

## Research Article

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# Adsorption and determination of polycyclic aromatic hydrocarbons in water through the aggregation of graphene oxide

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**Abstract:** In this study, a simple method was developed for the aggregation of graphene oxide (GO) with the addition of NaCl to concentrate and separate polycyclic aromatic hydrocarbons (PAHs) from water samples, and this method was used as an environmentally friendly method for the determination of PAHs. We demonstrate the uniform dispersion of GO sheets in aqueous samples for the fast high-efficiency adsorption of PAHs. Aggregation occurred immediately upon elimination of electrostatic repulsion by adding NaCl to neutralize the excessive negative charges on the surfaces of the GO sheets. The aggregates of GO and PAHs were separated and treated with hexane to form a slurry. The slurry was filtered and subjected to gas chromatography–mass spectroscopy (GC-MS) analysis. Based on a 40-mL sample volume, limits of detection of 10–30 ng L<sup>-1</sup> were obtained for 16 PAHs, with correlation coefficients ( $R^2$ ) exceeding 0.99. The method yielded good recovery, ranging from 80 to 111% and 80 to 107% for real spiked water samples at 100 and 500 ng L<sup>-1</sup>, respectively. Compared to traditional solid-phase extraction and liquid–liquid extraction methods, this method is free of organic reagents in the pretreatment procedure and uses only 1 mL hexane for sample introduction.

**Keywords:** graphene oxide; aggregation; polycyclic aromatic hydrocarbons.

## 1 Introduction

Environmentally friendly (green) analytical methodologies are in high demand to reduce the risks of chemical use to humans and the environment [1]. However, the traditional analytical methods used to detect environmental pollutants often contribute to further pollution through the chemicals used in analysis, as hazardous chemicals are required for analytical sample preparation, quality control, and calibration [2,3]. Sometimes these chemicals are more toxic than the original analyzed sample. Therefore, the development of novel green analytical methods remains necessary.

Polycyclic aromatic hydrocarbons (PAHs) are a class of common and persistent environmental pollutants containing three or more benzene rings, and they are toxic to aquatic animals and humans [4]. PAHs are frequently found in the soil, air and water, where they can negatively impact human health [5]. Therefore, the rapid and sensitive determination of PAH compounds in environmental samples is urgently needed [6–9]. However, the traditional liquid–liquid [10] and solid-phase (SPE) [11,12] methods for extraction before determination of PAHs usually consume large quantities of solvents, which lead to further polluting of the environment [13–16].

Graphene oxide (GO) is a two-dimensional carbon nanomaterial that has attracted significant scientific attention in recent years [17–19]. GO can be obtained by the strong oxidation of graphite; it possesses a layered structure and negatively charged surfaces [20]. At the edges of the carbon layers, dense carboxyl groups significantly affect the van der Waals interactions among adjacent graphene layers and render the material strongly hydrophilic [21,22]. Thus, many hydrophilic and polar substances including pigments [23,24], endogenous estrogen [25], heavy metal ions [26,27], phenols [28], and

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basic species[29] can be adsorbed onto the GO surface through hydrogen bonding, anion- $\pi$ , and electrostatic interactions [30,31].

GO has been reported to adsorb PAH compounds with high efficiency [31]. However, the complete removal of small GO sheets from a well-dispersed solution is difficult. The traditional separation methods of high-speed centrifugation and filtering through 0.22- $\mu\text{m}$  porous membrane filters are usually relatively cumbersome, time-consuming, and inefficient, and they typically result in incomplete separation. When GO is used to adsorb target compounds, the separation of GO from the solution remains slow and difficult. Fortunately, GO can form stable aqueous colloids that aggregate by changing the pH [32,33] or adding electrolyte solutions [34,35]. Based on this theory, GO was successfully used to extract and separate trace toxic metals including Pb, Cd, Bi, and Sb [36].

Recently, carbon nanomaterials were also applied successfully to the extraction and separation of organic compounds through SPE. For example, graphene has been used as a sorbent for the isolation of propyl gallate and butylated hydroxyanisole from complex food sample matrices [37]. Magnetic SPE based  $\text{Fe}_3\text{O}_4$ @GO nanocomposite was also used to extract ethyl vanillin, trans-cinnamic acid, methyl cinnamate, ethyl cinnamate, and benzyl cinnamate from food samples [38]. However, carbon nanomaterial packed in a SPE cartridge usually becomes increasingly more compact during elution due to an aggregation phenomenon, which decreases extraction and purification efficiency over time. Moreover, large amounts of organic solvent are consumed in the elution of SPE column. Therefore, the aggregation of GO by adding electrolytes in liquid samples was applied to potentially improve the efficiency of the nanomaterial and to reduce the consumption of organic solvents.

The aim of this work was to investigate the impact of the aggregation of GO by introducing NaCl as an electrolyte solute during the extraction of PAHs from water. The isolated GO-adsorbed PAH aggregates were transferred to a GC-MS detection system using a hexane solution for the introduction of a liquid sample. By exploiting the superior properties of GO, the proposed method showed excellent extraction efficiency and minimal organic solvent consumption compared to those in traditional methods.

