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GREEN METHODS OF ANALYSIS OF PESTICIDES IN CEREALS: OVERVIEW

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Abstract. Pesticides have been used all over the world since the mid-twentieth century to protect cereals and their derivatives in agriculture from pests, insects and fungi. The release of pesticides into the environment makes up a fraction of one percent of the total amount of chemical pollutants, but given that these compounds are aimed at suppressing certain groups of organisms, pesticides and their transformation products have a toxic effect on various forms of biota and on human health when ingested with vegetables and fruits, including from their surface, if they are poorly washed. And also, from cereals, as they can be absorbed into them from the soil. There are no safe pesticides, even when used in small quantities, they can cause various allergic reactions and poisoning. In the production of agricultural products, approved pesticides are used, but this does not negate the fact that long-term use of the drug can have negative consequences. Therefore, constant monitoring of the residual amount of pesticides in these products reduces the risk to human health and the environment. Hence, there is a need for efficient, rapid and cost-effective methods for the determination of pesticide residues. The article reflects the methods of sample preparation in the analysis of pesticides in grain crops, as well as features of the method of solid-phase micro extraction of one of the methods of environmental, green chemistry in the preparation of samples.

Key words: cereals, pesticides, methods of sample preparation, solid-phase micro extraction method, chromatography.

Balanced nutrition plays an important role in one's health and life. Fresh fruits and vegetables and cereals are an important part of a balanced diet because they contain a significant amount of nutrients and minerals [1]. The growing populations around the world have led to the increased demand for food, hence using pesticides have become important to protect the plants before and after harvest [2]. Although the use of pesticides has played a key role in providing large quantities of inexpensive fruits and vegetables [3], they have side effects. Insecticides, herbicides, and fungicides have been used effectively to combat pests, fungi, and weeds. However, they enter fruit and vegetable cells and remain in waste. This process may possibly result in contamination of the products and poses a threat to human health due to their toxicity. Moreover, the entry of pesticides into the soil, in addition to their direct application is associated with watering plants and the runoff of sediments from the surface of plants, the drift of drugs during the processing of fields, forest lands, etc. The possibility of accumulation of pesticides in the soil is determined by the conditions of their use (consumption rates, frequency of treatment), stability and solubility of drugs, soil type, its pH, temperature and humidity, leaching conditions, inactivating effect of plants, penetration depth, etc. As a result of chemical and biological processes in the soil, the content of pesticides in it usually decreases, nevertheless, their residual amounts range from hundredths to tens of micrograms per 1 kg. The least stable pesticides are in sandy soils, the most stable in soils with a high content of clay, organic matter, iron, aluminum and manganese ions. Being in the soil, pesticides are exposed to the action of abiotic factors, and microorganisms play a significant role in their decomposition [4].

Grain is one of the products that is produced and consumed worldwide. This is because they supply essential minerals, vitamins and other microelements as a source of energy due to their high content of essential fatty acids, nutrients and dietary fibers. They are the basis for making a large variety of products. Various types of agrochemicals are used in agriculture to increase productivity. Insecticides, fungicides, herbicides and plant growth regulators are administrated to cereal production throughout the growing season, insecticides being the most frequently used Chlorpyrifos-methyl, pirimifos-methyl, chlorpyrifos, malathion, dichlorodiphenylethane are illustrative examples. Chlorpyrifos and its derivatives, malathion, chlorpyrifos, dichlorodiphenylethane (DDD) was banned in several states of US and in EU due to the health complications in young children (especially in fetuses) and adults [5-6]. Unfortunately, some of these pesticides were accumulated during Soviet Union and are still finding application in most Central Asian countries. Grain crops are often sprayed with insecticides even though some of them are banned in certain countries (for example, malathion, pirimiphos-methyl, chlorpyriphos-methyl, deltamethrin, d-phenothrin, tetramethrin, pirimicarb, or dichlorvos) [7-10]. To reduce the effect of the fungus, strobilurin, azoxystrobin, trifloxistrobin, kresoxim-methyl, as well as nitrogen fungicides chlorothalonil, propiconazole, epoxiconazole, tebuconazole, and boskalid are usually used. In cereal production, chlormecate, mepiquat, imazaquin, trinexapac-ethyl and 2-chlorethylphosphonic acid are used to reduce plant stems and thus reduce their ability to move [11, 12].

In conclusion, pesticide residue monitoring is important not only to ensure food security but also for the good industry practice, so it is important to develop highly sensitive, selective analytical methodologies that can now identify them by the required MPL (maximum permissible levels). Analysis of pesticide residues in various food and grain samples is currently a top priority in laboratories for controlling human health and quality.

Methods of sample preparation in the analysis of pesticides in cereals

Monitoring the residual quantities of pesticides in cereals and their derivatives contributes to the development of analytical methods aimed at detecting large numbers of pesticides through a single analysis. In addition, although research methods have been developed for the residual amount of one type pesticide, their cost and volume of work performed are generally a problem for laboratories. Due to the variety of pesticides and the intrinsic complexity of the matrices, different methods of sample pretreatment have been proposed. In some samples, high lipid content prevented the analysis. Most of the work on solvent extraction of pesticides from grain samples used gas chromatography with selective detection systems. Other methods have also been proposed (i.e., spectrofluorometry, resonance scattering, voltamperometry, enzyme-linked immunoenzyme analysis), but these methods can only identify one pesticide [13-15].

The determination of residual amounts of pesticides in food requires a long and labor-consuming sample preparation using highly toxic organic solvents (acetonitrile, chloroform, methylene chloride, acetone, methanol, toluene, etc.). Classical sample preparation involves extraction with an organic solvent, purification by passing through an adsorbent and concentrating by evaporation of the solvent. On average, 100-150 mL of solvent is required to prepare 1 sample, most of which is released into the atmosphere during the analysis or is sent to waste [16].

In recent years, the QUEChERS method (fast, simple, inexpensive, efficient, durable and safe) has been proposed as an effective means of detecting pesticides in matrices. However, other methods, such as ultrasonic extraction, pressurized liquid extraction, sorbent-based processes, such as solid phase extraction, matrix solid phase extraction, sorption extraction, solid phase microextraction, have their own advantages and disadvantages.

