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Ionic liquid based in situ solvent formation microextraction coupled to thermal desorption for chlorophenols determination in waters by gas chromatography/mass spectrometry☆

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ABSTRACT

A simple and efficient method for the determination of ten chlorophenols (including mono, di, tri, tetra and pentachlorophenols) in water samples is presented. The analytical method is based on a previous derivatization of the target compounds with acetic anhydride, being the derivatized compounds finally isolated/preconcentrated by an in situ solvent formation microextraction. Later on the extractant (an ionic liquid) containing the analytes is recovered by centrifugation and thermally desorbed. The analytes are finally separated and determined by gas chromatography/mass spectrometry. The main variables involved in the extraction and thermal desorption steps have been studied in depth. Once evaluated, the analytical method has been characterized in terms of linearity, sensitivity, precision and accuracy. The limits of detection were in the range from 60 ng L^{-1} (4-chlorophenol) to 440 ng L^{-1} (pentachlorophenol) while the precision, expressed as relative standard deviation, was in the interval from 4.5% (2,6-dichlorophenol) to 9.9% (3-chlorophenol). In addition, acceptable recovery values were obtained in samples of different nature, including river, tap and reservoir water samples.

1. Introduction

Chlorophenols are organic compounds widely used as disinfectants, pesticides, herbicides, wood preservatives and pulp bleaching agents. Chemically, they are phenols substituted with chlorine atoms (in the range from 1 to 5) in any position and they can be classified according to their substitution degree in mono, di, tri, tetra and pentachlorophenols. Chlorophenols can be found in different environmental compartments due to their widespread use [1]. In this sense, the most volatile compounds (mono and dichlorophenols) can be found in the air although they are usually degraded by sunlight [1]. They present a great tendency to be retained in soils and sediments due to their interaction with the organic fraction [2]. In addition, they can be found in water, especially in drinking water due to the chlorination process [3].

Chlorophenols are considered toxic chemical substances by some international agencies according to their potential harmful effects and their high bioaccumulation tendency [4,5]. In fact, they may affect the liver and the immune system and they present a negative effect on the metabolism through the inhibition of the enzyme ATP synthase [6]. Moreover, the International Agency of Research on Cancer (IARC) has determined that chlorophenols, as a family of compounds, are possibly carcinogenic [7]. According to these health risks, the United States Environmental Protection Agency (US-EPA) and the European Union (EU) have included chlorophenols in their priority pollutants list [8,9].

The determination of chlorophenols in water is usually accomplished by an extraction of the analytes followed by their separation by liquid chromatography (with ultraviolet, fluorimetric or mass spectrometric detection) or gas chromatography (with flame ionization, electron capture or mass spectrometric detection) [10]. In the latter case, a derivatization of the analytes by acetylation [11] or silylation [12] is required due to the low volatility of the parent compounds.

Liquid–liquid extraction is the conventional technique used for the isolation and preconcentration of these target compounds from water samples [13] although it has been successfully substituted by solid phase extraction (SPE) which can be considered a greener and simpler technique [14,15]. Microextraction techniques have emerged in the last years as suitable alternatives to classical sample treatments due to their special and favourable characteristics. In this sense, solid phase microextraction (SPME) has been applied in the direct immersion [16] or headspace [17] modes with excellent analytical features. The latter approach minimizes the matrix interferences but it is limited to more volatiles analytes. On the other hand, liquid phase microextraction (LPME) has been also proposed for the resolution of this analytical problem working under

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different modes. Thus, single drop microextraction [18], solvent bar microextraction [19], dynamic liquid microextraction [20], vortex assisted microextraction [21] and stir membrane liquid microextraction [22,23] have been applied for the efficient extraction of chlorophenols from water samples.

Some of the described methodologies usually present a slow extraction kinetic due to the low contact surface between the sample and the extractant phase. Dispersive liquid–liquid microextraction (DLLME), proposed for the first time in 2006 [24], enhances this surface area by the efficient dispersion (chemically assisted or by the application of an external energy source) of the extractant into the sample. DLLME has been applied using conventional solvents for the extraction of chlorophenols in water samples [25,26]. In the DLLME context, ionic liquids play a key-role as solvents due to their excellent extraction properties [27,28]. In addition, they allow the development of new dispersive microextraction modes such as temperature controlled ionic liquid dispersive liquid-phase microextraction [29] and in situ solvent formation microextraction [30,31]. Moreover, due to their thermal stability they can be used as thermal desorption solvents for gas chromatographic analysis [32].

