Short communication

Pressurised liquid extraction of pentachlorophenol from dyestuffs and cotton

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Abstract

Pressurised liquid extraction (PLE) was used to extract pentachlorophenol from cotton and dyestuffs. Five dyes and one dyed cotton were investigated for pentachlorophenol. The dyed cotton was found to have between 5.3 and 5.9 μg g^{-1} pentachlorophenol, while the dyes were found to have between 42 and 2569 μg g^{-1} pentachlorophenol present. The latter were found to be dye and manufacturing site dependant. Recovery experiments, in all cases, were found to be quantitative indicating appropriate sample work-up and manipulations. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The extraction and analysis of organic contaminants currently on the US Environmental Protection Agency (EPA) ''Red List'' [1] of high priority pollutants is important. Pentachlorophenol (PCP), for example, has high toxicity and persistence in the environment [2] hence levels need to be monitored carefully. PCP is deposited in the environment through several channels: from the petroleum industry [3]; as a by-product of the dye manufacturing process [2]; as a means of termite control [2]; and, as a herbicide [2]. Derivatives of PCP are also used as fungicides to protect against fungal rot of wood [2].

Pressurised liquid extraction (PLE; also known

under the Dionex trade name accelerated solvent extraction, ASE) is a relatively new technique (introduced in 1995), quickly gaining importance in an environmentally conscious world. Not only does it reduce sample extraction time, allowing alternative tasks to be completed, but also reduces solvent consumption, a factor many industries now recognise as crucial. PLE has been used on various occasions to extract phenols from soils and sediments [4,5]. Comparisons between PLE and conventional solvent extraction methods for organophosphorus pesticides and herbicides [6], yielded similar results for the two methods, indicating PLE is potentially a replacement for older, high solvent consumption methods, such as Soxhlet extraction. Frost et al. [7] also used PLE in a comparative study for the extraction of hexaconazole residues from weathered soil, with excellent preci-

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sion on three varying soil types. The results were comparable to those obtained by Soxhlet extraction, and significantly better than those obtained from either microwave-assisted extraction or supercritical fluid extraction. PLE has also been used to successfully extract polynuclear aromatic hydrocarbons (PAHs) from contaminated soil [8].

The aim of this paper is to investigate the extraction of PCP from dyestuffs using an experimental design approach. Then, using the optimum extraction conditions, apply the method to other dyestuffs and dyed cotton.

2. Experimental

An ASE 200 accelerated solvent extractor [Dionex (UK), Camberley, UK] was used to perform the extractions. 11-ml cells were used for all the extractions. The system is automated and capable of 24 sequential extractions. Typical extraction conditions are based on a pressure of 2000 p.s.i. (1 p.s.i.= 6894.76 Pa), a temperature of 100°C and a total extraction time of 10 min.

2.1. Dyestuffs and dyed cotton

Five samples of vat dyes and a sample of vat dyed cloth contaminated with PCP were obtained from Zeneca Specialties. The vat dyes are all based on chlorinated violanthrones.

2.2. Solvents and standards

The toluene used for the extractions was certified analytical-reagent grade (Fisher Scientific, Loughborough, UK), hexachlorobenzene and *N,O*-bis-(trimethylsilyl)acetamide derivatising agent were purchased from Aldrich (Gillingham, UK).

2.3. Gas chromatographic–mass spectrometric analysis

The gas chromatography–mass spectrometry (GC–MS) system (HP G1800A GCD system, Hewlett-Packard, Palo Alto, CA, USA) was operated in the selected-ion monitoring mode with a splitless injection volume of 0.5 μl.

The column used was a DB-1 (J&W Scientific, Folsom, CA, USA) of 30 m×0.25 mm I.D., 0.25 μm film thickness. The temperature program used for the analysis was: 90°C for 2 min to 250°C at 10°C min^{-1} with a final hold time of 12 min. The injection port temperature was set at 250°C, and the detector temperature was set at 280°C.

GC–MS in the selected-ion monitoring mode was used to determine the presence of PCP. The ions monitored were m/z 323 and m/z 321. Quantification was achieved by use of a 10-point calibration curve from 0 μg ml^{-1} to 50 μg ml^{-1} for the dye work (r^2=0.9995). For cotton a seven-point calibration from 0 μg ml^{-1} to 5 μg ml^{-1} (r^2=0.9993) was generated. Selected standards were run on a daily basis to assess analytical performance.

