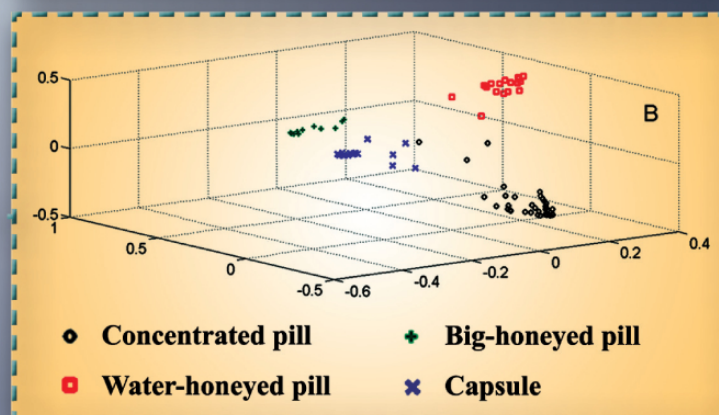
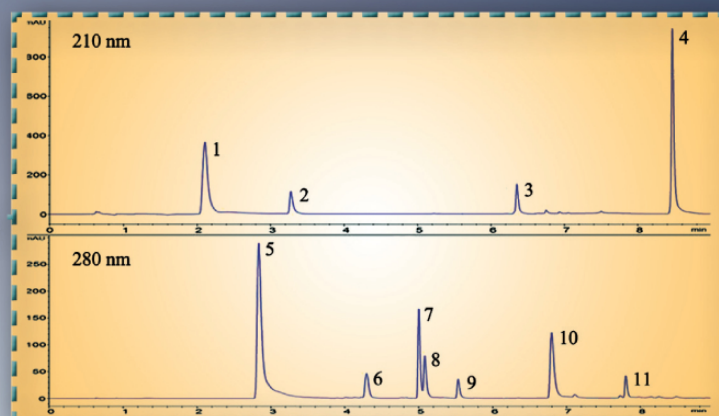


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## Research Article

# Octyl-modified magnetic graphene as a sorbent for the extraction and simultaneous determination of fragrance allergens, musks, and phthalates in aqueous samples by gas chromatography with mass spectrometry

An effective, simple, and low-cost sample preparation method based on dispersive SPE followed by GC with MS is developed for the multianalyte determination of fragrance allergens, musks, and phthalates, at sub-ppb levels. The extraction procedure is based on a novel magnetic graphene sorbent, which is functionalized with octylamine, taking advantage of the functionalization's hydrophobic properties and  $\pi$ - $\pi$  interactions with the analytes. Two alkyl amines, the octylamine and octadecylamine are studied to introduce alkyl chains in the basal plane of graphene. Magnetic graphene-octadecylamine is proved to be highly hydrophobic to such a degree that is hard to disperse in the bulk aqueous matrixes. Because of this behavior, its extraction efficiency for the target analytes is low. The synthesis and applicability of the magnetic graphene-octylamine as more favored sorbent are optimized in terms of the most determining experimental conditions. The detection and quantification limits, which are calculated based on S/N ratio of 3 and 10, respectively, ranged from 0.29 to 3.2 ng L<sup>-1</sup> and from 0.89 to 9.6, respectively. The dispersive SPE is successfully applied to routine analysis for the determination of the target analytes in samples from municipal treatment plant of Ioannina (Greece), from Pamvotis Lake and baby bathwater. The reproducibility of the spiked biological treatment plant water sample is evaluated and the relative standard deviation values range between 2.1 and 9.4%.

**Keywords:** Allergens / GC-MS / Magnetic octyl-graphene / Musks / Phthalates  
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Additional supporting information may be found in the online version of this article at the publisher's web-site

## 1 Introduction

Nowadays, a wide variety of chemical compounds, either natural or synthetic are used in commercially available products. Among them, fragrance allergens, musks, and phthalates are three major groups with numerous applications in commercial cosmetics, household products etc. [1–3]. According to the International Fragrance Association, fragrances are compounds with odorous properties, which confer a pleasant scent to a product, mask the smell of malodorous materials, or in some cases, they are used for mood benefits, stress, or pain relief [http://www.ifraorg.org]. Thus, compounds like limonene, linalool, and citral are

widely used, since they inspire feelings of welfare and are directly correlated to the quality of products [4]. Nonetheless, studies have proven that some of the active ingredients of fragrances can cause severe allergic reactions to people, including a variety of symptoms such as skin sensitivity, rashes, dermatitis, coughing, asthma attacks, migraine, etc. [5, 6]. Synthetic musks can also be found in personal care products, detergents, commercial cosmetics, and many other consumer products, in addition to fragrance allergens, [1]. Polycyclic musks is a class of synthetic musks which are extensively used in industry for the scent enhancement of products and they have replaced the naturally derived musks due to their significantly lower cost [7]. However, it was not until recently that studies rose concern over their impact on human health [8]. Endocrine disrupting effects of musk compounds like galaxolide and tonalide have been proved in vitro [9] while another investigation indicated that galaxolide can inhibit cellular detoxification processes [10]. As far as phthalates are concerned, they are nonhalogenated esters of phthalic acid

