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Development of solid-phase extraction and solid-phase microextraction methods for the determination of chlorophenols in cork macerate and wine samples☆

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Abstract

Tri-, tetra- and pentachlorophenol (TCP, TeCP and PCP) can be considered the precursors in the formation of corresponding chloroanisoles, known to be powerful odorants in corks and wine. Determining the presence of these chlorophenolic compounds in cork soaking solutions (ethanol/water mixtures, 12% (v/v) ethanol used for cork quality control testing), or in wine can be achieved by acetylation/gas chromatography electron-capture detection. In order to reach the required sensitivity, a previous preconcentration step is necessary. Solid-phase extraction (SPE) and headspace solid-phase microextraction (HS-SPME) have given good results for the preconcentration of TCP, TeCP and PCP in such matrices. The use of Oasis HLB cartridges gives acceptable recoveries for the three compounds when different volumes (50–250 mL) of cork macerate with concentrations ranging from 20 to 150 ng/L are processed. Preconcentration based on HS-SPME has also been optimised with a 100 μm polydimethylsiloxane fibre and in situ derivatization. The HS-SPME method allows chlorophenols in a cork soaking solution and in wine to be determined with a limit of detection of 1 ng/L for each compound (in cork macerate) and a repeatability of around 0.5%–5% (n = 8) for a concentration level of 30 ng/L.

Keywords: Cork; Wine; Food analysis; Chlorophenols

1. Introduction

The organoleptic defect known as cork taint is associated with a musty or mouldy aroma in wine. The appearance of this off-flavour represents a serious problem for the wine industry, with an estimated annual loss of more than 10 billion dollars worldwide [1]. Several substances, such as geosmin, 2-methyl-isoborneol, guaiacol, 1-octen-3-one, 1-octen-3-ol and chlorophenols, have been reported to be responsible for cork taint [2]. However, 2,4,6-trichloroanisole (TCA), which presents an extremely low odour threshold, is considered to be the main contributory compound to this sensory defect [2,3]. Current literature indicates that about 80% of tainted bottled wines are contaminated by TCA [4]. It is believed that TCA is produced through a process of detoxification by fungal methylation of chlorophenolic compounds. The presence of such chlorophenolic compounds in corks may have different origins, including the use of fungicides, biocides, herbicides, wood preservatives and washing products containing 2,4,6-trichlorophenol (TCP), 2,3,4,6-tetrachlorophenol (TeCP) and pentachlorophenol (PCP), either in the cellar or during cork manufacturing. Nonetheless, chlorophenolic compounds can be considered the main precursors of TCA, so their determination becomes of great interest to cork and wine industries. Recently, the cork industry has implemented quality control tests consisting of determining the amounts of TCA and chlorophenols released into hydroalcoholic solutions (wine simulant) [5], as a way of testing the quality of cork stoppers.

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The main objective of testing is to ensure the necessary levels of control of any substances that might be transferred to the food by contact with the cork material.

Among the various methods developed for the analysis of chlorophenols in aqueous samples, gas chromatographic methods are most often used because of their high sensitivity and power of resolution [6–8]. In general, due to adsorption problems, tailed peaks and detectability, chlorophenols have to be derivatized prior to separation and quantification by gas chromatography. A large number of derivatizing reagents, such as diazomethane [9], pentafluorobenzyl bromide [10], methyl iodide [11] or acetic anhydride [12–14], have been used for this purpose. Acetylation is one of the procedures most widely employed to convert chlorophenols into less polar compounds, thus increasing extraction efficiency [15].

The need to determine chlorophenols at low concentrations requires sample preparation steps prior to injection into a gas chromatograph. Appropriate sample-handling techniques such as solid-phase extraction (SPE) and solid-phase microextraction (SPME) are extensively applied taking into account their well-known advantages [16,17]. Recently, the development of new SPE sorbents has encouraged the use of this extraction and preconcentration technique in different types of samples. According to published studies, C_{18} and polymeric sorbents are considered the most effective for trapping phenolic compounds, especially for water analysis [18,19]. Likewise, a new macroporus polydivinilbenzene-*N*-vinylpirrolidone copolymer (Oasis HLB) has been used for extracting a variety of pollutants including chlorophenols [19–21]. Nevertheless, the use of SPE to determine the presence of chlorophenols in cork extracts is not so common. For example, Soleas et al. [22] applied a C_{18} sorbent for the preconcentration of the sample after the extraction of trichloroanisole and trichlorophenol from cork stoppers with an ethanol/water mixture.

