daily prepared by diluting the appropriate amount of stock solutions in Milli-Q water.  $\text{NaBPh}_4$  was used as the derivatization agent, and these solutions were prepared immediately before the derivatization step. Sodium acetate/acetic acid buffer solutions (2 M,  $\text{pH} \sim 5$ –6) were used for pH adjustment. Seawater was collected from Persian Gulf.

### 2.2. Apparatus

Scanning electron microscopy (SEM) measurements were performed on a S4160 Hitachi (Tokyo, Japan) microscope equipped with energy dispersive X-ray spectrometry (EDS). Fourier transform infrared (FTIR) spectra of KBr powder-pressed pellets were recorded on an ABB BOMEM model FTLA 200-100 instrument.

The gas chromatography–mass spectrometry (GC–MS) analysis was performed using a model 6890N network GC system (Agilent, USA) equipped with a 5973 mass selective detector (Agilent, USA) and a MSD chemstation software on a HP-5 fused silica capillary column (30 m  $\times$  0.25 mm I.D.). The oven temperature program was isothermal for 1 min at  $60^\circ\text{C}$ , raised to  $120^\circ\text{C}$  at a rate of  $25^\circ\text{C min}^{-1}$  and then raised to  $240^\circ\text{C}$  at a rate of  $15^\circ\text{C min}^{-1}$ . Helium was used as the carrier gas at a flow rate of  $1.0\text{ mL min}^{-1}$ . The mass spectrometer was operated in the selected ion-monitoring (SIM) mode at 292, 294 and 297  $m/z$ . The injector and auxiliary temperatures were set at 250 and  $280^\circ\text{C}$ , respectively.

### 2.3. Synthesis of $\text{Fe}_3\text{O}_4$ nanoparticles

$\text{Fe}_3\text{O}_4$  nanoparticles were synthesized by co-precipitation of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions in the presence of alkaline solution under hydrothermal treatment. 5.2 g of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and 2.0 g of  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  were dissolved in 25 mL of 0.4 M HCl. The solution of the mixed iron-salts was added drop-wise into a 1.5 M NaOH solution (250 mL) with vigorous stirring under an atmosphere of nitrogen gas. Then the obtained black precipitate was heated at  $75^\circ\text{C}$  for 30 min. The precipitate was collected through centrifugation at 4000 rpm, washed sequentially with distilled water and ethanol. A black colored powder ( $\text{Fe}_3\text{O}_4$  nanoparticles) was obtained upon drying under vacuum at  $60^\circ\text{C}$  for 6 h.

### 2.4. Synthesis of $\text{Fe}_3\text{O}_4/\text{PANI}$ nanocomposite

$\text{Fe}_3\text{O}_4/\text{PANI}$  was synthesized by a self-assembly method in the presence of HCl as dopant [50] with some modification. 0.3 mL HCl (0.1 M) was dissolved in 10 mL of deionized water. 0.2 mL aniline monomer and definite amount of  $\text{Fe}_3\text{O}_4$  (0.25 g) nanoparticles were added to the above reaction mixture and stirred at room temperature. An aniline/HCl complex containing  $\text{Fe}_3\text{O}_4$  nanoparticles was obtained. Five milliliters aqueous ammonium peroxydisulfate (2.2 mmol) was added drop wise to the solution of PANI/HCl complex containing  $\text{Fe}_3\text{O}_4$  nanoparticles. The mixture was left over night. The product was washed with deionized water, methanol and ether three times, respectively, and then dried in vacuum for 24 h to obtain green-black powder of  $\text{Fe}_3\text{O}_4/\text{PANI}$  nanocomposites. Fig. 1a shows the schematic diagram of preparation procedure of  $\text{Fe}_3\text{O}_4/\text{PANI}$  sorbent.

