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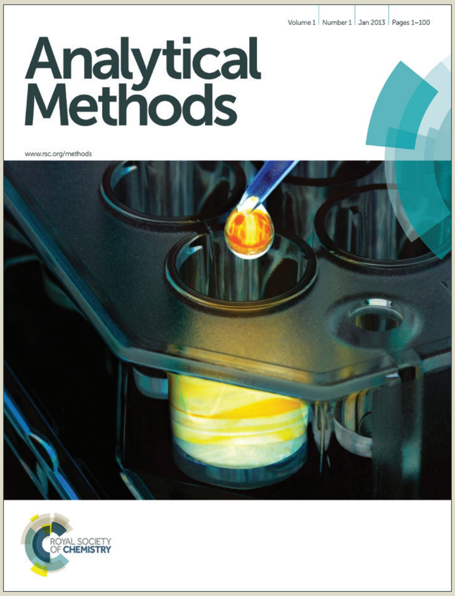

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# Graphene grafted magnetic microspheres for solid phase extraction of bisphenol A and triclosan from water samples followed by gas chromatography-mass spectrometric analysis

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**Abbreviations:** BPA, bisphenol A; BSTFA, N, O-bis(trimethylsilyl)-trifluoroacetamide ; EDC, Endocrine disrupting compound; $Fe_3O_4@SiO_2$-NH-G, graphene grafted magnetic ferroferric oxide microspheres; GC/MS, gas chromatography/mass spectrometry; G-$Fe_3O_4$, magnetic graphene nanocomposite; LC/MS, liquid chromatography/mass spectrometry; LOD, limit of detection; MSPE, magnetic solid phase extraction; RSD, relative standard deviation; SEM, scan electronic microscopy; TCS, Triclosan; TMS, trimethylsilyl; TEM, transmission electron microscope;

Graphene grafted magnetic microspheres were prepared and used as the adsorbent for magnetic solid phase extraction (MSPE) of bisphenol A and triclosan from water samples prior to their determination by gas chromatography-mass spectrometric (GC-MS) detection. A new customized ground-glass stoppered conical flask with a side tube was used for the MSPE operations to simplify the separations of the magnetic adsorbent from the sample solution. The main experimental factors affecting the extraction recoveries of the analytes, including the amount of adsorbent, pH of the sample solution, extraction time, salt concentration, desorption conditions, and derivatization conditions were investigated. Under the optimal conditions, a linear response was observed in the concentration range of 0.05-2.50 μg $L^{-1}$ for bisphenol A and 0.10-5.00 μg $L^{-1}$ for triclosan. The limits of detection ($S/N = 3$) were 10.0 ng $L^{-1}$ for bisphenol A and 20.0 ng $L^{-1}$ for triclosan. The established method was applied to the determination of bisphenol A and triclosan residues in environmental water samples with satisfactory results. The recoveries of the analytes for the method from lake, river, bottled and tap water samples were in the range from 93.9% to 104.3% (intra-day), and from 93.5% to 99.5% (inter-day) with the relative standard deviations varying from 2.1% to 5.8% (intra-day), and from 3.1% to 5.7% (inter-day).

## Introduction

Endocrine disrupting compounds (EDCs) are exogenous substances that can alter some functions of the endocrine system of intact organisms.[1, 2] Human exposure to these compounds have been associated with various adverse health effects including reproductive and endocrine disorders, cardiovascular disease, obesity and metabolic syndrome, cancer, immune system dysfunction and neurobehavioral defects.[2-5]

Bisphenol A (2,2'-bis-[4-hydroxyphenyl]propane) and triclosan (2,4,4'-trichloro-2'- hydroxy-diphenyl ether) are two typical EDCs with numerous industrial and commercial applications in the past decade.[6-9] With over 6 billion pounds produced worldwide each year,[7] bisphenol A (BPA) is mainly used as monomer to manufacture polycarbonate plastics and epoxy resins，which are then used to produce various products of daily life. Trace amounts of BPA can leach out from polycarbonate containers.[3] Because of its weak estrogenic and anti-androgenic activity,[1, 3, 5] BPA has been banned as the additive in baby bottles in China since 2011.[10] Triclosan (TCS) is a broad spectrum antimicrobial and antifungal agent which is extensively used as preservatives and disinfectant (usually in mixtures) in a wide range of personal care products (e.g., shampoos, soaps, toothpastes, skin care formulations, mouthwashes, acne medications, etc.).[1, 3, 5]

The wide use of BPA and TCS has made wastewater become an important transport route for these compounds into the aquatic environment.[3-5] Increasing numbers of water samples obtained from lakes, streams, aquifers and even municipal supplies have been found contaminated by trace BPA and TCS typically at a level in the range from micrograms to nanograms per liter.[2-4]