1.1 Solvent extraction method

Simple solvent-based extraction methods are used to detect pesticides in wheat, rice, corn, soybeans and some derivatives [17-19]. Solid samples (e. g. millet) are often finely stirred before extraction and then sonicated by mixing with solvents to facilitate extraction. Solvents such as acetonitrile, ethyl acetate, methanol and ethanol are often used for the extraction of polar pesticides. For example, even if ethyl acetate is not mixed with water [20], it is equivalent to solvents in detecting polar and non-polar pesticides and has shown good results in detecting pesticides in high fat foods. However, most polar pesticides are easily extracted from ethyl acetate and their degree of extraction is relatively small, so in their work Na_2SO_4 is added to enhance extraction process. Acetone, n-hexane and dichloromethane are used to extract low-polar pesticides, for the better extraction additional stages of cleaning can be used to eliminate compounds that may interfere with chromatographic analysis [21,22].

A liquid separation process after solvent extraction has been used [23-24]. However, as a result, the volume of organic solvents used and the sample pretreatment time for analysis increased. In some cases, gel-conducting chromatography was used for additional cleaning instead of separating the fluid. Uygun et al. Identified phosphor organic pesticides (malaoxon, isomalathion, and fenitrooxone) in barley and malt, and Zhang et al. in multicellular pesticides [25]. Chen et al. Identified carbofuran in rice extracting pesticide samples using Triton X-100 as extractant, which is a non-ionic surfactant containing a hydrophilic polyethylene oxide group and a hydrophilic lipophilic or hydrophobic group [26]. As a result, the average value of the high-performance liquid chromatography after extraction was in the range of 88-92 % [27]

Soler C. Proposed the use of dichloromethane to detect carbosulfan in rice. The detection threshold was in the range of 58-93 % of 3-15 mcg / kg [28].

1.2 Pressurized liquid extraction method

When extracting compounds under pressure, solvents are used at high or low temperatures and pressures (vaporized) to extract solid or semi-solid matrices, which has been developed as an alternative to current extraction methods [29-33]. During liquid extraction under pressure, the solubility of the target analytes increases at high temperatures due to a decrease in the viscosity of the solvents, which also reduces the interaction of analytes and increases the diffusion of analytes through the matrix. Compared to other methods, liquid extraction under pressure consumes a small amount of solvent, works quickly and has high efficiency, high degree of automation, good sample ability and safe operation.

1.3 Solid phase extraction method

Solid-phase extraction is one of the most used methods for sorbent extraction [34-38], sometimes being coupled with pressurized liquid extraction [39] or microwave extraction [40]. Solid-phase extraction allows e.g. the detection of pesticides in rice, wheat, as well as corn, oats, barley. The method also shows good results in the detection of pesticides in wheat flour and in bread made from that flour [41].

Pang et al. Identified 362 of 405 multicellular pesticides in corn, wheat, oats, rice and barley with GC-MS but the 43 pesticides that were not detectable by GC-MS were analyzed immediately after extraction with LC-MS/MS acetonitrile solvent. The extracted solutions are subjected to two different solid-phase extraction methods based on the properties of the pesticides being analyzed. The analysis was tested on NH_2 and acetonitrile cartridges. Preliminary tests have shown that the cartridge has less adsorption on pesticides detected with the GC-MS than on the Alumina N cartridge, which was more effective on LC-MS/MS carbonate-based pesticides [42].

In conclusion, these parameters are crucial for obtaining relevant information in the target analyzes. Solid phase extraction reduces the amount of extractable compounds but increases the extraction time. And this is a disadvantage of the solid-phase extraction method.

1.4 Matrix solid-phase dispersion method

In addition to solid-phase extraction, matrix solid-phase dispersion (MSPD) has been used in several cases to detect pesticides from cereals [43, 44]. Moreover, MSPD and MSPD followed by gas chromatography coupled with electron capture detection GC-ECD methods, used to detect pesticide residues in wheat or rice, are mixed in appropriate solid sorbents such as acetonitrile n-hexane, ethylacetate (10-40 ml range), which are used to achieve complete sample disintegration and dispersing [45].

As with any other method, pesticide detection is influenced by several experimental parameters (e.g. sample size, solid sorbent, type and amount of eluting solvent) for solid phase dispersion. In previous studies, these parameters have been studied and optimized using a step-by-step approach that varies by one factor, despite the emergence of chemometric methods [46].

Matrix solid-phase dispersion is a good alternative to classical extraction methods. Since the cereals are solid specimens, the use of a solid-phase matrix dispersion method will allow no prior solvent extraction. The complete destruction of the specimen and the dispersion of its particles into very small dimensions provide an enlarged surface area for subsequent specimen removal. Sample preparation and cleaning are performed simultaneously using a small amount of adsorbent and solvent. In table 1 gas chromatographic methods for determining the residual amount of pesticides in cereals for the last ten years are summarized.

Table 1 – Gas chromatographic methods for determining the residual amount of pesticides in cereals.

Identifiable substance	Sample	Methods and conditions of analysis	Results of pre-sample preparation and specification	Reference
1	2	3	4	5
Ametryn, prometryn, terbutryn, atrazine, simazine, propazine, cyanazine	rice	Method: SPME-GC-MS Equipment: Shimadzu GC-2014 gas chromatograph. Mass spectrometer in electronic shock ionization mode (70 eV). Column: SPB-50 (50 м×0.25 mm×0.12μm) Fiber: 20 mm polymer coated aluminum wire τ_{ex} = 12 min; t_{ex} = 25°C; τ_{desorb} = 1 min; t_{desorb} = 250°C;	10 g of rice is replaced with a 25 ml vial. 12.5 ml of methanol and very pure water (pH = 7) are poured over. Detection limit: 9 - 85 ng/ml Recovery Rate:> 85 %	[42]

