



# Magnetic headspace adsorptive extraction of chlorobenzenes prior to thermal desorption gas chromatography-mass spectrometry



Lorena Vidal <sup>a,\*</sup>, Mazaher Ahmadi <sup>b</sup>, Elena Fernández <sup>a</sup>, Tayyebeh Madrakian <sup>b</sup>, Antonio Canals <sup>a,\*\*</sup>

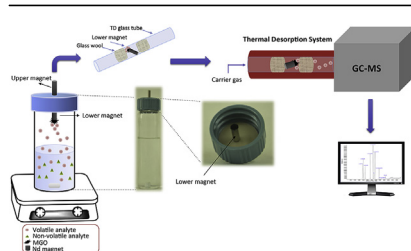
<sup>a</sup> Department of Analytical Chemistry, Nutrition and Food Sciences and University Institute of Materials, University of Alicante, P.O. Box 99, E-03080, Alicante, Spain

<sup>b</sup> Faculty of Chemistry, Bu-Ali Sina University, Hamedan, Iran

## HIGHLIGHTS

- A new extraction technique named Magnetic Headspace Adsorptive Extraction is presented.
- Graphene oxide/iron oxide composite deposited on a neodymium magnet as sorbent.
- Sorbent of low cost, rapid and simple synthesis, easy manipulation and portability options.
- Fast and efficient extraction and sensitive determination of chlorobenzenes in water samples.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 27 October 2016

Received in revised form

29 March 2017

Accepted 1 April 2017

Available online 10 April 2017

### Keywords:

Solid-phase microextraction  
Chlorobenzenes  
Magnetic graphene oxide  
Magnetic headspace adsorptive extraction  
Gas chromatography-mass spectrometry  
Water samples

## ABSTRACT

This study presents a new, user-friendly, cost-effective and portable headspace solid-phase extraction technique based on graphene oxide decorated with iron oxide magnetic nanoparticles as sorbent, located on one end of a small neodymium magnet. Hence, the new headspace solid-phase extraction technique has been called Magnetic Headspace Adsorptive Extraction (Mag-HSAE). In order to assess Mag-HSAE technique applicability to model analytes, some chlorobenzenes were extracted from water samples prior to gas chromatography-mass spectrometry determination. A multivariate approach was employed to optimize the experimental parameters affecting Mag-HSAE. The method was evaluated under optimized extraction conditions (i.e., sample volume, 20 mL; extraction time, 30 min; sorbent amount, 10 mg; stirring speed, 1500 rpm, and ionic strength, non-significant), obtaining a linear response from 0.5 to 100 ng L<sup>-1</sup> for 1,3-DCB, 1,4-DCB, 1,2-DCB, 1,3,5-TCB, 1,2,4-TCB and 1,2,3-TCB; from 0.5 to 75 ng L<sup>-1</sup> for 1,2,4,5-TeCB, and PeCB; and from 1 to 75 ng L<sup>-1</sup> for 1,2,3,4-TeCB. The repeatability of the proposed method was evaluated at 10 ng L<sup>-1</sup> and 50 ng L<sup>-1</sup> spiking levels, and coefficients of variation ranged between 1.5 and 9.5% (n = 5). Limits of detection values were found between 93 and 301 pg L<sup>-1</sup>. Finally, tap, mineral and effluent water were selected as real water samples to assess method applicability. Relative recoveries varied between 86 and 110% showing negligible matrix effects.

© 2017 Elsevier B.V. All rights reserved.

## 1. Introduction

Analytical chemists have always benefited from the availability of numerous instruments such as chromatographs, spectrometers,

\* Corresponding author.

\*\* Corresponding author.

E-mail addresses: [lorena.vidal@ua.es](mailto:lorena.vidal@ua.es) (L. Vidal), [a.canals@ua.es](mailto:a.canals@ua.es) (A. Canals).

and microscopes, as well as sensors and microdevices. However, these instruments cannot fully satisfy analytical chemists' need to perform trace analysis of analytes of interest in complex matrices. In this respect, one or more pretreatment steps are usually necessary to improve instrument sensitivity and selectivity, referred to as "Sample Preparation", whose goal is enrichment, clean-up, and signal enhancement [1]. Sample preparation is important in all aspects of chemical, biological, materials, and surface analysis, thus researchers are always looking for more advanced techniques. Notable among recent developments are faster, more economical, more efficient and greener extraction methods like microextraction techniques. In addition, advanced microfabrication techniques have resulted in the development of miniaturized chemical analysis systems, including microscale sample preparation on a chip [2].

Solid-phase microextraction (SPME) is a rapid, solventless and environmentally-friendly extraction technique for the isolation and preconcentration of solutes from liquid, solid or gaseous matrices. Nowadays, many researchers use SPME as an efficient sample preparation technique to extract and subsequently introduce desired analytes into detection instruments such as the gas chromatograph (GC) and liquid chromatograph (LC) with different detectors [3–6]. At first, SPME was used to analyze volatile compounds using fused silica fibers [7], but nowadays, its use has been extended to the analysis of a wide range of analytes from volatile to nonvolatile compounds using uncoated and coated fibers with liquid and solid phases [4–6,8]. The SPME process comprises two steps: In the first, the fiber is exposed to the sample or its headspace and the target analytes partition from the sample matrix to the coating. In the second step, the fiber bearing the concentrated analytes is transferred to the analytical instrument (e.g., GC or LC) where desorption, separation, and quantification of the extracted analytes take place [9,10].