Liquid chromatography/mass spectrometry (LC/MS) and gas chromatography/mass spectrometry (GC/MS) are the most commonly used techniques for the determination of EDCs. Compared with LC/MS, GC/MS is much more widely applied due to its less cost and easier operations.[2-5, 11, 12] However, the high polarities of the compounds often require the use of derivatizations prior to GC analysis to reduce their polarity and enhance their volatility.[2, 4, 11] For the determination of low concentration level of these compounds, sample pretreatment is also often needed to achieve a high sensitivity for GC/MS analysis. A number of sample pretreatment techniques including liquid–liquid extraction (LLE),[13] single-drop microextraction,[14] dispersive liquid–liquid microextraction,[15] solid-phase extraction (SPE),[2] solid-phase microextraction,[16] stir-bar sorptive extraction,[17] focused ultrasonic solid-liquid extraction[18] and hollow fiber based liquid phase microextraction (HF-LPME)[19] have been reported to extract and concentrate EDCs from environmental samples. Among them, SPE is more preferred as it is well suited to multi-residue analysis of the compounds with a wide range of polarities or diverse physico-chemical properties.[20] SPE followed by GC/MS detection is recommended by the U.S. Geological Survey (USGS) National Water Quality Laboratory (NWQL) as an official method for the analysis of known and suspected EDCs in domestic and industrial wastewater samples.[21] Recently, a new mode of SPE, known as magnetic solid-phase extraction (MSPE) has been developed. Compared with traditional SPE methods, MSPE is based on the use of magnetic adsorbents which can make the phase separation between the adsorbent and the aqueous sample solution easier and faster by using only a magnet without the need of additional centrifugation or filtration procedures.[22-25] Also, MSPE can avoid the time-consuming column passing operations encountered in common SPE. In our previous work, graphene grafted magnetic ferroferric oxide microspheres have been successfully applied as the MSPE absorbent for the extraction of polycyclic aromatic hydrocarbons,[22] phthalateesters,[23] pyrethroid pesticides[24] and triazole fungicides.[25] Developing a new alternative analytical method for the determination of trace EDCs by the introduction of MSPE process is therefore of great interest.

In this study, the graphene grafted magnetic ferroferric oxide microspheres ($Fe_3O_4$@$SiO_2$-NH-G) was further explored as the magnetic absorbent for the MSPE of BPA and TCS from water samples followed by GC/MS analysis. Furthermore, a new customized ground-glass stoppered conical flask with a side tube was developed and used in the MSPE process to simplify the phase separations between the magnetic adsorbent and the aqueous sample solution. Prior to determination by GC/MS, the analytes were derivatized with *N*, *O*-bis(trimethylsilyl)- trifluoroacetamide (BSTFA) to facilitate their analysis by GC. Several important experimental parameters affecting the extraction efficiencies such as the amount of the $Fe_3O_4@SiO_2$-NH-G, extraction time, sample pH, salt addition, desorption conditions, and derivatization conditions were optimized. The established method was applied for the determination of the BPA and TCS residues from environmental water samples.

## Experimental

### Reagents and materials

Ammonium ferrous sulfate [$(NH_4)_2Fe(SO_4)_2$•$6H_2O$] and ammonium ferric sulfate [$NH_4Fe(SO_4)_2$•$12H_2O$] were both obtained from Huaxin Chemical Reagents Company (Baoding, China). Graphite powder (50 meshes) was purchased from Boaixin Chemical Reagents Company (Baoding, China). $NH_3$•$H_2O$ (30 wt%), ethylsilicate (TEOS), 3-aminopropyltriethoxysilane (APTES), dimethylformamide (DMF), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC), n-hydroxysuccinimide (NHS) and polyvinylpyrrolidone (PVP) were obtained from Chengxin Chemical Reagents Company (Baoding, China). Acetonitrile, acetone, hydrochloric acid (HCl), sodium hydroxide (NaOH), and all other reagents were purchased from Beijing Chemical Reagents Company (Beijing, China). The water used throughout the work was double-distilled on a SZ-93 automatic double-distiller purchased from Shanghai Yarong Biochemistry Instrumental Factory (Shanghai, China).

Bisphenol A (BPA，CAS：80-05-7) and triclosan (TCS，CAS：3380-34-5) powder were purchased from Boaixin Chemical Reagents Company (Baoding, China). The derivative reagent *N*,*O*-bis(trimethylsilyl)-trifluoroacetamide (BSTFA, CAS：25561-30-2) was purchased from Aladdin Industrial Corporation (Shanghai, China). A mixture stock solution containing BPA and TCS each at 1.0 g $L^{-1}$ was prepared in ethyl acetate. A series of standard solutions were prepared by mixing an appropriate amount of the stock solution with ethyl acetate in a 10-mL volumetric flask. All the standard solutions were stored at 4 °C and protected from light.

