

NEW APPROACH IN PESTICIDE RESIDUE ANALYSIS METHODS INFLUENCED BY FOOD MATRIX

R.M. MADJAR¹ and G. Vasile SCĂEȚEANU^{1*}

¹Department of Soil Sciences, University of Agronomic Sciences and Veterinary Medicine Bucharest, Romania
*Corresponding author: ginavasile2000@yahoo.com

Accepted

Pesticides have largely benefited the human life through enhancement of agricultural products but in turn have influenced human health. Nowadays, assessment of pesticide residues in different food products present a great importance and a priority in order to ensure food quality that therefore to protect consumers against different health issues. The analytical methods for the determination of pesticides depend on of the matrix complexity origin and of the chemical classes. The challenge in pesticide residues quantification is represented by the number of analytes in complex matrices and therefore analytical methods suppose accuracy, precision, sensitivity, specificity and selectivity, robustness and ruggedness, acceptable time of analysis. In most cases according to matrix complexity, prior quantification of pesticide residues must fulfill the following steps: preliminary characterization of pesticide residues, extraction from sample matrix using proper solvents, separation procedure that is based on removal of the interfering species, concentration of the pesticide residues.

Keywords: pesticide; food matrix; extraction.

Pesticides use has obviously increased the agricultural production but beside beneficial effects, persistent residues present hazardous effects on environment. As lately, it has been observed that exposure to pesticides is increasingly linked with serious diseases it is mandatory to monitor the pesticide residues in food. Accordingly, determination of pesticide residue in food matrix it has been proven to be challenging since requires separation methods able to assure accuracy, precision, sensitivity, specificity and selectivity, robustness and ruggedness, acceptable time of analysis. In most cases according to matrix complexity, prior quantification of pesticide residues must fulfill the following steps: preliminary characterization of pesticide residues, extraction from sample matrix using proper solvents, separation procedure that is based on removal of the interfering species, concentration of the pesticide residues.

The methods used for pesticide residues analysis must fulfill some requirements: **(i)** to be capable of analyzing low and very low levels of residues; **(ii)** it is necessary to have analytical standards that contain analyte on the level comparable to

concentration in real matrix; **(iii)** sample preparation must not contribute to environmental pollution¹.

This chapter is an overview of the methods approached to quantify of pesticide residues that originates from different food matrix (milk and dairy products, fruits, vegetables, fish and meat, cereals, juices and wine) and present a comparison between traditional and innovative analytical methods used to fulfill this objective.

1. EXTRACTION PROCEDURES

The extraction procedure is the most time consuming from total analysis time and it is the primary source of errors. Even if there are available many extraction procedures, the complexity of the matrix still produces inconvenient and almost every time extraction is followed by cleanup procedures. Depending of the origin and type of analysed food product, there are different extraction methods presented briefly below.

Direct solid-liquid extraction (SLE) includes accelerated solvent extraction (ASE) and microwave-assisted extraction (MAE). ASE, also known as pressurized liquid extraction (PLE) has been proven its efficiency for determination of

pesticides in various types of matrices. It uses small quantities of water and organic solvents under temperatures up to 200°C and pressures up to 20 mPa for short periods of time. MAE supposes usage of microwave energy and assures high extraction efficiency at low temperature, the main disadvantage being low selectivity [2]. For the extraction of polar pesticides are used mainly acetonitrile and ethyl acetate, but other solvents have been employed for SLE extraction: acetone, n-hexane, dichloromethane [3].

Solid phase extraction (SPE) is based on passing of the extract through the column filled with appropriate sorbent or passing the proper solvent through column that contain sample. In pesticide analysis are used as sorbents reverse-phase octadecyl, normal-phase aminopropyl and primary-secondary amine (PSA), anion-exchanger three methyl ammonium (SAX) and adsorbents (graphitized carbon black, GCB). Florisil (MgSiO_3), aluminum oxide and silica (SiO_2) are used together with already mentioned sorbents [4].

Liquid-liquid extraction (LLE) is the most common extraction method even if is laborious and requires both large volumes of organic solvents and sample. The most used solvents for LLE are acetonitrile (effective for extraction of polar and non-polar pesticide residues), ethylacetate, chloroform, diethylether and occasionally hexane, cyclohexane and light petroleum [4]. As disadvantages, LLE requires large amounts of hazardous organic solvents and in the case of target compounds with different polarities is difficult to obtain a proper sample using single LLE, being recommended to perform an additional SPE [5].

Dispersive liquid-liquid microextraction (DLLME) was introduced in 2006 and is a sample preparation technique that offers high enrichment from low volumes of water samples. The extraction takes place in dispersion of the extracting solvent in water and to achieve dispersion a dispersing solvent is used. The extracting solvent must be able to extract analytes and to be soluble in dispersing solvent and the dispersing solvent (acetone, acetonitrile, and methanol) has to be fully soluble with the water phase. Also, the density of the extracting solvent has to different from the density of water to assure phase separation [6].

Dispersive liquid-liquid microextraction combined with solidification of floating organic droplet (DLLME-SFO) supposes the use of extractants with lower density than water and lower toxicity [7]. DLLME-SFO was reported as suitable

for non-polarity organic substances in aqueous samples and was subjected to simultaneous analysis of polychlorinated biphenyls (PB), organochlorine (OC) and pyrethroid pesticides [8].

Supercritical fluid extraction (SFE) is a technique that uses supercritical fluids (mainly CO_2) to diffuse into the solid matrix and to extract non-polar species and moderately ones. The efficiency of the extraction may be increased by using certain modifiers (acetone, methanol) [2,4]. The advantage of SFE is high sensitivity for a limited amount of sample, low cost, and does not generate hazardous wastes.

Solid phase microextraction (SPME) is very used for quantification of pesticide residues from different samples and the main advantage is that purification and concentration of the sample occurs in the same time. SPME is based on the partition of the analyte between sample matrix and stationary phase coated on fused silica fiber. To extract analytes are used two types of fiber techniques: headspace (HS-SPME) when fiber is exposed to the vapor phase above a gas and direct immersion (DI-SPME) when fiber is immersed in the samples. A great applicability has received SPME coupled with HPLC, GC, GC-MS, LC-MS [1,4].

Matrix solid-phase dispersion (MSPD) is based on the complete fractionation of the solid, semisolid and/or highly viscous samples [9] with the dispersion of the components into a solid sorbent. MSPD combine into a single step the extraction and cleanup procedure. As solid support is used mainly C_8 and C_{18} -bonded silica [10]. MSPD has proven its efficiency for the extraction of various pesticides from different matrices [9], lately being applicable to pesticide residue analysis of fatty food matrixes [11]. The difference between MSPD and SPE is that in the latter, the samples is necessary to be liquid before application to the column, meanwhile in the case of MSPD may be used solid/viscous liquid samples [3].

QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) method was described for the first time by Anastassiades et al [12] for the extraction of multi-class pesticide residues from fruit and vegetables. It is based on single-phase extraction of 10 g sample with 10 mL acetonitrile, followed by liquid-liquid partitioning formed by addition of 4 g anhydrous MgSO_4 plus 1 g NaCl. Then it follows a cleanup step with d-SPE with primary secondary amine (PSA) with the aim of eliminating the possible interfering compounds such as organic acids, certain polar pigments, and sugars.

Having in view that the method provides high recoveries of pesticides with a various range of polarities and also produce significant elimination of matrix components, were introduced many modified QuEChERS methods [13-20]. The importance of this procedure it has been demonstrated since out of a total of 55 published multi-residue methods between 2000 and 2014, 21 (38%) are based on QuEChERS (using acetonitrile and ethylacetate as extractants) [21].

2. INSTRUMENTAL TECHNIQUES OF ANALYSIS

In separation and quantification of the pesticides, traditional chromatographic methods such as gas chromatography (GC) and high performance liquid chromatography (HPLC) coupled with mass spectrometry (MS) are effective for measuring levels of some pesticide and its residues in food products [22]. OC pesticides are determined using GC with electron capture detector (ECD), OP and nitrogenated pesticides by GC with nitrogen and phosphorus detector (NPD) and sulphur and phosphorus pesticides are analyzed by GC with flame photometric detector (FPD).

The GC-MS detectors for pesticide analysis are single quadrupole (Q), triple quadrupole (QqQ), ion trap (IT), hybrid quadrupole ion trap (QTrap), time of flight (TOF), Orbitrap [21]. Also, multiresidue methods including GC-MS have been reported for pesticide analyses of pesticides from different classes [23] due to high sensitivity, selectivity and quantification potential to wide range polarities of pesticides.

