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Determination of phenols in waters by stir membrane liquid–liquid–liquid microextraction coupled to liquid chromatography with ultraviolet detection

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ABSTRACT

A simple and rapid method for the determination of eleven phenols in water samples is presented. The target analytes are isolated by stir membrane liquid–liquid microextraction working under the three-phase mode. An alkaline aqueous solution is used as extractant phase while octanol is selected as supported liquid membrane solvent. The target analytes are separated and determined by liquid chromatography (LC) with ultraviolet detection (UV). All the variables involved in the extraction process have been studied in depth. Low detection limits (in the range from 82.1 ng/L for phenol to 452 ng/L for 2,4,5-trichlorophenol) were obtained. The repeatability, expressed as relative standard deviation (RSD), varied between 1.3% (for 4-nitrophenol) and 8.0% (for 4-chlorophenol). The enrichment factors were in the range from 168 (for 2,4,5-trichlorophenol) to 395 (for 3-chlorophenol). The proposed procedure was applied for the direct determination of the eleven phenols in some real water samples including river, well and tap waters. The accuracy was evaluated by means of a recovery study, the results being in the range of 87–120%.

1. Introduction

Due to their toxicity, persistence and unpleasant organoleptic properties [1,2] both the US Environmental Protection Agency (EPA) and the European Union (EU) have classified several phenols as priority pollutants [3]. Their input into the ecosystems results directly from the human activity or indirectly from the transformation of natural or synthetic chemicals and they are usually found in waters from different sources [4–7].

Several strategies have been described for the quantification of phenolic compounds in water samples, including separation techniques such as liquid chromatography (LC) [8–10] or gas chromatography (GC) [11–13] coupled to different detectors. Due to the low volatility character of phenolic compounds, LC is employed more often than GC because analyte derivatization is not required. As a result of the complex nature of some environmental samples and the low concentration of phenols in such samples, their isolation and preconcentration is commonly necessary prior to their quantitative determination. Liquid–liquid extraction (LLE) [14] and solid-phase extraction (SPE) [15] are the most usual techniques for this purpose. However, these techniques require an appreciable amount of toxic organic solvents either for the extraction or elution steps, which are hazardous to the operators and environmental unfriendly. Therefore, a variety of microextraction techniques that reduce or even avoid the use of organic solvents have been developed in recent years. Among them, solid-phase microextraction (SPME) and liquid-phase microextraction (LPME) are the two predominant techniques for analysis of phenols. SPME presents some drawbacks such as limited lifetime, fragility of fibers and possibility of sample carry-over [16]. In addition, the SPME of highly polar compounds like phenols is usually complicated, an appropriate derivatization step being necessary. In this context LPME results to be an excellent alternative to SPME. LPME is very versatile taking into account its different formats and the great variety of solvents that can be employed (covering a wide range of polarities).

The usefulness of membranes for the development of new sample enrichment techniques has been widely described [17,18]. Polymeric membranes are very attractive in the extraction context taking into consideration their high surface to length ratio, availability, wide chemical composition and formats. The use of a hydrophobic membrane for phases separation allows the proposal of efficient and automated sample pre-treatment techniques, such as supported liquid membrane extraction (SLME). SLME [19,20] is based on a three-phase system with an organic solvent immobilized in the pores of a porous-membrane that acts as a physical barrier between two aqueous phases (the sample and the acceptor phase). SLME has been employed for the extraction of chlorinated phenols in waters providing limits of detection in the low ng/L range using liquid chromatography coupled to electrochemical detection [21].