In this article, a new method for the extraction and determination of ten chlorophenols in water samples is presented. The analytical procedure is based on a previous derivatization of the analytes with acetic anhydride, being the derivatized compounds finally isolated/preconcentrated by an in situ solvent formation microextraction. The generated ionic liquid is finally recovered by centrifugation and analyzed by GC/MS. In this article, a thermal desorption step is employed for the injection of the target analytes taking advance of the characteristics of the solvent employed. The proposed method has been successfully applied to the determination of ten chlorophenols in reservoir, river, bottled and tap water.

2. Experimental

2.1. Reagents and samples

All reagents were of analytical grade or better. Chlorophenols (2-chlorophenol, 3-chlorophenol, 4-chlorophenol, 2,6-dichlorophenol, 2,3-dichlorophenol, 3,4-dichlorophenol, 2,4,5-trichlorophenol, 2,4,6-trichlorophenol, 2,3,5,6-tetrachlorophenol and pentachlorophenol) were purchased from Sigma–Aldrich (Madrid, Spain). Stock standard solutions of each analyte were prepared in acetone (Panreac, Barcelona, Spain) at a concentration of 500 mg L^{-1} and stored at 4 °C. Working solutions of chlorophenols were prepared by dilution of the stocks in milli-Q water (Millipore Corp; Madrid, Spain).

4-Bromophenol (internal standard), potassium hexafluorophosphate (KPF_6), acetic anhydride, potassium carbonate, 1-methyl-3-octylimidazolium chloride ([Omim] [Cl]) and hydroxylamine were also purchased from Sigma–Aldrich.

River, tap and reservoir water samples were collected in amber-glass bottles without headspace. Bottled water samples were purchased in a local market. The samples were stored in the dark at 4 °C until their analysis.

2.2. Apparatus

Gas chromatographic/mass spectrometric analyses were carried out on an Agilent (Palo Alto, CA) HP6890 gas chromatograph equipped with an HP5973 mass spectrometric detector based on a quadrupole analyzer and a electron multiplier detector. System control and data acquisition was achieved with an HP1701CA MS ChemStation software.

A column split ratio of 1:10 was selected for injection, using Helium (6.0 grade, Air liquid, Seville, Spain) at a flow rate of 1 mL min^{-1} as carrier gas. Chromatographic separations were performed on a fused silica capillary column (30 m × 0.25 mm i.d.) coated with 5% diphenylsiloxane and 95% dimethylsiloxane (film thickness 0.25 μm) (Supelco, Madrid, Spain). The column temperature program was as follows: 2.5 min at 40 °C, raised up to 100 °C at 25 °C min^{-1}, then immediately ramped at 4 °C min^{-1} up to 180 °C and raised up to 300 °C at 40 °C min^{-1} and kept finally at this temperature for 5 min. The quadrupole mass spectrometer detector was operated in selected ion monitoring mode, recording the following fragment-ions: 128 (from 8.00 to 11.50 min), 162 and 172 (from 11.50 to 14.50 min), 196 (from 14.50 to 19.00 min), 232 (from 19.00 to 22.50 min), and finally 266 (from 22.50 min to the end of the chromatogram). Electron impact ionization (70 eV) was used for analytes fragmentation. The injector, MS source and quadrupole temperatures were kept at 250 °C, 230 °C and 150 °C, respectively. The peak areas were used for quantification of individual analytes.

A vortex stirrer and a centrifuge, both from J. P. Selecta (Barcelona, Spain), were also used in the extraction procedure.

2.3. Extraction procedure

The target analytes should be derivatized prior to their extraction. For this purpose, 50 mL of the sample or aqueous standard containing the analytes and the internal standard (4-bromophenol at 5 ng mL^{-1}) are placed in a 125 mL amber-glass bottle. Later on, 1 mL of 5 M K_2CO_3 solution and 1 mL of acetic anhydride (derivatization reagent) are added. The solution is shaken during 5 min, opening the bottle in regular intervals to release the carbon dioxide.