2.4. Extraction procedures: PLE

Dye (0.2 g accurately weighed) or cotton (three pieces, 1.5 cm×1.5 cm accurately weighed) were placed in a stainless steel extraction cell that had been prefitted with a filter paper [Dionex (UK), specifically for ASE]. The headspace was filled with an inert matrix, hydromatrix (Varian, Surrey, UK). The cell was placed in the carousel and the extraction was started. Each of the extracts were strongly coloured (burgundy). Sonication was required for 2 min to ensure all the dye was in solution. The extract was then quantitatively transferred into a volumetric flask (50 ml capacity) and made up to the mark using toluene. A 1-ml aliquot was removed and placed in a tapered tube (10 ml capacity). Internal standard (hexachlorobenzene, at the 10 μg ml^{-1} level) was added along with 100 μl of the derivatising agent [*N,O*-bis-(trimethylsilyl)acetamide]. The solution was mixed thoroughly and 0.5 μl of the derivatised extract was injected.

2.5. Extraction procedures: solvent extraction

An accurately weighed (5 g) sample (dye or dyed cloth) was dissolved in 250 ml of concentrated H$_2$SO$_4$ and placed on a Ludwig extractor (rotation perforator). The acidified sample solution was then extracted using *n*-hexane for 2 h. After extraction, the extract was dried with 2 g of anhydrous sodium

sulphate. The extract was then derivatised, as described above.

2.6. Recovery experiments

2.6.1. Spot spike procedure

Hydromatrix (5×1 g), or cotton (5×3 g) was spiked at each of the following levels of PCP in 25 µl dichloromethane; 20, 300 and 1000 µg ml^{-1}. The solvent was allowed to evaporate and the hydromatrix or cotton were extracted immediately.

2.6.2. Slurry spike procedure

Hydromatrix (3×5 g), or undyed cotton (3×5 g) was spiked with pentachlorophenol in 25 ml of dichloromethane at three different levels to give a final concentration of 20, 300 and 1000 µg ml^{-1}. The solvent was allowed to evaporate overnight and then left for approximately 4 days before extraction to allow some interaction of the pentachlorophenol with the matrix. Portions (1 g) of the hydromatrix or cotton were extracted each time.

3. Results and discussion

The reproducibility of the GC analysis was assessed by monitoring the area of a 5 µg ml^{-1} PCP standard. The average signal response was 20 184

counts s^{-1} with an RSD of 0.3%, based on nine determinations determined over 3 weeks.

3.1. Optimisation of PLE operating conditions

A central composite design (CCD) was used to optimise the PLE conditions. A single dye was used for this process. A CCD consists of a two-level full factorial design superimposed on a star design with the centres of the two designs coinciding. A CCD with three variables takes the form of a cube with star points located in the centre of each face. The three ASE operating parameters investigated were pressure, temperature and time. Each of these operating parameters were investigated between the following limits: pressure, 1100 and 2400 p.s.i.; temperature, 40 and 200°C; and, static extraction time 2 and 16 min. The CCD was generated using a statistical software package (CSS Statistica/W, Release 5.0 with Industrial units, Statsoft UK, Letchworth, UK). Sixteen experiments were required. Each experiment was performed in duplicate. The operating parameters and the quantity of PCP that was removed from the dye for each experiment are shown in Table 1. Multilinear regression (MLR) was then performed on the data using a mathematical package (Statistica). The equation for the central composite design was as follows:

Table 1
Central composite design for the extraction of pentachlorophenol from a dyestuff

Experiment No.	Pressure (p.s.i.)	Temperature (°C)	Time (min)	µg ml^{-1} PCP ($n=2$)
1	1300	170	13	1670
2	2100	170	5	1263
3	1700	120	16	902
4	2100	70	13	1228
5	1700	200	9	1254
6	1700	120	2	1121
7	1300	170	5	994
8	1300	70	5	1090
9	2100	170	13	878
10	1700	120	9	1140
11	2400	120	9	1329
12	1700	120	9	1230
13	1000	120	9	1299
14	2100	70	5	860
15	1300	70	13	1108
16	1700	40	9	775

$$y = b_0 + b_1 P + b_2 T + b_3 t + b_4 P^2 + b_5 T^2 + b_6 t^2$$
$$+ b_7 PT + b_8 Pt + b_9 Tt + b_{10} PTt$$

where y is the concentration of PCP (μg g^{-1}) extracted from the dye, b_0 is the intercept, and P, T and t are pressure, temperature and extraction time, respectively. The correlation coefficient was 0.9076 ($r^2 = 0.8237$). From the results of the MLR a model for the extraction of PCP from the dye can be determined. The significant parameters are highlighted in bold in Table 2. It can be seen that the temperature and combined static extraction time (Tt), together with the three-term interaction (PTt) were the most significant parameters at the 95% confidence level. Individual and quadratic parameters were deemed not to be significant at the 95% confidence level. It should be noted however that the intercept, combined pressure and temperature (PT), and pressure and time (Pt) terms are also significant at the 90% confidence interval.

A graphical representation of the model (Fig. 1) showed that the optimum conditions for the extraction of pentachlorophenol from dye were an extraction temperature of 140°C and a static extraction time of 10 min (pressure was fixed at 2000 p.s.i.).