Liquid chromatography (LC) has been employed for polar and/or non-volatile and/or thermally labile pesticides in the case of which GC was not suitable (carbamates, triazines and their degradation products). Also, LC has been coupled with different MS detectors: Q, IT, tandem-MS, TOF-MS for determination of pesticide residues from various food matrixes [23].

Moreover, some optical and electrochemical methods of determination have been developed and among them, flow-based methods present advantageous characteristics (miniaturization, simplicity, low-cost and in situ measurements ability). For pesticide detection, the most popular methodologies are flow injection analysis (FIA), sequential injection analysis (SIA) and multi-commuted flow techniques such as multi-commuted

flow analysis (MCFA) and multi-syringe flow analysis (MSFIA) [24].

In many cases, traditional methods have limitations (complexity, time-consuming procedure, high costs, and trained operators) and therefore, new methods are recommended for pesticide residues detection. Some examples from this category are based on enzymatic sensors or immunoassays as ELISA a very selective methods for a specific target pesticide, that present potential to simplify or even to eliminate sample preparation, to reduce costs and analysis time [25].

3. DAIRY PRODUCTS MATRIX

Organochlorine pesticides and their metabolites are lipophilic, resistant to microbial degradation and therefore accumulate in fatty tissues and fatty products (milk, cheese, yogurt, etc). The quantification of organochlorines in food products is achieved mainly using chromatographic methods.

A study developed by Darko and coworkers [26] presented the assessment of six OC pesticides (lindane, aldrin, dieldrin, endosulfan, dichlorodiphenyltrichloroethane (DDT) and dichlorodiphenyldichloroethylene (DDE) from dairy products (cheese yogurt, milk) collected from six communities from Kumasi metropolis, Ghana. Portions of 10 grams each of milk and yogurt were grounded with anhydrous sodium sulphate and transferred into a column that was eluted with 80 mL dichloromethane. In the case of cheese samples, the pesticide extraction was laborious and the protocol indicates to use 1 g cheese sample, 20 mL methanol, 2 mL H₂SO₄ 10% and 1 g of sodium oxalate. Also, at the resulted mixture must be added 20 mL ethyl ether/petroleum. After separation of the extract, the solvent was evaporated and the fat extracted with 10 mL methylene chloride. The extracts were dissolved in 10 mL hexane and passed through octadecyl C₁₈ columns. The sample was eluted five times with 0.5 mL aliquots of hexane and finally, was performed the GC analysis. The residues found in all analyzed samples are lower than maximum residue level, but having in view their tendency to accumulate in fatty tissues it is mandatory to monitor their levels.

Other study conducted in Jordan [27]. The food samples constituting in milk, butterm cheese, labaneh, yogurt were subjected to analysis in order to evaluate the presence of some OCs (aldrin, dieldrin, endrin, heptachlor, hexachlorobenzene, DDT)

banned in Jordan. Extraction procedure supposes use of petroleum ether (40 mL for 3 grams) for fats dissolution followed by partitioning in acetonitrile and petroleum ether and finally concentration to a volume less than 5 mL. The cleanup procedure was performed using glass chromatographic column filled with activated Florisil. The elution was done using a mixture of dichloromethane (20%) and petroleum ether (80%). The analysis of the extract was performed using GC-ECD. The reproducibility of the method is satisfactory since the average recoveries of OC were 89.4-102.3% for milk and 79.4-103.6% for dairy products. From total number of samples (233) only 4.3% (10 samples) exceeded the maximum residue limit and the order of contamination in the analyzed dairy products was labaneh>cheese>yoghurt>butter>milk.

Assessment of OC pesticides and its metabolites from dairy and buffalo milk has been performed in India [28]. For extraction, in two steps, was used a mixture formed from acetone, acetonitrile and hexane and then the solvent layer was washed with acetonitrile, 2% Na₂SO₄ and hexane. For cleanup was used a column with Florisil and anhydrous Na₂SO₄ and for elution was used hexane and 1% methanol in hexane. The resulted extracts were evaporated to dryness and dissolved in hexane and subjected to GC-ECD. The percentage of the recoveries was 95-98% meanwhile the results indicated that all milk samples were contaminated with DDT and its metabolites (DDE and DDD), isomers of HCH, heptachlor and its epoxide, aldrin. From all these, levels of aldrin, HCH, heptachlor exceeded the tolerance limits imposed by WHO (0.15, 0.1 and 0.15 mg/kg, respectively), whereas levels of DDT and its metabolites were below limit (1.25 mg/kg).

A study developed by Rengasamy and coworkers [29] presented the comparison between ELISA and GC results of DDT analysis investigated in milk and dairy products. In the case of ELISA method the sample was extracted with methanol and used directly for loading in the ELISA reader and for GC the milk and milk product samples have been extracted in n-hexane. The percentage recovery of DDT in the case of cheese and kalakhand samples was almost the same by GC and ELISA techniques. The recovery was 70% and above and the levels of DDT in milk and milk products were found to be well below detectable limits in both methods.

The presence of OC (alachlor, dieldrin, hexachlorobenzene, lindane and methoxychlor) and

OP (chlorpyrifos, malathion, parathion-methyl) was evidenced in buffalo milk samples from Egypt [30]. For the extraction and cleanup was adopted MSPD, according to which 5.0 mL of milk was blended with 2.0 g C₁₈, 2 g of anhydrous Na₂SO₄ and 1.5 mL acetonitrile. After aqueous phase was removed, the pesticide residues were eluted from C₁₈/milk matrix with acetonitrile and then were eluted through a Florisil solid-phase extraction column. After acetonitrile evaporation, the residue was dissolved in petroleum ether, concentrated and analyzed using GC-MS. The quality of the method was assured by assessing the average recoveries of fortified pesticides that ranged from 76.0-97.8% for OC and 75.0-104.5% for OP. The results indicated that in 44% of the buffalo milk samples, lindane and malathion maximum residue levels (MRLs) exceeded tolerance limits set by European Commission in 2008 [31]. The residue levels of chlorpyrifos, methoxychlor and hexachlorobenzene exceeded MRLs [31] in 33,6 and 88% of the samples, respectively.

Pesticide from OP (coumaphos, fenthion, malathion, dimethoate) and carbamate (carbaryl, aldicarb, carbofuran) classes were identified in milk samples collected from cattle farms [32]. Extraction was done using 25 mL acetone:acetonitrile (1:4), followed by partition with 50 mL dichloromethane. The extracts were evaporated and treated with 1 mL acetonitrile. The cleanup procedure was carried out by SPE, eluting with 2 mL acetonitrile and 1 mL 2-propanol. The sample was concentrated, redissolved in acetone and analyzed using GC. From 30 milk samples that were analyzed, 6 (20%) were contaminated with OP pesticide, 5 (16.7%) with carbamate pesticides and in the case of one sample were identified both organophosphate and carbamate pesticides.

Even if there are many analytical methods that are suitable for OP residues extraction and quantification in milk and dairy products, a modified QuEChERS method combined with DLLME-SFO (dispersive liquid-liquid microextraction combined with solidification of floating organic droplets technique) was optimized by Miao and coworkers [13]. The OP pesticides (chlorpyrifos, chlorpyrifos-methyl, isocarbophos, malathion, phorate) were extracted from milk (15 mL) by QuEChERS method by centrifugation using 1g NaCl, 2 mL acetonitrile. Acetonitrile extract was concentrated using DLLME-SFO. The extraction efficiency was adjusted by investigating and optimization of the extraction solvent, dispenser

solvent, volume of extraction, salt effect, sample pH and extraction time. Under optimized conditions (15 μL 1-dodecanol as extractant, 300 μL methanol as dispersant, 1 minute extraction time) was obtained good linearity from 0.01 to 1.0 mg/L with correlation coefficients higher than 0.9968. Also, limit of detection of the subjected OP pesticides ranged between 0.1-0.3 $\mu\text{g/L}$, meanwhile limits of quantification were between 0.3-1.0 $\mu\text{g/L}$.