Aliquots of 10 mL of the sample/aqueous standard containing the derivatized analytes are placed in a conical-bottom tube where 50 mg of [Omim] [Cl] are previously placed. The solution is agitated using a vortex during 1 min to facilitate the dissolution of the ionic liquid. Subsequently, an excess of KPF_6 (50 mg) is added, a cloudy solution being immediately formed. Then, the solution is stirred in a vortex for 1 min in order to dissolve the salt completely. The ionic liquid (1-methyl-3-octylimidazolium hexafluorophosphate, [Omim] [PF_6]) formed by the metathesis reaction (ca. 29 mg), is finally separated by centrifugation (5000 rpm, 5 min) and transferred to a glass vial where the thermal desorption will take place following a similar approach to the proposed by Hino et al. [33]. In this case, the vial is hermetically closed and two needles are introduced through the septum. The first one allows the introduction of a helium stream (100 mL min^{-1}) in the vial while the second acts as transference line with the injector of the chromatograph. In order to favour the thermal desorption of the analytes, the vial is heated at 300 °C during 6 min.

3. Results and discussion

The extraction procedure has as reference the European standard EN 12673:1999 [13], which describes a gas chromatographic method for the determination of some chlorophenols in water samples. The analytes are previously derivatizated following an acylation reaction with acetic anhydride in the presence of K_2CO_3. The derivatized analytes are subsequently isolated by mean of a classical liquid–liquid extraction (LLE) using hexane as extractant solvent. Lastly, a few microlitres of extract are injected into the gas chromatographic system for analytes determination.

In the present method, several innovations have been introduced in the standard procedure. First, the conventional LLE has been substituted by an in situ solvent formation microextraction which involves a greener extraction alternative. This approach reduces the volume of organic solvent and increases the extraction

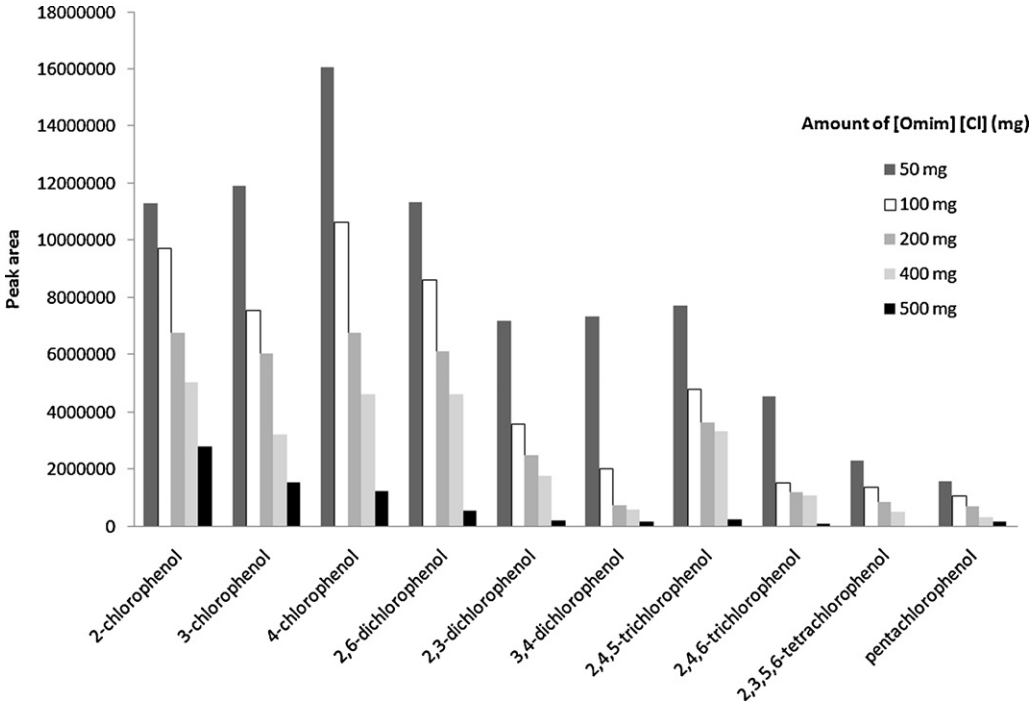

Fig. 1. Influence of the amount of the ionic liquid [Omim] [Cl] on the analytical signals for the different derivatized chlorophenols. The study was performed maintaining the amount of KPF_6 in an excess of 20% and the concentration of the analytes at 50 $\mu g\,L^{-1}$. The desorption temperature and He flow rates were 300 °C and 100 mL min^{-1}, respectively.