Continuation of the table 1

1	2	3	4	5
24 pesticide	wheat	Method: QuEChERS GC-MS Equipment: CP-8400 gas chromatograph Varian CP-3800 equipped with autosamplers. Mass spectrometer in electronic shock ionization mode (70 eV). Column: VF-5 MS (30 м×0.25 mm×0.25 µm)	In 10 g of wheat sample, mix for 10 minutes with 10 ml of acetonitrile and 1 % acetic acid. Then, 3 g of anhydrous $MgSO_4$, 1.7 g of CH_3COONa, 1.0 g of $Na_3C_6H_5O_7$, and centrifuged for 8 min (4500 rpm). The supernatant was then centrifuged again with 600 mg $MgSO_4$ and 600 mg C18. Detection Range: 2.5-5 mcg/kg Recovery Rate: 70-120 %	[43]
simeconazole	wheat, rice	Method: QuEChERS GC-MS Equipment: Trace GC Ultra Gas Chromatograph Mass spectrometer in ionization mode with positive charge (70 eV). Column: BGB-172 (30 м×0.25 mm×0.25 µm)	20 g of wheat, 20 ml of acetonitrile were added to the rice sample and incubated for 60 minutes at room temperature. Then 4 g of anhydrous $MgSO_4$ and 1 g of NaCl are added and the mixture is dehydrated. Detection range: 0.4 – 0.9 mcg/kg	[44]
Fluroxypyr-meptyl	wheat	Method: SPE GC–ECD Equipment: Shimadzu 2014 Gas Chromatograph Mass spectrometer in electronic shock ionization mode (70 eV). Column: HP-5 (30 m×0.25 mm×0.25 µm)	10 g of wheat sample is ground and 30 ml of methanol: water (5:1 ratio) are extracted. It is then filtered and extracted 3 times with 20 ml of dichloromethane. Then they are eluted on Florisil cartridge. Detection limit: 0.0005 ng/ml Recovery Rate: 84.45 – 108.2 %	[45]
alachlor, acetochlor, pretilachlor, butachlor, metolachlor, propanil	wheat, rice	Method: SPE GC–ECD Equipment: Trace GC Ultra Gas Chromatograph Mass spectrometer in electronic shock ionization mode (70 eV). Column: DB-5 (30 m×0.25 mm×0.25 µm)	2 g of wheat and rice were ground and extracted with 50 ml of acetone. The extract is then evaporated and extracted again with 1 ml of hexane. The graphite is then eluted on the secondary amino matrix. Detection range: 0.8-1.7 µg/kg Recovery Rate: 82.3–115.8 %	[46]

Continuation of the table 1

1	2	3	4	5
α, β, γ,δ-HCH p, p'-DDD, p, p'-DDE, o, p'-DDT, p, p'-DDT, α-endosulfan β-endosulfan heptachlor, heptachlor epoxide, dieldrin, aldrin	wheat, rice	Method: SPE GC–ECD Equipment Trace GC Ultra Gas Chromatograph Mass spectrometer in electronic shock ionization mode (70 eV). Column: DB-5 (30 m × 0.25 mm × 0.25 μm)	1 g of wheat and rice sample was homogenized with 2 ml of water and 8 acetonitrile. Then added 2 g of NaCl and shake for 2 minutes. The extract is then evaporated and extracted again with 1 ml of hexane. The graphite is then eluted on the secondary amino matrix. Detection Range: 1.5–4.2 μg/kg Recovery Rate: 78 –116 %	[47]
120 pesticides	wheat	Method: QuEChERS GC–MS/MS Equipment: Agilent 7890A gas chromatograph Column: HP-5ms Ultra Inert (30 m×0.25 mm×0.5 μm)	In 5 g of ground wheat sample, add 10 ml of water and 10 acetonitrile, and shake for 5 minutes. Then, 4 g $MgSO_4$, 1 g CH_3COONa, and 1.5 g $Na_3C_6H_5O_7$ were added and centrifuged for 10 min. Then, PSA was added and centrifuged. Recovery Rate: 70–120 %	[48]
219 pesticides	wheat, rice	Method: QuEChERS GC–MS/MS Equipment Agilent 7890A gas chromatograph Column: VF-1701 ms (30 m×0.25 mm×0.5 μm)	5 g of wheat and rice are moisturized by adding 10 ml of water. Then centrifuged for 5 minutes at 15 ml of acetonitrile, 6 g MgSO4, and 1.5 g CH3COONa. Then 400 ml of PSA, 400 mg of C18 and 1200 mg of MgSO4 were added to 8 ml of supernatant and centrifuged for 5 minutes. Then 3 ml of supernatant is sent for analysis. Detection Range: 5–50 mcg / kg	[49]
124 pesticide	rice	Method: QuEChERS GC–MS/MS Equipment: Gas chromatograph Varian 450 equipped with CP 8400 autosamplers Mass spectrometer in electronic shock ionization mode (70 eV). Column: VF-5 MS (60 m×0.25 mm×0.25 μm)	5 grams of rice is replaced with 50 ml of Teflon tube and 10 ml of water and 10 ml of acetonitrile are added. The mixture was kept in the fridge for 30 minutes. Detection range: 0.1–24.4 μg / kg Recovery Rate: 70–22.7 %	[50]

Continuation of the table 1

1	2	3	4	5
dimetoat, forat, diazinone, methyl parathion, forat sulfonate, forat sulfoxide, chlorpyrifos, chlorofenvinophos, fosalon	wheat, rice	Method: QuEChERS GC–NPD/MS Equipment: Shimadzu GC - 2010 Gas Chromatograph. Column: DB-1 (30 m×0.25 mm×0.5 μm)	In 10 g of sample, water is added and shaken. Then, 10 ml of ethyl acetate, 4 g of anhydrous $MgSO_4$, and 1.0 g of NaCl were added and centrifuged for 10 minutes (8000 rpm). Aliquot volume 1 ml. Detection Range: 0.001–0.010 μg/kg Recovery Rate: 70.2–95.25 %	[51]
demethon-s-methyl, phorate, diazinone, chlorpyrifos methyl, tolclophos-methyl, pirimifosmetil, malathion	rice	Method: MA-NPS-DME GC- MS Equipment: Gas chromatograph Shimadzu QP 2010 plus Mass spectrometer in electronic shock ionization mode (70 eV). Column: DB-5 MS (30 m×0.25 mm×0.5 μm)	1 g of rice was placed on the extractor-will be created. The 2.0 ml hexane was then infused for 200 seconds through the extractor and irradiated with a 150 W microwave. Detection Range: 0.45–1.06 μg/kg	[52]
chlorpyrifos, fenitrotion, malathion, metacriphos, phosphamidone	wheat	Method: HS-SPME-GC-FPD/MSD Equipment: HP 5890 II gas chromatographs. Column: DB-35 Ultra (50 m×0.25 mm×0.12 μm) Fiber: DVB/CAR/PDMS 50/30 μm τ_{ex} = 45 min t_{ex} = 60°C τ_{desorb} = 3 min t_{desorb} = 250°C	The 1.7 g wheat sample is replaced with a 4 ml vial. Detection limit: 0.05–100 ng/g	[53]
Tebuconazole, Carbofuran, Atrazine, simazine, Molinate	rice	Method: SPME-GC-MC Equipment: Shimadzu QP-Plus 2010 gas chromatograph. Column: Rtx-5MS (30 m×0.25 mm×0.5 μm) Fiber: DVB/CAR/PDMS 50/30μm τ_{ex} = 40 min tex = 80°C τ_{desorb} = 10 min tdesorb = 250°C	The 125 mg rice sample is replaced with a 40 ml vial. 25 ml of very clean water is poured into it, according to pH = 2.2. Detection range: 0.46 – 5.9 ng / g Recovery Rate: 76 –109 %	[54]

