

Low toxicity deep eutectic solvent-based ferrofluid for the determination of UV filters in environmental waters by stir bar dispersive liquid microextraction

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ABSTRACT

In this work, a low toxicity deep eutectic solvent-based ferrofluid is presented for the first time as magnetic fluid to be used as an efficient solvent in liquid-based microextraction techniques. This ferrofluid is made of a hydrophobic deep eutectic solvent, composed by menthol and thymol in a 1:5 molar ratio as carrier solvent, and oleic acid-coated cobalt ferrite (CoFe₂O₄@oleic acid) magnetic nanoparticles. This material was characterized via magnetism measurement, scanning electron microscopy, infrared spectroscopy and density measurement. The determination of UV filters in environmental water samples was selected as model analytical application to test the extraction performance of this new ferrofluid by employing stir bar dispersive liquid microextraction, prior to liquid chromatography-tandem mass spectrometry analysis. The response surface methodology was used as a multivariate optimization method for extraction step. Under the optimized conditions, good analytical features were obtained, such as low limits of detection between 7 and 83 ng L⁻¹, good repeatability (relative standard deviations, RSD (%) below 15%), enrichment factors between 46 and 101 and relative recoveries between 80 and 117%, proving the good extraction capability of this ferrofluid. Finally, the method was successfully applied to three environmental waters (beach and river waters), finding trace amounts of the target UV filters. The presented low toxicity deep eutectic solvent-based ferrofluid results to be a good alternative to conventional solvents used in liquid-phase microextraction techniques.

1. Introduction

The evolution of Analytical Chemistry has been traditionally focused on the development of new analytical methods able to achieve lower and lower limits of detection in an efficient way. In addition, due to the social concern for the environment, researchers have prioritized the development of greener strategies to reduce, not only their impact on the environment, but also the risks to the operator [1].

In this context, the implementation of liquid-phase microextraction techniques and sorbent-based microextraction techniques allowed to reduce drastically the amount of organic solvents employed in each analysis. From these two, those liquid phase-based microextraction

techniques usually needs higher amounts of organic solvents, although in the microliter range, including, in some cases, hazardous halogenated ones [2]. Moreover, these solvents employed as extractant phase present a lack of selectivity compared with the tailor-made sorbents used in solid phase-based microextraction techniques [3,4]. In any case, the employment of this kind of solvents is not recommended by the principles of the Green Analytical Chemistry [5] and the Green Sample Preparation [6], since they are not safe neither for environment nor for operators.

For this reason, in order to reduce the impact caused by these solvents when liquid-phase microextraction techniques are used, new greener tailor-made solvents, such as ionic liquids (ILs) and deep

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eutectic solvents (DESs), have been incorporated to these microextraction techniques [7]. These solvents are made from two individual components, which can be selected from different possibilities resulting in very interesting tunable properties that can be exploited for carrying out targeted extractions [8].

Concretely, DESs have attracted the attention of researchers during the recent years [9,10] due to different reasons. They are easily formed by mixing a hydrogen bond acceptor (HBA) and a hydrogen bond donor (HBD), which interact forming strong hydrogen bonds, resulting in the formation of a eutectic mixture with a lower melting temperature than that of each individual component [11]. Consequently, DESs may be liquids at room temperature, even if the original components are solid [12]. In addition, their preparation is easy to perform and can be done in a matter of minutes, just mixing the HBA and HBD, even *in situ* in the donor phase [13,14].

It should be noted that DESs share several properties with ILs, such as low vapour pressure, high thermal stability and low flammability. Nevertheless, the individual components of DESs are usually cheaper and quite less harmful than those for ILs, and generally, their preparation is easier and consumes less energy [15].

Although DESs boast of having high greenness and low toxicity, some individual components used to prepare them may be toxic. For this reason, the term natural DES (NADES) has been usually employed to distinguish those non-harmful DES [16,17]. However, NADES definition is an inaccurate term since it may not include all non-toxic DES. In this sense, the term low toxicity DESs (LT-DESs) should be more appropriate [7].

However, DESs and LT-DESs are not exempted from issues, since their lack of volatility may affect their introduction in some measurement devices such as in a gas chromatography system, of course, but also in a mass spectrometer [18]. Moreover, their lower density than water makes their retrieval after the extraction process tedious unless additional steps are conducted (e.g., solidification of floating organic droplet [19]).

The use of magnetic nanoparticles (MNPs) to form ferrofluids has allowed to easily retrieve low density solvents in microextraction techniques by applying magnetic forces [20–22]. Ferrofluids are stable colloidal and homogenous dispersions of MNPs in a carrier solvent [23]. Dispersive agents, such as surfactants (e.g., oleic acid (OA)) are usually employed to avoid the agglomeration of the MNPs in the bosom of the solvent [22,24]. In this sense, ferrofluids are easily prepared by simple sonication of OA-coated MNPs (i.e., MNPs@OA) with the carrier solvent.

During the last years, several liquid-phase microextraction strategies have been developed employing ferrofluids or other magnetic fluids such as magnetic ionic liquids (MILs) as extraction phase. Most of these strategies employ dispersive-based techniques, in such a way that tiny droplets of the fluid are formed in the sample solution, increasing the contact area between the sample and the extraction phase, and thus enhancing the extraction speed [25]. Finally, after the extraction, the fluid can be easily retrieved by applying an external magnetic field.

In this regard, some techniques, such as modifications of the well-known dispersive liquid-liquid microextraction (DLLME) [26,27] and other novelties like stir bar dispersive liquid microextraction (SBDLME) [28], have been proposed as magnetic fluid-based extraction approaches. Although the applications of SBDLME are scarce so far, its simplicity and good extraction performance [29,30], in addition to the no-need of an external magnetic field [28], makes it a good alternative to DLLME.

In SBDLME, a magnetic fluid and a neodymium-core magnetic stir bar are introduced into the sample allowing the magnetic fluid to coat the stir bar due to magnetic interactions. When low stirring rates are applied, the liquid is retained onto the neodymium magnet. However, when the stirring rate is increased, the rotational forces surpass the magnetic field and the material is dispersed into the sample. After extraction period, the stirring is stopped and the magnetic fluid

containing the analytes is attracted again by magnetic interactions onto the stir bar [28].

Up to now, only MILs [29,30] and just a DES [31] have been used as extraction phases in SBDLME. However, LT-DES-based ferrofluid may be a greener alternative. For that reason, the aim of this work was to develop a LT-DES-based ferrofluid for SBDLME, thus avoiding the use of toxic compounds and tedious synthesis processes, in addition to reduce the analysis cost.

In this work, an innovative ferrofluid is presented as a green and efficient solvent for liquid-phase microextraction techniques. This one is formed by a low toxicity menthol and thymol DES as carrier solvent and OA-coated cobalt ferrite (CoFe_2O_4 @OA) MNPs. This ferrofluid not only has the advantage of being quite safe and harmless for the environment, but also it can be easily separated into their volatile components employing a small amount of organic solvent, thus allowing it to be introduced in the mass spectrometer without harming it. As far as we know, this is the first time that this ferrofluid has been employed for analytical purposes.

As model analytical application of this new ferrofluid, the determination of UV filters in environmental waters by liquid chromatography-tandem mass spectrometry (LC-MS/MS) was selected. The high concern about the impact of solar radiation in human health has caused an increase of the use of cosmetic products containing UV filters. Consequently, high amounts of these compounds are able to reach the environment by direct or indirect sources and hence, to be bioaccumulated in environment [32]. Once there, these UV filters can alter aquatic fauna and flora. For that reason, these compounds are considered as emerging pollutants, and the development of sensitive analytical methods for their environmental monitoring is mandatory.

2. Experimental

2.1. Reagents and preparation of standard solutions

All reagents and solvents were purchased from major suppliers. Benzophenone-3 (BZ3) 98% and ethylhexyl salicylate (EHS) 99% from Sigma-Aldrich (Barcelona, Spain), isoamyl p-methoxycinnamate (IMC) 99.3% from Haarmann and Reimer (Parets del Vallés, Spain), 4-methylbenzylidene camphor (MBC) 99.7% from Guinama S.L. (Valencia, Spain), octocrylene (OC) > 98% from F. Hoffmann-La Roche Ltd. (Basel, Switzerland), ethylhexyl dimethyl PABA (EHDP) 100%, butyl methoxydibenzoylmethane (BMDM) 98% from Merck (Darmstadt, Germany), and diethylamino hydroxybenzoyl hexyl benzoate (DHHB) 99.8% from BASF (Barcelona, Spain) were used as standards. The chemical structures and relevant information are given in Table S1. Octocrylene (2-ethyl-d₅-hexyl-2,3,3,4,4,5,5,6,6,6-d₁₀) (OC-d₁₅) from Sigma-Aldrich (Barcelona, Spain) was used as surrogate.

