Application of hydrophobic magnetic nanoparticles as clean-up adsorbents for pesticide residue analysis in in fruit, vegetable and various soil samples

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Abstract. *A clean-up procedure based on hydrophobic magnetic nanoparticles for QuEChERS extraction followed by GC-MS method for the simultaneous determination of 16 organochlorine pesticides was developed. The type and amount of clean-up adsorbents ($C18/GCB/Fe_3O_4/Fe_3O_4@Triton$), the volume and polarity of the extraction solvent were optimized. The method was validated according to SANTE/11813/2017 and ICH/2005/Q2/R1 guidelines. Spiked-sample recoveries of 84 – 108% with RSD below 8% were obtained for all the tested pesticides in strawberry. Quantification was carried out using matrix-matched calibration plots, which displayed good linearity ($R^2 > 0.99$), the limits of quantification being less than the maximum residue limits (MRL) for food. The elaborated procedure with satisfactory results was applied in to determine the pesticides in fruit, vegetable (strawberries, avocadoes, watermelons, radishes, and flesh kiwis) and soil (agricultural, urban and lab-made) samples. The most frequently-founded pesticide residues were: 4,4'-DDE, 4,4'-DDD, lindane and 4,4'-DDT - in all cases were below MRL. The highest concentration of 4,4'-DDT was founded in agricultural and lab-made soils.*

Key words: sample preparation, intestacies, magnetic separation, matrix effect, multi-residue analysis, recovery.

Introduction

Pesticides including of the following insecticides, herbicides, fungicides, etc. are necessary for increasing agricultural productivity and harvest to protect the commodity from deterioration during storage and transport. However, their high toxicity poses a hazard to the ecosystem [1] and the

contamination air, water and soil [2], which leads to the direct transfer of pesticides from agricultural land to surrounding food products (fruits, berries or vegetables) at concentrations range from ng to µg·L^{-1} [3]. Among various organic pesticides, organochlorine pesticides (OCPs) are the most persistent, toxic and economical agricultural substances. Though their use is banned, they are still used illegally. But at the same time OCPs have accumulated and render themselves persistent in moistened agricultural soil, environmental and groundwater [4]. In contrast to OCPs, organophosphorus pesticides are less persistent and are used more extensively, while synthetic parathyroid pesticides are the least toxic and are used as insecticides.

The first multi-residue analysis method for organochlorine insecticides was developed in 1963 [5]. However, the efficient pesticide residue analysis is an important task not only in modern analytical chemistry, but also for the regulatory European Community authorities that control maximum residue limit (MRL) [6] based on European Regulation No. 396/2005. Methods for multiclass pesticide analysis based on mass-spectrometry (MS), which allows this type of detection [7], have recently gained considerable attention from researchers, as this technique is easy and more reliable in terms of confirmation and identification. The usage of GC-MS for multi-residue pesticides analysis commenced 1990 and is now a standard method for the quantification and identification of analytes in complex matrices [8]. Direct determination of trace level concentration of all pesticides including OCPs is complicated due to low sensitivity of methods and matrix interference (matrix effect). Therefore, prior to quantitative determination of analytes is often required an effective sample preparation and pre-concentration procedures.

The pesticide residue analysis employed in our research, the QuEChERS sample preparation assay was developed in 2003 for fruits and vegetables [9] and was shown to improve sensitivity of determination [10]. It has become a popular technique in most laboratories around the world for sample preparations of various matrices such as: cereals [11], fruits and vegetables [12] on account of its low cost and availability, combined with its high efficiency. In 2007, QuEChERS procedure in combination with the dispersive Solid Phase Extraction (dSPE) method was considered one of the advance approach for sample preparation was approved by the International Association of Official Analytical Chemists (AOAC) for the determination of multi-pesticide residues in veggies and fruits [13]. Moreover, use of QuEChERS has quickly expanded outside of its traditional field of application to determine a wide

variety of contaminants, antibiotics and other pharmaceuticals [14], in a broader variety of matrices such as meat, fish, tea [15], tobacco [16], blood [17], rice [22] and even soil [18, 19]. The method typically involves two stages. In the first stage, extraction is performed on the separation between the organic and aqueous layers by salting-out. In the second, dSPE is performed to attain enhanced purification of the matrix via $MgSO_4$ (anhydrous) with various adsorbents (octadecyl silica (C18), graphite carbon black (GCB), primary-secondary amine (PSA), etc.) depending on the interfering compounds to be removed [9]. PSA is generally in dSPE as adsorbent to eliminate organic acids, polar pigments, fatty acids and most of sugars from fruits [20]. However, the cleaning efficiency is not always satisfactory, especially for polar pigments [21]. The main drawback of PSA as clean-up adsorbent is acid-basic sensitive pesticides can suffer hydrolysis under basic modes and it needful to apply some organic acid (formic or acetic) to diminish pH. GCB is also applied to remove organic pigments and planar pesticides in improve QuEChERS procedure [22]. Some researchers use a freeze-out step to reduce the lipid-containing and other interfering compounds with scarce solubility. However, clean-up procedure with C18 for lipid removal is more simpleness and faster, although freeze-out also precipitates additional matrix components with limited solubility in extraction solvent during QuEChERS procedure. The most important task of extraction is not only to transfer the target analytes (OCP) from the complex matrix to the extraction solvent (especially soils), but also to minimize the co-extracted components of the matrix as much as possible, as this background may adversely affect to the reproducibility of analysis, GC equipment and require additional accessories. Therefore, the components that are co-eluted will be separated mainly. The higher the organic matter content, the better the pesticides adsorption. For example, the influence of organic matter in different soil on the extraction process was observed by Lesueur et al. [18]. The soils used in that study were EUROSOIL 7 and SO 26 (subsoil) standard samples with 11.52% and 1.81% organic compound contents, respectively, as well as sea sand (0% organic compound content). The 24 OCPs were studies in this work, which have a high affinity for humic substances in the soil, which highlight interpretive the chemical interactions with target analytes. For all tested active substances, the results were higher for EUROSOIL 7 than for SO 26. The clean-up step is required for complicated matrices (i.e. soils, honey, meat) in order to reduce interferences, improve quantification of target analytes through improving quality chromatograms (symmetry and separation peaks). Thus, developing a new clean-up agent (selective adsorbent) is important for OCPs residue analysis. Compared to other methods,

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the main insufficiency of this method is the absence the stage preconcentration of analyte (enrichment process), which leads to higher limit of detections. To overcome this effect in real matrix was proposed improving certain steps by using of dispersive liquid-liquid microextraction using organic compounds with similar to the functional groups of the traditional clean-up materials, for example, n-octadecylamine [23]. Also, for purification stage employing carbon-based nanomaterials [24], single-walled and multi-walled carbon nanotubes [25], using a mixture of various nature adsorbents [26] or amine-derivate polymer material [27].

Furthermore, the separation process in dSPE can be carried out directly in crude samples (with the exception of matrices of soil) containing suspended magnetic solid material without the need for any additional centrifugation or filtration, thus making separation fast and easier named as magnetic solid phase extraction. Magnetite (Fe_3O_4) magnetic nanoparticles (MNPs) have been shown to have excellent adsorption features in terms of purifying the complex sample and can easily be separated from the extract [28, 29, 30]. The most widely used MNPs for pesticide residue analysis using the QuEChERS method is bare magnetite (Fe_3O_4) [28]. Here, we propose using the non-ionic surfactant Triton X-100, which contains a hydrophilic polyethylene oxide part (with 9.5 ethylene oxide units) and an aromatic fragment combine with hydrophobic aliphatic groups as functional complexes as the clean-up adsorbent [31]. The hydrophobic motives of surfactant (4-(1,1,3,3-tetramethylbutyl)-phenyl groups) can selectively bind to pesticides. Hydrophilic polyethylene oxide groups of the non-ionic surfactant can be chemically grafted to the SiO_2 shell of MNPs-core with epoxy groups. This is a key issue to combine the features and advantages of both the hydrophobic properties of a non-ionic surfactant and superparamagnetic properties of magnetite to reach separation and determination of trace amount OCPs in real samples.