efficiency. In addition, in our proposal the sample injection is based on a thermal desorption approach taking advance of the non-volatile nature of the ionic liquid and the volatility of the derivatized analytes. However, the derivatization reaction, as well as the reagent concentrations, are maintained at the optimum values described in the standard. The use of higher amount of reagents would negatively affect to the subsequent microextraction since it results in an increase of the ionic strength affecting to the final metathesis reaction.

In the following sections, the optimization of the extraction and thermal desorption processes will be described in depth. For simplicity the variables are divided in two main groups, namely: extraction conditions and thermal desorption parameters.

3.1. Optimization of the extraction conditions

A general extraction procedure may be affected by several variables such as the pH, ionic strength, sample volume, extraction time and extractant volume. However, in the proposed method the pH has not influence on extraction procedure because the derivatized analytes do not present any ionizable groups. On the other hand, the ionic strength has a negligible influence in the extraction process because an excess of electrolytes were added during the derivatization process. In addition, the use of higher sample volumes should result in an improvement of the preconcentration factor but considering that the final separation is performed by centrifugation, the sample volume is limited by the centrifuge tubes used in the application (10 mL), Regarding the extraction time, the ionic liquid dissolved provides a large extraction surface, making the transference of analytes from the sample to the extraction medium almost instantaneous as it is common in dispersive microextraction approaches. All these aspects were experimentally confirmed.

The amount of extractant is the crucial factor in the microextraction and it is marked by the amounts of [Omim] [Cl] and KPF_6 which are involved in the metathesis reaction. In fact, each reagent provides the cation ($Omim^+$) and the anion (PF_6^-) required to form the water-insoluble ionic liquid ([Omim] [PF_6]) which is the real extractant. In our case, this reaction has been checked by means of infrared spectrometry. In this case, the [Omim] cation was selected instead to other counterparts (e.g. [Bmim] or [Hmim]) to enhance the hydrophobic interaction with the analytes. Moreover, the resulting [Omim] [PF_6] is less soluble in water and therefore their removal by centrifugation is easier. As a general rule[30,34], the reagent KPF_6 is usually added in excess in order to favour the metathesis reaction. Taking into consideration all these facts, the amount of [Omim] [Cl] was studied in a broad interval (from 50 to 500 mg) using KPF_6 in excess of 20%. Lower amounts were not studied due to their complex recovery by centrifugation. The results obtained for the extraction of 10 mL of an aqueous standard containing the analytes at a final concentration of 50 $\mu g\,L^{-1}$ are shown in Fig. 1. The effect of the ionic liquid volume on the extraction of the analytes involves two contradictory aspects. On the one hand, the absolute extraction recovery should increase when higher volumes of extractant are employed. On the other hand, the desorption process is improved when lower amount of extractant are considered since the surface-to-volume ratio is enhanced in these circumstances. Moreover, a crust of IL is observed when higher amounts are used. According to the results, the final aspects are predominant and 50 mg were selected as the optimum value for [Omim] [Cl]. Subsequent experiments showed that the addition of a 20% of excess is enough for the efficient recovery of the ionic liquid.

3.2. Optimization of the thermal desorption injection

The thermal desorption of the derivatized analytes is a crucial aspect in order to obtain good sensitivity levels. The desorption and subsequent transference of the derivatized chlorophenols to the gas chromatograph is controlled by three main variables, namely: desorption temperature, desorption time and gas flow rate. These variables were studied using aqueous standards containing the derivatized analytes at a concentration level of 50 $\mu g\,L^{-1}$. Each standard was extracted under the optimal

