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Development of a Modified QuEChERS Procedure for the Isolation of Pesticide Residues from Textile Samples, Followed by GC–MS Determination

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Abstract: Due to the use of pesticides during cotton production and/or textile storage, it is necessary to assure textile and clothing safety in order to improve the protection of human health. In this work, an efficient method was established for a multiresidue determination of 33 pesticides covering several pesticide classes such as organochlorine, organophosphate, pyrethroides, triazines, etc., in textiles by modified QuEChERS and followed by gas chromatography–mass spectrometry. Optimal conditions were selected, including the amount of the sample, type of the extraction solvent and cleaning up sorbents, until the method was finally validated. Sufficient accuracy and precision were presented by the method using spiked samples between 10 and 250 µg/kg, while recoveries from 70 to 120% and an RSD < 20% for all the pesticides were obtained; the limits of quantification were below 5 µg/kg for all studied pesticides. The presented method showed high separation efficiency with minimal sample and sorbent consumption. The validated method was successfully applied to the analysis of real samples and proved to be applicable to routine analyses.

Keywords: QuEChERS; textile samples; pesticide residues; GC-MS determination

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1. Introduction

One of the most important agricultural and industrial crops in the world, after food grains and soybeans, is cotton [1,2]. More than half of all its fibers are used in the manufacture of industrial fabrics for clothing and household furnishings [2,3]. The cotton crop contains more insects than any other crop in the world; around 1300 insects found in cotton have been registered worldwide. This has caused cotton production to suffer economic damage in many countries that are particularly challenging for entomologists [1,4]. Therefore, one of the main problems in the production of cotton is pest attacks, which can cause as high as 90% of yield losses in non-pesticide treated cotton fields. Especially in the mid- and late-production stage, the repeated application of pesticides in order to protect the cotton leaves and the developing cotton balls and fiber from pest attacks is essential [5]. To achieve high yields and quality, farmers widely use pesticides to protect cotton from pests and diseases [6]. Approximately 60% of all agrochemicals in the market are applied to cotton fields. Therefore, cotton can be considered the dirtiest agricultural crop and the most chemical-intensive crop in the world [1,4]. There is increasing concern for pesticides and other chemicals contained in cotton fiber. It has been proven that various pesticides are present in raw cotton fiber samples on the market, with a content of 0.02–1.58 mg kg^{-1} [5]. Pesticide residues could still be identified in textile products despite the fine processing of cotton fibers. Therefore, relevant risks could have negative impacts on human health, while being especially harmful to the skin, the respiratory system, and the digestive system [6]. Preventing the huge amount of textile damage that can be caused by fungus or small animals such as rats and mice during storage is always a challenging task. Therefore, before selling, insecticides, fungicides, and another kinds of pesticides are applied; however, this could still pass through the covering material and contaminate the textiles.

Controlling the pesticide residues and developing best management practices based on these data is one of the most important aspects in the minimalization of the potential hazards of pesticides to human and environmental health. Hence, there is a need to develop efficient methods of extraction and determination of pesticides in different media such as soil, sediment, water, and food [7]. Because of the wide variety and complexity of textile matrices, samples should first be cleaned up by using a compatible sample preparation technique before injecting them into the separation and detection system. Three primary types of sample preparation methods are currently applied to isolate pesticide residues from textiles: Soxhlet extraction, solid phase extraction, and accelerated solvent extraction (ASE). These extraction methods have certain disadvantages such as their labor-intensive processes, the need for large volumes of solvent as well as being time-consuming. Therefore, developing a greener and more convenient sample pretreatment method is very important. QuEChERS has been developed as a new sample preparation method in recent years, mainly for the extraction of pesticide residues from fruits and vegetables, but much less in textiles. The development of the multi-residue QuEChERS method has become more and more important in meeting the high demand of monitoring pesticide residues at low concentrations in different samples. In comparison with conventional extraction procedures, the QuEChERS approach requires less solvent and can obtain higher recoveries. This method is usually applied to crops such as vegetables and fruits [8–10].

Several studies have focused on the determination of different pesticides in the soil of cotton and wheat growing areas [11]. But no efforts have been made to determine the levels of these hazardous compounds in the final textile products. Thus, the present study focused on the determination of pesticide levels in textile samples, using the modified QuEChERS method for the extraction and GC–MS for the determination of pesticide residues. Organochlorine pesticides are checked by testing laboratories, but other groups of pesticides are currently not being tested. A multi-family mix of pesticides, a lot of which exhibit endocrine-disrupting properties after resorbing through the skin of textile users, was selected; the analytical method was subsequently developed and validated. The next aim of the study was to test various approaches for the analysis of white and colored textile materials.