The main motivation of this study is to use core-shell MNPs modified by hydrophobic Triton X-100 to analyse representative OCPs (16 intestacies) in a fruit (strawberry, avocado (as high oil matrix), watermelon and kiwi), vegetable (radish) and soil (agricultural, pesticide-enriched lab-made and urban) matrixes. We emphasise the point that hydrophobically-modified MNPs constitute excellent, novel clean-up materials compared to traditional adsorbents (C18 and GCB, bare MNPs). All-purpose practicability of the elaborated procedure was likewise validated. The modified method was applied to determine OCPs in fruits, vegetable and soil samples by a budget-conscious laboratory GC-MS system. A further aim was to determine the distribution between the selected main pesticides and various matrixes via simultaneous

analysis of soil samples and the corresponding lab-grown vegetables (e.g. radishes). Comprehension the distribution of OCPs residues in soil is crucial for determining the transportability of these residues into water, non-target plants, organisms, and humans.

Experimental part

Reagents. HPLC grade methanol (MeOH) and acetonitrile (MeCN), hexane, ethyl acetate (EtAc) and dichloromethane (CH_2Cl_2) were acquired from Sigma-Aldrich (Kyiv, Ukraine). Inorganic salts such as magnesium sulphate ($MgSO_4$, anhydrous), sodium acetate (NaAc), and cartridge Varian SPE Bulk Packing (C18 phase, polymeric bonded) were purchased in Sigma-Aldrich (Munich, Germany). $MgSO_4$ was pretreated (5 h at 500 °C) to remove any residual water. Reference standards of the pesticides were provided via the SUPELCO EPA Pesticide Mix (aldrin, α-BHC, β-BHC, γ-BHC, 4,4'-DDD, 4,4'-DDE, 4,4'-DDT, α-endosulfan, β-endosulfan, endosulfan sulphate, dieldrin, endrin, endrin aldehyde, heptachlor, heptachlor epoxide Isomer B) in MeOH:CH_2Cl_2 (98:2) and the EPA 8080 Pesticide Mix (aldrin, α-BHC, β-BHC, γ-BHC, 4,4'-DDT, 4,4'-DDD, 4,4'-DDE, endosulfan α, endosulfan β, endosulfan sulphate, endrin, endrin aldehyde, dieldrin, heptachlor epoxide Isomer B, heptachlor, methoxychlor) in toluene : hexane (50:50), while all other pesticides were purchased individually (Atrazine). The working standard mixture solution involving 10 mg·L^{-1} of each OCPs was prepared in methanol. All individual standard solutions(SS) of each pesticide (10 mg·L^{-1}) were prepared in MeOH to obtain a stock solution of 10,00 μg·L^{-1}. All prepared solutions stored in a refrigerator (at 4-6 °C) to avoid possible decomposition of pesticides.

Apparatus. A Thermo Scientific Espresso high-speed microcentrifuge was used for sedimentations. The disperser (T-18 Ultra Turrax Digital) was fabricated from IKA (China), as was a vortex shaker (Genius 3). T 18 digital ULTRA-TURRAX® dispenser was utilised. The magnetic stirrer with temperature controller AREX Hot Plate Stirrer was purchased from VELP Scientifica (Italy).

Internal standards. Octafluoronaphthalene (OFN) and 4,4′-DDT-d_8 were both used as internal standards (IS) at a concentration of 15 μg·L^{-1} in the MeOH solution. Intermediate working standards in MeOH were prepared by dilution of 1 mL of the solvent stock solution in flask (class A, 100 mL). Using two IS due to the different molecular structure of their benzene rings and weight enabled us to cover all

the target pesticides. Retention time intervals of 6.0-13.5 and 13.5-30.0 min were obtained when using atrazine-d$_5$ and 4,4′-DDT-d$_8$, respectively [32].

Adsorbents. Lab-made hydrophobic magnetite nanoparticles (Fe$_3$O$_4$@Triton), produced from core-shell MNPs modified with the non-ionic surfactant Triton X-100 [31], were used in this study. For the sake of comparison, GCB [33] and a commercial SPE sorbent (C18) [34] were used to remove polar compounds. The textural characteristics of all these adsorbents are given (Table 1).

Table 1. Textural parameters of applied adsorbents.

Adsorbent	Sorbent phase	Category phase	Carbon loading (%)	S, m^2/g	Particle size	Mean pore size (nm)
SiO$_2$C18	C18	Non-polar	14.90	500	40/120 (μm)	6
Fe$_3$O$_4$@Triton	Triton X-100		14.56	150	12-15 (nm)	3.2
Fe$_3$O$_4$	-	Low polar	-	25	8-11 (nm)	Non-porous
GCB	-		85.45	1890	1-5 (μm)	5.51

Samples. Different samples of fresh fruits (strawberries, avocadoes, watermelon and kiwis) and vegetables (radishes) were purchased from local supermarkets (Kyiv, Ukraine). A root-crop radish was also bought and used as a matrix for growing the plant under lab conditions.

The soil samples were gathered from 3 representative agricultural areas in Ukraine (Kyiv region), and 6 pesticides were selected on the basis of their use. The agricultural soil samples were collected, between May 2017 and September 2017 from conventional farming (more than 5 years of agricultural practices). The soils were collected in glass boxes (1 kg). Agricultural and urban soils were gathered with a stainless steel spatula at a profoundness of among 20 - 40 (cm from agricultural land (*soil 1, soil 2, soil 3*) and an urban plot (*soil 4, soil 5*) located in the central park of Kyiv (Ukraine). Soil samples were stored before analysis in glass boxes at (3-5) °C under lightless condition. Before use they were subsequently homogenized, sieved (2-mm mesh) and dried at room temperature.

The agricultural soil (*soil 1*) was used for radish grown completely in lab flower vials, watering the plants (radish seeds) with a mixture of 6 OCPs (lindane, heptachlor, dieldrin, 4,4'-DDD, 4,4'-DDE, 4,4'-

DDT, each at 10 μg/L) every week for 2 months at 25 °C until the time of analysis (soil and root-crop radish). These samples were denominated as *soil 1.1* and *radish 1.1*. The corresponding blank samples (watering the radish plants with distillate water) were denominated as *soil 1.2* and *radish 1.2*.

Description of developed samples preparation. The QuEChERS procedure was performed according to the methods described Anastassiades in [9] and Lehotay in J. AOAC [13] analysis. A modified QuEChERS extraction procedure was employed to pretreatment samples using different adsorbents (bare Fe_3O_4, Fe_3O_4@Triton, GCB and C18). Figure 1 shows an illustrative diagram for the proposed experimental procedure.
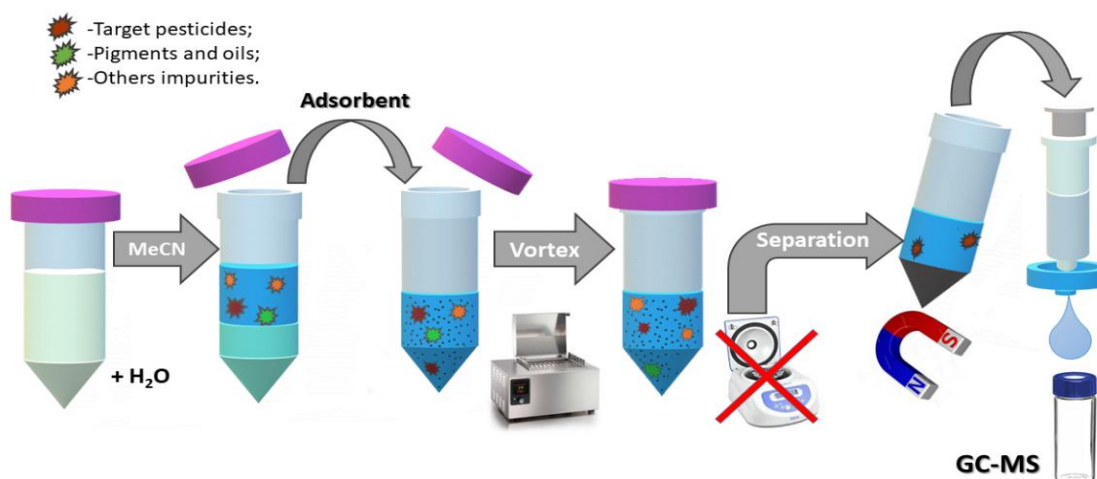

Fig. 1. Scheme of developed sample preparation for fruits and vegetables.