Jeong et al [14] reported an optimized method for sample preparation and determination of 14 pesticide (vinclozolin, penconazole, dieldrin, myclobutanil, endosulfan sulphate, bifenthrin, fenprothrin, cyhalothrin, permethrin, fenbuconazole, 2,4'-DDE, 4,4'-DDE, 2,4'-DDT, 4,4'-DDT) residues from milk. The extraction procedure was performed by QuEChERS method using acetonitrile in acetic acid as extraction solvent, anhydrous MgSO_4 to reduce the water phase and to favour partitioning of pesticides into organic layer, sodium acetate to dissolve the fat globules. For cleanup were used PSA to remove fatty acids and matrix co-extractants and C_{18} . The upper layer was analyzed by GC-ECD and GC-MS. The recovery of each subjected pesticide was investigated varying 3 variables: the amounts of sodium acetate, PSA and C_{18} that were investigated in the ranges 0.5-2.5 g, 200-600 mg and 200-600 mg, respectively. After optimization, the maximum predicted recovery was 99.73% for myclobutanil when were used 1.70 g sodium acetate, 600 mg PSA and 489.96 mg C_{18} . For 2,4'-DDE, 4,4'-DDE, 2,4'-DDT and 4,4'-DDT it was possible to detect and quantify the molecules by optimized method even though the recoveries were below 80%. The recoveries of these lipophilic pesticides were below 80% due the removal by C_{18} along with the other fatty compounds.

A modified version of QuEChERS method combined with HPLC-DAD for determination of triazines and phenylurea from yogurt and milk was reported by Li et al [15]. The efficiency of extraction was assured by the use of ethylacetate and hexane rather than acetonitrile, the amount of PSA was reduced (from 25 to 10 mg/mL) and the frozen centrifugation was applied to remove fatty matrix. It has been reported [33] that the simplest method for lipids removal is by freezing centrifugation because fatty substances have lower melting points than solvent and frozen lipids can be removed by centrifugation or filtering, the OC remaining dissolved in the solvent. The optimization of the method was done by modifying

experimental parameters (extraction solvent, extraction method, adsorbent, pH of sample solution, extraction time, amount of PSA and NaCl). The precision and absolute recoveries of the herbicides ranged from 0.07 to 5.86% and from 78.9 to 99.9%, respectively [15].

OC pesticides (aldrin, dieldrin, α -endosulfan, β -endosulfan, p,p'-DDE, p,p'-DDT, o,p'-DDT and lindane) from fresh and pasteurized milk collected from Kampala markets were determined by Kampire et al [34] by GC-ECD and confirmed by GC-MS. The extraction was done using petroleum ether as extractant meanwhile cleanup procedure was performed using Florisil and for elution hexane. The recoveries were determined by spiking each type of milk with solutions of known concentrations of each of the subjected pesticides and in most cases, the recoveries ranged between 70 and 120%. Concerning pesticide residue levels in milk samples, the results indicated that in 85% and in 76.5% of the samples, the detected residues were lindane at mean levels of 0.026 and 0.022 mg/kg fat basis in fresh and pasteurized milk, respectively.

4. VEGETABLE AND FRUIT MATRIX

Having in view that fruits and vegetables are consumed worldwide, it is important to monitor the presence of pesticide residues to prevent consumer health disturbances.

A study developed in Bogota, Columbia aimed the assessment of the pesticide in tomato [16]. The extraction procedure was based on a modified version of QuEChERS (10 g of homogenized sample was treated with 15 mL acetonitrile and acetic acid 1% (v/v), 6 g of anhydrous MgSO_4 , 1 g sodium acetate and centrifugated). For cleanup were used 25 mg of PSA (primary/secondary amine) and 150 mg of anhydrous MgSO_4 for each mL of extract. After centrifugation, the supernatant was analyzed by LC-MS. The pesticide residues detected using this method were acephate, azoxystrobin, benalaxyl, carbedazim, carbofuran, chlorfenapyr, cymoxanil, difenoconazole, dimethomorph, imazalil, imidacloprid, indoxacarb, metalaxyl, methomyl, methoxyfenozide, pyrimethanil, spinozad, tebuconazole, thiocyclam. Only one sample containing carbendazim exceeded the maximum residue limit. The results indicated that in 70.5% of samples was identified at least one pesticide, the most detected being pyrimethanil, carbendazim, dimethomorph and acephate.

Quantification of OP pesticide residues (acephate, chlorpyrifos, malathion, methamidophos, parathion-methyl) from tomatoes grown in Brazil was achieved through GC-NPD [35]. Extraction of the pesticides from tomatoes (25 g) was done using as solvent ethyl acetate (50 mL) in the presence of NaCl 10% (2.5 mL). GC-NPD technique presents the advantage that is selective and does not require purification of the extract. The recoveries of the pesticides calculated from the curve plotted with the matrix extract ranged between 88-118% and the quantification limits were between 0.0132-0.135 mg/kg. The analysis of tomatoes indicated the presence of acephate and methamidophos residues, in the case of one sample level of methamidophos being higher (2.4 mg/kg) than limit imposed by Brazilian legislation (0.3 mg/kg).

OC pesticides (lindane, heptachlor, endrin, dieldrin, o,p'-DDE, p,p'-DDE, o,p'-DDD, o,p'-DDT, p,p'-DDT) in vegetables were determined in 240 samples of vegetables collected from Greater Accra region of Ghana during 2010-2011 [36]. The extraction of the pesticides was done using 20 g of sample that was treated with 40 mL ethylacetate, 5 g NaHCO₃, 20 g anhydrous Na₂SO₄. After centrifugation, cleanup procedure through SPE using Florisil was done. Florisil column was conditioned with 10 mL ethylacetate and the elution of the pesticide was done with 10 mL ethylacetate. The determination of pesticide was fulfilled by GC-ECD technique. The results indicated that one or more residues from targeted pesticides were identified in 39.5% of cabbage samples (total 60), in 26.4% of carrot samples (total 60), 29.6% of tomato samples (total 60) and 16.7% in lettuce samples (total 60). From all analyzed samples, 31.48% were above MRLs and the most frequently found pesticides were metabolites of DDT (o,p'-DDE, p,p'-DDE, o,p'-DDD), lindane and o,p'-DDT. Also, the study revealed that vegetables collected from supermarket were higher than those collected from roadside grocery stores and open markets.

Other study [37] developed in Ghana aimed the assessment of OC pesticide residues in fruits (apples and pawpaw) and vegetables (tomato). The extraction of the pesticide and quantification was performed identically as in study reported by Bempah and coworkers [36]. The recoveries in spiked samples, calculated for three replicate samples were between 87% and 120%. Heptachlor epoxide, aldrin, γ -chlordane and o,p'-DDD were not detected in pawpaw samples, in tomato samples pesticide residues range from <0.01 to 0.02 $\mu\text{g/g}$ for

γ -HCH, 0.01-0.02 $\mu\text{g/g}$ for δ -HCH, <0.01-0.01 $\mu\text{g/g}$ for p,p'-DDT, 0.02-0.04 $\mu\text{g/g}$ for heptachlor epoxide, 0.01-0.02 $\mu\text{g/g}$ for heptachlor, <0.01-0.02 $\mu\text{g/g}$ for endrin ketone and <0.01-0.01 $\mu\text{g/g}$ for endrin aldehyde. In apple samples, pesticide levels varied from <0.01 to 0.02 $\mu\text{g/g}$ for γ -HCH, 0.01-0.02 $\mu\text{g/g}$ for δ -HCH, <0.01-0.01 $\mu\text{g/g}$ for p,p'-DDE, 0.01-0.05 $\mu\text{g/g}$ for heptachlor epoxide, 0.03-0.11 $\mu\text{g/g}$ for endrin aldehyde, 0.03-0.09 $\mu\text{g/g}$ for p,p'-DDT and <0.01-0.01 $\mu\text{g/g}$ for endrin ketone.

Dithiocarbamate are some of the most frequently detected pesticides in European Union and the methods for their quantification is based on acidic hydrolysis to CS₂ and its determination by GC, but the main problem is that it is hard to distinguish between subclasses of dithiocarbamates [17].

Lopez-Fernandez et al [17] proposed a method for the determination of the residues of mancozeb, maneb and propineb in fruits (apple, grape, strawberry) and vegetables (tomato, lettuce, pepper) by HPLC-DAD. Extraction of the pesticides was performed using a modified QuEChERS method. To remove matrix interferences, purification efficiency of PSA d-SPE was tested on organic extracts from spiked samples. Also, Florisil Plus (Waters), Strata silica-1(Phenomenex) and ENVI-CarbII/PSA (Supelco) cartridges were tested and after these investigations, it was found that PSA dispersive and Florisil Plus cartridge gave recoveries higher than 130%. High recoveries were corrected with the use of Strata silica-1 cartridges.

Application of the optimized method [17] indicated the presence of dithiocarbamate residues in all analyzed fruits (excepting strawberries) and vegetables. Peppers presented the most numerous positive samples (96.9%), followed by tomatoes (87.5%), lettuces (71.9%), grapes (33.3%) and apples (15.6%). The MRLs were exceeded in 6% from analyzed samples.