In the microextraction context, hollow fiber-protected liquid-phase microextraction (HF-LPME) [22] has been extensively employed due to its simplicity and robustness. In HF-LPME a hol-

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low porous polypropylene fiber of minimal dimensions is employed as the container of the acceptor phase. The target analytes are transferred from the sample (aqueous), through the organic solvent immobilized (as a supported liquid membrane) in the pores of the fiber, to the acceptor solution (aqueous or organic) located in the lumen of the hollow fiber. Depending on the number of phases involved in the extraction, HF-LPME can operate in the two-phase or the three- phase mode [23]. The two-phase mode is similar to classic LLE while the three-phase mode is analogous to classic LLE with back-extraction. HF-LPME presents a high sample-to-acceptor volume ratio, providing therefore high analyte enrichment factors without any evaporation and reconstitution steps. Moreover, it is a very efficient technique for sample clean-up, reducing or eliminating potential problems from matrix components. Despite its usefulness, HF-LPME develops under passive diffusion which negatively affects to the extraction recovery. The kinetics of the extraction may be improved using larger fibers and working under continuous stirring of the sample.

A new liquid microextraction approach, called stir membrane liquid–liquid microextraction (SM-LLME), has been recently proposed [24]. The extraction technique involves the advantages of LPME and stirring in the same unit allowing the extraction of the analytes in a simple and efficient way. In this case, the SM-LLME is proposed under a three-phase format for the extraction of selected phenolic compounds from water samples. All the variables involved in the extraction process have been considered in depth. The method has been characterized in terms of linearity, sensitivity, precision and accuracy with very good features.

2. Experimental

2.1. Reagents, materials and samples

All the reagents were of analytical grade or better. Sigma–Aldrich (Madrid, Spain) provided the analytes: phenol (P); 4-nitrophenol (4NP); 3-nitrophenol (3NP); 4-chlorophenol (4CP); 3-chlorophenol (3CP); 2,5-dimethylphenol (2,5DMP); 4-chloro-3-methylphenol (4C3MP); 2,6-dichlorophenol (2,6DCP); 3,4-dichlorophenol (3,4DCP); 3,5-dichlorophenol (3,5DCP) and 2,4,5-trichlorophenol (2,4,5TCP). Stock standard solutions of each analyte were prepared in methanol (Scharlab, Barcelona, Spain) at a concentration of 2 g/L and stored in the dark at 4 °C. Working solutions (containing either mixtures or individual compounds) were daily prepared by a rigorous dilution of the stock solutions with Milli-Q water (Millipore Corp., Madrid, Spain) or methanol as required.

Sodium hydroxide solutions were used as acceptor phases, while hydrochloric acid was employed to adjust the sample pH. Octanol was used as solvent for the supported liquid membrane. These reagents were also purchased from Scharlab.

Acetonitrile (Scharlab) and sodium dihydrogen phosphate (Sigma–Aldrich) (20 mM, pH 2.5) were employed as components of the mobile phase.

PTFE membranes (10 μm of pore size, 100 μm in thickness) were employed for the construction of the extraction unit. The 1 mL empty SPE cartridges and PTFE top-caps, necessary to construct the extraction devices, were obtained from Supelco (Madrid, Spain).

Water samples were collected in amber-glass bottles without headspace. The samples were all stored in the dark at 4 °C until their analysis.

2.2. Chromatographic system and conditions

Liquid chromatographic analyses were performed using a HP1100 series liquid chromatograph (Agilent, Palo Alto, CA) equipped with a binary high-pressure pump for mobile phase delivery, an autosampler and a single wavelength photometer (HP1100 series) for analytes determination. Data analysis was carried out using HP ChemStation software.

Chromatographic separation was developed on a LiChrosorb C_{18} (4.6 mm × 250 mm) column (Análisis Vínicos, Tomelloso, Spain), using acetonitrile (solvent A) and a 20 mM sodium dihydrogen phosphate buffer adjusted at pH 2.5 (solvent B) as mobile phase components. For analytes separation a slight gradient program was employed. From 0 to 3 min, the composition of the mobile phase remained constant in 50% of solvent A. Later on, the proportion of solvent A was linearly increased to 60% in 20 min. After each run, a 10 min re-equilibration period is required. The injection volume was 10 μL, the flow rate was maintained at 1 mL/min and the analytes were monitored at 220 nm.