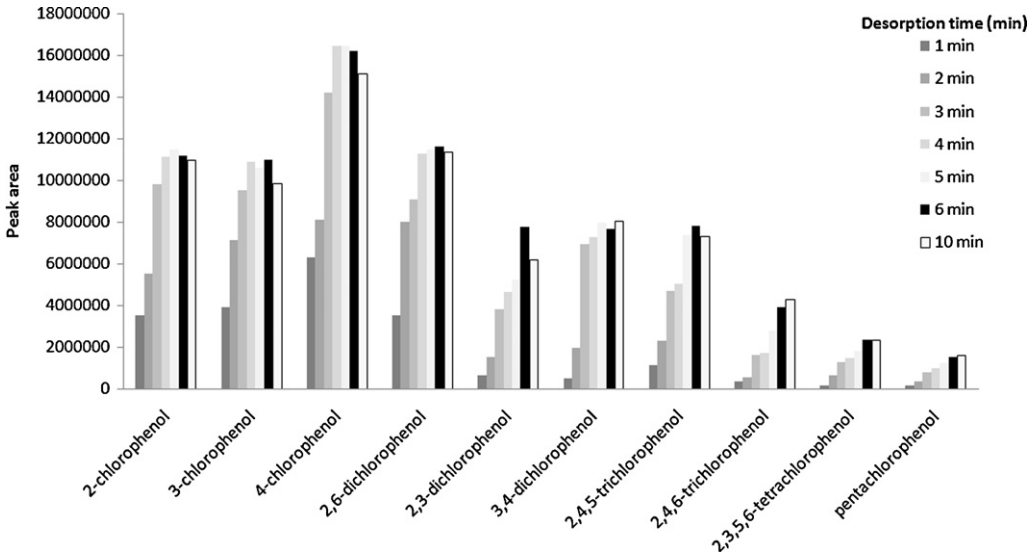

Fig. 2. Influence of the desorption time on analytical signal. The concentration of the analytes was fixed at 50 μg L^{-1} being the He flow rate of 100 mL min^{-1}.

extraction condition and the final extract was thermally desorbed and analyzed.

The desorption time was studied in the interval from 1 to 10 min; the results are shown in Fig. 2. As expected, the analytical signal increased when the desorption time increased, remaining almost constant over 4–6 min depending on the analyte. According to these results, 6 min was selected as optimum value.

Desorption temperature was studied at 300 °C and 500 °C. The results shows a slight effect of the temperature on the desorption in this interval. However, at 500 °C the thermal degradation of the ionic liquid is observed. According to these facts, 300 °C was selected as optimum desorption temperature value.

Finally, the flow rate of the transference gas (from the vial to the injector) was evaluated in the interval from 25 to 100 mL min^{-1}. In this case, higher flow rates were not considered due to overpressure problems in the injector of the gas chromatograph. The results, which are summarized in Fig. 3, show that the analytical signal increases with increasing the flow rates. The maximum signal was obtained at 100 mL min^{-1} which was finally selected as optimum value.

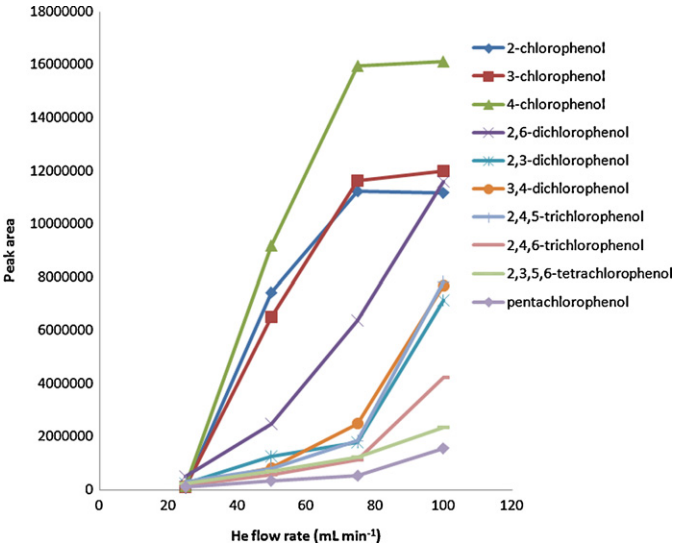

Fig. 3. Effect of the flow rate on the analytical signal. The concentration of the analytes was fixed at 50 μg L^{-1} being the desorption temperature of 300 °C.