Investigation of OC residues in 127 samples of fruits and vegetables in Qatar evidenced that 90% of the imported samples presented residues above MRLs, the most found compound being heptachlor [38]. Pesticide extraction was performed using 10 g of washed sample and 6 g of diatomaceous earth. Due to the complexity of the matrix, a cleanup procedure is required. Consequently, it was used SPE techniques based on Florisil and Silica gel. The interfering species that were not removed by Florisil cartridge were removed by the second cleanup based on Silica gel. The quantification of the extracted pesticide residue was done using GC-ECD and GC-MS.

A study [39] developed in Turkey present the results of investigation of 186 pesticide residues in 1423 sample of fruits and vegetables. Pesticide extraction was performed using a modified QuEChERS method. The performance of the method was evaluated on the basis of recovery, precision and detection limits. Consequently, the recovery values ranged between 73% and 115%, calculated RSDs were lower than 20% for all analytes and LOD and LOQ values were below 0.01 mg/kg for all pesticides. The assessment of pesticide residues levels were done through GC-ECD and GC-MS (43 pesticides) and the rest of them by LC-MS/MS. The results indicated that pomegranate, cauliflower, cabbage samples were pesticide free, meanwhile 754 samples contained detectable residues or below MRLs, 48 (8.4%) of fruit samples and 83 (9.8%) of the vegetable samples contained residues above MRLs. In the case of arugula, cucumber, lemon, grape MRLs were more often exceeded. The most detected pesticide residues were acetamiprid and chlorpyrifos.

Another study conducted in Turkey [18] aimed determination of 175 pesticide residues in various fruits and vegetables collected from Hatay. The extraction of the pesticide residues was performed using a modified QuEChERS method using for 15 g of sample 15 mL acetonitrile, 6 g MgSO₄ and 1.5 g CH₃COONa and centrifugated. To a portion of 4 mL supernatant were added 0.6 g MgSO₄ and 0.2 g PSA. The pesticide determination was done using LC-MS using a Synergy C₁₈ column and a mobile phase consisting of 5 mmol ammonium formate in methanol and 5 mmol ammonium formate in water at a flow rate of 500 µL/min. The limit of quantification for all analytes was 0.003 mg/kg in vegetable and fruit samples meanwhile the limit of detection was estimated at 0.001 mg/kg. The results indicated that in tomato, plum and apricot the pesticide residue levels were below limits of detection. A number of 12 pesticides (acetamiprid, carbendazim, chlorpyrifos, fenarimol, fludioxonil, hexythiazox, imidacloprid, metalaxyl, pyridaben, pyriproxifen, thiabenzazole, triadimelol) were identified at levels that ranged between 0.003 and 0.759 mg/kg.

5. FISH AND MEAT MATRIXES

In food control analysis, isolation of pesticides from fatty matrixes is very challenging because

requires complicated sample treatment procedures, proper solvents for extraction, cleanup and preconcentration strategies prior quantification. OC pesticides and PCB are encountered in almost living organisms having in view their tendency to concentrate in fatty tissues [40,41].

The analysis of these pesticides in fatty tissues requires extraction from matrix, cleanup of the obtained extract and GC analysis. In the case of meat samples, the difficulty is that fatty material is extracted also from the matrix and it is incompatible with GC systems. Consequently, the cleanup procedure is the most laborious step in the analysis [42].

Levels of PCB and OC pesticides were determined in 8 edible fish samples collected from largest Iranian wetland, the Shadegan Marshes. The extraction was performed with Soxhlet apparatus using hexane:acetone mixture and the cleanup was accomplished on a column filled with acidified silica gel and anhydrous sodium sulphate. The column was eluted with hexane/dichloromethane and the eluate was subjected to GC-ECD analysis after concentration under nitrogen stream. The results indicated the presence of organochlorine pesticides in concentrations higher than PCB [43]. The same extraction procedure and quantification method of OC pesticide from fish and molluscs collected from Liaoning, China was adopted by Liu et al. [44]. The results indicated that OC levels were higher in fish than in mollusks and are higher in freshwater fish than in marine fish.

Molina-Ruiz et al [45] reported a modified QuEChERS method for determination of OC and OP pesticides in fish muscle tissues of carp and sturgeon collected from Carp Valley, Lesser Poland. After extraction procedure (using acetonitrile as solvent), it were tested two d-SPE cleanup stages: one of them consisted in the addition of the d-SPE sorbent mixture (PSA+silica SAX SPE bulk sorbent+amino bulk sorbent) and the other consisted in addition of C₁₈ after extracts enrichment with d-SPE sorbent combination (PSA+silica SAX SPE bulk sorbent+amino bulk sorbent). The residue analysis was achieved by GC/Q-MS. The results indicated that better recoveries were obtained when C₁₈ addition. Recoveries were 70-120% with RDS lower than 10% at 0.030 mg/kg spiking level for most investigated pesticides.

Sun et al [46] reported a multiresidue method for determination of OC pesticides and their metabolites (chlorobenzilate, dieldrin, endosulfan

sulfate, endosulfan, endrin, heptachlor, heptachlor epoxide, lindane, methoxychlor, p,p'-DDE, p,p'-DDT) and nitrogen-containing pesticides (alachlor, trifluralin) from different fish samples with 1.2-23.3% fat content. Extraction of pesticides was performed using acetonitrile and cleanup was done using SPE column with Florisil and C₁₈ with acetonitrile as unique solvent. The pesticide residues were achieved by GC-ECD. The recoveries of the spiked pesticide residues were 73.4-119.6%.

Other multiresidue method for determination of OC and OP pesticide from meat was reported [47]. The extraction was done using acetonitrile:hexane mixture (1:1, v/v) and the pesticide quantification was achieved by GC-ECD. The recovery tests (2 g sample fortified at 3 levels) revealed that GC-ECD provide 64.4-96.0% recovery for all investigated pesticides, excepting 2,4'-DDE (46.6-50.4%), 4,4'-DDE (51.1-57.5%) and 2,4'-DDT (50.0-51.2%).

The investigation of distribution of HCH isomers and DDT analogues and selected PCB congeners in pork organs was reported by Covaci et al [48]. The extraction and cleanup procedure was done by validated a method and consisted in treatment of animal tissues with sodium sulphate followed by Soxhlet extraction with hexane:acetone (3:1, v/v). The cleanup procedure was done using a column filled with acidified silica and eluted with hexane and dichloromethane. The quantification of the pesticide residue was achieved by GC-ECD. Recoveries of target compounds ranged between 72–80% and the LOD for PCB individual congeners were 0.1–0.5 mg/g lipid and for HCHs and DDTs the detection limit was 0.2 ng/g lipid for each isomer. The results indicated that the most load of pesticide residues is found in adipose tissue, with HCHs between 16-27.7 ng/g lipid, meanwhile for DDTs were 65.9-344.5 ng/g lipid. In the case of PCB, the highest level was found in lung and liver (more than 32 ng/g lipid).

Garrido Frenich et al [42] optimised and validated a method for simultaneous determination of the OC and OP residues in meat (chicken, pork, lamb). The extraction was done with ethyl acetate using polytron homogenizer, but is also tested Soxhlet and ASE extraction. In the case of extraction using ethylacetate, the recovery ranged from 70.2 to 104.4% and RSD was lower than 15.0%. When Soxhlet extraction was tested it was obtained recoveries below 70% and RSD lower than 13.0%. Even if ASE is a very effective extraction method, in this case the recoveries ranged from 70.0 to 92.9% and RSD below 10.0%. The cleanup

procedure was performed by gel permeation chromatography with mobile phase cyclohexane:ethylacetate (1:1, v/v) and the determination was done with GC-QqQ-MS. The proposed method was applied to the analysis of pesticides from 10 chicken samples, 10 pork samples and 10 lamb samples. The results indicated the presence of endosulfan α , endosulfan sulfate and dichloran in 3 lamb samples. The endosulfan α was detected in one pork sample with level below LOQ. The analysed chicken samples were clean of investigated pesticides.

