Vortex-assisted Dispersive Solid-phase Extraction Using Schiff-base Ligand Anchored Nanomagnetic Iron Oxide for Preconcentration of Phthalate Esters and Determination by Gas Chromatography and Flame Ionization Detector

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Phthalate esters are synthetic chemicals that are widely used in plastic industries as plasticizer. They are harmful to humans and could be carcinogenic. In this research, a new nanosorbent was prepared via a Schiff-base reaction between p-dimethylaminobenzaldehyde and Fe3O4@SiO2-NH2 nanoparticles. A characterization of the sorbent was performed by Fourier-transform infrared spectroscopy, transmission electron microscopy, scanning electron microscopy, and energy-dispersive spectroscopy. A modified nanosorbent has a core shell structure, and shows a great tendency towards the sorption of phthalate esters. Hence, it was utilized for the dispersive solid-phase extraction of six phthalate esters and determination by gas chromatography-flame ionization detection. Several variables, such as the pH, sorbent amount, salt effects, extraction and desorption time, extraction solvent type and volume, were investigated to establish the optimal conditions. Calibration graphs were linear in the range of 1.0 – 150.0 μg L⁻¹ for dimethyl phthalate, bis-(2-ethylhexyl) phthalate, di-n-octyl phthalate and 0.1 – 200.0 μg L⁻¹ for diethyl phthalate, di-n-butyl phthalate and butyl benzyl phthalate, respectively. The obtained limits of detections (S/N = 3) were in the range of 0.02 – 0.31 μg L⁻¹. Application of the method for the enrichment and determination of phthalate esters in mineral water, natural low fat yogurt and sodium chloride infusion (0.9%, w/v) was investigated.

Keywords Phthalate esters, dispersive solid phase extraction, p-dimethylaminobenzaldehyde, nanosorbent, Schiff-base

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Introduction

Phthalic acid esters (PAEs) are among hazardous materials for humans at even low concentration levels because of their toxicity and bioaccumulation.1 PAEs are synthetic chemical compounds widely used as plasticizers for the fabricating polymeric containers, such as plastic bottles, food packages, and cosmetics to improve their persistence, transparency, performance and plasticity.2 They enter into foods, water and beverages through contact with plastic containers3 and into environment from industrial applications. PAEs can impress on the skin and endocrine system, cause carcinogenicity and also influence genital development.4–6 Scientific researchers have also proved that PAEs at high concentrations may hurt human organs, like the lung, kidney and liver.7 According to European Food Safety Authority (EFSA), tolerable daily intake (TDI) values for DEHP, DnBP, BBP and DBP are 0.05, 0.01, 0.15 and 0.04 mg kg⁻¹, respectively.8 The US Environmental Protection Agency (EPA) has also set the maximum admissible concentration (MAC) or maximum contamination level (MCL) of DEHP at 6 μg L⁻¹ and the threshold values (TLV) of DEP, DBP, DMP and DEHP are 0.55, 0.45, 5.0 and 5.0 mg L⁻¹, respectively.9 The World Health Organization (WHO) has also established a reference value of 8 μg mL⁻¹ for DEHP in drinking water.10 However due to the extensive use of phthalates in the plastic industries and their hazardous effects for humans, the attention of the scientific community has been attracted to this problem. Therefore, it is highly desirable to increase the sensitivity and reliability of analytical methods to measure PAEs at trace levels in a variety of samples.

Various methods such as: gas chromatography (GC),11,12 gas chromatography/mass spectrometry (GC/MS),13,14 gas chromatography/tandem mass spectrometry (GC/MS/MS),15 high performance liquid chromatography (HPLC),16 ultra-high performance liquid chromatography (UPLC),17 liquid chromatography/mass spectrometry (LC/MS),18,19 liquid chromatography/tandem mass spectrometry (LC/MS/MS),20 microwave plasma torch ionization tandem mass spectrometry (MPT/MS),21 supercritical fluid chromatography (SFC),2 and fluorimetry4 have been reported for the determination of PAEs in different samples.

