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Multiresidue Analysis of Organochlorine Pesticides in Milk, Egg and Meat by GC–ECD and Confirmation by GC–MS

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Abstract A multiresidue method was developed and optimized for the quantification of organochlorine pesticides (OCPs) in milk, egg and meat samples. Sample extraction was performed by adopting QuEChERS principle and the extracts were cleaned-up dispersive solid-phase extraction with primary secondary amine after salting out with NaCl and $MgSO_4$. Analysis was carried out by gas chromatography coupled with electron capture detector and confirmation by gas chromatography-mass spectrometry. The performance of the method was investigated in terms of linearity, accuracy, precision, detection limit and quantification limit (LOQ). Good linearity was obtained, with correlation coefficients (r^2) higher than 0.992. Mean recoveries were found in the ranges 72 %–108 %, 74 %–101 % and 75.27 %–104.56 % for the milk, egg and meat, respectively, RSD % turned out to range from 0.28 % to 10.05 %. The method developed was successfully tested on commercial milk, egg, and meat samples from the markets of Tamil Nadu (India), proving to be a useful tool in routine analysis of OCPs for monitoring purposes. None of the compounds of interest were observed above their respective LOQ.

Keywords QuEChERS · OCPs · Multiresidue analysis · Milk · Egg · Meat

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Organochlorine pesticides (OCPs) are the potential group of chemicals used to improve agricultural productivity. OCPs have been largely used worldwide against a variety of pests, since the middle of the twentyth century (Beyer and Biziuk 2008). These compounds have been applied for decades in preventing, repelling or mitigating the effects of pests. OCPs are one of the most persistent organic pollutants present in the environment and are responsible for their persistence in the environment and concentration in fatty tissues by means of the food chain, bioaccumulation can occur, particularly in products of animal origin such as meat, fat, butter and milk (Stefanelli et al. 2009).

Animals intended for human food may absorb pesticides from residues in their feed, water or during direct/indirect exposure in the course of pest control (Aulakh et al. 2006). The dairy cows and poultry chickens are mainly exposed to pesticide residues through their food (Nag and Raikwar 2008). Poultry feed and animal feed could be the major sources of contamination for chicken eggs and milk (Aulakh et al. 2006; Suganthy et al. 2009). In recent years, increasing attention has been paid to the risk to consumers posed by chemical contaminants or residues in animal feed. This was caused by various cases of milk, eggs or other animal products contaminated with environmental chemicals (Leeman et al. 2007).

In general, the analysis of organochlorine pesticide residues in milk follows the conventional approach of the multiresidue methods (MRMs) in which the total residues are extracted together with the total fatty material (Ahmed 2001) and supercritical fluid extraction (SFE) method for egg (Fiddler et al. 1999). Recently, QuEChERS method (quick, easy, cheap, effective, rugged and safe), introduced by Anastassiades et al. 2003 has been most applied extraction method for the determination of pesticide residues in food samples, providing acceptable recoveries for

acidic, neutral and basic pesticides (Prestes et al. 2009). This method was initially developed for the extraction of pesticides from fruits and vegetables (Anastassiades et al. 2003; Aysal et al. 2007), but later it was also used for the determination of pesticide residues in fatty food matrices viz., milk, eggs and avocados (Lehotay et al. 2005).

Therefore, determination and monitoring of OCPs in different environmental matrices are important for environment, especially for human health. To control and monitor the contamination of OCPs residues in animal origin foods it is necessary to develop an analytical procedure capable of detecting the pesticide residues at trace level. The aim of this study is to optimize and validate a simple and rapid QuEChERS method for the simultaneous determination of selected OCPs in milk, egg and meat samples by gas chromatography with electron capture detection (GC–ECD) and confirmation by gas chromatography mass spectrometry (GC–MS).

Materials and Methods

Pesticide standards (α-HCH, β-HCH, γ-HCH, δ-HCH, dicofol, aldrin, p,p′-DDD, p,p′-DDE, p,p′-DDT, α-endosulfan, β-endosulfan, and endosulfan sulphate) were obtained from Sigma Aldrich, Germany with purity ranging from 95.8 % to 99.8 %. Analytical grade acetone, acetonitrile, and hexane (HPLC grade), anhydrous magnesium sulphate, sodium chloride were purchased from M/s. Merck (Mumbai, India), primary secondary amine (Bondesil PSA, 40 μm particle size) was from M/s. Varian, India.