Continuation of the table 1

1	2	3	4	5
23 pesticides	wheat, rice	Method: QuEChERS GC–MS/MS Equipment: Agilent GC 6890N gas chromatograph Column: Rxi-5 ms (30 m×0.25 mm×0.5 µm)	In 5 g of ground wheat and rice samples was added 10 ml of water and 15 ml acetonitrile was shaken for 1 minute. Then added 6 g $MgSO_4$, 1.7 g CH_3COONa, 1.5 g $Na_3C_6H_5O_7$ and centrifuged for 10 min. Then 8 ml of supernatant was transferred to a 15 ml vial, 25 mg of PSA and 150 mg of $MgSO_4$ were added and centrifuged for 5 minutes	[55]

1.5 The method of solid phase microextraction during the pre-sample preparation

A sample preparation process is an important step in analysis, mainly used to enrich the matrix with analytes and to remove interfering components. However, the pre- sample preparation process usually takes a long time and a large amount of organic solvent. Therefore, the development of green technology for pre-sample specimens with high efficiency and simplicity of performed operations is one of the important areas of modern science.

One of the most important advances in sample preparation was the solid phase microextraction method originally described in 1990 by Arthur and Pawliszyn [47]. SPME is a simple and efficient sorption method eliminates the need for solvents and combines sample selection, extraction, and concentration at one stage. It is designed to solve long-lasting solvent-based problems using multi-stage methods that require the use of large quantities of solvent-bearing samples. In some literature, the SPME method is referred to as "green method" because of the non-use of environmentally hazardous solvents. Achieving a balance between the analytes as well as the phase of organic polymer deposited on the fused silica fiber and the matrix of the samples is the principle of SPME.

The solid phase microextraction method saves pre-sample treatment time and reduces the overall cost of the assay. The purpose of the method is to quickly prepare samples. It offers sample preparation, solvent-free extraction, solid, liquid or gaseous specimens, and low analyte concentrations.

SPME has helped eliminate some of the disadvantages of classical sample preparation methods. The easy automatization of the method has resulted in higher analytical performance [48-50]. Due to its excellent analytical characteristics, including linearity, repeatability, repeatability and low detection range, SPME is an effective and efficient method of extracting pesticide residues in fruits, vegetables and grains. The SPME tool is a quartz-roded syringe, coated with a thin polymer film connected to the plunger. For the extraction of components using SPME, the vial membrane is pierced, the component is extracted onto the film, and the syringe is removed for further desorption in the chromatograph. SPME is a very attractive alternative when preparing specimens that provide high selectivity, sensitivity and versatility at minimum matrix impedances [51, 52].

In conclusion, the need for frequent monitoring of residues of pesticides and other pollutants in food has led to the development of different methods of sample preparation. The SPME method was able to demonstrate good results in a quantitative analysis of pesticide residues in food and agricultural products.

Application of solid phase microextraction in pesticide analysis

Currently monitoring of pesticide residues in food products is the task of agrochemical research to conduct a comprehensive assessment of food quality and pollution. Therefore, the analysis of pesticides and agrochemical wastes (fertilizers, pesticides, soil conditioners, antibiotics etc.) in food is of paramount importance for monitoring and security purposes. Sample preparation is the most important step in achieving good quantitative results when determining the residual amount of pesticides from food matrices. The SPME technique has several advantages. Among them are the shortness of sample preparation time, separation and detection compatibility with chromatographic instruments and feed automation [53].

Cortes et.al [54] developed an analytical method in combination with the GC-MS and GC-MS/MS methods to determine the residual amount of 54 pesticides in orange, peach, pineapple juice. The rapid screening method was first performed to detect pesticide-containing juice specimens at concentrations above the predetermined threshold values. Samples were reanalyzed using simple, standard methods to confirm the predefined pesticides. This method reduced the total time of traditional analytical methods by 50 % [55].

SPME has been widely used recently to monitor the residual content of pesticides in water and soil and in edible plant samples. Chai et al. [56] presented the HS-SPME-GC-ECD method using 100 μm PDMS fiber to determine the residual pesticide content in fruits (strawberries, caramel and guava) and vegetables (cucumbers, tomatoes, and peas). The developed HS-SPME procedure provided a good linear range, accuracy, quantitative detection range and was adequate to analyze pesticide residues in fruits and vegetables. LOD (0.01-1 μg/l) and the quantitative detection limits of these pesticides were shown in LOQ (0.05-5 μg/l). The amount of pesticides detected was significantly lower than the permissible levels.

Feng et al. [63] proposed the HS-SPME/GC-MS method for identifying 8 pesticides in tea samples. Compared to simple sample preparation methods, the recommended method is quick, simple, highly sensitive, and saves extraction solvents. This optimized method allowed to improve good separation rate (86.7-112.8 %) and LOD (1.2-22.1 ng/g) using 100 μm PDMS fiber.

Saraji et al. prepared a polypyrrole/sol-gel composite coated SPME fiber by electrochemical deposition. The authors analyzed the phosphor-organic pesticides in cucumber and lettuce leaves using the GC-NPD method. Fiberglass-coated SPME has shown better extraction efficiency than commercial fiber. LOD levels and separation rates (80-109 %) were excellent [57]. Wang et al. Used the technique for preparing a water-compatible molecular imprinted polymer for SPME using a diazinon matrix as a sol-gel functional monomer and polyethylene glycol. MIP-coated fiber showed significantly higher extraction ability than unimpressed polymer and commercial fiber. Due to its unique adsorption, it showed excellent thermal and chemical stability. MIP-SPME-GC-NPD was developed and displayed on LOD (0.017-0.77 mg/kg) for OPP evaluation in agriculture samples [58].

Melo at al. [59-65] have developed a method to identify the 10 most frequently used pesticides in the production of lettuce (acetamiprid, azoxystrobin, cyprodinil, fenhexamid, fludioxonil, folpet, iprodione, metalaxil, pirimicarb, and tolyfluanid). This method has been efficient for quantitative determination of fludioxonil, folate, iprodione, azoxystrobin, cyprodinil, fenhexamid, and tolyfluanid in salad leaves at concentrations from 0.8 to 25.6 mg/kg. However, this SPME fiber does not extract acetamiprid, metalaxyl and pirimicarb were extracted only at concentrations greater than 20 mg/kg.

Detection of pesticides in food using SPME

Chromatographic analysis of pesticide residues in food, fruit and vegetable samples has been extensively studied since the introduction of SPME. Currently, SPME has been successfully used for analytical purposes in the identification of many pesticides in various foods [66, 67].