Since PAEs normally exist at very low concentrations in various samples with complex matrices, applying an effective pretreatment method is generally required to enrich these analytes and to remove them from sample matrices before an analysis by the gas chromatography flame ionization detector (GC-FID). In recent years, the extraction of PAEs from different matrices has been accomplished by sample pretreatment methods based on solid-phase extraction (SPE), headspace
solid-phase microextraction, dispersive solid-phase extraction (DSPE) and solid-phase microextraction (SPME) using various sorbent materials.\textsuperscript{18,19,22–27} The entrance of magnetic nanoparticles in the field of analysis has demonstrated major physicochemical characteristics such as a short diffusion route and a high surface area-to-volume ratio which make these substances noteworthy as solid phase sorbents for analytical purposes. These specific properties allow rapid extraction, high extraction capacity and great extraction efficiencies compared with microparticles. Particularly, magnetic iron oxide nanoparticles (MIONPs) have presented many applications as sorbents for the determination of various contaminants because no extra operation such as filtration and centrifugation of the sample, is required after a pretreatment, and an external magnetic field is used to separate the sorbent from the sample solutions.\textsuperscript{28,29}

Attention has been made to use Schiff-base coated sorbents for different purposes. These include a salophen Schiff base on silica to remove uranium and thorium,\textsuperscript{30} a 4-aminoantipyrine Schiff base impregnated on silica gel for the separation of Pt from water,\textsuperscript{31} and Schiff-base/SBA-15 nanosorbent for the removal of methylene blue.\textsuperscript{32} Modified magnetic nanoparticles with different Schiff-base ligands have also been used to determine or remove various compounds, such as phenols,\textsuperscript{33} organochlorine pesticides\textsuperscript{34} and metal ions.\textsuperscript{35} To the best of our knowledge $p$-dimethylaminobenzaldehyde (PDMAB) Schiff-base has not been used to modify the Fe$_3$O$_4$@SiO$_2$-NH$_2$ before. This Schiff-base was chosen because of its structure and possible strong π–π stacking affinity for PAEs. Therefore, the aim of the present study was to introduce new Schiff-base coated MIONPs sorbent for the simultaneous preconcentration and determination of six PAEs in different samples at trace levels.

This new nanosorbent was thus prepared by the Schiff-base reaction of $p$-dimethylaminobenzaldehyde (PDMAB) and Fe$_3$O$_4$@SiO$_2$-NH$_2$ nanoparticles. The modified nanoparticles by PDMAB were efficiently used for the preconcentration of six PAEs including dimethyl phthalate (DMP), diethyl phthalate (DEP), di-$n$-butyl phthalate (DBP), butylbenzyl phthalate (BBP), bis-(2-ethylhexyl) phthalate (DEHP) and di-$n$-octyl phthalate (DnOP) (Fig. S1) using DSPE, followed by GC-FID determination.