3.3. Analytical figures of merit

The analytical features of merit of the proposed method are summarized in Table 1. The calibration curves for the ten chlorophenols were constructed by using working aqueous standards prepared at concentrations between 0.25 ng mL^{-1} and 50 ng mL^{-1}. For this purpose, eight concentration levels were evaluated, each level being analyzed by triplicate. An internal standard (4-bromophenol) at a concentration of 5 ng mL^{-1} was used in order to obtain better repeatability values. Linearity was observed in the range of 0.25 ng mL^{-1} to 50 ng mL^{-1}. 4-Chlorophenol showed the wider linear range (0.25–50 ng mL^{-1}) while pentachlorophenol presented the narrowest one (1.5 ng mL^{-1} to 50 ng mL^{-1}). A chromatogram obtained for a standard containing the analytes at a final concentration of 10 ng mL^{-1} is presented in Fig. 4A.

The repeatability, expressed as relative standard deviation (RSD) was studied using seven replicate analyses of aqueous standards at a concentration of 0.5 ng mL^{-1} for mono, di and trichlorophenols and 2 ng mL^{-1} for tetra and pentachlorophenols. As can be seen in Table 1, the obtained values are ranged from 4.5% (2,6-dichlorophenol) to 9.9% (3-chlorophenol).

The sensitivity of the method was evaluated according to the limit of detection (LOD) and the method detection limit (MDL) defined by US-EPA [35]. The MDLs were in all cases in the nanogram per litre range and varied between 70 ng L^{-1} (2,6-dichlorophenol) and 470 ng L^{-1} (pentachloropenol). The LODs, based on signal-to-noise ratio (S/N) of 3, ranged from 60 ng L^{-1} (4-chlorophenol) to 440 ng L^{-1} (pentachlorophenol). A good correlation between MDLs and LODs values were observed for all the analytes.

3.4. Recovery study

Once optimized and analytically characterized, the proposed method was applied for the determination of the target analytes in water samples of different nature (reservoir, river, bottled and tap).

Taking into account that the analytes were not detected in the samples, a recovery study was performed to evaluate the applicability of proposed method to determine chlorophenols in waters. The recovery study was developed by spiking chlorophenol-free samples with the target compounds at 1 ng mL^{-1} for mono, di and trichlorophenols and 2 ng mL^{-1} for tetra and pentachlorophenols.

Table 1
Analytical figures of merit for the determination of ten chlorophenols in water samples.

Compounds	Linear range (ng mL^{-1})	R^a	MDL^b (ng L^{-1})	LOD^c (ng L^{-1})	RSD^d %
2-Chlorophenol	0.3–50	0.994	150	90	8.5
3-Chlorophenol	0.3–50	0.998	130	80	9.9
4-Chlorophenol	0.25–50	0.999	115	60	8.6
2,6-Dichlorophenol	0.3–50	0.998	70	100	4.5
2,3-Dichlorophenol	0.4–50	0.999	115	120	7.2
3,4-Dichlorophenol	0.4–50	0.996	115	130	8.2
2,4,5-Trichlorophenol	0.4–50	0.986	120	112	6.6
2,4,6-Trichlorophenol	0.5–50	0.994	125	140	8.3
2,3,5,6-Tetrachlorophenol	1.0–50	0.990	244	280	5.1
Pentachlorophenol	1.5–50	0.993	470	440	9.0

[a] *R*, regression coefficient.
[b] MDL, method detection limit.
[c] LOD, limit of detection.
[d] RSD, relative standard deviation ($n = 7$).

The samples were analyzed after 24 h to favour the potential interaction of the analytes with the sample matrix. Each sample was analyzed by triplicate and the results are shown in Table 2. As it can be seen, recovery values ranged between 72 ± 3% (2,3,5,6-tetrachlorophenol) and 102 ± 8% (2,3-dichlorophenol). In addition, Fig. 4B shows the chromatogram obtained for a water sample analyzed after enrichment with the analytes and analyzed following the proposed procedure.

