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Development of a solid-phase microextraction method for direct determination of pentachlorophenol in paper and board samples: Comparison with conventional extraction method

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Abstract

A solid-phase microextraction (SPME) method has been developed for the determination of pentachlorophenol (PCP) in paper and board samples. The analytical procedure involves direct extraction of PCP from paper and board samples and determination by gas chromatography with electron capture detection (GC–ECD). Two kinds of commercially available fibres; 100 μm polydimethylsiloxane (PDMS), apolar, and 85 μm polyacrylate (PA), quite polar, were evaluated to determine the extraction efficiency of pentachlorophenol. Parameters affecting the extraction process, such as temperature and time, were studied. Moreover, time of desorption and the effect of addition of salt were also investigated. The optimized procedure was applied to the analysis of pentachlorophenol (PCP) in five samples of virgin and recycled paper and board. The PCP content was determined by GC–ECD. To evaluate the effectiveness of the proposed method, it was compared with conventional extraction method with liquid–liquid extraction and derivatization. Detection limit of 0.015 μg/g for PCP in paper was achieved with a RSD of 14%.

Keywords: Solid-phase microextraction; Paper and board analysis; Pentachlorophenol; Derivatization; Standard addition

1. Introduction

Paper and board are widely used as food packaging materials, often in forms adapted to direct contact with foodstuffs. A number of chemicals, such as slimicides, bleaching agents and inks, are used during the production process. Virgin paper and board products are produced by pulping, bleaching, and treatment process. Recycled paper also requires chemical treatment to remove the inks and contaminants from this material. However, none of the processes used in obtaining virgin or recycled pulp are able to get the total elimination of persistent contaminants such as pentachlorophenol (PCP).

PCP is the most toxic compound among chlorophenols (CPs) and it has been widely used as fungicide in wood preservation for decades. It was demonstrated that PCP was a member of environmental endocrine disruptors (EEDs) [1] and its analysis has received special attention to ensure the necessary levels of control of any substances that might be transferred to the food in contact with the paper and board. Few toxicological studies of paper and board used as food packaging have been published. Fauris et al. [2] found that both virgin and recycled paper exhibited cytotoxicity in the form of an effect on RNA synthesis rate in human HeLa cells. PCP is reported to be a potential carcinogen [3,4]. Moreover, PCP has been reported genotoxic in chromosomal aberration test and sister chromatic exchanges test.

PCP is hydrophobic ionizable organic compound and its distribution is strongly dependent on the pH of the aqueous

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phase as well as the ionic strength (μ) and this μ dependence is only reflected for pH values in the aqueous phase above 7. PCP is the "strongest" acid of the phenols family, having a pK_a of 4.7. The fraction of the neutral form of PCP depends on the pH of the solution. Under pH 3 the fraction of neutral species is almost 100%, while above pH 7 the anionic PCP is predominant. Between these values, a combination of both species is present [5].

In order to asses the overall safety of recycled paper and board as food packaging, the Council of Europe approved a proposal which contains the "List of substances used in the manufacture of paper and board materials and articles intended to come into contact with foodstuffs" which established a limit value of pentachlorophenol as low as 0.15 mg/kg in paper and board [6]. Analysis for compliance with the purity restriction for pentachlorophenol of this resolution can be made using a method based on extraction of the total amount in the paper.

Among the various methods developed for the analysis of PCP in different samples, gas chromatographic methods are the most used because of their high sensitivity and good resolution [7–9], thus liquid chromatography has low resolution and is frequently affected by the sample matrix [10]. However, to determine PCP at low concentrations requires sample preparation steps prior to the injection into a gas chromatograph. Most of the published methods for chlorophenols including PCP are focused on their determination in water. In general, analysis of the CPs in water involve liquid–liquid extraction [11–13] and solid-phase extraction [14–18] whereas sonication and Shoxlet are mainly employed [19] for the analysis of PCP in wood.

Due to adsorption problems, tailed peaks and detectability, CPs are usually derivatized prior to separation and quantification by gas chromatography. A large number of derivatizing reagents, such as diazomethane [13], pentafluorobenzyl bromide [20], methyl iodide [21] or acetic anhydride [22–24], have been used for this purpose. Acetylation is one of the procedures most widely employed to convert chlorophenols into less polar and volatile compounds, thus increasing extraction efficiency and enhancing the sensitivity for the final detection by electron capture detection (ECD) [25].