Bottle water was purchased from local supermarket (Baoding, China), river water was collected near a plastic production factory (Baoding, China), lake water was collected from our campus (Baoding, China), and tap water was from our lab (Baoding, China). All of the solvents and water samples were filtered through a 0.45-μm membrane to eliminate particulate matters before analysis. Figure 1 depicts the procedures for the preparation of the $Fe_3O_4$@$SiO_2$-NH-G nanocomposite according to the method reported in our previous work. [22, 23]

Fig. 1

## MSPE and derivatization procedures

The MSPE procedures are shown in Figure 2. First, 100 mL of sample solution was transferred into a customized conical flask with side tube, to which 40 mg of $Fe_3O_4$@$SiO_2$-NH-G was added. The mouth of the flask was then covered by a ground-glass stopper and the side tube was sealed with a plastic cap. The mixture was placed on a slow-moving platform shaker for 30 min. Then, the plastic cap on the side tube was replaced with a 1.5-mL centrifuge tube. The flask was then tilted to make the solution flow to the side tube, and a strong magnet was placed outside of the flask wall. After the $Fe_3O_4$@$SiO_2$-NH-G was gathered together, the strong magnet was slowly moved along the flask wall to the bottom of the side tube. Then, the flask was put back to the upright position and the side tube with the isolated $Fe_3O_4$@$SiO_2$-NH-G was removed from the flask. Finally, the adsorbed analytes were eluted from the isolated particles with 0.5 mL methanol by vortexing for 1 min. After the magnet was put on the outside of the side centrifuge tube, the supernatant solution was collected using a pipette. Three replicate desorptions were performed. The desorption solutions were combined together and transferred into a 1.5-mL microcentrifuge tube. The solution was then evaporated to dryness under a mild nitrogen stream. The residue was dissolved in 90.0 µL ethyl acetate, followed by the addition of 10 µL BSTFA for derivatization. The derivative reaction (see Figure 3) was performed at 70 °C for 30 min. After the reaction, the reaction mixture (1.0 µL) was injected into the GC/MS system for analysis.

Fig. 2 Fig. 3

**GC–MS analysis**

A Shimadzu (Kyoto, Japan) GCMS-QP2010SE system equipped with a Rxi-5MS fused silica capillary column (30 m × 0.25 mm × 0.25 µm) (Restek Corporation, USA, www.restek.com) was used for analysis. The injector was operated in the splitless mode and then changed to the split mode (the split ratio was 1:15) after 1 min from the beginning of a run. The time for solvent delay was set at 8 min. The injection port temperature was maintained at 260 $^{o}$C. The column was first maintained at 70 $^{o}$C for 1 min and then was increased at a rate of 10 $^{o}$C min$^{-1}$ to 140 $^{o}$C, at 10 $^{o}$C min$^{-1}$ to 200 $^{o}$C, and finally at 5 $^{o}$C min$^{-1}$ to 260 $^{o}$C and held for 1 min. Ultra pure helium (99.9995%) was used as the carrier gas at a flow rate of 0.97 mL min$^{-1}$ corresponding to a constant linear velocity of 37.5 cm s$^{-1}$. GC-MS interface temperature was maintained at 250 $^{o}$C. The electron impact ionization source was operated at 70 eV and 200 $^{o}$C. The MS detection was made using full-scan mode at a voltage of 0.7 kV from 50-400 m/z for qualitative analysis and selected ion monitoring (SIM) mode for quantitative analysis. The retention times and mass spectrometric data of the analyte derivatives are shown in Table 1.

Table 1

## Results and discussion

### Characterization of the magnetic graphene nanocomposite

The TEM and SEM images of the $Fe_3O_4$@$SiO_2$-NH-G are shown in Figure 4. It can be seen from Figure 4A that the crumpled silk wave-like carbon sheets exist, which is a characteristic feature of the single-layer G sheets, and the $Fe_3O_4$ nanoparticles were well distributed on G sheets. The TEM image (Figure 4B) shows that the estimated average size of the $Fe_3O_4$ nanoparticle was about 20 nm.

Fig. 4

### Optimization of the MSPE procedures

In order to obtain the optimum MSPE conditions for the extraction process, 100 mL double-distilled water spiked with 2.5 μg $L^{-1}$ of BPA and 5.0 μg $L^{-1}$ of TCS was used to study the extraction efficiency of the MSPE under different experimental conditions. All the experiments were performed in triplicate and the means of the results were used for evaluation.

### Modification of the extraction flask

In our previous work,[26] G-$Fe_3O_4$ has been successfully applied as the MSPE adsorbent for water samples. However, it was found that it was a little hard to transfer the magnetically collected G-$Fe_3O_4$ to the centrifuge tube from the conical extraction flask after the extraction of the analytes. In order to overcome this drawback, a customized ground-glass stoppered conical flask with a side tube (see Figure 2) was developed and applied for the current extraction. As a result, with the use of the current extraction flask, the MSPE operations, especially for the transfer of the adsorbent after the extraction from the main extraction flask to the smaller side desorption tube, became much easier.