SPME constitutes a good alternative to other commonly used extraction methods as sampling can be done rapidly and directly, without solvent, and can be easily automated. The number of available coatings for SPME has increased in recent years, resulting in more selective analysis. In this way, chlorophenol determinations have been performed with or without derivatization procedures using more suitable stationary phases. Buchholz and Pawliszyn [23] analysed chlorophenols from water using a poly(acrylate) fibre or a poly(dimethylsiloxane) fibre with in situ derivatization. A poly(acrylate) fibre was also used by Ribeiro et al. [24] for chlorophenol determination in landfill leachates. Llompart et al. [25] applied SPME to the detection of 30 phenolic compounds in water samples. Additionally, fibres constituted by two or three different polymers demonstrated the possibility of simultaneously determining haloanisoles and halophenols in water [26]. Furthermore, several SPME–HPLC methodologies have been reported for the determination of chlorophenolic compounds [27,28].

The aim of the present study is to develop and apply two methodologies based on SPE and SPME coupled to GC–electron-capture detection (ECD) to determine tri-, tetra- and pentachlorophenol in cork macerate and wine samples. For this purpose, a C_{18} cartridge and a styrene–divinilbenzene-based sorbent (Oasis HLB) have been evaluated under different experimental conditions. In addition, we have optimised a SPME method using a polydimethylsiloxane fibre to achieve the best extraction conditions for the chlorophenolic compounds.

2. Materials and methods

2.1. Chemicals and reagents

The chlorophenol standards 2,4,6-trichlorophenol (Fluka,Vienna, Austria), 2,3,4,6-tetrachlorophenol (Riedel-de-Haën, Seelze, Germany) and pentachlorophenol (Sigma–Aldrich Química, Madrid, Spain) used in this study had a purity of at least 99%. Stock solutions were prepared for each of the standards in methanol (Carlo Erba Instruments, Milan, Italy) at a concentration level of 100 μg/mL. They were stored in a refrigerated environment at 4 °C and kept in darkness. Working solutions were made daily by diluting the standard solutions with water or hydroalcoholic mixture (12% (v/v) ethanol).

The reagents used, acetic anhydride, *n*-hexane (Panreac, Barcelona, Spain) and absolute ethanol (Carlo Erba Instruments, Milan, Italy), anhydrous sodium sulfate, NaCl and K_2CO_3 were of analytical-reagent grade. The high purity water was taken from a Milli-Qplus water system.

2.2. Cork closures

Natural-cork stoppers were kindly supplied by AECORK (the trade association of the Catalan cork manufacturers). The corks used for the experiments were graded according to the usual selection process (grade a).

2.3. Cork macerates and wine samples

Cork macerates were obtained after soaking 10 corks in a 300 mL hydroalcoholic solution (12% (v/v)) for 24 h. White wine produced in the Experimental Cellar of the Faculty of Oenology, Universitat Rovira i Virgili, Tarragona, Spain, was used in some experiments.

The spiked cork macerates and wine used in recovery studies were prepared by adding the appropriate volume of chlorophenolic stock solutions.

2.4. Acetylation of standards

The acetylation procedure to convert the chlorophenols into more suitable compounds was as in Rodríguez et al [14]. One milliliter of the standards in methanol, 2 mL of 5% K_2CO_3 and 200 μL of acetic anhydride were shaken for 1 min. After that, 1 mL of *n*-hexane was added and mixed

for another minute. The organic phase containing acetylated chlorophenols was separated and the aqueous phase was re-extracted with 1 mL of *n*-hexane. The two organic fractions were mixed, dried over anhydrous sodium sulphate and reduced to 1 mL under a gentle stream of nitrogen before their injection into the GC–ECD system.

2.5. Solid-phase extraction (SPE)

Two different SPE sorbents were tested: C_{18} cartridges (300 mg, Teknokroma) and Oasis HLB syringe barrels (macroporous polydivinylbenzene-*N*-vinylpirrolidone copolymer, 60 mg, Waters). Both sorbents were conditioned with 2 mL of methanol and 12% (v/v) ethanol/water at pH 2 (5 mL in the case of C_{18} cartridge and 2 mL for Oasis HLB). A known volume of a spiked sample was loaded at a flow-rate of 4 mL/min with the aid of a peristaltic pump (Miniplus 3, Gilson). Afterwards, in the case of C_{18} sorbent, the cartridge was dried using a vacuum system and elution was performed by adding 3 mL of methanol. Oasis HLB syringe barrels were rinsed with 1 mL of hydroalcoholic solution to remove matrix interferences. Finally, elution of the analytes was carried out with 3 mL of methanol.

