Gold-Nanoparticles-based Solid-Phase Microextraction Coatings for Determining Organochlorine Pesticides in Aqueous Environmental Samples

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Abstract

The use of gold nanoparticles (AuNPs) based solid-phase microextraction (SPME) coatings has been investigated, focusing the attention on the preparation of AuNPs with non-classical reduction agents of $HAuCl_4$ such as gallic acid and hydrogen peroxide, rather than the conventional sodium citrate. All AuNPs were characterized by diode array spectroscopy, whereas novel AuNPs prepared with gallic acid and hydrogen peroxide were also characterized by atomic force microscopy (AFM) and scanning tunneling microscopy (STM). AuNPs SPME coatings were prepared with a layer-by-layer (LBL) approach. Gallic acid permitted the preparation of stable AuNPs with milder experimental conditions (1 min, room temperature) and provided the most uniform SPME coatings with a thickness of ~3 μm, characterized by scanning electron microscopy (SEM). The analytical performance of the SPME coatings was tested with a group of seven organochlorine pesticides (OCPs) in different environmental waters using gas chromatography (GC) with electron capture detection (ECD). Despite the low thickness of the coatings obtained, limits of detection (LODs) of the SPME-GC-ECD method down to 0.13 $\mu g \cdot L^{-1}$ were obtained. A comparison with the commercial polyacrylate (PA) coating in terms of the partition coefficients (K_{fs}) of the analytes to the coatings gave $\text{Log}K_{fs}$ values two times higher with AuNPs SPME coatings prepared with gallic acid than PA (despite being 28 times thicker the PA fiber). Inter-fiber relative standard deviation (RSD) values (in %) ranged from 8.67% to 21.3%, thus proving the robustness of the coating method used to prepare the SPME fibers. Intra-fiber (and intra-day) RSD values were always lower than 19.8%, thus showing the precision of the entire SPME-GC-ECD method using the optimum AuNPs coating. Real sample analysis was also accomplished to evaluate matrix effect with tap waters and pond waters, obtaining RSD values from 6.7 to 15% for a spiked level of 1.5 $\mu g \cdot L^{-1}$ of OCPs, and relative recovery (RR) values ranging from 85.0 to 97.1%.

Keywords: Coatings; Environmental waters; Gold nanoparticles; Organochlorine pesticides; Solid-phase microextraction

1 Introduction

Solid-phase microextraction (SPME), initially developed by Pawliszyn in early 1990s [1], is nowadays one of the most widely used sample preparation techniques in laboratories worldwide [2-5]. SPME is characterized by its simplicity: a fiber coating of ~1 cm long is directly dipped into a sample solution for a certain period of time, followed by desorption of analytes trapped by the coating in the adequate analytical technique. The polymeric material of the coating is able to maintain its integrity after several extraction/desorption steps. The method also features easiness of automation, impressive enrichment factors, versatility, and low sample volume requirements, among others [6,7]. This microextraction method can be utilized for the analysis of gas, liquid, and solid samples, and for the determination of volatile, semi-volatile, and non-volatile compounds. Depending on the matrix as well as the nature of the target analytes, it can be operated in direct immersion mode (DI-) or in headspace (HS-) as simpler modes, but other improvements have been accomplished [8-11]. As disadvantage, SPME may include the carry-over, particularly in liquid chromatography and capillary electrophoresis. Furthermore, Supelco commercialize only seven materials, and the fibers have certain fragility.

Given the outstanding performance of SPME, it is not a surprise that an intensive search for novel coating materials has taken place in recent years. Thus, materials such as ionic liquids and polymeric ionic liquids [12,13], carbonaceous-based materials such as graphene and carbon nanotubes [14], molecularly-imprinted polymers [15], metal-organic frameworks [16], and metal (mainly Au and Ag) and metal oxide nanomaterials (mainly TiO_2, Co_3O_4, and ZnO) [14,17,18], among others, have been proposed as successful candidates to compete with commercial ones.

Among metallic nanomaterials in SPME, gold nanoparticles (AuNPs) have been probably the most employed as novel coatings. This is related to the advantages associated to gold with respect to other nanosized metals: robustness, stability, compatibility with biomolecules, interesting optical and catalytic properties, and mainly the fact that their synthesis has been the most studied and thus higher control over it can be achieved [19].

Feng *et al.* were the first describing a simple layer-by-layer (LBL) self-assembly process to prepare AuNPs coatings for SPME. [20]. Authors first prepared AuNPs using the classical reduction of $HAuCl_4$ wit sodium citrate. Afterwards, the stainless steel (SS) of the SPME support was immersed into the AuNPs solution, followed by formation of a well-organized self-assembled monolayer (SAM) of dithiol. It is well-known that organic molecules containing thiol can be adsorbed spontaneously onto the Au surface forming a SAM [21]. Several immersion steps trough a LBL method (timing ~12 days) ensured the formation of their AuNP SPME coating (stable at extreme pH values and high temperatures), which was used for determining polycyclic aromatic hydrocarbons (PAHs) in DI-SPME-gas chromatography (GC). Since that original study, a number of SPME works employing gold have been reported. Karimi *et al.* [22], modified a silica support of the SPME fiber with AuNPs, and used the novel coatings for determining PAHs in HS-SPME-GC. Yang *et al.* performed an electrochemical deposition of AuNPs [23] onto SS to decrease the time required in the coating preparation, and then formed a SAM of dithiol (~1 day). Their coating was tested with a high number of aromatic compounds through a DI-SPME-high-performance liquid chromatographic (HPLC) method. Further improvements of the method by the same group has implied the preparation of cedar-like AuNPs as SPME coatings [24], which were tested in the determination of phthalate esters and aromatic hydrocarbons using HPLC. Hafez and Wenclawiak electrochemically

supported gold to prepare a SPME coating, which as further treated to ensure the formation of a porous gold coating [25]. The porous gold SPME coating was employed to determine dodecanethiol using GC-mass spectrometry (MS). Liu *et al.* also prepared AuNPs SPME coating by supporting the material onto pretreated SS wires [26]. The application was devoted to the determination of UV filters in waters by HPLC. Recent improvements have implied the preparation of hybrid coatings incorporating AuNPs for SPME, like those containing poly(3,4-ethylenedioxythiophene) [27], polyaminithiophenol [28], or graphene oxide [29], and thus other materials are also responsible of the extraction efficiency of the final SPME coating.