2. Materials and Methods

2.1. Chemicals and Reagents

The standards of pesticides were acquired from different sources (Dr. Ehrenstorfer, Augsburg, Germany; Bayer, Leverkusen, Germany; Cheminova, Harboore, Denmark; Agrovita, Ivanka pri Dunaji, Slovak), with purity higher than 95%. Stock standard solutions of the individual pesticides, at a concentration 1 mg/mL, were prepared by weighing the pesticides and dissolving them in 10 mL of toluene (Merck KGaA, Darmstadt, Germany). The working standard solution of pesticides was prepared in toluene by dilution and stored at 4 °C. This working solution contained all of the 33 studied pesticides at a concentration of 0.020 mg/mL. The calibration standards were prepared by additional dilution into acetonitrile (Merck KGaA, Darmstadt, Germany). HPLC-grade acetonitrile, ethyl acetate, hexane, and water were also obtained from Merck (Darmstadt, Germany). Every solvent used was pesticide residue grade. Anhydrous magnesium sulfate and sodium chloride were purchased from Lachema (Lachema a.s., Brno, Czech Republic). Octadecyl silica (C18) and primary secondary amine were obtained from Agilent Technologies (Avondale, PA, USA). Ethyl acetate was received from Sigma-Aldrich (Sigma Aldrich, Steinheim, Germany).

2.2. Sample Preparation

The cotton-based textiles were cut into small pieces. A modified version of the original QuEChERS procedure [12] was applied. Briefly, one gram of sample was weighed into a 50 mL centrifuge tube. Ten mL of acetonitrile was added to the sample and shaken by hand for 1 min. Subsequently, 4 g of $MgSO_4$ and 1 g of NaCl were added, after which the

sample was mixed vigorously by hand for 1 min. Finally, the mixture was centrifuged at 3700 rpm for 5 min.

For the clean-up process by dispersive solid phase extraction, different sorbents were tested on white and colored textiles.

White textile samples: a total of 2 mL of the organic phase (supernatant) was transferred to a 15 mL centrifuge tube, which contained 50 mg of PSA (primary secondary amine). The tube was shaken by hand for 1 min and subsequently centrifuged at 4000 rpm for 5 min. Finally, 1 mL of the organic phase was transferred to a vial (2 mL) for GC–MS analysis.

Colored textile samples: a total of 2 mL of the organic phase was transferred to a 15 mL centrifuge tube, which contained 50 mg of PSA and 25 mg GCB (graphitized carbon black). The tube was shaken by hand for 1 min and subsequently centrifuged at 4000 rpm for 5 min. Finally, 1 mL of the organic phase was transferred to a vial for GC–MS analysis.

2.3. Instrument and Apparatus

Analytic MC1 scales (Sartorius, Göttingen, Germany) were used for standards weighting. A high-volume centrifuge ROTOFIX 32 Hettich (Tuttlingen, Germany) was used for centrifugation.

An Agilent 6890N GC system (Agilent Technologies, Little Falls, DE, USA) was used for the separation of the pesticides. The GC was equipped with a programmable temperature vaporization (PTV) injector and an autosampler (Agilent 7683B) from the same company, which was used for the injection of 2 µL of the solutions in solvent vent injection mode. A narrow-bore capillary column CP-Sil 8 CB (Agilent Technologies, Little Falls, DE, USA) with 5% diphenyl/95% dimethylsiloxane stationary phase and 15 m × 0.15 mm i.d. × 0.15 µm film thickness was utilized for GC separation. A fused silica untreated capillary column (1 m × 0.32 mm) was used as a pre-column. Helium was used as a carrier gas at a constant flow rate of 1.2 mL/min. The initial temperature of the injector was set at 40 °C and held for 0.2 min. After that, it was increased with a gradient rate of 400 °C/min until 300 °C and held for 2 min. The temperature was subsequently increased with the same gradient rate of 400 °C/min until 350 °C and held for 5 min. The initial temperature of the chromatographic oven was set at 60 °C and held for 1.75 min; subsequently, the temperature was increased to 150 °C at a 60 °C/min rate. After that, the temperature was increased to 220 °C at a rate of 30 °C/min, followed by a rate of 12 °C/min until 250 °C, and finally increased up to 300 °C with a rate of 30 °C/min and held for 3 min. In order to reach the initial injector temperature as fast as possible for the next injection, cryogenic cooling with CO_2 was used when the injector temperature reached 90 °C. The total run time was 12.75 min.