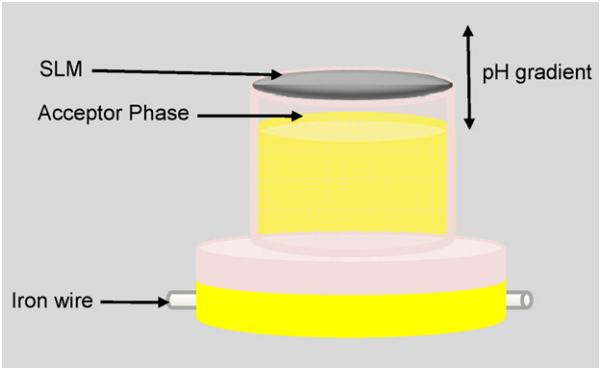

Fig. 1. Scheme of the extraction unit employed in stir membrane liquid–liquid–liquid microextraction. SLM, supported liquid membrane.

2.3. Extraction unit

The extraction unit, which was described elsewhere [24], is schematically presented in Fig. 1. It consists of a PTFE body which is pierced by an iron wire to allow its magnetic stirring. The polymeric body presents an internal chamber (internal volume of ca. 50 μL) which is filled with the acceptor phase. The internal chamber is protected by a polymeric membrane, avoiding potential losses of the acceptor phase during extraction. Considering that the device works under the three-phase mode, the membrane was impregnated with octanol to form a supported liquid membrane.

Between extractions, the unit can be re-used, only a soft cleaning process (with methanol and water) being required. The polymeric membrane is replaced every new extraction.

Finally, it should be noted that the extraction device is constructed using commercially available materials which are also characterized by their reproducible manufacturing. This is a key aspect to support the reproducibility of the extraction units.

2.4. Extraction procedure

The extraction unit was filled with 50 μL of a sodium hydroxide solution (pH 13) which acted as acceptor phase. Later on, the polymeric membrane was properly placed and fixed by displacing the external body of the unit through the internal one as it is described elsewhere [24]. In these conditions, the extraction unit remained completely closed during the extraction. Afterwards, the pores of the membrane were impregnated with octanol (forming the SLM) and the unit was directly immersed in 20 mL of the aqueous standard or sample. The extraction vial was finally located in a magnetic stirrer, the extraction of the analytes taking place at 500 rpm during 45 min.