The investigation of HCH isomers, DDT and its metabolites in chicken organs was reported by Tao et al [49]. The sample was homogenized with sodium sulphate and subjected to Soxhlet extraction with acetone:dichloromethane (2:8, v/v). After solvents removal, the extracts were treated with hexane, and hexane with acetonitrile. Then a new extraction was performed with hexane and the resulted extract was concentrated and passed to a column with filled silicon gel and eluted with hexane and dichloromethane:hexane (2:3, v/v). The analysis of the extracts was done by GC-ECD. The quality control indicated recoveries of spiked muscle samples of 74%, 64%, 73%, 50%, 107%, 123%, 82%, 78%, 121% and 95% for α -HCH, β -HCH, γ -HCH, δ -HCH, o,p'-DDT, o,p'-DDD, o,p'-DDE, p,p'-DDT, p,p'-DDD, p,p'-DDE, respectively. The mean detection limits were 0.01 ng/g fresh weight for all HCH isomers and 0.02-0.3 ng/g fresh weight for DDT, DDD and DDE. The fresh weight concentrations of the chicken samples ranged from 0.054 ng/g (muscle) to 2.76 ng/g (skin) for HCHs and from 0.123 ng/g (muscle) to 6.35 ng/g (skin) for DDT, respectively.

Ahmad et al [50] determined OC pesticide residues in chicken, lamb and beef samples collected from Jordan. The extraction of the pesticides from meat samples was performed by Soxhlet method with petroleum ether. The resulted fat was dissolved in petroleum ether, partitioned with acetonitrile saturated with petroleum ether and back-extracted into petroleum ether. The cleanup was performed by Florisil column chromatography and the final analysis was performed by GC-ECD. The obtained results indicated that 20% and 49% of chicken and meat samples respectively, were contaminated with organochlorine residues. Among those, HCHs and DDTs are the most encountered species. Other organochlorines (heptachlor, heptachlor epoxide, aldrin, andrin) were present in less than 7% in analyzed samples.

6. GRAIN MATRIX

Determination of pesticide residues in grain (barley, oat, rye, wheat) from Kazakhstan was performed using a multimethod based on MSPD and GC with dual detection ECD and NPD [51]. A quantity of 2 g of grain sample was mixed with 4 g of Florisil and then was further purified using a column that contain anhydrous Na_2SO_4 , silica gel, samples with Florisil. For elution was used 25 mL of mixture composed from acetone and methanol (9:1, v/v). After evaporation, the extract was placed in an SPE C_{18} column and the analytes were eluted with 15 mL acetonitrile. Mean recoveries for wheat spiked at three fortification levels (0.001-2.5 mg/kg) were between 70.07-118.90%. Exception were dicofol, pyridaben, dichloran, isofenphos, triazophos in the case of which recoveries were 122.2-127% and acetamiprid, captan, dichlofluanid, tecnazene, dichlobenil, endosulfan-sulfate, phorate, phosmet with recoveries 42.83-69.1%. In cereal grain were identified banned pesticides (DDT, γ -HCH, aldrin, diazinon). For 77.5% of the samples, were found no residues, 13.75% contained pesticides below MRLs and 8.75% above MRLs.

Halosulfuron-methyl residues in wheat grain were identified and quantified using an optimised QuEChERS preparation method associated with LC-MS/MS detection [19].

For herbicide extraction was used acetonitrile:water solution (10:1, v/v) and NaCl. The cleanup procedures for the cleanup efficiency were tested different sorbents (PSA, C_{18} , mixture of PSA and anhydrous MgSO_4 , mixture of GCB and PSA) and the highest recoveries were obtained when PSA was used.

The recovery tests were set at three levels for each matrix: 0.001; 0.01; 0.1 mg/kg for wheat brain and 0.005; 0.01; 0.1 mg/kg for wheat plant and the average recoveries ranged 86-92% for wheat grain and 92-109% for wheat plant. The results indicated that the residue level of halosulfuron-methyl in wheat grain were below 0.01 mg/kg at harvest.

QuEChERS method was optimized to provide acceptable results for various grain matrices (corn, oat, rice, wheat) for approximately 180 analytes [20]. The milled sample (2.5-5 g) was treated with water:acetonitrile 1:1 (v/v) (25 mL for rice and 20 mL for corn, oat, and wheat). Phase separation and accumulation of pesticide in upper acetonitrile layer was done by adding $\text{MgSO}_4/\text{NaCl}$ salt mixture (4:1, w/w). The cleanup procedure consisted in d-SPE

using PSA (150 mg), C_{18} (50 mg) and MgSO_4 (150 mg) for 1 mL aliquot. The quantification of the pesticide residues was performed by GC-TOFMS (gas chromatography combined with time-of-flight mass spectrometry) and GC-amenable pesticides were analyzed using UPLC-MS/MS (ultraperformance liquid chromatography coupled to tripole-quadrupole tandem mass spectrometry).

Santilio and coworkers [52] reported a rapid and effective method for detection of low levels of phenoxy acid herbicides (2,4-D, 2,4-Dichlorprop, Dichlorprop-p, Fluzifop, Fluroxypyr, Mecoprop, Mecoprop-p) in cereals. It has been stated [52] that the extraction of acidic pesticides is difficult to extract from complex matrixes, as cereals, because due to the other components from matrix the extraction efficiency is affected. Due to this behavior, in order to break-up the covalent bonds between acidic pesticides and matrix components, first it was done on alkaline hydrolysis with sodium hydroxide, followed by a QuEChERS extraction using acetonitrile as extractant, anhydrous MgSO_4 , disodium citrate sesquihydrate. The pesticide quantification was achieved using HPLC/MS/MS. Recoveries were determined at four spiking levels (0.02 mg/kg, 0.05 mg/kg, 0.1 mg/kg and 0.5 mg/kg) and mean recoveries ranged from 90 to 120%, meanwhile the RSD proved to be lower than 20%. The proposed method was used to quantify the levels of pesticides in cereals (rye flour, oat meal, oat flakes, dehusked oat) and the levels were below the limit of quantification of the method.

Monitoring of pesticide residues in northern Cameroon was carried out by Sonchieu et al [53]. The investigated grains were maize and millet and the subjected pesticides were OC (lindane, α -endosulfan, β -endosulfan), OP (malathion, pirimiphos-methyl), synthetic pyrethroids (permethrin) and carbamates (carbofuran). For the extraction procedure from grain matrix were used acetone:hexane (1:1, v/v). The cleanup procedure was performed using Florisil column and hexane saturated with acetonitrile for elution. The residue determination was performed using GC-ECD/NPD and GC-MS for confirmation. Recoveries ranged between $71\pm 3\%$ for permethrin in maize by ECD to $109\pm 16\%$ for carbofuran in maize by GC-NPD. For millet, recoveries were between $73\pm 3\%$ for permethrin by GC-ECD and $105\pm 16\%$ for carbofuran by GC-NPD. Among investigated pesticide residues, OC ones are found frequently and in higher levels, ranging from 0.02 ± 0.01 mg/kg for β -endosulfan in millet to 9.53 ± 4.00 mg/kg

lindane in maize. The OP residues were found in concentrations varying from 0.04 ± 0.03 mg/kg for pirimiphos methyl to 0.23 ± 0.38 mg/kg for malathion in maize. Concerning carbofuran levels, the analysis indicated its absence.

Assesment of OP and carbamate pesticides in maize collected from Lagos State was reported by Ogah et al [54]. Extraction of pesticides from the matrix was done using ethylacetate and the cleanup procedure was performed by SPE using Florisil. The eluting solvent was a mixture composed from hexane:ethylacetate (50:50). The resulted solution was evaporated to dryness and reconstituted then in ethylacetate. The analysis was performed by GC-MS analysis. The results indicated the presence of OP or carbamate in all samples with concentrations that ranged between 12.0 (fenitrothion) and 1565.4 $\mu\text{g}/\text{kg}$ (malathion).

7. JUICE AND WINE MATRIX

Pesticide residues in juices are an important issue taking into account the consumption by children and its monitoring is of great interest. Also, it is mandatory to provide precise and reliable results concerning pesticide levels to ensure food safety. For extraction and concentration of the pesticide in juices and wines are used LLE, SPE, SPME, SFE, MSPD, ASE, SBSE, MASE and SDME [5]. Most used and common detection techniques for pesticide residues determination in fruit juices and wines are GC, GC-MS, GC-MS/MS, GC-ECD, GC-NPD, GC-FID, GC-FPD, HPLC, LC-MS, LC-MS/MS [5].

A new method developed for carbamate (carbosulfan, benfuracarb, carbofuran, pirimicarb, diethofencarb) and phenylurea (diuron, monuron, monolinuron) residues in fruit juices was reported by Sagratini and coworkers [55] by SPME coupled with LC/MS and LC/QIT-MS. The extraction of the residues was performed after investigating several types of fibers (50 μm Carbowax/templated resin, 60- μm poly(dimethylsiloxane)divinylbenzene, 85- μm polyacrylate) and were chosen the best extraction parameters: 90 minutes (time), 20°C (temperature) and 1 mL (volume). The best recoveries between 25 to 82%, were obtained when were used Carbowax/templated resin and poly(dimethylsiloxane)divinylbenzene fibers.