In both off-line SPE processes, the methanolic extracts were derivatized prior to gas chromatography analysis following the same procedure used for the methanolic standards (see Section 2.4).

Recoveries of spiked cork macerates, which were analysed according to the SPE method, were calculated by interpolating the peak area in the calibration curve obtained with standard solutions prepared following Section 2.4.

2.6. SPME and in situ derivatization

SPME experiments were performed with a manual fibre holder supplied by Supelco. The commercially available fibre, 100 μm polydimethylsiloxane, was also from Supelco. Before use, each fibre was conditioned by inserting it into the GC injector for 1 h at 250 °C.

The sample (5 mL of wine or a hydroalcoholic solution 12% (v/v)) was introduced into a 10 mL screw-cap glass vial. After the addition of NaCl, 2 mL of a 5% K_2CO_3 solution and 200 μL of acetic anhydride, the vial was closed and clamped over a magnetic stirrer (Variomag®) in a water-thermostated bath (Bunsen) heated to different temperatures. Magnetic stirring (medium speed) was employed during the extraction using a PTFE-coated stir bar. The fibre was exposed to the headspace generated in the sample vial. After that, the fibre was pulled into the housing and the SPME device was removed from the vial and inserted into the injection port of the GC for thermal desorption (5 min).

Blanks were run periodically during the analysis to confirm the absence of contaminant chlorophenols.

Recoveries for cork macerates and wine samples spiked with target compounds were obtained by interpolating in the SPME calibration curve.

2.7. GC–ECD analysis

Gas chromatographic analysis was performed with a GC 8000 Series (8160) gas chromatograph equipped with an AS 800 autosampler and an ECD 80 electron-capture detector (Fisons Instruments, Milan, Italy). A DB-5 capillary column (J&W Scientific, Folsom, CA, USA) (30 m × 0.25 mm i.d.; film thickness, 0.25 μm) was used. The operating conditions were an injector temperature of 270 °C (250 °C in SPME); a detector temperature of 330 °C; helium was the carrier gas at 30 cm/s; N_2 was the make up gas at 43 cm/s; the oven temperature programme was 2 min at 70 °C, then increasing by 5 °C/min up to 180 °C and by 10 °C/min up to 270 °C, and finally 3 min at 270 °C. Splitless mode injections (1 μL) were performed with the purge valve opened at 1 min, or 5 min when SPME was used. The chromatographic data were analysed by Chrom-Card software.

In order to identify the target compounds, their retention times were compared with those obtained for standard solutions injected separately. Calibration curves were constructed as plots of the peak area of each derivative against the concentration. The ECD response was lineal in the range of concentrations considered (1–20 μg/L). Detection limits were not higher than 1 μg/L for all compounds. The repeatability expressed as relative standard deviation ranged between 4% and 6%.

3. Results and discussion

3.1. SPE experiments

3.1.1. Comparison of extraction process using C_{18} and Oasis HLB sorbents

Prior to the application of both SPE sorbents to real samples, it was necessary to evaluate their capability for the preconcentration of chlorophenols (TCP, TeCP and PCP) from Milli-Q water and a hydroalcoholic solution. Recovery tests were performed by applying 50 mL of each type of sample containing 200 ng/L of the analytes. The pH was adjusted to 2 before extraction to prevent the formation of phenolate ions. At this pH, chlorophenols are in neutral form and their affinity towards the sorbent increases. Table 1 shows the results obtained for the extraction of chlorophenolic compounds by two reversed solid-phase sorbents. No significant differences

Table 1
Mean recoveries and R.S.D. (in %) obtained by applying 50 mL of sample (water and hydroalcoholic solution) spiked at 200 ng/L of chlorophenols on Oasis HLB syringe barrel and C_{18} cartridge (n = 2)

Compound	Water		12% Ethanol	
	Oasis HLB	C_{18}	Oasis HLB	C_{18}
TCP	90.2 (12.1)	109.0 (15.3)	131.9 (4.2)	85.7 (4.6)
TeCP	106.9 (24.7)	97.9 (0.2)	133.2 (7.5)	124.3 (0.1)
PCP	135.6 (14.1)	76.0 (4.1)	96.3 (4.9)	79.2 (9.0)

Table 2
Mean recoveries and R.S.D. (in %) obtained by applying 50 mL of cork macerate spiked at 200 ng/L of chlorophenols on an Oasis HLB syringe barrel or a C_{18} cartridge (n = 2)