To perform the synthesis of CoFe_2O_4 @OA MNPs, cobalt (II) chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$) and iron (III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), both for analysis, were obtained from Acros Organics (New Jersey, USA), while oleic acid (OA) (90%) was acquired from Sigma-Aldrich (Steinheim, Germany). Thymol 99% and ($\pm$)-menthol 98% from Sigma-Aldrich (Steinheim, Germany) were used for the preparation of DES.

HPLC-grade ethanol and acetonitrile were purchased from Panreac (Barcelona, Spain). Deionized water was obtained from a Connect water purification system provided by Adrona (Riga, Latvia). Sodium chloride (NaCl, 99.5%, analytical grade), ortho-phosphoric acid (85%, analytical grade), di-sodium hydrogen phosphate dodecahydrate (reagent grade), hydrochloric acid (37%, reagent grade) and sodium hydroxide (analytical reagent grade) used as ionic strength and pH regulators, were acquired from Scharlau (Barcelona, Spain).

To prepare the chromatographic mobile phase, LC-MS grade methanol and LC-MS grade water were obtained from VWR Chemicals (Fontenay-sous-Bois, France), whereas formic acid (98%, for mass spectrometry) was purchased from Fluka (Steinheim, Germany).

Nitrogen used as nebulizer and curtain gas in the MS/MS ion source was obtained by means of a NiGen LCMS nitrogen generator from Claind S.r.l. (Lenno, Italy). Extra pure nitrogen (>99.999%) from Praxair (Madrid, Spain) was used as collision gas in the MS/MS collision cell.

Different stock solutions of the target compounds were prepared in ethanol at 500 $\mu\text{g mL}^{-1}$. From them, a multicomponent stock solution was prepared in ethanol at different concentration for each UV filter depending on their limits of detection (see Section 3.3): 50 $\mu\text{g mL}^{-1}$ for DHHB and EHDP, 100 $\mu\text{g mL}^{-1}$ for BZ3, IMC and OC, 200 $\mu\text{g mL}^{-1}$ for MBC and BMDM and 500 $\mu\text{g mL}^{-1}$ for EHS. This solution was kept at 4 °C and protected from UV radiation by using amber glassware. From this solution, an intermediate 1:1000 v/v solution was prepared also in ethanol. Afterwards, from this intermediate solution, working solutions between 30 and 750 ng L^{-1} for DHHB and EHDP, 70–1750 ng L^{-1} for BZ3, IMC and OC, 130–3250 ng L^{-1} for MBC and BMDM and 300–7500 ng L^{-1} for EHS were prepared by proper dilution with a 6% NaCl w/v aqueous solution. In addition, a 500 $\mu\text{g mL}^{-1}$ OC-d₁₅ stock solution (as surrogate) was prepared in ethanol and then diluted in ultrapure water at a concentration of 150 ng L^{-1} . All these solutions were kept at 4 °C and protected from UV radiation by using amber glassware. Under these conditions, these solutions were stable at least one month.

2.2. Sample collection and pretreatment

Three different water samples were analyzed. In this sense, sea water from Puzol beach (Puzol, Spain) and Patacona beach (Valencia, Spain), and river water from Mijares River (Montanejos, Spain) were collected during the summer season in a 1 L amber glass bottle and were kept at 4 °C until their analysis, as it will be described further on. Prior to analysis, they were filtered and their ionic strength was regulated to NaCl 6% w/v after measurement of their conductivity.

2.3. Apparatus

An Agilent 1100 Series HPLC system equipped with a G1379B degasser, a G1312A binary pump, a G1367A autosampler and a G1330B thermostatic column oven, coupled to an Agilent 6410B Triple Quad MS/MS was employed in the present study. MassHunter version B.08.00 was used as software for data acquisition. Separations were carried out in an Agilent Zorbax SB-C18 (50 mm $\times$ 2.1 mm, 1.8 μm) purchased to Agilent Technologies (Waldbronn, Germany).

For the preparation of MNPs, DESs and ferrofluids, a ZX3 vortex mixer from VELP Scientifica (Usmate Velate, Italy), an Incudigit lab stove, a Tectron water bath and an ultrasound bath (50 Hz, 360 W) all from J.P. Selecta (Barcelona, Spain) were employed.

A 10-position multiple stirring plate model MS-M-S10 from Labbox (Barcelona, Spain) and NdFeB magnets (54 MGO, 10 mm length $\times$ 3 mm diameter) from Supermagnete (Gottmadingen, Germany) were employed to perform the SBDLME process.

A Basic 30 conductimeter from Crison (Barcelona, Spain) was used for the study of the salt content in water samples, and a Basic 20 pH meter from Crison (Alella, Spain) was used for the adjustment of the pH of the solutions.

A Jasco FTIR 4100 Fourier transform infrared spectrometer (FT-IR) from Jasco Europe S.r.l. (Cremella, Italy) was used to confirm the preparation of menthol:thymol 1:5 DES. The surface morphology of the MNPs were provided by a HITACHI S-4800 field emission scanning electron microscope (SEM) operating at 10 kV and equipped with a RX Bruker backscattered electron detector (Krefeld, Germany). The magnetic measurements were assessed by a homemade vibrating sample magnetometer (VSM) fabricated by the Magnetism Unit of SGIker of University of the Basque Country (UPV/EHU).

2.4. Synthesis of the CoFe₂O₄@OA magnetic nanoparticles

The synthesis of the CoFe₂O₄@OA MNPs included two different

steps. First, CoFe₂O₄ MNPs were synthesized by wet chemical coprecipitation according to an adapted protocol [33] and then, they were coated with OA.

In this sense, 100 mL of a 0.4 M FeCl₃ aqueous solution and 100 mL of a 0.2 M CoCl₂ aqueous solution were mixed. Then, 100 mL of a 3 M sodium hydroxide aqueous solution were added dropwise under continuous stirring at 80 °C. After that, 2 mL of OA were added and the reaction mixture was stirred at 80 °C for 1 h. The black precipitate product was slowly cooled to room temperature and the MNPs were washed twice with ultrapure water and once with ethanol. Finally, the precipitate was dried overnight at 100 °C and pulverized into a fine powder.

2.5. Preparation of low toxicity menthol:thymol deep eutectic solvent

The menthol:thymol 1:5 DES was prepared by weighing separately 0.47 g of menthol, as HBA, and 2.76 g of thymol, as HBD, in two 15 mL polystyrene Falcon™ tubes. Then, they were heated at 60 °C in a water bath for 10 min, and mixed and vortexed for 1 min until a homogeneous transparent liquid was obtained. The resultant DES was left to reach room temperature before the synthesis of the ferrofluid.

2.6. Preparation of low toxicity deep eutectic solvent-based ferrofluid

To prepare the CoFe₂O₄@OA-menthol:thymol ferrofluid, 25 mg of CoFe₂O₄@OA MNPs were weighed in a microcentrifuge tube and 1 mL of DES was added. The resultant mixture was sonicated for 40 min leading to the formation of a stable ferrofluid.

2.7. SBDLME procedure

Firstly, a neodymium stir bar was introduced into a clean and dry 40-mL extraction vial. Then, 100 μL of ferrofluid, 15 mL of a standard solution or a sample, 200 μL of acetonitrile as dispersant agent, and 100 μL of 150 ng mL^{-1} OC-d₁₅ solution (as surrogate) were added into the vial and vigorously stirred (ca. 1000 rpm) for 10 min at room temperature to achieve the total dispersion of the ferrofluid throughout the aqueous donor solution. When stirring was stopped, the magnetic ferrofluid was collected on the stir bar. Subsequently, the stir bar was removed with plastic forceps, and it was introduced into a 5-mL desorption vial containing 100 μL of acetonitrile to accomplish the liquid desorption of the analytes. Finally, after 2 min of slow stirring rate (ca. 250 rpm), the acetonitrile extract was collected with a syringe, passed through a 0.22 μm nylon filter and transferred to a chromatographic vial for LC-MS/MS analysis. Fig. 1 shows a schematic diagram of the experimental SBDLME procedure.

2.8. LC-MS/MS analysis

The chromatographic method was carried out with a mobile phase consisted of solvent A (H₂O, 0.1% formic acid) and solvent B (methanol, 0.1% formic acid), by isocratic elution at a mixing ratio of 15:85 (v/v). The injection volume was 5 μL . The flow rate was set 0.2 mL min^{-1} and the column temperature was kept constant at 35 °C. The run time was 6 min.