In general, AuNPs SPME coatings are prepared by electrochemical deposition or using AuNPs prepared by reduction of $HAuCl_4$ with strong reduction agents such as sodium citrate [20,27] or $NaBH_4$ [22]. Zhang *et al.* recently proposed the formation of AuNPs SPME coatings by immersion of a pretreated SS wire (with HF) into a $HAuCl_4$ solution at room temperature with the purpose of utilizing milder conditions [24].

Our purpose is to test the performance of AuNPs SPME coatings employing AuNPs prepared with non-classical reduction agents, to evaluate if the preparation method of NPs exerts an influence in the final SPME coating, and also searching for milder preparation routes while decreasing the preparation times. Furthermore, a group of organochlorine pesticides as target analytes, which have not been tested with AuNPs SPME coatings, have been selected for this analytical application.

2 Experimental

2.1 Chemicals, reagents and materials

133 Seven organochlorine pesticide (OCPs) were utilized in this study: heptachlor
134 (97%), dieldrin (98%), methoxychlor (99%), 4,4'-DDT (99%), 2,4'-DDT (98.9%), α-
135 endosulfan (99.8%), and β-endosulfan (99.9%). These OCPs were supplied by Riedel-de
136 Haën (Seelze, Germany). Individual standard solutions of OCPs were prepared in
137 methanol at a concentration level of 510 $mg \cdot L^{-1}$ for heptachlor; 560 $mg \cdot L^{-1}$ for dieldrin;
138 920 $mg \cdot L^{-1}$ for methoxychlor; 610 $mg \cdot L^{-1}$ for 4,4'-DDT; 2140 $mg \cdot L^{-1}$ for 2,2'-DDT; 690
139 $mg \cdot L^{-1}$ for α-endosulfan; and 520 $mg \cdot L^{-1}$ for β-endosulfan. All solutions were stored at 4
140 ºC and protected from light. These individual stock solutions were used to prepare several
141 intermediate solutions in methanol. Methanol was supplied by Sigma-Aldrich (St. Louis,
142 USA) with HPLC grade (>99.9%).
143 In the optimization studies, a working standard solution of 3 $\mu g \cdot L^{-1}$ containing all
144 analytes was prepared by proper dilution of the intermediate solutions in ultrapure water.
145 Working standard solutions for the SPME calibrations were prepared containing all the
146 OCPs dissolved in ultrapure water (at different concentration levels) by proper dilution
147 of the intermediate solutions.
148 Deionized water (Milli-Q, ultrapure grade) was obtained by a water purification
149 system A10 MilliPore (Watford, UK).
150 The reagents used for the synthesis and preparation of the AuNPs-based SPME
151 coatings were as follows: tetrachloroauric (III) acid trihydrate ($HAuCl_4 \cdot 3H_2O$), gallic
152 acid (99.3%), hydrogen peroxide (30%, v/v), and 1,8-octanedithiol (dithiol) (>97%), all
153 purchased from Sigma-Aldrich. Sodium citrate (99%) was acquired from Sanofi-Aventis
154 (formerly May and Baker, London, UK).
155 The calibrations performed by GC-ECD without the SPME injection mode required
156 the preparation of individual standard solutions of the analytes in methanol with
157 concentrations of 5080 $mg \cdot L^{-1}$ for α-endosulfan; 5000 $mg \cdot L^{-1}$ for β-endosulfan; 5200

158 mg·L^{-1} for heptachlor; 5790 mg·L^{-1} for methoxychlor; 4970 mg·L^{-1} for Dieldrin; 5590
159 mg·L^{-1} for 2,4'-DDT, and 3350 mg·L^{-1} for 4,4'-DDT. An intermediate standard solution
160 containing all the analytes was then prepared in dichloromethane (Sigma Aldrich) at a
161 concentration of 500 mg·L^{-1}. GC-ECD calibration standard solutions in cyclohexane
162 (Sigma Aldrich) were prepared by proper dilution of this intermediate solution, with
163 concentrations of the analytes ranging from 0.5 to 5 mg·L^{-1}. These GC-ECD calibrations
164 without SPME were only used for the calculations of the partition coefficients of the
165 analytes to the SPME coatings selected.

166 The environmental waters studied in this work were collected from different
167 sampling points of Tenerife Island: tap water from the laboratory, one sample from a
168 pond, and two water samples coming from different wells. Sampling was carried out
169 avoiding the formation of bubbles, and using clean amber glass bottles of 1 L in volume.
170 They were kept in a portable fridge until reaching the lab, and then kept in the dark at 4
171 ºC until analysis.

172 A polyacrylate commercial SPME fiber (PA, 85 μm of film thickness) was also
173 utilized in this study for comparison purposes, and it was obtained from Supelco
174 (Bellefonte, PA, USA). Glass vials (15 mL) with screw taps and polytetrafluoroethylene
175 (PTFE)/silicone septa were also supplied by Supelco. A magnetic stirring bar of PTFE
176 (cylindrical shape, 12 mm × 4.5 mm o.d.) was obtained from Sigma-Aldrich.

177 All glassware, including the vials, were washed with detergent and tap water,
178 followed with washing with a mix of Derquim-Oxy purchased by Panreac (Barcelona,
179 Spain) and sulfuric acid supplied by Sigma-Aldrich. Finally, non-graduated glassware
180 and vials were heated in the muffle furnace (550 °C during 2.5 h) to ensure removal of
181 organic matter.

182

2.2 Instrumentation

The stability of the gold nanoparticles at different experimental conditions was studied using an Agilent 8453 a diode array spectrophotometer equipped with a quartz cuvette of 1 cm path length and 4 mL of internal volume.

A pH-meter Basic Meter PB-11 from Sartorius (Madrid, Spain) and a thermostat model Trade Digistat from Raypa (Barcelona, Spain) were also utilized.

The gas chromatographic analyses were performed using a Varian 3800 GC equipped with an electron capture detector (ECD), also from Varian (Palo Alto, CA, USA). A capillary column SPB^{TM}-5 Fused Silica (30 m × 0.32 mm × 0.25 μm) from Supelco was used.