## 2 Experimental Section

### 2.1 Materials and Reagents

All chemicals used in this work were of at least analytical grade. All solutions were prepared using 18 M $\Omega$ -cm deionized water (DIW) produced by a water-purification system (Millipore, USA). Commercial GO (thickness 0.55–1.2 nm, purity > 95 wt%; size 0.5–3  $\mu\text{m}$ ) was obtained from Chengdu Organic Chemicals Co., Ltd. (Chengdu, China). The GO solution of 1.0 mg mL<sup>-1</sup> prepared with DIW was used directly for the extraction. The liquid PAH standards (1000 mg L<sup>-1</sup>) dissolved in methanol were purchased from the Agro-Environment Protection Institute (Tianjin, China). The selected PAHs were defined and nominated as priority pollutants by the United States Environmental Protection Agency (EPA), including naphthalene (NAP), acenaphthylene (ANY), acenaphthene (ANA), fluorene (FLU), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLT), pyrene (PYR), benzo(a)anthracene (BaA), chrysene (CHR), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), indeno(1,2,3-cd)pyrene (IPY), dibenzo(a,h)anthracene (DBA), and benzo(g,h,i)perylene (BPE). A stock solution of each compound with the concentration of 10 mg L<sup>-1</sup> was prepared in acetone and stored in amber screw-capped glass vials in the dark at -20°C. Working solutions were prepared daily by the appropriate dilution of the stock solutions with hexane before use. NaCl and other reagents were purchased from Guangzhou Chemical Reagent Factory (Guangzhou, China).

### 2.2 Extraction Procedure

A total of 15 water samples were used to evaluate the accuracy of the proposed method. Five river, five lake and five sea water samples were collected from Nandu River, Hongcheng Lake and Holiday Beach of Haikou, Hainan province of China. The samples were collected in precleaned quartz bottles and directly transported to the laboratory for immediate study after filtration with 0.22- $\mu\text{m}$  membrane filters. A 40-mL portion of each water sample was accurately weighed and placed directly in a 50-mL precleaned Teflon centrifuge tube. After that, 4.0 mL of a high concentration (1 mg mL<sup>-1</sup>) of the GO dispersion was added to the tubes, which were allowed to mix for 5 min to achieve the complete adsorption of the analyte PAHs. When NaCl was added and mixed with the GO in the sample solution, GO aggregated quickly and was gradually deposited on the bottom of the tubes. Complete

**Table 1:** Analytical performances of the developed method.

PAHs	Retention time (min)	Selected ions	Regression equation	r <sup>2</sup>	Liner range (ng L <sup>-1</sup> )	LODs (ng L <sup>-1</sup> )
NAP	6.05	128 <sup>a</sup> , 129, 127	Y=0.982x+0.003	0.996	50-2000	10
ANY	9.29	152 <sup>a</sup> , 151, 153	Y=0.983x+0.003	0.998	50-2000	10
ANA	9.81	153 <sup>a</sup> , 154, 152	Y=0.970x+0.005	0.997	50-2000	10
FLU	11.74	166 <sup>a</sup> , 165, 167	Y=1.003x-0.001	0.999	50-2000	10
PHE	16.83	178 <sup>a</sup> , 179, 152	Y=0.995x+0.001	0.999	50-2000	15
ANT	16.55	178 <sup>a</sup> , 179, 176	Y=1.002x-0.001	0.999	50-2000	15
FLT	24.61	202 <sup>a</sup> , 101, 100	Y=0.987x+0.002	0.999	50-2000	15
PYR	26.71	202 <sup>a</sup> , 200, 203	Y=0.938x+0.008	0.995	50-2000	15
BaA	42.27	228 <sup>a</sup> , 226, 229	Y=0.944x+0.008	0.994	50-2000	15
CHR	42.50	228 <sup>a</sup> , 229, 226	Y=0.945x+0.008	0.994	50-2000	15
BbF	47.52	252 <sup>a</sup> , 253, 125	Y=1.003x-0.001	0.999	50-2000	20
BKF	47.65	252 <sup>a</sup> , 253, 250	Y=1.002x-0.001	0.999	50-2000	20
BaP	48.96	252 <sup>a</sup> , 253, 250	Y=1.022x-0.004	0.999	50-2000	20
IPY	55.49	276 <sup>a</sup> , 277, 138	Y=0.985x+0.003	0.997	50-2000	30
DBA	55.81	278 <sup>a</sup> , 276, 139	Y=0.996x-0.001	0.999	50-2000	30
BPE	57.40	276 <sup>a</sup> , 274, 138	Y=1.009x-0.001	0.999	50-2000	30

a Quantitation ion of each PAH for SIM.

phase separation was accomplished by centrifuging for 5 min at 15000 rpm (high-speed refrigerated centrifuge, CR22N, Hitachi, Japan). The supernatant was transferred to another pre-cleaned 50-mL centrifuge tube, and another 4.0 mL of GO solution was added for a second extraction as described above. The second supernatant was discarded and the GO aggregates were mixed to slurry with 1 mL hexane. The slurry was centrifuged for 1 min at 15000 rpm and the supernatant was filtered through 0.22  $\mu$ m membrane (Tianjin Jinteng Experiment Equipment Ltd., Co., Tianjin, China) automatic sampling and analyzed by GC-MS.