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and are widely used in various industrial and consumer-oriented applications [11]. They are also used as ingredients in inks, adhesives, lacquers, sealing, and packing materials, materials for treating surfaces, solvents, and fixing agents in fragrances, as well as additives in cosmetics [2]. Some of them, like dibutyl phthalate and diethylhexyl phthalate have been reported to be carcinogenic and estrogenic [12]. Considering the widespread use of all the above mentioned chemical groups, relatively large amounts of these compounds are released into the environment posing a threat to living organisms and ultimately to human health. Moreover, since some of these compounds have been restricted by the International Fragrance Association and the Scientific Committee on Cosmetic Products and Non-Food Products [13, 14] due to their harmful effects, their determination in aquatic samples is deemed critical [15, 16]. To date, several studies have been developed for the extraction, separation, and determination of fragrance allergens, musks, or phthalates, at  $\mu\text{g L}^{-1}$  levels in the aquatic environment. Extraction techniques, applied so far, include SPE [17, 18], SPME [16, 19], stir-bar sorptive extraction [2, 20], LLE [21], QuEChERS [22, 23], and others [3, 24–28]. The separation and determination are achieved by a variety of analytical methods including large-volume-injection GC–MS [26, 29], thermal desorption GC–MS [21], etc. [30–32].

Concerning SPE, several different materials are continuously being introduced as sorbents for such purposes. Among them, graphene (GR) and graphene-based nanomaterials are new sorbents, the applications of which have been documented and reviewed [33–35].

Integrating iron-based magnetic nanomaterials and GR into nanocomposites has recently become a hot topic of research due to their enhanced properties such as good dispersibility and rapid separation under an external magnetic field [36, 37]. Moreover, in comparison to single GR, the composite material has improved properties in microextraction as both the hydrophobic graphene surface and iron participate in the adsorption of molecules [38]. These features make magnetic GR favorable in determining analytes with a wide range of polarity. This can also result from its wettability in water due to the hydrophilicity of iron oxides [39].

Recently, our group has managed to prepare magnetic graphene nanocomposites and graphene-coated cotton fibers for the extraction of several pollutants, such as PAHs, PCBs, phenolic endocrine disruptors, haloacetic acids, and pesticides from aqueous matrices [40–42]. In the present study, a new, low-cost dispersive SPE method is developed based on magnetic GR, which has previously been modified with octylamine, for the simultaneous extraction and determination of fragrance allergens, musks and phthalates in aqueous samples by GC–MS, at sub-ppb levels. The magnetic graphene functionalized with octylamine is used as a sorbent capitalizing on the properties of  $\pi$ -conjugated electron system of GR, the hydrophobic character of octyl chain and the improved dispersibility.

## 2 Materials and methods

### 2.1 Reagents and solutions

Geraniol ( $\geq 96\%$ ), coumarin (99%), (*R*)-(+)-limonene (97%), *cis/trans*-isoeugenol (98%), amyl cinnamyl alcohol (95%), benzyl cinnamate (99%), ionone ( $\geq 90\%$ ), hexyl cinnamaldehyde ( $\geq 95\%$ ), hydroxycitronellal ( $\geq 95\%$ ), dibutyl phthalate (99%), diethyl phthalate (99.5%), dicyclohexyl phthalate (99%), and graphite powder (99.9%) were purchased from Aldrich (Sigma–Aldrich–Hellas, Greece). Eugenol (99%), *cis/trans*-citral (95%), linalool (97%), benzyl alcohol (99%), and cinnamyl alcohol (98%) were purchased from Merck (Darmstadt, Germany). The musks cashmeran, celestolide, phantolide, galaxolide, and tonalide ( $3.0 \text{ mg mL}^{-1}$ ) were purchased from LGC Promochem (Promochem, Wesel, Germany). The *n*-docosane (99%), used as internal standard (I.S.) was purchased from Alfa Aesar (Karlsruhe, Germany). Phosphoric acid 85% w/w, hydrochloric acid 37% w/w, ammonia solution 25% w/w, sulfuric acid 96% w/w, and  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  ( $\geq 99\%$ ) were purchased from Aldrich (Sigma–Aldrich–Hellas, Greece). Octylamine for synthesis  $\sim 100\%$  and  $\text{FeCl}_3$  (97%) were purchased from Merck (Schuchardt, Germany). All solvents were at least of analytical grade.