Concerning the extraction step there are also some differences. For example, Win [26] employs methanol to extract PCP and Buhr et al. [19] use sulphuric acid to liberate PCP from its salts and then total PCP is collected in toluene. But the main drawback of these classical methods is that they often involve extensive time consuming and potentially hazardous extraction and derivatization steps prior to GC–ECD.

In order to reduce the analysis steps, new techniques are being developed for this purpose. 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 SPME fibers has increased in recent years, resulting in more selective analysis. In this way, chlorophenols determinations have been performed with [27] or without derivatization [28] procedures using more suitable stationary phase. The purpose of derivatization in this case is to convert PCP in a volatile compound and simultaneously to facilitate its analysis by GC–ECD, taking advantage of the high sensitivity of this technique. Two different systems have been tested: (i) derivatization in solution and then applying the SPME extraction by total immersion mode, and (ii) derivatization in solution and using the SPME in headspace mode. The first case is not available for PCP, since the derivatizing agent affects the SPME fiber. In the headspace mode, it has been demonstrated that derivatization of PCP and the SPME analysis is not appropriate since the increase of the molecular size of the analyte has a negative impact on the transport [29]. Buchhlotz and Pawliszyn [30] analyzed 11 phenols in wastewaters by SPME-GC with Flame Ionization Detection and concluded that low pH levels and saturated salt conditions increased compound extraction efficiency, proving that it is possible to apply this extraction technique to more complex matrices but it has not been applied yet.

The analysis of chlorophenols by SPME and the optimization of several procedures based on SPME have been reported in several aqueous samples [31–36]. However, paper and board samples are complex solid matrices require a specific extraction procedure in order to avoid analysis interferences and to get the analytes out of the solid matrix, which is a difficult task. The European Comittee for Standarization established in 2003 [37] an analytical test for paper and board (P&B) using the extraction with hot water, further derivatization and analysis by GC–ECD or GC–MS. But such a procedure is time consuming and not as sensitive as required for the analysis of PCP in paper and board to accomplish with the proposal of the Council of Europe [6].

In this paper, a method for the direct analysis without derivatization of PCP in paper and board using SPME–GC–ECD is evaluated in comparison whit a conventional method using liquid extraction and further derivatization. The results obtained applying the two analytical procedures are shown and discussed.

2. Experimental

2.1. Chemicals

Pentachlorophenol (99%) and 2,4,6-trichlorophenol (TCP, 98%), used as internal standard (IS), from Fluka (Buchs, Switzerland) and methanol and acetonitrile HPLC grade were supplied by Merck (Darmstadt, Germany). Potassium chloride and hydrochloric acid were purchased from Panreac (Barcelona, Spain).

Pentafluorobenzyl bromide (PFBBr) from Sigma–Aldrich (Madrid, Spain) in 10% (v/v) solution in acetonitrile was used for the derivatization.

Water from a Milli-Q water purification system (Millipore, Bedford, MA, USA) was used.

Stock solution was prepared for TCP in ethylacetate at a concentration level of 10.6 μg/g. Standard solution (500 μg/g) of PCP was prepared by weight in methanol. For optimisation of the SPME procedure and calibration, water standards containing 5 and 50 μg/g of PCP were prepared.

2.2. Chromatographic conditions

A Hewlett-Packard Series 5890 (Wilmington, DE, USA) gas chromatograph equipped with electronic capture detection and a 60 m × 0.25 mm (i.d.) fused silica capillary column (SGL-1 of polydimethylsiloxane as stationary phase, 0.25 μm film thickness) were used for the study.

The GC operating conditions are as follows: initial temperature 60 °C; hold 1 min; ramp, 20 °C/min, til 190 °C; ramp 10 °C/min, final temperature 280 °C (1 min); injection port temperature 270 °C for PDMS and 290 °C for PA; detector temperature 300 °C; carrier gas helium, flow rate 1 ml/min; injection mode splitless (1 min).

The heater and magnetic stirrer was from Framo, Geratetecnik.

