Analysing organochlorine pesticides in strawberry jams using GC-ECD, GC-MS/MS and QuEChERS sample preparation

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This paper describes a comparison of adaptations of the QuEChERS (quick, easy, cheap, effective, rugged and safe) approach for the determination of 14 organochlorine pesticide (OCP) residues in strawberry jam by concurrent use of gas chromatography (GC) coupled to electron capture detector (ECD) and GC tandem mass spectrometry (GC-MS/MS). Three versions were tested based on the original QuEChERS method. The results were good (overall average of 89% recoveries with 15% RSD) using the ultrasonic bath at five spiked levels. Performance characteristics, such as accuracy, precision, linear range, limits of detection (LOD) and quantification (LOQ), were determined for each pesticide. LOD ranged from 0.8 to 8.9 $\mu g\,kg^{-1}$; LOQ was in the range of 2.5–29.8 $\mu g\,kg^{-1}$; and calibration curves were linear ($r^2 > 0.9970$) in the whole range of the explored concentrations (5–100 $\mu g\,kg^{-1}$). The LODs of these pesticides were much lower than the maximum residue levels (MRLs) allowed in Europe for strawberries. The method was successfully applied to the quantification of OCP in commercially available jams. The OCPs were detected lower than the LOD.

Keywords: chromatography – GC; extraction; GC/MS; pesticides – organochlorine; pesticide residues; processed foods; organic foods; cooked foods; fruit

Introduction

Pesticides are used globally for the protection of food, and more generally for human health. However, their excessive use/misuse, especially in developing countries, volatility and long-distance transport eventually results in widespread environmental contamination (Kaushik et al. 2009; Perez-Serradilla et al. 2010). Organochlorine pesticides (OCP) are a large class of very persistent pollutants. They stay in the environment after being applied for long periods. Many OCPs are endocrine-disrupting chemicals, meaning they have subtle toxic effects on the body's hormonal systems, contributing to adverse health effects (Mansilha et al. 2010).

The use of OCPs has been highly restricted in European countries, but they have been reported in several food samples (Correia et al. 2000; Barriada-Pereira et al. 2003, 2007; Da Silva et al. 2010; Dubois et al. 2010; Rashid et al. 2010; Fernandes et al. 2011a) in the last decade. It is, therefore, not surprising that residues of OCP in food have given rise to major concerns. OCPs have been found in both raw and processed foodstuffs (Keikotlhaile et al. 2010). A reduction of pesticide residue levels occurred due to processing techniques in most of the food materials due to pesticide degradation. In the case of juicing fruits and pressing or extraction of oil from vegetable seeds, the food material was concentrated (Holland et al. 1994; Kaushik et al. 2009; Dasgupta et al. 2010; Keikotlhaile et al. 2010). Jam processing may be considered a concentration given that water from fruit is lost during the procedure.

The aim of this study was the development of a useful method for the determination of OCP in strawberry jam. The major analytical problem was due to the complexity of the matrix. The potential interferences from the complex matrix requires a sample preparation step. The preparation of fruit preserves (jams, jellies and marmalades) usually involves the use of pectin as a gelling agent, although sugar or honey may be used as well. Pectin is required to provide thickening or gel formation (Fúgel et al. 2005). The fact that the samples are strawberry jam increases the analytical difficulties when compared with the methods used for the determination of OCP in fresh strawberries (Fernandes et al. 2011b).

There are a few studies of samples with processed fruit, with Sannino (1995) reporting a study of fungicides in jams. Furthermore, in 2004 an analytical method was proposed for pesticide control in concentrated lemon juice (Sannino et al. 2004).

In this context, liquid–liquid extraction (LLE) (Navickiene et al. 1999; Fontcuberta et al. 2008), solid-phase extraction (SPE) (Di Muccio et al. 2006), and solid-phase micro-extraction (SPME) (Wennrich et al. 2001; Beltran et al. 2003; Lambropoulou and Albanis 2003; Sanusi et al. 2004) have frequently been applied in strawberry analysis. Anastassiades et al. (2003) introduced a new method described as 'quick, easy, cheap, effective, rugged and safe' (QuEChERS) for the quantification of pesticide residues in fruit and vegetables. In a follow-up study, Koesukwiwat et al. (2010) conducted validation experiments of the QuEChERS method for 150 pesticides in several matrixes.