Mass spectrometric detection was carried out with an Agilent 5975 mass-selective detector (Agilent Technologies, Little Falls, DE, USA) operating in full scan (FS) and selected ion monitoring (SIM) mode, using electron ionization (EI, 70 eV). The ion source temperature was kept at 250 °C and a 3 min solvent delay time was selected.

2.4. Validation Process

Matrix-matched calibration curves were used to evaluate the linearity of the method by using blank sample extracts spiked at a concentration ranging from 0.1 µg/kg to 250 µg/L. The lowest calibration level (LCL) was determined for pesticides individually, according to the pesticide response. Each spiked extract was analyzed in triplicate. The peak area, as an analytical signal (quantification ion in SIM mode was used), was applied to a linear least-squares regression analysis.

The accuracy of the method was expressed as the recovery. It was performed in five replicates at three spiking levels (10, 50, and 250 µg/kg). The fortification of the blank textile samples with pesticides was performed before the extraction by the solution of pesticide standards at the required spiking levels, calculated to be the final concentration of the spiked sample. Standards were dissolved in acetone, which is a highly volatile

solvent; the solution was applied to the sample by spraying. Spiked samples were left to stand for 30 min before their extraction. For the recovery studies, the relative peak areas of pesticides were compared with relative peak areas of matrix-matched standards. Precision was expressed as relative standard deviation (RSD) and studied as intra- and inter-day precision. Spiked samples at 10, 50, and 250 μg/kg were analyzed for intra-day precision (five replicates). Inter-day precision was studied at the same concentration levels by processing spiked samples on five different days.

As the last validation parameter, the limits of detection (LODs) and the limits of quantifications (LOQs) were calculated. LODs and LOQs were determined for the quantification ion by the signal-to-noise ratio (S/N) criteria. They were established as the lowest concentration of the analytes yielding an S/N of 3 (LODs) or 10 (LOQs).

3. Results

Thirty-three pesticides were investigated in this study using a modified QuEChERS procedure, followed by GC–MS separation and quantification. The selection of the pesticides was based on the following criteria: (i) pesticides, which could be expected in cotton materials; (ii) reported real findings of pesticides in soil and water samples near cotton fields or in cotton balls [13–15]; or (iii) pesticides that are suspected to be endocrine disrupting chemicals and that could possibly be resorbed through the skin.

At first, the working solution of pesticide standards solutions (prepared in acetonitrile, ethyl acetate, hexane, hexane: acetonitrile 1:1) at a concentration of 1 ng/μL was analyzed in full scan (FS) mode, followed by their classification into SIM groups according to their retention times. The fast GC–MS conditions, particularly the oven temperature program, was optimized taking into consideration the good separation of the analytes. Table 1 summarizes the studied pesticides, their retention time, and characteristic ions for the SIM method. Multi-family groups of pesticides with a wide range of physical and chemical properties were studied. Therefore, the development of a multi-residual analytical method for the determination of pesticide residues in the cotton-based textile matrix was needed.

3.1. Modification of the QuEChERS Method

In order to acquire operative extraction efficiency, the parameters, which influence the extraction performance, had to be optimized. The QuEChERS method is affected by several factors such as the sample processing or pre-treatment, sample/solvent ratio or sample weight, hydrolysis by deionized water, type of extraction solvent, and sorbent types for dispersive SPE (dSPE).

To select the optimal parameters for the QuEChERS method, fortified samples at 100 μg/kg were used. The selection of the best extraction parameters was performed by simultaneously changing and screening the different factors that affect the extraction performance according to the design of the experimental approach [1,16]. Each optimization experiment was replicated three times, and the extraction recoveries (ER) were used for the evaluation of the proposed method. The QuEChERS method is the ideal extraction procedure for the isolation of pesticides from samples with high water content; therefore, in the case of matrices with a low moisture percentage, the adding of water is necessary to prepare a slurry of the matrix before the extraction in order to make the extraction of the compounds more efficient [17–19]. The addition of water not only improves sample homogeneity, but also enables the effective extraction of the compounds by hydrating the particles and facilitating the access of the extraction solvent to the pesticides [17,20]. Therefore, the cotton-based textile was mixed with water before the extraction in the ratio of 1:1 sample:water (*w/w*).

Table 1. List of the pesticides, their chemical classes, and GC–MS parameters (retention time, monitored ions, SIM groups).