## 2.3 GC-MS Analysis

The selected PAHs were analyzed on a Trace GC Ultra equipped with a DSQ quadrupole MS system (Thermo, USA). Liquid samples of 1  $\mu$ L each were injected to the GC apparatus via a TriPlus RSH Autosampler by the headspace and liquid mode, respectively. The GC analyzer was equipped with a Thermo Scientific TR-5MS column (30 m  $\times$  0.25 mm  $\times$  0.25  $\mu$ m). He (purity  $\geq$  99.999%) was used as the carrier gas at the flow rate of 1.5 mL min<sup>-1</sup>. The oven temperature program was set as follows: 45°C for 0.8 min, heated to 150°C at 25°C min<sup>-1</sup>, then to 200°C at 3°C min<sup>-1</sup>, and finally to 280°C at 8°C min<sup>-1</sup> for 18 min. The injection

port, ion source, and interface temperatures were 250, 230, and 280°C, respectively. The MS detector was operated in the electron ionization (EI) mode with an ionizing energy of 70 eV. The selective ion monitoring mode was adopted for the quantitative determination of the analytes, and the selected ion masses are listed in Table 1.

Ethical approval: The conducted research is not related to either human or animals use.

## 3 Results and Discussion

### 3.1 Proposed Mechanism of Aggregation

GO is regarded as a promising nanomaterial for the adsorption of pollutants because it features abundant O-containing functional groups, large surface areas, highly negative surface charge, and high adsorption capacity. The first study was designed to test whether PAHs could be adsorbed onto GO from water samples with high efficiency. Therefore, the river, lake, and sea water samples were treated for 10 min in the presence of GO to permit adsorption, and the contents of PAHs in pre- and post-treatment samples were determined with a standard SPE method [39]. The results (Fig 1) demonstrate that GO successfully adsorbed the PAHs.

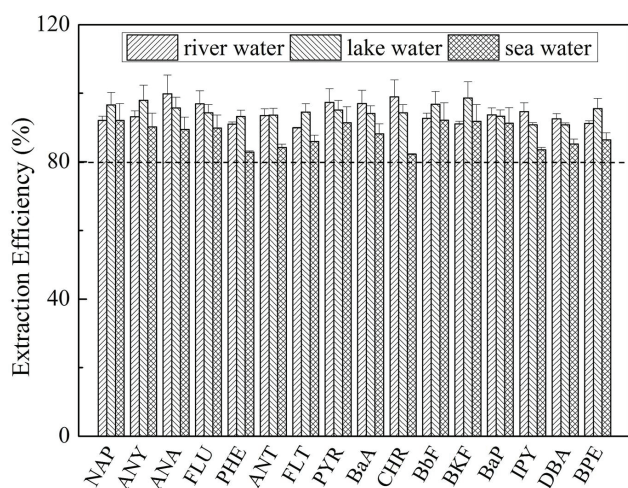
After adsorption, the GO solution must be aggregated for the separation of PAHs from the water sample. The GO sheets are highly negatively charged because of the edge carboxyl groups. Aqueous colloids and dispersions are stabilized *via* electrostatic repulsion; therefore, the dispersion and aggregation of GO depend on the degree of ionization of its carboxylic acid and phenolic hydroxyl groups. In this study, NaCl was chosen to neutralize the excessive negative charges and decrease the electrostatic repulsion to accomplish GO aggregation. The effect of NaCl on the zeta potential of GO was thus evaluated by an MPT-2 Zetasizer Nano (Malvern, England), with results

summarized in Figure 2. The change in zeta potential upon the introduction of  $1000 \mu\text{g}\cdot\text{L}^{-1}$  PAHs was negligible (Figure 2a), demonstrating that the GO solvent maintains good dispersion under high concentrations of PAHs. However, once  $0.04 \text{ g mL}^{-1}$  of NaCl was added to the GO solvent, the zeta potentials decreased sharply from  $-48.4$  to  $-25.0 \text{ mV}$ . The effects of different NaCl masses on the zeta potential of  $1 \text{ mg mL}^{-1}$  GO were studied as shown in Figure 2b. When the mass of NaCl was increased from  $0.04$  to  $0.20 \text{ g mL}^{-1}$ , the zeta potential gradually increased from  $-25.0$  to  $-4.4 \text{ mV}$ . A previous study found that instability in colloid dispersions, caused by insufficient mutual repulsion, appeared when the absolute zeta potential values were  $<30 \text{ mV}$  [34,40]. This proves that the introduction of NaCl can achieve GO aggregation and phase separation.