The carrier gas was nitrogen at a flow rate of 1 mL·min^{-1}. GC injection was performed under splitless mode in all cases. The selected desorption temperature in the injector was 260 ºC with all fibers. The optimum desorption time selected was 3 min with all fibers. When SPME was not used, 2 μL was used as injection volume (also in splitless mode).

The GC oven temperature program employed was the following: initially isothermal for 1 min at 100 ºC, and then increased at 15 ºC·min^{-1} up to 260 ºC, holding this temperature during 6 min. The temperature of the detector was kept at 300 ºC, using a make-up flow of nitrogen of 30 mL·min^{-1}.

The microscopic morphology of the NPs was evaluated by atomic force microscopy (AFM) in tapping mode in air with a MultiMode 8 microscope and Nanoscope V control unit from Digital Instruments–Bruker (Santa Barbara, CA, USA) at a scan rate of 1.0–1.2 Hz. Scanning tunneling microscopy (STM) images, in constant current mode, were taken with a Nanoscope IIE (from Digital Instrument/Veeco). It was operated in air at room temperature and using commercial Pt/Ir tips. The tunneling current was 0.3 – 0.5 nA and

the applied bias voltage was 0.1 – 0.5 V, at scan rates ranging from 0.5 to 10 Hz. Evaporated Au onto chromium-coated glass plates (Arrandee™) were used as substrates. Theses plates, after flame annealing, consist of μm-sized Au (111) preferred-oriented crystals with atomically smooth triangular terraces separated by monatomic steps in height. The height of these steps (0.24 nm) is used to test the Z piezotube of the STM.

A Digital Microscope camera Leica m 205 c from Leica Microsystems Ltd, Industry Division (Switzerland) was initially used to screen the aspect of the gold nanoparticles-based SPME coatings. The surface characterization of the SPME coating of Au-NPs was carried out using a JSM 630 scanning electron microscope (SEM) (JEOL, Tokyo, Japan).

2.3 Procedures

2.3.1 Preparation of Au nanoparticles

Au nanoparticles (AuNPs) were prepared through the reduction of $HAuCl_4$ using three different reagents: sodium citrate, gallic acid, and hydrogen peroxide. AuNPs were prepared at different Au:reduction agent molar ratios, pH (by adjusting with diluted HCl and/or NaOH solutions), and temperature conditions.

Under optimum conditions, the following synthetic procedure was used when using sodium citrate as reduction reagent: 2.5 mL of $4.4 \cdot 10^{-4}$ M $HAuCl_4$ (aqueous solution) was heated at 95 ºC under vigorous stirring. While boiling, 2.5 mL of $2.0 \cdot 10^{-3}$ M sodium citrate was added very quickly. The color of the solution turned to wine red in 2 min. After 15 min of reaction, the heating was stopped but the stirring was kept until the solution was cooled to room temperature.

Under optimum conditions, the following synthetic procedure was utilized when using gallic acid as reduction reagent: 2.5 mL of $2.0 \cdot 10^{-3}$ M gallic acid was added very

quickly to 2.5 mL of $4.4 \cdot 10^{-4}$ M $HAuCl_4$. The color of the solution turned to blue in 1 minute. No heating followed by cooling was required in this case.

Under optimum conditions, the following synthetic procedure was utilized when using hydrogen peroxide as reduction reagent: 2.5 mL of $3.0 \cdot 10^{-1}$ M hydrogen peroxide was added to 2.5 mL of $4.4 \cdot 10^{-4}$ M $HAuCl_4$ at 60 ºC. The color of the solution turned to pink quickly.

2.3.3 Preparation of AuNPs-based SPME coatings

Commercial SPME fibers (already over their lifetime due to prolonged used in other applications) were employed for the preparation of AuNPs-based SPME coatings. Thus, the original commercial coating was removed and 0.5 cm of the needle was eliminated using a LC columns cutter. The inner steel of the needle (where the coating was originally attached) was then exposed and softly cleaned using acetone, ethanol, and ultrapure water, during 10 minutes each in an ultrasounds bath.

Once the steel has been conditioned, it is immersed into a 0.05% (w/w) $HAuCl_4$ solution during 3 hours. Afterwards, it is washed with ultrapure water. The formation of a red film over the steel was observed during the exposure time.

The steel was then immersed into a 1,8-octanedithiol solution (0.1%, w/w) for 12 hours. Then, the excess of 1,8-octanedithiol was removed washing with ethanol.

Afterwards, the steel was immersed in one of the three AuNPs solution selected, prepared according to Section 2.3.1., for another 12 hours. After this time required for generating the AuNPs film, the excess of AuNPs was removed by washing with ultrapure water.

256 The immersion of the fiber in 1,8-octanedithiol (12 h) followed by immersion in
257 AuNPs (12 h) constitutes one cycle. It was necessary to repeat this cycle eight times.
258 Therefore, 8 days were required in the preparation of each SPME fiber.
259 For the activation of the AuNPs-based SPME coating, the fiber was exposed at 300
260 ºC for 30 minutes in the GC injector.
261
262 **2.3.4 SPME procedure**
263 All SPME extractions were carried out in DI mode. Each working vial was filled
264 with 15 mL of the aqueous standard solution of all analytes or with 15 mL of the water
265 samples.
266 The SPME method was optimized, being the optimum conditions the following: the
267 extraction is performed at ambient temperature for 60 minutes while stirring at 700 rpm
268 using a stir bar. Once the extraction time is over, the fiber is subjected to desorption in
269 the GC injector for 3 min and using splitless mode. No carry over was observed with any
270 of the SPME fibers tested.
271
272 **2.3.5 Estimation of partition coefficients**
273 When a SPME fiber is directly immersed into an aqueous solution, the analytes
274 already present in the water sample experience partition to the SPME sorbent coating (if
275 adequate affinity analyte-coating is achieved). Under equilibrium conditions, the partition
276 coefficient of the analytes between the two phases (K_{fs}) can be expressed according to the
277 following equation:
278 $$K_{fs} = \frac{V_s}{V_f\left[\frac{n_0}{n_f} - 1\right]} \quad \text{(Equation 1)}$$
279 being V_s the initial sample volume (15 mL in all cases of this study). V_f is the coating
280 volume. It can be calculated for the AuNPs-based coatings using the total radius of the

fiber coating (considering the radius of the solid support and the film thickness) and the coating length (1 cm). Calculated V_f value for AuNPs-based coating formed with gallic acid was 5 nL. The V_f value for the commercial PA SPME fiber was obtained from Supelco, being 0.520 µL. Finally, n_0 and n_f indicate the amount of analytes present initially in the sample and on the fiber once the equilibrium is achieved, respectively. The n_f values were estimated using the GC-ECD calibrations performed without SPME. These calibrations were above described in Section 2.1., but are basically performed under the same GC-ECD conditions that those selected for SPME experiments. Thus, n_f values were calculated through the peak area obtained after the corresponding extraction of an initial amount of n_0 amount via SPME-CG-ECD, while using the CG-ECD calibrations.