### 2.5. SPE procedure with *in situ* phenyl derivatization

The following steps were applied to extract and determine the MeHg from the sample solution: (1) the pH of sample solution ( $\sim 47\text{ mL}$ ) was adjusted at 5.0 by 1.0 mL of acetate buffer (2 M) in conical glassware tube ( $V = 150\text{ mL}$ ); (2) 2 mL of the  $\text{NaBPh}_4$  solution (1%, w/v) was added into the sample solution as the derivatization reagent; (3) after shaking, 20 mg of  $\text{Fe}_3\text{O}_4/\text{PANI}$  nanocomposites were added into the solution and final volume of the solution was adjusted at 50 mL using ultra-pure water; (4) the mixture was shaken under sonication and allowed to complete the extraction process within 15 min; (5) the mixture was exposed to a strong magnet (15 cm  $\times$  12 cm  $\times$  5 cm, 0.8 T) at 5 min then the

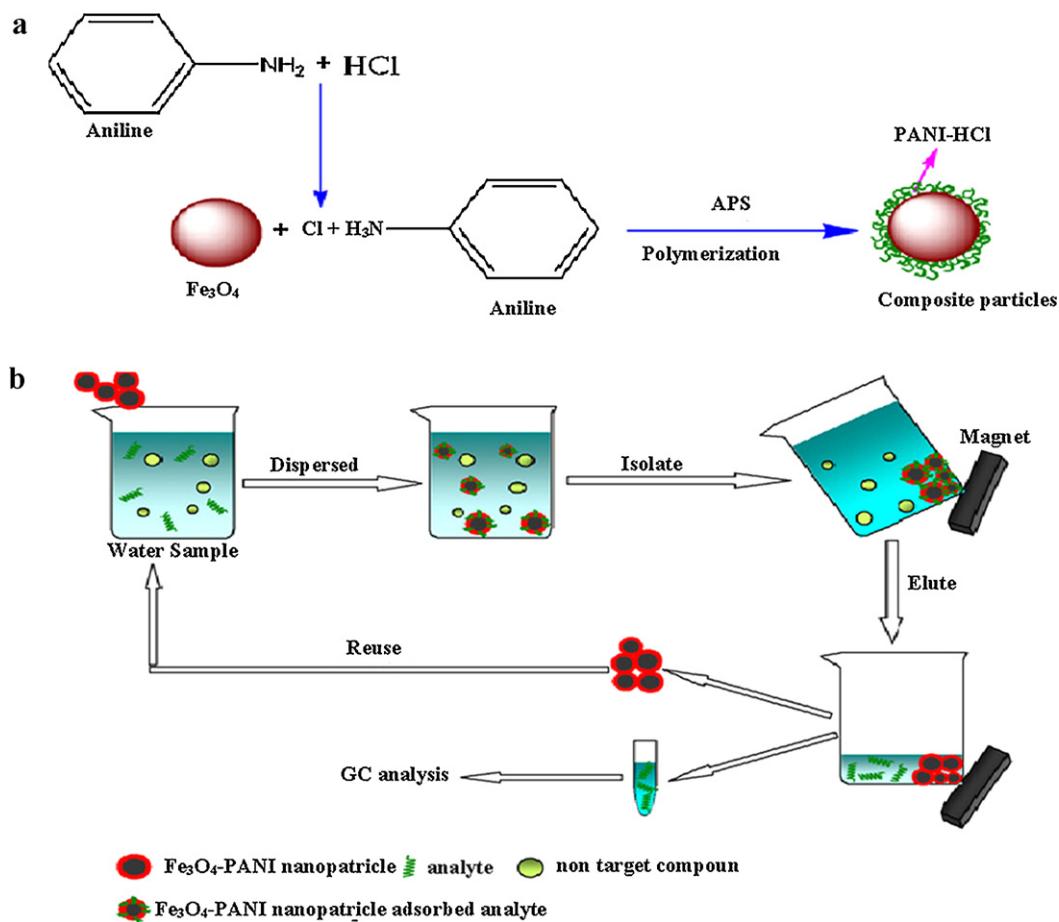


Fig. 1. Schematic diagrams of (a) the preparation of Fe<sub>3</sub>O<sub>4</sub>/PANI sorbent, and (b) its application for enriching analyte as MSPE-NP sorbent.

solution became limpid and the supernatant solution was completely decanted; (6) (3 × 1.5 mL) hexane (eluent solvent) was added to the isolated adsorbent to desorb the target analyte and the hexane extract was collected into a 10 mL test tube; (7) the hexane extract was then dried with a stream of nitrogen to 0.5 mL; (8) 1 μL of obtained hexane extract was injected into the GC system for analysis. Fig. 1b shows the schematic diagram of analyte enrichment by MSPE-NP method. The derivatization reaction of MeHg with NaBPh<sub>4</sub> was as follows:



### 3. Results and discussion

#### 3.1. Characterization of new sorbent

Characterization of the sorbent was performed by SEM, EDS and FTIR studies. The surface characteristic of prepared Fe<sub>3</sub>O<sub>4</sub>/PANI NPs was investigated by SEM technique. As illustrates in Fig. 2a, the morphology of NPs surface was fibrous with fibers with nano-sized diameters between 50 and 100 nm. Porous structure of the NPs surface is evenly distributed. The nanoparticles provide large surface area and then high extraction capacity [51]. Fig. 2b also displays the

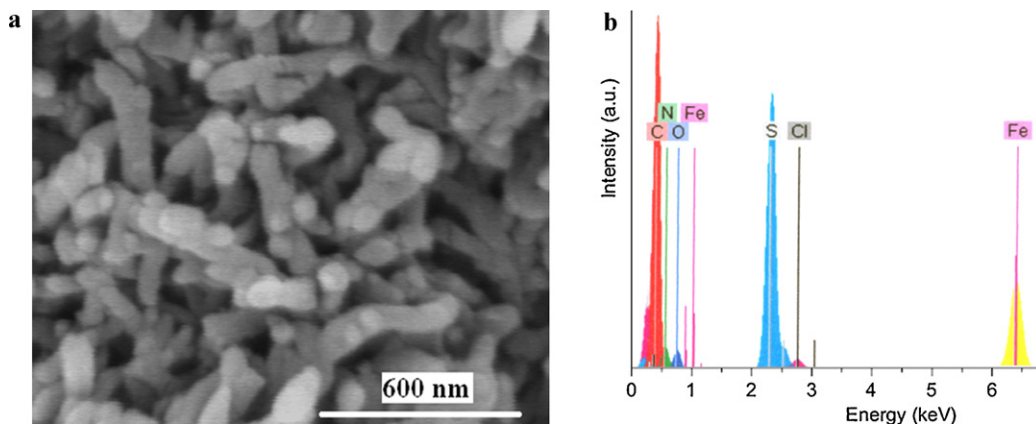


Fig. 2. (a) SEM image of Fe<sub>3</sub>O<sub>4</sub>/PANI sorbent surface at 30,000× magnifications. (b) The EDS spectra of Fe<sub>3</sub>O<sub>4</sub>/PANI nanocomposites.

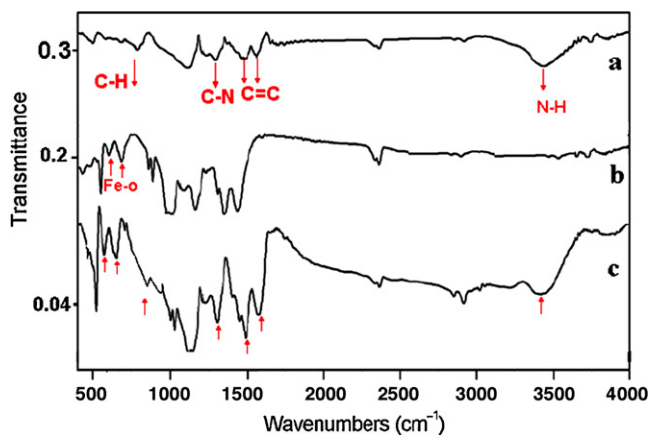


Fig. 3. FTIR spectra of pure PANI (a), pure  $\text{Fe}_3\text{O}_4$  (b), and  $\text{Fe}_3\text{O}_4/\text{PANI}$  nanocomposites (c).

EDS spectra for  $\text{Fe}_3\text{O}_4/\text{PANI}$  nanoparticles. As shown in this figure C, O, Fe, Cl, S and N peaks were found at 0.24 keV, 0.52 keV, 0.69 keV and 6.41 keV, 2.61 keV, 2.43 keV and at 0.52 keV. The weight ratios were: C, 60.4%; N, 17.73%; O, 8.97%; Fe, 7.46%; Cl, 0.15%; S, 5.29%. These results proved that the iron (II and III) chloride slats were not formed during the synthesis of nanocomposites because of the low concentration of HCl used. The small Cl and S peaks observed in the spectrum are related to the dopant of HCl and oxidant of APS used during the preparation of  $\text{Fe}_3\text{O}_4/\text{PANI}$ .

