

# Determination of siloxanes in water samples employing graphene oxide/Fe<sub>3</sub>O<sub>4</sub> nanocomposite as sorbent for magnetic solid-phase extraction prior to gas chromatography-mass spectrometry

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*Running title:* GO/ Fe<sub>3</sub>O<sub>4</sub> as sorbent for siloxanes determination in water samples

## *List of abbreviations:*

cVMS Cyclic volatile methyl siloxanes  
D4 Octamethylcyclotetrasiloxane  
D5 Decamethylcyclopentasiloxane  
D6 Dodecamethylcyclohexasiloxane  
GO Graphene oxide  
L3 Octamethyltrisiloxane  
L4 Decamethyltetrasiloxane  
L5 Dodecamethylpentasiloxane  
LLE Liquid-liquid extraction  
mLOD Methodological limit of detection  
mLOQ Methodological limit of quantification  
MOFs Metal-organic frameworks  
MSPE Magnetic solid-phase extraction  
RR Relative recovery  
SIM Selected ion monitoring  
SPME Solid-phase microextraction  
TEM Transmission electron microscopy  
USA-DLLME Ultrasound-assisted dispersive liquid-liquid microextraction

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VMSs Volatile methylsiloxanes  
VSM Vibrating sample magnetometer  
WWTPs Wastewater treatment plants  
XPS X-ray photoelectron spectroscopy  
XRD X-ray diffraction

*Keywords:* gas chromatography-mass spectrometry, graphene oxide/Fe<sub>3</sub>O<sub>4</sub> nanocomposite, magnetic solid-phase extraction, siloxanes, water samples.

## **Abstract**

A new, fast, simple and environmentally friendly analytical method has been developed to determine six siloxanes in water samples: octamethyltrisiloxane, octamethylcyclotetrasiloxane, decamethyltetrasiloxane, decamethylcyclopentasiloxane, dodecamethylpentasiloxane and dodecamethylcyclohexasiloxane. The analytical method consists of magnetic solid-phase extraction employing graphene oxide/Fe<sub>3</sub>O<sub>4</sub> as sorbent for the separation and preconcentration of siloxanes prior to GC-MS determination. The extraction procedure was optimized by means of a Plackett-Burman design. Under the optimized extraction conditions (graphene oxide/Fe<sub>3</sub>O<sub>4</sub>, 20 mg; extraction time, 10 min; eluent volume, 0.5 mL ACN; elution time, 2.5 min; sample volume, 20 mL), the method rendered repeatability levels with a relative standard deviation between 9 and 20% (n=6, 10 µg L<sup>-1</sup>). Methodological limits of detection ranged from 0.003 µg L<sup>-1</sup> to 0.1 µg L<sup>-1</sup>. The linearity of the method was studied between the methodological limit of quantification and 100 µg L<sup>-1</sup>, obtaining correlation coefficient values between 0.990 and 0.999. The applicability of the method was assessed by analyzing drinking, river and wastewater samples. Relative recovery values ranged between 70 and 120% (1 and 60 µg L<sup>-1</sup> spiking level) showing that the matrix had a negligible effect on extraction. Finally, the greenness of this method was confirmed by the semiquantitative Eco-Scale metrics.

## 1 Introduction

Siloxanes are used in various products, such as electronics, cosmetics, paints, food additives, medical devices, cosmetic surgery, needle coating, pacemaker coating, etc. Volatile methylsiloxanes (VMSs) are the most detected in the environment because they are not effectively removed from wastewater and may migrate through different matrices. Their lipophilicity allows VMSs to spread in the environment and to accumulate in wildlife and humans [1]. The cyclic siloxanes D5 and D6 are currently the most used in personal care products, including perfumes, hair care products, deodorants, antiperspirants, nail polishes, lotions, and skin cleansers [2]. Consequently, VMSs are present in several types of water. Sparham et al. [3] reported D5 concentrations between 0.013 and 0.027  $\mu\text{g L}^{-1}$  in river water which serves a population of more than 3 million people. Wang et al. [4] determined concentrations of D4, D5, and D6 in the influent (entrance) wastewater of 11 wastewater treatment plants (WWTPs) (0.282-6.69  $\mu\text{g L}^{-1}$ , 7.75-135  $\mu\text{g L}^{-1}$ , and 1.53-26.9  $\mu\text{g L}^{-1}$ , respectively) and in the receiving water (at the point of discharge of the effluent into a waterbody) (<0.009-0.023  $\mu\text{g L}^{-1}$ , <0.027-1.48  $\mu\text{g L}^{-1}$ , and <0.022-0.151  $\mu\text{g L}^{-1}$ , respectively). D4, D5 and D6 were also detected in the receiving water and their concentrations varied depending on those in the effluent (tertiary treatment in the WWTP) (<0.009-0.045  $\mu\text{g L}^{-1}$ , <0.027-1.56  $\mu\text{g L}^{-1}$ , and <0.022-0.093  $\mu\text{g L}^{-1}$ , respectively). Siloxanes also impair the efficient energy production by biogas combustion due to significant amounts of siloxanes in the sludge of WWTPs. The volatility of some siloxanes means that they are present in the gas resulting from the anaerobic digestion process of the sludge. At high temperatures siloxanes become silicon dioxide ( $\text{SiO}_2$ ), which quickly deteriorate biogas facilities for energy recovery (engine power generation, cogeneration, fuel cells, etc.). Biofuel combustion produces solid  $\text{SiO}_2$ , which erodes engines and other equipment, causing damage [5]. Such biogas-related damage and poor performance are promoting the search for