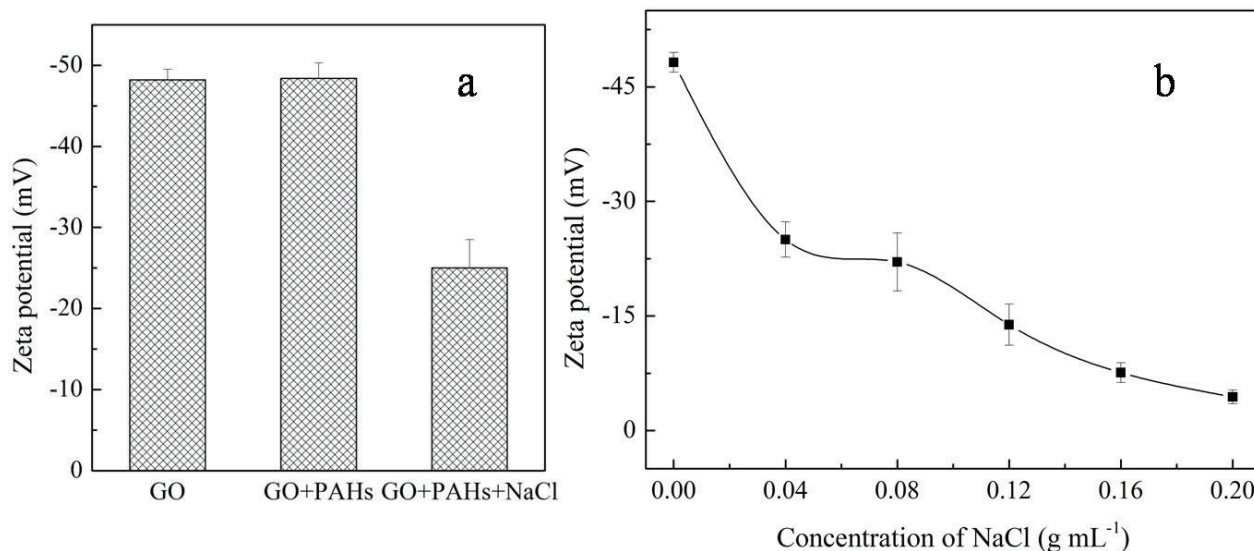
To further illuminate the morphologies of the GO sheets, transmission electron microscopy (TEM, HT7700, Hitachi, Japan) was used to observe changes in the images of GO after the addition of NaCl, with results summarized in Figure 3. In Figure 3a, a large GO sheet with intrinsic wrinkles is observed. Figure 3b shows the aggregated GO sheets, confirming that the neutralization of GO negative charges by NaCl induced GO aggregation in aqueous GO suspensions.

### 3.2 Optimization of Extraction Conditions

To optimize the adsorption conditions of PAHs by GO, DIW water spiked with the sixteen kinds of PAHs at

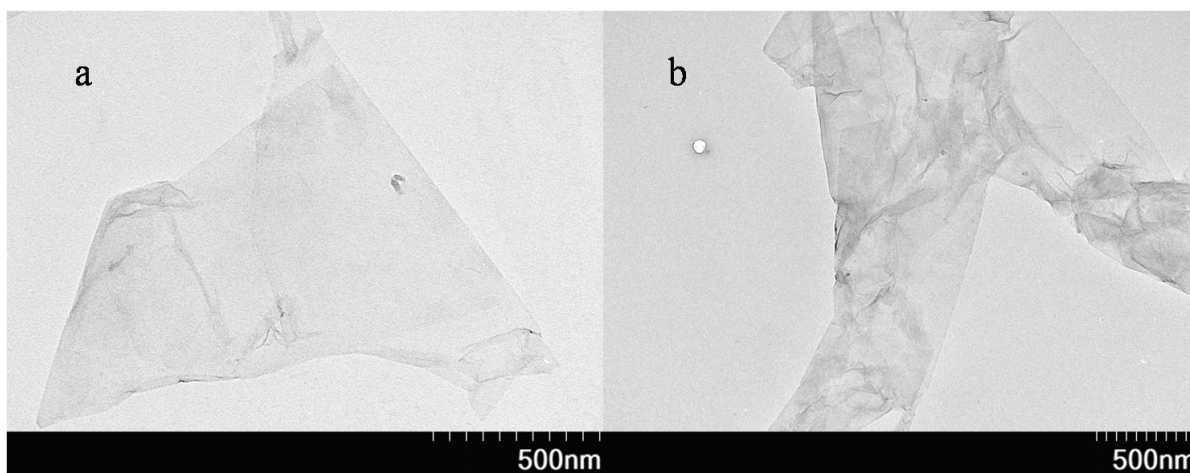


**Figure 1:** Extraction efficiency of PAHs with GO from river, lake and sea water.



**Figure 2:** Zeta potential measurement of GO suspensions: (a) Zeta potential values after addition of PAHs ( $1000 \mu\text{g mL}^{-1}$ ) and NaCl ( $0.04 \text{ g mL}^{-1}$ ) into GO suspensions ( $1 \text{ mg mL}^{-1}$ ), and (b) Zeta potential of GO at  $1 \text{ mg mL}^{-1}$  as a function of NaCl.