Chlororganic semi-and pyrethroid pesticides, bifenthrin residues in celery, garlic, and cabbage were identified by Zeng et al. [68] Good results were obtained by using 70 µm polymethylphenylsiloxane-coated fibers obtained by Sol-gel technology. The above-mentioned fiber demonstrated the best efficiency of pesticide extraction compared to commercially available fibers. The extraction efficiency is explained by the long fiber cover, the porous nature and the presence of a phenyl group. Vegetable samples are mixed with a solution, then acetone is added, dried, and treated with ultrasound. Then, it was extracted in DI-SPME mode at room temperature. The obtained data showed good results compared to the analyses performed in the HS-SPME mode. The acquired specimens are desorbed using the GC-ECD method. Quantitative evaluation was analyzed in three copies by addition of fresh vegetables. The degree of recovery pesticides ranged from 42.9 to 105.3 %, the RSD has shown 2.6 to 16.2 %, and the LOD 0.13 - 1.45 ng/g [69].

Chai et al. [70] have developed the HS-SPME-GC-ECD method for the analysis of phosphororganic (diazinon, profenophos and quinalphos) and α- and β-endosulfan and chlorothalonil in tomatoes and guava. In the developed method, 100 µl of 20 % methanol-acetone (1+1 vol/vol.), 10 % NaCl in purified water were used to obtain a total mass of 5 g. The resulting mixture was extracted with 100 µm PDMS fiber which was selected due to its low LOD and high sensitivity to all the studied pesticides. The extraction was performed in HS mode (800 rpm) by constant stirring at 60 °C for 30 minutes. Desorbed at 240 °C for 6 minutes after optimizing the required parameters. Addition of water provides recovery from 82 to 97 %, and LOD ranges from 0.1 to 1 µg/l.

Chai et al. Evaluated the use of GC-NPD in combination with SPME to identify five OPPs from tomatoes. This method involves simultaneous cooling of the fiber used in the HS mode and heating of the sample matrix. The developed method demonstrated better extraction efficiency in terms of sensitivity, linearity and recovery than traditional HS-SPME. The homogenized sample of 5 g of tomatoes was extracted at 80 °C for 30 min and desorbed at 270°C for 2 min. The method showed acceptable linearity, recovery and LOD [71].

Chai and Tan validated HS-SPME optimized parameters for detection of profenophos, quinalphos, α- and β-endosulfan in strawberries, guava, cucumber, tomato, bag, using a previously developed method [72]. Thermal desorption was performed at 240 °C for 10 minutes instead of 6 minutes, which helped to overcome the problem of reducing the temperature of the gas chromatography injector port and transporting. As a result, 10 minutes of desorption compared to 4 minutes of desorption yielded the best extraction efficiency. The median recovery rates for each pesticide were 71 to 98 % when enriched at three levels and RSD less than 5 % (n=3). Relapse (0.3-3.7 %) and intermediate accuracy (0.8-2.5 %) were satisfactory for all the studied samples. LOD showed quantitative determination using 0.01-1 µg/l and LOQ 0.05-5 µg/l.

Cortes-Aguado et al. Provided an analytical method for detecting 54 pesticide residues in orange, peach and pineapple juice samples. A fast screening is an analytical method that is quite new. In this method, the sample process is semiautomatic, which significantly reduces human error. Preprocessing of the specimen includes pretreatment of 1 ml of ethylacetate with 1ml of homogenized samples and centrifugation within 2 minutes. The resulting mixture was extruded at 250 °C for 9 minutes at room temperature in DI-SPME mode using 65 μm PDMS/DVB fiber. The RSD showed good recovery rates between 2-17 %. The LOD and LOQ were between 0.01 and 16.7 and 0.1 and 50 μg/l, respectively, and the linear range was from 0.01 to 1 μg/l, above 0.99 for all r^2 specimens [73].

Menezes et al. Developed an analytical method for the simultaneous detection of 14 pesticide residues in mango using the SPME-GC/MS method. The 3g sample was transferred to a 10 ml measuring flask and filled with an alcohol-water mixture of 50 μl of the concentrated pesticide solution. The resulting mixture was extracted for 30 min in a 10-ml hermetically sealed in the DI-SPME mode at 50°C for 50 minutes and stirring at 250 rpm. The mean relative recovery rate (n = 3) ranged from 71.6 to 117.5 %. The method was of good accuracy, selective and sensitive. The residual pesticide levels were below the maximum permissible values [74].

Guillet et al. Developed a method that involves the use of microwave energy for rapid and controlled pre-extraction of the residual amount of pesticides from 25 tomatoes. Extraction was performed using 100 μm PDMS fiber (for water-insoluble pesticides) and 60 μm PDMS/DVB fiber (for water-soluble pesticides) and a room temperature of 45 rpm for 500 min. LOD (0.01-7.62 μg/kg) and LOQ (0.20–25.4 μg/kg) were significantly lower than the permissible threshold values for all pesticides studied [75].

CONCLUSION

QuEChERS has been found to be a fast and effective method that allows you to extract residual amounts of target compounds while removing unwanted interferences such as organic acids, lipids, pigments, sugars, and others. It was revealed that the QuEChERS method is free of the drawbacks of traditional methods of sample preparation, such as the duration of the extraction procedure, the use of hazardous solvents, and radically simplifies the analysis of pesticide residues in food.

It has been established that to achieve accurate and complete determination of pesticides, new modern analysis systems are used. Chromato-mass spectrometry in combination with QuEChERS technology opens new opportunities in the analysis of residual amounts of pesticides in agricultural products. Tandem mass spectrometry detectors with HPLC or GLC allow for a group analysis of many compounds with exceptionally high selectivity and sensitivity and extrude methods such as gas and high-performance liquid chromatography with various detectors.

However, because of the high cost of chromatographs with tandem mass spectrometric detectors, the institutions and laboratories of developing countries cannot afford to purchase these devices.

The method of solid phase microextraction (SPME) is the most promising and most widespread of alternative "green" methods of sample preparation in the analysis of volatile pesticides. Solid phase microextraction, which combines sample selection, extraction, concentration and simultaneous enrichment, is a simple and efficient method of sample preparation. This method has gained advantages over traditional methods such as ease of use, low cost, low solvent consumption, speed, high enrichment and ease of automation. Due to its high elasticity, SPME is widely used for the analysis of volatile and non-volatile compounds in complex matrices, especially in food samples. Given that microextraction is one of the important fields in pre-modern sample processing, it is expected that the use of the SPME method for food analysis will increase in the future. The need to regularly monitor pesticide residues and identify other contaminants in food has led to the development of various sampling methods. Currently, the SPME method involves world scientific laboratories to determine the residual amount of pesticides

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REFERENCES

1 Sharma D., Nagpal A., Pakade Y. B., Katnoria J. K. Analytical methods for estimation of organophosphorus pesticide residues in fruits and vegetables //Talanta. – 2010. – Vol. 82. – P. 1077-1089.