For vegetables and fruits. Lab-prepared vegetables (radishes) and commercial available fruits (strawberries, avocadoes, watermelon, kiwis) were crushed by means knife and comminuted using a disintegrator for 30 s to achieve homogeneousness. Briefly, 5 g of sample were transferred in a centrifuge tube (50 mL) and appropriate volumes of pesticide standards were also added after that put on 8 mL of MeCN. Thereupon the mixture was shacked during 1 min and 4 g of $MgSO_4$ (anhydrous) were added. Then, the tube was agitated intensive for 1 min by vortex and centrifuged at 8000 rpm for 5 min using a microcentrifuge. 1 mL of the MeCN extracts (upper layer) was transferred in an Eppendorf vial (1.5 mL) containing a certain amount of Fe_3O_4@Triton (0.05 g), C18 (0.05 g) or GCB (0.05 g) and 0.15 g $MgSO_4$ for clean-up (optimized condition). The samples were agitate during 10 min at room temperature, and

then magnetically separated by an NdFeB magnet (diameter - 2 cm). The supernatant layer (0.5 mL) was placed in the centrifuge tube (2 mL) containing water (0.5 mL). After that the solution was passed through membrane filter (0.22 μm) for assays. A 1 μL of the aforementioned solution was injected into the GC-MS. The total chromatography time of tested injection was 35.92 min.

For soils. The soil sample from the radish flower vial (5 g) was transferred in the centrifuge tube (50 mL). 8 ml of the water then added to the centrifuge tube and vigorously vortexed, subsequently adding 8 mL MeCN (without formic acid). The centrifuge tube with sample mixture was vortexed during 1 min. Then, tube putted in a refrigerator for 30 min and reached at 4 °C. $MgSO_4$ (4 g) and NaCl (1 g) were subsequently added to the soil/acetonitrile/water suspension and the mixture was vortexed for 1 min. The sample was centrifuged for 5 min at 4000 rpm. The grey MeCN extract (2 mL) was transferred to 5 mL microcentrifuge Eppendorf vial containing 0.05 g of Fe_3O_4@Triton (or 0.05 g of C18), 0.15 g of $MgSO_4$ and 0.05 g of GCB, followed by vortexing within 1 min. The Eppendorf vial was centrifuged at 5000 rpm for 5 min. The extract (1.2 mL) was transferred to a Eppendorf vial (1.8 mL) and the vial was vortexed and centrifuged at 10000 rpm during 5 min. The extract was transferred to the vial for GC-MS analysis. Blank samples of the soil previously tested for the presence of OCPs were used for the purposes of method validation and optimization.

Gas chromatography-mass spectrometry assay. The GC-MS analysis was performed on an Isq LT GC-MS (Thermo Fisher Scientific). The OCPs were separated in an HP-Ultra-1MS column (60 m × 0.25 mm × 0.25 μm). The oven temperature was initially held at 85 °C and then increased to 150 °C at a rate of 10 °C·min^{-1}. The temperature was subsequently increased to 350 °C at a rate of 5 °C/min and was finally held for 5.0 min at 350 °C. The injection volume was 2 mL in split mode. Helium (purity ≥ 99.999%) was used as carrier gas at a flow rate of 1.0 mL·min^{-1}. The injection port, ion source and interface temperatures were held at 200 °C, 250 °C and 300 °C, respectively. Selective ion monitoring (SIM) mode was adopted for the quantitative analysis.

Validation method and matrix effect. The validation process of the procedure followed European guidelines for pesticide residue analysis in food (SANTE/11813/2017 [35]) and pharmaceuticals (ICH/2005/Q2/R1 [36]) protocols. Thus, precision, linearity (expressed as R^2), uncertainty, limits of detection (LOD) and quantification (LOQ), accuracy (expressed as recovery), matrix effects and intra-

/inter-day precision were evaluated. Matrix-matched calibration curves with spiked blank samples at five concentrations levels (0.5, 1, 10, 50, 100 µg·kg^{-1}) were used for linearity determination. Precisions and recoveries (%) as view of reproducibility and repeatability were determined by analysis of blank samples spiked with SS at two concentration levels. According to European ICH/2005/Q2/R1 guideline, LOD and LOQ values were calculated from the same curves, using the following equations: *LOD = 3 σ/S* and *LOQ = 10 σ/S*, where σthe standard deviation of the response and S is the average slope of the calibration plots.

The evaluation of matrix effects (ME) in the strawberry and soil samples was carried out by comparing the slopes of the OCPs calibration plots in pure solvent and the investigated matrices. The ME (%) was calculated via the following equation:

$$ME(\%) = \frac{\text{slope of calibration plot in matrix}}{\text{slope of calibration plot in solvent}} \cdot 100\%$$

Results and discussions

Several parameters were investigated to achieve optimal performance of the modified QuEChERS procedure for the target OCPs, including purification time, nature and amount of adsorbents, volume and polarity of solvent.

GC-MS optimization. Standard solutions and samples were analysed in SIM mode. This mode based on the use of two identification ions and one quantitation ion, as two multiple reaction monitoring ions may not be enough to provide positive identification of the target pesticides [37]. In this study, monitoring was set to select the highest *m/z* value and abundance of the precursor ion, establishing a trade-off between selectivity and sensitivity. For this reason, the pesticides were identified in accordance with their retention time and three ions (two identification ions and one quantitation ion) using the NIST pesticides library (Table 2). Quantitative determination was based on the ratio of the peak area of the quantitation ion to one of the ions of IS. Peak areas were calculated based on the corresponding quantification ion (Fig. S2). Moreover, addition of the internal standard (OFN and 4,4'-DDD-d$_8$) to the samples after the extraction solvent enables controlling the whole analytical process, thus helping to minimization of the error generated in the multiple steps and improving precision and accuracy. The results show that identity verification was possible for all pesticides in samples of fruits and vegetables.

SIM segments were established containing a specific ion mass-to-charge ratio (*m/z*) for each compound, followed by MS characterization. The method yield optimum separation of the 16 OCPs and IS within 30 min (Fig. S3).

Table 2. Retention times (*t*$_R$), molecular weights, quantification parameters of target ions for the GC-MS analysis of the pesticides.

Analyte	*t*$_R$ (min)	Molecular weight (g·mol^{-1})	Quantifier and qualifier (*m/z*)	Range (nm)
Aldrin	14.37	364.91	**263**, 193, 191	190-264
OFN (IS)	6.91	272.09	**219**, 170, 131	104-206
α-HCH	9.83	290.83	**181**,145,146	108-184
Lindane	9.59	290.83	**183**,147, 111	109-184
4,4'-DDT	25.64	354.49	**235**, 165, 199	117-236
4,4'-DDD	23.50	320.04	**235**, 165, 199	162-236
4,4'-DDD·HCl	25.75	356.54	**282**, 212, 176	176-272
4,4'-DDE	19.88	318.03	**246**, 176, 175	174-247
4,4'-DDD-d$_8$ (IS)	23.68	362.50	**243**, 173, 206	172-244
Dieldrin	21.42	379.81	**263**; 345; 237	166-239
α-Endosulfan	26.10	406.93	**241**, 206, 205	165-242
β-Endosulfan	26.88	406.93	**241**, 206, 205	165-242
Endosulfan sulphate	27.91	422.93	**272**, 237, 235	234-273
Endrin	29.57	380.91	**243**, 207, 173	172-244
Heptachlor	15.60	373.32	**272**, 237, 235	236-275
Heptachlor epoxide	16.67	389.32	**353**, 263, 282	262-354