Pesticide	Retention Time [min]	Chemical Function	Fragment Ions [m/z]			Starting Time of SIM Group [min]
Carbofuran	4.207	Carbamate	164	149	131	3.00
Trifluralin	5.499	Dinitroanyline	306	264	307	
Hexachlorobenzene	5.796	OCP	284	286	282	5.70
Dimethoate	5.894	OPP	87	93	164	
Atrazin	5.968	Triazine	200	215	202	
Propazin	5.979	Triazine	214	229	172	
Diazinone	6.025	OPP	179	137	152	
Lindane	6.042	OPP	181	183	109	
Parathion-methyl	6.579	OPP	263	125	211	6.30
Prometrin	6.642	Triazine	241	184	226	
Fenitrothion	6.768	OPP	277	125	260	6.74
Malathion	6.808	OPP	173	127	125	
Chlorpyrifos	6.899	OPP	197	314	199	
Parathion-ethyl	6.977	OPP	291	109	139	
Aldrin	6.997	OCP	263	261	265	
Dicofol	7.117	OCP	139	111	250	
Pendimethalin	7.242	Dinitroanyline	252	162	281	7.19
Oxychlordane	7.379	OCP	353	355	115	
Heptachlor epoxide	7.408	OCP	353	355	351	
Bromophos-ethyl	7.557	OPP	359	357	303	
o,p-DDE	7.642	OCP	246	248	318	
p,p-DDE	7.997	OCP	246	318	316	7.75
Endosulfan-alfa	7.808	OCP	241	239	195	
Endrin	8.368	OCP	263	265	281	8.15
Endosulfan-beta	8.471	OCP	237	239	216	
o,p-DDT	8.500	OCP	235	237	165	
p,p-DDT	8.883	OCP	235	237	165	8.80
Endosulfan sulfate	8.923	OCP	229	272	387	
Bifenthrin	9.243	Pyrethroid	181	165	166	
Methoxychlor	9.391	OCP	227	228	274	
Cyhalothrin lambda	9.746	Pyrethroid	181	197	208	9.56
Cypermethrin	10.797	Pyrethroid	163	165	181	
Deltamethrin	11.952	Pyrethroid	181	253	251	

Note: fragment ions in the first column were selected as quantification ions, OCP—organochlorine pesticides, OPP—organophosphorus pesticides.

3.2. Sample Weight Selection

Increasing the extraction sample weight causes the decrease of the dilution factor and the increase of the target pesticide sensitivity. The low density of cotton means that the increase in cotton-based textile sample weight is limited [1]. Three different weights were proposed: 1.0, 2.0, and 3.0 g. It was difficult to use the 2.0 or 3.0 g textile samples because of the high volume these would create in the QuEChERS tube. Furthermore, after the addition of 10 mL of the extraction solvent, the volume of the organic phase was too small for further clean-up and analysis. Thus, 1.0 g of the cotton-based textile was used as the optimum sample weight for the analytical procedure.

3.3. Selection of Extraction Solvent

To select the optimal extraction solvent, the recoveries of pesticides were studied by using three extracting solvents (acetonitrile, ethyl acetate, hexane) and one mixed extraction

agent (hexane:acetonitrile 1:1), respectively. It should be stated that in multi-residual analytical methods, acetonitrile and ethyl acetate have usually been used as extraction solvents. To test their extraction ability for cotton-based textile samples, the effect of the extraction solvent was evaluated. Despite the many advantages of acetonitrile in extraction, it is seldom used in GC analysis due to its high toxicity, large solvent expansion volume during GC vaporization, and low volatility. The method gave satisfactory mean recoveries for all target analytes in the case of using acetonitrile or ethylacetate as the extraction solvent (Figure 1). The apparent recoveries varied from 81 to 120% when acetonitrile was the extraction solvent, and from 75 to 107% for ethylacetate. The extraction efficiency of hexane and the mixture of hexane:acetonitrile were not enough for some of the pesticides, and the recoveries ranged between 56–156% and 46–147%, respectively. The strong extraction capability of acetonitrile contributed to the satisfactory recoveries of the pesticides. It can be seen that 79% of the analyzed pesticides showed recoveries higher than 90%, with acetonitrile as the extraction solvent; therefore, acetonitrile was selected.