Considering the assay of OCP, gas chromatography (GC) can be coupled to an electron capture detector (ECD) (Barriada-Pereira et al. 2005, 2007; Berrada et al. 2010), a mass spectrometer (MS) and a tandem mass spectrometer (MS/MS) (Colume et al. 2001; Bolanos et al. 2007; Medina et al. 2009; Wong et al. 2010). GC-MS/MS has been recommended for use to minimise interference effects in complex sample matrices (Cortes-Aguado et al. 2008). Tao et al. (2009) used GC ion-trap mass spectrometry (IT/MS) to detect multi-residues of pesticides in vegetables. IT/MS is good for qualitative analysis, but not efficient for quantitative analysis. A two-dimensional GC coupled with time-of-flight MS (GCxGC-ToF-MS) method is generally recommended for multi-residue analysis of a large number of compounds, as it resolves many co-elution problems and provides a much improved chromatographic separation of target compounds from each other as well as from the matrix background (Feo et al. 2010).

In this work two alternative methodologies using GC-ECD and GC-MS/MS were performed for the sensitive and selective determination of 14 OCP residues in strawberry jam after an optimisation of the preparation process, with different approaches involving QuEChERS methods.

Materials and methods

Reagents and samples

A total of 14 OCPs was selected for this study: α-, β-, γ- and δ-hexachlorocyclohexanes (HCHs), hexachlorobenzene (HCB), *o,p′*-DDT ([1,1,1 trichloro-2, 2-*bis*-(*p*-chlorophenyl) ethane]), *p,p′*-DDE ([2,2-*bis*(*p*-chlorophenyl)-1,1-dichloroethylene]), *p,p′*-DDD (dichlorodiphenyldichloro-ethane), aldrin, dieldrin, endrin, α,β-endosulfan, and methoxychlor. Pesticide standards (purity > 97.0%) were obtained from Chemservice (West Chester, PA, USA), Dr. Ehrenstorfer GmbH (Augsburg, Germany), and Sigma-Aldrich Co (Steinheim, Germany). Standard solutions of OCP were prepared in *n*-hexane (HPLC grade) supplied by Merck (Darmstadt, Germany). Acetonitrile (Merck) were also HPLC grade. 4,4′-Dichlorobenzophenone was purchased from Sigma-Aldrich and used as an internal standard (IS) for chromatographic analysis. The selected QuEChERS (EUMIV50CT-VP) from UCT (Bristol, PA, USA) were 50 ml extraction tubes containing 6 g anhydrous magnesium sulfate ($MgSO_4$), 1.5 g sodium chloride, 1.5 g trisodium citrate dehydrate and 0.75 g disodium hydrogencitrate sesquihydrate. Clean-up was performed with micro-centrifuge clean-up tubes (CUMPS15C18CT) from UCT containing 150 mg of anhydrous $MgSO_4$, 150 mg of PSA and 50 mg of C18.

Samples

Nine commercially available strawberry jams from different types of production were obtained from local shops and supermarkets in Porto, Portugal. One of them was produced by organic farming strawberries and the other eight from conventional farming (five jams were produced by traditional methods and the other four by industrial procedure).

Preparation of standard solutions

The IS solution of 4,4′-dichlorobenzophenone was prepared at 350 $\mu g\, l^{-1}$ in *n*-hexane. Using the same solvent, a stock standard mixture solution with a concentration of 350 $\mu g\, l^{-1}$ for each of the 14 OCPs was prepared. Calibration matrix-matched standard solutions, with concentration levels ranging from 5 to 100 $\mu g\, kg^{-1}$, were prepared by an appropriate dilution of the more concentrated mixture (350 $\mu g\, l^{-1}$) in blank extracts of the matrix. All solutions were stored under refrigeration (2–6°C).

Sample preparation

Nine bottles of strawberry jam were directly blended and stored in a deep freezer (−20°C). The samples were homogenised in a grinder (Krups). A modified QuEChERS extraction based on Standard Method EN 15662 (Anastassiades 2008) citrate buffering was developed. The homogenised jam samples (10 g) were weighed into 50 ml polypropylene centrifuge tubes. A known pesticide concentration mixture and the IS were spiked into the samples, which were allowed to stand for 1 h at room temperature to allow solvent evaporation and then shaken vigorously. A total of 10 ml of acetonitrile (ACN) was added to the samples and mixed using an automatic vortex for 5 min to swell the matrix and extract the samples. The citrate buffering salts were added to each tube, which was shaken for 1 min, ensuring that the powders did not agglomerate. A total of 1 ml aliquots of the ACN extracts (upper layer) were transferred to 2 ml mini centrifuge clean-up tubes, which were shaken for 30 s. The dispersive solid-phase (d-SPE) extraction tubes were centrifuged at 4000 rpm for 5 min and an aliquot of 1.0 ml was transferred into a vial and put under a mild stream of nitrogen to dryness. Finally, 1 ml of hexane was added to redissolve the extract and then 2 µl of this solution were injected into the gas chromatography.