Individual stock standard solutions of each fragrance allergen were prepared in acetone, at a concentration range  $1.0$ – $1.5 \text{ mg mL}^{-1}$ . Individual stock solutions were also prepared for musks and phthalates in acetone, at concentrations of  $3.0 \text{ mg mL}^{-1}$  and  $1.0 \text{ mg mL}^{-1}$ , respectively. Mixtures were prepared in acetone after proper dilutions. All solutions were stored in glass vials, at  $-18^\circ\text{C}$ .

### 2.2 Instrumentation

A Shimadzu GC–17A gas chromatograph (Kyoto, Japan), coupled to a Shimadzu QP 5000 mass spectrometer, equipped with a split/split less injector and a DB5-MS column ( $30 \text{ m} \times 0.25 \text{ mm id}$ ,  $0.25 \mu\text{m}$  film thickness, Agilent J&W, Agilent Technologies, CA, USA) was used for the chromatographic analysis of the targeted compounds. Chromatographic conditions are given in the Supporting Information.

Elemental analysis was performed on a Vario Macro CNS (Elemental Analyzen systeme, Hanau, Germany). Ultrasonication was performed on an Elmasonic S40 unit, purchased from Elma, Germany. To characterize the functionalized GR and ensure proper fabrication, FTIR spectra were recorded on a Spectrum Two FTIR using an attenuated total reflectance accessory (PerkinElmer, MA, USA).

### 2.3 Synthesis of graphene oxide (GO)

Graphite powder was oxidized using a mixture of acids and  $\text{KMnO}_4$ , as described elsewhere [40]. Details are provided in the Supporting Information.

## 2.4 Synthesis of magnetic graphene oxide and graphene composites

Magnetic GO and GR nanoparticles were synthesized according to a previously reported method by the in situ chemical co-precipitation of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  (molar ratio  $\text{Fe}^{3+}/\text{Fe}^{2+}$  2:1) in an alkaline solution, in the presence of GO [43]. Details are given in the Supporting Information.

## 2.5 Synthesis of magnetic octyl-GR (magnetic GR- $\text{C}_8$ )

A quantity of magnetic GO (200 mg) was dispersed in 10 mL of DDW using ultrasonication at 140 Watt, for 10 min. Then, it was added to a solution of 600 mg octylamine (or octadecylamine) in 40 mL of warm ethanol ( $\sim 30^\circ\text{C}$ ). The whole mixture was refluxed at  $80^\circ\text{C}$  under stirring, for 24 h. A magnet was used to isolate the material, which was subsequently washed with a hot mixture of DDW: ethanol (1:1) three times, followed by three more washings with ethanol. The sorbent was finally dried at  $70^\circ\text{C}$ , for 24 h, ground in an agate mortar, and stored at room temperature.

## 2.6 Dispersive SPE procedure

The extraction procedure was carried out as follows: first, 30 mg of magnetic GR- $\text{C}_8$  sorbent was rinsed successively with 1.5 mL of methanol for activation and 3 mL of water and then it was added into 100 mL aqueous sample solution. The mixture was stirred for 15 min using a magnetic stirrer to trap the analytes. Subsequently, the magnetic nanoparticles were isolated from the mixture with a magnet positioned at the bottom of the glass beaker while the supernatant was poured away. The nanoparticles, attached to the magnetic bar, were removed by washing with DDW. The isolated particles were dried under a gentle stream of nitrogen. Target analytes were desorbed after the addition of 100  $\mu\text{L}$  of a mixture of ethyl acetate: methyl-*tert*-butyl ether (1:1) containing 120  $\text{ng mL}^{-1}$  of *n*-docosane solution (I.S.) with the aid of ultrasonication, for 2 min. The procedure was repeated twice and the eluates were combined and evaporated to a final volume of 100  $\mu\text{L}$ , after the addition of three drops of toluene to prevent possible losses of analytes during evaporation. Finally, 1  $\mu\text{L}$  of the final solution was injected into the GC-MS system. The I.S. was used to compensate for variations in evaporation, final volume of eluate, and injection volumes.

# 3 Results and discussion

## 3.1 Preliminary evaluation of the material

A simple approach for preparing magnetic GR- $\text{C}_8$  sorbent is proposed by chemical deposition of iron oxide nanoparticles onto GO, followed by chemical grafting of alkylamine

on magnetic GO sheets through the nucleophilic substitution reaction of amine groups with epoxy groups, under refluxing and stirring, at  $80^\circ\text{C}$ , for 24 h. The synthetic procedure for magnetic GR- $\text{C}_8$  sorbent is schematically illustrated in Fig. 1. Two alkyl amines, the octylamine and octadecylamine were initially studied to introduce alkyl chains in the basal plane of GO. The chosen functionalization was undertaken in order to improve the extraction efficiency for the target analytes. Magnetic GR- $\text{C}_{18}$  was proved to be highly hydrophobic to such a degree that it was hard to disperse in the bulk aqueous matrices even after an exhaustive preconditioning with methanol. Therefore, the low extraction efficiencies observed for the target analytes were attributed to the low dispersibility of the sorbent in water.