alternatives in order to remove siloxanes before they reach the landfill gas [6]. The increased presence of siloxanes in wastewater calls for reliable analytical methods to determine these compounds, which end up in biogas [5]. Likewise, to improve the use of biogas as a renewable energy source, methods to eliminate the compounds that can damage gas-burning equipment are needed, siloxanes being the most difficult compounds to remove [7]. Studies on the preconcentration/determination of volatile siloxanes in water [3,4,8-14] are scarce compared to number of similar studies on biogas and sewage sludge. Previous studies favor gas chromatography-mass spectrometry (GC-MS) as the preferred separation and detection technique for siloxanes determination. The high volatility of methylsiloxanes and the potential sources of background contamination affecting their final determination are the main limiting factors for their analysis. Thus, there is a need to develop methods for siloxanes determination in water and wastewater to enable a more efficient VMS elimination in WWTPs. Such determination methods normally require a sample preparation step because organic compounds are contained at trace levels or in a matrix that interferes. The solid-phase extraction (SPE) technique is simple, fast and economical. It consumes fewer reagents than liquid-liquid extraction and can be combined with different detection techniques in off-line and on-line modes [15]. Graphene has been used as an adsorbent for SPE, increasing adsorptive capacity due to its high theoretical surface area ( $2630 \text{ m}^2 \text{ g}^{-1}$ ) [16]. Graphene has an electron delocalization system which can form  $\pi$ - $\pi$  bonds with benzene rings and adsorbing aromatic compounds [16-20]. Graphene oxide (GO), a derivative of graphene synthesis by the Hummers method [21], possess an important amount of -COOH, -C=O and -OH groups on the surface [22]. These surface functional groups of GO indicate the high capability of forming hydrogen bonds or electrostatic interactions with aromatics and polar compounds or metal ions [23-25]. GO has been proved to be an ideal sorbent for SPE [26] and its miniaturization, the solid-phase microextraction (SPME) technique [27].

Recently, magnetic solid-phase extraction (MSPE) has been employed as a sample preparation technique, using adsorbents decorated with a magnetic phase mainly composed of an iron mineral or iron oxides such as magnetite ( $\text{Fe}_3\text{O}_4$ ) or maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ). In this extraction procedure the magnetic sorbent is dispersed directly into the liquid phase (standard solution or water sample), and after extraction, phases separation is performed by means of an external magnetic field (neodymium magnet). Various possible materials can be used as sorbent phase of the adsorbents, including GO [28], silica [29], carbon nanotubes [30] and more recently, zeolites [31] and metal-organic frameworks (MOFs) [32]. The sorbents decorated with magnetic solids synergistically combine an excellent sorbent capacity with easy sorbent handling by the external magnetic field, helping to reduce processing time, amount of sorbent and solvent consumption.

Reported herein is a magnetic solid-phase extraction method employing graphene oxide/ $\text{Fe}_3\text{O}_4$  as sorbent for the fast and ecological extraction of siloxanes prior to GC-MS determination. To the best of our knowledge, this is the first time that MSPE/GC-MS has been used to determine siloxanes in water samples. The method was optimized by experimental design, validated and applied to real-world samples. Finally, Eco-Scale metrics [33] were used to assess the greenness of the new method.