Three versions were studied. (1) Only the vortex was used (described above). (2) After adding 10 ml of ACN, the sample was introduced into a homogeniser (Thomas Teflon homogeniser) for 2 min. The extract was then homogenised at high rpm using a homogeniser with a Teflon tip. (3) The 50 ml tubes with ACN extracts were placed into ultrasonic bath for 5 min (Figure 1).

Gas chromatography-electron capture detector (GC-ECD)

OCPs were analysed using a Shimadzu GC-2010 with an ECD apparatus, equipped with a capillary column of 30 m, TRB-5MS (0.25 mm i.d., 0.25 µm film thickness, Teknokroma). The oven temperature was programmed starting at 65°C and held for 2 min, followed by increases of 8°C min^{-1} to 160°C, then 2°C min^{-1} to 235°C, and then 15°C min^{-1} to 250°C. The injection port was at 250°C in splitless mode, and the detection was carried out at 300°C. Helium (Linde Sogás) was used as carrier gas at a constant flow rate of 1.3 ml min^{-1}; while nitrogen (Linde Sogás; purity ≥ 99.999%) was employed as a make-up gas at the flow of 30 ml min^{-1}. The system was operated by GC solution Shimadzu software.

GC-MS/MS analysis

A Trace GC Ultra gas chromatograph Polaris Q coupled with an ion-trap mass spectrometer (Thermo Fisher Scientific) operated in electron impact ionisation (EI) mode at 70 eV controlled by Xcalibur 1.3 software was used for the determination of residues. Confirmation of residues was carried out by GC-MS/MS using a Supelco column fitted with a SLBTM-5MS (30 m × 0.25 mm, 0.25 µm film thickness). The injector operating in the splitless mode and an ultrapure grade helium (Linde Sógas; purity ≥ 99.999%) were used as the carrier gas at 1.3 ml min^{-1} flow. The GC oven temperature was programmed from an initial temperature of 40°C (2 min hold), ramped at 30°C min^{-1} to 220°C (5 min hold) and finally at 10°C min^{-1} to 270°C with holding for 1 min. This programme resulted in a total run time of 21 min. The other optimised parameters included a transfer line temperature of 250°C and an ion source of 250°C. The MS/MS conditions were fixed for each compound, trying to select as the precursor ion the one with the highest *m/z* ratio and abundance (Table 1).

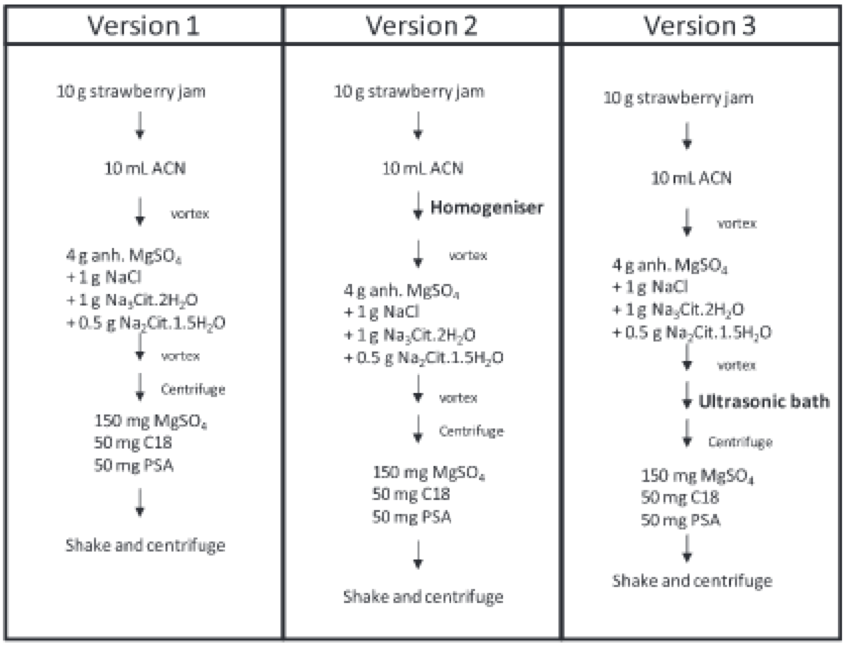
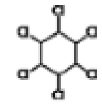
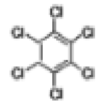
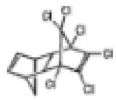
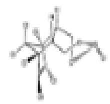
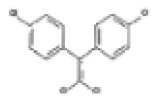
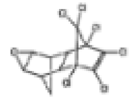
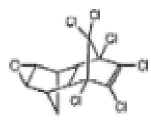
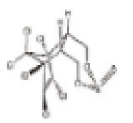
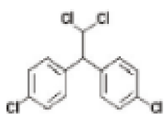
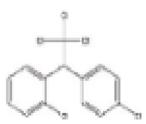
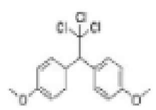