The FTIR spectra of PANI (a),  $\text{Fe}_3\text{O}_4$  (b) and  $\text{Fe}_3\text{O}_4/\text{PANI}$  NP (c) were shown in Fig. 3. The typical absorption peaks of pure PANI in Fig. 3a at 1304, 832, 1500/1550 and 3450  $\text{cm}^{-1}$  were attributable to C–N, C–H, C=C and N–H bonds, respectively. The chemical structure of PANI was confirmed due to these peaks. The peaks appeared at 571 and 572  $\text{cm}^{-1}$  in Fig. 3b, is attributed to the Fe–O stretching band of  $\text{Fe}_3\text{O}_4$ . On the other hand, both absorption peaks of PANI and Fe–O were appeared in Fig. 3c that clearly demonstrates the successful modification of  $\text{Fe}_3\text{O}_4$  nanoparticles surface with PANI.

X-ray diffraction elemental analysis, thermal gravimetric analysis (TGA) and UV–visible spectroscopic studies were also discussed in details in some papers [52,53].

The extraction efficiency results obtained from  $\text{Fe}_3\text{O}_4/\text{PANI}$  NPs were compared to the results of  $\text{Fe}_3\text{O}_4$  NPs in Fig. 4. As illustrates in this figure,  $\text{Fe}_3\text{O}_4/\text{PANI}$  NPs show higher extraction efficiency than  $\text{Fe}_3\text{O}_4$ . The results indicated that PANI improves extraction efficiencies of  $\text{Fe}_3\text{O}_4$  NPs through its high extraction capability.

### 3.2. Optimization of extraction conditions

In this study, one-variable-at-a-time optimization approach was used for the optimization of MSPE-NP conditions.

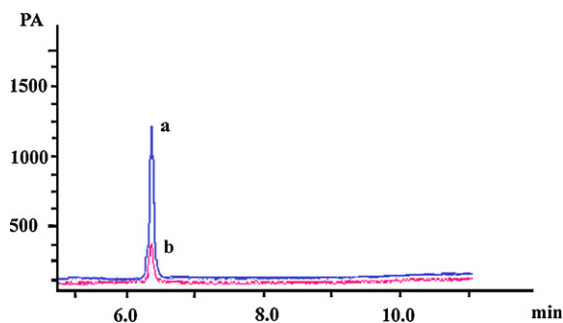


Fig. 4. Chromatograms of standard solutions ( $100 \text{ ng mL}^{-1}$ ) of MeHg extracted by  $\text{Fe}_3\text{O}_4/\text{PANI}$  (a) and  $\text{Fe}_3\text{O}_4$  (b) NPs sorbent.

#### 3.2.1. Effect of amount of nanoparticles sorbent

To obtain the maximum extraction efficiencies of target analyte, the amount of adsorbent is optimized by varying mass of  $\text{Fe}_3\text{O}_4/\text{PANI}$  sorbent from 10 to 60 mg in 50 mL water. The extraction efficiencies of MeHg increased with adding amount of magnetic adsorbents. Fig. 5a shows the MeHg extraction efficiencies reached the maximum when the amount of adsorbent was 20 mg, and then kept invariant. According to the above results, 20 mg was selected as the final amount of magnetic adsorbents used in the following studies.

#### 3.2.2. Effect of extraction time

Generally, sufficient contact time is required to attain adsorption equilibrium for target compound on sorbents. For studying the effect of extraction time on MeHg extraction efficiency, extraction times were varied in the range of 5–30 min. It was observed (Fig. 5b) that after 15 min, the GC response intensities of MeHg had no significant variation. Thus, the extraction time of 15 min was selected for further studies.

#### 3.2.3. Effect of derivatizing agent volume

One important parameter affecting MSPE-NP with in situ derivatization was the volume of the derivatization reagent. In this regard, optimization of the volume of 1% NaBPh<sub>4</sub> solution was performed using  $10 \text{ ng mL}^{-1}$  standard solutions of MeHg. The results showed the phenylated MeHg gave a maximum response in the 2 mL volume of 1% NaBPh<sub>4</sub> solution. Therefore 2 mL was considered to be the optimal volume of 1% NaBPh<sub>4</sub> solution (Fig. 5c).