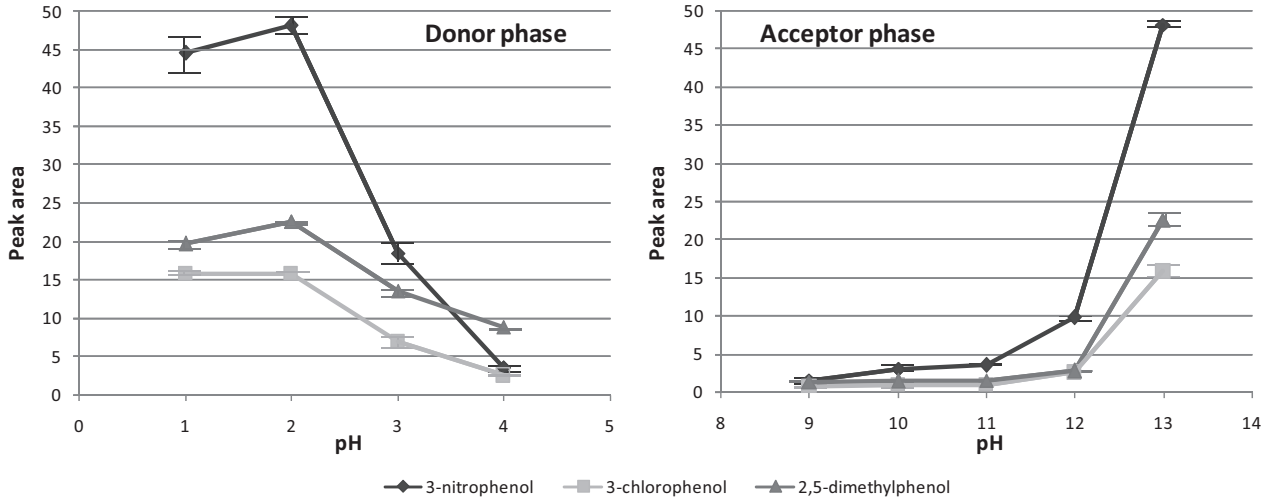

Fig. 2. Effect of the pH of the donor and acceptor phases on the extraction of three model analytes, namely: 3-nitrophenol; 3-chlorophenol and 2,5-dimethylphenol.

The final extracts, which were collected using a 100 μL glass-syringe, were transferred to a HPLC vial and neutralized by adding 0.5 μL of HCl in order to achieve a good chromatographic resolution. 10 μL of the neutralized extracts were finally injected into the chromatograph for analysis.

3. Results and discussion

Three-phase LPME mode is especially appropriate for the extraction of phenolic compounds since these analytes present ionizable groups in their chemical structure. In this mode, the pH gradient established at both sides of the SLM is the driving force of the extraction providing high isolation recoveries. For this reason, the SM-LLME was evaluated under the three-phase format. The main aims of the proposed extraction technique were (i) to isolate the analytes from the sample matrix for clean-up purposes and (ii) to preconcentrate the analytes improving the sensitivity of the determination. In order to obtain high enrichment factors and extraction recoveries of the phenols, the stir membrane liquid–liquid–liquid microextraction (SM-LLLME) was previously optimized taking into consideration some variables such as sample and acceptor phases pH, ionic strength, stirring speed, extraction time and sample volume. The method was optimized following a one-at-a-time variable approach using the areas of the chromatographic peaks as analytical signals.

3.1. Sample and acceptor phases pH

In order to help the transference of the analytes between the donor and acceptor phases, a pH gradient at both sides of the SLM should be created. As the target compounds are acidic, the pH of the donor solution (sample) should be adjusted to promote the formation of the uncharged species, which are easily transferred to the SLM. For this reason, the pH of donor phase was studied in the range from 1 to 4 maintaining the acceptor phase at pH 13. The peak areas for all the analytes increased inversely to the pH, the highest value being obtained at pH 2.

The pH of the acceptor phase was studied in the range of 9–13. The peak areas of all the analytes increased with pH from 9 to 13. Thus, pH 13 was chosen as the optimum value.

The effect of both variables on the extraction of three model analytes, corresponding to the three different phenols families (nitrophenols, chlorophenols and alkylphenols) is presented in Fig. 2.

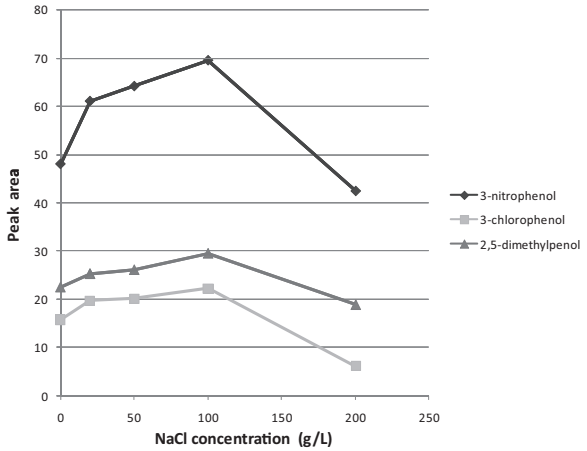

Fig. 3. Effect of the ionic strength (expressed as the concentration of sodium chloride) on the extraction of three model analytes, namely: 3-nitrophenol; 3-chlorophenol and 2,5-dimethylphenol.