Figure 1. Flowchart of the analysis of OCP in strawberry jams.

Table 1. Optimised MS/MS conditions of the analysed pesticides.

Pesticide	Molecular weight ($g\,mol^{-1}$)	Structure	Solubility in water ($mg\,l^{-1}$) at 20°C	Segment	Precursor ions (m/z)	Product ions for MS/MS method (m/z)
α-HCH	290.8		1.0	5.00	219	109, 146
β-HCH			0.1			
γ-HCH (lindane)			1.0			
δ-HCH			6.5	8.10		
HCB	284.8		0.04	7.50	142	141
Aldrin	364.9		0.02	9.54	263	191
α-Endosulfan	406.9		0.15	11.20	195	170
p,p′-DDE	318.0		0.04	11.90	318	176, 211
Dieldrin	380.9		0.17		243	206, 211
Endrin	380.9		0.23	12.75	245	211
β-Endosulfan	406.9		0.15	13.22	195	170
p,p′-DDD	320.0		0.05		235	165, 199
o,p′-DDT	354.5		0.003		235	165, 199
Methoxychlor	345.7		0.1	15.00	227	152, 169

Method validation

The analytical method was validated as per the single-laboratory validation approach. The performance of the method was evaluated considering the following validation parameters.

The calibration curves of the compounds in the matrix were obtained by plotting the peak area against the concentration at seven calibration levels ranging from 5 to 100 μg kg^{-1}.

Limits of detection (LOD) and quantification (LOQ) were determined by considering the slope of the calibration line and the residual standard deviation of a regression line (ICH 1996). The recovery experiments were carried out on strawberry jam by fortifying the samples (10 g) in three replicates with the pesticide mixture separately at five concentration levels of 0.005, 0.010, 0.030, 0.090 and 0.180 mg kg^{-1}, extracting by the method described above. The quantification of recovery samples was done by using the peak area of the analyte and calculating the concentration by preparing a calibration curve. The optimised method was applied to the screening of nine strawberry jams samples.

Results and discussion

The major analytical problem was due to the complexity of the matrix (Fügel et al. 2005) combined with potential interferences from the presence of co-extractives such as pigments and added pectin in the jams. Consequently, the determination of pesticides in jams must involve a sample preparation step including an extraction process followed by a clean-up.

Optimisation of extraction and clean-up

The QuEChERS method is commonly used for fruit and vegetables, but it can be applied to the analysis of other different types of food samples. This present method has been conceived and is presented as a versatile tool, which can be easily adapted to accomplish the legislation. The QuEChERS extraction followed by a d-SPE clean-up gave very clean extracts, with good results and short clean-up times. The sample preparation required, before the extraction, an additional step based on the use of an ultrasonic bath in order to release analytes from the pectin gel which severely affect the accurate identification and quantification of the analytes, in this case OCP. IS was added to the strawberry jam at the beginning of the analytical procedure in order to monitor critical stages of the extraction clean-up process.

The QuEChERS extractions followed by the clean-up step were evaluated by measuring the recoveries. The results (Figure 2) proved that the inclusion of a homogenisation (version 2) or an ultrasonic bath (version 3) in the pre-treatment increased the recoveries. The range obtained was 43–132%, which implies that some values are not in compliance with the reference range (70–120%) defined by SANCO (2009). The HCH isomers and HCB had lowest recoveries in all versions of the procedure. Although there was an increase of 10% in version 3, the result was not sufficient to reach 70%. However, aldrin, dieldrin, endrin, α,β-endosulfan and p,p'-DDE achieved acceptable values as defined by the SANCO (2009) criteria. The OCP, p,p'-DDD, o,p'-DDT and methoxychlor with the version 3 procedure appear to be affected by matrix effects because the recovery results were greater than 120%. In these cases, the matrix induced chromatographic response enhancement, which causes higher analyte transfer efficiency, thus a greater signal in the presence of the matrix (Lehotay et al. 2010; Mansilha et al. 2010).