2.3. Samples

Five paper and board samples intended to use in contact with food were analyzed. Four samples were of recycled paper and board: Interliner (IL), Smedium (SM), Testliner (ET), HidroS (HS) and one was virgin paper and board (Kraft).

Three replicates of the same lot number were analyzed. The samples were cut into pieces (0.5 cm × 0.5 cm) and 2 g of each were placed in 20 ml vial for the analysis.

For the experimental design, a standard solution containing 6.3 μg/g for PCP was used. A spiked paper sample (ET) containing PCP was prepared to optimize the experimental design. This sample was prepared by adding the 0.15 g of the standard solution of PCP in methanol to the paper sample and then dried at room temperature.

The sample (2 g) with the standard PCP was introduced into a 20 ml screw-cap glass vial and was completely immersed in the water (10 ml), and the pH adjusted with HCl to 1.

2.4. Conventional extraction method

The procedure proposed by Gabelish et al. [38] was followed. In a 100 ml glass flask, add 1 g of paper and board sample, an ethylacetate solution of 50 μl of TCP (10.6 μg/g) used as internal standard and 5 ml of dichloromethane.

Extract in an ultrasonic bath for 5 min, remove the extract obtained and keep it in a 50 ml round bottom flask. Repeat eight times the extraction process and put together all the extracts. Evaporate the total extract to dryness under N_2 stream.

After extraction, the derivatization of PCP was achieved by addition of 100 μl of acetonitrile, 80 μl *N*,*N*-diisopropylethylamine and 120 μl of PFBBr to the 50 ml flask and wait for 60 min at room temperature.

The organic extract was evaporated to dryness and was diluted to a final volume of 1 ml with acetonitrile and passed through a 0.22 μm nylon filter before their injection into the GC–ECD system. The final solution was gravimetrically controlled.

2.5. Solid phase microextraction procedure

The polyacrylate (PA) and polydimethylsiloxane (PDMS), coated SPME fibers were used. They were obtained from Supelco (Bellefonte, PA, USA) with thicknesses of 85 and 100 μm, respectively. The fibers were conditioned under helium at a flow-rate of 1.0 ml/min in the hot injection port of a gas chromatograph at 300 °C for 2 h for PA and 250 °C and 1 h for PDMS.

In a 20 ml glass vial, add 2 g of paper and board sample, 5 g of KCl, HCl, 5 ml of water and a magnetic stirrer. Crimp the vial with a PTFE-lined septum and shake by hand for 30 s to allow the salt dissolution. Place in a thermostatized water bath at 60 °C. Introduce the 100 μm PDMS SPME fiber through the septum and keep it in the headspace of the vial for 60 min. Then, remove the fiber and proceed to its desorption in the injection port of a GC, and analyze the compounds under the conditions above described.

3. Results and discussion

3.1. Experimental design

A considerable number of variables are involved in SPME performance [39,40]. In order to reduce the time to achieve the optimum working conditions, an experimental design [41] with four variables was used for the PCP extraction. First, all the possible variables were considered, but due to that the number of experiments is high, a reduction to the strictly necessary variables was done. Table 1 shows the variables finally evaluated: addition of salt (A) and fiber (B), extraction time (C), extraction temperatures (D). Other important variables such as desorption time was further evaluated. Magnetic stirring and headspace mode were used in all cases.

The optimization basically consisted of a factorial design where 18 experiments, plus several replicates and statistical validity of results, must be carried out. With respect to the central point, four experiments were done in the following conditions: extraction temperature, 45 °C; extraction time, 50 min, PDMS fibre and 2.5 g of KCl.

The following variables were fixed for different reasons: 2 g were chosen as sample amount, since the concentration of PCP is expected to be very low; pH was fixed at 1.0 to assure that PCP was as molecular protonated specie, in principle easier for being extracted, as was above mentioned [42]; desorption temperature was 270 °C for PDMS fibre

Table 1
Experimental conditions used in the experimental design

Experiment	Salt (g)	Fibre	Extraction time (min)	Extraction temperature (°C)
1	2.5	PDMS	50	45
2	0	PA	80	60
3	5	PA	80	30
4	0	PDMS	80	30
5	5	PA	80	60
6	5	PA	20	30
7	0	PA	20	30
8	0	PDMS	80	60
9	0	PDMS	20	30
10	0	PA	20	60
11	5	PDMS	20	30
12	0	PA	80	30
13	5	PDMS	80	60
14	5	PDMS	80	30
15	5	PDMS	20	60
16	0	PDMS	20	60
17	5	PA	20	60
18	2.5	PA	50	45

and 290 °C for PA fibre, to avoid the carryover effect and be sure that the compounds were completely removed from the SPME fiber; and the desorption time was fixed at 2.5 min.