Focusing on the synthesis of magnetic GR- $\text{C}_8$  sorbent, subsequently, the reflux time needed for the covalent attachment of octylamine on the surface of magnetic GR was studied. Elemental analysis of the resulting materials, refluxed for different time periods (6, 12, 24, 48, 72 and 90 h) indicated that no significant differences (at 95% confidence level) among preparations were noticed with respect to the percentage of carbon loading while nitrogen diminished (See Supporting Information Table 1).

Consequently, the magnetic GR- $\text{C}_8$  based composites were evaluated in terms of their extraction efficiency in spiked aqueous samples. It was noticed that the material arising from a refluxing process of 12 h was more efficient by almost 10% than that of 6 h, on the basis of the total chromatographic peak area. The material refluxed for 24 h, demonstrated an increase in the total chromatographic peak area of around 40%, compared to 6 h refluxing. No further increase was noticed for refluxing process of 48, 72, and 90 h. For this reason, a refluxing of 24 h was selected as the optimum for the functionalization of magnetic-GR. The resulting material can easily be dispersed in water after activation with 1.5 mL of water-miscible organic solvent (methanol).

## 3.2 Characterization of magnetic GR- $\text{C}_8$

FTIR spectroscopy was employed to ensure successful chemical synthesis and modification of the materials (Supporting Information Fig. S1). Characteristic bands appear for aromatic C–C groups ( $1621\text{ cm}^{-1}$ ) as well as for C=O ( $1733\text{ cm}^{-1}$ ), epoxy C–O ( $1220\text{ cm}^{-1}$ ) and alkoxy C–O ( $1045\text{ cm}^{-1}$ ) chemical groups, which evidently confirm the successful oxidation of graphite. After the chemical functionalization, two weak peaks at  $2929$  and  $2857\text{ cm}^{-1}$  reveal the asymmetric and the symmetric extension vibration of  $\text{CH}_2$  respectively, in the  $-(\text{CH}_2)_7\text{CH}_3$  group. Moreover, a new peak appears at  $1574\text{ cm}^{-1}$  (N–H stretching vibration) indicating the formation of  $-\text{C}-\text{NH}-\text{C}-$  due to the reaction between the epoxide group and the amine group. Finally, the presence of a strong band at  $554\text{ cm}^{-1}$  represents the stretching vibration of  $\text{Fe}-\text{O}-\text{Fe}$  while the dramatic reduction of the bands of oxygen-functional groups mentioned above, signifies an

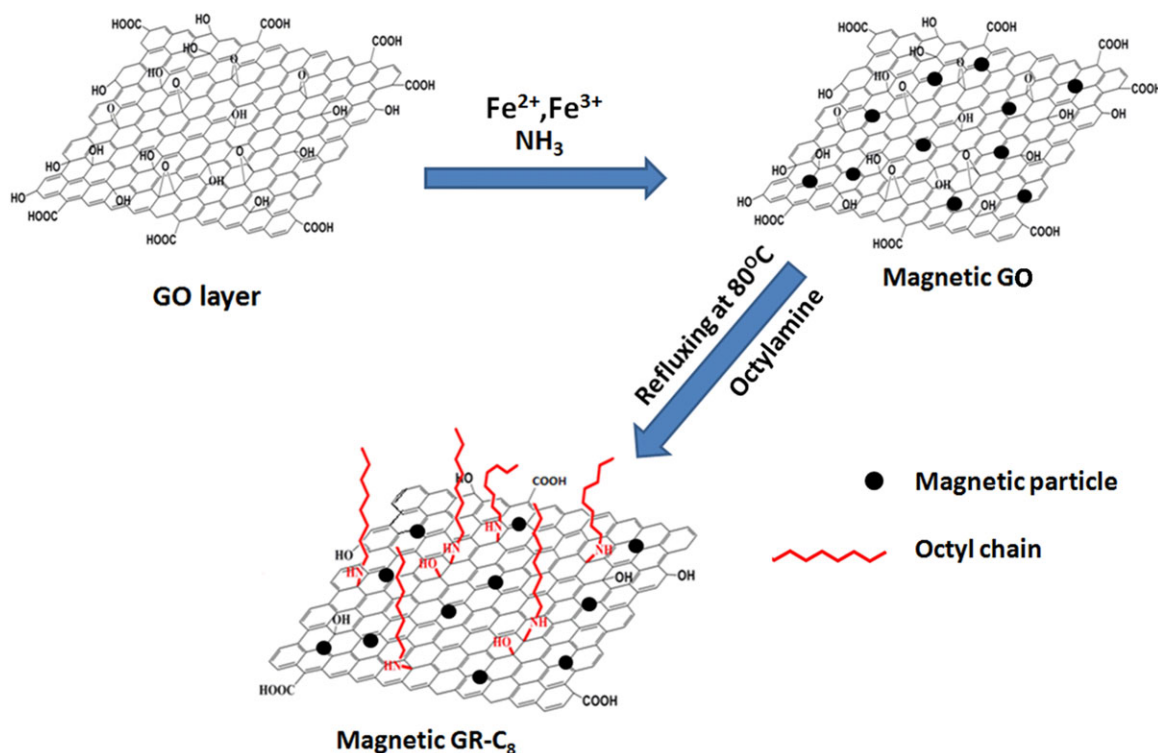


Figure 1. Synthetic route of magnetic-GR-C<sub>8</sub>.