3.2. Effect of the ionic strength on the extraction

Ionic strength is an interesting factor since it can affect the analyte recovery when supported liquid membranes (SLM) are employed [25]. For this purpose, the influence of the ionic strength was evaluated in the range from 0 to 200 g/L using sodium chloride as model electrolyte. As can be seen in Fig. 3, the peak areas of the phenols increased with the electrolyte concentration up to 100 g/L, decreasing for higher concentrations. The initial addition of salt decreases the solubility of the analytes in the aqueous matrix by a salting-out effect, increasing their partitioning into the SLM [26]. When the ionic strength is further increased the molecules of the electrolyte begin to interact with the analyte molecules, reducing their extraction [27]. Therefore, 100 g/L of sodium chloride was selected for subsequent experiments.

3.3. Effect of the stirring rate on the extraction

The stirring of the sample during a LPME procedure plays a key role since it improves the mass transference of the analytes from the donor to the acceptor phase. In fact, the stirring induces the convection of the sample affecting directly to the Nerst layer. Therefore, the distribution equilibrium between the involved phases can be achieved quickly. This aspect has two different connota-

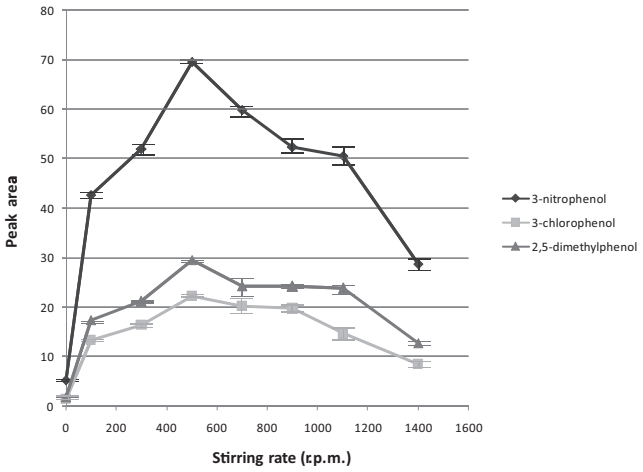

Fig. 4. Effect of the stirring rate on the extraction of three model analytes, namely: 3-nitrophenol; 3-chlorophenol and 2,5-dimethylphenol.

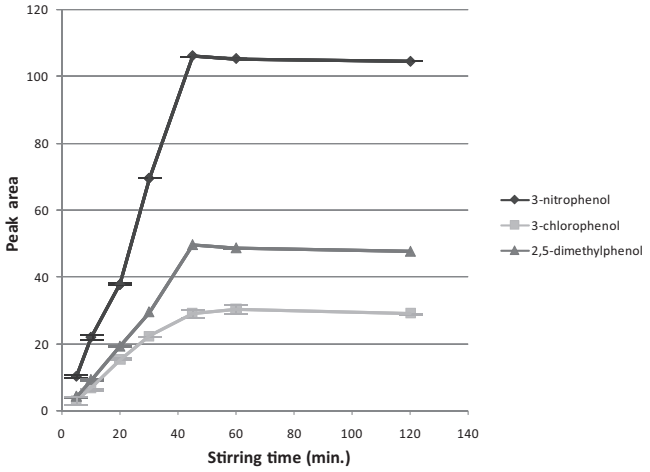

Fig. 5. Effect of the stirring time on the extraction of three model analytes, namely: 3-nitrophenol; 3-chlorophenol and 2,5-dimethylphenol.

tions. On the one hand, the sample throughput is increased since the extraction time is reduced. On the other hand, the sensitivity is improved as the extraction is facilitated. The stirring rate was evaluated in the range from 0 to 1400 rpm, each point being evaluated in triplicate. In the light of the results presented in Fig. 4, the extraction increased with the stirring rate from 0 to 500 rpm. When the stirring rate was further increase from 500 to 1400 rpm, the enrichment factor decreased. This behavior could be ascribed to different causes. First of all, the use of high stirring rates may induce the loss (detaching) of the organic solvent employed as SLM, reducing the extraction efficiency. Moreover, at higher velocities a vortex is created directly above of the extraction device reducing the contact between the sample and extractant. Consequently, a stirring rate of 500 rpm was chosen as the optimum value.