Different types of juices (orange, pineapple, peach, apple, mango, strawberry, tomato, pear,

mandarin, grape, banana, greppfruit) were selected for the development of a method for pesticide analysis by direct injection in LC-MS/MS [56]. The main important issue when a pesticide is analysed is the matrix effect and a minimization of this inconvenient may be achieved by diluting the extracts and in this way it is reduced the amount of matrix that is going in the system. The efficiency of the method was demonstrated when it was applied to real juice samples. The results indicate that 57% from juices did not contain pesticide at detectable levels at the levels were lower than the practical limits of quantification, while 43% of them contained one or more of the investigated pesticides.

Miele and coworkers [57] analyzed the pesticide content (azoxystrobin, cyproconazole, tebuconazole, thiophanate-methyl, triadimefon, fenthion, carbaryl, fenitrothion, simazine, diuron) in grape juices using classical QuEChERS method [12] for extraction and quantification by LC-MS/MS. The pesticide residues were not detected in analyzed grape juices (27 samples).

Pesticide residues (trifluralin, atrazine, acetochlor, alachlor, endosulfan-alpha, endosulfan-beta, endosulfan-sulphate) presence in 80 samples of sugarcane juice collected from Brazilian cities were investigated by QuEChERS method associated with GC-ECD [58]. QuEChERS method involved acetonitrile extraction (10 mL) and liquid-liquid partition using MgSO_4 (4 g) and NaCl (1g) for 10 mL of sample. The cleanup procedure was done by d-SPE with PSA sorbent. The recoveries ranges between 62.9 to 107.5% for sugarcane juice spiked at 0.025, 0.10 and 0.20 mg/L. The proposed method is suitable for pesticide residue analysis in matrixes with high sugar content.

Analysis of pesticides from wine samples it has been proven to be very difficult and challenging due to the complexity of the matrix. The technique used for quantification is related with pesticide nature.

Carpinteiro and coworkers [59] reported a new procedure for determination of fungicides (metalaxyl-M, azoxystrobin, myclobutanil, flusilazole, penconazole, tebuconazole, propiconazole, diniconazole, difenoconazole) encountered in wine samples. Sample concentration and purification were done using mixed-mode, anion exchange and reverse phase, Oasis MAX cartridges (for SPE). The authors optimized the parameters that affect chromatographic determination. Accordingly, 10 mL of wine samples were diluted with 10 mL ultrapure water and

concentrated on mixed-mode SPE cartridges conditioned with methanol and ultrapure water (Ph = 4 and pH = 6, 5 mL each). Analytes were recovered using 1 mL methanol after previously it was added 5 mL NH₄OH 5%. The resulted extract was injected in LC-MS/MS system without any further purification. The recoveries determined as against pure standards in methanol were higher than 72%.

A pretreatment method based on MMLLE for GC-FID determination of pesticides (endosulfan, iprodione, lindane, procymidone, quinalphos, tetradifon, vinclozolin) in wine was reported by Hyötyläinen and co-workers [60]. MMLLE using cyclohexane as extraction solvent favoured an efficient, selective and repeatable extraction. Further, an improvement of the above proposed method was reported [60] and the sensitivity of the developed system gave on average 2–13 timer better sensitivity.

Lately, the most advantageous manner to determine the pesticide residue content in food is the application of multiresidue methods that allow assessment of many species in a single step. For example, a new multiresidue method for the screening, identification and quantification of more than 160 pesticides in red, rosé and white wines was validated and reported by Walorczyk and his team [61].

It were investigated three sample preparation procedures using acetonitrile as extractant (unbuffered, citrate-buffered and acetate buffered) and three d-SPE cleanup procedures using PSA sorbent (1), combination of PSA combined with C₁₈ sorbents (2) and combination of PSA, C₁₈ and CGB sorbents (3). The use of citrate-buffered extraction method followed by d-SPE cleanup with PSA and C₁₈ provided the most consistent recoveries with the less result variability and accordingly, this sample preparation was considered the most favourable sample preparation before quantification by GC-QqQ-MS/MS analysis. With this method, were detected captan, chlorothalonil, dichfluaniid, folpet and tolylfluaniid. The recoveries were 80–110% with RSD lower than 10% at three spiking levels of 0.01, 0.05 and 0.2 mg/kg.

Other method suitable for multiresidue analysis in wine and grapes [62] was developed for 11 new generation fungicides (benalaxyl, benalaxyl-M, boscalid, cyazofamid, famoxadone, fenamidone, fluquinconazole, iprovalicarb, pyraclostrobin, trifloxystrobin, zoxamide). The extraction procedure was done with ethylacetate:hexane (1:1,

v/v) and cleanup by SPE with GCB/PSA using a mixture of acetonitrile and toluene (3:1, v/v) as eluent. The quantification of was performed by GC-ITMS. The proposed method was applied for determination of residues of benalaxyl, benalaxyl-M and iprovalicarb in white wines previously treated with these compounds. The results indicated that benalaxyl and benalaxyl-M levels were close to 0.2 mg/kg (European MRLs) and irpovalicarb were lower than 2 mg/kg.

Navarro and co-workers [63] reported a validated a multiresidue gas chromatographic method for quantification of 17 fungicides in grapes, must and wine. For pesticide extraction was used a simple on-line microextraction using acetone-dichloromethane mixture. The subjected fugicides were benalaxyl, captan, chlozolinat, cyprodinil, dichlofuanid, fenarimol, fludioxonil, folpet, hexaconazole, metalaxyl, myclobutanil, nuarimol, penconazole, procymidone, pyrimethanil, triadimefon, vinclozolin. An advantage of the proposed method is that cleanup is not necessary because chromatograms of untreated samples are free of interfering peaks. Also, the method assures good recoveries (78–107%) and RSDs were below 14%. The identification and quantification of the pesticides was performed by GC-NPD and GC-ECD and for confirmation was used MS detection.

A similar extraction method based on dichloromethane:acetone (1:1, v/v) extraction mixture with recoveries 79–109.1% for OP pesticides in Chinese health wines was reported [64]. For simultaneously determination of the pesticides was applied GC-FPD technique. The proposed method presents the advantage of being simple, easy with high extraction recoveries and less time consuming. Out of all 80 health wines, 18 OP pesticides were found in 8 samples at levels of 8.2–37.9 ng/mL. The pesticide presence was confirmed by GC-MS.

LIST OF ABBREVIATIONS

ASE – accelerated solvent extraction;
DDD – p,p'-dichlorodiphenyldichloroethane;
DDE – dichlorodiphenyldichloroethy lene;
DDT – dichlorodiphenyltrichloroethane;
DI-SPME – direct immersion solid phase microextraction;
DLLME – dispersive liquid-liquid microextraction;
DLLME-SFO – dispersive liquid-liquid microextraction combined with solidification of floating organic droplet;
d-SPE – dispersive solid phase extraction;
ELISA – enzyme – linked immunosorbent assay;
FIA – flow injection analysis;
GC – gas chromatography;

GCB – graphitized carbon black;
GC-ECD – gas chromatography with electron capture detector;
GC-FID – gas chromatography with flame ionization detector;
GC-FPD – gas chromatography with flame photometric detector;
GC-ITMS – gas chromatographic ion trap mass spectrometry;
GC-NPD – gas chromatography with phosphorus detector;
GC/Q-MS – gas chromatographic quadrupole mass spectrometry;
GC-QqQ-MS – gas chromatography coupled to triple quadrupole mass spectrometry detection;
GC-TOFMS – gas chromatography combined with time-of-light mass spectrometry;
HCH – hexachlorocyclohexane;
HPLC – high performance liquid chromatography;
HPLC-DAD – high performance liquid chromatography with diode array detector;
HS-SPME – headspace solid phase microextraction;
IT – ion trap;
LC – liquid chromatography;
LC-ESI-MS/MS – liquid chromatography-electrospray ionization-tandem mass spectrometry;
LC/QIT-MS – liquid chromatography quadrupole ion trapped mass mass spectrometry;
LLE – liquid-liquid extraction;
LOD – limit of detection;
LOQ – limit of quantification;
MAE – microwave-assisted extraction;
MASE – membrane assisted solvent extraction;
MCFA – multi-commuted flow analysis;
MMLE – microporous membrane liquid-liquid extraction;
MRLs – maximum residue levels;
MS – mass spectrometry;
MSFIA – multi-syringe flow analysis;
MSPD – matrix solid-phase dispersion;
OC – organochlorine;
OP – organophosphate;
PBDE – polybromodiphenylethers;
PCB – polychlorinated biphenyls;
PLE – pressurized liquid extraction;
PSA – primary-secondary amine;
Q – single quadrupole;
QqQ – triple quadrupole;
QuEChERS – Quick, Easy, Cheap, Effective, Rugged and Safe method;
RSDs – relative standard deviation;
SBSE – stir bar sorptive extraction;
SDME – single drop microextraction;
SFE – supercritical fluid extraction;
SIA – sequential injection analysis;
SLE – solid-liquid extraction;
SPE – solid phase extraction;
SPME – solid phase microextraction;
TOF – time of flight;
UPLC-MS/MS – ultraperformance liquid chromatography coupled to tripole-quadrupole tandem mass spectrometry.