Stocks solutions (1,000 μg mL^{-1}) of each pesticide standard were prepared by dissolving 0.025 g of the pesticide in 25 mL of hexane/acetone (9/1, v/v). A pesticide intermediate standard solution (100 μg mL^{-1}) was prepared by transferring 10 mL from each pesticide solution to a 100 mL volumetric flask and diluting to volume with hexane. An intermediate stock standard mixture of 10 μg mL^{-1} was prepared by mixing appropriate quantities of the individual stock solutions and diluted accordingly. Several standard solutions, with concentrations of 0.01–0.1 μg mL^{-1}, were injected to obtain the linearity of detector response. All substances were stored at −4°C until further use.

Representative milk, egg and meat samples were purchased from the local market of Coimbatore city (Tamil Nadu, India). The whole egg sample was blended after removing and discarding shells, using a blender and mixed thoroughly. Milk samples were homogenized properly and representative sample was taken for extraction. The meat sample was blended with high volume blade homogenizer and used for the recovery study.

The extraction method was carried out according to the original QuEChERS principle established by Anastassiades et al. 2003 with slight modifications. Exactly 10 g of the well-homogenized samples (milk, egg and meat) were weighed in a 50 mL screw-capped centrifuge tube and 20 mL of acetonitrile was added, screw cap was closed and the tube vigorously shaken by hand for 1 min. Afterwards, 4 g of anhydrous magnesium sulfate and 1 g of sodium chloride was added, and again tube was shaken by hand for 1 min to prevent agglomeration of magnesium sulfate. Then, it was placed in a centrifuge (Plasto crafts, Mumbai, India), and centrifuged at 5,000 rpm for 10 min at room temperature.

For cleanup step, a 6 mL aliquot of the extract (upper layer) was transferred to a 15 mL centrifugation tube containing 100 mg primary secondary amine (PSA) and 600 mg anhydrous $MgSO_4$. Tube was closed, and then shaken for 30 s using a vortex mixer and then it was centrifuged again for 5 min at 3,000 rpm. Finally, 4 mL of the clear extract, (2 g of sample per mL), was evaporated under a gentle stream of nitrogen (15 psi) by using the Turbovap LV (Caliper Life Sciences, Russelsheim, Germany) set at 40°C, until near dryness. The residues were then reconstituted with 1 mL of n-hexane and the solution was analysed in GC–ECD and confirmation by GC–MS.

The recovery rate was determined by spiking appropriate OCPs standard mixture solutions into milk, egg and meat samples (10 g homogenized) at three different concentrations (10, 50, and 100 μg kg^{-1}). In controlled sample, same amount of hexane was added. The spiked samples were permitted to equilibrate for 30 min before extraction, to allow the spiked solution to penetrate the matrix. The samples were processed by adopting the above extraction procedure. Replicated ($n = 3$) samples were run and the recovery values were calculated for each. Repeatability of the method was evaluated through the relative standard deviation (RSD %).

Quantification of OCPs was performed using GC (Shimadzu GC-2010) equipped with an EC detector, an autosampler (AOC 20 s) and an auto injector (AOC 20i). The OCPs were separated using DB-5 (30 m × 0.25 mm i.d, 0.25 μm film thickness) fused silica capillary column (J & W Scientific Co., Agilent Technologies, USA). The injection was performed at split (1:10) mode with 1 μL injection volume. High purity (purity 99.999 %) nitrogen was used as carrier and makeup gas flow at 2 mL min^{-1} and 30 mL min^{-1}, respectively. The injector temperature was 280°C and the detector temperature was 300°C. The oven temperature was programmed as follow: 160°C, for 1 min, increased to 200°C (3°C/min) for 2 min, increased to 220°C (4°C/min) for 4 min and finally, increased to 250°C, (5°C/min) for 18 min.