**Figure 3:** TEM images of GO suspensions (a), and GO+PAHs+NaCl (b).

concentrations of  $200 \text{ ng L}^{-1}$  were used for sequential assessments. The extraction efficiency was evaluated by the recovery of the spiked PAHs.

As mentioned earlier, GO displays high affinity for the PAHs. However, the mass of the GO strongly affected the adsorption capacity for the analytes, which affected the extraction efficiency. In this work, the adsorption capacities of GO for PAHs were first investigated by adding 4.0 mL of GO dispersion solutions with different concentrations ( $0.10\text{--}1.00 \text{ mg mL}^{-1}$ ) to a series of 40-mL solutions containing  $200 \text{ ng L}^{-1}$  PAHs. The results are summarized in Figure 4a, which shows that the extraction efficiencies of all four tested PAH targets increased with increased mass of GO. A plateau for each analyte was obtained in the range of 2.0 to 4.0 mg GO. Lower masses of GO resulted in the inefficient adsorption of the analytes because of the limited adsorption capacity of GO. Therefore, 4 mL of GO at  $0.75 \text{ mg mL}^{-1}$  was used for all subsequent extractions in this work.

The adsorption time of the PAHs onto GO is another critical parameter for the proposed method. Therefore, the effects of adsorption time were also studied, with results summarized in Figure 4b. All PAH compound recoveries increased with adsorption time in the range of 5 to 15 min. A plateau occurred for times exceeding 15 min, indicating that the GO and PAHs reach equilibrium in 15 min. The adsorption time of 15 min was thus applied in subsequent experiments.

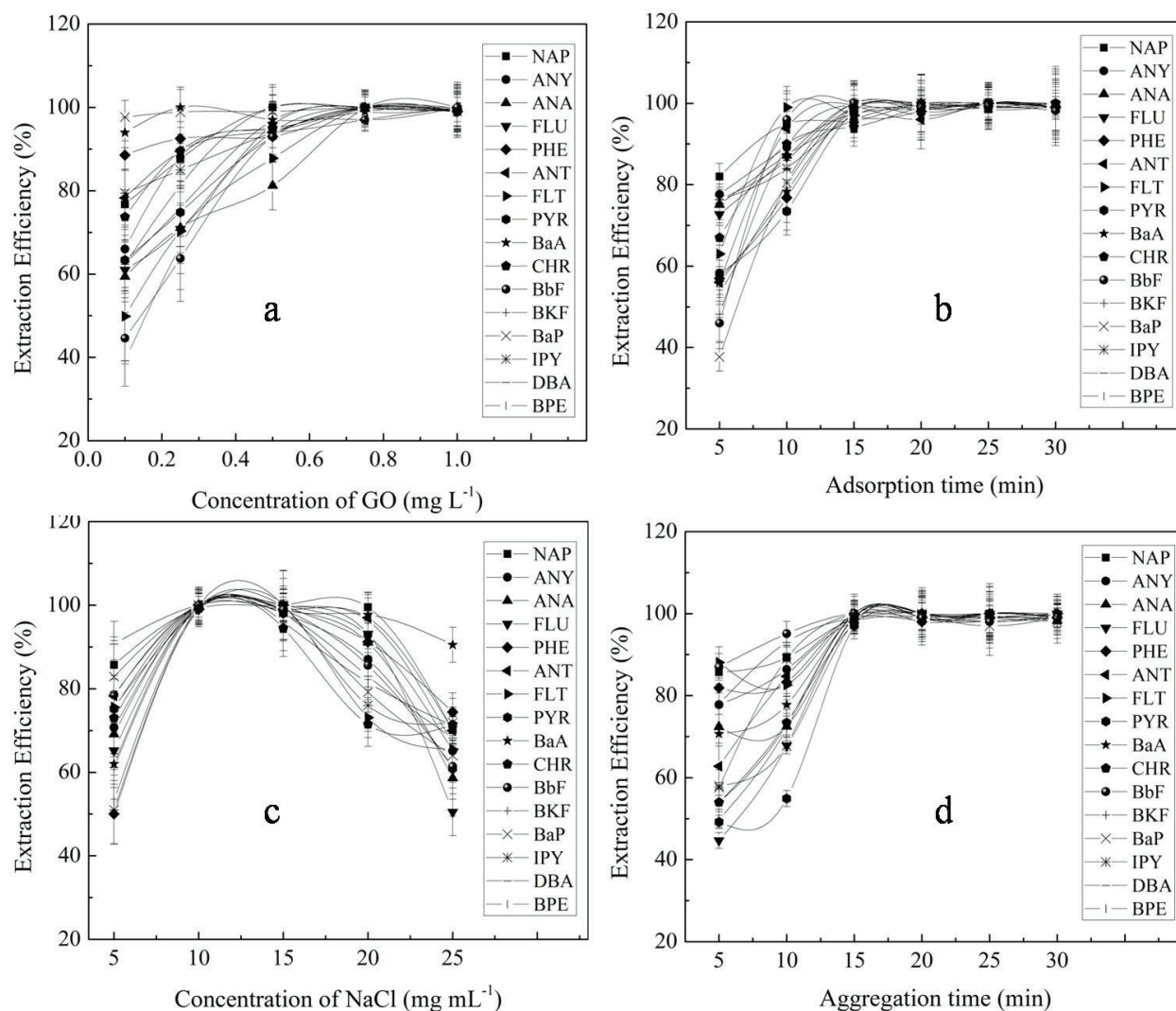
In the extraction, NaCl was chosen to neutralize the excessive negative charges and decrease the electrostatic repulsion to induce GO aggregation. Therefore, the effect of the concentration of NaCl on the extraction efficiency was investigated using  $200 \text{ ng L}^{-1}$  PAHs as the test samples. Results of these experiments are shown in