Two grams of the spiked sample were placed in a 20 ml screw.cap vial and water was added to cover the paper sample. pH was adjusted with HCl and 5 g of potasium chloride (5 g) were added. The vial was closed and clamped inside a water thermostatic bath placed on a magnetic stirrer.

A comparison of the sensitivity of the PCP extraction for the PA and PDMS coating fiber was performed.

All experiments were carried out in triplicate and the average GC peak area counted for comparison. Fig. 1 shows a comparison of the response factor obtained for PCP in each experiment.

The experiments E19, E20, E21 and E1 are identical and were used to check the repeatability of the method.

As can be seen, the highest values were obtained for the experiment 13; that used the PDMS fiber and 60 °C extraction temperature; 80 min extraction time and addition salt (5 g).

3.2. Performance of SPME method

3.2.1. Variables influence

Once all the experiments were carried out, the results were statistically evaluated by *t*-test. Fig. 2 summarises all the obtained results applying *t*-test. It must be pointed out that *y*-axis has been normalised, corresponding 100% to the average value of the design.

When studying the individual variables in detail, the type of fiber showed to be the most significant variable followed by extraction temperature and extraction time. Less influence was obtained with the salt addition.

As can be seen, some cross-effects between variables were significant according to *t*-test as, as expected, between the type of fiber and the extraction temperature. These variables are the most significant as in the others crossed effects were not observed. Some negative values but not very important were found between fiber and extraction time (BC), salt and fiber (AB) and extraction time and extraction temperature (CD).

According to the optimisation criterium, PDMS fiber showed to be considerably more effective than PA.

After the fiber material, two of the most important variables are the extraction temperature and the extraction time, being the optimum value critically affected by small differences in time. To check this behaviour, the extraction temperature and the extraction time were studied in depth.

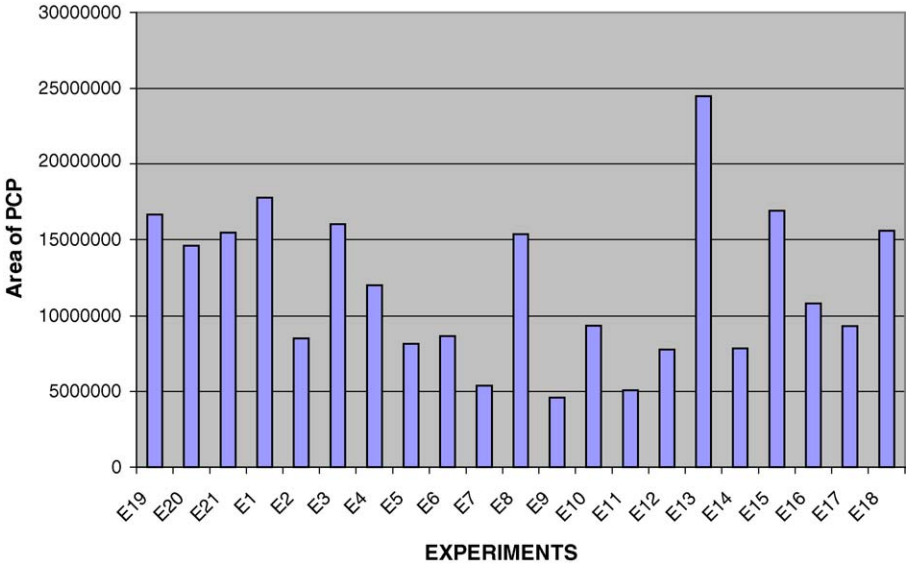

Fig. 1. Response factor obtained for PCP in each experiment. Experimental conditions described in Table 1.