extended reduction of graphene oxide during functionalization. Earlier study has reported that chemically prepared GO consisting of epoxy groups in its basal plane, undergoes simultaneous nucleophilic substitution reaction with  $-\text{NH}_2$  groups of alkylamines and reduction of oxygen groups [44]. Also, this study has shown that further reduction of the magnetic GR-C<sub>8</sub> with hydrazine scarcely reduces the peaks of oxygen-containing chemical groups. This seems to have been achieved with octylamine in our study, after refluxing for 24 h.

### 3.3 Optimization of the proposed method

The fragrance allergens, musks, and phthalates studied along with some of their physicochemical properties are listed in Supporting Information Table S2. The optimization was carried out by extracting a mixture of all fragrance allergens, musks, and phthalate esters under study, at concentrations in the range 100–200 ng L<sup>-1</sup>, unless otherwise stated. Unless striking differences were observed among individual analytes within classes of compounds during optimization, the total chromatographic area for each class was considered to be the criterion of extraction efficiency.

The pH of the sample, in a wide range of pH values (i.e. 2.5–9.0) was proved to have an insignificant bearing on the extraction yield because all the target analytes are nonionic. As for temperature, extractions were performed at 20, 30, and 40°C and results indicated that the higher the temper-

ature the lower the total chromatographic area. Specifically, temperatures of 30 and 40°C showed a decrease in the total response by 40 and 80%, respectively, as compared to that at 20°C. This could be explained by the facts that some of the analytes are volatile and adsorption process is exothermic and rising the temperature inhibits the transfer of the analytes to the sorbent. Thus, all experiments were conducted at neutral pH and room temperature. Several other parameters, including sorbent amount, sample volume, stirring rate and time of extraction, ultrasonication time, salting out effect, and desorption conditions were found to be more influential to the analytical signal and were examined in order to achieve the optimum extraction efficiency of the target analytes.

#### 3.3.1 Effect of the amount of adsorbent and sample volume

To achieve enhanced extraction and recoveries regarding the targeted analytes, the amount of the magnetic GR-C<sub>8</sub> sorbent was studied in a range from 10 to 40 mg. The total peak areas of the analytes increased significantly, when the sorbent amount increased to 30 mg. The overall total areas remained unchanged by further increasing the amount of the adsorbent indicating that the enrichment ability of magnetic GR-C<sub>8</sub>, as sorbent, reached a plateau. Considering the adsorption ability of the composite material, 30 mg of the sorbent was employed in the study.

Sample volume was studied by varying the volume of the aqueous solution from 20 to 150 mL, at a constant spiking

level in the range 100–200 ng L<sup>-1</sup> for each of the 22 analytes. From the results shown in Supporting Information Fig. S2, it is found that the maximum total area for fragrance allergens and phthalates was obtained at 150 mL while for musks the maximum total areas were alike for 100 and 150 mL. These results indicate that the proposed composite magnetic nanomaterials could be used for relatively large volumes of water. Because of the difficulties encountered with the quantitative collection of the sorbent when volumes higher than 100 mL are employed, that volume was chosen as the optimum. The sorbent amount was re-evaluated by changing the sample volume from 20–100 mL and the absorption ability of 30 mg of magnetic GR-C<sub>8</sub> was invariably the same at constant spiked amounts of the analytes in the aqueous samples.

### 3.3.2 Effect of stirring time and stirring rate

The effect of stirring time was studied in time intervals of 15 min, at stirring rates of 300, 600, and 900 rpm. Generally, an increase in the stirring rate results in accelerated mass transfer of the analytes to the solid sorbent. However, from Supporting Information Fig. S3, it is concluded that as the stirring rate rises, especially at elevated stirring times, the total area of fragrance allergens diminishes. This could be explained by their failure to interact effectively with the sorbing material, under the stated conditions. As regards musks and phthalates, the total area is not dramatically affected by the combinations of stirring time and rate. To avoid possible loss of analytes and to save time, a 15-min stirring time at a stirring rate of 600 rpm was chosen as optimum.