2 Ibrahim W., Farhani W. A., Sanagi H., Aboul-Enein M. M. Solid phase microextraction using new sol-gel hybrid polydimethylsiloxane-2-hydroxymethyl-18-crown-6-coated fiber for determination of organophosphorous pesticides //Journal of Chromatography A. – 2010. – Vol. 1217. – P. 4890-4897.

3 Bidari A., Ganjali M. R., Norouzi P., Hosseini M. R. M., Assadi Y. Sample preparation method for the analysis of some organophosphorus pesticide's residues in tomato by ultrasound-assisted solvent extraction followed by dispersive liquid–liquid microextraction //Food Chemistry. – 2010. – Vol. 126. – P. 1840-1844.

4 Araoud M., Douki W., Rhim A., Najjar M. F., Gazzah N. Multiresidue analysis of pesticides in fruits and vegetables by gas chromatography-mass spectrometry //Journal of Environmental Science and Health. –2007. –Vol. 42. –P. 179-187.

5 Saunders, M., Magnanti, B. L., Correia Carreira, S., Yang, A., Alamo-Hernández, U., Riojas-Rodriguez, H., Calamandrei, G., Koppe, J. G., Krayer Von Krauss, M., Keune, H., Bartonova, A. Chlorpyrifos and neurodevelopmental effects: A literature review and expert elicitation on research and policy //Environmental Health: A Global Access Science Source. – 2012. – Vol. 11. P. 1-11.

6 Grandjean, P., Landrigan, P. J. Neurobehavioural effects of developmental toxicity // *The Lancet Neurology*. –2014. –Vol. 13. –P. 330-338.

7 Li, Y. F., Zhulidov, A. V., Robarts, R. D., Korotova, L. G., Zhulidov, D. A., Gurtovaya, T. Y., & Ge, L. P. Dichlorodiphenyltrichloroethane usage in the former Soviet Union // Science of the Total Environment. –2005. –Vol. 357. –P. 138-145.

8 Barron, M. G., Ashurova, Z. J., Kukaniev, M. A., Avloev, H. K., Khaidarov, K. K., Jamshedov, J. N., Rahmatullova, O. S., Atolikshoeva, S. S., Mamadshova, S. S., & Manzenyuk, O. Residues of organochlorine pesticides in surface soil and raw foods from rural areas of the Republic of Tajikistan //Environmental Pollution. – 2017. – Vol. 224. – P. 494-502.

9 Li, Y. F., Zhulidov, A. V., Robarts, R. D., & Korotova, L. G. Hexachlorocyclohexane use in the former Soviet Union //Archives of Environmental Contamination and Toxicology. – 2005. – Vol. 48. – P. 1-15.

10 Aliyeva, G., Halsall, C., Alasgarova, K., Avazova, M., Ibrahimov, Y., Aghayeva, R. The legacy of persistent organic pollutants in Azerbaijan: An assessment of past use and current contamination //Environmental Science and Pollution Research. – 2013. – Vol. 20. – P .1993-2008.

11 Wołejko, E., Łozowicka, B., Kaczyński, P., Jankowska, M., & Piekut, J. The influence of effective microorganisms (EM) and yeast on the degradation of strobilurins and carboxamides in leafy vegetables monitored by LC-MS/MS and health risk assessment // Environmental Monitoring and Assessment. –2015, -Vol. 188. –P. 1-14.

12 Walorczyk S. Development of a multi-residue method for the determination of pesticides in cereals and dry animal feed using gas chromatography-tandem quadrupole mass spectrometry // Journal of Chromatography A. –2008. –Vol. 1208. –P. 202-214.

13 Mastovska K., Dorweiler K. J., Lehotay S. J., Wegscheid J. S., Szpylka K. A. Pesticide multiresidue analysis in cereal grains using modified quechers method combined with automated direct sample introduction GC-TOFMS and UPLC-MS/MS techniques // Journal of Agricultural and Food Chemistry. –2010. –Vol. 58. –P. 5959-5972.

14 Balinova A., Mladenova R., Shtereva D. Solid-phase extraction on sorbents of different retention mechanisms followed by determination by gas chromatography-mass spectrometric and gas chromatography-electron capture detection of pesticide residues in crops // Journal of Chromatography A. –2007. –Vol. 1150. –P. 136-144.

15 Boccacci-Mariani M., Aiuto V., D, Giannetti V. Multiresidue method for the determination of organophosphorus pesticides in cereal matrixes //Journal of AOAC International. – 2010. – Vol. 93. – P. 999-1006.

16 Ballesteros-Gomes A., Rubio S., Recent Advances in Environmental Analysis // Analytical Chemistry. – 2011. – Vol. 83. – P. 4579-4613.

17 Goto T., Ito, Y., Yamada S., Matsumoto H., Oka H., Nagase H., Ito Y. High throughput analysis of no methyl carbamate pesticides in cereals and beans by dual countercurrent chromatography and liquid chromatography electrospray ionization tandem mass spectrometry //Journal of Liquid Chromatography & Related Technologies. – 2006. – Vol. 29. – P. 2651-2661.

18 Lee S. J., Park H. J., Kim W., Jin J. S., Abd E.A, Shim A. M., Shin J.H. Multiresidue analysis of 47 pesticides in cooked wheat flour and polished rice by liquid chromatography with tandem mass spectrometry //Biomedical Chromatography. – 2009. – Vol. 23. – P. 434-442.

19 Uygun U., Senoz B., Öztürk S., Koksel H. Degradation of organophosphorus pesticides in wheat during cookie processing //Food Chemistry. – 2009. – Vol. 117. – P. 261-264.

20 Uygun U., Özkara R., Özbey A., Koksel H. Residue levels of malathion and fenitrothion and their metabolites in postharvest treated barley during storage and malting // Food Chemistry. –2005. –Vol.100. –P. 1165-1169.

21 Hiemstra M., Kok de A. Comprehensive multi residue method for the target analysis of pesticides in crops using liquid chromatography-tandem mass spectrometry // Journal of Chromatography A. –2007. –Vol. 1154. – P. 3-25.

22 Vela G. N., Perez G., Navarro S. Gas chromatographic determination of pesticide residues in malt, spent grains, wort, and beer with electron capture detection and mass spectrometry //Journal of AOAC International. – 2007. – Vol. 90. – P. 544-549. PMID: 17474524.