## **2 Materials and Methods**

### **2.1 Reagents and real-world water samples**

The six siloxanes studied in this work were octamethyltrisiloxane (L3) (98%), octamethylcyclotetrasiloxane (D4) (98%), decamethyltetrasiloxane (L4) (97%), decamethylcyclopentasiloxane (D5) (97%), dodecamethylpentasiloxane (L5) (97%) and dodecamethylcyclohexasiloxane (D6) (95%). All siloxanes as well as HPLC-grade acetonitrile, methanol, ethanol and hexane were purchased from Sigma-Aldrich (St. Louis, MO, USA). The stock standard solution of  $1 \text{ g L}^{-1}$  of the six siloxanes was prepared in

acetonitrile. Deionized water (resistivity of 18.2 MΩ cm at 25 °C) was prepared on a water purification system (GradientA10) supplied by Millipore (Billerica, MA, USA). Working solutions were prepared daily by diluting the stock standard solution with deionized water. All solutions were stored in the dark at 4 °C. It is important to highlight that preparation of aqueous working solutions, at a higher concentration than that of the siloxanes solubility in water, was possible due to the presence of the co-solvent (acetonitrile) that comes from the stock standard solution.

Iron oxide II, III (Fe<sub>3</sub>O<sub>4</sub>) (50-100 nm) was obtained from Sigma-Aldrich and graphene oxide (GO) from Graphenano nanotechnologies (Yecla, Spain).

HNO<sub>3</sub> 65% from Merck (Darmstadt, Germany) and NaOH pellets from Scharlau (Barcelona, Spain) were employed for the nanocomposite synthesis.

Drinking water from a water purification plant (Murcia, Spain), a river water sample (Alcoy, Spain), wastewater samples from three different points of Rincón de León WWTP (three samples, WWTP1) (Alicante, Spain), from Monte Orgegia WWTP (one sample, WWTP2) (Alicante, Spain) and from a WWTP in Portugal (one sample) were used in the study as real-world water samples. All samples were stored in the dark at 4 °C.

## **2.2 Apparatus and instrumentation**

A Ni-coated neodymium magnet, N45 grade, 45x30mm, from Supermagnete (Gottmadingen, Germany) was used as external magnetic field in the MSPE procedure. Automatic vortex from Heidolph Instruments GmbH (Schwabach, Germany) was used for the extraction procedure and an ultrasonic bath from Elma Schmidbauer GmbH (Singen, Germany) for the elution procedure.

Two chromatographic systems were employed. The inlet septa used in both systems was Premium Non-Stick Inlet Septa, Bleed and Temperature Optimized from Agilent Technologies (Santa Clara, CA, USA). For MSPE optimization and nanocomposite reuse

study, chromatographic analyses were performed on a gas chromatograph (model 7820A) from Agilent Technologies equipped with a split/splitless automatic injector and a flame ionization detector. A capillary column HP-5 (5% phenyl-95% dimethylpolysiloxane, 30 m x 0.32 mm I.D., 0.25  $\mu\text{m}$  film thickness) was from Agilent. The injector temperature was maintained at 250  $^{\circ}\text{C}$  and the injection volume was 1.0  $\mu\text{L}$  in the splitless mode. The oven temperature program was initially set at 40  $^{\circ}\text{C}$  and was raised by 6  $^{\circ}\text{C min}^{-1}$  up to 120  $^{\circ}\text{C}$  (held 5 min), followed by an 8  $^{\circ}\text{C min}^{-1}$  ramp up to— 150  $^{\circ}\text{C}$ , where it was held for 5 min. Helium (99.999%) from Air Liquide (Madrid, Spain) was used as the carrier gas at a constant flow rate of 1  $\text{mL min}^{-1}$ . The detector temperature was set at 200  $^{\circ}\text{C}$ .

Method validation and real sample analyses were carried out by Agilent 7890A gas chromatograph coupled to a mass spectrometry detector Agilent 5975C with electron impact ionization at an ionization energy of 70 eV. The capillary column employed was HP5-MS UI (5% phenyl-95% dimethylpolysiloxane, 30 m x 0.25 mm I.D., 0.25  $\mu\text{m}$  film thickness) from Agilent J&W GC Column (Santa Clara, CA, USA). Extracts (1  $\mu\text{L}$ ) were injected in the splitless mode with the split closed for 0.75 min. Helium (99.999%) was used as the carrier gas at a flow rate of 1  $\text{mL min}^{-1}$ . The oven temperature was initially set at 35  $^{\circ}\text{C}$  for 5 min, programmed to 140  $^{\circ}\text{C}$  at 5  $^{\circ}\text{C min}^{-1}$  rate, where it was held for 1 min, followed by a 20  $^{\circ}\text{C min}^{-1}$  ramp up to 300  $^{\circ}\text{C}$ , where it was held for 5 min. The mass spectrometer source and quadrupole were set at 230 and 150  $^{\circ}\text{C}$ , respectively. Measurements were taken with a solvent delay of 4 min and in selected ion monitoring (SIM) mode. All target compounds were identified by their mass spectra and GC retention times (Fig. 1). The (m/z) ratio to quantify significant ions and the retention times of the six siloxanes using the GC-MS method are (73), (221), and (222) from minute 8.50-11 for L3; (73), (193) and (281) from minute 11-15 for D4; (73), (207) and (295) from minute 15-17.50 for L4; (73), (267) and (355) from minute 17.50-20 for D5; (73), (147), (281) and (369) from minute 20-22.50 for L5; and (73),

(341) and (429) from minute 22.50-24 for D6 determinations. Fig. 1 shows typical chromatograms after MSPE of a blank and a standard solution spiked at  $10 \mu\text{g L}^{-1}$  with the six siloxanes.

