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# Graphene-dispersive solid-phase extraction of phthalate acid esters from environmental water

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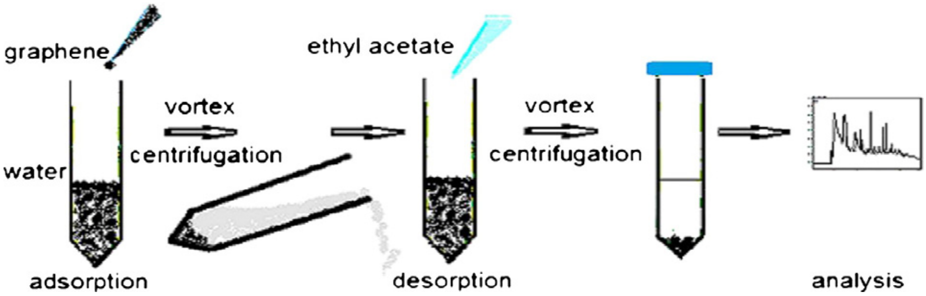
## HIGHLIGHTS

- ► Graphene-dispersive solid-phase extraction was firstly used in sample preparation.
- ► The amount of graphene used was only 3 mL (1.5 mg/mL) for enrichment of 15 PAEs.
- ► The method was applied for 9 river and 2 sea water samples from 7 areas in China.

## GRAPHICAL ABSTRACT

Graphene-dispersive solid-phase extraction of phthalate acid esters from environmental water.



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## ABSTRACT

Graphene is a novel carbon nanomaterial with an ultra-high specific surface area. In this paper, we explored graphene as adsorbent for efficient enrichment of 15 phthalate acid esters (PAEs) under different water matrixes (ultrapure water, river and sea). A simple and inexpensive method of dispersive solid-phase extraction (DSPE) combined with gas chromatography–mass spectrometry (GC–MS) was used and acceptable results were provided for most PAEs with overall average recoveries between 71 and 117%. The extraction conditions such as the amount of graphene, the desorption solvent, adsorption time, desorption time and the solution pH were optimized. Finally, the method was applied for the determination of PAEs in environmental water samples including 9 rivers and 2 seas from 7 areas in China.

## 1. Introduction

Phthalate acid esters (PAEs) are widely used in industrial plastics, polyvinyl chloride (PVC) products and personal care products. As PAEs are not chemically bound to plastic, they can readily leach, migrate or evaporate into various environmental matrices. These pollutants are refractory to the environmental microorganisms. Their accumulation in natural waters causes wide distribution within aqueous systems like rivers, lakes and ground waters, as well as a noticeable influence on the ecological environment (Daiem et al., 2012). Being suspected to have carcinogenic and estrogenic properties (Harris et al., 1997; Heudorf et al., 2007), the determination of the PAEs has attracted considerable attention.

The most widely used analysis methods for sample preparation of PAEs include liquid–liquid extraction (LLE) (Mori, 1976; Holadová and Hajslová, 1995; Kambia et al., 2001) and solid phase extraction (SPE) (Jobling et al., 1995; Jara et al., 2000). Recently some new techniques have been developed for the preconcentration of phthalate esters such as solid-phase microextraction (SPME) (Peñalver et al., 2000; Prokůpková et al., 2002; Saito et al., 2002), ultrasonic extraction (USE) (Ma et al., 2003), liquid-phase micro extraction (LPME) (Batlle and Nerín, 2004; Psillakis and Kalogerakis, 2003), microwave-assisted extraction (MAE) (Bartolomé et al., 2005), and accelerated solvent-based

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**Table 1**
The retention time, qualitative ions and quantitative ions for the GC/MS analysis of 15 PAEs.

| Analyte | Abbreviation | Retention time (min) | Qualitative ion | Quantitative ion |
|---|---|---|---|---|
| Dimethyl phthalate | DMP | 5.57 | 77, 135, 194 | 163 |
| Diethyl phthalate | DEP | 6.42 | 121, 177, 222 | 149 |
| Diisobutyl phthalate | DIBP | 8.06 | 167, 205, 223 | 149 |
| Dibutyl phthalate | DBP | 8.75 | 121, 205, 223 | 149 |
| Bis(2-methoxyethyl) phthalate | DMEP | 9.08 | 149, 193, 251 | 59 |
| Bis(4-methyl-2-pentyl) phthalate | BMPP | 9.73 | 121, 167, 251 | 149 |
| Bis(2-ethoxyethyl) phthalate | DEEP | 10.06 | 45, 121, 149 | 72 |
| Dipentyl phthalate | DPP | 10.39 | 167, 219, 237 | 149 |
| Di-n-hexyl phthalate | DHXP | 12.40 | 76, 104, 251 | 149 |
| Benyl butyl phthalate | BBP | 12.54 | 91, 206, 238 | 149 |
| Bis(2-n-butoxyethyl) phthalate | DBEP | 13.93 | 57,193, 249 | 149 |
| Dicyclohexyl phthalate | DCHP | 14.53 | 83, 167, 269 | 149 |
| Bis(2-ethylhexyl) phthalate | DEHP | 14.79 | 113, 167, 279 | 149 |
| Di-n-octyl phthalate | DNOP | 17.13 | 179, 261, 279 | 149 |
| Dinonyl phthalate | DNP | 19.60 | 57, 71, 293 | 149 |
| Triphenyl phosphate | TPP | 13.14 | 170, 215, 325 | 326 |