3 Results and Discussion

3.1 Preparation and characterization of AuNPs-based SPME coatings

3.1.1 Synthesis and characterization of AuNPs

AuNPs were prepared under different experimental conditions to evaluate the influence of the surrounding environment during the synthesis of the NPs and their stability. The final goal is to evaluate if the synthetic procedure used for obtaining AuNPs exerts an influence in the final SPME coating.

It has been described that the use of weak reducing agents leads to the formation of NPs of larger size than those obtained with more aggressive agents [19]. Best results for AuNPs have been reported with the chemical reduction of $HAuCl_4$ in presence of sodium citrate, sodium borohydride, cyclic and linear ketones, hydrazine, or formamide [30,31]. Thus, the formation of AuNPs through reduction of $HAuCl_4$ was the synthetic mode

306 selected in this study. We decided to focus on three different reduction agents: sodium
307 citrate (the most common agent for preparation of AuNPs), gallic acid, and hydrogen
308 peroxide, while evaluating the influence of the amount of the reduction agent, the pH, and
309 the temperature during the synthesis.

310 Table ESM-1 of the electronic supplementary material (ESM) summarizes the main
311 experimental variables studied during the synthesis and characterization of AuNPs, and
312 their ranges. Regarding the concentration values required for the reduction agents to
313 obtain AuNPs, they were in the range 10^{-4} to 10^{-3} *M* for sodium citrate and gallic acid,
314 whereas higher values (in the range 10^{-2} to 10^{-1} *M*) were needed when using H_2O_2.
315 Regarding temperature, temperatures higher than 95 ºC were not tried to avoid water
316 evaporation. Regarding pH, values from 3.0 to 9.0 were covered.

317 The monitoring of the AuNPs formation was carried out by diode array
318 spectroscopy. It is well-known that one of the most noticeable properties of metal NPs is
319 that they form a surface plasmon, due to the collective oscillation of free electrons
320 confined in the electron cloud of each NP under an electromagnetic field. Figure 1 shows
321 the absorption spectra of different AuNPs in water, obtained under the three main
322 different approaches and experimental conditions. The peaks occurring at ~535–548–598
323 nm correspond to the formation of the typical SP of gold NPs (~20 to 100 nm).
324 Furthermore, the obtaining of symmetric peaks indicates that the AuNPs solutions do not
325 contain highly aggregated particles.

326 The use of sodium citrate as reduction agent of $HAuCl_4$ to form AuNPs is well-
327 known as the Turkevich/Frens method. It requires energy and constant stirring to take
328 place at an acceptable kinetic. A summary of the characterization studies of AuNPs
329 formation using sodium citrate can be observed in Figure 1 (A and D). Figure 1 (A) shows
330 that the spectra obtained at low molar ratios of Au:sodium citrate presented a maximum

absorption wavelength at 540 nm, and such maximum experiences a hypsochromic shift at 520 nm when increasing the molar ratio. This shift is also accompanied by an increase in the intensity when increasing the molar ratio. The maximum is obtained at the molar ratio 1:6. Higher molar ratios were accompanied by slight decreases in the intensities, and thus were discarded. Figure 1 (D) shows the effects of temperature and pH when using the optimum molar ratio. At high temperature, the absorbance values are the highest (thus supporting the need of overcoming the activation energy to have acceptable kinetics), being such values almost constants at pH 3.0 and 6.0, but sharply decrease at pH 9.0. The same behavior is observed at 25 and 60 ºC, but with much lower absorbance values. In any case, it was observed that acidic pH values were favorable for the AuNPs. The optimum synthetic conditions for AuNPs when using sodium citrate as reduction agent are: a molar ratio gold:sodium citrate of 1:6, a pH value of 6.0, and a temperature of 95 ºC. Figure ESM-1 (A) of the ESM shows the visual aspect of all AuNPs solutions tested in these studies with sodium citrate.

A similar study was carried out for the reduction of $HAuCl_4$ with gallic acid, as shown in Figure 1 (B and E); and with H_2O_2, as shown in Figure 1 (C and F). In these cases, there is a hypsochromic shift, reaching values of the absorbance maximum of 548 nm for gallic acid at 1:6 molar ratio; and a bathochromic shift for H_2O_2 when reaching a value of 598 nm at 1:500 molar ratio. In both cases, higher molar ratios than those selected were accompanied by decreases in the maximum absorbance. Figure ESM-1 (B) and ESM-1 (C) of the ESM shows the visual aspect of AuNPs solutions tested in these studies for gallic acid and H_2O_2, respectively.

Regarding the influence of the temperature and the pH during the synthesis, there are practically no variations in the spectra with the temperature for gallid acid (Figure 1 (E)), with increases in the signal at pH 9.0. For H_2O_2 (Figure 1 (F)), higher absorbance

peaks are obtained at 60 ºC and a pH value of 9.0. Therefore, the optimum conditions with gallic acid include a molar ratio of 1:6, a pH value of 9.0, and a mild temperature of 25 ºC. The optimum conditions in the third approach require a molar ratio of 1:500 for Au:H_2O_2, a pH value of 9.0, and a temperature of 60 ºC.

If solely attending to the experimental procedure, AuNPs are obtained in a simpler manner (milder conditions) when using gallic acid than when using sodium citrate or H_2O_2.

Given the low number of studies using gallic acid and H_2O_2 as reduction agents to obtain AuNPs, the characterization of these AuNPs has been performed using AFM and STM, as described in Section 2.2. The obtained images are included in Figure ESM-2 of the ESM. From these studies it can be seen that AuNPs obtained using gallic acid are randomly distributed with a NPs density of ~4500 μm^{-2}, and with an average size of 2 – 4 nm. When using H_2O_2, AuNPs are practically spherical and are mono-dispersedly present. They are also randomly distributed with a NPs density of ~1600 μm^{-2}, and present an average size between 2 and 3 nm.