Selection of optimum extraction and elution solvents and their volumes. One of the most important steps when developing a new sample preparation approach is the choice extraction solvent with optimal parameters. Many effects and parameters need to be considered, such as: a high dissolving ability for the desired analyte (full spectrum nonpolar OCPs) and good permeability in the food matrix; the selectivity degree of that can be achieved during extraction, partitioning and clean-up; achieving a separation from

aqueous medium; compatibility with chromatographic detection without any hardware issues; cost, safety and environmental issues; and finally, ease of evaporation and clean volume transfers. Accordingly, several extraction solvents with an increasing polarity index (EtAc, acetone, dichloromethane, hexane and MeCN) were studied (Fig. 2). Such solvents choice among the most commonly used ones for multi-residue analysis of pesticides is due to that each has been shown to provide high recoveries of a wide range of OCPs for fruit and vegetable matrices [38, 39]. Each solvent has some advantages and drawbacks. The drawbacks of hexane versus MeCN and EtAc for determination of pesticides include: 1) a greater volume of solvent expansion during evaporation in gas chromatography conditions; 2) lower volatility (though comparable with EtAc and MeCN, which means longer evaporation times); and 3) hexane's agglutinate effect on MNPs can be dissolved in the mixture with low magnetic separation. The same degree of recovery efficiency is detected for all the contaminants: MeCN > dichloromethane > EtAc > acetone; hence, MeCN was elected for QuEChERS method as extraction solvent. The main drawbacks of MeCN and EtAc (i.e., co-extraction of nonpolar compounds such as lipids or waxes), which is evident in the extraction of fruits and vegetables, may be not significant in the case of soil samples, and these solvents are suitable for the extraction of different soil types [40].
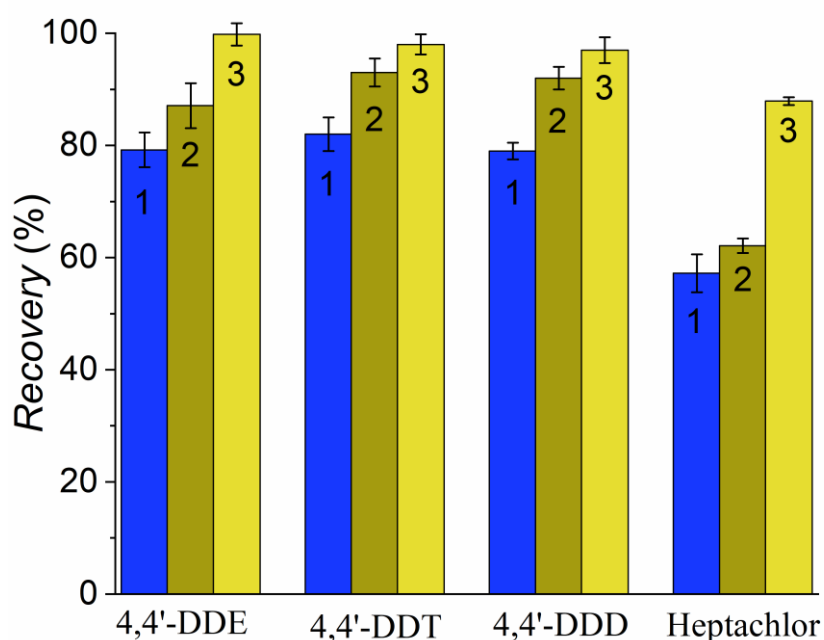

Fig. 2. Effect of various solvents (1– EtAc, 2 – CH_2Cl_2, 3 – MeCN) on the extraction efficiency toward OCPs in strawberries with dSPE clean-up step using the adsorbent Fe_3O_4@Triton: (extraction conditions: Fe_3O_4@Triton 50 mg; time 10 min; temperature 20 °C; V = 8 mL).

Other factor that can affect the extraction efficiency the selected OCPs from the food matrix is volume extraction solvent. The original QuEChERS method uses 10 mL extraction solvent [9]. The other studies reported using from 2.5 [40] to 30 mL [41] solvent for extraction. The optimization of solvent volume is resulted in higher recoveries of OPCs and economical effect. Different volumes of MeCN (1.0, 2.0, 5.0, 8.0, 10.0, and 15.0 mL) were used to estimate this parameter. The extraction efficiency of the selected OCPs increases up to 8.0 mL to then decrease with increasing MeCN volume (Fig. S1). This may be explain that at low volumes of MeCN (less than 8.0 mL), extraction of the OCPs from the extract was insufficiently for high recovery values. Thus, 8.0 mL of MeCN was employed as an optimum volume for OCPs extraction.

Optimization of the amount of adsorbent and contact time. To achieve satisfactory removal effect for co-extracted interference compounds in food samples, two types of clean-up absorbents (Fe_3O_4@Triton and GCB) were tested for the five OCPs (heptachlor, dieldrin, 4,4'-DDD, 4,4'-DDE, 4,4'-DDT) from strawberry samples (as model sample). The recoveries of these compounds in different amounts of tested adsorbents (30-100 mg) are shown in Figure 3. The recoveries of 20 mg and 30 mg GCB were above 90% and meet test requirements. The recoveries planar OCPs began to diminish after more than 50 mg GCB were added. Thus understanding purification efficiency into account, 50 mg GCB was chosen for the clean-up procedure. Moreover, the recovery of more planar target compounds decreased noticeably intensively. When the amount of added Fe_3O_4@Triton was below 20 mg, the absorbent mixture could not be magnetic separated quickly by using NdFeB magnet. In this case, the concentration of Fe_3O_4@Triton in the adsorbent mixture may be too low. The magnetic properties of adsorbent were effective begun at 40 mg. When the amount of added Fe_3O_4@Triton solid was close to 50 mg, recoveries improved to maximum. Additionally, the decrease in the recovery of planar OCPs caused by increased amounts Fe_3O_4@Triton was significantly less than that decreased by increased amounts of GCB adsorbent.
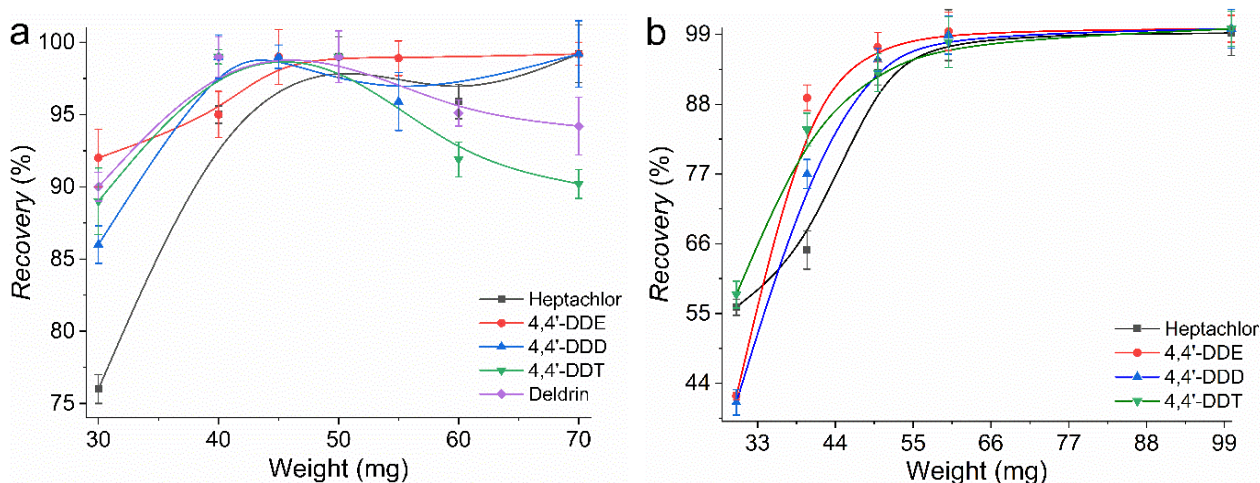
Fig. 3. Effect of weight of GCB (a) and Fe$_3$O$_4$@Triton (b) as clean-up adsorbents on the extraction of the analysed pesticides (60 µg kg^{-1} each).