Compound	Cork macerate	
	Oasis HLB	C_{18}
TCP	99.5 (0.4)	59.4 (10.4)
TeCP	91.3 (11.5)	85.6 (6.1)
PCP	72.6 (4.8)	85.6 (8.4)

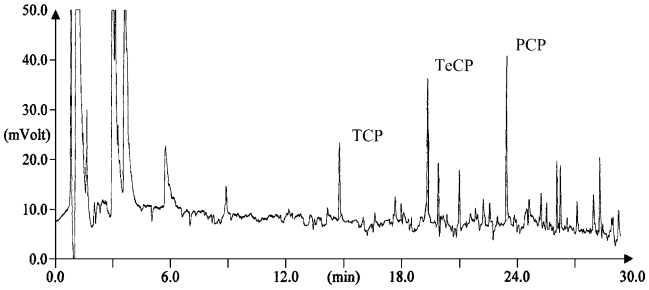

Fig. 1. GC–ECD Chromatogram for 50 mL cork macerate spiked at 200 ng/L of chlorophenols. Extraction and preconcentration was performed with Oasis HLB syringe barrel.

were obtained when the sample contained 0% and 12% (v/v) of ethanol, when C_{18} cartridges or Oasis HLB syringe barrels were employed.

Due to the importance of the possible matrix effects, spiked cork macerates were assessed. The results thus obtained with Oasis HLB (Table 2) provided better recoveries in almost all cases. Therefore, C_{18} cartridges were excluded from any further attempts.

Fig. 1 illustrates a gas chromatogram from a cork macerate spiked at 200 ng/L with the target compounds studied. After extraction and derivatization, analyte peaks were clearly identified showing the high sensitivity of the SPE method as well as the benefits derived from the derivatization process.

3.1.2. Volume of the sample and concentration of analytes

In order to determine the capacity of Oasis HLB sorbent, 100 and 250 mL of cork macerate containing the three chlorophenols at 10 ng level were evaluated. As can be seen in Table 3, with the exception of 2,4,6-triclorophenol in 250 mL of macerate, acceptable recoveries were obtained according to the AOAC [29]. In order to shorten the analysis time, a sample volume of 100 mL was selected for further examination.

Table 3
Recovery results and R.S.D. (in %) obtained with Oasis HLB for the extraction of chlorophenols from 100 mL (n = 3) and 250 mL (n = 2) cork soaking solution spiked at 10 ng level

Compound	Volume sample (mL)	
	100	250
TCP	90.0 (12.7)	117.4 (1.5)
TeCP	99.7 (11.8)	94.2 (7.1)
PCP	77.2 (7.8)	66.0 (4.2)

Table 4
Recovery results and R.S.D. (in %) obtained with Oasis HLB for the extraction of chlorophenols from 100 mL of cork macerate at different analyte concentrations (n = 2)

Compound	Analyte concentration (ng/L)		
	150	50	20
TCP	92.6 (14.4)	114.5 (2.2)	159.6 (3.0)
TeCP	86.7 (17.8)	93.7 (7.1)	102.7 (9.3)
PCP	67.7 (21.9)	94.0 (8.3)	94.5 (4.3)

The recovery of the method was also examined by adding different quantities of chlorophenolic compounds to cork soaking solutions. In every case, the sample volume was fixed at 100 mL and the concentration levels studied were 150, 50 and 20 ng/L for each chlorophenol. Polymeric Waters Oasis HLB sorbent seems to be the most suitable for determining the chlorophenols in a complex sample such as a cork macerate (see Table 4). Good recoveries were shown in almost all concentrations studied. These results demonstrate that SPE with Oasis HLB sorbent followed by derivatization of the methanolic eluate provides a highly sensitive method for the analysis of chlorophenols in cork macerate solution in the low ng/L range.

3.2. Development of SPME method

3.2.1. Selection of the fibre and extraction mode

Poly(dimethylsiloxane) (PDMS) has been employed in a large number of applications [30]. According to Llompart et al. [25], PDMS fibre provides the most efficient extraction for tri-, tetra- and pentachlorophenol from water samples. When chlorophenolic compounds are converted to less polar species, carryover or memory effect is prevented. At the same time, derivatization also offers chromatographic advantages in terms of sensitivity and peak shape [23]. SPME can be performed without derivatization of the chlorophenols using more polar coatings such as polyacrylate (PA) and carbowax-divinylbenzene (CW–DVB). However, a rigorous control of pH, especially when chlorophenols are not derivatized, together with a control of ionic strength, sampling time and temperature of the solution must be ensured.