### **2.3 Synthesis and characterization of graphene oxide/Fe<sub>3</sub>O<sub>4</sub> nanocomposite**

In a previous work the GO/Fe<sub>3</sub>O<sub>4</sub> nanocomposite was synthesized and characterized [34]. The composite is formed by electrostatic attraction between magnetic nanoparticles of Fe<sub>3</sub>O<sub>4</sub> with a positively charged surface and negatively charged nanosheets of GO. Optimal conditions for GO/Fe<sub>3</sub>O<sub>4</sub> nanocomposite synthesis were: stirring on a magnetic stir plate, pH 2 and GO/Fe<sub>3</sub>O<sub>4</sub> ratio (w/w) 1/5. Transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and vibrating sample magnetometer (VSM) were used to test nanocomposite formation and determine its composition and magnetic properties [34].

### **2.4 Magnetic solid-phase extraction procedure**

Firstly, 20 mg of GO/Fe<sub>3</sub>O<sub>4</sub> nanocomposite (40 mg for wastewater samples) was placed in a 22 mL vial. Then, 20 mL of standard solution or water sample was added, and the mixture was vortex stirred for 10 min. After full extraction, the nanocomposite was separated from the liquid phase placing the vial over a neodymium magnet and discarding the liquid with a glass pipette. Elution was carried out with 0.5 mL of acetonitrile and 2.5 min in ultrasonic bath. It is important to highlight that the total extraction procedure time (i.e., extraction, phases separation, sample removal and elution) is about 16 min. Finally, 1  $\mu\text{L}$  of the eluate was injected into the GC-FID or GC-MS system. Two more elution processes with 0.5 mL of acetonitrile and 2.5 min in ultrasonic bath were performed to clean the nanocomposite for reuse.

It should be noted that due precaution was taken, such as cosmetics use, protection and cleaning (i.e., filter mask, gloves and hair covers, and proper cleaning with deionized water



and organic solvents), during the extraction procedure to avoid false positives and cross-contaminations. Additionally, Fig. 1 shows the chromatogram of a blank solution (i.e., deionized water) after MSPE/GC-MS and the signals obtained could be considered negligible; therefore, blank corrections were not performed.

## **2.5 Data handling and processing**

For the screening study, the response of the GC-FID system used was based on the peak area of the eluate for each siloxane individually. The Plackett-Burman [35] design was carried out to screen the significant factors for the MSPE procedure. A concentration level of  $10 \text{ mg L}^{-1}$  was used for screening to ensure a detectable signal (peak area) in all experimental runs of the six siloxanes. An experimental design matrix was constructed, and the results were evaluated using the statistical software NEMRODW<sup>®</sup> version 2007/2010 ("New Efficient Methodology for Research using Optimal Design") from LPRAI (Marseille, France).

## **3 Results and Discussion**

### **3.1 Study of graphene oxide/Fe<sub>3</sub>O<sub>4</sub> nanocomposite**

Previous nanocomposite characterization studies [34] by X-ray photoelectron spectroscopy (XPS) confirmed the chemical composition. Transmission electron microscopy (TEM) characterized the morphology of GO/Fe<sub>3</sub>O<sub>4</sub> nanocomposite. Fig. S1 shows a TEM image of the GO/Fe<sub>3</sub>O<sub>4</sub> nanocomposite synthesized under optimum conditions. The Fe<sub>3</sub>O<sub>4</sub> nanoparticles (darker) are anchored as clusters to the surface of the GO sheets (paler sheets) due to electrostatic self-assembly between the positively charged surface of the Fe<sub>3</sub>O<sub>4</sub> and the negatively charged GO.

A batch-to-batch repeatability study was carried out for three different batches, using each batch for MSPE of an aqueous standard solution spiked at  $10 \text{ } \mu\text{g L}^{-1}$  in triplicate. The

synthesis process was considered repetitive with relative standard deviations (RSD) between 5 and 8%.