Also, the clean-up time for the analysed main OCPs using Fe$_3$O$_4$@Triton as adsorbents was analysed. The clean-up time varied from 30 to 180 sec under constant other extraction parameters and strawberry sample. According to Fig. 4 the extraction efficiency raised with increased clean-up time from 30 to 120 sec, becoming stable from 120 to 180 sec. Finally, the clean-up time at 120 sec was selected for developed procedure.
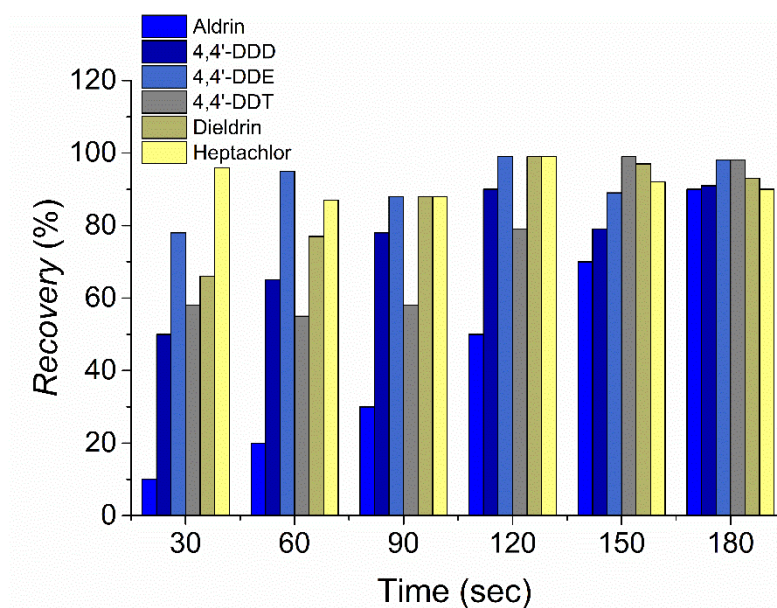

Fig. 4. Effect of clean-up time on the extraction efficiency the target OCPs (each 50 µg kg^{-1}) by *Fe$_3$O$_4$@Triton* adsorbent from strawberry samples

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Comparison with other clean-up adsorbents. After selecting the optimal extraction solvent, the next step was to determine the most suitable purification adsorbent. Samples that contain large amounts of pigments or those that contain very large amounts of fat may require specific, additional clean-up for these matrices. To certify the purification effect of the modified QuEChERS procedure with developed magnetic adsorbents (Fe_3O_4@Triton) was compared with the commonly used adsorbents (C18, GCB and bare MNPs) that supplement the clean-up step for the most complicate and critical extract (avocado) (Fig. 5).
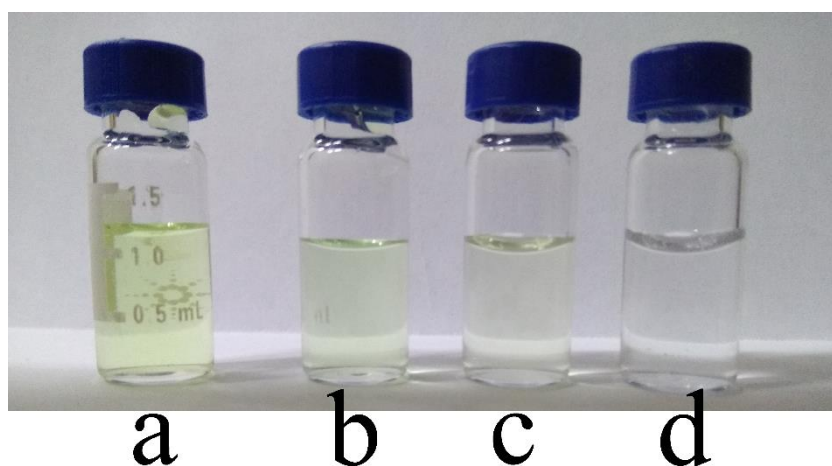

Fig. 5. Images of avocado extracts (2 mL) with clean-up using 0.15 g $MgSO_4$ (anhydrous) and different adsorbents: (a) 0.15 g bare MNPs; (b) 0.05 g GCB; (c) 0.05 g C18; (d) 0.10 g Fe_3O_4@Triton.

Comparing the data presented in Figure 5, it can be seen that bare MNPs are only slightly useful in cleaning up pigment-containing matrices. Since MNPs with a low specific surface (< 100 $m^2 \cdot g^{-1}$) do not adsorb planar-ring OCPs, significantly increasing the amount of MNPs 3-fold will not be helpful and will lead to the loss of these pesticides. Thus, it is difficult to simultaneously achieve good purification (Fig. 5a) and satisfactory separation of these pesticides when cleaning-up using bare MNPs. Experimental data (Fig. 5 b and c) demonstrate that C18 showed enhanced clean-up performance compared to GCB in removing pigments. The avocado sample treated by Fe_3O_4@Triton present clear colorless solution as depicted in Fig. 5d. Moreover, the chromatograms in Figure S3b represent that the developed magnetic adsorbents shown lower concentration levels of co-extracted interferences from the matrices. To obtain the number and amount target compounds (5 pesticides) keep in each of the acetonitrile extracts. The extraction effectivity were analysed by areas of chromatography peak (Fig. 6).
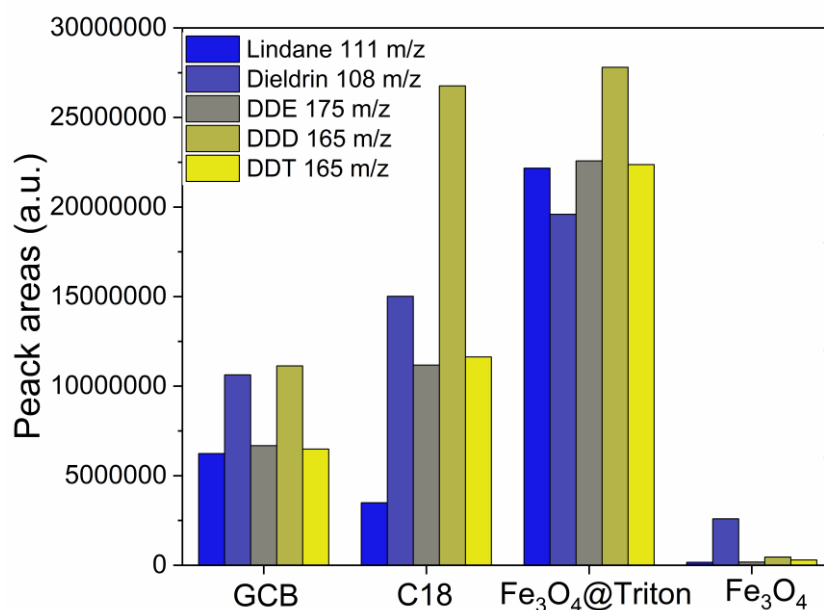
Fig. 6. Adsorption ability of different adsorbents with respect to representative target OCPs.

It is evident that Fe_3O_4@Triton could effectively eliminate organic pigments from studied samples with good OCPs recovery (see Fig. 6). Thus, Fe_3O_4@Triton displayed a high affinity towards matrix impurities (including organic pigments) together with in satisfactory recovery of multiple OCPs, including planar-ring pesticides (Fig. 6) in food samples.

Also, we can assess the experimental data with compared to the full-scan chromatograms of strawberry extract after using two different clean-up approach. The chromatograms of the spiked sample of strawberry with C18 and Fe_3O_4@Triton adsorbents for clean-up procedures are shown in Fig. S3. The strawberry extract chromatograms are practically identical, a differences in initial part of the chromatogram for the sample preparation with using C18 where the peaks for some analytes is lower and non-separated than in the chromatogram after injection extract after developed clean-up procedure. The chromatogram of the spiked sample based on Fe_3O_4@Triton adsorbent was relatively clean with well separated peaks, thus proving that the present method has good clean-up ability (Fig. S3b). Compared to developed method to the QuEChERS procedure applying the typical 50 mg kg^{-1} C18 clean-up agent, at 50 mg kg^{-1} in a strawberry matrix sample, all of the 16 OCPs was characterized with recovery in the 80–110% range. With respect to the avocado matrix procedure had lower recovery values (55-114%).