### Materials and Methods

#### Apparatus

The PAEs determination was carried out by the GC-FID Model GC-2550TG (Teif Gastar Fraz, Iran) and a BP5 capillary column (25 m length; 32 mm i.d. and film thickness of 0.5 μm). The temperature programming of the column was: initial oven temperature of 60°C for 1 min, increasing to 180°C at a rate of 25°C min$^{-1}$ and to 260°C at a rate of 15°C min$^{-1}$ and finally to 290°C at a rate of 10°C min$^{-1}$ and held at this temperature for 5 min. The temperatures of the injector and detector were set at 290 and 300°C, respectively. The inlet operated in the split mode with a split ratio of 10:1. Hydrogen gas ($0.9999\%$ purity) was applied as the carrier gas at a flow rate of 15 mL min$^{-1}$. Additional make-up gas was nitrogen (high-purity) at a flow rate of 30 mL min$^{-1}$. Scanning electron microscopy (SEM) analysis was performed using a Hitachi S5200 (Tokyo, Japan) in the scanning mode at 30 kV. An energy dispersive X-ray spectrometer (EDX) attached to the SEM instrument was used to determine the chemical compositions. The magnetic properties of prepared magnetic nanoparticles were studied by a vibrating sample magnetometer, VSM/AGFM (Meghnatis Daghigh Kavir Co., Kashan, Iran) at room temperature and cycling field from −15 to 15 kOe. The morphology of nanomagnetic iron oxide was investigated by transmission electron microscopy (TEM) images (Zeiss, EM10C, 100 KV, Germany). To identify the functional groups and chemical bonding of the modified magnetic nanoparticles, Fourier-transform infrared spectroscopy (FTIR) (Rayleigh, WQF-510, Beijing, China) was used. An Orbital Shaker (Ariateb, Tehran, Iran), an ultrasonic bath (Parsonic, Iran) and a vortex-mixer (IKA, Staufen, Germany) were used during the experiments. A Metrohm pH meter Model 632 (Herisau, Switzerland) equipped with a combined glass electrode was used for adjusting the pH.

#### Chemicals

Analytical-grade chemicals were used throughout the work. Ultrapure water produced by a Milli-Q Water (Millipore, France) was used throughout the experiments. Phthalate ester standard solutions (200 mg L$^{-1}$) including DMP, DEP, DBP, BBP, DEHP and DnOP were purchased from Dr. Ehrenstorfer GmbH (Germany). All of the reagents including iron(III) chloride hexahydrate (FeCl$_3$·6H$_2$O), iron(II) chloride tetrahydrate (FeCl$_2$·4H$_2$O), tetraethyl orthosilicate (TEOS), (3-aminopropyl)-triethoxysilane (APTES), $p$-dimethylaminobenzaldehyde (PDMAB), ammonia ($d = 0.91$ g mL$^{-1}$, 25%), methanol, dichloromethane, n-hexane, ethanol, acetone, glacial acetic acid and NaCl were obtained from Merck Company (Darmstadt, Germany).

#### Preparation of modified magnetic nanoparticles with Schiff-base PDMAB

The iron oxide magnetic nanoparticles (Fe$_3$O$_4$NPs), SiO$_2$ coated Fe$_3$O$_4$NPs and Fe$_3$O$_4$@SiO$_2$-NH$_2$ nanoparticles were prepared based on a previously reported method.\textsuperscript{36,37} For preparing Fe$_3$O$_4$@SiO$_2$-NH$_2$ nanoparticles modified with Schiff-base PDMAB, 0.6 g of Fe$_3$O$_4$@SiO$_2$-NH$_2$ nanoparticles was added to a 100 mL mixture of ethanol and methanol (1:1), and then 0.2 g of PDMAB was slowly added to the mixture under a nitrogen atmosphere while stirring at 60 – 70°C. To increase the collision rate and the reactivity between PDMAB and Fe$_3$O$_4$@SiO$_2$-NH$_2$ nanoparticles, the mixture was sonicated for 5 min. Then, 5 drops of glacial acetic acid were added and stirred under a nitrogen atmosphere at 60 – 70°C for 12 h. The prepared Fe$_3$O$_4$@SiO$_2$-NH-PDMAB nanoparticles were separated by an external magnet, washed with ethanol three times and dried in a desiccator. Different steps for preparing the nanocomposite are schematically presented in Fig. 1.

#### General DSPE procedure

DSPE was performed by a batch procedure. During the extraction process, 15 mg of the sorbent was added to 25 mL of a phthalate esters sample solution containing 10% NaCl in a falcon tubes and mixed on a vortex for 90 s. A vortex was used to assist in dispersing the sorbent in the sample. After extraction, the magnetic nanosorbent was separated by an external magnet and the solution was discarded. A desorption process was carried out by adding 2.0 mL of n-hexane under sonication for 3 min. The sorbent was separated by an external magnet and the solution containing the analytes was placed in a vial and the remaining solution was evaporated to dryness under nitrogen gas. Then, 100 μL of the n-hexane was added to dissolve the residue and analyzed by GC-FID. All glassware was washed with acid, deionized water and acetone prior to use, and a blank (pure solvent) was run before each analysis to prevent any carryover of the PAEs. Typical chromatograms for 50 μg L$^{-1}$ of phthalate esters before and after preconcentration are shown in