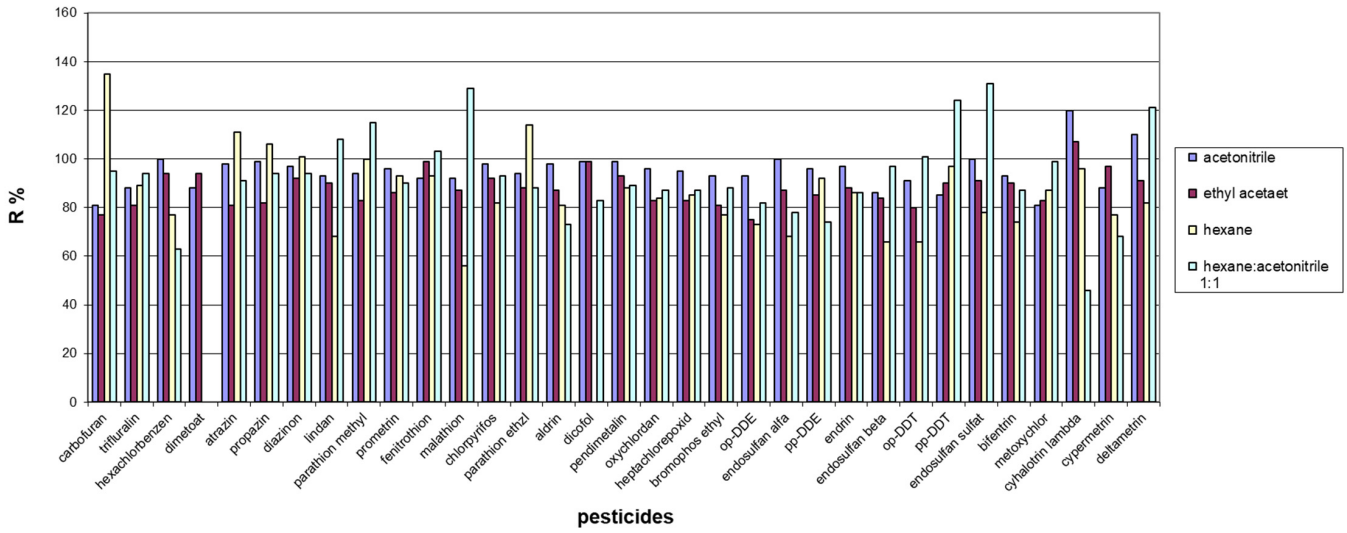

Figure 1. Selection of extraction solvent. The dependence of the extraction recovery of individual pesticides on the selection of the solvent.

3.4. Selection of an Appropriate Sorbent for Dispersive SPE

The interfering components from the sample matrix may negatively affect the ruggedness of the GC analysis. Therefore, the most important role of extraction is not only transferring the interested analytes from the sample matrix into the extraction solvent, but also the elimination of the coextracted components of the matrix. Due to the presence of potential interferences from matrices in the final extract, the cleanup sorbents should be used to clean the extract. PSA was mainly used as the cleanup sorbent for the reduction of the interferences in several methodologies for the analysis of pesticides in various commodities. The effectiveness of the QuEChERS method was estimated with and without the purification step. The PSA sorbent was used in the cleanup step, the need for a further purification step was surveyed, and the results obtained without the cleanup were compared. It was observed that the cleanup step was necessary to reduce interferences, to improve quantification, and to not affect the signal of the chromatographic system. A consistent chromatographic response was obtained when PSA was used as a cleaning sorbent, as well as with the reduction of the GC–MS equipment maintenance and the improvement of the robustness of the proposed method. Therefore, the PSA sorbent was used for further studies.

However, for colored textiles, cleaning with PSA was not enough to obtain colorless extracts. For this reason, the mixture of PSA and GCB was tested and the results were compared with the results obtained from the use of only the PSA cleanup sorbent. Recovery

values depending on the type of textile used and the selected cleaning sorbent are depicted in Figure 2. The extracts obtained with the use of a mixture of sorbents (PSA and GCB) were exactly colorless, and despite the use of the PSA and GCB, it was observed that maintenance operations of the GC system (liner and pre-column replacement) are not needed until the analysis of approximately 100 samples. The recoveries of pesticides were statistically evaluated (ANOVA test); PSA was used for the purification of white textiles, and the mixture of PSA and GCB was used for the cleanup of colored textiles. There was no significant difference between the sets of data; therefore, the white textile samples were used to validate the method.