Reusability of Fe₃O₄@Triton. With an eye to investigate the reusability of Fe_3O_4@Triton, the adsorbent was separated and washed with solvents to desorption of the impurities from its surface. As shown in Figure 7, Fe_3O_4@Triton can be reused twice times without significantly decreasing its clean-up efficiency, which can significantly reduce costs in sample preparation procedures.
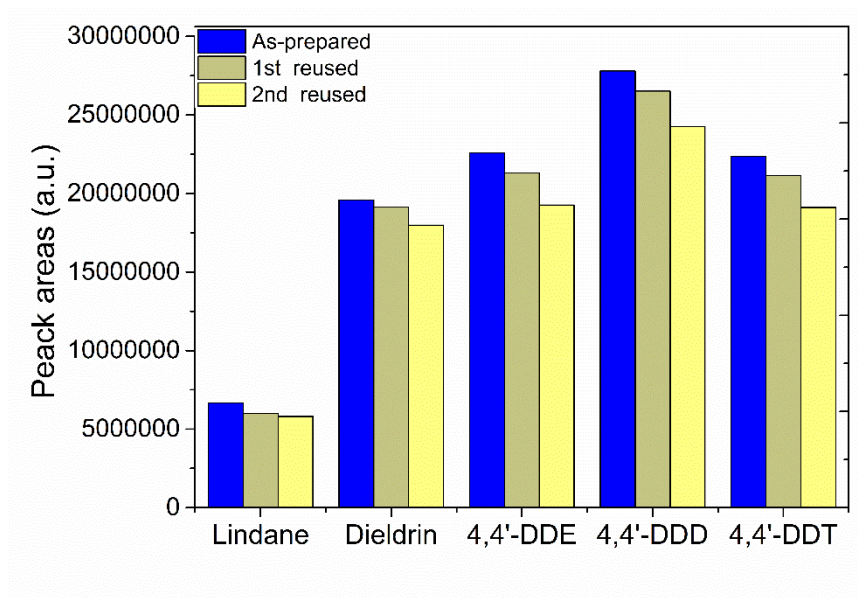

Fig. 7. Clean-up properties of Fe_3O_4@Triton toward various OCPs in the experiment comprising several consecutive regeneration cycles.

Considering the comparison our experimental data with the standard QuEChERS procedure [9] only with otherness clean-up adsorbents, it was shown that magnetic Fe_3O_4@Triton can be used as a suitable alternative adsorbent to C18/GCB/bare MNPs for the extract clean-up various complex food or other matrices. In this aspect, it was used for further full validation studies.

Validation studies. The developed procedure based on the use of Fe_3O_4@Triton as clean-up adsorbent, was validated following SANTE/11813/2017 and the ICH/2005/Q2/R1 guidelines. According to SANTE/12682/2017 to assess the accuracy and precision of the method can be based on recovery experiment results; a minimum of five replicates are required at two different spike levels. Target LOQ of the method and leastwise one higher level from 2LOQ to 10LOQ or the MRL of determine analyte. The LOQ value is defined as the lowest spike concentration level according to these performance criteria.

Calibration curves for studied analytes were obtained by the matrix-matching method at concentrations ranging from 0.5 to 100 µg·L⁻¹ and both IS (each at 15 µg·L⁻¹) in blank sample extracts.

The calibration curves were linear plotted using the dependence between the amount of OCPs and the chromatographic relative peak area. Linearity values were evaluated as correlation coefficients from calibration plots for each pesticide (Table 3). Also, two calibration curves in matrix extract were used for validation method in agricultural soil (Table S2). Accuracy was evaluated as recovery by spiking the blank samples with the added corresponding volume of the multi-components working standard solution at two concentration levels (LOQ and 10LOQ) in strawberry sample (Table 3).

Table 3. Mean metrological parameters of the developed QuEChERS-GC-MS method (using *Fe₃O₄@Triton* as adsorbent) with spiked samples for 16 pesticides in strawberry (n = 5)

Analyte	Calibration plots (R²)	LOD, μg·kg⁻¹	LOQ, μg·kg⁻¹	ME, %	Spiking level			
					LOQ		10LOQ	
					Recovery, %	RSD, %	Recovery, %	RSD, %
Aldrin	$Y=4156.1+440.1x(0.9997)$	1.85	5.45	3	95	6.8	98	4.7
α-HCH	$Y=7782.8+920.5x(0.9992)$	1.54	4.61	4	96	2.5	105	5.1
β-HCH	$Y=9128.7+929.6x(0.9916)$	1.51	4.55	9	96	6.2	88	4.1
δ-HCH	$Y=4602.7+589x(0.9994)$	1.69	5.06	3	103	3.0	105	3.9
Lindane	$Y=7108.9+358.3x(0.9980)$	1.20	3.63	1	106	8.0	95	7.8
4,4'-DDT	$Y=18397.6+1921.7x(0.9986)$	1.16	3.49	1	89	7.4	85	4.6
4,4'-DDD	$Y=9385.5+275x(0.9990)$	1.41	4.28	1	94	6.2	95	3.5
4,4'-DDD·HCl	$Y=6857.2+266.9x(0.9993)$	1.49	4.53	0	96	5.1	108	3.8
4,4'-DDE	$Y=3953.8+1056.1x(0.9999)$	1.27	3.95	33	99	7.5	103	7.7
Dieldrin	$Y=2113.2+201.4x(0.9987)$	0.11	0.34	1	86	2.5	94	6.4
Endosulfan(alpha)	$Y=3179.1+146.1x(0.9983)$	1.17	3.53	1	89	4.4	103	6.4
Endosulfan(beta)	$Y=2146.2+95.6x(0.9985)$	1.14	3.44	28	90	3.1	105	4.7
Endrin	$Y=1294.8+72.5x(0.9970)$	0.55	1.71	12	90	4.0	84	4.7
Heptachlor	$Y=1692.6+212.6x(0.9996)$	1.28	3.87	9	90	6.7	101	9.3
Heptachlor epoxide	$Y=1704.2+547.4x(0.9998)$	1.39	4.21	12	96	4.1	105	4.7

Table 3 shows that obtained calibration plots based on matrix-matching experiment for all tested OCPs were good plotted by linear approximation with high correlation coefficients (R² ≥ 0.9916). All the OCPs had recoveries and RSD within the 84-108% and of 2.5-7.8 % range, respectively. Though, it is worth noting that for several pesticides, such as 4,4'-DDD (Table S2), recoveries were lower in soil. In case of agriculture soil, RSD results varied from 1 to 12 %, where the highest values were attained for the lowest

concentrations (LOQ and 10LOQ). In accordance with the SANTE/11813/2017 guideline, mean recoveries should be in the range of 70 – 120%, with RSDs ≤ 20% [35]. Thus, the repeatability and reproducibility of developed QuEChERS-GC-MS procedure using Fe_3O_4@Triton as adsorbent were characterized with acceptable precision.

According to the ICH/2005/Q2/R1 guideline, LOD ranged from 0.11 µg·kg⁻¹ to 1.85 µg·kg⁻¹ and LOQ ranged from 0.34 µg·kg⁻¹ to 5.45 µg·kg⁻¹. All OCPs exposed LOQs lower than the lowest MRL based on EU requirements [42].

Inter- and intra-day precision. Precision as one of the main parameter for validation of the developed QuEChERS-GC-MS procedure, exposed as intra- and inter-day variability, were obtained after evaluation of RSD (table S1); for all the OCPs in the strawberry sample, these ranged from 0.8 to 3.3% for intra-day (n=5) and from 1.5 to 14.2% for inter-day (over 5 days) precision, respectively. Regarding SANTE/11813/2017 guidelines [35], the RSD ≤ 20% is recommended as criterion. This criterion was used for all components in the strawberry matrix.

Matrix effect. Matrix interferences constitute one of the major problems of residue OCPs analysis in different complex matrices, especially complicated such as soil, meat or blood, because they can suppress or enhance the chromatographic peaks [43]. For example, some soil parameters universally increase the possibility of a pesticide binding to the soil and thus persisting in the environment. Clay content and organic motives in soil including petroleum are considered to be two of the most important factors positively influencing the potential for OCP residues to bind to the soil [44, 45]. These effects can lead to low or high recovery of the each analyte, respectively. However, other factors like pH have effects on different compounds [46]. Furthermore, the possibility of persistence of residues can even be influenced by conditions at the time of application, like soil water content following a rainfall event [45]. This problem was solved by using matrix-matched working standard solution instead of pure extraction solvent. We proposed the variability of matrix effects for several OCPs were estimated not only in soil samples as the most complicate matrix among using in study and also for fruit (as typical object of analysis by QuEChERS procedure). For evaluation ME for samples was extracted using QuEChERS procedure without clean-up stage for GC-MS analysis.

The results of the calculated ME in the fruit and soil matrixes are shown in Table 3 and Table S2, respectively. The tested pesticides exhibited low matrix effect (between − 20 and 20% [35]) in the strawberry (Table 3). As seen from Table S2, most of the tested OCPs exhibited matrix influence effects in soil sample. Approximately 69% of the pesticides exhibited soft matrix effects, 19% - medium matrix effects and only12% - strong matrix effects (Table S2). Pesticides with longer time for fatty acid elution or retention time in chromatogram close to 20 min did not exhibited stronger matrix effects compared to other OCPs outside of these conditions. It was not an unexpected result. In general, matrix effect in soil is slightly stronger than that in fruits and vegetables [44]. The obtained results shown that matrix-matched calibration plots are necessary for trueness determination and quantification of soil samples by developed QuEChERS-GC-MS procedure.