The triple quadrupole MS detector operated in positive electrospray ionization mode (ESI⁺, capillary voltage at 6 kV), by multiple reaction monitoring (MRM). The other conditions were: gas temperature at 230 °C, nebulizer gas flow rate at 13 L min^{-1} , nebulizer gas pressure at 35 psi, and dwell time at 50 ms. The *m/z* precursor $\rightarrow$ product ion transitions for quantification and for identification, the collision energies and fragmentor values for each analyte are shown in Table S2.

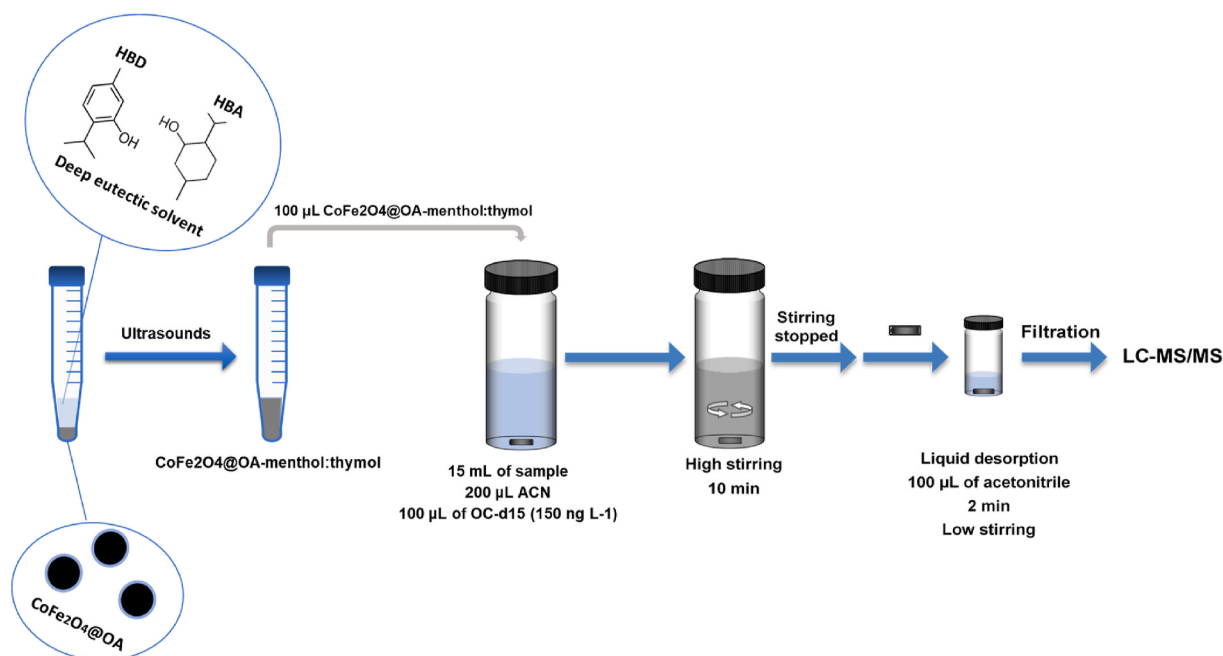


Fig. 1. Schematic diagram of proposed SBDLME-LC-MS/MS method.

3. Results and discussion

3.1. Selection of the ferrofluid and characterization

The combination of menthol and thymol was selected for the formation of the ferrofluid due to their hydrophobic character and aromaticity, improving the interactions with the analytes. Furthermore, both HBA and HBD are volatile, thus after decomposing the DES into the original components it can be introduced into the mass spectrometer system without risk of fouling it.

Three different molar ratios of menthol:thymol (i.e., 1:1, 1:2 and 1:5) were tested in order to select which resulting ratio provided the best extraction of the analytes. The extractions were performed in 5 mL of aqueous standard solution with 2 ng mL^{-1} of the target analytes, and 50 μL of the ferrofluid. Higher molar ratios of menthol were not tested in order to favor π - π interactions between thymol and UV filters. The DES with 1:1 ratio was not properly formed and then it was discarded. Between 1:2 and 1:5, the latter provided better results in terms of extraction capability (Fig. S1), due to their major number of aromatic rings provided by thymol molecules. Thus, the 1:5 ratio was selected for further experiments.

Afterwards, different amounts of $\text{CoFe}_2\text{O}_4\text{@OA}$ MNPs (i.e., 6, 12, 25, 50 and 100 mg) to form the ferrofluid were studied in 1 mL of menthol:thymol 1:5 DES. The assay was performed in 5 mL of aqueous standard solution with 2 ng mL^{-1} of the target analytes, and 50 μL of the ferrofluid. Higher presence of MNPs (i.e., >25 mg) formed ferrofluids with huge viscosity hindering their aspiration with conventional micropipettes, impairing the repeatability. Lower amounts were not enough to form the $\text{CoFe}_2\text{O}_4\text{@OA}$ -menthol:thymol ferrofluid properly making it less magnetic and thus reducing its retrieval, as it was visually observed. Then, the ferrofluid was prepared with 25 mg of $\text{CoFe}_2\text{O}_4\text{@OA}$ MNPs per 1 mL of menthol:thymol 1:5 DES.

3.1.1. Characterization of menthol:thymol 1:5 DES

The preparation of menthol:thymol 1:5 DES was studied by FT-IR analysis. The spectra of DES and its individual components are presented in (Fig. S2). As it is shown in Fig. S2a, the stretching vibration bands at 3158 cm^{-1} (O-H), $2866\text{--}1956 \text{ cm}^{-1}$ (C-H), $1584\text{--}1619 \text{ cm}^{-1}$ (aromatic C=C) and 1239 cm^{-1} (C-O) of thymol can be identified. In

the FT-IR spectra of menthol (Fig. S2b) it is possible to identify the stretching vibrations of 3291 cm^{-1} (O-H), $2843\text{--}2948 \text{ cm}^{-1}$ (C-H) and 1023 and 1042 cm^{-1} (C-O). However, as can be seen in the DES spectra (Fig. S2c), the band corresponding to the O-H stretching in menthol:thymol 1:5 DES is wider than the individual O-H stretching bands of thymol and menthol and, moreover, it appears shifted. Likewise, the stretching vibration band of C-O in menthol appears shifted in DES spectra, proving the existence of strong interactions between the protons on the hydroxyl groups from menthol and thymol, thus inferring that hydrogen bonds were formed between these hydroxyl groups [34]. Therefore, it suggests the successful formation of menthol:thymol 1:5 DES.

The density of menthol:thymol 1:5 DES was also determined, measuring it at room temperature by weighing 500 μL of DES, resulting in a density of 0.905 g cm^{-3} .

3.1.2. Characterization of $\text{CoFe}_2\text{O}_4\text{@OA}$ MNPs

The surface morphology of $\text{CoFe}_2\text{O}_4\text{@OA}$ MNPs was investigated with SEM. Fig. S3 shows the spherical and uniform shape of the MNPs with a particle size around 50 nm.

3.1.3. Characterization of $\text{CoFe}_2\text{O}_4\text{@OA}$ -menthol:thymol ferrofluid

For the characterization of the ferrofluid, the magnetization curve of the $\text{CoFe}_2\text{O}_4\text{@OA}$ MNPs and the resultant $\text{CoFe}_2\text{O}_4\text{@OA}$ -menthol:thymol ferrofluid were measured at room temperature (Fig. S4). A hysteresis loop may be observed in $\text{CoFe}_2\text{O}_4\text{@OA}$ MNPs, showing a residual magnetism when the magnetic field is stopped [35]. The magnetic saturation (M_s) of the ferrofluid was 24 emu g^{-1} , which, as expected, is lower than the M_s obtained for $\text{CoFe}_2\text{O}_4\text{@OA}$ MNPs (i.e., 57 emu g^{-1}). It could be attributed to, for one hand, the less amount of the magnetic component (i.e., MNPs) per gram of material, and on the other hand, to the shielding that DES produces in the MNPs. This shielding may also be responsible of the observed loss of retentivity and coercivity. Even though, its magnetic behavior is enough to efficiently retrieve the ferrofluid from an aqueous solution employing a magnetic field and thus to be employed in SBDLME.

3.2. Optimization of the SBDLME variables

Before the multivariate optimization of the conditions of the extraction step (see Section 3.2.1.), preliminary studies were performed to evaluate the employment of acetonitrile as disperser solvent. It was observed that adding 200 μL of acetonitrile the ferrofluid was more efficiently dispersed. It should be emphasized that under these conditions, the DES was not decomposed and maintained its structure, since there are not significant differences between the IR spectra after (Fig. S2d) and before (Fig. S2c) the extraction.