The stability of the AuNPs once prepared was also evaluated by spectroscopy studies, by measuring the spectroscopic signals at regular timings during 14 days. Figure ESM-3 of the ESM shows the obtained results. AuNPs obtained by the three methods experienced a slight decrease in the absorbance signals during the first ~5-10 hours, (which is related to the tendency of NPs to form agglomerates followed by sedimentation), and afterwards remain stable for at least 14 days.

3.1.2 Preparation and characterization of AuNPs-based SPME coatings

The preparation of the SPME coatings initially started following the LBL self-assembly method proposed by Feng *et al.* [20], which used sodium citrate as reduction

agent to form AuNPs. SS is a useful support because it stabilizes NPs while avoiding their aggregation. Thus, cleaned and etched SS wires were immersed into a 0.05% (w/w) $HAuCl_4$ solution for 3 h, followed by immersion into a 1,8-octanedithiol solution (0.1% w/w) for 12 h. This way, SH_2 and NH_2 groups are spontaneously adsorbed onto the reduced gold surface of the fiber, thus forming a well-organized self-assembled monolayer (SAM) in which AuNPs can be further supported.

Afterwards, it is immersed into the optimum AuNP solution obtained with sodium citrate for 12 h in the case of the SPME coating denoted by Fiber type 1, and for 24 h in the case of the SPME coating denoted by Fiber type 2. These times are much lower than those previously reported (48 h) [20]. Sodium citrate was used for these screening studies for being the most common reduction agent reported and thus to establish comparisons. The purpose of the current study was to minimize the experimental time required to obtain efficient and reproducible SPME coatings. The whole cycle (immersion in 1,8-octanedithiol followed by immersion in AuNP solution) was repeated 8 times (as in [20]).

The coating method is detailed in Section 2.3.3, and summarized in Figure 2. The specific conditions are listed in Table 1, together with several characteristics of the coatings obtained. Figure ESM-4 of the ESM shows the microscopy images obtained for both coatings, which provide an estimation of the coating thickness formed. From the Figure, it can be observed a more uniform coating with granularity aspect in the case of Fiber type 1; whereas Fiber type 2 has few areas covered by AuNPs, also presenting the appearance of flake. The estimated thicknesses were of ~2.0 μm for Fiber type 1 and ~1.0 μm for Fiber type 2. The increase of the immersion time in the AuNPs solution is not favoring the formation of thicker neither uniform coatings. Given these findings, it was decided to proceed preparing the AuNPs-based coatings with shorter immersion times.

405 Once the preparation time was selected, it is important to perform a comparison
406 among AuNPs-based SPME coatings as a function of the AuNPs preparation mode. Thus,
407 not only AuNPs formed using sodium citrate were employed (Fiber type 1), but also with
408 gallic acid (Fiber type 3) and H_2O_2 (Fiber type 4). Their estimated thicknesses have been
409 also included in Table 1, obtaining a higher thickness for Fiber type 3 (~3.0 μm), and
410 lower thickness for Fiber type 4 (~1.5 μm). Coating thickness is an important parameter
411 to ensure adequate extraction efficiency in SPME [1]. Figure 3 (A-F) shows the
412 microscopy images obtained for the three SPME fibers. It can be clearly observed that
413 Fiber type 3 and Fiber type 4 present a more intense gold color than Fiber type 1, which
414 may be due to the presence of very close nanoparticle colonies. This, in turn, implies a
415 rougher coating for Fiber type 3 and Fiber type 4, in contrast with the uniformity of Fiber
416 type 1. It can be also observed several areas without proper coating in Fiber type 4, which
417 is already pointing out for inadequacy. Therefore, it seems that better coating for SPME
418 is that of Fiber type 3 (which is also convenient considering the simple preparation of
419 these AuNPs), and thus a SEM image was obtained for this coating (Figure 3 (G)). The
420 formation of AuNPs onto the SS can be clearly observed in the image.
421

422 **3.2 Analytical performance of the SPME-GC-ECD method using different**
423 **coatings**

424 To test the adequacy of AuNPs obtained with gallic acid (at optimum conditions)
425 as SPME coating for determining OCPs by GC-ECD, the SPME method was first
426 optimized. The selection of the optimum GC-ECD conditions was carried out using the
427 commercial PA SPME fiber, which has been successfully utilized before for these
428 compounds and GC-MS [32]. The optimization of the SPME method was focused on the
429 extraction and desorption time, using 260 ºC as desorption temperature in the GC injector.

430 The ionic strength and the pH were not studied, taken into account previous reports on
431 the SPME-GC determination of these pesticides [32-34]. The sample volume was fixed
432 to 15 mL in all optimization studies, and using a standard of 3 $\mu g \cdot L^{-1}$ for the pesticides in
433 ultrapure water. The extraction time profiles were studied in the range 0 to 120 min.
434 Longer times were not tested to avoid the use of a tedious procedure. Figure ESM-5 (A)
435 of the ESM shows the extraction profiles obtained (using a fixed desorption time of 5
436 min). As a compromise solution, an extraction time of 60 min was selected to avoid long
437 timings and also adequate extraction efficiency for the majority of pesticides. Figure
438 ESM-5 (B) of the ESM includes the desorption time profiles obtained (using a fixed
439 extraction time of 60 min). Given the obtained results, a desorption time of 3 min was
440 selected. No carry-over was observed when further utilizing this desorption time with any
441 of the SPME fibers tested.

442 Under optimum SPME-GC-ECD conditions (Sections 2.2. and 2.3.4. for details),
443 pesticides were completely separated in less than 16 minutes, as it can be observed in
444 Figure 4. Table ESM-2 of the ESM shows the chromatographic retention times of the
445 OCPs together with the obtained reproducibility. In all cases, relative standard deviation
446 (RSD) values, in %, lower than 0.094% (n = 50, inter-day study) were obtained for the
447 retention times.