### 3.3.3 Effect of ionic strength

The presence of a salt can either enhance the salting-out effect or decrease the extraction capability and diffusion coefficient through increasing the viscosity of the solution [45]. Different concentrations of Na<sub>2</sub>SO<sub>4</sub> and NaCl ranging from 0 to 5% w/v were used to examine the effect of ionic strength on the extraction yield. The addition of 2% w/v Na<sub>2</sub>SO<sub>4</sub> was found to be the optimum since it increased the total area by 40% for allergens and 30% for musks and phthalates in comparison to the absence of salt. The addition of NaCl was proved to be less efficient than Na<sub>2</sub>SO<sub>4</sub>. This could be explained by the fact that NaCl and Na<sub>2</sub>SO<sub>4</sub> exhibit different ionic strength. (Supporting Information Fig. S4 represents graphically, the total chromatographic areas of fragrance allergens, musks, and phthalate esters after their chromatographic analysis).

### 3.3.4 Elution procedure

The elution efficiency of six organic eluents, which can directly be injected into a gas chromatograph and cover a wide range of polarity, was studied. The eluents tested were: acetone, *n*-hexane, methyl-*tert*-butyl ether, *n*-hexane/ethyl acetate (1:1), ethyl acetate, and ethyl acetate/methyl-*tert*-butyl ether (1:1). Supporting Information Fig. S5 demonstrates that

among the studied solvent systems acetone and *n*-hexane exhibited the lowest elution yields, expressed as the total chromatographic area for all analytes. The rest of the studied eluents showed practically the same total chromatographic areas for musks and phthalates. As for fragrance allergens, the elution efficiency of ethyl acetate/methyl-*tert*-butyl ether (1:1) was superior to the other eluents. A mixture of ethyl acetate/methyl-*tert*-butyl ether (1:1) was chosen as the optimum eluent considering the polarity for the targeted analytes and the ability of the eluent to sufficiently disrupt the interactions between the analytes and the sorbent. In an effort to minimize the volume of organic eluent and at the same time increase the preconcentration factor, the volume of the eluent was also optimized. Three portions of 100 µL of ethyl acetate/methyl-*tert*-butyl ether (1:1) followed by ultrasonication, ensured complete immersion of the sorbent during elution and proper desorption. The combined eluates (~300 µL) were condensed under a gentle stream of nitrogen, up to a final volume of 100 µL to increase the preconcentration factor. Further increase in the eluent volume (greater than 300 µL) followed by condensation to 100 µL did not heighten the total chromatographic areas.

Ultrasonication was applied to the elution step, to desorb more efficiently the analytes (Supporting Information Fig. S6 shows the total chromatographic area in relation to the ultrasonication time, at the elution step). For allergens, the highest total chromatographic area was achieved with 2 min of ultrasonication, which was twice as high as that without ultrasonication or ultrasonication for 1 min. Further increase in the ultrasonication time, resulted in insignificant changes of the total area, for all three classes of analytes.

## 3.4 Analytical characteristics

A series of experiments were conducted to determine the quality parameters of the method such as the linear range, reproducibility, LODs, and LOQs. The calibration plots were drawn by analyzing 100 mL of DDW, spiked with the standard solutions of all analytes, at five concentration levels, from the LOQs up to the upper concentration of each calibration curve (a typical chromatogram is given in Supporting Information Fig. S7). The response ratios (analyte-to-I.S. chromatographic areas) versus the concentrations of analytes (in ng L<sup>-1</sup>) were considered. All the results, along with the fragment ions for quantification and qualification are listed in Table 1. The coefficients of determination (*R*<sup>2</sup>) of these curves (analyte-to-I.S. versus concentration) were above 0.9910. The detection and quantification limits, which were calculated based on *S/N* ≥ 3 and 10, respectively, ranged from 0.29 to 3.2 ng L<sup>-1</sup> and from 0.89 to 9.6 ng L<sup>-1</sup>, respectively.

## 3.5 Analysis of real samples

The adsorbent was successfully applied as a dispersive SPE material for quantitative applications. Real water samples

**Table 1.** Analytical parameters for fragrance allergens, musks, and phthalates determined by GC-MS (SIM), after extraction with magnetic GR-C<sub>8</sub>