Figure 4c. A plateau of extraction efficiency for each PAH compound occurs in the range of  $10\text{--}15 \text{ mg mL}^{-1}$  NaCl solution. The recoveries are decreased for both higher and lower concentrations of NaCl. Lower NaCl concentrations resulted in inefficient GO aggregation and poor extraction efficiency of the analytes from the aqueous phase, while higher NaCl concentrations induced low analyte recovery from GO because of competition between  $\text{Na}^+$  and the PAHs. Therefore, the NaCl concentration of  $10 \text{ mg mL}^{-1}$  was used for further experiments.

The GO aggregation could be observed immediately upon the addition of NaCl. However, the deposition time was assessed to determine whether GO was completely deposited. Different deposition times were selected to evaluate the efficiency of GO aggregation, and the results were summarized in Figure 4d. The recoveries of all analytes reached 40–80% for the deposition time of 5 min, and recoveries increased to 60–90% after 10 min. For longer times, the recoveries plateau at approximately 100% for each analyte, indicating a deposition balance between NaCl and the GO solution. Therefore, we repeated the GO extraction and aggregation twice with 15 min allotted for each aggregation in subsequent studies to enhance the recoveries of the PAH compounds.

### 3.3 Interference

GO demonstrated high efficiency for PAH adsorption. However, some coexisting chemicals may affect the adsorption efficiencies of analytes if competitive adsorption occurs between the tested targets and potential interferential chemicals, such as inorganic ions and organic materials. Consequently, the effects of several

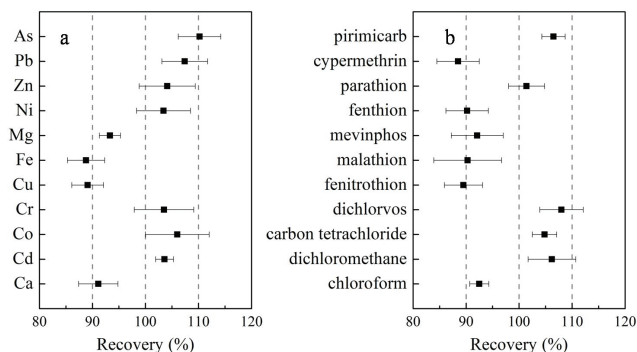


**Figure 4:** Optimization of the effects of influencing parameters on the extraction efficiency of PAHs. (a) Effect of concentration of GO. Adsorption time, 15 min; concentration of NaCl, 10 mg mL<sup>-1</sup>; and aggregation time, 15 min. (b) Effect of concentration of Adsorption time. Concentration of GO, 1.0 mg L<sup>-1</sup>; concentration of NaCl, 10 mg mL<sup>-1</sup>; and aggregation time, 15 min. (c) Effect of concentration of NaCl. Concentration of GO, 1.0 mg L<sup>-1</sup>; adsorption time, 15 min; and aggregation time, 15 min. (a) Effect of aggregation time. Concentration of GO, 1.0 mg L<sup>-1</sup>; adsorption time, 15 min; and concentration of NaCl, 10 mg mL<sup>-1</sup>.

inorganic ions and organic materials were carefully studied. In these experiments, standard solutions of 200 ng L<sup>-1</sup> of the PAHs were used, and 13 inorganic ions (namely As<sup>3+</sup>, Ca<sup>2+</sup>, Cd<sup>2+</sup>, Co<sup>2+</sup>, Cr<sup>3+</sup>, Cu<sup>2+</sup>, Fe<sup>3+</sup>, Mg<sup>2+</sup>, Mn<sup>2+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup>, Pb<sup>2+</sup>, and Se<sup>2+</sup>) and 11 organic chemicals (namely chloroform, dichloromethane, carbon tetrachloride, dichlorvos, fenitrothion, malathion, mevinphos, fenthion, parathion, cypermethrin, and pirimicarb) at concentrations of 100 µg mL<sup>-1</sup> were introduced. The results are summarized in Figure 5. With the tolerance limits defined as the largest concentrations of coexisting ions causing less than 15% signal variation, no significant interferences were observed.