The OCPs in the investigated samples was confirmed by GC–MS analysis using a Shimadzu GC 2010 (Shimadzu, Japan) system equipped with a GCMS-QP 2010 plus mass spectrometer. The DB-1 MS fused-silica capillary column, 30 m × 0.25 mm i.d, 0.25 μm film thickness (J & W

Scientific Co., Agilent Technologies, USA) was used. The injector temperature was 250°C and sample injection was performed in split mode with ratio of 1:5 and the injection volume was 1 μL. The oven ttemperature was programmed as follows: 160°C for 1 min, increased to 200°C (3°C/min) for 2 min, and finally increased to 220°C (4°C/min) for 4 min to facilitate separation of all the target compounds. High purity (over 99.999%) helium was used as the carrier gas with flow rate of 2 mL/min. The mass conditions were set as follows: ionization mode with EI, ionization energy of 70 eV, ion source temperature at 200°C, transfer line temperature at 250°C, full scan mode and scan range between 50 and 450 amu. The mass spectrometer with electron impact (EI) was used in selected ion monitoring (SIM) mode and three ions were selected and monitored for each pesticide. Retention times, molecular weight, selected ion for SIM of studied pesticides are listed in Table 1. Detected pesticides were confirmed by matching the mass spectrum and the retention time of the compound to that of a known standard using the SIM mode. Data recording and instrument control were performed by the with GCMS solution 2.5 software.

Results and Discussion

Gas chromatography coupled with electron capture detector (GC–ECD) provided good responses even at very low concentrations because of its selective and sensitive detectors (Zawiyah et al. 2007). GC–MS operating in SIM mode, allowed higher instrumental sensitivity and lower detection limits and was applied for confirmation of peak identity. Three fragment ions were selected for each pesticide used in this study. The use of target ions and their retention time allowed to positively confirm the pesticide identity.

In the present study, OCPs namely α-HCH, β-HCH, γ-HCH, δ-HCH, dicofol, aldrin, p,p′-DDD, p,p′-DDE, p,p′-DDT, α-endosulfan, β-endosulfan and endosulfan sulphate were investigated under the same optimized temperature programs and analysis time, to obtain the most efficient quantitative results with maximum separation. Each pesticide was injected and retention times were recorded. In the case of close retention times, separation by changing temperature programs was achieved. Several tests were performed in order to obtain the best optimized separation-resolution of the analytes used in this study. The GC operating conditions and optimized oven temperature programs were explained in experimental section. The chromatograms of the standard pesticides for their multiple analyses were successfully obtained under optimized conditions. The applied temperature program resulted in a good separation of the analytes by employing the stated chromatographic conditions. The mixtures of OCPs compounds under study were well resolved in a run time of 25 min.

In the present study, QuEChERS (Anastassiades et al. 2003) principle was adopted for the extraction of pesticides in milk, egg and meat with few modifications. Acetonitrile was used as the solvent for extraction of pesticides because of its effectiveness for polar and nonpolar pesticides from a diverse range of matrices and also gives high recoveries of a wide polarity range of pesticides (Bennet et al. 1997; Lehotay et al. 2001). Earlier studies by Lehotay et al. (2005) indicated that acetonitrile is very useful for low fatty foods such as milk and egg but cannot be used for highly lipidic food.

The cleanup of the samples was performed by using dispersive solid phase extraction (d-SPE), which involved mixing the extract in a mixer of PSA and $MgSO_4$. The d-SPE with PSA effectively removes many polar matrix components, such as organic acids, certain polar pigments,

Table 1 Selected ion groups of OCPs in GC–MS (SIM) analysis

Pesticide	Retention time (min)	Molecular mass (g mol^{-1})	Target ion (m/z)	Qualifier ion (m/z)
α-HCH	5.62	290.83	183	181, 219, 111
β-HCH	6.20	290.83	219	181, 109, 183
γ-HCH	6.53	290.83	181	183, 109, 219
δ-HCH	6.88	290.83	109	219, 183, 217
Dicofol	11.03	370.49	139	251, 141, 253
Aldrin	11.08	364.91	66	263, 91, 293
α-endosulfan	14.24	406.93	241	239, 195, 339
p,p′ DDD	15.72	320.04	235	165, 237, 199
β-endosulfan	16.83	406.93	195	241, 237, 235
p,p′ DDE	17.91	316.0	246	248, 318, 316
Endosulfan sulphate	19.20	422.93	387	389, 272, 237
p,p′ DDT	20.17	355.0	235	237, 165, 199

and sugars, to some extent from the food extracts (Anastassiades et al. 2003).

The analytical performance of the proposed method was studied in order to evaluate its usefulness for quantitative determination of pesticide residues in milk, egg and meat extract.

All measurements were performed over five different levels ranging between 0.01 and 0.1 μg mL^{-1} (three replicates for each level were analyzed). The calibration graphs obtained by plotting concentration versus average peak area and the results are summarized in Table 2. The calibration curves were found to have good linearity by correlation coefficients (r^2) of more than 0.992 in all analyses, indicating that the linear regression method can answer the concentrations of the analyses under study within the concentration range investigated.