However, any technique has its drawbacks. Some disadvantages of SPME are: (i) fibers are fragile and can easily be broken; (ii) conditioning should always be performed on each new fiber or when a fiber has not been used for some time; (iii) when a high percentage of suspended matter is present in the sample, the fiber coating can be damaged during agitation, and; (iv) high-molecular-mass compounds can adsorb irreversibly to the fiber, thus changing the properties of the coating and making it unusable, although the latter has been somewhat resolved by over coated fibers. However, the main restriction of SPME is the small amount of sorbent present on the fiber, which leads to certain sensitivity problems [11–13], thus limiting extraction capacity and, consequently, sensitivity cannot be increased by increasing sample volume. To overcome these problems, there are certain modifications to conventional SPME, based on other configurations of SPME and miniaturization of the conventional solid-phase extraction method such as micro-solid-phase extraction ( $\mu$ -SPE) [14], stir-cake sorptive extraction (SCSE) [15], rotating-disc sorbent extraction (RDSE) [16], stir-rod sorptive extraction (SRSE) [17], stir-bar sorptive extraction (SBSE) [18], microextraction by packed syringe (MEPS) [19], dispersive  $\mu$ -SPE (dispersive  $\mu$ -SPE) [20] and headspace sorptive extraction (HSSE) [11,21].

However, all the techniques named above not only present advantages, but also have some drawbacks such as commercial dependence, high cost, complex set-ups, difficult handling, small or limited amount of sorbent, among others. Therefore, the purpose of the present manuscript is to present magnetic graphene oxide (MGO) nanomaterial as sorbent supported on a neodymium magnet (Nd), providing a new extraction technique called Magnetic Headspace Adsorptive Extraction (Mag-HSAE), which overcomes the drawbacks of most of the extraction techniques described above.

One of the advantages of the developed technique is that Nd

magnets were used instead of traditional stir bars (which are relatively more expensive and weaker than Nd magnets) to prevent any magnetic nanomaterial leakage, and to fix the extraction material (MGO). In addition, it should be pointed out that MGO was chosen as adsorbent because of its relatively low production cost, easy manipulation, simple synthesis procedure, wide accessibility, and high extraction capacity of aromatic compounds [22–24]. In this work, as model compounds, nine chlorobenzenes were successfully separated and preconcentrated from water samples using Mag-HSAE prior to thermal desorption gas chromatography-mass spectrometry (TD-GC-MS) as a separation/detection system. The results showed that by using relatively cheap Nd magnets, MGO and the proposed set-up rapid and easy handling extraction, stability of the sorbent, high extraction capacity and high sensitive determination of the investigated chlorobenzenes was achievable under the optimized conditions. To our knowledge, this is the first time that Mag-HSAE has been reported.

## 2. Experimental

### 2.1. Chemicals and real samples

Nine chlorobenzene compounds were used in the present work, namely: 1,2-dichlorobenzene (1,2-DCB), 1,3-dichlorobenzene (1,3-DCB), 1,4-dichlorobenzene (1,4-DCB), 1,2,3-trichlorobenzene (1,2,3-TCB), 1,2,4-trichlorobenzene (1,2,4-TCB), 1,3,5-trichlorobenzene (1,3,5-TCB), 1,2,3,4-tetrachlorobenzene (1,2,3,4-TeCB), 1,2,4,5-tetrachlorobenzene (1,2,4,5-TeCB), and pentachlorobenzene (PeCB), all obtained from Riedel-de Haën (Seelze, Germany). 1,4-dibromobenzene (1,4-DBB) as internal standard (IS) was also purchased from Riedel-de Haën. All chlorobenzenes and the internal standard were dissolved in HPLC-grade acetonitrile available from Scharlau Chemie (Barcelona, Spain) at  $100 \text{ mg L}^{-1}$  to obtain stock solutions. These solutions were kept in the dark at  $4^\circ\text{C}$ . Multicomponent working standard solutions were freshly prepared from the stock solutions for each experiment in deionized water (resistivity of  $18.2 \text{ M}\Omega \text{ cm}$  at  $25^\circ\text{C}$ ), supplied using a water purification system (Milli-Q Biocel A10) from Millipore (Billerica, MA, USA).

For the synthesis of the magnetic materials, graphene oxide (GO),  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and  $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  from Sigma-Aldrich (St. Louis, MO, USA), and ammonium hydroxide solution (32%, w/w) and ethanol from Merck (Darmstadt, Germany) were used. To adjust ionic strength of the aqueous samples, sodium chloride from Merck was used. For GC-MS measurements, high-purity helium (99.9999%) from Air Liquide (Valencia, Spain) was used as a carrier, for both thermal desorption and GC processes. Liquid nitrogen, also from Air Liquide, was used as a coolant for the cooled GC injection system.

Tap water sample from San Vicente del Raspeig (Alicante, Spain), a mineral water sample from a local supermarket (Alicante, Spain) and an effluent water sample from a municipal wastewater treatment plant (Alicante, Spain) were used as real water samples. The water samples were collected in 1 L Pyrex borosilicate amber glass containers, and stored in the dark at  $4^\circ\text{C}$  until their analysis. In the case of the effluent water, the sample was filtered through syringe filters (Acrodisc<sup>®</sup>, pore size  $0.45 \mu\text{m}$ ) before extraction.

### 2.2. Apparatus and instruments

Size and morphological properties of the synthesized magnetic nanomaterial were investigated using a transmission electron microscope (TEM) from JEOL Co. (JEM-2010, 200 KV, Tokyo, Japan). The crystal structure of the synthesized nanomaterial was determined by an X-ray diffractometer (XRD, D8-Advance, Bruker

Download English Version:

<https://daneshyari.com/en/article/5131038>

Download Persian Version:

<https://daneshyari.com/article/5131038>

[Daneshyari.com](https://daneshyari.com)