### 3.4 Analytical performance

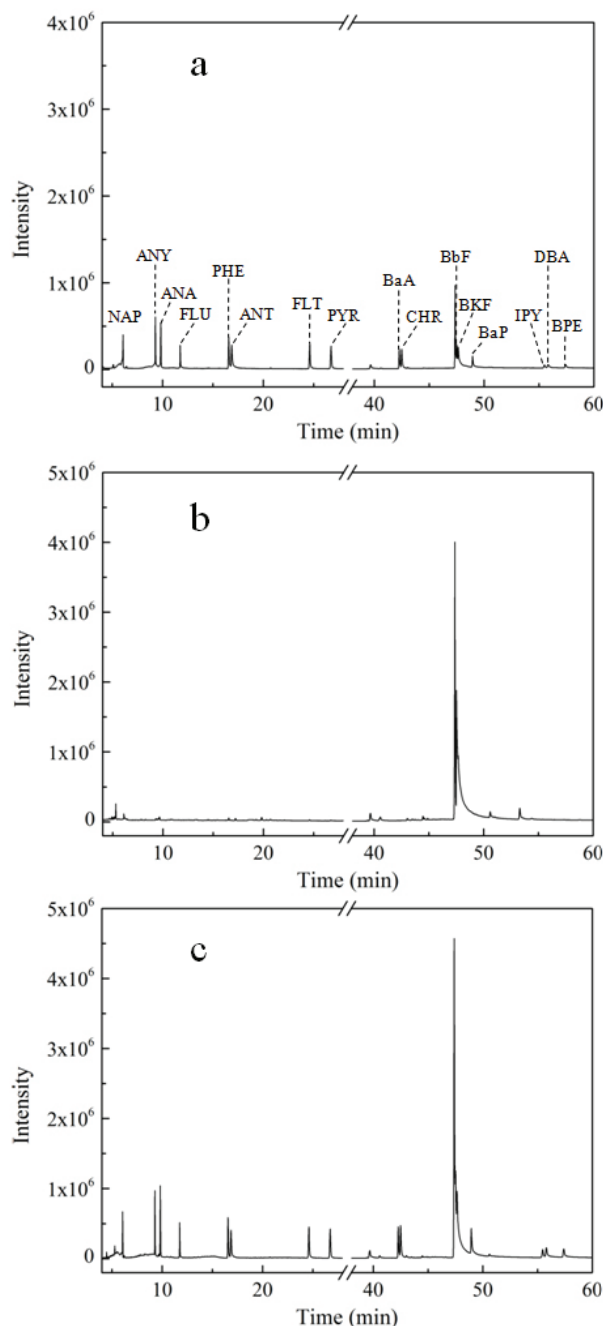
Analysis of PAHs by GC-MS was accomplished in the SIM mode based on the use of one target as quantification ion and two confirmation ions. PAHs were recognized according to their retention times, target and confirmation ions. The retention time, diagnostic ions and quantification ion for each analyte are presented in Table 1. Representative selected ion chromatograms of non-spiked and spiked water samples are shown in Figure 6. The method showed no interfering background signal and therefore excellent selectivity for PAHs in the presence of other sample constituents.



**Figure 5:** (a) Interferences owing to the coexistence of different inorganic ions at a concentration of  $100 \mu\text{g mL}^{-1}$ . (b) Interferences owing to the coexistence of different organic materials at a concentration of  $100 \mu\text{g mL}^{-1}$ .

The analytical performance of the PAHs obtained using GC-MS were evaluated under optimal experimental conditions. The linearity, regression, and linear ranges of the PAHs compounds are presented in Table 1. The linear coefficient ( $R^2$ ) was better than 0.99. The determined limits of detection (LODs), as defined as the lowest analyte concentration that yielded a signal of three times the signal-to-noise ratio (S/N), ranged from 10 to  $30 \text{ ng L}^{-1}$ . Considering that the Chinese Ministry of Health has established maximum residue limits (MRLs) of PAHs in drinking water at a value of  $2 \mu\text{g L}^{-1}$  (GB 5749-2006, Chinese national standard), this method meets requirements for the determination of PAHs in water samples.