3.4. Effect of the stirring time on the extraction

The stirring time is another important parameter that influences the analytes transport across the SLM. Its influence on the extraction of the target phenols was investigated in the range from 0 to 120 min. According to the results showed in Fig. 5, the extraction of the analytes increases almost linearly with the time up to 45 min. A slight increase is observed for further times. According to the results, the optimum value was fixed at 45 min for sensitivity enhancement.

3.5. Effect of the sample volume on the extraction

The preconcentration factors can be improved increasing the volume ratio of donor solution (sample) and acceptor phase. The effect of the sample volume on the analytical signal was evaluated in the range from 10 to 100 mL. The signals increased up to 20 mL (data not shown) for all analytes, remaining almost constant for higher volumes. This behavior can be ascribed to the octanol solubility in water which increases with the sample volume. According to these results, 20 mL was selected as the optimum value in order to quantify the target analytes at lower concentration. In these conditions, the volume ratio between phases is ca. 400.

3.6. Analytical figures of merit

The optimized SM-LLLME procedure was characterized in terms of linearity (linear ranges and correlation coefficient), precision (expressed as relative standard deviation), sensitivity (limits of detection) and extraction efficiency (enrichment factors and absolute extraction recovery). The results are summarized in Table 1. In this sense, a calibration graph for each analyte was constructed by extracting in triplicate 8 working aqueous standards containing all the analytes at concentrations in the range from 100 ng/L to 500 μg/L. For all the analytes, a good linearity ($R > 0.998$) was observed.

The detection limits, calculated from the calibration curve parameters, varied between 82.1 ng/L (for phenol) and 452 ng/L (for

Table 1
Figures of merit of the proposed method for the determination of 11 phenols in water.

Analyte	LOD[a]	RSD[b]	EF[c]	ER[d]
Phenol	82.1	1.9	331	82.7
4-Nitrophenol	91.6	1.3	344	85.9
3-Nitrophenol	115.1	3.1	365	91.4
4-Chlorophenol	284.2	8.0	317	79.2
3-Chlorophenol	200.0	5.7	395	98.7
2,5-dimethylphenol	152.6	2.5	390	97.4
4-Chloro-3-methylphenol	198.1	3.4	374	93.4
2,6-Dichlorophenol	381.8	7.8	363	90.8
3,4-Dichlorophenol	363.6	5.4	359	89.6
3,5-Dichlorophenol	354.8	5.3	263	65.8
2,4,5-Trichlorophenol	452.6	6.7	168	42.0

[a] LOD, limit of detection, expressed in ng/L.
[b] RSD, relative standard deviation ($n = 6$), calculated at 2 μg/L level.
[c] EF, enrichment factor.
[d] ER, absolute extraction recovery.

Table 2
Recovery study performed on real samples spiked with the analytes at a concentration of 2 μg/L.