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The above text provides a detailed description of the methods and results of a study on the preparation and characterization of magnetic nanoparticles, specifically focusing on their use in the analysis of phthalate esters. The text discusses the development of a Schiff-base modified nanoparticle for enhanced extraction efficiency and the use of GC-FID for the analysis of these compounds. The study involves the preparation of magnetic iron oxide nanoparticles (MIONPs) and their modification with $p$-dimethylaminobenzaldehyde (PDMAB) for enhanced preconcentration of phthalate esters. Features such as easier extraction, high extraction capacity, and simplified analysis procedures are highlighted.

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5. **General DSPE procedure**
Sample preparation
The real samples used included natural low-fat yogurt, sodium chloride infusion serum (0.9% w/v) and mineral water. To prepare the yogurt sample, 2.0 g of the sample were added to a 50 mL falcon tube; 15 mL of 5% trichloroacetic acid in water and 5 mL of acetonitrile was added and capped. The tube was sonicated for 10 min, placed on a vertical shaker for 10 min and centrifuged for 10 min at 4000 rpm. A wetted filter paper with 5% trichloroacetic acid was used to filter the solution. The filtrate was transferred to a 10 mL volumetric flask and made up to the mark with water.38,39 No special preparation was made concerning the mineral water sample and sodium chloride infusion serum 0.9%; they were directly used for extraction. An aliquot of each sample was treated under the DSPE procedure.

Results and Discussion
Characterization of the sorbent
The nanocomposite was characterized at each step by various techniques such as FTIR, TEM, SEM, EDX and VSM. Figure S3 shows the FTIR spectra of four compounds prepared at each stage. Figure S3a presents the FTIR of Fe₃O₄ for a comparison. As can be observed in Fig. S3b, the characteristic peaks of Fe₃O₄@SiO₂ NPs appear at 1050 cm⁻¹ and the peak at 1455 cm⁻¹ belongs to Si-O-C stretching. From Fig. S3c, related to Fe₃O₄@SiO₂-NH₂ two peaks at 2850 and 2925 cm⁻¹ are attributed to the C-H stretching of propyl groups of APTES. The final coating of the sorbent with PDMAB was confirmed by the presence of two peaks at 1240 cm⁻¹ related to C-N stretching (N is bonded to C of an aromatic ring) and 1600 cm⁻¹ belonging to C-H stretching of the aromatic portion of PDMAB.
The morphology, size and structure of magnetic Fe$_3$O$_4$ nanoparticles, Fe$_3$O$_4$@SiO$_2$, Fe$_3$O$_4$@SiO$_2$-NH$_2$ and Fe$_3$O$_4$@SiO$_2$-NH-PDMAB, were investigated by SEM images. As shown in the SEM images, Fe$_3$O$_4$ nanoparticles have an average diameter of 18 nm. After coating of Fe$_3$O$_4$ with SiO$_2$, NH$_2$ and PDMAB, the diameter of the nanoparticles increased to 20.5, 25.5 and 50 nm, respectively. The SEM images show that a core-shell structure was formed in the nanocomposite after coating the APTES, PDMAB on the Fe$_3$O$_4$@SiO$_2$ surface, which is relatively uniform and almost spherical in shape.