### Effect of $Fe_3O_4$@$SiO_2$-NH-G dosage

The effect of the amount of the $Fe_3O_4$@$SiO_2$-NH-G on the extraction recoveries of TCS and BPA was investigated in the range from 10 to 50 mg. As can be seen from Figure 5A, the extraction recoveries of TCS and BPA was linearly increased with the amount of the $Fe_3O_4$@$SiO_2$-NH-G being increased from 10 mg to 25 mg, and then remained almost constant when the amount of the adsorbent exceeded 30 mg. According to the above results, 40 mg of the $Fe_3O_4$@$SiO_2$-NH-G was chosen for the following studies.

### Effect of pH

The pH of the sample solution plays an important role for the adsorption of the analytes to the sorbent by both affecting the existing forms of the analytes and their charge species and densities on the sorbent surface. In this work, the influence of the sample pH on the extraction efficiency of TCS and BPA was studied over the pH range from 1 to 12. The pH of the sample was adjusted by 0.1 mol $L^{-1}$ HCl or 0.1 mol $L^{-1}$ NaOH. . As shown in Figure 5B, the extraction recoveries of the two analytes were almost unchanged when the sample pH was increased from 1 to 3, and then the extraction recoveries were decreased sharply after the sample pH was increased to above 4. The reason for this could be that TCS and BPA would exist mostly in ionic forms in alkali conditions, which is unfavorable for the extraction. Therefore, the pH of the sample solution in this study was adjusted to 2.

### Effect of extraction time

The effect of the extraction time on the extraction recoveries of TCS and BPA was investigated at varying extraction times in the range from 10 to 50 min while the other experimental conditions were held constant. As can be seen from Figure 5C, the extraction recoveries of the analytes were increased rapidly when the extraction time was increased from 10 to 30 min, and then remained almost unchanged after that. Hence, the extraction time of 30 min was selected. This result showed that the extraction equilibrium could be attained in a short time.

### Effect of sample salinity

The addition of salt, such as NaCl, to the sample solution will increase the ionic strength of the solution. In most cases, higher ionic strength would decrease the solubility of organic analytes due to salting-out effect and increase the distribution constant of the analytes, which is favorable for the extraction. On the other hand, salt addition can also increase the viscosity of the solution, which will reduce the extraction capability and the diffusion coefficient. To investigate the effect of sample salinity on the extraction recoveries of the analytes, various amounts of NaCl, i.e. 1.0, 2.0, 3.0 and 4.0 g were added into 100 mL of sample solution with other parameters being held at constant. Figure 5D shows that no significant changes of the extraction recoveries for either TCS or BPA were observed with the addition of NaCl from 0 to 2%, and then decreased recoveries for the analytes were observed. Therefore, no addition of salt to the sample solution was adopted for the study.

### Desorption conditions

Complete desorption of the adsorbed analytes from the magnetic adsorbent is favorable for the sensitive determination of the analytes. In this study, the effects of different desorption solvents (acetone, methanol, ethanol and acetonitrile)[27] on the extraction recoveries of TCS and BPA were investigated. As shown in Figure 5E, the eluting power of methanol was stronger than either acetone, ethanol or acetonitrile. Thus methanol was selected as the desorption solvent. Then, varying desorption times between 0.5 and 5 min were also tested. As a result, no obvious increase of the extraction recoveries for the analytes was observed after the desorption time was longer than 1.0 min. Thus, vortexing for 1 min was selected for the desorption of the analytes from the adsorbent.

Fig. 5

## Optimization of the derivatization conditions

Both BPA and TCS are high polar compounds due to the presence of polar phenolic groups. Their high polarities require their prior derivatizations before their GC/MS analysis, so as to reduce their polarity and enhance their volatility. As a commonly used derivative agent for phenols or alcohols, BSTFA[28] was selected as the derivative agent for their derivatizations in the current study. The reaction equations are presented in Figure 3.

### Effect of reaction temperature

The effect of the derivative reaction temperature ranging from 25 to 80 $^{o}$C on the extraction recoveries of TCS and BPA was investigated. As shown in Figure 6A, the extraction recoveries of TCS and BPA were both higher than 50 % under room temperature; they were gradually increased with the reaction temperature being increased to 60 $^{o}$C and then remained almost after 60 $^{o}$C. According to the results, the derivative reaction temperature was selected at 70 $^{o}$C.

### Effect of reaction time

Derivative reaction time is another important parameter for derivatization reaction. In this study, the effect of derivative reaction time on the extraction recoveries of TCS and BPA was investigated in the range from 20 to 70 min. Figure 6B shows that the recoveries of TCS and BPA were increased with increased derivative reaction time to 40 min, and then remained almost unchanged. Hence, 40 min was finally selected as the derivative reaction time.