## **3.2 Optimization of the extraction procedure**

### **3.2.1 Study of elution solvent**

Prior to optimizing the MSPE procedure, extractions were performed with four different solvents in the elution step. These solvents need to offer a high analyte desorption ability and good chromatographic behavior during the course of chromatographic separation. Accordingly, acetonitrile, methanol, ethanol and hexane were chosen to study solvent elution.

The MSPE procedures were performed as described in section 2.4. using 20 mL of standard solution at 10 mg L<sup>-1</sup> concentration of each siloxane. Results are shown in Fig. S2. Acetonitrile and methanol showed the highest peak areas and all the analytes were eluted. Hexane and ethanol responded for only some of the six siloxanes. Hence, acetonitrile and methanol were selected for the screening study (i.e., Plackett-Burman design).

### **3.2.2 Plackett-Burman design**

The extraction yield in the MSPE procedure can be affected by different factors and in most cases these factors are correlated. Therefore, a multivariate approach is recommended for their optimization. Based on the literature and previous experience, the multivariate approach selected was the Plackett-Burman design. For identifying the significant factors, this two-level fractional factorial design sustains that interactions between factors can be completely ignored. Thus, the main effects are calculated with a reduced number of experiments [35].

The saturated Plackett-Burman matrix with eleven factors was constructed (seven real factors and four dummy factors), and twelve different experiments were randomly conducted employing 20 mL of standard solution at 10 mg L<sup>-1</sup> concentration level of each siloxane

(Table S1). The value of the levels attributed to each factor was selected according to previous studies on MSPE using the GO/Fe<sub>3</sub>O<sub>4</sub> nanocomposite as sorbent [34].

Variations in pH were not contemplated as a factor since pH does not affect the chemical structure of these compounds. Moreover, previous studies about the determination of cyclic volatile methyl siloxanes (cVMS) in freshwaters estimated that the half-lives of D4 and D5 siloxanes were short at both high and low pH values. Therefore, the highest half-life values were found at pH 7, proving that in the pH range of natural water samples, siloxanes remain longer [2].

Data were evaluated by ANOVA and results were visualized with the Pareto chart for each siloxane (Fig. S3). The length of each bar was proportional to the influence of the corresponding factor, while the effects exceeding the reference vertical lines may be considered significant with 95% of probability.

Results indicate that the sample volume was the only significant factor for five out of the six siloxanes (L3, D4, L4, D5 and L5), exhibiting a positive effect for all siloxanes, including D6. The higher the sample volume, the larger the amount of analytes extracted. As 22 mL was the maximum volume of the vial used in the extractions, 20 mL was selected as optimum for all experiments. The other non-significant factors were selected considering the sign of effect. The amount of nanocomposite, extraction time and type of eluent were non-significant with a positive effect, hence larger amounts of nanocomposite and longer extraction times showed to increase analyte extraction, thus they were fixed at the maximum level (i.e., 20 mg and 10 min, respectively). For the type of eluent, the bar length was very short. According to a previous study (Section 3.2.1), both methanol and acetonitrile were considered suitable eluents for the optimization study, but the highest elution was achieved with acetonitrile. Therefore, acetonitrile was selected as elution solvent. Volume of eluent, elution time and NaCl amount were non-significant with a negative effect. This effect could be related to the

fact that the lower the volume of eluent, the higher the analyte concentration, and a higher elution time in ultrasound could affect the nanocomposite structure. Regarding the effect of salt, Han et al. [36] observed that NaCl concentrations between 0 and 0.6% suggested a negligible effect for polycyclic aromatic hydrocarbons extraction. The present study employed a concentration 25 times higher than Han et al. [36] (15% w/v), but this factor proved also a non-significant effect. Thus, we can conclude that salt does not affect the extraction process. Therefore, these factors were fixed at a minimum level (i.e., 0.5 mL of acetonitrile, 2.5 min and 0% of NaCl, respectively).

The optimal MSPE conditions obtained for the preconcentration of the six siloxanes were: 20 mg of GO/Fe<sub>3</sub>O<sub>4</sub> nanocomposite, 10 min of vortex extraction, 0.5 mL of acetonitrile as eluent, 2.5 min of elution in ultrasound, 20 mL of sample and no addition of NaCl in the sample.

### **3.3 Reuse of graphene oxide/Fe<sub>3</sub>O<sub>4</sub> nanocomposite**

Five consecutive MSPEs using a 10 mg L<sup>-1</sup> solution for each siloxane were carried out to evaluate GO/Fe<sub>3</sub>O<sub>4</sub> nanocomposite reusability. Results for the six siloxanes revealed maintenance of GO extraction capacity and Fe<sub>3</sub>O<sub>4</sub> magnetic properties for all the extractions (Fig. S4). However, from the first to the fourth extraction, the peak areas were similar for all siloxanes obtaining RSD values between 9 and 12%, but, in the fifth extraction the signal decreased between 50 and 81%. Hence, the same nanocomposite could be reused for up to four MSPEs without losing adsorptive capacity, saving costs and generating less waste.