23 Shin E.H., Choi J.H., Khay S., Kim S.J., Shim J. H. Simultaneous determination of three acidic herbicide residues in food crops using HPLC and confirmation via LC-MS/MS // Biomedical Chromatography. –2010. – Vol. 25. – P. 124-135.

24 Guler G.O., Cakmak Y. S., Dagli Z., Aktumsek A., Ozparlak H. Organochlorine pesticide residues in wheat from Konya region, Turkey // Food and Chemical Toxicology. – 2010. – Vol. 48. – P. 1218-1221.

25 Zhang W., Wu P., Li C. Study of automated mass spectral deconvolution and identification system (AMDIS) in pesticide residue analysis // Rapid communications in mass spectrometry. – 2006. – Vol. 20. – P. 1563-1568.

26 Chen J., Zhao W., Liu W., Zhou Z., Yang M. Cloud point extraction coupled with derivative of carbofuran as a preconcentration step prior to HPLC //Food Chemistry. – 2008. – Vol. 115. – P. 1038-1041.

27 Pang G.F., Liu Y.M., Fan C.L., Zhang J.J., Cao Y.Z., Li X. M. Simultaneous determination of 405 pesticide residues in grain by accelerated solvent extraction then gas chromatography-mass spectrometry or liquid chromatography-tandem mass spectrometry //Analytical and Bioanalytical Chemistry. –2006. –Vol. 384. –P. 1366-1408.

28 Carabias-Martínez R., Rodríguez-Gonzalo E., Miranda-Cruz E., Domínguez-Álvarez J., Hernández-Méndez J. Sensitive determination of herbicides in food samples by nonaqueous CE using pressurized liquid extraction //Electrophoresis. – 2007. – Vol. 28. – P. 3606-3616.

29 Soler C., Hamilton B., Furey A., James K.J. (2007). Liquid chromatography quadrupole time-of-flight mass spectrometry analysis of carbosulfan, carbofuran, 3-hydroxycarbofuran, and other metabolites in food // Analytical Chemistry. – 2007. – Vol. 79. – P. 1492-1501.

30 Cho S.K., Abd El-Aty A. M., Park Y.S., Choi J.H., Khay S., Kang C.A., Shim J.-H. A multiresidue method for the analysis of pesticide residues in polished rice (Oryza sativa L.) using accelerated solvent extraction and gas chromatography and confirmation by mass spectrometry //Biomedical Chromatography. –2007. –Vol. 21. –P. 602-609.

31 Marchese S., Perret D., Bafile E., Gentili A., Caretti F., Berardino M. Pressurized liquid extraction coupled with LC–ESI–MS–MS for the determination of herbicides chlormequat and mepiquat in flours //Chromatographia. –2009. –Vol. 70. –P. 761-767.

32 Brutti M., Blasco C., Picó Y. Determination of benzoylurea insecticides in food by pressurized liquid extraction and LC-MS //Journal of Separation Science. – 2009. – Vol. 33. – P. 1-10.

33 Zhang W.G., Chu X.G., Cai H.X., An J., Li C.J. Simultaneous determination of 109 pesticides in unpolished rice by a combination of gel permeation chromatography and Florisil column purification, and gas chromatography/mass spectrometry //Rapid Communications in Mass Spectrometry. – 2006. – Vol. 20. – P. 609-617.

34 Navarro S., Pérez G., Navarro G., Mena L., Vela N. Decay of dinitroaniline herbicides and organophosphorus insecticides during brewing of lager beer //Journal of Food Protection. – 2206. – Vol. 69. – P. 1699-1706.

35 Lee W. Y., Lee E. K., Kim Y. J., Park W. C., Chung T., Lee Y. T. Monoclonal antibody-based enzyme-linked immunosorbent assays for the detection of the organophosphorus insecticide isofenphos //Analytica Chimica Acta. – 2005. – Vol. 557. – P. 169-178.

36 Chen L. S. Shi Z., Shan Q. Determination of organochlorine pesticide residues in rice and human and fish fat by simplified two-dimensional gas chromatography //Food Chemistry. – 2006. – Vol. 104. – P. 1315-1319.

37 Esparza X., Moyano E., Galceran M. T. Analysis of chlormequat and mepiquat by hydrophilic interaction chromatography coupled to tandem mass spectrometry in food samples //Journal of Chromatography A. – 2009. – Vol. 1216. – P. 4402-4406.

38 Takatori S., Okihashi M., Okamoto Y., Kitagawa Y., Kakimoto S., Murata H., Sumimoto T., Tanaka Y. A rapid and easy multiresidue method for the determination of pesticide residues in vegetables, fruits, and cereals using liquid chromatography/ tandem mass spectrometry //Journal of AOAC International. – 2008. – Vol. 91. – P. 871-873. PMID: 18727548.

39 Chen L., Ding L., Jin H., Song D., Zhang H. The determination of organochlorine pesticides based on dynamic microwave-assisted extraction coupled with on-line solid phase extraction of high-performance liquid chromatography //Analytica Chimica Acta. – 2007. – Vol. 589. – P. 239-246.

40 Tsochatzis E.D., Menkissoglu-Spiroudi U., Karpouzas D. G., Tzimou-Tsitouridou R. A multi-residue method for pesticide residue analysis in rice grains using matrix solid phase dispersion extraction and high-performance liquid chromatography-diode array detection //Analytical and Bioanalytical Chemistry. – 2010. – Vol. 397. – P. 2181-2190.

41 Abhilash P.C., Singh V., Singh N. Simplified determination of combined residues of lindane and other HCH isomers in vegetables, fruits, wheat, pulses and medicinal plants by matrix solid-phase dispersion (MSPD) followed by GC–ECD //Food Chemistry. – 2008. – Vol. 113. – P. 267-271.

42 Djavanshir D., Bahram E., Mehrdad M., Mir Ali F. Evaluation of a new method for chemical coating of aluminum wire with molecularly imprinted polymer layer // Analytica Chimica Acta. – 2010. – Vol. 674. – P. 40-48.

43 Diana I.K., Osmar D. P., Martha B. A., Renato Z. Development of a fast multiresidue method for the determination of pesticides in dry samples (wheat grains, flour and bran) using QuEChERS based method and GC–MS // Food Chemistry. – 2011. – Vol. 125. – P. 1436-1442.

44 Jing L., Fengshou D., Jun X., Xingang L., Yuanbo L., Weili S., Yongquan Z. Enantioselective determination of triazole fungicide simeconazole in vegetables, fruits, and cereals using modified QuEChERS (quick, easy, cheap, effective, rugged and safe) coupled to gas chromatography/tandem mass spectrometry //Analytica Chimica Acta. – 2011. – Vol. 702. – P. 127-135.