Afterwards, the desorption solvent and sample volume were also evaluated using a univariate approach. In this regard, 250 μL of different organic solvents (namely methanol, ethanol and acetonitrile) were evaluated as desorption solvents. The extractions were performed intra-day in 5 mL of aqueous standard solution with 2 ng mL^{-1} of the target analytes, and 50 μL of the ferrofluid. The peak area was considered as response function. Results in Fig. S5 show that acetonitrile significantly increased the signals of the analytes with lower sensitivity (BMDM and EHS) and the signals of BZ3 and IMC. Furthermore, acetonitrile decomposes the DES into the individual volatile components (i.e., menthol and thymol). This can be observed in Fig. S2d, where the O–H stretching band of the DES after the desorption in pure acetonitrile is narrower than in Fig. S2c. This gives rise to the dissolution of the analytes into the desorption solvent and the introduction of the extract into the LC-MS/MS without risk of fouling it as might happen if the DES was introduced. Consequently, acetonitrile was selected as desorption solvent for the next experiments.

Regarding to sample volume, 5, 10, 15 and 20 mL were evaluated. In general terms, the highest signals were obtained at a sample volume of 15 mL (Fig. S6). The lower signals observed employing 20 mL may be

produced because part of the ferrofluid was accumulated in the top layer of the sample solution and the magnetic forces were insufficient to recover it. Thus, 15 mL was chosen as sample volume to enhance the efficiency of the analysis.

3.2.1. Multivariate optimization of the extraction conditions

The factors of influence in the extraction procedure were optimized using the response surface methodology (RSM). In this sense, Box-Behnken design was performed to evaluate four significant extraction variables, performing 27 experimental runs with three levels for each factor (see Supplementary Material). The StatGraphics Centurion XVI software from StatGraphics Technologies, Inc. (The Plains, VA, USA) was employed for the statistical analysis. The studied independent factors were the ferrofluid volume (20–200 μL), the extraction time (2–20 min), pH of the donor phase (2–10) and the ionic strength of the donor phase (0–10% NaCl (w/v)). All experiments are summarized in Table S3 and were carried out intra-day in 15 mL of aqueous standard solution at a concentration of 2 ng mL^{-1} ; and the desorption was accomplished with 250 μL of acetonitrile for 5 min. The adequacy of the model was evaluated by the coefficient of determination (R^2), which was ≥ 0.81 for all the UV filters. This value indicates that the designed model is efficient for the prediction of response.

Fig. 2 shows the response surface plots in terms of desirability (estimated as described in Supplementary Material) for the four factors. In Fig. 2a, it can be observed that the best responses were obtained using 100–140 μL of ferrofluid, getting the proper dispersion of the whole material and the highest elution of the analytes. For that reason, 100 μL was established for further experiments in order to minimise the use of ferrofluid. In addition, when the amount of ferrofluid was higher than 140 μL , the extraction capacity decreased because huge amounts of

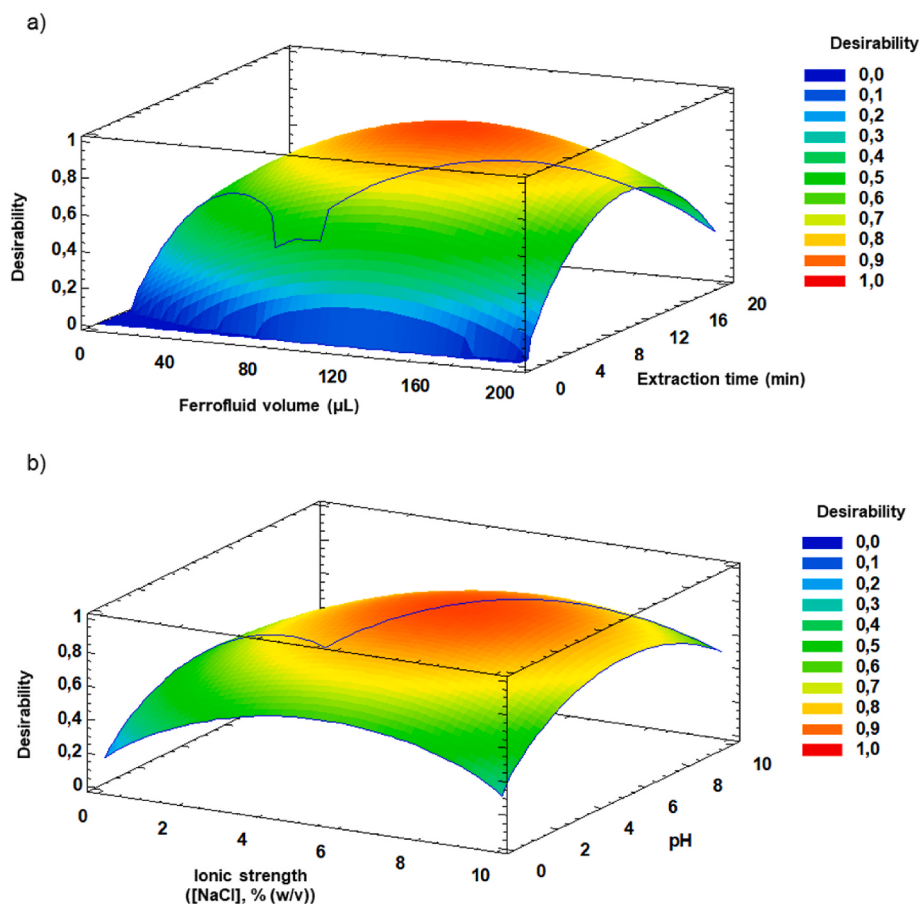


Fig. 2. Response surface of the desirability function representing the relation between the different variables: a) ferrofluid volume vs extraction time, and b) ionic strength vs pH.

ferrofluid may have difficulties to be retrieved by the magnet, thus decreasing the signal.

Regarding the extraction time, in Fig. 2a it is observed that the signal increased until ca. 10 min. At longer times, the signal decreased probably because the ferrofluid was partially separated into the $\text{CoFe}_2\text{O}_4\text{@OA}$ MNPs and the DES under vigorous stirring. This phenomenon is known as leaching effect [36]. In consequence, the stir bar only retrieved the remaining ferrofluid and the naked MNPs, but not the released DES and the analytes it contained.

On the other side, as it is shown in Fig. 2b, an improvement was observed working in the pH range of 4–6 due to the pK_a values of the UV filters (see Table S1). In this pH range, the UV filters remain in their neutral form, increasing the interaction with the hydrophobic DES and, thus, favouring their extraction.

Finally, the optimal extraction efficiency was achieved employing 6% NaCl (w/v) due to the known salting-out effect (see Fig. 2b). The extraction capacity increased at low-medium amounts of salt (i.e., 1–6%), however it decreased at high amounts. This may be produced due to the fact that the aqueous medium becomes highly ionic and viscous, causing the bad dispersion of the ferrofluid in the aqueous samples.

In summary, the optimized method consisted of 100 μL of ferrofluid, 10 min of stirring time and NaCl adjustment to 6%. The pH was not

adjusted since the normal pH in environmental waters is within the optimum interval.

3.2.2. Optimization of the desorption variables

Different desorption times (0, 2, 5 and 10 min) were tested. The obtained results (Fig. 3a) show that 2 min were enough to complete the desorption of UV filters from the extraction phase showing the maximum signals at this time. Therefore, this desorption time was selected.

The effect of the desorption solvent volume (i.e., acetonitrile) was explored. Different acetonitrile volumes (100, 250 and 500 μL) were tested. As it is shown in Fig. 3b the best results were obtained employing 100 μL . Volumes below 100 μL were insufficient to cover the neodymium magnet so they were discarded. Therefore, 100 μL of acetonitrile was selected as the appropriate volume for the desorption solvent.