Fig. 6

## Analysis of environmental water samples

### Linearity and limits of detection (LODs)

The analytical parameters for the developed method were evaluated using double-distilled waters containing various concentrations of TCS and BPA under the optimized conditions. The results are listed in Table 2. A good linear response was obtained in the concentration range of 0.05-2.50 μg $L^{-1}$ for BPA and 0.10-5.00 μg $L^{-1}$ for TCS, respectively. The LODs (*S/N = 3*) were 10.0 ng $L^{-1}$ for BPA and 20.0 ng $L^{-1}$ for TCS, respectively. These results indicate that the developed method is feasible for the analysis of trace TCS and BPA in water samples.

Table 2

**Real water sample analysis**

The established method was further applied for the analysis of TCS and BPA in real water samples including lake, river, bottled and tap water samples under the optimized experimental conditions. As a result, BPA was found to be 34.6 ng $L^{-1}$ in one of the river water samples.

In order to test the accuracy of the method, the recoveries of the analytes in real water samples spiked with TCS and BPA each at three different concentrations were investigated. For each concentration level, six replicate experiments were performed. The results are listed in Table 3. The spiked recoveries for the two analytes were 95.1%-103.2% for lake water samples, 93.5%-97.1% for river water samples, 93.9%-101.7% for bottle water samples, and 94.1%-104.3% for tap water samples, respectively. The RSDs of intra-day and inter-day variations for the two analytes were from 2.1% to 5.8 % and from 3.1% to 5.5%, respectively. The results indicate that the established MSPE/GC-MS method has a good precision and accuracy, which could meet the demand for the determination of the analytes in environmental water samples. Figure 7 shows the typical chromatograms of a river water sample before (Figure 7A) and after (Figure 7B) being spiked at 2.5 μg $L^{-1}$ of TCS and 1.0 μg $L^{-1}$ of BPA.

Table 3

Fig.7

## Conclusions

The graphene grafted magnetic microspheres $Fe_3O_4@SiO_2$-NH-G were successfully prepared and applied as the magnetic adsorbent for the MSPE of BPA and TCS from environmental water samples including lake, river, bottled and tap water samples, followed by GC-MS analysis. The established method exhibited a high extraction efficiency. With the introduction of a specially designed conical flask in the MSPE process, the phase separations between the magnetic adsorbent and the aqueous sample solution were simplified. The results indicate that the developed method can be a potential alternative for the determination of BPA and TCS in environmental water samples.

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## Table captions

**Table 1.** Retention time and mass spectrometric data of the analyte derivatives.

**Table 2**.The linear range (LR), coefficient of correlation (*r*), limits of detection (LODs), and limits of quantification (LOQs) of the analytes by the MSPE-GC-MS analysis.

**Table 3.** The recoveries and precisions for MSPE/GC-MS method in lake water, river water, bottle water and tap water samples spiked with three different concentrations of the TCS and BPA.

## Figure captions

**Figure 1.** Illustration for the preparation of the graphene magnetic particles with chemical bonding.

**Figure 2.** Procedures for the MSPE of BPA and TCS with the $Fe_3O_4$@$SiO_2$-NH-G.

**Figure 3.** Alkylation reaction of BPA and TCS with BSTFA

**Figure 4.** The typical SEM (A) and TEM (B) images of the $Fe_3O_4$@$SiO_2$-NH-G.

**Figure 5.** Effect of different extraction conditions on MSPE efficiency of TCS and BPA: (A) effect of the amount of the magnetic G sorbents; (B) effect of the pH of sample solution; (C) effect of extraction time; (D) effect of the concentration of NaCl in sample solution; and (E) effect of the desorption solvent.

**Figure 6.** Effect of different derivatization conditions on the extraction recoveries of TCS and BPA: (A) effect of the derivative reaction temperature; (B) effect of derivative reaction time.

Fig. 7 Chromatograms of (A) a river water sample and (B) the river water sample spiked with 2.5 μg $L^{-1}$ TCS and 1.0 μg $L^{-1}$ BPA.

Table 1. Retention time and mass spectrometric data of the analyte derivatives.

| Analytes | Retention time (min) | M. W. | Quantification ion (m/z) | Qualification ion (m/z) |
|---|---|---|---|---|
| TCS- TMS[a] | 15.795 | 362 | 362 | 345, 310 |
| BPA-TMS | 16.837 | 372 | 372 | 357 |

a: TMS: Trimethylsilyl

Table 2. The linear range (LR), coefficient of correlation (*r*), limits of detection (LODs), and limits of quantification (LOQs) of the analytes by the MSPE-GC-MS analysis.

| Analytes | LR (μg $L^{-1}$) | *r* | LOD (ng $L^{-1}$) | LOQ (ng $L^{-1}$) |
|---|---|---|---|---|
| TCS | 0.1-5.0 | 0.9986 | 20.0 | 60.0 |
| BPA | 0.05-2.5 | 0.9977 | 10.0 | 30.0 |