#### 3.2.4. Effect of elution solvent type

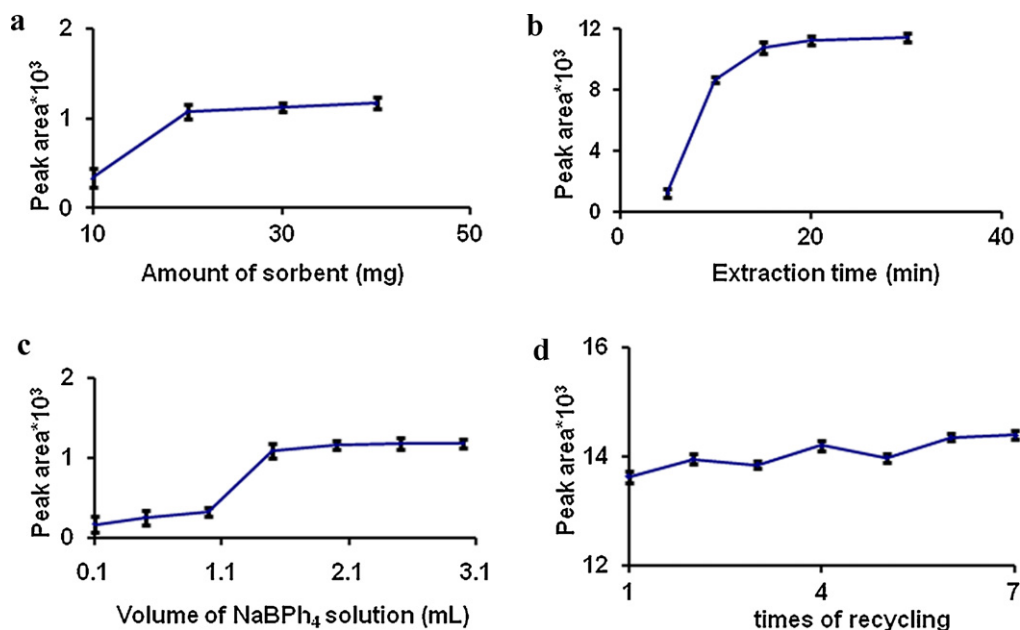
Desorption of derivatized MeHg from  $\text{Fe}_3\text{O}_4/\text{PANI}$  sorbents was studied using acetonitrile, hexane and methanol. Results showed that hexane, acetonitrile and methanol are able to desorb target compound from the sorbents but hexane was selected as elution solvent because it was more selective and effective due to its non-polar feature and is suitable for extraction of non-polar compound. Also it is immiscible with water. It is in agreement with the result obtained by the pervious works [54,55] on MeHg extraction.

#### 3.2.5. Effect of salinity

To investigate the effect of salinity on the recoveries of target compound, NaCl with concentrations of 0–20% (w/v) was added into solution. Any decrease or increase was not observed for the extraction efficiencies of analyte with the concentration range of 0–20% (w/v) of NaCl. The results (data not shown) indicated that ionic strength had no significant effect on the extraction efficiency. There is a possible for this observation that derivatization occurs after adsorption of MeHg ions on the sorbent surface. Therefore, due to the specific tendency of modified  $\text{Fe}_3\text{O}_4$  nanoparticle for MeHg ions, engaging of water molecules with NaCl ions has no significant effect on the adsorption of MeHg ions on the sorbent [56]. Therefore, the effect of salinity on the extraction efficiencies of target compound in real water sample is negligible.

### 3.3. Reusability of $\text{Fe}_3\text{O}_4/\text{PANI}$ sorbents

In order to investigate the recycling of the nanoparticle sorbents, the  $\text{Fe}_3\text{O}_4/\text{PANI}$  sorbents were rinsed with 5 mL of acetonitrile twice before application in the next time. The recoveries of MeHg were indicated in Fig. 5d. After seven times of recycling, there was no obvious decrease or increase for the recoveries of analytes. The results indicate that the  $\text{Fe}_3\text{O}_4/\text{PANI}$  sorbent were reusable with no analyte carryover during SPE procedure.