After the optimisation method, five spiking levels (0.005, 0.010, 0.030, 0.090, 0.180 mg kg^{-1}) were studied

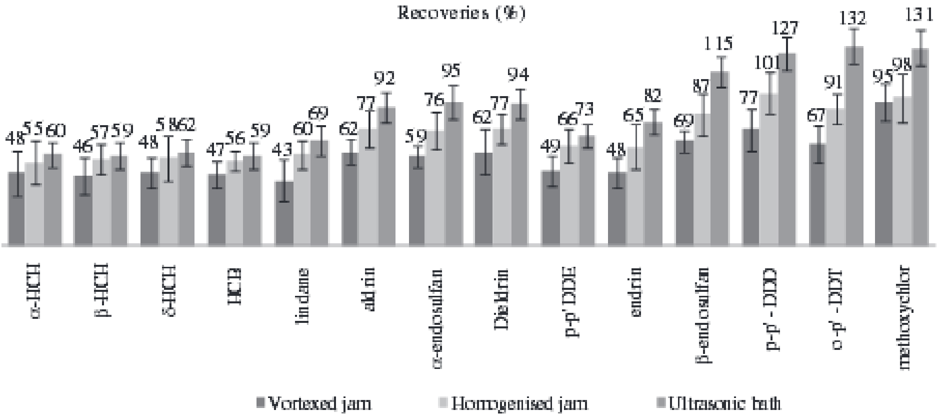


Figure 2. Average recoveries for strawberry jam samples spiked at 50 μg kg^{-1} and analysed by three different sample preparation procedures ($n = 2$).

and the recovery of each compound at each concentration was replicated three times (Table 3). The recoveries were in the range of 62–129%. Precision was expressed as relative standard deviation (RSD). The precision was very similar for all OCP with RSD ($n = 3$) varying from 5% to 15%. The recovery results have some variation in the three different samples: commercial, traditional and organic jams. In commercial jam, the recovery values obtained from *o,p′*-DDT, *p,p′*-DDD and methoxychlor for the five spiked levels were similar and higher than 120%. In the case of traditional jams, recoveries were less than 120% for the *o,p′*-DDT and *p,p′*-DDD for samples spiked with 0.005, 0.010 and 0.180 mg kg^{-1}. The recoveries obtained from methoxychlor were lower than 120% for all spiking levels in traditional jam extract. In organic jam, all the recovery results were within the limits set. Therefore, the spiking levels as well as the way the sample is produced and its processing influence the results of recoveries.

Some of the OCP targets are easily affected by matrix-induced enhancement. These compounds may be overestimated and increase chromatographic response (Figure 3).

p,p′-DDD, *o,p′*-DDT and metoxychlor showed recoveries above 120% when using an ultrasonic bath. The matrix effects are most evident in version 3, in OCPs with higher retention times. The OCPs with shorter retention times and higher solubility in water showed a negative matrix effect because they had recoveries below 70%.

Validation

The most common way to avoid matrix effects is to use matrix-matched calibration standards, which was done in this study for both GC-ECD and GC-MS/MS techniques. Jam samples spiked with OCP were used for the preparation of the calibration curves. They were obtained by using three replicate injections of the mix standard solution in each matrix at seven calibration levels, from 5 to 100 µg kg^{-1}, all containing 50 µg kg^{-1} of dichlorobenzophenone as the IS. Calibration curves were linear over the whole range of concentrations tested for all pesticides, as indicated by the very good values of the determination coefficients (R^2) which were between 0.9970 and 0.9996, as shown in Table 2. LOD and LOQ were determined as 3.3 and 10 times $s_{x/y}/b$, respectively, where b and $s_{x/y}$ are the slope of the regression line and the standard deviation of the intercept (ICH 1996). LODs were in the range of 0.8–8.9 µg kg^{-1}, while LOQs were from 2.5 to 29.5 µg kg^{-1}. Generally, the lower LOD values are obtained by using GC-ECD, although some pesticides have similar LOD values with the two techniques. There is no legislation regulating the maximum residue limits (MRL) of OCPs in jams; nevertheless, the MRL of OCPs in strawberries ranges from 0.01 to 0.05 mg kg^{-1}, depending on the specific OCP (European Union Database). The LOD values of the method are low enough to determine the target pesticides in strawberry jam samples with concentrations far lower than the MRL of OCPs in strawberries.