Application of the developed procedure in real matrices. Considering the previously mentioned features, the procedure presented in this paper should be both a satisfactory and suitable method for the multi-analysis of OCPs in real samples. Consequently, the proposed QuEChERS-GC-MS procedure for the detection of pesticides was successfully applied in the study of real samples compared to the traditional clean-up methodology using the commercial adsorbent C18 (Table 1). To test the possibility application of the proposed procedure, fresh fruit, vegetable and also three soil samples with various genesis were studied (Table 4).

Table 4. OCPs levels ($\mu g \cdot kg^{-1}$) found by traditional and developed QuEChERS-GC-MS procedure in real samples of fruits, vegetables and soil (mean of the three extraction cycles).

Pesticide	Fe_3O_4@Triton					C18		
	Fruits and vegetable samples							
	Strawberry	Avocado	Watermelon	Radish	Kiwi	Strawberry	Avocado	Watermelon
Aldrin	<LOQ	<LOQ	8.11	<LOQ	<LOQ	<LOQ	<LOQ	7.96
α-HCH	9.58	n.d.	<LOQ	5.68	<LOQ	8.63	n.d.	<LOQ
β-HCH	<LOQ	<LOQ	n.d.	10.42	<LOQ	<LOQ	<LOQ	<LOQ
δ-HCH	<LOQ	<LOQ	<LOQ	2.11	<LOQ	<LOQ	<LOQ	<LOQ
Lindane	14.26	<LOQ	19.11	<LOQ	11.15	12.82	<LOQ	15.26
4,4'-DDT	2.63	<LOQ	<LOQ	<LOQ	<LOQ	2.00	<LOQ	<LOQ
4,4'-DDD	n.d.	5.30	11.23	14.92	<LOQ	n.d.	3.2	7.56
4,4'-DDD·HCl	<LOQ	n.d.	n.d.	<LOQ	n.d.	<LOQ	n.d.	n.d.

4,4'-DDE	<LOQ	<LOQ	12.31	2.15	<LOQ	<LOQ	<LOQ	<LOQ
Dieldrin	<LOQ	2.4	<LOQ	<LOQ	5.23	<LOQ	1.9	<LOQ
α-Endosulfan	<LOQ	n.d.	<LOQ	n.d.	<LOQ	<LOQ	n.d.	<LOQ
β-Endosulfan	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	n.d.
Endrin	n.d.	<LOQ	<LOQ	8.2	n.d.	<LOQ	<LOQ	<LOQ
Heptachlor	4.5	<LOQ	n.d.	<LOQ	<LOQ	6.87	<LOQ	<LOQ
Heptachlor epoxide	<LOQ	n.d.	<LOQ	n.d.	<LOQ	<LOQ	n.d.	<LOQ

	Soil samples							
Pesticide	**Agricultural**			**Urban**		**Agricultural**		
	Soil 1	**Soil 2**	**Soil 3**	**Soil 4**	**Soil 5**	**Soil 1**	**Soil 2**	**Soil 3**
Lindane	<LOQ	<LOQ	7.11	<LOQ	<LOQ	<LOQ	<LOQ	5.21
Heptachlor	<LOQ	n.d.	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Dieldrin	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
4,4'-DDD	12.82	<LOQ	15.26	1.61	2.96	12.82	<LOQ	15.04
4,4'-DDT	14.26	18.13	19.09	1.98	5.67	12.00	17.54	12.21
4,4'-DDE	12.63	<LOQ	<LOQ	<LOQ	6.89	n.d.	<LOQ	<LOQ

Note: n.d. denotes that this component was not detected.

Analysis of the pesticides content in fresh fruits and vegetable showed the presence of ten pesticides (Table 4). Most of tested samples contain pesticide at a quantifiable concentration level (equal to or above the LOQ value) for at least one OCPs residue. OCPs were measured in the fruits from some supermarkets, such as strawberry (α-HCH, lindane, 4,4'-DDT, heptachlor), avocado (4,4'-DDD, dieldrin), watermelon (aldrin, lindane, 4,4'-DDE, 4,4'-DDD) and kiwi flesh (lindane and dieldrin) samples, as well as in radish (α, β-HCH isomers, 4,4'-DDD) samples. The most frequently-founded pesticide (lindane, 4,4'-DDD, 4,4'-DDE and 4,4'-DDT) residues were detected in many of the samples analyzed. The highest OCPs concentration were for lindane- and 4,4'-DDD-found, respectively, in radish - at 14.92 µg kg^{-1} and in strawberry - at 14.26 µg kg^{-1}. OCPs were detected in concentrations lower than the MRL allowable by the European Union [6]. Except for lindane for strawberries, which is persistent pesticide in the environment, most of the other is commonly used in conventional practices of strawberry cultivation.

The clean-up Fe$_3$O$_4$@Triton adsorbent compared to commercial C18 for fruits and vegetables, the ME was found to decrease significantly and the LOD was reduced for several OCPs (Table 4). Once again, it

is proved that developed QuEChERS extraction with *Fe$_3$O$_4$@Triton* improves the sensitivity and simplicity of the clean-up stage of this method.

Pesticides like OCPs used as protection for plant products in the 1970s were detected in soil samples (Table 4). Table 4 is also a summary of OCPs and their frequency in various soil samples. Overall four OCPs were detected in agricultural soils, fewer than the 3 compounds detected in the city urban soil samples. This result shown that the co-eluting of fatty acid in soil extracts still had not some negative effects consequences on trueness determination of main OCPs, despite the fact that presence of silica and petroleum in the city urban soil samples. Nonetheless, higher concentrations of 4,4'-DDT, 4,4'-DDD and lindane were found in the sample from conventional farming. It's no wonder, 4,4'-DDT and 4,4'-DDD found at a very high frequency, especially in agriculture soil [45]. 4,4'-DDT often exceeds target levels and is present at concentrations great enough to transfer to some plants. However, it was absent from the vegetable despite being found just as frequently in the topsoil as in the frequently in the urban soil (Table 4). Although OCPs have been banned, in Ukraine (USSR) in the 1980s, these compounds are known to be persistence and this present study proved that they can still be found in Ukrainian soils or do indicate that farmers have been applying pesticides after they have been banned. Other compounds that have not been banned, but have been used onsite for at least 20 years were found. These banned compounds pose potential human and environmental health risks.

In the present study, OCPs determination in radish from lab-made pesticide-containing (soil 1.1) and conventional (soil 1.2) farming also revealed the presence of OCPs in samples from both types of farming (table S3). The soil samples collected from conventional fields (soil 1, table S3) and conventional lab-made farming (soil 1.2, table S3) did not exhibit differences related to the type of farming and OCPs presence. Nonetheless, a significantly higher concentration value was found in the soil and plant (radish 1.1, table S3) from lab-made pesticide-containing farming. Previously mode of application was not reported as an important factor in the fate of pesticide residues. When compared the results from the agriculture soil to those of lab-prepared soil and partner these findings with vegetable (radish) studies we see that this is indeed an important factor.

Comparison with other methods. To further evaluate the efficiency of the method for the determination of OCPs presented here, it was compared with recently presented in literature approaches and procedures for food products and soil samples (Table 5).