3.2. Recovery experiments

The recovery experiments (Table 3) from the hydromatrix and undyed cotton demonstrated that near quantitative recovery occurred irrespective of the spike level and method (spot and slurry) investigated. The spot spike gave average recoveries of
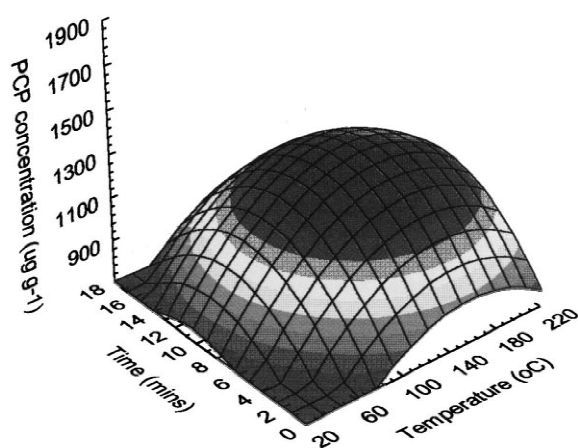

Fig. 1. Response surface for PCP recovery from a dyestuff.

86.1% ($n = 3$) from cotton and 92.6% ($n = 3$) from hydromatrix, while the slurry spike gave average recoveries of 89.3% ($n = 3$) from hydromatrix and 87.8% ($n = 3$) from cotton. Good precision was achieved by both methods (RSD < 3.8%). This showed that the analytical procedure was robust, and that hydromatrix and undyed cotton did not influence the extraction of PCP.

3.3. Extraction from dye and dyed cotton

Dye samples were extracted using the optimum conditions determined above. The average results ($n = 6$) were as follows [mean (RSD, %)]: 42 μg g^{-1} (1.8), 152 μg g^{-1} (4.2), 726 μg g^{-1} (1.5), 828 μg g^{-1} (3.7), 2570 μg g^{-1} (4.8). These differences in the amount of PCP extracted from the dye were due to different manufacturing processes and their origin. In addition, one of the dyes (2570 μg g^{-1}) was also extracted using the Ludwig extractor. The mean result by this approach was 1162 μg g^{-1} ($n = 2$). This result was of the order of two-times lower than that recorded by the optimised PLE approach.

As PLE was originally optimised using a CCD for dyestuffs only. It was appropriate to confirm that the operating conditions were also appropriate for dyed cotton. As the experimental design approach identified temperature and time as key operating variables (as can be seen in Fig. 1) for dyestuffs it was considered appropriate to investigate these further. A

Table 2
Multilinear regression for the extraction of PCP from a dyestuff

Variable	Coefficient	P-value
Intercept	3971.6	0.0977
P	−2.704	0.1114
T	−21.313	0.1761
t	−286.424	0.1569
P^2	0.000	0.3766
T^2	−0.023	0.3685
t^2	−3.143	0.3605
PT	0.017	0.0585
Pt	0.209	0.0751
Tt	3.689	**0.0321**
PTt	−0.002	**0.0277**

Table 3
PLE of pentachlorophenol from inert hydromatrix and undyed cotton ($n=6$)

Method of spiking		Hydromatrix			Cotton		
		Spike level (μg g^{-1})			Spike level (μg g^{-1})		
		20	300	1000	25	300	1000
Spot	Mean	18.7	273	932	22.0	254	856
	RSD (%)	3.5	1.5	1.7	1.5	1.5	3.8
Slurry	Mean	18.4	251	923	22.1	268	856
	RSD (%)	1.5	2.6	1.7	3.0	0.8	1.6

sub-sample of dyed cotton was selected. As the static extraction time selected was considered to be appropriate and within recommended guidelines (the US EPA approach for analytes recommends 10 min [9]) no further investigation of time was done. However, temperature was investigated. Three temperatures were investigated; 100, 140 and 170°C. The mean results ($n=2$) recorded were as follows: 2.6, 5.7 and 5.6 μg g^{-1}, respectively. It was concluded therefore, that the original optimum PLE conditions for dyestuffs were also amenable to dyed cotton, i.e., a temperature of 140°C was required. Sub-samples of dyed cotton were subsequently analysed. The average results ($n=6$) were as follows [mean (RSD, %)]: 5.3 μg g^{-1} (3.9), 5.7 μg g^{-1} (5.6), 5.9 μg g^{-1} (3.2), 5.7 μg g^{-1} (3.1), 5.5 μg g^{-1} (1.6). No differences in the PCP level were noted for the dyed cotton. In addition, a subsequent sub-sample of dyed cotton was extracted using the Ludwig extractor and found to contain 5.0 μg g^{-1} PCP ($n=2$). This was considered to be in agreement with the PLE results.

Acknowledgements

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