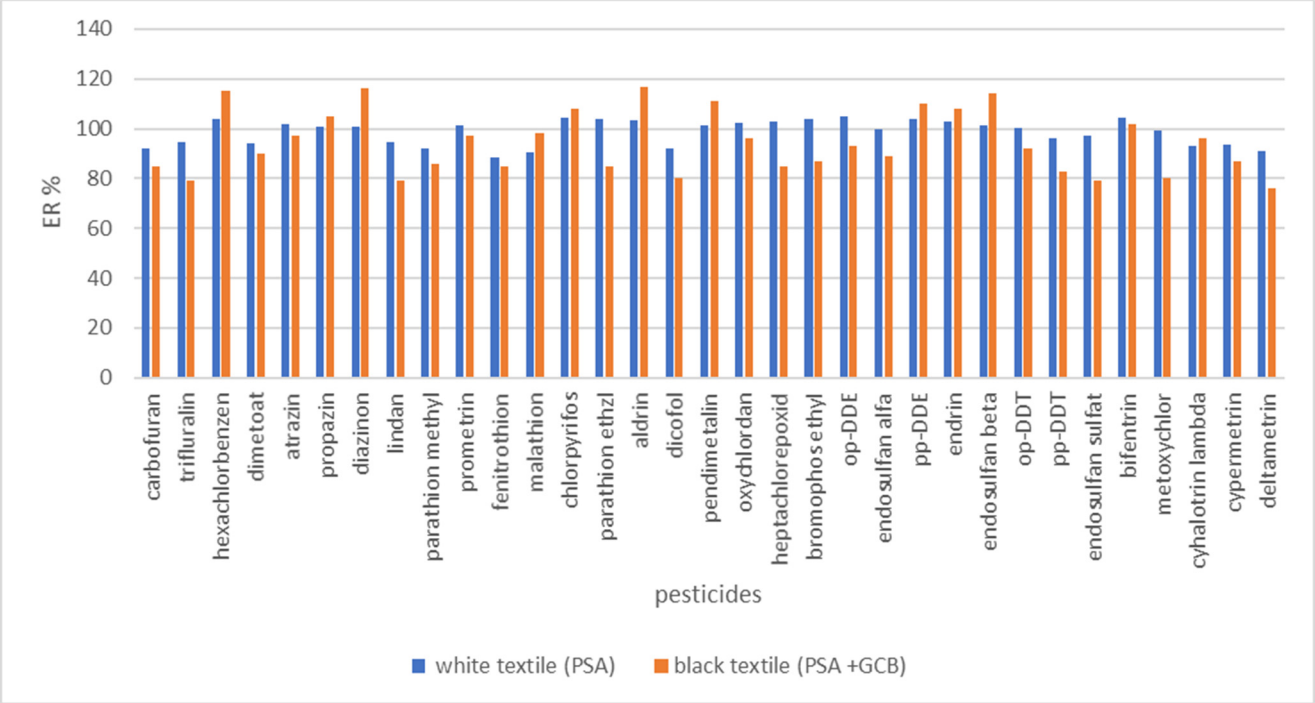

Figure 2. Extraction recovery (ER) of pesticides depending on the type of textile used and the selected cleaning sorbent.

3.5. Method Validation

The developed method was validated for white and colored textiles in terms of precision, linearity, trueness, LODs, and LOQs. The trueness of the method was formulated as recovery and the precision was expressed as relative standard deviation (RSD). The precision was evaluated as inter- and intra-day precision.

Matrix-matched standard solutions were used for the evaluation of linearity. An adequate volume of the pesticide working solution was added to the blank sample extracts after the extraction. Linearity was investigated at eight concentration levels, between 0.1 and 250 µg/kg. The method showed satisfactory linearity in the whole range of studied concentrations. The obtained determination coefficients (R^2) were higher than 0.98 for all of the pesticides.

Trueness was evaluated at three concentration levels in terms of recovery; the results can be seen in Table 2. The majority of pesticides indicated recoveries between 70 and 102%, at a concentration level of 10 µg/kg. In the case of some pesticides (dimethoate, parathion methyl, malathion), the recoveries were higher than 60% but lower than 70%. However, one pesticide, dicofol, had a recovery value higher than 120%. At a concentration level of 50 µg/kg, the recoveries always ranged from 86 to 106%; and at 250 µg/kg, from 88 to 105%. The established requirements for the pesticide residue analysis were fulfilled by RSD values lower than 15%.

Table 2. Validation results of the developed analytical method and MRLs of pesticides in cotton textile samples.