### **3.4 Validation of the method**

The proposed method was validated by determining the analytical parameters including the working range, correlation coefficient (r), RSD, methodological limit of detection (mLOD) and methodological limit of quantification (mLOQ). A calibration study was performed to define the working range and correlation coefficient of the calibration curve of

each siloxane (Table 1). The working ranges were 0.3-100  $\mu\text{g L}^{-1}$  (N=6) (L3); 0.01-100  $\mu\text{g L}^{-1}$  (N=7) (D4, D5, L5 and D6); 0.03-100  $\mu\text{g L}^{-1}$  (N=7) (L4) and r ranged from 0.990 to 0.999. The repeatability of the method, expressed as RSD was obtained by six consecutive extractions within a day and the inter-day RSD values were obtained by repeating the extraction in triplicate on three different days. MSPEs of an aqueous solution of 10  $\mu\text{g L}^{-1}$  for each siloxane were carried out, obtaining RSD values from 9 to 20% for the intra-day repeatability, and from 18 to 24% for the inter-day repeatability. The mLODs for all siloxanes were empirically determined, analyzing progressively more diluted concentrations of the analytes. mLOD values were found between 0.003 and 0.1  $\mu\text{g L}^{-1}$  (Table 1). mLOQs were calculated as 3.3 times the mLODs [37], being the lowest concentration of the working range. Recorded mLOQ values were between 0.01 and 0.3  $\mu\text{g L}^{-1}$  (Table 1).

The method developed (MSPE/GC-MS) presents shorter or similar extraction times compared to other analytical methods used to determine siloxanes in water samples (Table S2) and its great advantage is that it uses an environmentally friendly eluent rather than chlorobenzene [8] and hexane [13]. Additionally, mLODs were empirically determined and they were in the same order as those obtained with the liquid-phase extraction techniques (i.e., LLE and USA-DLLME) (Table S2). On the one hand, compared to the previous work using SPME [12], the LOD values obtained in the present work for lineal siloxanes were higher, although the LOD values for cyclic siloxanes were similar. Furthermore, the present work employed a sorbent for MSPE that is easily synthesized and manipulated, and the extraction time proved much shorter (10 min versus 53 min), thereby avoiding temperature control.

### **3.5 Real-world water sample analysis**

The MSPE/GC-MS method was applied to determine six siloxanes in drinking, river and wastewater samples. Sample analysis using the proposed method reveal the presence of

siloxanes in two of the seven samples studied. D5 was found at  $2.7 \pm 0.3 \mu\text{g L}^{-1}$  concentration level in the wastewater collected from Monte Orgegia WWTP (WWTP2). D4, D5 and D6 at  $3.1 \pm 0.6 \mu\text{g L}^{-1}$ ,  $4.4 \pm 0.7 \mu\text{g L}^{-1}$  and  $0.18 \pm 0.04 \mu\text{g L}^{-1}$ , respectively, were found in the sample from the Portuguese WWTP. To investigate the effects of sample matrix on the MSPE/GC-MS procedure, three analyses were conducted for one drinking water and for four wastewater samples (WWTP1 and WWTP2) spiked at  $1 \mu\text{g L}^{-1}$  and  $60 \mu\text{g L}^{-1}$  before the MSPE procedure. Relative recovery (RR) values for each siloxane were determined as the ratio of the area found in real-world and deionized water samples, spiked at the same level (Table 2).

Drinking water samples showed a good RR between 70 and 120% (Table 2). On the other hand, siloxane L3 was not found in the eluates of the wastewater samples at  $1 \mu\text{g L}^{-1}$  spiking level. This could be due to the fact that the organic matter in wastewater retains the siloxane, and thus avoids its adsorption onto GO/Fe<sub>3</sub>O<sub>4</sub>. At highest spiking level ( $60 \mu\text{g L}^{-1}$ ), RR values decreased by up to 40% for the wastewater samples, showing a matrix effect (data not shown). This effect might be explained by the fact that the organic matter blocks the nanocomposite; accordingly, 40 mg of GO/Fe<sub>3</sub>O<sub>4</sub> was used instead of 20 mg. As a result, RR increased and ranged from 70 and 120%, considered acceptable values [38].

In conclusion, matrix effects were not significant for all siloxanes except for L3 in the wastewater samples at  $1 \mu\text{g L}^{-1}$  spiking level.