Table 5. The reported results for the determination of OCPs in various samples by QuEChERS procedure using dSPE with clean-up adsorbents

Sample matrix	Analyte	Extraction procedure(briefly)/ Shaking time/Centrifuge time	Technique	LOD, µg·kg^{-1}	LOQ, µg·kg^{-1}	Ref
Lettuce, strawberries	22 pesticides (2-4 OCPs)	10 g homogenized samples in 40 mL tube + 10 mL MeCN + 1 mL MeCN + in 1.5 mL vial PSA (25 mg) and anhydrous MgSO$_4$(150 mg)/30 sec/1 min(6000 rpm)	GC-MS	n.a.	n.a.	[9]
Strawberries	7 pesticides	10 g homogenized samples in 50 mL tube + spiking standard +10 mL MeCN + 1 mL, 0.5 mL aliquot of upper MeCN tube for d-SPE, micro d-SPE, recently + Fe$_3$O$_4$/Fe$_3$O$_4$@TEOS/Fe$_3$O$_4$@TEOS@ MPS/Fe$_3$O$_4$@TEOS@MPS@PMAA) / 30 s /4 min(4500 rpm)	GC/MS/MS, GC/MS, GC/FPD	3.64 – 10.38	3.64 – 10.38	[30]
Egg	60 pesticides	5 g of the sample in 50-mL centrifuge tube + 15-mL 1% HAc in MeCN + 6 g of MgSO$_4$ and 1.5 g of NaAc with PSA (400 mg) vortex 1min/10 min at 4 °C	LC-MS/MS GC-MS/MS	1.0-5.0	3.0-17.0	[47]
Lettuce, cucumbers and tomatoes	12 pesticides	5 g sample shaken (2 min) + centrifuged + C18 (50 mg)/1 min / 5 min (4500 rpm)+ extract again (9 mL) with PSA (400 mg) + GCB (200 mg)/ 2 min /5 min(4500 rpm)	GC-MS	n.a.	1-3	[48]

Pears and oranges	16 post-harvest fungicides	5 mL sample into 15-mL tube + MWCNTs/PSA/yttria-stabilized ZrO_2 as adsorbents/0.5 min/5 min	LC-ESI-MS/MS	n.a.	≤ 10	[49]
Pear, orange, apple, pepper, lettuce and tomato, cucumber	16 pesticides	2 mL sample into tube (10 mL) + 2 mL of MaCN, 1 g of $MgSO_4$, and 0.5 g of NaCl, 1 min, 5000 rpm for 2min. (40 mg) extract again (1.5 mL) with 1 g of $MgSO_4$ +PSA/C18/PSA+C18/n-octadecylamine 55 °C for 1 min and then −10 ° C for 5 min centrifuged	GC-MS	04-3.6	1.2-11.8	[23]
Kiwi fruit and juice	33 pesticides (7 OCPs)	1 mL into 2-mL centrifuge tube + m-PFC /n.a./n.a.	GC-MS	1-4	3-10	[50]
Apples, cucumbers, oranges and Tomatoes	101 pesticides residues	1 mL into centrifuge tube (2 mL) + MNPs (40 mg), PSA (50 mg), GCB (10 mg) and anhydrous $MgSO_4$ (100 mg)/1 min/n.a.	GC-MS/MS	0.1-7.2	< 10.5	[28]
Blood	7 pesticides (4 OCPs)	2 mL blood into vial (10 mL) + (40 mg) PSA/(25 mg) C18/ (30 mg) Fe_3O_4/1 min /(5000 rpm, 5 min)	GC-MS	0.011-0.163	0.036-0.538	[17]
Strawberries, grapes, celery and cabbage	16 amide fungicides	1 mL into 50-mL volumetric tube + MWCNTs (10 mg)/1 min/3 min	UHPLC-MS/MS	≤ 3	≤ 10	[25]
Garland chrysanthemum, lettuce leaves and leeks	70 pesticides	1 mL into 2-mL centrifuge tube + MWCNTs (10 mg) and $MgSO_4$ (150 mg)/1 min/3 min	LC-MS/MS	0.1–2.4	0.3–7.9	[21]
Kiwi fruit	52 pesticides, 8	Fe_3O_4-PSA and the commercial adsorbent C18	UPLC-MS/MS	-	-	[26]

Matrix	Analytes	Procedure	Detection	LOD	LOQ	Ref
	metabolites					
Rice paddies	203 pesticides	5 g sample into a 50 mL centrifuge tube + 50 mg PSA, 300 mg $MgSO_4$ and 20 mg GCB/1 min/ 5 min at 4000 rpm	GC-MS		2-50	[22]
Soil	Chlorinated compounds (HCB)	2.5 mL EtAc shaken 1 min; salt: 1 g $MgSO_4$ 1 min/5 min(5000 rpm)	GC–ECD	10	-	[40]
Soil	34 aromatic organochlorine pesticides	15 mL CH_2Cl_2 + 4 g $MgSO_4$, 1 g NaCl, 1 g NaCit·2 H_2O, 0.5 g (no clean-up)/1 min/2 min (5000 rpm)	GC-MS	2.1–147.5	6.9–491.8	[51]
Strawberries, avocadoes, watermelon, radish, kiwi, agricultural and urban soils	16 pesticides	1 mL into 2-mL volumetric tube + *Fe₃O₄@Triton* (50 mg)/1 min/non-centrifuged	GC-MS	0.11-1.85	0.34-5.45	

Note: n.a. – not available, MWCNTs – multi-walled carbon nanotubes, m-PFC – multiplug filtration clean-up.

The advantages of our method compared with dSPE consist in the fact that centrifugation is not required for fruit and vegetable matrices and phase separation is simplified. Our experimental data indicates that the LOD obtained using the present method were comparable with those obtained by C18 and PSA with GC-MS/MS and better than those obtained when using a similar approach for sample preparation with GC-MS. Thus, the recovery value was higher and better suited to the OCPs analysis requirements. The technique exhibits excellent economically friendly enhanced purification efficiency, time analysis and sensitivity. The using *Fe₃O₄@Triton* in advanced QuEChERS procedure combined with lab-budget GC-MS yields satisfactory results in multiple OCPs analysis in soils, veggies and fruits

Conclusions

In this study, a very simple, fast and effective procedure based on a modified QuEChERS extraction was elaborated for the determination of multi-residue OCPs in fruits, veggies and various soil samples by GC-MS determination. We tested hydrophobic MNPs as an effective clean-up adsorbent in the extract purification of various matrices for the QuEChERS procedure as a potential alternative clean-up agent to commercial C18, GCB and bare MNPs. However, bare MNPs have not exhibited useful power as clean-up adsorbents for purification these matrices (especially avocado). The developed procedure in this paper exhibits the enhanced purification and simultaneous recovery various OCPs. Magnetic Fe_3O_4@Triton adsorbents provided the lowest level of co-extracted interference compounds (including organic pigments) in the food samples and shown better clean-up performance than the commercial adsorbent (C18 and GCB). The validation of a extraction QuEChERS procedure for the analysis of 16 pesticides in fruits and veggies from supermarkets by GC-MS was successfully carried out. Under the determined optimum conditions, parameters such as precision (intra-/inter-day), sensitivity and accuracy (as recovery), matrix effects were evaluated for the target analytes by GC-MS detection. The results of analytical performance showed good linearity ($R^2 \geq 0.9916$) and the average recoveries were considered satisfactory, obtaining values of between 84.0 and 108.0% (71.0-103.0 % for soil), RSD of 2.5-7.8% (1.0-12.0 % for soil). Quantification and detection limits ranged from 0.11 to 1.85 $\mu g \cdot kg^{-1}$ and from 0.34 to 5.45 $\mu g \cdot kg^{-1}$, respectively. OCPs were detected in strawberry (α-HCH, lindane, 4,4'-DDT, heptachlor), avocado (4,4'-DDD, dieldrin), watermelon (aldrin, lindane, 4,4'-DDE, 4,4'-DDD), radish (α, β-HCH isomers, 4,4'-DDD) and kiwi flesh (lindane and dieldrin) samples. The applicability of the developed procedure to very different soil types was demonstrated by analysis of OCPs for various soil samples. Matrix effects were accurately investigated and with a few exceptions, were not much relevant, permitting quantification of the compounds using solvent standard solutions. In spite of the soils used in this study not being applied for agricultural practices for many years, four insecticides (lindane, 4,4'-DDE, 4,4'-DDD and 4,4'-DDT) were detected at low concentrations (mostly below 20 $\mu g \ kg^{-1}$). Therefore, the analytical technique proposed in this work can be easily implemented in routine practice as universal for monitoring pesticide residues in different types of samples. Compared with the QuEChERS method based on GCB and C18, the present method can provide savings in terms of pretreatment time, becomes simpler, as well as a high throughput compared with aforementioned techniques. This is the new

approach on the usability of magnetic core-shell MNPs to remove matrix impurities based on switchable high hydrophobic functional group in the QuEChERS procedure and indicating potential for development of clean-up materials for determination various pesticides in complex matrixes.

Supplementary data

Supplementary data associated with this article can be found in the online Appendix.

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