Chromatographic analysis

The GC-ECD demonstrated high performance compared with GC-MS/MS for the detection and quantification of OCP (Table 2). The chromatograms obtained by these two different techniques show a better chromatographic resolution by GC-ECD at a concentration of 50 µg l^{-1} when compared with the

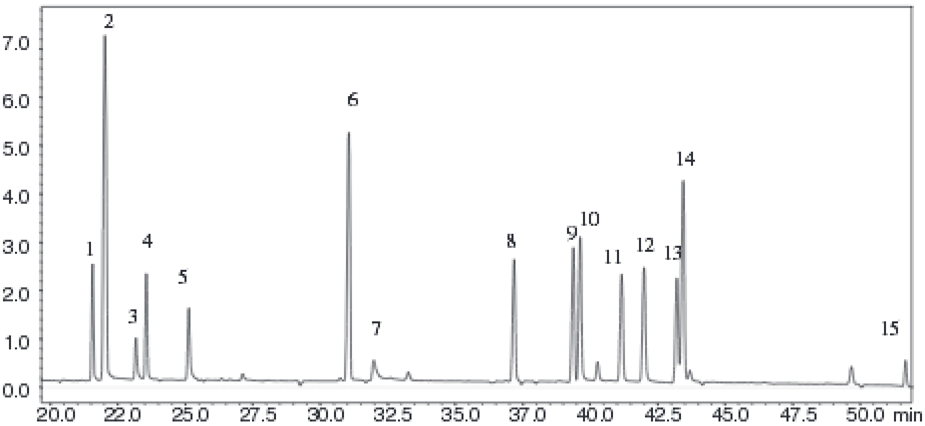


Figure 3. GC-ECD chromatogram of mixture OCP (50 µg l^{-1}). Peak identification in order of increasing retention time is as follows: 1, α-HCH; 2, HCB; 3, β-HCH; 4, γ-HCH; 5, δ-HCH; 6, aldrin; 7, IS; 8, α-endosulfan; 9, dieldrin; 10, *p,p′*-DDE; 11, endrin; 12, β-endosulfan; 13, *p,p′*-DDD; 14, *o,p′*-DDT; and 15, methoxychlor.

chromatogram obtained by MS/MS at a concentration of 100 μg l^{-1} (Figures 3 and 4). In the case of GC-MS/MS analysis, the identifications criteria are the acceptable values of the relative ion abundances in the sample spectra versus the reference spectrum. In MS/MS analysis, the identification of pesticide peaks was confirmed by matching retention times and by the presence of major ions and precursor ion with highest *m/z* ratio (greater selectivity) and abundance (greater sensitivity).

GC-MS/MS is generally acknowledged to provide greater selectivity in the analysis of complex extracts. The samples were analysed by GC-MS/MS because multiple ion monitoring is more prone to interferences and typically gives higher LODs, especially in complicated matrices (Lehotay and Gates 2009). Optimisation of the GC-MS/MS conditions, such as the selection of both precursor and product ions, and optimisation of collision energies were required for each target compound in order to achieve the identification of the chromatographic peaks, and the best commitment between sensitivity (the highest signal-to-noise ratio) and selectivity (characteristic *m/z*).

Application to the analysis of real samples

The new methodology was applied to nine strawberry jams and the analyses of pesticide residues were determined. The elimination of interfering substances and background noise, obtained by the efficient clean-up step, gave a high precision and accuracy in the determination of each compound. One strawberry jam sample from conventional farming and traditional production showed the presence of HCB and aldrin. Quantification of pesticides was carried out through the matrix-matched calibration curves by GC-ECD, obtained in terms of μg kg^{-1} of sample according to the recovery value (Table 3). The highest concentration found was 1.3 μg kg^{-1} of δ-HCH in a sample from conventional farming and industrial production. The other results were always lower than the LOD presented in Table 2. No OCP contamination was achieved in the organic farming jams. Nevertheless, all the pesticides detected have been banned for several years in countries of the European Union. Some of them are still present in the environment because of their resistance to degradation. The results emphasise the need for the maintenance of continuous monitoring of pesticide OCP residues.

Conclusions

The proposed multi-residue methodology for the determination of 14 OCPs in strawberry jam samples by GC-ECD and GC-MS/MS using QuEChERS coupled with a clean-up process is considered appropriate, except for α-, β-, δ-HCH, HCB and δ-HCH. The use of an ultrasonic bath achieved better results compared with the two versions previously tested. The use of matrix-matched calibration standards avoids matrix interference effects. The method yields recoveries between 62% and 129%, and the LOQs were, in all cases, significantly lower than the MRL established for strawberries (10 or 50 μg kg^{-1} depending on the OCP) in the European Union. The presence of organochlorines in several samples has been frequently reported in

Table 2. Analytical parameters of both chromatographic methods.