| Compound               | t <sub>R</sub> (min) | Ions (m/z) <sup>a</sup> | Coefficient of determination (R <sup>2</sup> ) | LOD <sup>b</sup> (ngL <sup>-1</sup> ) | Linear range (ngL <sup>-1</sup> ) |
|------------------------|----------------------|-------------------------|------------------------------------------------|---------------------------------------|-----------------------------------|
| Fragrance allergens    |                      |                         |                                                |                                       |                                   |
| Limonene               | 13.6                 | <b>68</b> , 93, 121     | 0.9960                                         | 0.57                                  | 1.7–450                           |
| Benzyl alcohol         | 13.8                 | <b>79</b> , 107, 108    | 0.9910                                         | 0.71                                  | 2.1–695                           |
| Linalool               | 16.4                 | <b>71</b> , 80, 93      | 0.9960                                         | 1.2                                   | 3.6–390                           |
| Citral                 | 21.7                 | <b>69</b> , 94, 109     | 0.9940                                         | 1.5                                   | 4.5–340                           |
| Geraniol               | 22.1                 | <b>69</b> , 93, 111     | 0.9970                                         | 2.7                                   | 8.3–620                           |
| Hydroxycitronellal     | 23.4                 | 59, <b>71</b> , 96      | 0.9940                                         | 2.9                                   | 9.0–320                           |
| Cinnamyl alcohol       | 24.2                 | 78, <b>92</b> , 134     | 0.9960                                         | 3.2                                   | 9.6–530                           |
| Eugenol                | 25.8                 | 103, 149, <b>164</b>    | 0.9910                                         | 2.2                                   | 6.7–219                           |
| Ionone                 | 28.3                 | 93, <b>121</b> , 136    | 0.9940                                         | 0.84                                  | 2.5–219                           |
| Coumarin               | 28.8                 | 90, <b>118</b> , 146    | 0.9940                                         | 1.2                                   | 3.5–550                           |
| Isoeugenol             | 29.1                 | 91, 103, <b>164</b>     | 0.9980                                         | 3.2                                   | 9.6–240                           |
| Amyl Cinnamyl alcohol  | 36.5                 | <b>91</b> , 133, 115    | 0.9950                                         | 2.8                                   | 8.5–255                           |
| Hexyl cinnamaldehyde   | 38.3                 | 117, <b>129</b> , 216   | 0.9973                                         | 2.5                                   | 7.7–550                           |
| Benzyl cinnamate       | 45.6                 | <b>91</b> , 131, 192    | 0.9992                                         | 0.90                                  | 2.7–550                           |
| Musks                  |                      |                         |                                                |                                       |                                   |
| Cashmeran              | 30.8                 | 191, <b>206</b> , 163   | 0.9960                                         | 1.4                                   | 4.3–750                           |
| Celestolide            | 37.2                 | <b>229</b> , 244, 173   | 0.9980                                         | 0.75                                  | 2.2–250                           |
| Phantolide             | 38.4                 | 187, <b>229</b> , 244   | 0.9990                                         | 0.76                                  | 2.3–750                           |
| Galaxolide             | 41.0                 | 213, <b>243</b> , 258   | 0.9990                                         | 0.83                                  | 2.5–750                           |
| Tonalide               | 41.2                 | 187, <b>243</b> , 258   | 0.9990                                         | 0.64                                  | 1.9–750                           |
| Phthalate esters       |                      |                         |                                                |                                       |                                   |
| Diethyl phthalate      | 33.5                 | <b>149</b> , 177        | 0.9910                                         | 0.79                                  | 2.4–250                           |
| Dibutyl phthalate      | 43.1                 | <b>149</b> , 205        | 0.9990                                         | 0.29                                  | 0.89–750                          |
| Dicyclohexyl phthalate | 50.8                 | <b>149</b> , 167, 279   | 0.9920                                         | 0.63                                  | 1.9–250                           |

<sup>a</sup>Quantification ions are in bold. The rest of the ions are qualifiers which are used for identification purposes.

<sup>b</sup>LOD, Limit of detection. Calculated based on S/N ratio  $\geq 3$ .

The LOQs, calculated based on S/N ratio  $\geq 10$ , is the lower value of the linear range for each analyte.

**Table 2.** Concentrations of fragrance allergens, musks, and phthalates in real samples using the magnetic GR-C<sub>8</sub> sorbent

| Sample compound        | Baby bath water   | Effluent of municipal treatment plant<br>Concentration ( $\mu\text{g L}^{-1}$ ) | Lake water        |
|------------------------|-------------------|---------------------------------------------------------------------------------|-------------------|
| Limonene               | nd                | 0.17 $\pm$ 0.01                                                                 | nd                |
| Linalool               | 0.095 $\pm$ 0.004 | 0.017 $\pm$ 0.003                                                               | 0.22 $\pm$ 0.01   |
| Eugenol                | 0.70 $\pm$ 0.02   | nd                                                                              | nd                |
| Hexylcinnamaldehyde    | nd                | 0.17 $\pm$ 0.02                                                                 | nd                |
| Galaxolide             | nd                | 6.00 $\pm$ 0.09                                                                 | 0.013 $\pm$ 0.003 |
| Tonalide               | nd                | 0.33 $\pm$ 0.02                                                                 | nd                |
| Dibutyl phthalate      | 2.86 $\pm$ 0.06   | 11.2 $\pm$ 0.3                                                                  | 3.71 $\pm$ 0.05   |
| Dicyclohexyl phthalate | 0.59 $\pm$ 0.01   | 0.93 $\pm$ 0.02                                                                 | 0.48 $\pm$ 0.01   |

nd, nondetectable.