SPME can be carried out by immersing the fibre directly in the sample or by exposing it in the gas phase (headspace) over the liquid. The choice of the extraction mode is based on sample matrix, volatility of analytes and their affinity to the matrix. In this study, extraction in the headspace of the sample and cork macerates has been employed using a 100 μm PDMS fibre. This type of extraction allows the extension of the operative time of the fibre thus protecting it from damage by interferences contained in the matrix sample.

3.2.2. Extraction time

To study the dependence of the amount of analyte extracted as a function of time, experimental conditions were

Table 5
Effect of the time on the extraction of acetylated chlorophenols at 40 ng/L with a PDMS fibre

Compound	Response ($\times 10^5$)[a]				
	20 min	30 min	40 min	50 min	60 min
TCP	4.7 (4.0)	5.6 (0.2)	6.6 (10.4)	8.1 (0.8)	10.8 (n.a.)[b]
TeCP	5.8 (2.3)	7.8 (3.2)	9.3 (13.5)	10.1 (5.4)	11.7 (13.0)
PCP	4.4 (3.2)	5.4 (10.0)	7.2 (26.8)	9.0 (13.4)	13.0 (n.a.)[b]

[a] Mean area (R.S.D. in %) ($n = 2$).
[b] R.S.D. in % not available.

Table 6
Optimisation of extraction temperature in the HS-SPME process applied to chlorophenolic derivates at 40 ng/L using a PDMS fibre

Compound	Response ($\times 10^5$)[a]				
	25 °C	35 °C	45 °C	55 °C	65 °C
TCP	3.0 (15.0)	3.6 (3.9)	3.9 (7.0)	4.0 (2.2)	2.0 (31.1)
TeCP	4.4 (13.3)	5.1 (9.2)	7.7 (20.2)	11.1 (3.3)	8.5 (5.5)
PCP	4.0 (7.7)	4.1 (0.7)	6.8 (10.6)	10.0 (14.2)	13.3 (15.3)

[a] Mean area (R.S.D. in %) ($n = 2$).

chosen according to the optimised SPME method for TCA, i.e. 1.2 g of NaCl and 25 °C [31]. The extraction time profiles of the acetylated chlorophenols were studied increasing the time of fibre exposure from 20 to 60 min obtaining higher responses by increasing the extraction time (Table 5). As a compromise, an extraction time of 30 min was selected for subsequent experiments. Although the system did not reach the equilibrium, the amount of extracted analytes was high enough to allow their quantification. Other studies have reported achieving the optimum extraction period of chlorophenols after 15 min [23] and 60 min [32] with a PDMS fibre.

3.2.3. Effect of temperature

The effect of temperature on the acetylchlorophenols extraction was tested from 25 to 65 °C in 10 °C increments. Extraction time was 30 min in all cases. As can be seen in Table 6, the amount of analyte recovered depends on the temperature selected. In general, an increase in the temperature until reach 55 °C leads to an increase of analyte concentration in the headspace, and helps to facilitate faster extraction. Temperatures up to 55 °C result in a decrease of the extraction yield, with the exception of pentachlorophenol. Thus, a temperature of 55 °C was selected for further experiments. This value corresponds with published data where temperatures between 50 and 60 °C were found to give optimum results [25,28].

3.2.4. Effect of ionic strength and ethanol content

The addition of salt enhances the extraction of organics from aqueous solutions. This makes organic compounds less soluble, therefore improving the affinity for the fibre and increasing the partition coefficients several times. The salt effect was investigated by adding different quantities of NaCl ranging from 0.8 to 4 g. As observed in Table 7, there is no real advantage observed for salt contents higher than 0.8 g. On the other hand, additional experiments with NaCl content lower than 0.8 g also showed a decrease of the response (data not shown). So, 0.8 g was taken as the optimum NaCl content. This result does not coincide with other studies in which an important increase in the SPME response was achieved under NaCl saturation conditions [25]. However, we must take into account that in our study the SPME process is applied to a hydroalcoholic matrix and this fact might necessary affect the extraction parameters.