The applicability of the proposed method was first used to analyze 15 real samples from river, lake, and sea water to allow comparison with standard methods. The river and lake water samples were concentrated directly after filtering through a  $0.22 \mu\text{m}$  membrane filter. However, as mentioned earlier, GO aggregation occurred immediately upon GO addition because of the high salt content of sea water, which decreased the extraction efficiency. Therefore, with this method, sea water should be diluted before analysis, and no additional NaCl is needed to trigger GO aggregation in this case. However, the PAH contents in the water samples collected in Haikou were below the limits of quantitation (LOQs) of both the proposed and standard methods (data not shown). Therefore, river and sea water samples were chosen to further validate the accuracy of the proposed method *via* the evaluation of the recoveries of the spiked PAHs, because no certified PAH values in these samples are available. The results are summarized in Table 2. Satisfactory spike recoveries were measured in the ranges of 80–111% and 80–107% for real



**Figure 6:** GC-MS chromatograms under SIM mode of PAHs in (a) PAHs standard solution, (b) blank water sample and (c) spiked water sample.

spiked water samples at  $100$  and  $500 \text{ ng L}^{-1}$ , confirming the suitability of the proposed method for PAH analysis.

Comparisons of PAH analysis by the proposed and standard methods are summarized in Table 3. Extraction and separation by the aggregation of GO using NaCl as the electrolyte solution coupled to GC-MS detection is friendlier to the environment, simpler in operation,

**Table 2:** Analytical performances of the developed method.

PAHs	Added, 100 ng L <sup>-1</sup>				Added, 500 ng L <sup>-1</sup>			
	Found <sup>a</sup> (ng L <sup>-1</sup> )	Recovery <sup>a</sup> (%)	Found <sup>b</sup> (ng L <sup>-1</sup> )	Recovery <sup>b</sup> (%)	Found <sup>a</sup> (ng L <sup>-1</sup> )	Recovery <sup>a</sup> (%)	Found <sup>b</sup> (ng L <sup>-1</sup> )	Recovery <sup>b</sup> (%)
NAP	90.4±4.8	90	106.1±7.9	106	535.2±24.7	107	451.0±34.8	90
ANY	103.2±7.0	103	102.8±3.6	103	440.8±37.3	88	511.2±13.2	102
ANA	81.1±8.0	81	103.3±6.0	103	470.1±54.7	94	466.8±19.0	93
FLU	103.1±6.9	103	91.4±3.3	91	448.3±40.3	90	462.2±42.4	92
PHE	110.4±1.8	110	89.5±5.7	89	471.8±14.4	94	453.8±25.2	91
ANT	110.3±8.2	110	88.8±3.0	89	441.7±19.4	88	511.0±16.7	102
FLT	93.7±6.5	94	94.2±4.3	94	423.0±35.9	85	462.2±19.3	92
PYR	81.7±5.9	82	88.8±4.9	89	438.3±16.9	88	437.7±35.2	88
BaA	80.1±6.0	80	96.7±7.3	97	502.7±20.2	101	509.0±39.9	102
CHR	84.8±4.6	85	106.2±2.0	106	438.6±15.6	88	406.9±41.1	81
BbF	88.3±6.9	88	109.0±2.0	109	479.3±26.4	96	457.8±22.1	92
BKF	110.3±2.0	110	110.7±7.3	111	495.8±37.0	99	514.0±25.5	103
BaP	95.2±4.0	95	89.2±5.5	89	429.0±36.1	86	443.2±23.4	89
IPY	87.9±3.4	88	84.6±4.4	85	470.2±35.6	94	533.7±37.2	107
DBA	99.3±4.7	99	100.3±8.3	100	452.8±12.6	91	474.4±25.9	95
BPE	86.7±6.5	87	106.9±5.9	107	489.8±26.9	98	401.3±14.6	80

a Spiked river water samples, n=3; b Spiked seawater samples, n=3.

**Table 3:** Comparison of the features of the proposed method and the standard methods.

	pretreated method	determined instrument	organic reagents for pretreatment	organic reagents for determination	enrichment coefficient	LODs (ng L <sup>-1</sup> )
GB/T 26411-2010	solid phase extraction	GC-MS	methylene chloride, 13 mL; methanol, 1.5 mL; actone, 1.5 mL	hexane, 0.5 mL	2000	1-2
EPA method 610	Liquid-liquid extraction	HPLC-UV	methylene chloride, 150 mL	acetonitrile, 1 mL	500	13-2300
[15]	multi-walled carbon nanotubes SPE	GC-MS	25 mL n-hexane, 10 mL methanol	hexane, 1 mL	500	2.0-8.5
[18]	molecularly imprinted SPE	GC-MS	2.0 mL methanol/H <sub>2</sub> O (1:9, v/v); 10 mL DCM/acetic acid (9:1, v/v)	0.5 mL DCM/acetic acid (9:1, v/v)	60	5.2-12.6
this method	adsorption/aggregation	GC-MS	-	hexane, 1.0 mL	50	10-30

and enhanced in both sample throughput and cost-effectiveness.

## 4 Conclusions

In this work, GO was successfully applied for the preconcentration/separation of PAHs from water samples through aggregation by the addition of NaCl. The method is free of organic reagents in the pretreatment procedure

and uses only 1 mL hexane for sample introduction in GC-MS. The proposed method is environmentally friendly and demonstrates great applicability for the green analysis of PAH contents in surface waters.

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**Conflict of interest:** Authors state no conflict of interest.

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