The instrumental limit of detection (LOD) and limit of quantification (LOQ) of the prepared in overall method were estimated for signal-to-noise ratio of 3 (S/N = 3) and 10 (S/N = 10), respectively, measured by peak-to-peak method at the lowest calibration level. The limit of quantification (LOQ) for this method was defined as the lowest concentration of compounds in a sample that could be quantitatively determined with suitable precision and accuracy. LOQ for the OCPs were found to be 0.01 μg g^{-1}.

In order to assess the extraction efficiency of the proposed method the recovery studies were carried out by spiking milk, egg and meat samples with mixture of OCPs (α-HCH, β-HCH, γ-HCH, δ-HCH, dicofol, p,p′-DDT, p,p′-DDD, p,p′-DDE, alpha endosulfan, beta endosulfan, and endosulfan sulphate) at three different concentration levels (10, 50 and 100 μg kg^{-1}) and repeated three times to determine repeatability. Meanwhile, milk, egg and meat samples were analyzed and the results indicated the blank extracts did not contribute any interference with the target compounds. The method validation phase of this work because it was found to result in clean extracts for analysis with milk, egg and meat samples. These results indicated that the QuEChERS method was indeed applicable for the determination of all the analytes of interest for the present study in a milk, egg and meat matrix. The percentage of recovery of each pesticide was calculated by comparing the peak area ratio of the spiked standards with those of the pure standards.

Recovery studies were performed at three levels in three commodities. Average recovery data and relative standard deviations (RSD) obtained for selected matrix spiked with OCPs compounds are shown in Table 3. The results were ranged from 72.27 % to 108.21 % with most of the recoveries being greater than 80 %. The most unfavourable relative standard deviation (RSD) was <10.05 %.

Satisfactory results were found with mean recoveries between 72 % and 108 %, and relative standard deviation (RSD) between 0.28 % and 7.55 %, in milk sample as shown in Table 3. The recoveries obtained for all OCPs in egg samples ranged from 72 % to 101 %, and the RSD values were <9 %. The mean recoveries obtained for meat samples spiked with all OCPs ranged from 79.45 % to 104.56 % with the RSD values from 0.36 % to 6.57 %. The results shows that the recovery rate for selected pesticides were within acceptable range (Chai and Tan 2009). The method is applicable for the determination of OCPs residues in milk, egg and meat samples.

The milk, egg and meat samples purchased from local markets in Coimbatore city of Tamil Nadu (India) and analysed following the proposed sample preparation

Table 2 Retention time, linear range, regression equation, determination coefficient of OCPs in GC–ECD and MRL for milk, egg and meat

Pesticide	Retention time (min)	Linear range (μg mL^{-1})	Regression equation (Y = ax ± b)	R^2	MRL[a] (μg g^{-1})		
					Milk	Egg	Meat
α-HCH	7.069	0.01–0.1	Y = 76742x − 1748.0	0.993	0.02	–	–
β-HCH	8.024	0.01–0.1	Y = 54652x + 464.2	0.997	0.02	–	–
γ-HCH	8.240	0.01–0.1	Y = 73715x − 576.9	0.995	0.01	0.1	2.0
δ-HCH	9.151	0.01–0.1	Y = 72538x − 731.6	0.995	–	–	–
Aldrin	12.81	0.01–0.1	Y = 76287x − 85.56	0.993	0.15	0.1	0.2
Dicofol	13.26	0.01–0.1	Y = 92345x + 456.8	0.997	–	–	–
α-Endosulfan	16.85	0.01–0.1	Y = 88279x + 15533	0.992	–	–	–
p,p′ DDE	18.54	0.01–0.1	Y = 71798x + 571.0	0.997	1.25	0.5	7
β-Endosulfan	20.13	0.01–0.1	Y = 73152x + 1936	0.998	–	–	–
p,p′ DDD	20.90	0.01–0.1	Y = 54234x + 315.8	0.998	1.25	0.5	7
Endosulfan sulphate	22.58	0.01–0.1	Y = 53985x + 896.4	0.998	–	–	–
p,p′ DDT	23.07	0.01–0.1	Y = 69084x − 388.3	0.997	1.25	0.5	7