REFERENCES

- [1] Aulakh JS, Malik AK, Kaur V, Schmitt-Kopplin P. A review on solid phase micro extraction-high performance liquid chromatography (SPME-HPLC) analysis of pesticides. *Critical Reviews in Analytical Chemistry*. 2005; 35(1):71-85.
- [2] Durovic R, Dordevic T. Modern extraction techniques for pesticide residues determination in plant and soil samples. *Pesticides in modern world - trends in pesticide analysis*. Available from <http://www.intechopen.com/books/pesticides-in-the-modern-world-trends-in-pesticides-analysis/modernextraction-techniques-for-pesticide-residues-determination-in-plant-and-soil-samples>.
- [3] Pareja L, Fernandez-Alba AR, Cesio V, Heinzen H. Analytical methods for pesticide residues in rice. *Trends in Analytical Chemistry*. 2011; 30(2): 270-291.
- [4] Zhang L, Liu S, Cui X, Pan C, Zhang A, Chen F. A review of sample preparation methods for the pesticide residue analysis in foods. *Central European Journal of Chemistry*. 2012; 10(3):900-925.
- [5] Jin B, Xie L, Guo Y, Pang G. Multi-residue detection of pesticides in juice and fruit wine: a review of extraction and detection methods. *Food Research International*. 2012; 46:399-409.
- [6] Zgola-Grzeskowiak A, Grzeskowiak T. Dispersive liquid-liquid microextraction. *Trends in Analytical Chemistry*. 2011; 30(9):1382-1399.
- [7] Wu C, Zhao B, Wu Q, Wang C, Wang Z. Development of dispersive liquid-liquid microextraction based on solidification of floating drop for the sensitive determination of trace copper in water and beverage samples by flame atomic absorption spectrometry. *Bulletin of Korean Chemical Society*. 2011; 32(3):829-835.
- [8] Zuo M, Cheng J, Matsadiq G, Liu L, Li M-L, Zhang M. Application of dispersive liquid-liquid microextraction based on solidification of floating organic droplet multi-residue method for the simultaneous determination of polychlorinated biphenyls, organochlorine, and pyrethroid pesticides in aqueous sample. *Clean – Soil, Air, Water*. 2012; 00(0):1-8.
- [9] Barker S. Matrix solid phase dispersion (MSPD). *Journal of Biochemical and Biophysical Methods*. 2007; 70:151-162.
- [10] Turiel E, Martin-Esteban A, 2008. Sample Handling of Pesticides in Food and Environmental Samples, *in* J.L.Tadeo (ed.), *Analysis of pesticides in food and environmental samples*. CRC Press Taylor&Francis Group, 35-58.
- [11] Lehotay S, Mastovska K. Evaluation of two fast and easy methods for pesticide residue analysis in fatty food matrixes. *Journal of AOAC International*. 2005; 88(2):630-638.
- [12] Anastassiades M, Lehotay SJ, Stajnbaher D, Schenck FJ. Fast and easy multiresidue method employing acetonitrile extraction/partitioning and dispersive solid-phase extraction for the determination of pesticide residue in produce. *Journal of AOAC International*. 2003; 86(2): 412-431.
- [13] Miao X-X, Liu D-B, Wang Y-R, Yang Y-Y, Yang X-Y, Gong H-R. Modified QuEChERS in combination with dispersive liquid-liquid microextraction based on solidification of the floating organic droplet method for the determination of organophosphorus pesticides in milk samples. *Journal of Chromatographic Science*. 2015; 53(10):1813-1820.
- [14] Jeong I-S, Kwak B-M, Ahn J-H, Jeong S-H. Determination of pesticide residues in milk using a QuEChERS-based

- method developed by response surface methodology. *Food Chemistry*. 2012; 133:473-481.
- [15] Li N, Lei L, Nian L, Zhang R, Wu S, Ren R, Wang Y, Zhang H, Yu A. A modified QuEChERS method for the determination of some herbicides in yogurt and milk by high performance liquid chromatography. *Talanta*. 2013; 105:219-228.
- [16] Arias LA, Bojaca CR, Ahumada DA, Schrevels E. Monitoring of pesticide residues in tomato marketed in Bogota, Columbia. *Food Control*. 2014; 35:213-217.
- [17] Lopez-Fernandez O, Rial-Otero R, Gonzalez-Barreiro C, Simal-Gandara J. Surveillance of fungicidal dithiocarbamate residues in fruits and vegetables. *Food Chemistry*. 2012; 134:366-374.
- [18] Sungur S, Tunur C. Investigation of pesticide residues in vegetables and fruits grown in various regions of Hatay, Turkey. *Food Additives and Contaminants: Part B*. 2012; 5(4):265-267.
- [19] Feng M, Li W, Hao X, Han L. Determination of halosulfuron-methyl residues and dissipation in wheat by QuEChERS and LC-MS/MS. *Food Additives&Contaminants: Part A*. 2014; 31(11): 1879-1885.
- [20] Mastovska K, Dorweiler K, Lehotay S, Wegscheid J, Szylla K. Pesticide multiresidue analysis in cereal grains using modified QuEChERS method combined with automated direct sample introduction GC-TOFMS and UPLC-MS/MS. *Journal of Agricultural and Food Chemistry*. 2010; 58:5959-5972.
- [21] Grimalt S, Dehouck P. Review of analytical methods for the determination of pesticide residues in grapes. *Journal of Chromatography A*. 2016; 1433: 1-23.
- [22] Alder L, Greulich K, Kempe G, Vieth B. Residue analysis of 500 high priority pesticides: better by GC-MS or LC-MS/MS?. *Mass Spectrometry Reviews*. 2006; 25: 838-865.
- [23] LeDoux M. Analytical methods applied to the determination of pesticide residues in foods of animal origin. A review of the past two decades. *Journal of Chromatography*. 2011; 1218:1021-1036.
- [24] Llorent-Martinez EJ, Ortega-Barrales P, Fernandez-de Cordova ML, Ruiz-Medina A. Trends in flow-based analytical methods applied to pesticide detection: a review. *Analytica Chimica Acta*. 2011; 684:30-39.
- [25] Verma N, Bhardwaj A. Biosensor technology for pesticides - a review. *Applied Biochemistry and Biotechnology*. 2015; 175:3093-3199.
- [26] Darko G, Acquah SO. Levels of organochlorine residues in dairy products in Kumasi, Ghana. *Chemosphere*. 2008; 71:294-298.
- [27] Salem NM, Ahmad R, Estaitieh H. Organochlorine pesticide residues in dairy products in Jordan. *Chemosphere*. 2009; 77:673-678.
- [28] John PJ, Bakore N, Bhatnagar P. Assessment of organochlorine residue levels in dairy milk and buffalo milk from Jaipur City, Rajasthan, India. *Environment International*. 2001; 26:231-236.
- [29] Rengasamy PT, Kantharimuthu A, Balaraman M, Sivanesan S. Development of ELISA kit for the assay of dichlorodiphenyltrichloroethane in milk and milk products. *African Journal of Food Science*. 2016; 10:41-47.
- [30] Shaker E, Elsharkawy E. Organochlorine and organophosphorus pesticide residues in raw buffalo milk from agroindustrial areas in Assiut, Egypt. *Environmental Toxicology and Pharmacology*. 2015; 39:433-440.
- [31] EC (Commission Regulation) No 149/2008 of 29 January 2008 amending Regulation (EC) No 396/2005 of the European Parliament and of the Council by establishing Annexes II, III and IV setting maximum residue levels for products covered by Annex I (Official Journal L58/1,1.3.2008).
- [32] Fagnani R, Beloti V, Battaglini APP, Dunga KS, Tamanini R. Organophosphorus and carbamates residues in milk and feedstuff supplied to dairy cattle. *Pesquisa Veterinaria Brasileira*. 2011; 31(7): 598-602.
- [33] Chung S, Chen B. Determination of organochlorine pesticide residues in fatty foods: A critical review on the analytical methods and their testing capabilities. *Journal of Chromatography A*. 2011; 1218:5555-55567.
- [34] Kampire E, Kiremire B, Nyanzi S, Kishimba M. Organochlorine pesticide in fresh and pressurized cow's milk from Kampala markets. *Chemosphere*. 2011; 84:923-927.
- [35] Gobo A, Kurz M, Pizzutti I, Adaime M, Zanella R. Development and validation of methodology for the determination of residues of organophosphorus pesticides in tomatoes. *Journal of Brazilian Chemical Society*. 2004; 15(6): 945-950.
- [36] Bempah CK, Buah-Kwofie A, Enimil E, Blewu B, Agyei-Martey G. Residues of organochlorine pesticides in vegetables marketed in Greater Accra region of Ghana. *Food Control*. 2012; 25: 537-542.
- [37] Bempah CK, Donkor A, Yeboah PO, Dubey B, Osei-Fosu P. A preliminary assessment of consumer's exposure to organochlorine pesticides in fruits and vegetables and the potential health risk in Accra Metropolis, Ghana. *Food Chemistry*. 2011; 128:1058-1065.
- [38] Al-Shamary N, Al-Ghouti M, Al-Shaikh I, Al-Meer S, Ahmad T. Evaluation of pesticide residues of organochlorine in vegetables and fruits in Qatar: statistical analysis. *Environmental Monitoring and Assessment*. 2016; 188:198, DOI 10.1007/s10661-016-5169-7.
- [39] Bakirci GT, Yaman Acay DB, Bakirci F, Otlas S. Pesticide residues in fruits and vegetables from the Aegean region, Turkey. *Food Chemistry, Food Chemistry*. 2014; 160: 379-392.
- [40] Turusov V, Rakitsky V, Tomatis L. DDT: ubiquity, persistence, and risks. *Environmental Health Perspectives*. 2002; 110(2):125-128.
- [41] De Voogt P, Wells DE, Reutergardh L, Brinkman UA. Biological activity, determination and occurrence of planar, mono- and di-ortho PCBs. *International Journal of Environmental Analytical Chemistry*. 1990; 40:1-46.
- [42] Garrido Frenich A, Martinez Vidal JL, Cruz Sicilia AD, Gonzalez Rodriguez MJ, Plaza Bolanos P. Multiresidue analysis of organochlorine and organophosphorus pesticides in muscle of chicken, pork and lamb by gas chromatography-triple quadrupole mass spectrometry. *Analytica Chimica Acta*. 2006; 558: 42-52.
- [43] Davodi M, Esmaili-Sari A, Bahramifarr N. Concentration of polychlorinated biphenyls and organochlorine pesticides in some edible fish species from the Shadegan Marhes (Iran). *Ecotoxicology and Environmental Safety*. 2011; 71:294-300.
- [44] Liu Z, Zhang H, Tao M, Yang S, Liu Y, Ma D, He Z. Organochlorine pesticides in consumer fish and molluscs of Liaoning province, China: distribution and human