Name	ER% 10 µg/kg (RSD%)	ER% 50 µg/kg (RSD%)	ER% 250 µg/kg (RSD%)	LCL [µg/kg]	LOD [µg/kg]	LOQ [µg/kg]	MRL [µg/kg]
Carbofuran	88 (6)	91 (4)	92 (2)	5	0.980	3.240	100
Trifluralin	101 (2)	86 (6)	95 (1)	0.5	0.057	0.190	10
Hexachlorobenzene	96 (7)	97 (1)	104 (1)	5	0.750	2.470	20
Dimethoate	62 (13)	96 (11)	94 (7)	5	1.400	4.620	10
Atrazine	97 (6)	96 (4)	102 (1)	5	1.210	3.980	50
Propazin	98 (4)	94 (3)	101 (2)	0.1	0.090	0.290	
Diazinon	100 (4)	102 (9)	101 (2)	5	1.402	4.673	20
Lindane	70 (10)	97 (9)	95 (7)	5	1.490	4.910	10
Parathion methyl	63 (13)	90 (9)	92 (7)	5	1.360	4.500	20
Promethryn	100 (2)	97 (3)	101 (2)	0.1	0.060	0.190	
Fenitrothion	70 (15)	97 (9)	88 (9)	5	1.500	4.950	20
Malathion	64 (9)	95 (8)	90 (9)	5	1.520	5.000	20
Chlorpyrifos	101 (3)	101 (3)	104 (1)	0.1	0.060	0.190	300
Parathion ethyl	99 (2)	98 (6)	104 (2)	1	0.149	0.495	
Aldrin	98 (3)	95 (5)	104 (1)	5	0.980	3.240	20
Dicofol	122 (11)	103 (9)	92 (9)	5	1.520	5.000	100
Pendimethalin	96 (5)	92 (5)	101 (4)	5	1.320	4.350	50
Oxychlordan	98 (4)	96 (2)	102 (1)	0.5	0.366	1.220	
Heptachlorepoxid	100 (1)	96 (1)	103 (2)	0.5	0.366	1.220	10
Bromophos ethyl	101 (1)	96 (2)	104 (1)	0.1	0.045	0.149	20
O,p-DDE	98 (3)	97 (6)	105 (2)	0.1	0.035	0.118	50
Endosulfan alfa	70 (8)	92 (4)	100 (3)	5	1.130	3.740	30
P,p-DDE	97 (1)	95 (4)	104 (1)	0.5	0.161	0.538	50
Endrin	75 (9)	96 (2)	103 (1)	5	1.390	4.600	
Endosulfan beta	100 (2)	106 (5)	101 (2)	5	1.290	4.250	30
O,p-DDT	102 (3)	98 (5)	100 (6)	5	1.260	4.170	50
P,p-DDT	99 (1)	106 (10)	96 (7)	5	0.843	2.809	50
Endosulfan sulfat	72 (14)	89 (13)	97 (8)	5	1.520	5.000	30
Bifenthrin	99 (1)	95 (1)	105 (1)	0.5	0.128	0.427	500
Methoxychlor	94 (11)	95 (15)	99 (13)	0.1	0.030	0.090	10
Cyhalotrin lambda	98 (3)	95 (8)	93 (8)	1	0.280	0.910	200
Cypermethrin	96 (2)	99 (7)	93 (7)	1	0.260	0.850	200
Deltamethrin	100 (4)	102 (8)	91 (5)	1	0.270	0.900	20

Notes: LCL—lowest calibration level, LOD—limit of detection, LOQ—limit of quantification, MRL—maximum residue level, ER—extraction recovery, RSD—relative standard deviation.

The precision of the method was formulated as repeatability (intra-day precision) and intermediate precision (inter-day precision). The obtained values are shown in Table 2, expressed as RSD. The repeatability of the method ranged from 1 to 15%. In the case of inter-day precision, the RSD values were a little bit higher, but lower than 20% for all pesticides.

For the calculation of the LODs and LOQs, the signal-to-noise ratio (S/N) values of 3 and 10 were used, respectively. The LODs were in the range of 0.057–1.520 µg/kg and the LOQs were at 0.190–5.000 µg/kg; details are summarized in Table 2. The obtained LODs for all of the pesticides were lower than the MRLs set by the European Union for cotton seeds as the closest possible matrix. The lowest LOD and LOQ were identified for trifluralin, while the highest values were established for malathion, dicofol, and endosulfan sulfate.

For example, the obtained LODs for malathion, dicofol, and endosulfan sulfate were 1.52 µg/kg, and the MRLs for these pesticides in cotton seeds were 20, 100, and 30 µg/kg, respectively. The rated MRLs by the European Union for the studied pesticides in cotton seeds are in the range of 10–500 µg/kg (Table 2), which is much higher than the obtained LODs and LOQs by the method developed for this study. The limit of quantification for this proposed method was lower than that reported in a previously published paper [1].

An illustration of the separation of the studied mixture of pesticides is shown in Figure 3. The picture shows the overlap of ion chromatograms (quantification ions were selected and measured in SIM mode) of matrix-matched standards, at a concentration level of 50 µg/L.