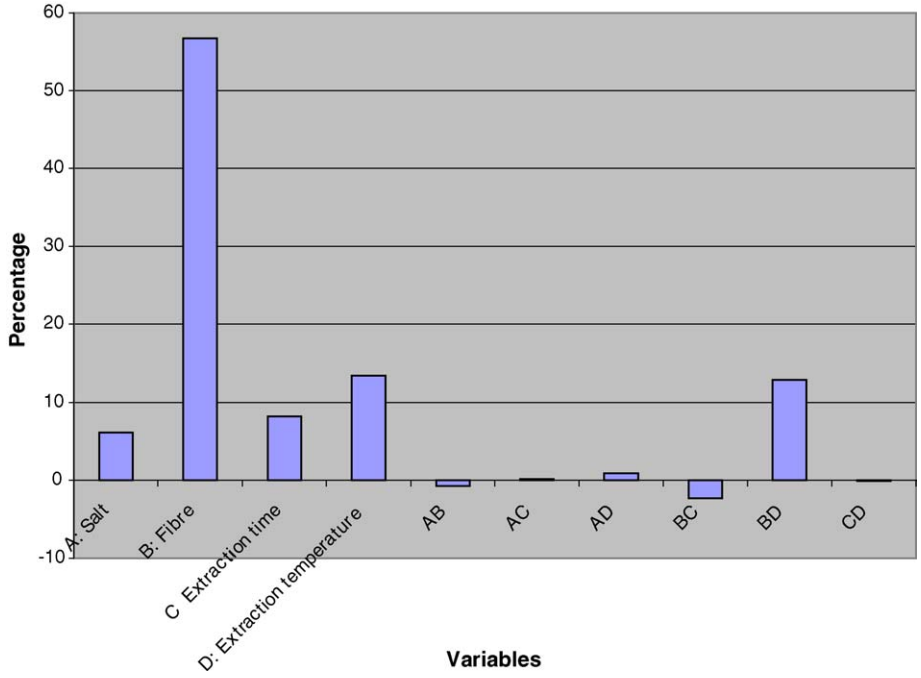

Fig. 2. Variables influence.

3.2.2. Effect of temperature of extraction

To study the dependence of the amount of analyte extracted as a function of extraction temperature, experimental conditions were studied increasing the range of temperature. The effect of sample temperature values 35, 40, 45, 50, 55, 60, 65 and 70 °C was examined. The conditions from the experiment with the best response factor, PDMS fiber, 80 min extraction time and the salt addition (5 g) were used. The extraction profiles of PCP are shown in Fig. 3.

As can be seen, the highest values were obtained at 60 °C of extraction temperature.

3.2.3. Effect of extraction time

The effect of extraction time on the extraction efficiency was studied. Values of time of 30, 40, 45, 50, 60 and 80 min of extraction time were applied. The conditions are the experiment with the best response factor, as was above mentioned. The extraction time profile of PCP is shown in Fig. 4.

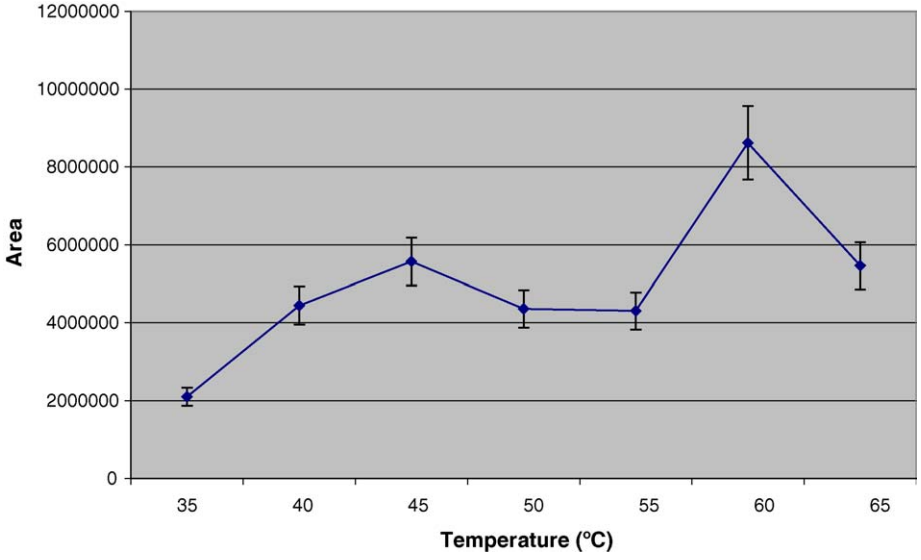

Fig. 3. Optimization of extraction temperature.