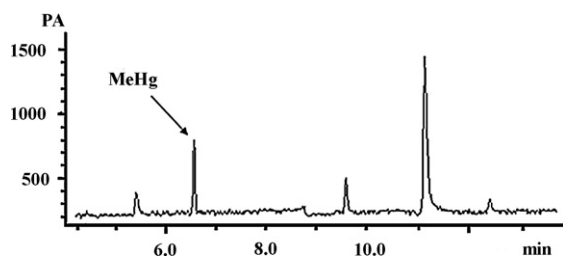


**Fig. 5.** (a) Effect of the amount of  $\text{Fe}_3\text{O}_4/\text{PANI}$  sorbent added for the adsorption of MeHg. (b) Effect of extraction time on the extraction efficiency of MeHg. (c) Effect of derivatization reagent volume on the extraction efficiency of MeHg. (d) Effect of recycling times on the extraction efficiency of MeHg. The concentration of all used standard solutions was  $10 \text{ ng mL}^{-1}$ , except in (d), which it was  $15 \text{ ng mL}^{-1}$ .

#### 3.4. Precision, limit of detection and linearity

The method figures of merit under optimum conditions conclude linear dynamic range in the concentrations of  $0.5\text{--}300 \text{ ng mL}^{-1}$  with good correlation coefficient ( $R^2=0.993$ ). Limit of detection (LOD,  $S/N=3$ ) was  $0.1 \text{ ng mL}^{-1}$ . The LOD and limit of quantitation (LOQ) in the spiked real sample were obtained as  $0.15$  and  $0.5 \text{ ng mL}^{-1}$ , respectively. Relative standard deviation (RSD) of the method for triplicate determination of the  $10 \text{ ng mL}^{-1}$  standard solutions of MeHg was 4.1%. Enrichment factor for the MeHg was 91. The content of MeHg in seawater was obtained as  $12.0 \text{ ng mL}^{-1}$ . The recovery values were estimated by spiking of MeHg standard solution in two concentration levels of 2 and  $50 \text{ ng mL}^{-1}$  and they were  $98 \pm 10\%$  and  $105 \pm 10\%$ , respectively.

Natural “dissolved organic matter” (DOM), often represented as “dissolved organic carbon” (DOC), have important effects on the extraction of many contaminants (such as MeHg, Hg (II)) from natural water samples. MeHg in water generally tend to associate with DOC because MeHg form strong “complex” with DOC [57]. Field measurements show that the concentrations of complexes of Hg (II)/MeHg–DOC increase with increasing DOC concentrations. However, when DOC concentrations are low ( $<5 \text{ mg L}^{-1}$ ), the formation of complexes of Hg (II) and MeHg with DOC is limited [58]. In this work, the DOC content of seawater was  $0.7 \text{ mg L}^{-1}$  and therefore, the effect of DOMs on the extraction efficacy of MeHg was negligible. The recovery values also proved this subject.



**Fig. 6.** Chromatogram of MSPE-NP-GC-MS analysis of seawater.

A typical GC–MS chromatogram of seawater sample was shown in Fig. 6.

The analytical performance data obtained from the proposed sorbent were compared to the results of commercial sorbent ( $\text{C}_{18}$  cartridge) [59]. The results showed that the recovery ( $>98\%$  versus  $93\%$ ) and LOD ( $0.1$  versus  $3 \text{ ng mL}^{-1}$ ) values of the proposed sorbent were better than the commercial sorbent of  $\text{C}_{18}$ .

#### 4. Conclusions

The determination of trace amounts of MeHg in seawater sample using magnetic solid-phase extraction nanoparticle sorbent with in situ derivatization was described. The proposed method has following merits: (a) convenient and rapid collection of analyte from adsorbent surface using of magnet elution, which avoids the time-consuming column passing or filtration operation. (b) A few adsorbent requirements. (c) Relatively low cost of proposed magnetic adsorbents compared with the commercial SPE adsorbents of  $\text{C}_{18}$ ,  $\text{C}_8$ . (d) Higher extraction efficiency of  $\text{Fe}_3\text{O}_4/\text{PANI}$  NPs than  $\text{Fe}_3\text{O}_4$  NPs. (e) Simultaneous extraction and derivatization procedure.

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