TEM images were also taken as: (a) Fe$_3$O$_4$(b) Fe$_3$O$_4$@SiO$_2$(c) Fe$_3$O$_4$@SiO$_2$-NH$_2$(d) Fe$_3$O$_4$@SiO$_2$-NH-PDMAB. The dispersed uncoated Fe$_3$O$_4$ microspheres (Fig. 4a) exhibited a regular sphere morphology with an average size of about 15 to 20 nm and Fe$_3$O$_4$ coated by silica shell microspheres with an average size of about 21 to 23 nm (Fig. 4b). Fe$_3$O$_4$@SiO$_2$-NH$_2$ particles have a relatively uniform core-shell structure with an average size of about 25 to 33 nm, as indicated in Fig. 4c. The TEM image presented in Fig. 4d shows that the coating of PDMAB on the surface of Fe$_3$O$_4$@SiO$_2$-NH$_2$ affected the size of the particles, and that the average size is about 50 to 75 nm with a clear core-shell structure.

To evaluate the elemental composition of the materials, EDX analysis was performed. The EDX spectra of Fe$_3$O$_4$, Fe$_3$O$_4$@SiO$_2$ (Fig. S3d), Fe$_3$O$_4$@SiO$_2$-NH$_2$, Fe$_3$O$_4$@SiO$_2$-NH-PDMAB. The dispersed uncoated Fe$_3$O$_4$ microspheres (Fig. 4a) exhibited a regular sphere morphology with an average size of about 15 to 20 nm and Fe$_3$O$_4$ coated by silica shell microspheres with an average size of about 21 to 23 nm (Fig. 4b). Fe$_3$O$_4$@SiO$_2$-NH$_2$ particles have a relatively uniform core-shell structure with an average size of about 25 to 33 nm, as indicated in Fig. 4c. The TEM image presented in Fig. 4d shows that the coating of PDMAB on the surface of Fe$_3$O$_4$@SiO$_2$-NH$_2$ affected the size of the particles, and that the average size is about 50 to 75 nm with a clear core-shell structure.
SiO\textsubscript{2}, Fe\textsubscript{3}O\textsubscript{4}@SiO\textsubscript{2}-NH\textsubscript{2} and Fe\textsubscript{3}O\textsubscript{4}@SiO\textsubscript{2}-NH-PDMAB are presented in Fig. S4a - S4d, respectively. As illustrated in Fig. S4a, Fe\textsubscript{3}O\textsubscript{4} shows typical elemental peaks for Fe and O. A silicon peak was detected for Fe\textsubscript{3}O\textsubscript{4}@SiO\textsubscript{2}, as shown in Fig. S4b, confirming the silanization. Peaks related to N, O, Fe and Si were observed for Fe\textsubscript{3}O\textsubscript{4}@SiO\textsubscript{2}-NH\textsubscript{2} (Fig. S4c) after modification of the surface. The elemental peak of C in the EDX image of Fe\textsubscript{3}O\textsubscript{4}@SiO\textsubscript{2}-NH-PDMAB is observed more clearly in Fig. S4d due to the carbon contents of PDMAB in Fe\textsubscript{3}O\textsubscript{4}@SiO\textsubscript{2}-NH-PDMAB.

The magnetic features of the prepared compounds at each stage were investigated by VSM. As presented in Fig. S5, the saturation magnetization (Ms) of as-prepared compounds decreased in the order of Fe\textsubscript{3}O\textsubscript{4} > Fe\textsubscript{3}O\textsubscript{4}@SiO\textsubscript{2} > Fe\textsubscript{3}O\textsubscript{4}@SiO\textsubscript{2}-NH\textsubscript{2} > Fe\textsubscript{3}O\textsubscript{4}@SiO\textsubscript{2}-NH-PDMAB. The reduction of Ms is due to the different coating layers on the surface of magnetic nanoparticles. As expected, due to the shield effects of the layers, a considerable decrease in the Ms values was observed as the number of coating layers increased. The saturation magnetization of Fe\textsubscript{3}O\textsubscript{4}@SiO\textsubscript{2}-NH-PDMAB was found to be 5.0 emu g\textsuperscript{-1}, which was much lower than that of the Fe\textsubscript{3}O\textsubscript{4}, Fe\textsubscript{3}O\textsubscript{4}@SiO\textsubscript{2}, Fe\textsubscript{3}O\textsubscript{4}@SiO\textsubscript{2}-NH\textsubscript{2}. Although the Si\textsubscript{2}, amine and PDMAB coating layers significantly reduced the Fe\textsubscript{3}O\textsubscript{4}@SiO\textsubscript{2}-NH-PDMAB composite, the final product still shows sufficiently strong Ms, which is still good enough for magnetic separation.