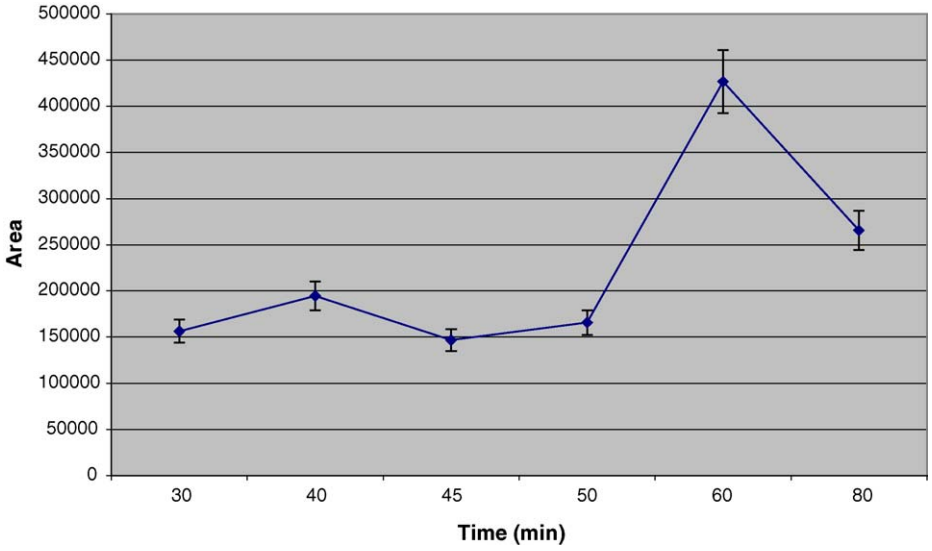

Fig. 4. Optimization of extraction time.

As can be seen, the highest values were obtained for 60 min of extraction time.

3.2.4. Effect of the fiber desorption time in the GC injector

According to our previous experience, one variable that could affect the procedure is the desorption time in the injection port of the GC. As was above mentioned the other conditions were those from the experiment with the best response factor. The desorption time of the PCP from the fiber was determined for 1.5, 2.0 and 2.5 min. The highest response factor was obtained for 2.0 min of desorption time.

3.2.5. Recommended procedure

The optimum conditions are as follows: place 2 g of the paper sample in small pieces (0.5 cm × 0.5 cm) in a 20 ml glass vial and add 10 ml of distilled water. Add 5 g of KCl 0.5 M and 5 g of HCl 0.1 M to adjust the pH of the sample at 1.0. Shake with magnetic stirrer at 1000 rpm. Use a 100 μm PDMS fiber of SPME at 60 °C for 60 min in headspace mode.Once the sorption step is finished, desorb the fiber in the injection port of the GC–ECD for 2 min at 270 °C.

3.3. Application of the SPME method in paper and board samples and comparison of conventional extraction method

3.3.1. External calibration procedure

To evaluate the effectiveness of the proposed method, the SPME procedure was used to determine the amount of pentachlorophenol in real samples of paper and board. It was compared with conventional extraction method of PCP also described in Section 2. GC–ECD was used to quantify PCP in all cases. Five samples were analyzed in triplicate.

Fig. 5 shows the chromatogram of paper and board sample using the SPME procedure. As PCP appears in the first 15 min, this was the selected chromatographic time to collect the data.

Quantitative analysis was carried out using external calibration, being the calibration range 0.064–1.1 μg/g of PCP.

The linearity of the optimized HS-SPME method was tested in the 0.051–2.1 μg/g PCP in water solution. Good linearity was found with correlation coefficient (r^2) greater than 0.971. The limit of detection was calculated from the signal-to-noise ratio (S/N) of the lowest detectable concentration and the value is 0.015 μg/g of PCP of water solution.