Table 3. The recoveries and precisions for MSPE/GC-MS method in lake water, river water, bottle water and tap water samples spiked with three different concentrations of the TCS and BPA.

| Analytes | Spiked (μg L$^{-1}$) | Lake water | | | | River water | | | | Bottle water | | | | Tap water | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Intra-day | | Inter-day | | Intra-day | | Inter-day | | Intra-day | | Inter-day | | Intra-day | | Inter-day | |
| | | R[b] (%) | RSD (%) | R (%) | RSD (%) | R (%) | RSD (%) | R (%) | RSD (%) | R (%) | RSD (%) | R (%) | RSD (%) | R (%) | RSD (%) | R (%) | RSD (%) |
| TCS | 0.5 | 98.6 | 3.4 | 97.3 | 4.5 | 94.3 | 4.2 | 93.6 | 4.6 | 94.1 | 2.8 | 93.9 | 5.2 | 104.3 | 3.6 | 98.6 | 4.9 |
| | 2.5 | 103.2 | 2.7 | 99.5 | 3.7 | 96.4 | 3.4 | 95.3 | 5.5 | 100.7 | 2.2 | 97.5 | 4.3 | 99.5 | 2.1 | 96.2 | 3.5 |
| | 4.5 | 99.5 | 2.4 | 96.5 | 5.2 | 94.8 | 5.3 | 93.8 | 3.9 | 101.7 | 3.2 | 96.2 | 3.7 | 100.9 | 3.0 | 97.8 | 3.9 |
| BPA | 0.2 | 95.1 | 3.4 | 97.4 | 4.8 | 95.2 | 4.4 | 93.5 | 4.7 | 99.8 | 3.9 | 95.8 | 3.1 | 102.9 | 5.8 | 98.8 | 4.1 |
| | 1.0 | 99.2 | 2.3 | 96.8 | 5.7 | 97.1 | 5.2 | 95.6 | 4.5 | 95.3 | 4.1 | 94.2 | 5.0 | 102.3 | 4.1 | 96.4 | 4.6 |
| | 2.2 | 98.9 | 4.6 | 97.1 | 3.5 | 93.9 | 4.3 | 94.4 | 5.4 | 101.4 | 2.5 | 96.7 | 4.5 | 99.7 | 4.5 | 94.1 | 5.3 |

b: R: recovery of the method

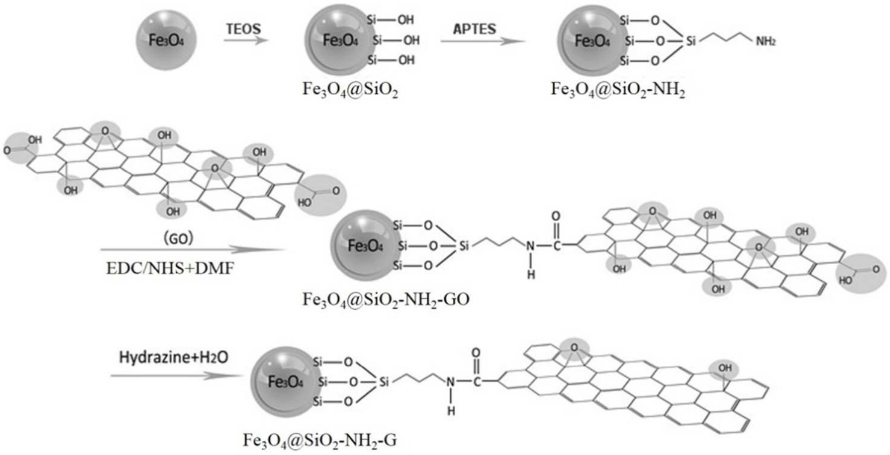

Fig.1 Illustration for the preparation of the graphene magnetic particles with chemical bonding.