### **3.6 Eco-scale metrics**

In order to assess the greenness of the new MSPE/GC-MS method, semiquantitative Eco-Scale metrics were used to calculate the penalty points of the whole analytical process. Introduced by A. Gałuszka et al. [33], the Eco-Scale metrics can classify an analytical method as green, assigning penalty points to parameters of the analytical process that are not in agreement with the ideal green analysis.

Thus, Eco-Scale metrics were applied to the method developed herein, the results of which appear in Table S3. Penalty points were attributed to the synthesis of GO/Fe<sub>3</sub>O<sub>4</sub> nanocomposite for one MSPE and MSPE/GC-MS method applied to a sample of 10 mg L<sup>-1</sup> for each siloxane and two sorbent cleaning stages.

The result obtained in the Eco-Scale metrics was >50 and <75, representing an acceptable green analysis.

#### **4 Concluding remarks**

An ecological MSPE/GC-MS procedure using GO/Fe<sub>3</sub>O<sub>4</sub> nanocomposite as sorbent has been developed to analyze six siloxanes in water samples. The magnetic nanocomposite combines the excellent extraction capabilities of GO with the easy handling of Fe<sub>3</sub>O<sub>4</sub> under an external magnetic field. Advantages such as the simple synthesis of the nanocomposite, easy manipulation and potential reuse, reduce both costs and impact of waste. According to LOD values obtained, the proposed method is sufficiently sensitive to determine siloxanes at trace levels in real-world water samples. This is the first time that a GO/Fe<sub>3</sub>O<sub>4</sub> nanocomposite has been used for siloxanes extraction and preconcentration from water samples.

Finally, given the importance of developing environmentally friendly analytical methods, it is noteworthy that this novel and promising method is classified as green on the Eco-scale metrics.

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### **Conflict of interest statement**

The authors declare that they have no conflicts of interest.

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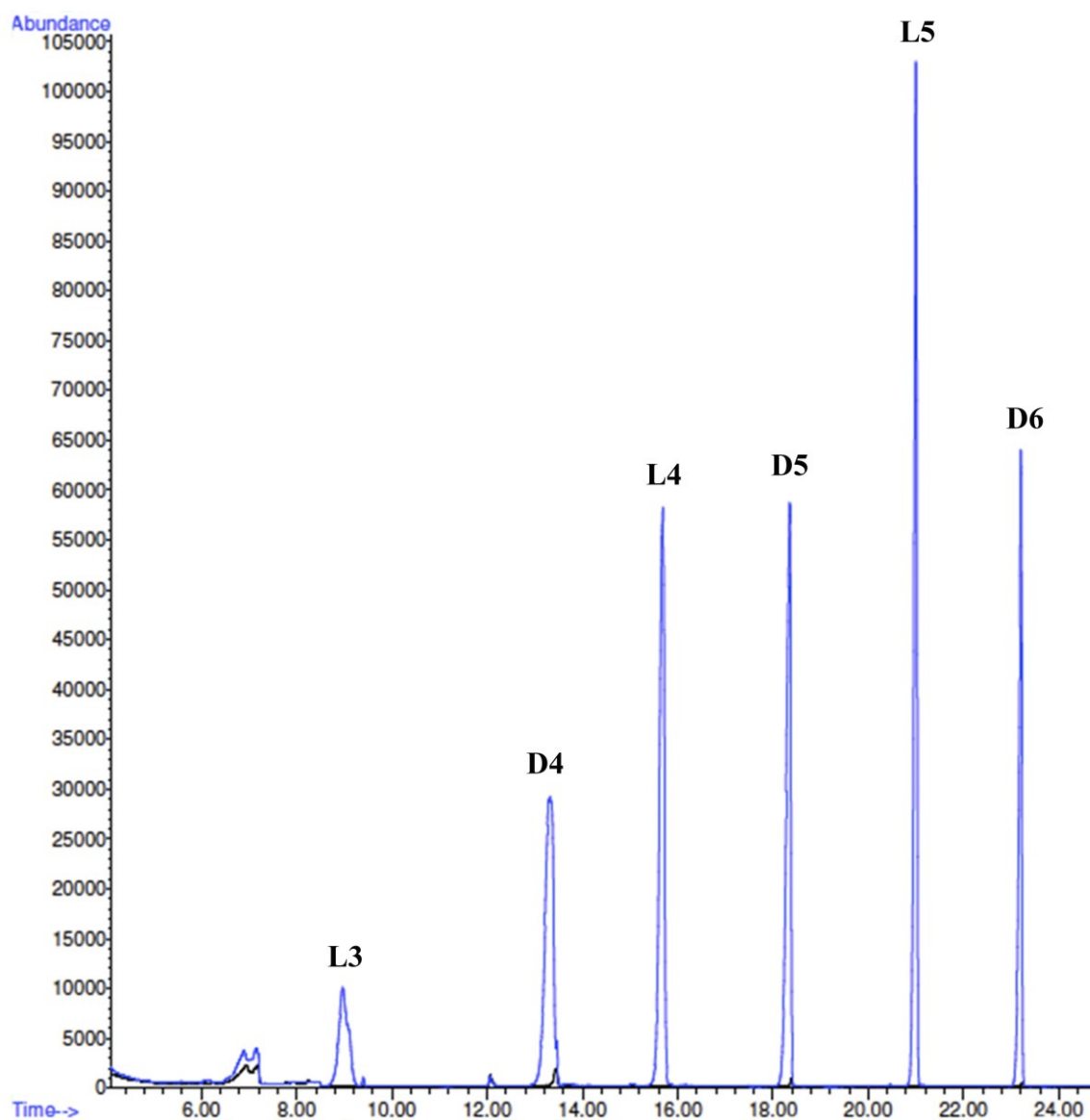
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## Figure Captions