Organochlorine pesticide	Linearity (R^2)		LOD (μg kg^{-1})		LOQ (μg kg^{-1})	
	ECD	MS/MS	ECD	MS/MS	ECD	MS/MS
α-HCH[a]	0.9996	0.9989	0.8	0.8	2.7	2.5
β-HCH[a]	0.9994	0.9991	1.1	0.9	3.5	2.9
δ-HCH[a]	0.9986	0.9993	1.5	0.9	5.1	3.0
HCB[b]	0.9970	0.9994	7.6	6.1	25.4	20.4
Lindane[b]	0.9986	0.9995	1.5	5.6	5.1	18.6
Aldrin[c]	0.9972	0.9989	7.3	7.9	24.4	26.3
α-Endosulfan[d]	0.9974	0.9985	7.0	7.3	23.4	24.5
p,p'-DDE[e]	0.9980	0.9991	6.2	8.9	20.6	29.5
Dieldrin[c]	0.9974	0.9986	7.1	6.7	23.7	22.3
Endrin[b]	0.9977	0.9991	6.7	8.5	22.3	28.3
β-Endosulfan[d]	0.9988	0.9992	4.7	6.3	15.7	21.1
p,p'-DDD[e]	0.9987	0.9994	5.1	6.0	16.9	20.3
o,p'-DDT[e]	0.9996	0.9990	2.9	6.3	9.6	21.1
Methoxychlor[b]	0.9995	0.9989	3.1	7.7	10.3	25.7

Notes: [a]HCH (sum of isomers, except the gamma isomer) = 10 μg kg^{-1}.
[b]MRL for each pesticide in Europe in strawberries = 10 μg kg^{-1}.
[c]Aldrin and dieldrin combined = 10 μg kg^{-1}.
[d]Sum of α- and β-isomers and endosulfan-sulphate = 50 μg kg^{-1}.
[e]Sum of *p,p'*-DDT, *o,p'*-DDT, *p,p'*-DDE and *p,p'*-DDD = 50 μg kg^{-1}.

Table 3. Influence of five spiked levels on the recovery efficiency using the version 3 procedure.