448 Calibration curves using aqueous standards (in deionized water) were obtained
449 with the optimized SPME-GC-ECD method for the OCPs using the best AuNPs coating
450 (obtained with gallic acid at optimum conditions). Table 2 includes several quality
451 analytical parameters of the method. Limits of quantitation (LOQs) of the method were
452 calculated as ten times the signal to noise ratio, and verified by preparation of aqueous
453 standards of OCPs at such levels and subjected to the entire SPME-GC-ECD method.
454 LOQs ranged between 0.44 and 0.81 $\mu g \cdot L^{-1}$. OCPs are currently forbidden, but their past

455 extensive use, together with the fact that a number of them are still in use in South Asian
456 countries [35] or their illegal use in certain developing areas, justifies the necessity of
457 analytical methods for their determination. LODs have been reported to range from 0.04
458 μg L^{-1} (for dieldrin) to 0.41 μg L^{-1} (aldrin) in aqueous extracts of textiles using
459 polydimethylsiloxane (PDMS) as coating (100 μm) in a SPME-GC-MS method [34].
460 Lower LOQs have been described for OCPs using SPME-GC-ECD and the triple fiber
461 divinylbenzene/carboxen®-PDMS (50/30 μm), with values ranging from 0.004 to 1.5
462 ng·L^{-1} [33].

463 As a comparison, calibrations of the entire SPME-GC-ECD method were also
464 obtained with the PA commercial coating (Table ESM-3 of the ESM). A summary of the
465 quality analytical parameters obtained with AuNPs-based SPME coatings prepared with
466 sodium citrate and H_2O_2 have been also included in the supplementary material (Table
467 ESM-4 of the ESM). Better LOQs were obtained with the commercial PA coating for all
468 OCPs, with values between 0.01 and 0.07 μg·L^{-1}, which *a priori* is a non-adequate result
469 for the AuNPs coatings. However, this comparison must be carefully considered, because
470 both coating fibers present quite different thicknesses, and this is also exerting a
471 considerable influence in the extraction efficiency.

472 Among AuNPs-SPME based coatings, the coating prepared with gallic acid
473 clearly performed better, as expected giving the characterization studies already
474 described.

475

476 **3.3 Estimating the affinity analytes-coatings by calculating the partition**
477 **coefficients**

478 The differences in sensitivity achieved when comparing the AuNPs coatings with
479 that of the commercial SPME coating can be justified by the differences in thicknesses.

In general terms, the thicker the coating the higher the extraction efficiency in SPME. Thus, the thicknesses are 85 μm for PA and 3 μm for the AuNPs coating prepared with gallic acid at optimum conditions (Fiber type 3). In other words, the comparison among the nature of the coating is highly influence for the coating thickness, and thus a normalized comparison is required. Therefore, it results useful the obtaining of the partition coefficients of target analytes to the SPME coatings if proper comparison of the ability of the coatings to establish interaction with target pesticides regardless of the coating thickness is pursued [36]. Partition coefficients of target analytes to the coatings were estimated according to SPME theory, as described in Section 2.3.5. (Table ESM-5 of the ESM as support of the calculations). Table 3 includes calculated LogK_{fs} values for OCPs to PA and AuNPs obtained with gallic acid at optimum conditions. From the Table 3, it is clear than the affinity of the analytes for the AuNP fiber is much higher than for the PA coating. In fact, the affinity (as estimated LogK_{fs}) is on average two times higher with AuNPs than with PA, and this is despite the fact the PA fiber is 28 times thicker than the AuNP fiber formed by gallic acid. These results highlight the affinity of AuNPs coating for these pesticides *versus* commercial coatings, and also point out the interest of improving the preparation of these SPME nanomaterials as coatings.

Table 3 also includes the octanol-water partition coefficients of the analytes studied. It is observed that for 2,4'-DDT, 4,4'-DDT, and methoxychlor, the correlations obtained between their LogK_{ow} and the estimated LogK_{fs} values were very high (with R^2 > 0.9999), being not that high for PA (R^2 = 0.9160). Despite the low number of analytes considered, this could point out for a hydrophobic interaction mechanism for these analytes and the Au-NP fiber formed by gallic acid at optimum conditions.

3.4 Inter-fiber reproducibility

505

506 The evaluation of the reproducibility of the fiber coating method is another
507 important parameter that needs to be performed to support the suitability of the method
508 proposed. Thus, three fibers were prepared with gallic acid at optimum conditions
509 (labelled as *a*, *b*, and *c*). Once prepared, they were used to determine OCPs from an
510 aqueous standard (3 $\mu g \cdot L^{-1}$). Each fiber was tested in intra-day (n = 3 each day, each fiber
511 in a different day), and inter-day (3 different days, non-consecutive) studies using the
512 entire SPME-GC-ECD method. The obtained results are shown in Table 4. Inter-fiber
513 RSD values (in %) ranged from 8.67% for β-endosulfan to 21.3% for 2,4'-DDT, thus
514 proving the robustness of the LBL method used to coat the fibers. Intra-fiber (and intra-
515 day) RSD values were always lower than 19.8%, thus showing the precision of the entire
516 SPME-GC-ECD method utilized, despite the low coating thickness obtained for the
517 fibers. These values are quite in agreement with literature. Thus, RSD values lower than
518 11.3% have been reported for OCPs using SPME-GC-MS for a spiked level of 100
519 $\mu g \cdot L^{-1}$ (in deionized water) [34]. Feng *et al.* reported RSD values lower than 26.4% for
520 their inter-fiber study using AuNPs coatings and their LBL method [20].

521

522 **3.5 Real samples analysis**

523

524 The SPME-GC-ECD method, using the AuNPs SPME coatings obtained with
525 gallic acid at optimum conditions, was used to analyze four water samples: tap water,
526 pond water, and two well waters. All samples were shown to be free of OCPs or, if
527 present, at contents below the LOD of the method.

528 Tap water and pond water were then selected to perform matrix-matched
529 calibrations. These SPME-GC-ECD calibrations presented adequate analytical

performance (as shown in Tables ESM-6 and ESM-7 of the ESM, for tap water and pond water, respectively). Thus, LOQs in tap waters ranged from 0.19 to 2.53 $\mu g \cdot L^{-1}$ and in pond waters from 0.19 to 1.26 $\mu g \cdot L^{-1}$, being comparable but a bit lower for the majority of compounds in pond waters than those obtained with standards in deionized water.