3.3. Extraction performance of $\text{CoFe}_2\text{O}_4\text{@OA}$ and ferrofluid

The extraction efficiency of $\text{CoFe}_2\text{O}_4\text{@OA}$ MNPs and the ferrofluid (i.e., $\text{CoFe}_2\text{O}_4\text{@OA}$ -menthol:thymol) were compared in order to study the influence of the DES in the extraction performance. Fig. 4 shows how the extraction with the ferrofluid increased the signals of the analytes with lower sensitivity such as BZ3, IMC, MBC and BMDM. For OC, EHDP and

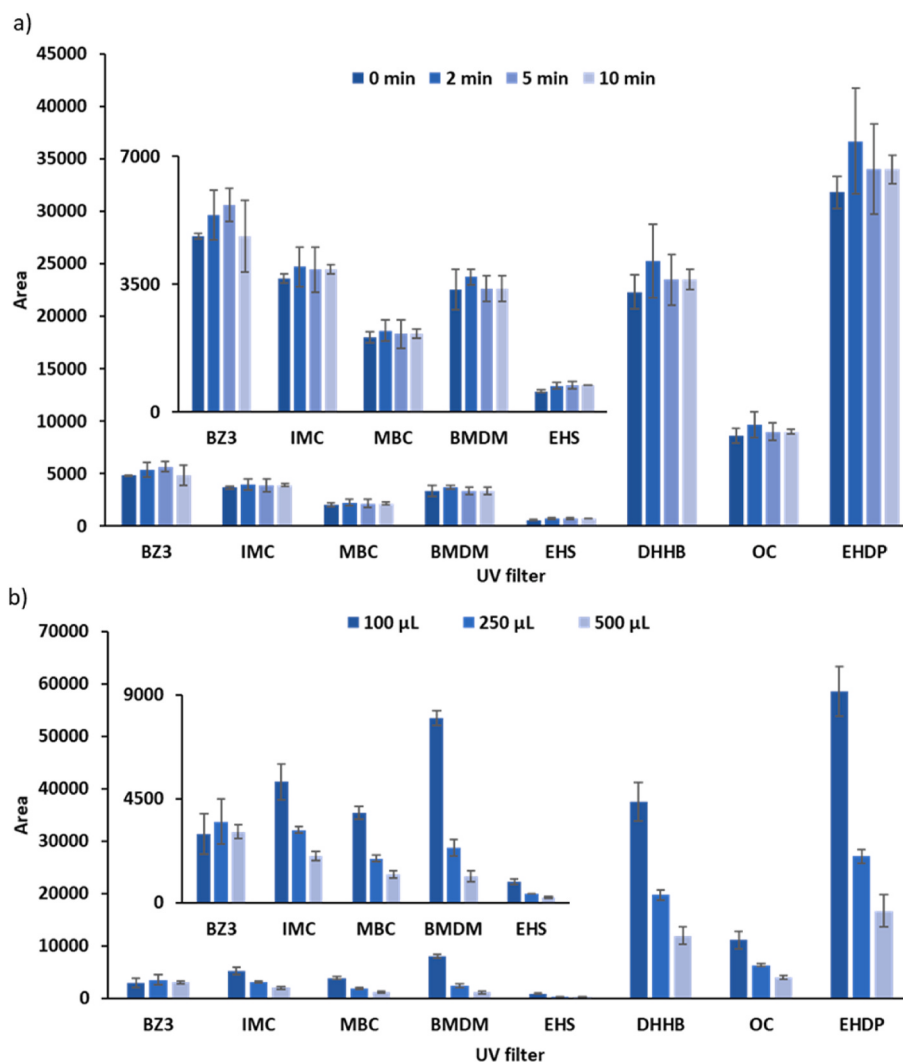


Fig. 3. a) Effect of the desorption time. Extraction conditions: 10 mL aqueous solution with 2 ng mL^{-1} of the target analytes at pH 5, 100 μL of ferrofluid and 6% NaCl (w/v). Error bars show the standard deviation of the results ($n = 3$). b) Effect of the desorption volume. Extraction conditions: 10 mL aqueous solution with 2 ng mL^{-1} of the target analytes at pH 5, 100 μL of ferrofluid and 6% NaCl (w/v). Error bars show the standard deviation of the results ($n = 3$).

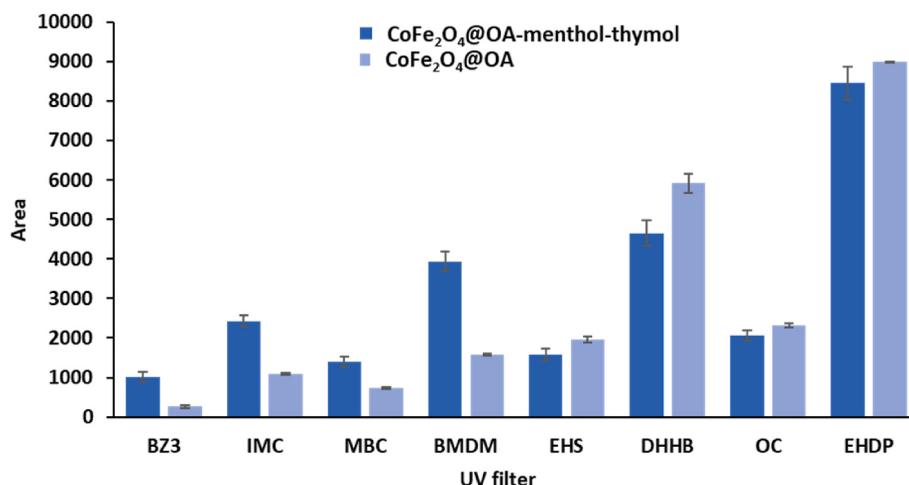


Fig. 4. Comparison of the extraction performance of the CoFe₂O₄@OA MNPs and the ferrofluid. Extraction conditions: 10 mL aqueous solution with 3 ng mL⁻¹ of EHS, 0.6 ng mL⁻¹ of BZ3, IMC and OC, 1.2 ng mL⁻¹ of MBC and BMDM, and 0.03 ng mL⁻¹ of DHHB and EHDP at pH 5, 100 μ L of ferrofluid and 6% NaCl (w/v). Error bars show the standard deviation of the results ($n = 3$).

EHS, there were not great differences employing the ferrofluid or the CoFe₂O₄@OA MNPs.

Therefore, it can be concluded that the addition of the DES to the CoFe₂O₄@OA provides a synergistic effect improving, in overall terms, the extraction efficiency for the UV filters, which increases the sensitivity of the method.

3.4. Inter-batch repeatability of the synthesis of the ferrofluid

The inter-batch repeatability of the synthesized ferrofluid was evaluated by comparing the extraction capacity of three different synthesis batches on the extraction of a 750 ng L⁻¹ standard solution under the optimized conditions. Results in Fig. 5 show that there were not significant differences ($p < 0.05$) between the three batches proving the good repeatability of the synthesis process.

3.5. Method validation

Limits of detection (LOD) and quantification (LOQ), linear working range (LR), repeatability (expressed as relative standard deviation (RSD

(%)) and enrichment factors (EF) were evaluated for method validation. In order to correct for the variability during the SBDLME process, OC-d₁₅ was used as surrogate. As consequence, the calibration was performed by plotting A_i/A_{sur} (where A_i is the peak area of the target analyte and A_{sur} is that of the surrogate) versus the target analyte concentration. The results are presented in Table 1.

The LODs and LOQs were estimated by measuring 3 and 10 times the signal to noise ratio from a 1000 ng L⁻¹ multicomponent aqueous standard solution. Then, standard solutions were injected at different concentrations after the SBDLME approach in order to find the signal with a $S/N = 3$ (for LOD) and $S/N = 10$ (for LOQ). The LODs and LOQs ranged from 7 to 83 ng L⁻¹ and from 24 to 276 ng L⁻¹, respectively, depending of the analyte.