Name	Recoveries (%)														
	Commercial jam ($n = 3$)					Traditional jam ($n = 3$)					Organic jam ($n = 3$)				
	0.005 mg kg^{-1}	0.010 mg kg^{-1}	0.030 mg kg^{-1}	0.090 mg kg^{-1}	0.180 mg kg^{-1}	0.005 mg kg^{-1}	0.010 mg kg^{-1}	0.030 mg kg^{-1}	0.090 mg kg^{-1}	0.180 mg kg^{-1}	0.005 mg kg^{-1}	0.010 mg kg^{-1}	0.030 mg kg^{-1}	0.090 mg kg^{-1}	0.180 mg kg^{-1}
α-HCH	66 ± 10	66 ± 11	62 ± 8	59 ± 10	62 ± 5	71 ± 11	68 ± 12	69 ± 10	72 ± 10	70 ± 12	72 ± 11	72 ± 11	70 ± 9	72 ± 6	70 ± 9
β-HCH	67 ± 11	69 ± 10	65 ± 10	60 ± 11	60 ± 6	75 ± 6	70 ± 12	71 ± 11	69 ± 11	74 ± 12	70 ± 5	75 ± 13	71 ± 11	76 ± 11	72 ± 11
δ-HCH	65 ± 7	67 ± 10	60 ± 5	62 ± 6	61 ± 10	73 ± 5	69 ± 5	70 ± 9	71 ± 9	73 ± 9	71 ± 5	73 ± 13	74 ± 8	77 ± 9	75 ± 7
HCB	64 ± 8	63 ± 8	63 ± 9	64 ± 11	62 ± 8	69 ± 7	73 ± 5	71 ± 8	70 ± 8	71 ± 7	71 ± 9	72 ± 12	71 ± 6	72 ± 10	70 ± 9
Lindane	62 ± 13	65 ± 11	62 ± 11	72 ± 9	69 ± 10	70 ± 9	70 ± 7	74 ± 7	76 ± 7	72 ± 7	70 ± 8	70 ± 13	73 ± 7	78 ± 8	75 ± 8
Aldrin	96 ± 8	92 ± 10	91 ± 12	95 ± 10	91 ± 8	90 ± 11	92 ± 9	93 ± 9	95 ± 9	94 ± 11	90 ± 9	90 ± 11	96 ± 10	100 ± 12	98 ± 11
α-Endosulfan	90 ± 9	95 ± 6	94 ± 10	99 ± 12	93 ± 11	91 ± 9	90 ± 12	96 ± 11	98 ± 11	91 ± 10	91 ± 11	93 ± 10	95 ± 9	102 ± 10	97 ± 12
Dieldrin	96 ± 11	94 ± 5	92 ± 8	98 ± 7	89 ± 10	89 ± 9	89 ± 10	92 ± 6	95 ± 6	90 ± 8	86 ± 13	88 ± 13	89 ± 12	95 ± 13	89 ± 10
***p,p′*-DDE**	70 ± 12	74 ± 9	72 ± 5	80 ± 9	79 ± 7	69 ± 8	70 ± 10	72 ± 11	76 ± 11	71 ± 12	75 ± 12	78 ± 11	74 ± 10	79 ± 11	78 ± 11
Endrin	90 ± 12	97 ± 9	92 ± 6	96 ± 9	90 ± 10	88 ± 10	93 ± 8	90 ± 12	95 ± 12	92 ± 10	86 ± 9	88 ± 9	85 ± 5	90 ± 7	89 ± 9
β-Endosulfan	115 ± 9	110 ± 11	114 ± 8	119 ± 10	110 ± 9	100 ± 13	116 ± 6	106 ± 8	110 ± 8	104 ± 9	113 ± 9	107 ± 13	103 ± 10	110 ± 12	105 ± 15
***p,p′*-DDD**	121 ± 11	124 ± 9	121 ± 10	123 ± 12	125 ± 9	112 ± 11	114 ± 9	124 ± 10	122 ± 10	118 ± 11	110 ± 10	110 ± 13	105 ± 11	110 ± 11	107 ± 10
***o,p′*-DDT**	122 ± 8	120 ± 13	128 ± 12	129 ± 13	125 ± 8	112 ± 9	113 ± 13	124 ± 12	126 ± 12	115 ± 10	109 ± 6	111 ± 10	103 ± 12	109 ± 9	105 ± 7
Methoxychlor	121 ± 8	121 ± 12	123 ± 9	121 ± 9	122 ± 11	113 ± 8	114 ± 8	119 ± 8	119 ± 8	116 ± 9	103 ± 7	112 ± 12	106 ± 11	110 ± 10	113 ± 8

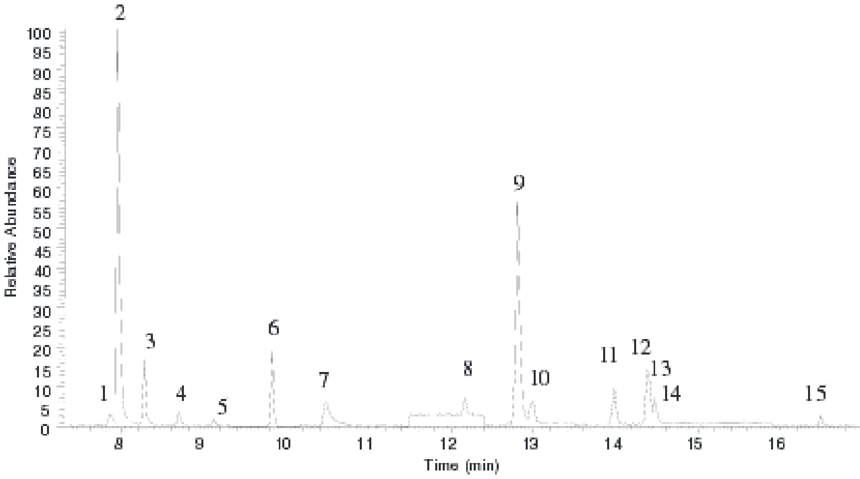


Figure 4. GC-MS/MS chromatogram of a mixture of OCP ($100\,\mu g\,l^{-1}$). Peak identification in order of increasing retention time is as follows: 1, α-HCH; 2, HCB; 3, γ-HCH; 4, β-HCH; 5, δ-HCH; 6, aldrin; 7, IS; 8, α-endosulfan; 9, dieldrin; 10, *p,p'*-DDE; 11, endrin; 12, β-endosulfan; 13, *p,p'*-DDD; 14, *o,p'*-DDT; and 15, methoxychlor.

previous studies (Fernandes et al. 2011a, 2011b, 2012). Considering the good results, this method has great potential in the field of OCP monitoring in strawberry jams.

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