Matrix effects were then assessed by comparing the slopes of the calibrations obtained with standards in deionized water (Table 2) with the slopes of the calibrations obtained with standards in tap water (Table ESM-6 of the ESM) or in pond water (Table ESM-7 of the ESM), using a Student's t-test and following the recommendations given by Andrade and Estévez-Pérez [37]. Briefly, regression variances are first compared using a F-test; and finally, a Student's t-test is carried out. The specific details of calculations of F_{exp} and t_{exp} have been included in Scheme ESM-1 of the ESM, and the obtained values are shown in Table ESM-8 of the ESM.

For tap waters, $F_{critical} > F_{exp}$ was encountered for all pesicides, except for α-endosulfan and β-endosulfan. Only for β-endosulfan, it was obtained that $t_{exp} > t_{critical}$, proving that a matrix effect existed. For the remaining pesticides, heptachlor, α-endosulfan, dieldrin, 2,4'-DDT, 4,4'-DDT, and methoxychlor, t_{exp} was always lower than $t_{critical}$. Therefore, there is not matrix effect for these compounds in tap waters.

For pond waters, $F_{exp} < F_{critical}$ was encountered for dieldrin and 2,4'-DDT. For the remaining pesticides $F_{exp} > F_{critical}$. Attending to the t_{exp} values obtained with respect to the $t_{critical}$, there is an important matrix effect for heptachlor, β-endosulfan, 4,4'-DDT, and methoxychlor.

Thus, matrix-matched calibrations or the standard addition method are suggested to avoid the problem of matrix effects, which was more significant for pond waters than for tap waters (being concordant with the increasing complexity of the matrix).

554 Finally, an intra-day (n = 3) precision and recovery study was carried out with
555 pond waters (those with the higher matrix effect) using the entire SPME-GC-ECD method
556 and the AuNPs coatings of gallic acid. Results have been included in Table ESM-9 of the
557 ESM. RSD values (in %, using a content of 1.5 $\mu g \cdot L^{-1}$ of OCPs) ranged from 6.7 to 15%,
558 being totally comparable to those obtained with standards in deionized water, and indeed
559 better. Slight saltiness of the samples (compared to that of deionized standards and even
560 to that of tap waters) can help in improving the efficiency and reproducibility by a salting-
561 out effect. These values are in agreement, and even better to literature precision values
562 using SPME-GC. Thus, RSD values lower than 11.3% at a spiked level of 100 $\mu g \cdot L^{-1}$ and
563 lower than 12.3% at a spiked level of 500 $\mu g \cdot L^{-1}$ have been reported for real aqueous
564 extracts of textiles using a commercial fiber coating of PDMS (100 μm) and SPME-GC-
565 MS [34].
566 Relative recovery (RR) values (also in %) were totally acceptable, with values
567 ranging from 85.0 to 97.1%, which also indicated that a higher matrix effect was observed
568 in pond waters. These values are also comparable with literature data. Thus, as simple
569 comparison with commercial SPME coatings, RR values from 70.0 to 112.6% (spiked
570 levels between 100-500 $\mu g \cdot L^{-1}$) have been reported for OCPs using SPME-GC-MS [34].
571
572 **Conclusions**
573
574 The comparison of the preparation routes of AuNPs by reduction of $HAuCl_4$ with
575 different agents (non-conventional: gallic acid and hydrogen peroxide, and conventional
576 sodium citrate) showed that milder conditions were required when using gallic acid: only
577 1 min for their preparation and at room temperature. The other agents required higher
578 temperatures: 60 ºC for hydrogen peroxide (1 min) and 95 ºC for sodium citrate (15 min).

579 Furthermore, the most uniform and thick AuNPs SPME coatings prepared by the LBL
580 method were those obtained with AuNPs prepared with gallic acid, being thus selected as
581 optimum material for SPME. In this sense, the preparation method of the NPs is exerting
582 a tremendous influence in the SPME coating formed. More attention on this aspect is
583 advisable for future research on the use of metallic NPs as SPME materials.

584 The optimum AuNPs SPME coating prepared with gallic acid was tested in a
585 SPME-GC-ECD method for determining OCPs in waters, obtaining LODs down to 0.13
586 $\mu g \cdot L^{-1}$, adequate linearity, and good inter-fiber reproducibility with RSD values in the
587 range 8.67–21.3 %. Matrix-matched calibrations were constructed with tap waters and
588 pond waters, showing also adequate analytical performance. Recovery and
589 reproducibility studies were carried out with pond waters (those with higher matrix
590 effect), and adequate values of analytical performance were also obtained: RSD values
591 lower than 15% and average RR values of 89.9%.

592 The partition coefficients of the analytes to the coatings (K_{fs}) were estimated to
593 efficiently compare the efficiency of the materials as SPME sorbents independently on
594 the coating thicknesses of the fibers. Thus, LogK_{fs} values of the OCPs to the PA
595 commercial SPME coating (84 μm thick) ranged between 1.35 ± 0.04 and 3.28 ± 0.05,
596 whereas those obtained with AuNPs of gallic acid (~3 μm thick) between 2.88 ± 0.08 and
597 4.41 ± 0.04, pointing out the high strength of the interactions OCPs – AuNPs as SPME
598 material.

599 Ongoing work is aimed to modify the coating strategy to obtain thicker metallic
600 NPs-based coatings.

601

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718 **Figure Captions**

719 **Fig. 1**. UV-Vis studies of AuNPs obtained at different ratios Au:reduction agent, being:
720 **A**) sodium citrate (at 95 ºC and no pH control during the synthesis), **B)** gallic acid
721 (at room temperature and no pH control during the synthesis), and **C)** H_2O_2 (at 60
722 ºC and no pH control during the synthesis). The influence of the pH and the
723 temperature during the synthesis on the spectra of resulting AuNPs (obtained with
724 the optimum ratios Au:reduction agent) is shown in: **D)** for sodium citrate, **E)** for
725 gallic acid, and **F)** for H_2O_2. Remaining UV-Vis conditions as described in the
726 manuscript.

727 **Fig. 2**. Scheme summarizing the entire LBL process followed to obtain AuNP-based
728 SPME coatings.