from Pamvotis Lake, municipal treatment plant of Ioannina as well as baby bathwater were collected, filtered through a paper filter, and analyzed. The results shown in Table 2 (typical chromatograms are given in Supporting Information Figs. S7 and S8 ) demonstrate their occurrence in aquatic environment. A real water sample from municipal treatment plant was spiked with fragrance allergens, musks, and phthalate esters, at concentrations equal to the LOQs and ten times the LOQs. The spiked sample was analyzed so as to calculate the recoveries of the method for the 22 an-

alytes. Recoveries were calculated as the ratio between the detected amount and the spiked amount ( $\times 100$ ). Supporting Information Table S3 lists the recoveries of the analytes, the repeatability (three replicates on the same day) and reproducibility (three consecutive days) RSDs. All the recoveries were in the range of 83–105%. The high recoveries in relation to the low final volume of the desorption solvent ensure high preconcentration efficiency. The reproducibility of the extraction of spiked municipal treatment plant water samples was evaluated and the RSD values (expressing the

repeatability and reproducibility) ranged between 2.1 and 9.4%.

### 3.6 Comparison between magnetic GR-C<sub>8</sub> nanoparticles and magnetic GR: Appraisal of the sorbent

To highlight the need for functionalization of the magnetic graphene with octyl-chain toward extracting the analytes, the procedure detailed above was also applied without prior functionalization of magnetic GR with the octyl chain. The recovery yields compared to those with magnetic GR-C<sub>8</sub>, on average, were 50% lower for musks and 80 and 70% for phthalates and fragrance allergens, respectively. Even lower was the extraction capability of the more hydrophilic magnetic GO. The results can be explained taking into consideration the chemical properties of the analytes and the sorbents. From the  $\text{Log}K_{\text{o/w}}$  (shown in Supporting Information Table S2) it is clear that most of the target analytes are hydrophobic with the exception of certain fragrance allergens, like benzyl alcohol, linalool, citral, hydroxycitronelal, cinammyl alcohol, and coumarin, which are rather hydrophilic ( $\text{Log}K_{\text{o/w}} < 2$ ). Cinammyl alcohol justifiably shows the highest recovery among the five previously mentioned analytes (see Table 3), as it has the highest  $\text{Log}K_{\text{o/w}}$  (stronger hydrophobic interactions) and its chemical structure facilitates the formation of  $\pi$ - $\pi$  interactions. Coumarin and benzyl alcohol have lower  $\text{Log}K_{\text{o/w}}$  than linalool but citral and hydroxycitronelal are extracted in higher yield owing to the presence of benzene rings in their structure (stronger  $\pi$ - $\pi$  interactions). It is known that GR offers strong affinity for carbon-based ring structures and small, medium-sized molecules due to its large delocalized  $\pi$ - $\pi$  electron system. Therefore, the extraction of the target analytes takes place by  $\pi$ - $\pi$  and hydrophobic interactions with the sorbent. This feature combined with the improved dispersibility and the adsorption capability make magnetic GR-C<sub>8</sub> nanoparticles ideal for extraction purposes. Finally, a comparison of the analytical performance of the proposed method with other analytical approaches for the determination of fragrance allergens, musks, and phthalates (Supporting Information Table 4) showed comparable figures of merit or even better in some cases.

### 3.7 Reusability

To investigate the reusability of the sorbent, portions of magnetic GR-C<sub>8</sub> were reused in dispersive SPE, for next samples, after thorough cleaning with a mixture of ethyl acetate : methyl-tert-butyl ether (1:1) to remove target analytes remnants. The magnetic sorbent was regenerated by washing with methanol and DDW. After two successive cycles of reuse, the recoveries of the analytes remained constant indicating good stability and reusability. A change in the texture of sorbent became visible in the fourth cycle of reuse.

## 4 Concluding remarks

In recent years, the chemical functionalization of GR has attracted tremendous attention due to the unique applications of the resulting materials. In this study, magnetic GR-C<sub>8</sub> has been synthesized and superior performance was achieved in the dispersive SPE of fragrance allergens, musks, and phthalic acid esters relatively to magnetic GR. The employment of magnetic GR, functionalized with octylamine as sorbent, capitalized on the properties of  $\pi$ -conjugated electron system of GR, the hydrophobic character of octyl chain, and the improved dispersibility due to the magnetic iron oxides. Overall, the average recoveries of the analytes were between 83 and 105% and consistent RSDs were <9.4%. The validated dispersive SPE was successfully applied for routine analysis for the determination of the target analytes in aqueous samples demonstrating the method suitability for a variety of aqueous matrices. This simple and rapid extraction method provides good repeatability and reproducibility range, high extraction efficiency and the total time needed is short. On balance, most of the intrinsic characteristics of the proposed method are comparable or even better than those of other approaches in terms of volume of sample needed, linear ranges, LOQs, recoveries, and time needed for the performance.

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