[a] Prevention of Food Adulteration (Fourth Amendment) Rules, 2005

Table 3 The relative recoveries of milk, egg and meat spiked with different concentrations of OCPs

Pesticides	Average recovery ± RSD %								
	Milk			Egg			Meat		
	10 (μg kg^{-1})	50 (μg kg^{-1})	100 (μg kg^{-1})	10 (μg kg^{-1})	50 (μg kg^{-1})	100 (μg kg^{-1})	10 (μg kg^{-1})	50 (μg kg^{-1})	100 (μg kg^{-1})
Alpha HCH	94.75 ± 4.24	81.87 ± 0.77	72.27 ± 1.57	83.01 ± 8.15	73.46 ± 4.41	74.03 ± 0.50	85.91 ± 2.44	88.59 ± 1.09	97.71 ± 1.12
Beta HCH	94.48 ± 1.82	91.03 ± 0.38	94.63 ± 1.20	93.75 ± 6.42	95.22 ± 1.90	99.37 ± 3.17	96.27 ± 0.36	95.54 ± 1.35	104.56 ± 0.98
Gamma HCH	91.25 ± 2.56	93.66 ± 0.48	98.66 ± 0.28	75.06 ± 3.49	72.08 ± 1.32	100.64 ± 2.14	79.45 ± 1.39	82.76 ± 1.94	101.34 ± 0.82
Delta HCH	101.84 ± 3.34	103.37 ± 2.63	108.21 ± 0.48	81.98 ± 9.08	91.70 ± 10.05	101.53 ± 0.51	93.97 ± 3.52	75.27 ± 5.57	88.36 ± 1.78
Dicofol	97.29 ± 7.55	99.42 ± 2.92	98.03 ± 2.31	92.46 ± 1.62	95.24 ± 3.34	100.25 ± 4.98	89.75 ± 4.68	96.48 ± 3.60	95.83 ± 3.23
Aldrin	90.27 ± 3.28	94.65 ± 4.60	89.33 ± 1.27	95.07 ± 2.85	94.15 ± 3.01	87.64 ± 4.96	92.98 ± 2.45	87.70 ± 1.44	96.62 ± 0.79
Alpha Endosulfan	101.83 ± 5.46	89.11 ± 0.45	96.15 ± 1.34	95.96 ± 1.72	83.85 ± 9.82	90.44 ± 2.76	87.86 ± 1.47	92.20 ± 1.67	100.22 ± 1.51
p,p′ DDE	86.71 ± 1.81	80.23 ± 0.99	75.19 ± 1.21	79.92 ± 4.71	79.01 ± 4.07	91.06 ± 2.61	94.27 ± 5.10	83.83 ± 2.43	95.36 ± 0.75
Beta Endosulfan	100.17 ± 2.50	82.48 ± 1.92	87.73 ± 1.47	94.76 ± 1.60	91.06 ± 3.50	94.53 ± 2.88	82.57 ± 0.94	87.22 ± 1.75	98.15 ± 1.37
p,p′ DDD	102.11 ± 5.74	89.21 ± 1.23	99.44 ± 0.99	94.09 ± 0.74	85.27 ± 4.39	95.21 ± 0.61	100.99 ± 2.82	88.07 ± 1.18	96.32 ± 2.05
Endosulfan sulphate	98.61 ± 1.40	101.93 ± 1.92	99.95 ± 4.78	88.20 ± 6.26	95.05 ± 9.53	100.69 ± 3.67	82.65 ± 1.61	97.34 ± 1.25	86.64 ± 1.98
p,p′ DDT	95.95 ± 5.07	86.30 ± 2.64	94.42 ± 2.57	72.96 ± 0.79	83.10 ± 1.41	92.53 ± 0.73	94.38 ± 6.57	90.84 ± 3.88	99.87 ± 2.51

method for the determination of selected OCPs residues. The results showed that no pesticide residues at concentrations above the quantification limit.

A simple and rapid method was developed to determine residues of selected OCPs residues in milk, egg and meat samples. This method using QuEChERS sample preparation and GC–ECD analysis showed a high sensitivity and confirmatory (GC–MS–SIM) power necessary for the determination of pesticide residues at the low levels. In addition, the present method offers considerable saving in terms of solvent consumption, cost of materials, sample manipulation and analysis time. The proposed method not only allowed the simultaneous determination and confirmation of very large number of pesticides with satisfactory recoveries and low detection limits but also useful in routine analysis due to fast and easy to carry out.

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