729 **Fig. 3**. Microscopy images (digital microscope camera Leica m 205 c) obtained for
730 AuNPs-based SPME coatings using: **A**) Fiber type 1 (sodium citrate as reduction
731 agent under optimum conditions) with zoom × 2, **B**) Fiber type 1 with zoom × 10,
732 **C**) Fiber type 3 (gallic acid as reduction agent under optimum conditions) with
733 zoom × 2, **D**) Fiber type 3 with zoom × 10, **E**) Fiber type 4 (H_2O_2 as reduction
734 agent under optimum conditions) with zoom × 2, **F**) Fiber type 4 with zoom × 10.
735 **G**) SEM images for the SPME Fiber type 3 coating (gallic acid as reduction agent
736 under optimum conditions).

737 **Fig. 4.** Representative chromatograms obtained by SPME-GC-ECD of an aqueous
738 standard solution containing OCPs at 3 $\mu g \cdot L^{-1}$, using the AuNPs coatings formed
739 using **A)** gallic acid as reduction agent (at optimum conditions), and **B)** H_2O_2 as
740 reduction agent (also at optimum conditions). SPME and GC-ECD conditions as
741 described in the text.

742

743 **Table 1**. Several characteristics of the AuNPs-based SPME fiber coatings prepared.

SPME fiber code	SPME coating preparation			Estimated coating thickness (μm)
	Reduction agent	Immersion time in AuNPs (h)	Number of coating steps	
Fiber type 1	sodium citrate	12	8	~2.0
Fiber type 2	sodium citrate	24	8	~1.0
Fiber type 3	gallic acid	12	8	~3.0
Fiber type 4	H_2O_2	12	8	~1.5

[a]Estimated by microscopy as described in the experimental section

744

745 **Table 2.** Several quality analytical parameters of the SPME-GC-ECD method obtained using as coatings AuNPs prepared with gallic acid at
746 optimum conditions (Fiber type 3).

Pesticide	Working range ($\mu g \cdot L^{-1}$)	(Slope ± SD[a])×10^{-4}	(Intercept ± SD[a])×10^{-4}	R[b]	$S_{y/x}$[c]×10^{-4}	LOD[d] ($\mu g \cdot L^{-1}$)	LOQ[e] ($\mu g \cdot L^{-1}$)
heptachlor	1.42 – 7.00	0.91 ± 0.34	0.98 ± 1.50	0.988	1.37	0.13	0.44
α-endosulfan	0.81 – 10.0	7.15 ± 0.13	-10.4 ± 0.7	0.999	0.80	0.24	0.81
dieldrin	0.65 – 10.0	15.4 ± 0.3	-20.8 ± 1.5	0.999	1.65	0.20	0.65
β-endosulfan	0.59 – 10.0	6.89 ± 0.33	-8.32 ± 1.90	0.997	2.08	0.18	0.59
2,4'-DDT	0.68 – 6.00	23.8 ± 1.4	-37.1 ± 5.7	0.997	4.23	0.20	0.68
4,4'-DDT	0.56 – 6.00	29.6 ± 1.3	-41.0 ± 5.1	0.998	4.03	0.17	0.56
methoxychlor	0.64 – 10.0	6.23 ± 0.14	-5.32 ± 0.82	0.999	0.90	0.18	0.60

[a] Standard deviation of slope and intercept, for n = 6 calibration levels
[b] Correlation coefficient
[c] Standard deviation of the residuals
[d] Limits of detection, calculated as three times the signal to noise ratio (and verified by preparation of standards at such levels)
[e] Limits of quantification, calculated as ten times the signal to noise ratio (and verified as above mentioned)
747

748 **Table 3.** Estimated partition coefficients, expressed as LogK_{fs}, for the target analytes and

749 the best SPME coatings.

Pesticide	LogK_{fs} ± error[a]		LogK_{ow}[b]
	AuNPs of gallic acid at optimum conditions (Fiber type 3)	PA commercial SPME coating	
heptachlor	3.07 ± 0.06	1.51 ± 0.03	6.10
α-endosulfan	2.88 ± 0.08	1.70 ± 0.02	3.83
dieldrin	3.12 ± 0.04	1.46 ± 0.03	5.40
β-endosulfan	2.94 ± 0.12	1.35 ± 0.04	3.64
2,4'-DDT	3.38 ± 0.04	1.84 ± 0.04	4.89
4,4'-DDT	4.03 ± 0.04	2.38 ± 0.04	5.01
methoxychlor	4.41 ± 0.04	3.28 ± 0.05	5.08

[a] Error in the determination of the LogK_{fs}, calculated from the error in the prediction of n_f (with $\alpha = 0.05$ and $m+n-3$ degrees of freedom, being m the number of replicates and n the calibration levels), and considering the mathematical propagation of errors
[b] Logarithm of the octanol-water partition coefficient, obtained from NCBI PubChem 2016 database

750

751 **Table 4.** Precision study performed with three different AuNPs SPME coatings prepared
752 with gallic acid at optimum conditions (Fiber type 3: *a*, *b*, and *c*).

Pesticide	SPME fiber	Intra-fiber precision[a]	Inter-fiber precision[b]
heptachlor	Fiber type 3 *a*	4.80	14.1
	Fiber type 3 *b*	10.5	
	Fiber type 3 *c*	6.85	
α-endosulfan	Fiber type 3 *a*	1.99	13.3
	Fiber type 3 *b*	13.6	
	Fiber type 3 *c*	15.7	
dieldrin	Fiber type 3 *a*	3.37	15.1
	Fiber type 3 *b*	6.70	
	Fiber type 3 *c*	13.5	
β-endosulfan	Fiber type 3 *a*	15.4	8.67
	Fiber type 3 *b*	18.0	
	Fiber type 3 *c*	16.3	
2,4'-DDT	Fiber type 3 *a*	19.7	21.3
	Fiber type 3 *b*	11.4	
	Fiber type 3 *c*	11.3	
4,4'-DDT	Fiber type 3 *a*	19.8	20.2
	Fiber type 3 *b*	6.99	
	Fiber type 3 *c*	11.9	
methoxychlor	Fiber type 3 *a*	11.8	14.9
	Fiber type 3 *b*	14.8	
	Fiber type 3 *c*	13.6	

[a] Relative standard deviation (n = 3), using an aqueous standard of OCPs (3 $\mu g \cdot L^{-1}$)
[b] Relative standard deviation (n = 9), using an aqueous standard of OCPs (3 $\mu g \cdot L^{-1}$)
753