This method provided good linearity until 20 ng mL⁻¹. However, due the low levels of UV filters expected in environmental waters, working ranges were set at different ng L⁻¹ levels according to the LOQs obtained for each UV filter and the samples requirements. Thus, 30–750 ng L⁻¹ was selected for EHDP and DHHB, 70–1750 ng L⁻¹ for BZ3, IMC and OC, 130–3250 ng L⁻¹ for BMDM and MBC and 300–7500 ng L⁻¹ for EHS. In this sense, good determination coefficients ($R^2 > 0.998$) were obtained

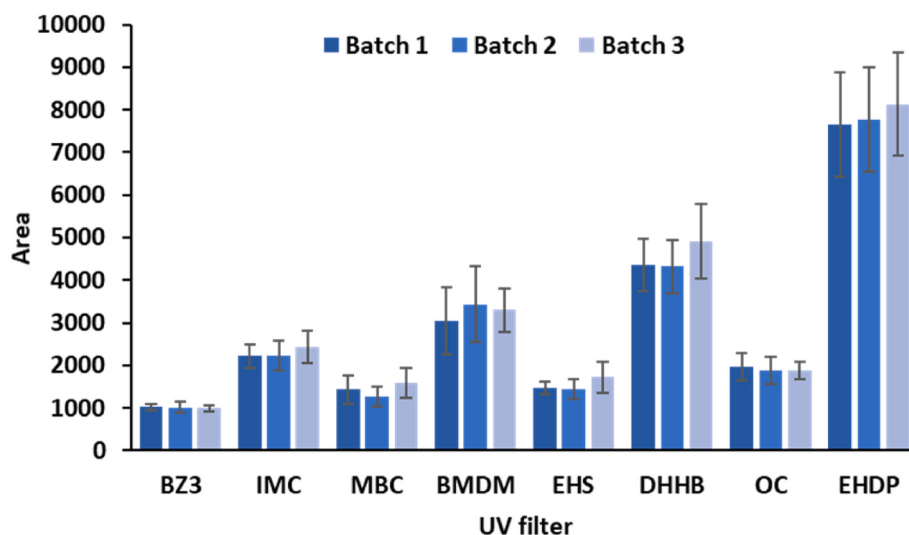


Fig. 5. Inter-batch repeatability of the synthesis process of the ferrofluid. Extraction conditions: 10 mL aqueous solution with 3 ng mL⁻¹ of EHS, 0.6 ng mL⁻¹ of BZ3, IMC and OC, 1.2 ng mL⁻¹ of MBC and BMDM, and 0.03 ng mL⁻¹ of DHHB and EHDP at pH 5, 100 μ L of ferrofluid and 6% NaCl (w/v). Error bars show the standard deviation of the results ($n = 3$).

Table 1

Figures of merit of the proposed SBDLME method.

UV filter	R ^{2a}	EF ^b	LOD ^c (ng L ⁻¹)	LOQ ^c (ng L ⁻¹)	Repeatability (RSD (%)) ^d					
					Intra-day			Inter-day		
					Level 1 ^e	Level 2 ^f	Level 3 ^g	Level 1 ^e	Level 2 ^f	Level 3 ^g
BZ3	0.9999	93	20	67	4.5	13.8	9.6	12.2	12.7	5.6
IMC	0.9998	75	16	54	6.6	6.1	5.0	9.9	12.8	14.2
MBC	0.9993	80	39	130	5.2	9.3	5.0	12.5	8.0	4.8
DHBB	0.9998	73	8	25	8.3	8.8	2.7	12.8	14.9	10.7
OC	0.9999	46	18	60	10.8	9.5	3.2	7.3	2.8	4.5
EHDP	0.9993	101	7	24	12.8	10.1	1.8	8.6	11.1	9.1
BMDM	0.9993	71	36	116	8.6	9.1	4.5	13.0	4.9	8.6
EHS	0.998	78	83	276	6.0	10.7	3.4	12.5	11.1	10.8

^a Coefficient of determination; Number of calibration points: 5.^b EF: Enrichment factor.^c LOD: Limit of detection (S/N = 3); LOQ: Limit of quantification (S/N = 10).^d RSD: relative standard deviation (%) (n = 5).^e Level 1: 30 ng L⁻¹ for DHBB and EHDP; 70 ng L⁻¹ for BZ3, IMC and OC; 130 ng L⁻¹ for MBC and BMDM; 300 ng L⁻¹ for EHS.^f Level 2: 190 ng L⁻¹ for DHBB and EHDP; 340 ng L⁻¹ for BZ3, IMC and OC; 690 ng L⁻¹ for MBC and BMDM; 1875 ng L⁻¹ for EHS.^g Level 3: 750 ng L⁻¹ for DHBB and EHDP; 1350 ng L⁻¹ for BZ3, IMC and OC; 2750 ng L⁻¹ for MBC and BMDM; 7500 ng L⁻¹ for EHS.

for all the analytes.

The intra- and inter-day repeatability was established by the extraction of five aqueous standard solutions at three different concentration levels in the same day (n = 5) and in five consecutive days (n = 5), respectively. The resultant RSD (%) were under 15% in all cases, proving the good repeatability of the proposed method.

The EFs were calculated as the ratio of the signal obtained before and after the extraction of a 2000 ng L⁻¹ aqueous standard solution, and they ranged from 46 to 101.

3.6. Analysis of environmental water samples

Three environmental waters (beach and river water) were analyzed to determine the amount of UV filters in these samples in order to evaluate this method in a real case application. Prior to analysis, the conductivity of the samples was measured to estimate their ionic strength value (i.e., 0.05% in river water, and 4% in seawater). Then, it was regulated to 6% w/v by adding NaCl. Table 2 shows the results after the SBDLME-LC-MS/MS method. As can be seen, the measured concentrations in beach 1 were noticeable higher than in beach 2, likely due to the fact it was a more crowded area for bathers and thus higher quantities of sunscreen arrive to the nearshore. On the contrary, most UV filters were not detected in river water despite it was sampled from a bathing area, probably due to the constant circulation of the water stream. As example, a chromatogram of sample beach 1 is shown in Figure S7.

Anyway, it should be added that the concentration of UV filters in that kind of aquatic samples depends on several factors, such as number

Table 2

Concentration of UV filters in three environmental water samples. Results are presented as the average value $\pm$ the standard deviation of three replicates (n = 3).

UV Filter	Found concentration (ng L ⁻¹)		
	Beach 1	Beach 2	River
BZ3	225 $\pm$ 25	<67 ^b	<20 ^a
IMC	<16 ^a	<16 ^a	<16 ^a
MBC	148 $\pm$ 13	<130 ^b	<39 ^a
DHBB	58 $\pm$ 6	<25 ^b	<25 ^b
OC	78 $\pm$ 9	84 $\pm$ 7	208 $\pm$ 2
EHDP	<24 ^b	<24 ^b	<7 ^a
BMDM	240 $\pm$ 20	<116 ^b	<36 ^a
EHS	<276 ^b	<276 ^b	<83 ^a

^a < limit of detection.^b < limit of quantification.

of swimmers, water tide and water recirculation rates along the day.

Finally, for the study of the accuracy of the method, these three samples were spiked at three different concentration levels in order to calculate the relative recoveries for each analyte. As can be seen in Table 3, good relative recoveries were obtained (80–117%), proving the absence of a significant matrix effect.

3.7. Comparison with previously reported methods

A comparison between the proposed method and some previously reported methods based on the determination of the same UV filters in environmental waters is presented in Table 4. As can be seen, the analytical performance is comparable or better than these previous methods. In general terms, compared to non-dispersive techniques (i.e., SPME and SBSE), the dispersive-based techniques (i.e., SBSDE and SBDLME) require lower extraction times. Nevertheless, SBDLME present even lower extraction times compared with those employing solid sorbents. Moreover, comparing the two SBDLME-based methods, similar results were obtained (the high limit of detection obtained for EHS attributed to its low signal employing LC-MS/MS and not to the extraction technique), proving that this new LT-DES-based ferrofluid can be employed as a cheaper and greener alternative to MILs.

Additionally, a greenness study of the presented method and the previous MIL-based SBDLME method is presented in Supplementary Material employing the ComplexGAPI [37] and AGREEprep [38] apps. As can be seen, employing complexGAPI (Fig. S8), there are not significant differences in the analysis (5 upper pentagons). However, if the synthesis of the materials is included (hexagon), a huge difference employing the MIL (Fig. S8a) and the LT-DES-based ferrofluid (Fig S8b) can be noticed, thus proving the greener synthesis of the menthol: thymol ferrofluid.

On the other side, according to AGREEprep (Fig. S9), minimum differences are observed employing the MIL (Fig. S9a) or the LT-DES-based ferrofluid (Fig. S9b), since the synthesis process is not included and it is mainly focused on the sample preparation.

4. Conclusions

A new low toxicity deep eutectic solvent (LT-DES)-based ferrofluid has been presented as an extraction phase for microextraction purposes. This ferrofluid, composed by CoFe₂O₄@OA MNPs and a 1:5 ratio of menthol and thymol DES, has two main advantages over other magnetic fluids (i.e., MILs). First of all, its components are quite less toxic and less harmful to the environment. Moreover, the synthesis is simple and safe, since only a water bath was needed for the preparation of the DES and a

Table 3

Relative recoveries after the application of the SBDLME method on three environmental water samples spiked at three concentration levels. Results are presented as the average value $\pm$ the standard deviation of three replicates ($n = 3$).