**Plausible mechanism**

The possible mechanism of this adsorption process is supposed to be the interactions between the PAEs molecules and PDMAB on the surface of Fe\textsubscript{3}O\textsubscript{4}@SiO\textsubscript{2}-NH-PDMAB nanoparticles (e.g., London dispersion force, hydrogen bonding and π-π stacking interaction). It has already been mentioned that there is strong π-π stacking affinity between the benzene rings on the surface of the sorbent toward aromatic rings of PAEs in previous studies.

**Influence of pH**

The solution pH is known to affect the adsorption process of the analytes on the sorbent; this parameter should be studied. Thus, the influence of the pH on the adsorption of six PAEs was studied. The pH variation showed no significant effect over a wide range from 2.0 to 12.0 on the extraction efficiency of the analytes from water samples (Fig. S6). The relative standard deviations (RSD) of the peak areas obtained in these pH values were in the range of 0.74 – 4.44%. It seems that the sorbent and the analytes are not sensitive to the concentration of H\textsuperscript{+} in the solution, and the pH variation cannot affect the adsorption process. This could be an advantage in real sample analysis. Thus, in subsequent experiments, no pH adjustment was required before the analysis.

**Influence of sorbent amount**

The influence of the sorbent amount for the effective sorption of PAEs by DSPE was investigated over the range of 2 – 30 mg. According to the results (Fig. S7), the peak areas of the analyzed PAEs were increased significantly by increasing the amounts up to 15 mg, and became almost constant for sorbent amounts of more than 15 mg. Therefore, 15 mg was applied as the optimum value in further work.

**Influence of desorption solvent type and its volume**

Several solvents such as dichloromethane, acetone, methanol, ethanol, acetonitrile and n-hexane were selected and tested in order to find a suitable desorption solvent for the procedure. As shown in Fig. 5, for all of the investigated analytes, except for DnOP, the highest peak areas were obtained when n-hexane was used as the desorption solvent, while for DnOP the best solvent was acetone. Thus n-hexane was selected as the most effective desorption solvent for the analytes; also the effect of the n-hexane volume as desorption solvent was investigated in the range of the 0.5 – 4.0 mL. It was observed that the peak areas of all PAEs reached a maximum up to 2.0 mL of the desorption solvent, and remained almost constant after that. For further studies, 2.0 mL of n-hexane was utilized to desorb the analytes from the sorbent. This solution was evaporated to dryness by the assistance of a nitrogen gas stream and then dissolved in 100 μL of the n-hexane before analysis by GC-FID.

**Influence of sorption and desorption times**

A good dispersion of the sorbent would considerably increase the contact of the sorbent and analytes in the sample, which could lead to a higher sorption efficiency. Both a vortex and sonication were applied in the sorption/desorption processes; it was found that vortex and sonication were more effective and faster for the sorption and desorption, respectively. Thus, the vortex was chosen as the desired method for performing sorption of the analytes. The time required to reach the partition equilibrium is an important factor because it influences the extraction efficiency of analytes from solution by the sorbent. Thus, different extraction times between the sample solutions and the sorbent using the vortex were investigated from 5 to 180 s; the results are shown in Fig. S8. Although the efficient vortex times were different for the analyzed PAEs, no perceptible changes were observed after 90 s for all analytes. Thus, an extraction time of 90 s was used in further experiments.

The desorption time is also an essential factor which needs to be considered. Hence, the influence of the desorption time under sonication was studied in the range of 20 – 300 s. The results of desorption time optimization with the assistance of an ultrasonic bath are illustrated in Fig. S9. The extraction efficiencies were different for the analyzed PAEs with time, but after 180 s of desorption, no significant improvement was observed for all PAEs. Thus, 180 s of sonication was chosen as the optimum desorption time to perform the experiments.