extraction (Reid et al., 2009). The traditional method of LLE is time consuming and requires large amounts of organic solvents. SPE is expensive relatively. Compared to LLE and SPE, these new extraction methods are simple and time saving.

More recently other methods based on the application of carbon materials such as activated carbon (Özer and Gücer, 2011), multi-walled carbon nanotubes (MWNTs) (Cai et al., 2003) and magnetic MWCNTs (Luo et al., 2012) were also developed. The magnetic solid-phase extraction (MSPE) coupling with gas chromatography/mass spectrometry (GC/MS) (Luo et al., 2012) showed limits of detection (LOD) of 16 PAEs ranged from 0.003 to 0.06 ng/L, which was more sensitive compared to other methods.

These carbon materials showed great potential for the enrichment of PAEs. Graphene is a new type of carbon nanomaterial with one

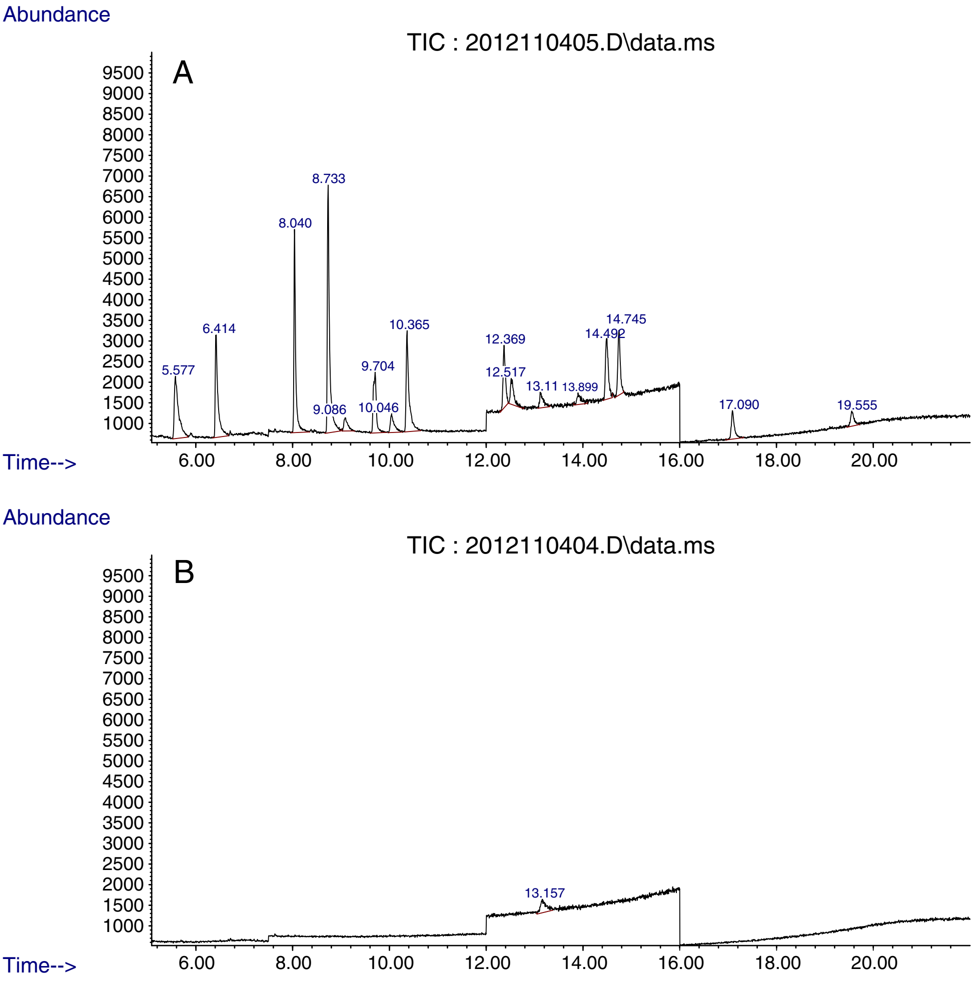

**Fig. 1.** The total ion chromatograms of 15 PAEs and TPP obtained by GC–MS analysis. A) The total ion chromatograms of 15 PAEs and TPP. B) The solvent blank with TPP.