The influence of ethanol on pesticide extraction in aqueous solution by SPME has been evaluated by several authors [5,33]. It is assumed that ethanol, as a co-solvent, can induce some variations of the partition coefficient of the organic compounds between the polymeric stationary phase and the aqueous solution in the SPME. For this reason, the role of ethanol in the extraction of chlorophenols was evaluated at three percentages: 0%, 6% and 12% (v/v). It was found that for a 6% (v/v) ethanolic solution the reduction of the response was only of 10%, while a 12% (v/v) ethanol content results in a 50% reduction of peak area (chlorophenol concentration of 40 ng/L). In spite of the lower extraction rates obtained when using hydroalcoholic solutions of 12% (v/v) ethanol, the method is sensitive enough for the determination of acetylated compounds in cork macerate and wine.

3.2.5. Validation parameters and application of the HS-SPME method

The linearity of the optimised HS-SPME method was tested in the 1–40 ng/L range in a hydroalcoholic solution 12% (v/v) ethanol (see Table 8). For all compounds, good linearity was found with correlation coefficient (r^2) greater than 0.993. The repeatability of the proposed procedure was also tested. For this purpose, eight standards at 30 ng/L were consecutively extracted under the same conditions. Relative standard deviation ranged from 0.5% to 5.3%. Detection limits, calculated based on a signal-to-noise ratio of 3:1, were close to 1 ng/L for TCP, TeCP and PCP.

Table 7
Influence of the amount of NaCl added on the solid-phase microextraction of selected acetylchlorophenolic compounds at 40 ng/L using a PDMS fibre

Compound	Response ($\times 10^5$)[a]					
	0.8 g NaCl	1.2 g NaCl	1.6 g NaCl	2 g NaCl	3 g NaCl	4 g NaCl
TCP	2.6 (2.3)	2.1 (2.1)	1.8 (0.8)	1.7 (6.2)	1.4 (11.2)	1.4 (n.a.)[b]
TeCP	3.2 (0.2)	3.0 (2.7)	2.1 (3.0)	2.6 (8.5)	2.7 (n.a.)[b]	1.6 (n.a.)[b]
PCP	4.7 (8.6)	5.2 (2.9)	3.2 (4.0)	3.8 (17.6)	3.5 (n.a.)[b]	2.5 (n.a.)[b]

[a] Mean area (R.S.D. in %) ($n = 2$).
[b] R.S.D. in % not available.

Table 8
Linear ranges, parameters of calibration lines and limits of detection of the HS-SPME procedure

Compound	Linear range (ng/L)	a (S_a) ($\times 10^3$)	b (S_b) ($\times 10^3$)	LOD (ng/L)
TCP	3.4–34.0	52.1 (9.5)	14.1 (0.4)	1.5
TeCP	1.7–34.0	94.4 (8.1)	29.8 (0.5)	0.8
PCP	1.8–44.1	105.7 (9.9)	33.1 (0.4)	1.0

a, independent term; S_a, standard deviation of a; b, slope; S_b, standard deviation of b and LOD, limit of detection.

Table 9
Recovery results (in %) and R.S.D. of chlorophenols from cork macerate (n = 3) and white wine

Compound	Matrix	
	Cork macerate	Wine
TCP	131.9 (3.5)	109.2(4.5)
TeCP	92.4 (8.3)	92.0(4.6)
PCP	97.8 (7.5)	n.d.

n.d.: not detected; analyte concentration was 10 ng/L in both cases.

Finally, spiked cork macerate and white wine samples were analysed using the optimised methodology. Table 9 shows recovery results of analytes at 10 ng/L in both types of samples. Acceptable recoveries were obtained for most of the compounds studied with the exception of pentachlorophenol in wine.

4. Conclusions

In this study, a SPE–GC–ECD and an HS-SPME–GC–ECD methods have been evaluated for the extraction of chlorophenols in cork macerate and wine samples. Extraction and clean-up studies were conducted with two different SPE sorbents, C_{18} and Oasis HLB. The highest recoveries for TCP, TeCP and PCP in cork soaking solutions were obtained using Oasis HLB syringe barrels for different sample volumes and analyte concentrations. When SPE is combined with the acetylation/detection method, chlorophenols at low ppt levels can be determined in cork macerate.

The influence of several parameters on the extraction of the derivatized chlorophenols with a PDMS fibre has been evaluated in the development of a HS-SPME method. Under the optimised conditions (addition of 0.8 g NaCl and extraction for 30 min at 55 °C), detection limits of 1.5, 0.8 and 1.0 ng/L for TCP, TeCP and PCP, respectively, were obtained with standards prepared in hydroalcoholic solution (12% (v/v) ethanol). The method also allows quantification of TCP and TeCP in wine in the range of concentrations studied.

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