**Salting effect**

It has been observed that in some cases, the addition of salt to the system has a significant impact on SPE methods. By increasing the ionic strength of the aqueous solutions, the solubility of organic compounds is reduced, and more
compounds are removed from the aqueous medium. Therefore, the extraction efficiency is thought to be increased in the presence of a salt. Sample solutions with different concentrations of NaCl (0 – 20%, w/v) were prepared to evaluate the effect of salt on the extraction efficiency. As shown in Fig. S10, the extraction efficiencies were increased when the concentration of NaCl was raised and after reaching a maximum value at a salt concentration of 10%, the results were slightly decreased again. It is thought that a salting-out effect is responsible for this increase in the extraction efficiency upon increasing the NaCl concentration. Thus, the extraction procedure was performed using a NaCl concentration of 10%.

Reusability of the sorbents

The reusability of the sorbent is an important parameter for low-cost analysis. Thus the reusability of the Fe₃O₄@SiO₂-NH₂-PDMAB sorbent was studied by a sorption/desorption test. The sorption/desorption was performed using the general DSPE procedure. The sorbent was separated using a magnet and rinsed with 5 mL of an acetonitrile and n-hexane mixture (1:1) twice before being applied in the next DSPE procedure. This sorption/desorption was performed using the general DSPE procedure. The sorbent was separated using a magnet and rinsed with 5 mL of an acetonitrile and n-hexane mixture (1:1) twice before being applied in the next DSPE procedure. This procedure was performed several times for the same batch of the sorbent. The results of this investigation are shown in Fig. 6. The sorbent can be used eight times without any significant change in the percent recoveries of PAEs.

![Fig. 6 Reusability of the sorbent, conditions: vortex shaking time, 90 s; elution solvent, 2 mL; sonication time, 3 min; final volume, 100 μL; amount of sorbent, 15 mg.](image)

**Working graphs and analytical performance**

The DSPE procedure was evaluated by measuring the analytical parameters. The calibration graphs for determining the analytes were produced according to a procedure using optimum conditions, and was found to be linear in the range of 1.0 – 150.0 μg L⁻¹ for DMP, DEHP and DnOP and 0.1 – 200.0 μg L⁻¹ for DEP, DBP and BBP, respectively. The limit of detection (LOD) and the limit of quantification (LOQ) were calculated using 3Sₒ/m and 10Sₒ/m, respectively, where Sₒ was obtained by performing replicate (n = 5) extractions for a standard solution with concentration level to meet the S/N = 3 and m was the slope of the calibrations graph. The obtained LODs and LOQs were in the range of 0.02 – 0.31 and 0.05 – 0.82 μg L⁻¹, respectively. The enrichment factor, expressed as the ratio of the analyte concentration after and before extraction was calculated; the results were in the range of 144 – 202. More details concerning the results of the regression equations, the determination coefficient (R²), and the intra-day and inter-day repeatability (the concentration of PAEs were 125 μg L⁻¹) are given in Table S1.

**Analysis of different samples**

To specify the usability of the method, several samples were treated as described previously (please see Sample preparation). The selected samples had plastic storage bottles in which PAEs are usually used as plasticizers for their fabrication. The samples were also spiked with two concentrations of 5 and 25 μg L⁻¹, and analyzed. Then, the sorption and desorption processes were performed under the optimized condition. The results given in Table 2 show that there is a satisfactory agreement between the added and found quantities of PAEs, indicating that the developed procedure is applicable for PAEs measurements in different samples with a sophisticated matrix. The results indicated the presence of DMP in mineral water and natural low fat-yogurt and DBP in mineral water (Table 2). As reported by Ueta et al., the Ministry of Health, Labour and Welfare, Japan, has established reference values for DBP and DEHP of 10 and 80 μg mL⁻¹, respectively, in drinking water. Looking at these values and the daily intake (TDI) values for DEHP, DnBP, BBP and DBP, the LOQ obtained by the method is as good as or better than some of these methods.