**Fig.1.** Chromatogram of a blank solution (black line) and chromatogram of a standard solution (blue line) containing all siloxanes ( $10 \mu\text{g L}^{-1}$  each) both subjected to the developed method (MSPE/GC-MS). MSPE conditions: amount of nanocomposite, 20 mg; extraction time, 10 min; 0.5 mL of acetonitrile for elution; elution time, 2.5 min; sample volume, 20 mL.



**Table 1.** The main analytical figures of merit of the developed MSPE/GC-MS method.

Analyte	Working range ( $\mu\text{g L}^{-1}$ )	Correlation coefficient ( $r$ ) <sup>a</sup>	RSD (intra-day precision) (%) <sup>b</sup>	RSD (inter-day precision) (%) <sup>c</sup>	mLOD ( $\mu\text{g L}^{-1}$ ) <sup>d</sup>	mLOQ ( $\mu\text{g L}^{-1}$ )
<b>L3</b>	0.3-100	0.993	20	18	0.1	0.3
<b>D4</b>	0.01-100	0.999	19	23	0.003	0.01
<b>L4</b>	0.03-100	0.997	10	23	0.01	0.03
<b>D5</b>	0.01-100	0.990	9	22	0.003	0.01
<b>L5</b>	0.01-100	0.997	12	24	0.003	0.01
<b>D6</b>	0.01-100	0.997	13	24	0.003	0.01

<sup>a</sup> N=6 (L3) and N=7 (D4; L4; D5; L5 and D6).

<sup>b</sup> Intra-day repeatability (n=6, 10  $\mu\text{g L}^{-1}$ ).

<sup>c</sup> Inter-day repeatability (n=3 in 3 different days, 10  $\mu\text{g L}^{-1}$ ).

<sup>d</sup> Empirically determined.

**Table 2.** Relative recoveries and RSD values of the six siloxanes studied in real-world water samples.

Analyte	Relative recovery and RSD values in parentheses (%)									
	Drinking water (n=3)		WWTP 1 entrance (n=3)		WWTP 1 secondary (n=3)		WWTP 1 tertiary (n=3)		WWTP 2 entrance (n=3)	
	1 $\mu\text{g L}^{-1}$	60 $\mu\text{g L}^{-1}$	1 $\mu\text{g L}^{-1}$	60 $\mu\text{g L}^{-1}$	1 $\mu\text{g L}^{-1}$	60 $\mu\text{g L}^{-1}$	1 $\mu\text{g L}^{-1}$	60 $\mu\text{g L}^{-1}$	1 $\mu\text{g L}^{-1}$	60 $\mu\text{g L}^{-1}$
<b>L3</b>	85 (5)	71 (8)	Not found	104 (7)	Not found	91 (17)	Not found	116 (2)	Not found	109 (1)
<b>D4</b>	105 (11)	70 (3)	102 (9)	94 (5)	96 (7)	102 (13)	92 (9)	113 (3)	92 (2)	120 (3)
<b>L4</b>	80 (8)	70 (3)	71 (26)	120 (10)	88 (6)	101 (16)	120 (3)	76 (8)	116 (2)	71 (5)
<b>D5</b>	99 (5)	70 (3)	84 (12)	118 (10)	95 (18)	100 (16)	86 (19)	75 (7)	112 (1)	70 (4)
<b>L5</b>	120 (2)	71 (5)	70 (13)	115 (9)	78 (10)	94 (16)	113 (1)	73 (2)	96 (3)	89 (5)
<b>D6</b>	91 (1)	70 (4)	81 (6)	120 (11)	88 (10)	103 (16)	82 (2)	76 (8)	92 (1)	92 (4)