Anomalous results were obtained for tap water since an abrupt decrease in the peak area was observed for the internal standard. This fact has been attributed to the residual concentration of hypochlorite in water due to the disinfection process. The residual

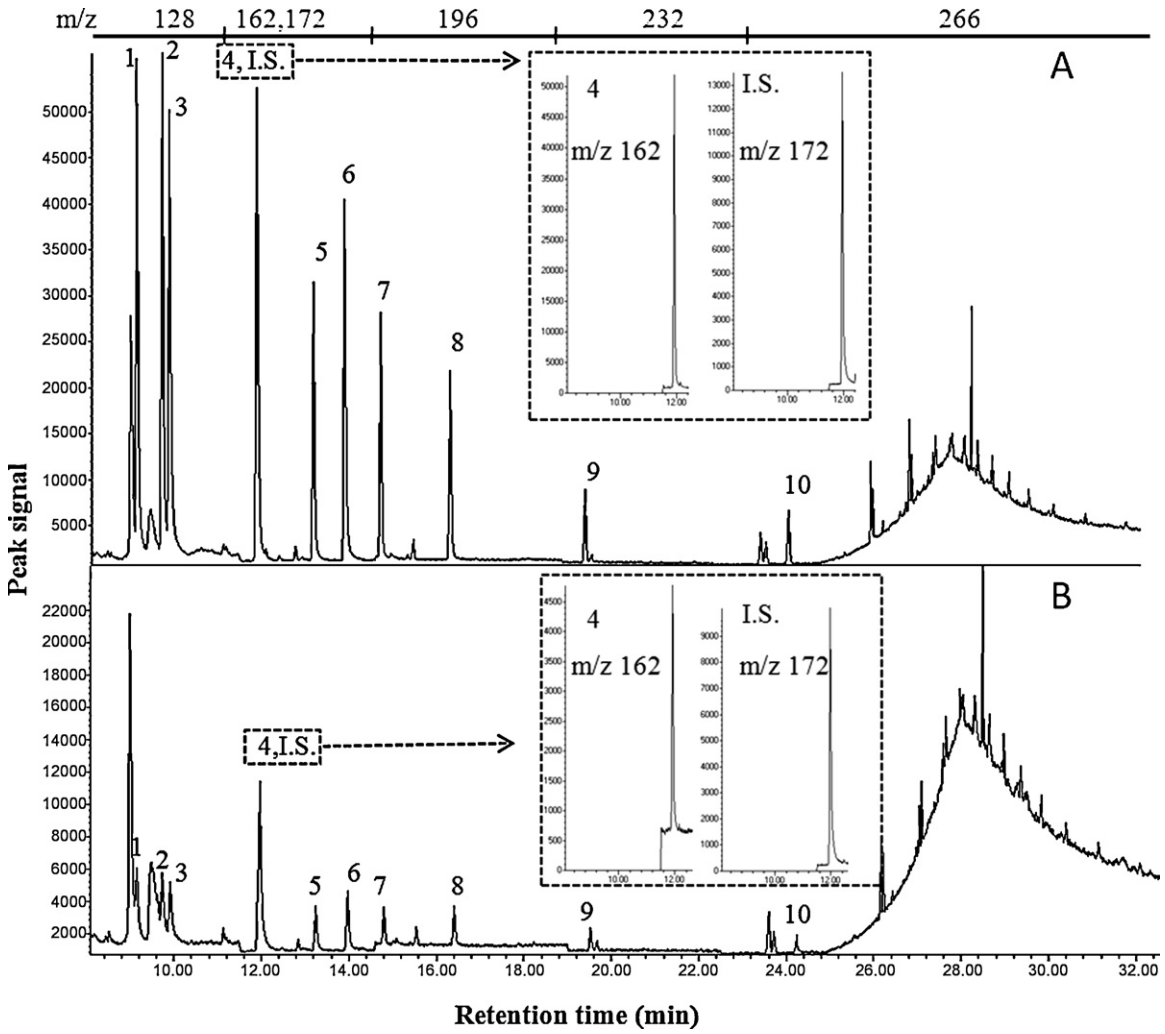

Fig. 4. Chromatograms obtained from analysis of (A) an aqueous standard containing the derivatized analytes at a concentration of 10 ng mL^{-1} and (B) a water sample containing the derivatized analytes at a concentration of 1 ng mL^{-1}. (1) 2-Chlorophenol, (2) 3-chlorophenol, (3) 4-chlorophenol, (4) 2,6-dichlorophenol, (5) 2,3-dichlorophenol, (6) 3,4-dichlorophenol, (7) 2,4,5-trichlorophenol, (8) 2,4,6-trichlorophenol, (9) 2,3,5,6-tetrachlorophenol, (10) pentachlorophenol. A detail showing the selected ion monitoring chromatograms is also included. The *m*/*z* 162 corresponds to the derivatized 2,6-dichlorophenol while the *m*/*z* 172 corresponds to the derivatized 4-bromophenol. (I.S.)