Analyte	River I	River II	River III	Well I	Well II	Well III
Phenol	101 ± 2	96 ± 2	98 ± 2	102 ± 2	101 ± 2	102 ± 2
4-Nitrophenol	103 ± 1	99 ± 1	102 ± 1	99 ± 1	98 ± 1	99 ± 1
3-Nitrophenol	108 ± 3	95 ± 3	103 ± 3	100 ± 3	96 ± 2	101 ± 4
4-Chlorophenol	120 ± 10	94 ± 8	105 ± 8	106 ± 8	91 ± 7	95 ± 8
3-Chlorophenol	93 ± 5	92 ± 5	99 ± 6	92 ± 5	103 ± 6	95 ± 5
2,5-Dimethylphenol	95 ± 2	103 ± 3	100 ± 2	97 ± 2	98 ± 2	103 ± 3
4-Chloro-3-methylphenol	102 ± 3	100 ± 3	98 ± 3	96 ± 3	106 ± 4	100 ± 3
2,6-Dichlorophenol	118 ± 9	102 ± 8	97 ± 8	110 ± 9	97 ± 8	106 ± 8
3,4-Dichlorophenol	103 ± 6	104 ± 6	95 ± 5	96 ± 5	97 ± 5	94 ± 5
3,5-Dichlorophenol	105 ± 6	101 ± 5	95 ± 5	108 ± 6	104 ± 6	90 ± 5
2,4,5-Trichlorophenol	119 ± 8	102 ± 7	95 ± 6	93 ± 6	103 ± 7	95 ± 6

Analyte	Well IV	Well V	Tap I	Tap II	Tap III	Tap IV
Phenol	99 ± 2	100 ± 2	99 ± 2	101 ± 2	100 ± 2	102 ± 2
4-Nitrophenol	100 ± 1	102 ± 1	101 ± 1	100 ± 1	100 ± 1	99 ± 1
3-Nitrophenol	99 ± 3	98 ± 3	96 ± 3	103 ± 3	102 ± 3	98 ± 3
4-Chlorophenol	98 ± 8	108 ± 9	89 ± 7	106 ± 8	102 ± 8	94 ± 8
3-Chlorophenol	97 ± 5	105 ± 6	99 ± 6	105 ± 6	102 ± 6	109 ± 6
2,5-Dimethylphenol	99 ± 2	100 ± 2	97 ± 2	98 ± 2	101 ± 3	104 ± 3
4-Chloro-3-methylphenol	100 ± 3	102 ± 3	105 ± 4	98 ± 3	94 ± 3	100 ± 3
2,6-Dichlorophenol	86 ± 7	100 ± 8	105 ± 8	105 ± 8	97 ± 8	87 ± 7
3,4-Dichlorophenol	109 ± 6	104 ± 6	103 ± 6	95 ± 5	95 ± 5	103 ± 6
3,5-Dichlorophenol	102 ± 5	93 ± 5	106 ± 6	97 ± 5	96 ± 5	101 ± 5
2,4,5-Trichlorophenol	107 ± 7	93 ± 6	100 ± 7	101 ± 7	95 ± 6	98 ± 7

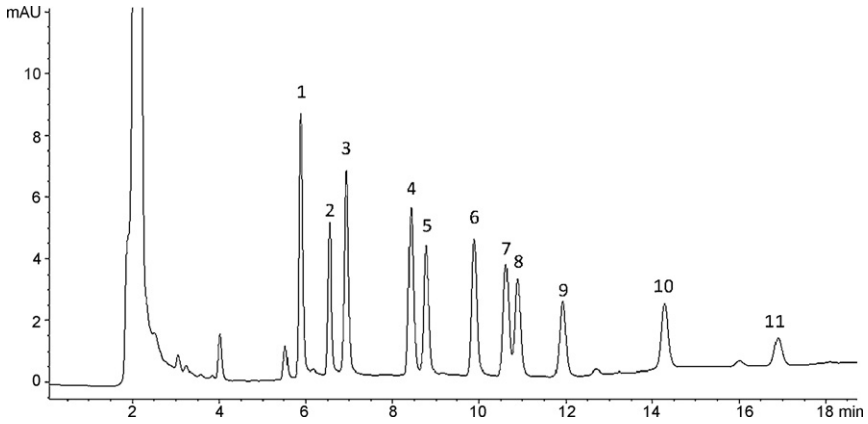

Fig. 6. Chromatogram obtained after the extraction (following the previously optimized SM-LLLME procedure) of a sample spiked with the 11 phenols at a concentration level of 1 μg/L. (1) phenol; (2) 4-nitrophenol; (3) 3-nitrophenol; (4) 4-chlorophenol; (5) 3-chlorophenol; (6) 2,5-dimethylphenol; (7) 4-chloro-3-methylphenol; (8) 2,6-dichlorophenol; (9) 3,4-dichlorophenol; (10) 3,5-dichlorophenol and (11) 2,4,5-trichlorophenol.