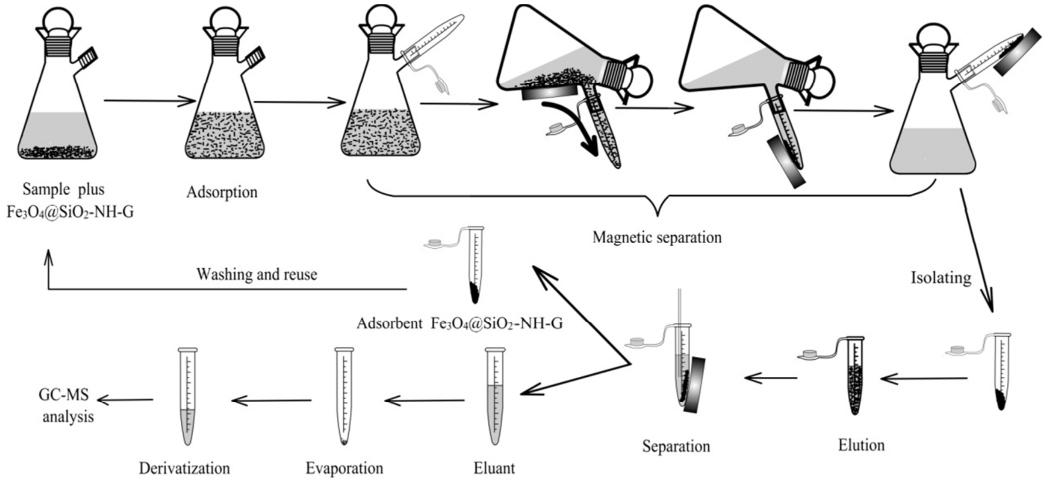

Fig.2 Procedures for the MSPE of BPA and TCS with the $Fe_3O_4@SiO_2$-NH-G.

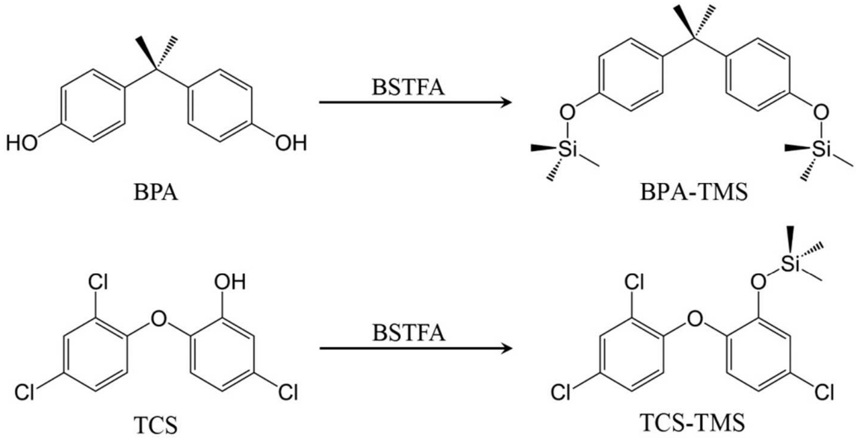

Fig. 3 Alkylation reaction of BPA and TCS with BSTFA

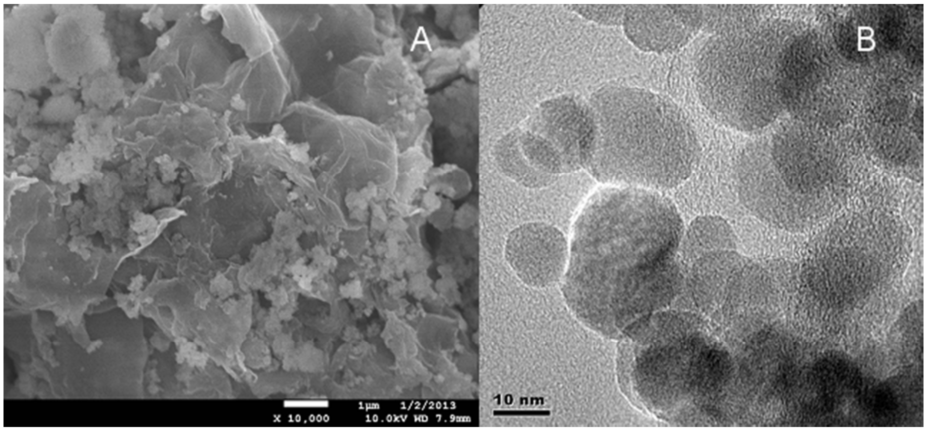

Fig. 4 The typical SEM (A) and TEM (B) images of the $Fe_3O_4$@$SiO_2$-NH-G.