Table 2
Recovery values obtained for the determination of ten chlorophenols in different water samples.

Compounds	Recovery (% ±SD[a], $n = 3$)				
	Reservoir water	River water	Bottled water	Tap water[b]	Tap water[c]
2-Chlorophenol	90 ± 7	99 ± 8	99 ± 8	92 ± 7	121 ± 10
3-Chlorophenol	88 ± 8	97 ± 9	90 ± 8	93 ± 9	191 ± 12
4-Chlorophenol	88 ± 8	99 ± 8	87 ± 7	87 ± 7	120 ± 10
2,6-Dichlorophenol	99 ± 4	99 ± 4	100 ± 5	98 ± 4	150 ± 8
2,3-Dichlorophenol	102 ± 8	102 ± 7	100 ± 7	100 ± 7	171 ± 13
3,4-Dichlorophenol	101 ± 8	100 ± 8	102 ± 8	100 ± 8	197 ± 14
2,4,5-Trichlorophenol	99 ± 6	102 ± 7	100 ± 7	101 ± 7	173 ± 11
2,4,6-Trichlorophenol	89 ± 7	96 ± 8	101 ± 8	97 ± 8	180 ± 28
2,3,5,6-Tetrachlorophenol	73 ± 3	72 ± 3	81 ± 4	79 ± 5	102 ± 12
Pentachlorophenol	82 ± 7	78 ± 7	79 ± 7	76 ± 8	107 ± 16.6

[a] SD, standard deviation.
[b] Tap water sample treated with hydroxylamine.
[c] Tap water sample without hydroxylamine.

Table 3
Comparison of the proposed method with other reported approaches based on dispersive microextraction for the determination of chlorophenols in water.

Microextraction procedure	Instrumental technique	Derivatization required	Sample volume (mL)	LOD (ng mL^{-1})	RSD (%)	Reference
Vortex assisted microextraction	HPLC-UV	NO	100	0.3–3.0	<7.6	[21]
Dispersive liquid-liquid microextraction (DLLME)	GC-ECD	YES	5	0.01–2.0	<4.7	[25]
Temperature controlled ionic liquid DLLME	HPLC-UV	NO	10	0.27–0.68	<3.7	[29]
Surfactant assisted DLLME	HPLC-UV	NO	11	0.1	<6.9	[36]
Dispersive liquid-liquid based on solidification drop	HPLC/MS	NO	5	0.002–0.02	<8.5	[37]
In situ solvent formation microextraction	GC/MS	YES	10	0.06–0.44	<9.9	Proposal

hypochlorite reacts with the 4-bromophenol inducing its chlorination. This effect was corrected adding 100 μL of hydroxylamine to the tap water before the addition of the internal standard and the derivatizaton process.

4. Conclusions

The analytical method presented in this article is based on a dual use of an ionic liquid. On the one hand, the ionic liquid is used as extractant under an in situ solvent formation microextraction procedure achieving the efficient isolation and preconcentration of the target analytes. On the other hand, the low vapour pressure of the solvent is exploited in a thermal desorption step which facilitates the injection of the extracted analytes in the gas chromatograph. The analytical method is quite simple, only a previous derivatization of the analytes being necessary in order to promote their extraction and to make easier their gas chromatographic analysis.

The proposal has been optimized considering those variables, related to the extraction and thermal desorption steps, which have a clear influence in its performance. Once optimized, the proposed method was analytically characterized in terms of linearity, sensitivity and precision, being finally applied to the determination of the target compounds in water samples of different origin.

Table 3 compares the proposed method with other analytical procedures based on dispersive microextraction [21,25,29,36,37]. The proposed method provides the best results in terms of sensitivity, only surpassed by the procedure which uses liquid chromatography and mass spectrometry as instrumental technique. However, it presents a lower precision which will be considered as a key-aspect in further investigations.

Acknowledgement

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