- exposure implications. *Archives of Environmental and Contamination Toxicology*. 2010; 59: 444-453.
- [45] Molina-Ruiz JM, Cieslik E, Cieslik I, Walkowska I. Determination of pesticide residues in fish tissues by modified QuEChERS method and dual-d-SPE cleanup coupled to gas chromatography-mass spectrometry. *Environmental Science and Pollution Research*. 2015; 22(1), 369-378.
- [46] Sun F, Lin F-Y, Wong S-S, Li G-C. Determination of organochlorine and nitrogen-containing pesticide residues in fish with different fat content. *Journal of Food and Drug Analysis* 2000. 8(2); 103-111.
- [47] Park J-W, El-Aty AMA, Lee M-H, Song SO, Shim JH. Residue analysis of organophosphorus and organochlorine pesticides in fatty matrices by gas-chromatography coupled with electron-capture detector. *Zeitschrift fur Naturforschung*. 2006; 61: 341-346.
- [48] Covaci A, Gheorghe A, Schepens P. Distribution of organochlorine pesticides, polychlorinated biphenyls and a-HCH enantiomers in pork tissues. *Chemosphere*. 2004; 56:757-766.
- [49] Tao S, Liu WX, Li XQ, Zhou DX, Yang YF, Yue DP, Coveney RM. Organochlorine pesticide residuals in chickens and eggs at a poultry farm in Beijing, China. *Environmental Pollution*. 2009; 157:497-502.
- [50] Ahmad R, Salem NM, Estaitieh H. Occurrence of organochlorine pesticide residues in eggs, chicken and meat in Jordan. *Chemosphere*. 2010; 78:667-671.
- [51] Lozowicka B, Kaczynski P, Paritova AE, Kuzembekova GB, Abzhaliyeva AB, Sarsembayeva NB, Alihan K. Pesticide residues in grain from Kazakhstan and potential health risks associated with exposure to detected pesticides. *Food and Chemical Toxicology*. 2014; 64:238-248.
- [52] Santilio A, Stefanelli P, Girolimetti S, Dommarco R. Determination of acidic herbicides in cereals by QuEChERS extraction and LC/MS/MS. *Journal of Environmental Science and Health, Part B*. 2011; 46:535-543.
- [53] Sonchieu J, Ngassoum MB, Tchatchueng, Srivastava AK, Srivastava LP. Survey of pesticide residues in maize, cowpea and millet from northern Cameroon: part I. *Food Additives and Contaminants: part B*. 2010; 3(3):178-184.
- [54] Ogah CO, Coker HB. Quantification of organophosphate and carbamate pesticide residues in maize. *Journal of Applied Pharmaceutical Science*. 2012; 2(9):093-097.
- [55] Sagratini G, Manes J, Giardina D, Damiani P, Pico Y. Analysis of carbamate and phenylurea pesticide residues in fruit juices by solid-phase microextraction and liquid chromatography-mass spectrometry. *Journal of Chromatography A*. 2007; 1147:135-143.
- [56] Ferrer C, Martinez-Bueno MJ, Lozano A, Fernandez-Alba AR. Pesticide residue analysis of fruit juices by LC-MS/MS direct injection. One year pilot survey. *Talanta*. 2011; 83:1552-1561.
- [57] Miele A, Rizzon LA, Queiroz S, Gianello C. Physicochemical composition, minerals, and pesticide residues in organic grape juices. *Food Science and Technology*. 2015; 35(1): 120-126.
- [58] Furlani Zanes Prado R, Marcilio KM, Leme Moralez F, Tfouni Verdiani SA. Analysis of pesticide residues in sugarcane juice using QuEChERS sample preparation and gas chromatography with electron capture detection. *Food Chemistry*. 2011; 126: 1283-1287.
- [59] Carpinteiro I, Ramil M, Rodriguez I, Cela R. Determination of fungicides in wine by mixed-mode solid phase extraction and liquid chromatography coupled to tandem mass spectrometry. *Journal of Chromatography A*. 2010; 1217: 7484-7492.
- [60] Hyötyläinen T, Tuutijärvi T, Kuosmanen K, Riekkola ML. Determination of pesticide residues in red wines with microporous membrane liquid-liquid extraction and gas chromatography. *Analytical and Bioanalytical Chemistry*. 2002; 372:732-736.
- [61] Walorczyk S, Drozdzyński D, Gnusowski B. Multiresidue determination of 160 pesticides in wines employing mixed-mode dispersive-solid phase extraction and gas chromatography-tandem mass spectrometry. *Talanta*. 2011; 85:1856-1870.
- [62] Gonzalez-Rodriguez R, Cancho-Grande B, Simal-Gandara J. Multiresidue determination of 11 new fungicides in grapes and wines by liquid-liquid extraction/cleanup and programmable temperature vaporization injection with analyte protectants/gas chromatography/ion trap mass spectrometry. *Journal of Chromatography A*. 2009; 1216: 6033-6042.
- [63] Navarro S, Barba A, Navarro G, Vela N, Oliva J. Multiresidue method for the rapid determination - in grape, must and wine - of fungicides frequently used on vineyards. *Journal of Chromatography A*. 2000; 882:221-229.
- [64] Liu Q, Kong W, Qiu F, Wei J, Yang J, Yang S, Zheng Y, Yang M. One-step extraction for gas chromatography with flame photometric detection of 18 organophosphorus pesticides in Chinese medicine health wines. *Journal of Chromatography B*. 2012; 885-886:90-96.