UV Filter	Beach 1			Beach 2			River		
	Level 1 ^a	Level 2 ^b	Level 3 ^c	Level 1 ^a	Level 2 ^b	Level 3 ^c	Level 1 ^a	Level 2 ^b	Level 3 ^c
BZ3	104 $\pm$ 13	105 $\pm$ 9	91 $\pm$ 9	113 $\pm$ 15	83 $\pm$ 2	87 $\pm$ 7	100 $\pm$ 4	109 $\pm$ 16	91 $\pm$ 12
IMC	96 $\pm$ 15	112 $\pm$ 11	94 $\pm$ 7	83 $\pm$ 3	80 $\pm$ 3	93 $\pm$ 7	84 $\pm$ 1	85 $\pm$ 6	98 $\pm$ 14
MBC	120 $\pm$ 1	91 $\pm$ 8	80 $\pm$ 8	109 $\pm$ 10	84 $\pm$ 7	82 $\pm$ 6	116 $\pm$ 4	80 $\pm$ 2	96 $\pm$ 5
DHMB	109 $\pm$ 7	115 $\pm$ 4	111 $\pm$ 10	89 $\pm$ 7	104 $\pm$ 8	101 $\pm$ 3	114 $\pm$ 8	107 $\pm$ 3	96 $\pm$ 6
OC	96 $\pm$ 6	107 $\pm$ 1	98 $\pm$ 4	107 $\pm$ 1	112 $\pm$ 9	112 $\pm$ 8	91 $\pm$ 3	86 $\pm$ 10	98 $\pm$ 2
EHDP	116 $\pm$ 4	101 $\pm$ 5	88 $\pm$ 7	97 $\pm$ 3	107 $\pm$ 4	102 $\pm$ 3	115 $\pm$ 6	100 $\pm$ 4	91 $\pm$ 8
BMDM	104 $\pm$ 8	94 $\pm$ 16	97 $\pm$ 13	107 $\pm$ 14	112 $\pm$ 13	104 $\pm$ 3	106 $\pm$ 3	115 $\pm$ 3	102 $\pm$ 6
EHS	80 $\pm$ 7	90 $\pm$ 10	84 $\pm$ 12	81 $\pm$ 1	103 $\pm$ 14	102 $\pm$ 2	98 $\pm$ 9	97 $\pm$ 11	96 $\pm$ 8

^a Level 1: 30 ng L⁻¹ for DHMB and EHDP; 70 ng L⁻¹ for BZ3, IMC and OC; 130 ng L⁻¹ for MBC and BMDM; 300 ng L⁻¹ for EHS.

^b Level 2: 190 ng L⁻¹ for DHMB and EHDP; 340 ng L⁻¹ for BZ3, IMC and OC; 690 ng L⁻¹ for MBC and BMDM; 1875 ng L⁻¹ for EHS.

^c Level 3: 750 ng L⁻¹ for DHMB and EHDP; 1350 ng L⁻¹ for BZ3, IMC and OC; 2750 ng L⁻¹ for MBC and BMDM; 7500 ng L⁻¹ for EHS.

Table 4

Comparison of the proposed SBDLME method and other methods focused on the determination of UV filters in environmental waters.

UV filters ^a	Extraction technique ^b	Measurement technique ^c	Extraction phase ^d	Extraction time (min)	Sample volume (mL)	LOD (ng L ⁻¹)	RR%	Ref.
BZ3, MBC, IMC, OC, EHMC, EHDP, BMDM, EHS, HMS	SBSE	TD-GC-MS	PDMS	180	20	0.2–64	75–116	[39]
BZ3, MBC, IMC, OC, EHMC, EHDP, EHS, HMS	SBSDME	LC-UV	CoFe ₂ O ₄ @OA	20	25	2400–30000	87–120	[40]
BZ1, BZ3, BZ4, BZ8, MBC, IMC, OC, EHMC, EHDP, EHS, HMS, BS, Eto, MA	SPME	GC-MS/MS	DVB/CAR/PDMS	30	10	2–1000	80–106	[41]
BZ3, MBC, IMC, OC, EHMC, EHDP, EHS, HMS	SBDLME	TD-GC-MS	[P ⁺ _{6,6,6,14}][Ni(hfacac) ₃]	10	25	9.9–27	87–117	[28]
BZ3, MBC, IMC, DHMB, OC, EHDP, BMDM, EHS	SBDLME	LC-MS/MS	CoFe ₂ O ₄ @OA-menthol:thymol	10	15	7–83	80–117	This work

^a BZ: benzophenone; MBC: methybenzylidene camphor; IMC: isoamyl p-methoxycinnamate; OC: octocrylene; EHMC: ethylhexyl methoxycinnamate; EHDP: ethylhexyl dimethyl PABA; EHS: ethylhexyl salicylate; HMS: homosalate; BMDM: butyl methoxydibenzoylmethane; BS: benzyl salicylate; Eto: octocrylene; MA: menthyl anthranilate.

^b SBSE: stir bar sorptive extraction; SBSDEME: stir bar sorptive-dispersive microextraction; SPME: solid phase microextraction; SBDLME: stir bar dispersive liquid microextraction.

^c TD-GC-MS: thermal desorption-gas chromatography-mass spectrometry; LC-UV: liquid chromatography-ultraviolet spectrometry; GC-MS/MS: gas chromatography-tandem mass spectrometry; LC-MS/MS: liquid chromatography-tandem mass spectrometry.

^d PDMS: polydimethylsiloxane; CoFe₂O₄@OA: oleic acid-coated cobalt ferrite nanoparticles; DVB/CAR/PDMS: divinylbenzene-carboxen-polydimethylsiloxane; [P⁺_{6,6,6,14}][Ni(hfacac)₃]: trihexyl(tetradecyl)phosphonium nickel(II) hexafluoroacetylacetonate ionic liquid; CoFe₂O₄@OA-menthol:thymol: oleic acid-coated cobalt ferrite nanoparticles-menthol:thymol deep eutectic solvent ferrofluid.

sonication step to form the ferrofluid.

This new ferrofluid was tested in the determination of UV filters in environmental waters employing SBDLME as microextraction technique obtaining good analytical features. This method was compared with the previous SBDLME methodology used for the same purpose, but employing a MIL as an extraction phase [28]. The proposed method showed similar results, proving the potential of this ferrofluid as a cheaper and greener alternative of MILs to be employed in future analytical approaches.

Credit author statement

A. Duque: Investigation, Data treatment, Writing – original draft; J. Grau: Investigation, Data treatment, Writing – original draft; J.L. Benédé: Methodology, Writing - reviewing and editing; R.M. Alonso: Conceptualization, Supervision, Methodology, Writing - reviewing and editing; M.A. Campanero: Conceptualization, Supervision, Methodology, Writing - reviewing and editing; A. Chisvert: Conceptualization, Supervision, Methodology, Project organization, Funding acquisition, Writing - reviewing and editing.

Declaration of competing interest

The authors declare that they have no known competing financial

interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.talanta.2022.123378>.