Table 3
Comparison of the presented method for the determination of phenols in water with other microextraction techniques also coupled to liquid chromatography with UV detection.

Extraction technique	Vs[a] (mL)	Et[b] (min)	LOD[c] (μg/L)	RSD[d] (%)	Reference
SM-LLLME	20	45	0.08–0.45	1.3–8.0	Present article
SPME	4	40	1–10	0.7–12.0	[28]
LPME with back extraction	2	35	0.5–2.5	5.4–11.5	[29]
SPME	3.5	30	0.4–23	8.9–18.1	[30]
In tube SPME	0.7	10	4–16	1.2–23	[31]
HF-LPME	15	60	0.5–1	4.3–5.9	[32]
SPME	4	40	1.1–5.9	6.3–15	[33]
SPME	4	30	0.25–3.67	1.52–6.38	[34]
LLLME	14	40	0.049–0.081	3.3–5.4	[35]

[a] Vs, volume of sample.
[b] Et, extraction time.
[c] LOD, limit of detection.
[d] RSD, relative standard deviation.

2,4,5-trichlorophenol). These values were concordant with those obtained using a signal-to-noise ratio of 3.

The repeatability of the method (expressed as relative standard deviation) was evaluated at 2 μg/L in septuplicate resulting to be in the range from 1.3% (4-nitrophenol) to 8% (4-chlorophenol).

The enrichment factors for all the analytes, which were obtained by comparing the calibration graphs before and after the extraction process, were in the range from 168 (for 2,4,5-trichlorophenol) to

395 (for 3-chlorophenol). The extraction recoveries were in the range from 79.2 to 98.7 which highlight the good performance of the proposed technique. Only two of the analytes, 3,5-dichlorophenol and 2,4,5-trichlorophenol present lower extraction recoveries.

In order to validate the proposed method, twelve real environmental water samples, including well, river and tap water were analyzed. The results show that the contents of phenols in the 12 samples were under the detection limits for all the analytes. A recovery study was therefore performed by spiking the samples at the concentration level of 1 μg/L. Taking into account their detection limits, the recovery study for 2,6-dichlorophenol, 3,4-dichlorophenol, 3,5 dichlorophenol and 2,4,5-trichlorophenol was performed at the concentration level of 2 μg/L. Table 2 shows that the recoveries were all in the range of 87 between 120. As an example, a chromatogram obtained for the analysis of a spiked water sample at 1 μg/L of each phenol is presented in Fig. 6.

4. Conclusions

The potential of stir membrane liquid–liquid–liquid microextraction has been demonstrated as a sample preparation technique prior to HPLC. The developed technique allows the efficient isolation and preconcentration of the target analytes from environmental water samples providing high enrichment factors.

The method has been completely characterized studying in depth the influence of all the variables on the analytical signal. Furthermore, the methodology was successfully validated through a recovery study using independent water samples containing the analytes. Stir membrane liquid–liquid–liquid microextraction combined with HPLC–UV has been illustrated to be viable, easy to use, rapid and economical technique for analysis of phenols in aqueous samples.

Table 3 presents a critical comparison of the proposed technique with other microextraction techniques. For comparative purposes, only those procedures coupled to liquid chromatography with UV detection have been considered. As can be seen, within all the approaches [28–35] liquid phase microextraction working under the three-phase format provides the best results in terms of sensitivity and precision. This aspect is due to the ionic nature, which is pH-dependent, of the target phenols. Except for the LLLME approach [35], which requires a more complicated assembly, SM-LLLME surpasses to its counterparts.

Further research will be focused on the evaluation of more complex matrixes and the potential automation of the technique.

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