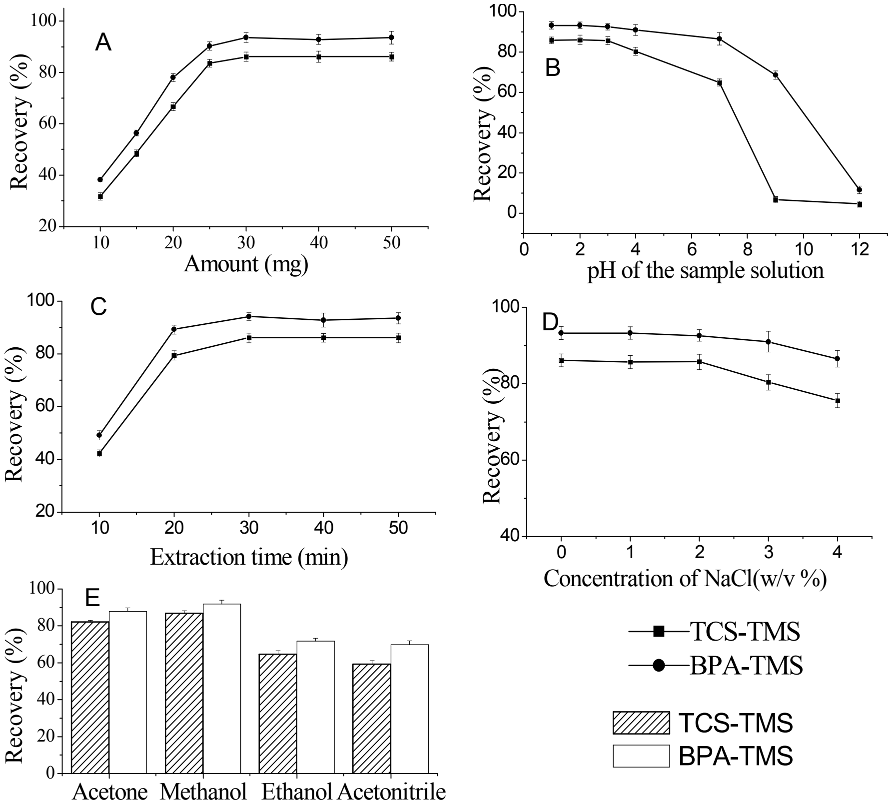

Fig.5 Effect of different extraction conditions on MSPE efficiency of TCS and BPA: (A) effect of the amount of the magnetic G sorbents; (B) effect of the pH of sample solution; (C) effect of extraction time; (D) effect of the concentration of NaCl in sample solution; and (E) effect of the desorption solvent.

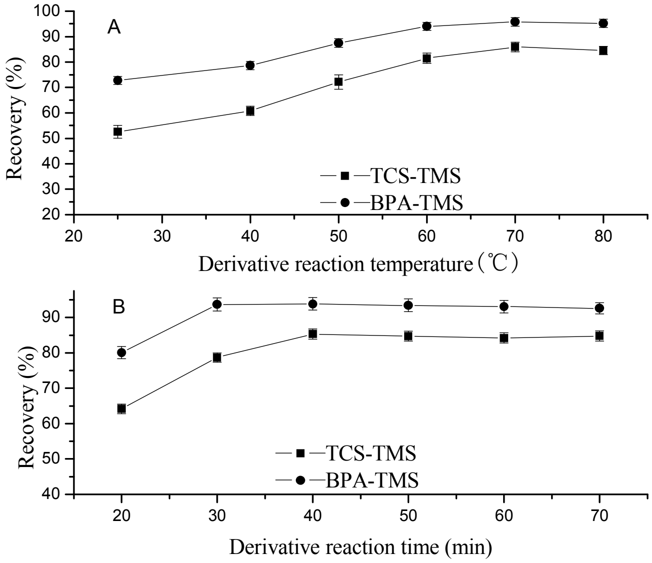

Fig. 6 Effect of different derivatization conditions on the extraction recoveries of TCS and BPA: (A) effect of the derivative reaction temperature; (B) effect of derivative reaction time.

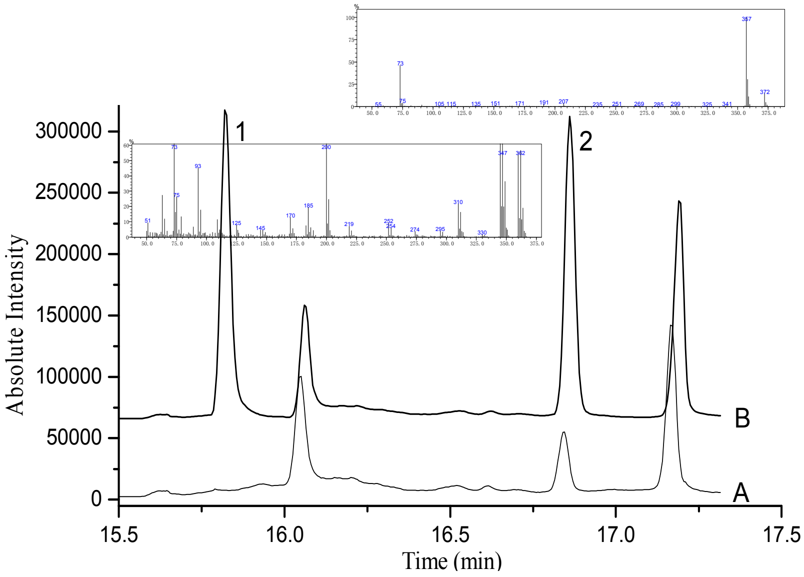

Fig. 7 Chromatograms of (A) a river water sample and (B) the river water sample spiked with 2.5 μg $L^{-1}$ TCS and 1.0 μg $L^{-1}$ BPA.

1．TCS-TMS；2．BPA-TMS

# Graphene grafted magnetic microspheres for solid phase extraction of bisphenol A and triclosan from water samples followed by gas chromatography-mass spectrometric analysis

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