The results of concentration of PCP in the five samples obtained using direct analysis with external calibration with the SPME and conventional extraction methods are shown in Table 2. The RSD, calculated with three replicates, was in the range of 6–10% for conventional extraction method and 9–14% for SPME method.

First, it can be emphasize that none of the samples surpass the established limit of 0.15 mg/kg on paper basis.

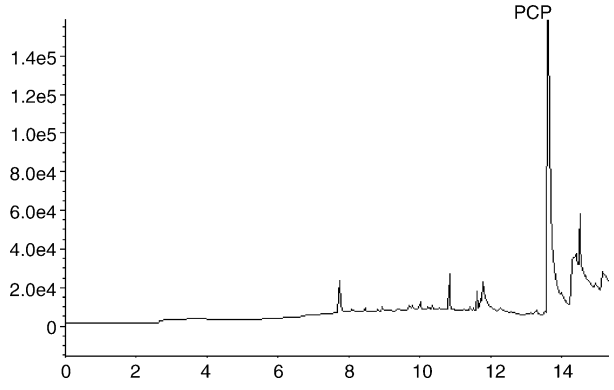

Fig. 5. Analysis of PCP in a real Kraft paper sample analysed by SPME–GC–ECD in optimum conditions.

Table 2
Concentration of PCP on five samples of paper and board (P&B) obtained by conventional extraction and SPME

SAMPLE	Conventional method (mg/kg)	SPME (mg/kg)
Testliner (ET)	0.08 ± 0.005	0.057 ± 0.007
HidroS (HS)	0.092 ± 0.008	0.065 ± 0.009
InterLiner (IL)	0.135 ± 0.01	0.091 ± 0.009
Kraft (K)	0.103 ± 0.01	0.087 ± 0.008
SMedium (SM)	0.114 ± 0.02	0.065 ± 0.007

The highest value obtained was 0.134 mg/kg and the lowest 0.080 mg/kg. The value obtained in the Kraft sample a virgin paper, is not the lowest, which demonstrates that the origin of PCP in the paper is from wood treatment and the recycled paper does not provide additional concentration of PCP.

The results showed that using the SPME procedure the efficiency ranges from 60 to 84% with respect to the values obtained by the conventional extraction method. Having recovery values lower than 80% could be attributed to the strong absorption of PCP in the paper matrix, which makes the extraction very difficult. The differences of the recovery of PCP obtained with the different samples could be attributed to the matrix influence which PCP is linked with. Besides, the experimental procedure can be modified so that the presence of other components does not influence the results. To overtake this difficult and facilitate the quantitative analysis, the standard addition procedure can be applied.

3.3.2. Standard addition procedure

The sample with the lowest extraction efficiency by SPME (SM, recycled paper) was analysed by the standard addition procedure. It consisted of adding a standard solution of PCP to several aliquots of paper sample to obtain the calibration plot and then, once dried, applying the SPME procedure.

To perform the standard addition method to nine aliquots of paper and board samples which contain possible interferences, different volumes of standard solution containing PCP were added. Then the final concentration added was between 0.088 and 0.373 μg/g of PCP in the paper sample.

In these conditions the regression curve was as good ($r^2 = 0.9854$) as that of external calibration, but the slopes are very different (396,904 for standard addition and 256,745 for external calibration), as expected due to the matrix effect above mentioned.

The result obtained was 0.099 μg/g with a regression coefficient of 0.985. This value is closer to the value of 0.114 μg/g used as reference, which demonstrates that using the standard addition procedure, the quantitation is better, as the recovery is much higher.

4. Conclusions

SPME has been proposed as a direct, solvent-less and attractive procedure for the analysis of PCP in paper and board samples. However, as this analyte is strongly linked to the solid matrix, the standard addition procedure using SPME is required.

In the case of PCP, the strong reduction of extraction time and the possibility of carrying out the analysis directly on the paper and board can be considered as enough advantage to accept the procedure, even using the external calibration, although knowing that the values obtained by SPME are between 70 and 84% of those obtained by the conventional procedure using a derivatization step. For this reason the standard addition procedure should be necessary to get a higher recovery of PCP.

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