References

- [1] S. Armenta, S. Garrigues, F.A. Esteve-Turrillas, M. de la Guardia, Green extraction techniques in green analytical chemistry, *TrAC Trends Anal. Chem.* (Reference Ed.) 116 (2019) 248–253.
- [2] G. Li, K.H. Row, Utilization of deep eutectic solvents in dispersive liquid-liquid micro-extraction, *TrAC Trends Anal. Chem.* (Reference Ed.) 120 (2019) 115651.
- [3] S. Peng, X. Huang, Y. Huang, Y. Huang, J. Zheng, F. Zhu, J. Xu, G. Ouyang, Novel solid-phase microextraction fiber coatings: a review, *J. Separ. Sci.* 45 (2022) 282–304.
- [4] P. Ścigalski, P. Kosobucki, Recent materials developed for dispersive solid phase extraction, *Molecules* 25 (2020) 1–27.
- [5] A. Gałuszka, Z. Migaszewski, J. Namieśnik, The 12 principles of green analytical chemistry and the SIGNIFICANCE mnemonic of green analytical practices, *TrAC Trends Anal. Chem.* (Reference Ed.) 50 (2013) 78–84.
- [6] A.I. López-Lorente, F. Pena-Pereira, S. Pedersen-Bjergaard, V.G. Zuñin, S.A. Ozkan, E. Psillakis, The ten principles of green sample preparation, *TrAC Trends Anal. Chem.* (Reference Ed.) 148 (2022) 116530.
- [7] J. Grau, C. Azorín, J.L. Benedé, A. Chisvert, A. Salvador, Use of green alternative solvents in dispersive liquid-liquid microextraction: a review, *J. Separ. Sci.* 45 (2022) 210–222.
- [8] P. Makoś, E. Stupek, J. Gębicki, Hydrophobic deep eutectic solvents in microextraction techniques—A review, *Microchem. J.* 152 (2020) 104384.
- [9] Á. Santana-Mayor, R. Rodríguez-Ramos, A.V. Herrera-Herrera, B. Socas-Rodríguez, M.Á. Rodríguez-Delgado, Deep eutectic solvents. The new generation of green solvents in analytical chemistry, *TrAC Trends Anal. Chem.* (Reference Ed.) 134 (2021) 116108.
- [10] A. Shishov, A. Pochivalov, L. Nugbienyo, V. Andrich, A. Bulatov, Deep eutectic solvents are not only effective extractants, *TrAC Trends Anal. Chem.* (Reference Ed.) 129 (2020) 115956.
- [11] M.Q. Farooq, N.M. Abbasi, J.L. Anderson, Deep eutectic solvents in separations: methods of preparation, polarity, and applications in extractions and capillary electrochromatography, *J. Chromatogr., A* 1633 (2020) 461613.
- [12] Q. Zhang, K. De Oliveira Vigier, S. Royer, F. Jérôme, Deep eutectic solvents: syntheses, properties and applications, *Chem. Soc. Rev.* 41 (2012) 7108–7146.
- [13] B.B. Hansen, S. Spittle, B. Chen, D. Poe, Y. Zhang, J.M. Klein, A. Horton, L. Adhikari, T. Zelovich, B.W. Doherty, B. Gurkan, E.J. Maginn, A. Ragauskas, M. Dammun, T.A. Zawodzinski, G.A. Baker, M.E. Tuckerman, R.F. Savinell, J. R. Sangoro, Deep eutectic solvents: a review of fundamentals and applications, *Chem. Rev.* 121 (2021) 1232–1285.
- [14] H. Musarurwa, N.T. Tavengwa, Emerging green solvents and their applications during pesticide analysis in food and environmental samples, *Talanta* 223 (2021) 121507.
- [15] O.E. Plastiras, E. Andreassidou, V. Samanidou, Microextraction techniques with deep eutectic solvents, *Molecules* 25 (2020) 6026.
- [16] M. de los Á. Fernández, J. Boiteux, M. Espino, F.J.V. Gomez, M.F. Silva, Natural deep eutectic solvents-mediated extractions: the way forward for sustainable analytical developments, *Anal. Chim. Acta* 1038 (2018) 1–10.
- [17] J. Plotka-Wasyłka, M. Rutkowska, K. Owczarek, M. Tobiszewski, J. Namiesnik, Extraction with environmentally friendly solvents, *TrAC Trends Anal. Chem.* (Reference Ed.) 91 (2017) 12–25.
- [18] J. Plotka-Wasyłka, M. Rutkowska, M. de la Guardia, Are deep eutectic solvents useful in chromatography? A short review, *J. Chromatogr., A* 1639 (2021) 461918.
- [19] J. Lee, D. Jung, K. Park, Hydrophobic deep eutectic solvents for the extraction of organic and inorganic analytes from aqueous environments, *TrAC Trends Anal. Chem.* (Reference Ed.) 118 (2019) 853–868.
- [20] R. Nayeibi, F. Shemirani, Ferrofluids-based microextraction systems to process organic and inorganic targets: the state-of-the-art advances and applications, *TrAC Trends Anal. Chem.* (Reference Ed.) 138 (2021) 116232.
- [21] M.Á. Aguirre, A. Canals, Magnetic deep eutectic solvents in microextraction techniques, *TrAC Trends Anal. Chem.* (Reference Ed.) 146 (2022) 116500.
- [22] M. Sajid, K. Kalinowska, J. Plotka-Wasyłka, Ferrofluids based analytical extractions and evaluation of their greenness, *J. Mol. Liq.* 339 (2021) 116901.
- [23] M. Ebrahimi, A short review on ferrofluids surface modification by natural and biocompatible polymers, *Nanomedicine J* 3 (2016) 155–158.
- [24] R. González-Martín, A. Gutiérrez-Serpa, V. Pino, The use of ferrofluids in analytical sample preparation: a review, *Separations* 8 (2021) 1–14.
- [25] E. Psillakis, Vortex-assisted liquid-liquid microextraction revisited, *TrAC Trends Anal. Chem.* (Reference Ed.) 113 (2019) 332–339.
- [26] M. Sajid, Magnetic ionic liquids in analytical sample preparation: a literature review, *TrAC Trends Anal. Chem.* (Reference Ed.) 113 (2019) 210–223.
- [27] B. Hashemi, P. Zohrabi, K.H. Kim, M. Shamsipur, A. Deep, J. Hong, Recent advances in liquid-phase microextraction techniques for the analysis of environmental pollutants, *TrAC Trends Anal. Chem.* (Reference Ed.) 97 (2017) 83–95.
- [28] A. Chisvert, J.L. Benedé, J.L. Anderson, S.A. Pierson, A. Salvador, Introducing a new and rapid microextraction approach based on magnetic ionic liquids: stir bar dispersive liquid microextraction, *Anal. Chim. Acta* 983 (2017) 130–140.
- [29] J.L. Benedé, J.L. Anderson, A. Chisvert, Trace determination of volatile polycyclic aromatic hydrocarbons in natural waters by magnetic ionic liquid-based stir bar dispersive liquid microextraction, *Talanta* 176 (2018) 253–261.
- [30] M.J. Trujillo-Rodríguez, J.L. Anderson, In situ generation of hydrophobic magnetic ionic liquids in stir bar dispersive liquid-liquid microextraction coupled with headspace gas chromatography, *Talanta* 196 (2019) 420–428.
- [31] A.R. Zarei, M. Nedaei, S.A. Ghorbanian, Deep eutectic solvent based magnetic nanofluid in the development of stir bar sorptive dispersive microextraction: an efficient hyphenated sample preparation for ultra-trace nitroaromatic explosives extraction in wastewater, *J. Separ. Sci.* 40 (2017) 4757–4764.
- [32] A. Chisvert, J.L. Benedé, A. Salvador, Current trends on the determination of organic UV filters in environmental water samples based on microextraction techniques – a review, *Anal. Chim. Acta* 1034 (2018) 22–38.
- [33] K. Maaz, A. Mumtaz, S.K. Hasanain, A. Ceylan, Synthesis and magnetic properties of cobalt ferrite (CoFe₂O₄) nanoparticles prepared by wet chemical route, *J. Magn. Magn. Mater.* 308 (2007) 289–295.
- [34] S.A.M. Hussin, P. Varanusupakul, S. Shahabuddin, B.Y. Hui, D. Mohamad, Synthesis and characterization of green menthol-based low transition temperature mixture with tunable thermophysical properties as hydrophobic low viscosity solvent, *J. Mol. Liq.* 308 (2020) 113015.
- [35] L. Kafi-ahmadi, S. Khademinia, M.N. Nansa, A.A. Alemi, M. Mahdavi, A.P. Marjani, Co-precipitation synthesis, characterization of CoFe₂O₄ nanomaterial and evaluation of its toxicity behavior on human leukemia cancer K562 cell line, *J. Chil. Chem. Soc.* 65 (2020) 4845–4848.
- [36] V. Vázquez-Gomis, J. Grau, J.L. Benedé, D.L. Giokas, A. Chisvert, A. Salvador, Fundamentals and applications of stir bar sorptive dispersive microextraction: a tutorial review, *Anal. Chim. Acta* 1153 (2021) 338271.
- [37] J. Plotka-Wasyłka, W. Wojnowski, Complementary green analytical procedure index (ComplexGAPI) and software, *Green Chem.* 23 (2021) 8657–8665.
- [38] W. Wojnowski, M. Tobiszewski, F. Pena-Pereira, E. Psillakis, AGREEprep – analytical greenness metric for sample preparation, *TrAC Trends Anal. Chem.* (Reference Ed.) 149 (2022) 116553.
- [39] R. Rodil, M. Moeder, Development of a method for the determination of UV filters in water samples using stir bar sorptive extraction and thermal desorption-gas chromatography-mass spectrometry, *J. Chromatogr., A* 1179 (2008) 81–88.
- [40] J.L. Benedé, A. Chisvert, D.L. Giokas, A. Salvador, Development of stir bar sorptive-dispersive microextraction mediated by magnetic nanoparticles and its analytical application to the determination of hydrophobic organic compounds in aqueous media, *J. Chromatogr., A* 1362 (2014) 25–33.
- [41] M. Vila, M. Celeiro, J.P. Lamas, C. Garcia-Jares, T. Dagnac, M. Llopart, Simultaneous in-vial acetylation solid-phase microextraction followed by gas chromatography tandem mass spectrometry for the analysis of multiclass organic UV filters in water, *J. Hazard Mater.* 323 (2017) 45–55.