**Table 1** Comparison of this method with some of the previously reported methods for PAEs determination

| Method                  | Compound            | Sorbent                        | LOD (μg L⁻¹) | Extraction time (min) | LR (μg L⁻¹) | Ref.
|-------------------------|---------------------|--------------------------------|--------------|----------------------|-------------|-------
| MSPE-HPLC-UV⁺           | DPP/DPB/BBP        | Fe@SiO₂@PEI                    | 0.26 – 0.45  | 40                   | 0.5 – 100.0 | 5     |
|                         | DPIP/DCHP          |                                |              |                      |             |       |
| UASEME-GC/FID³          | DMP/DEP/DCHP       | Triton X-100                   | 0.41 – 0.79  | 2                    | 0.86 – 251  | 11    |
|                         | DIOP/DnOP          |                                |              |                      |             |       |
| DSPE-GC-FID⁺           | BBP/DPB            | Fe₂O₃@dMIP                     | 0.53 – 1.20  | 40                   | 4 - 400     | 12    |
| DSPE-GC-MS⁺            | DPP/DBP/DnOP       | Graphen                        | 2 – 7        | 3                    | 5 – 100     | 14    |
| MSPE-HPLC-UV⁻           | DAP/DPP/BBP        | Fe₂O₃@Fe³⁺-TA                  | 0.10 – 0.62  | 6                    | 3 – 200     | 16    |
|                         | DCP/DEHP           |                                |              |                      |             |       |
| HPLC-UV⁻                | DBP/DEHP           | PET nanofiber                  | 0.1 – 1      | 20                   | 100 – 1000  | 27    |
| DSPE-GC-FID             | DMP/DEP/BBP        | Fe₂O₃@SiO₂-NH-PDMAB            | 0.019 – 0.308| 5                    | 0.1 – 200.0 | Present study

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a. Limit of detection. b. Linear range. c. Magnetic solid phase extraction-high performance liquid chromatography-ultraviolet detector. d. Ultrasound-assisted surfactant-enhanced emulsification microextraction gas chromatography-flame ionization detector. e. Dispersive-solid phase extraction-chromatography flame ionization detector. f. Dispersive solid phase extraction-gas chromatography-mass spectrometry detector. g. High performance liquid chromatography-ultraviolet detector.
fulfills the safety legal requirements. The matrix effect (ME%) was calculated by:

\[
\text{ME\%} = \left( \frac{A_{\text{spiked sample}} - A_{\text{non-spiked sample}}}{A_{\text{spiked DW}}} \right) \times 100
\]

where \(A\) is the peak area of the analyte for the samples, and the spiked concentration was 5 \(\mu\)g L\(^{-1}\) of the PAEs to the real samples. The results are presented in Table 2. It is apparent from the results that the ME\% for determining the analytes is within an acceptable range.\(^{45}\)

### Conclusions

A simple, low-cost and reproducible vortex-assisted DSPE coupled to GC-FID was developed for the simultaneous preconcentration and determination of six phthalate esters in different samples. The adsorption rate was increased with the aid of the vortex because the magnetic nanoparticles were more dispersed and the rate of collisions between the analytes and the nanoparticles were significantly accelerated. The pH variation showed no significant effect over a wide range from 2.0 to 12.0 concerning the extraction efficiency of the analytes from water samples. The results show that the obtained recoveries for six phthalate esters in real samples were at an acceptable level. The superiority of the proposed method is its requirement of a small amount of the sorbent (15 mg); also a short time is required to extract the analytes from samples and to recover them prior to an analysis by GC-FID. Besides, magnetic nanoparticles are easily separated from the samples using a magnet without needing any extra filtration apparatus. The method shows a high analytical potential for determining phthalate esters at ultra-trace levels with satisfactory precision.

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### Supporting Information

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