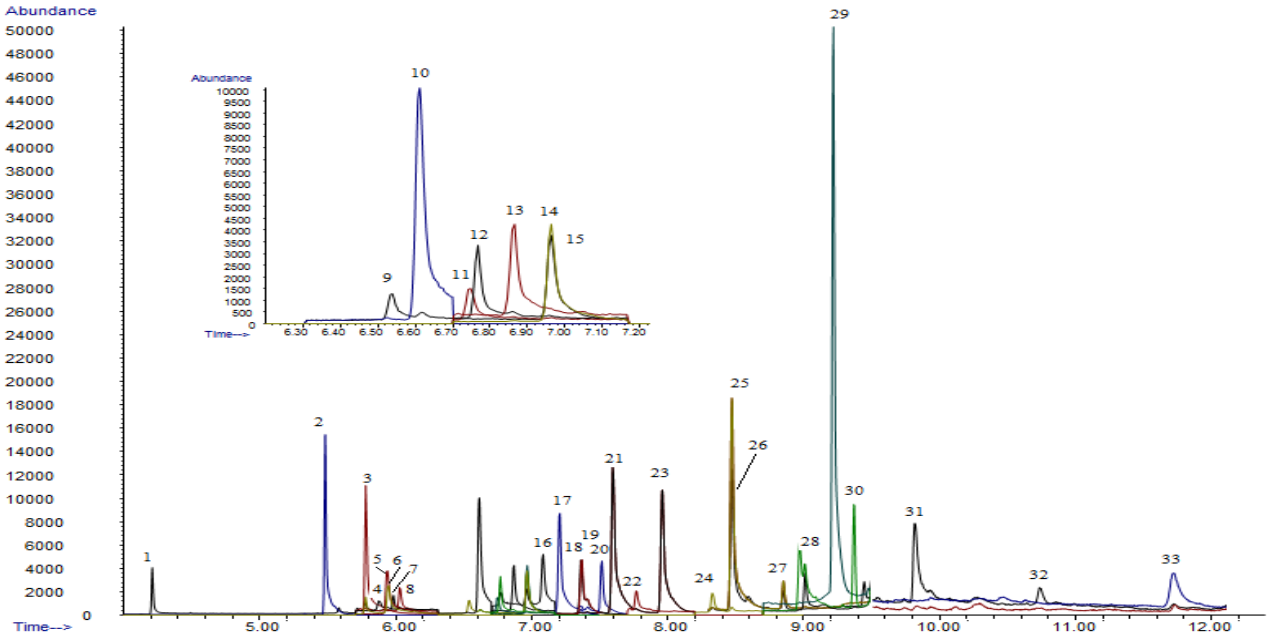

Figure 3. Extracted ion chromatogram of matrix-matched standards, at a concentration level of 50 µg/L. Peak assignments are the following: 1 carbofuran, 2 trifluralin, 3 hexachlorobenzene, 4 dimethoate, 5 atrazin, 6 propazin, 7 diazinone, 8 lindane, 9 parathion-methyl, 10 prometrin, 11 fenitrotion, 12 malathion, 13 chlorpyrifos, 14 parathion ethyl, 15 aldrin, 16 dicofol, 17 pendimethalin, 18 oxychlordane, 19 heptachlor epoxid, 20 bromophos ethyl, 21 op DDE, 22 pp DDE, 23 endosulfan alfa, 24 endrin, 25 endosulfan beta, 26 op DDT, 27 pp DDT, 28 endosulfan sulfat, 29 bifenthrin, 30 metoxychlor, 31 cyhalotrin lambda, 32 cypermetrin, 33 deltametrin.

For the analysis of materials with changed textile composition, a re-validation of the method is recommended.

3.6. Real Sample Analysis

The applicability of the method was tested by real sample analyses under optimized conditions. The samples were purchased from local markets. Ten textile samples were analyzed for the verification of the developed method. All the textile samples were made of 100% cotton without any material additions. For white textile samples, PSA was used in the cleanup step, and for colored samples, the mixture of PSA and GCB was applied. No pesticides were detected or quantified in the analyzed samples above the presented LODs and LOQs.

4. Conclusions

The simultaneous determination of 33 pesticides from different chemical classes in textiles was insured by a rapid, low cost, and sensitive method. Analytes were extracted by the modified QuEChERS protocol and the extracts were analyzed via the GC–MS method. Under the optimized conditions, low detection and quantification limits, wide

linearity, satisfactory recoveries with good repeatability were obtained. The simplicity and versatility of the validated method allow the product safety and management departments to monitor pesticide residues in textiles. The control of pesticide residues in textiles is essential to guaranty the safety of populations against pesticides. Furthermore, an update of the legislation is needed to fill the current gap regarding the lack of residual limits, particularly for a broad range of pesticides suspected to exhibit endocrine disruption properties for textiles.

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