45 Ji Y.H., Ya Q.H., Zi H.Z., Zhu B.D. Residue analysis of fluroxypyr-meptyl in wheat and soil by GC–ECD // Chromatographia. – 2011. – Vol. 74. – P. 291-296.

46 Zhang Y., Yang J., Shi R., Su Q., Yao L., Li P. Determination of acetanilide herbicides in cereal crops using accelerated solvent extraction, solid-phase extraction and gas chromatography-electron capture detector //Journal of Separation Science. – 2011. – Vol. 34. – P. 1675-1682.

47 Zhang Y., Yang J., Shi R., Su Q., Yao L. Development of an analytical method based on accelerated solvent extraction, solid-phase extraction clean-up, then GC–ECD for analysis of fourteen organochlorine pesticides in cereal crops //Chromatographia. – 2011. – Vol. 73. – P. 385-391.

48 Walorczyk S., Drożdżyński D. Improvement and extension to new analytes of a multi residue method for the determination of pesticides in cereals and dry animal feed using gas chromatography-tandem quadrupole mass spectrometry revisited //Journal of Chromatography A. – 2012. – Vol. 1251. – P. 219-231.

49 Rasche C., Fournes B., Dirks U., Speer, K. Multi-residue pesticide analysis (gas chromatography-tandem mass spectrometry detection). Improvement of the quick, easy, cheap, effective, rugged, and safe method for dried fruits and fat-rich cereals //Journal of Chromatography A. –2015. –Vol. 1403. –P. 21-31.

50 He Z., Wang L., Peng Y., Luo M., Wang W., Liu X. Multiresidue analysis of over 200 pesticides in cereals using a QuEChERS and gas chromatography–tandem mass spectrometry-based method // Food Chemistry. – 2014. – Vol. 169. – P. 372-380. .

51 Hou X., Han M., Dai X., Yang X., Yi S. A multi-residue method for the determination of 124 pesticides in rice by modified QuEChERS extraction and gas chromatography -tandem mass spectrometry // Food Chemistry. –2012. –Vol. 138. –P. 1198-1205.

52 Trivedi P., Sharma V. P., Srivastava L.P. Determination of organophosphorus pesticide residues in wheat and rice by QuEChERS method // Journal of environmental research and development. – 2014. – Vol. 8. – P. 859-866.

53 Wu L., Song Y., Xu X., Li N., Shao M., Zhang H., Wang Z. Medium-assisted non-polar solvent dynamic microwave extraction for determination of organophosphorus pesticides in cereals using gas chromatography-mass spectrometry //Food Chemistry. – 2014. – Vol. 162. – P. 253-260.

54 Du X., Ren Y., Beckett S. J. An innovative rapid method for analysis of 10 organophosphorus pesticide residues in wheat by HS-SPME-GC-FPD/MSD //Journal of AOAC International. – 2016. – Vol. 99. – P. 520-526.

55 Omena E., Oenning A. L., Merib J., Richter P., Rosero-Moreano M., Carasek E. A green and simple sample preparation method to determine pesticides in rice using a combination of SPME and rotating disk sorption devices //Analytica Chimica Acta. – 2019. – Vol. 1069. – P. 57-65.

56 Herrmann S. S., Poulsen, M. E. Clean-up of cereal extracts for gas chromatography -tandem quadrupole mass spectrometry pesticide residues analysis using primary secondary amine and C18 //Journal of Chromatography A. – 2015. – Vol. 1423. – P. 47-53.

57 Arthur C. L., Pawliszyn J. Solid phase microextraction with thermal desorption using fused silica optical fibers // Analytical Chemistry. – 1990. – Vol. 62. – P. 2145-2148.

58 Risticevic S., Niri V. H., Vuckovic D., Pawliszyn J. Recent developments in solid phase microextraction // Analytical and Bioanalytical Chemistry. – 2009. – Vol. 393. – P. 787-795.

59 Fatima de Alpendurada M. Solid-Phase Microextraction: A promising ´ technique for sample preparation in environmental analysis //Journal of Chromatography A. – 2000. – Vol. 889. – P. 3-14.

60 Fytianos K., Drimaropoulou G., Raikos N., Theodoridis G., Tsoukali H. Headspace solid phase microextraction for the gas chromatographic analysis of organophosphorus insecticides in vegetables // Journal of AOAC International. – 2007. – Vol. 90. – P. 1677-1682.

61 Cortes-Aguado S., Sanchez-Morito N., Arrebola F.J., Frenich A.G., Vidal J.L.M. Fast screening of pesticide residues in fruit juice by solid-phase microextraction and gas chromatography-mass spectrometry //Food Chemistry. – 2007. – Vol. 107. – P. 1314-1325. .

62 Chai M.K., Tan G.H. Validation of a headspace solid-phase microextraction procedure with gas chromatography-electron capture detection of pesticide residues in fruits and vegetables //Food Chemistry. –2009. –Vol. 117. –P. 561-567.

63 Feng J., Tang H., Chen D.Z., Wang G.N., Li L. Determination of pesticides in tea by isotope dilution gas chromatography-mass spectrometry coupled with solid-phase microextraction //Analytical Methods. –2012. –Vol. 4. –P. 4198-4203.

64 Saraji M., Rezaei B., Boroujeni M.K., Bidgoli A.A.H. Polypyrrole/sol-gel composite as a solid-phase microextraction fiber coating for the determination of organophosphorus pesticides in water and vegetable samples //Journal of Chromatography A. – 2013. – Vol. 1279. – P. 20-26.

65 Wang Y.L., Gao Y.L., Wang P.P., Shang H., Pan S.Y., Li X.J. Sol-gel molecularly imprinted polymer for selective solid phase microextraction of organophosphorous pesticides // Talanta. – 2013. – Vol. 115. – P. 920-927.

66 Melo A., Aguiar A., Mansilha C., Pinho O. Optimization of a solid phase microextraction/HPLC/diode array method for multiple pesticide screening in lettuce //Food Chemistry. – 2012. – Vol. 130. – P. 1090-1097.

67 Zeng J., Chen J., Lin Z., Chen W., Chen X., Wang X. Development of polymethylphenylsiloxane-coated fiber for solidphase microextraction and its analytical application of qualitative and semi-quantitative of organochlorine and pyrethroid pesti-

cides in vegetables //Analytica Chimica Acta. –2008. –Vol. 619. –P. 59-66. Chai M. K., Tan G. H., Asha I. Optimization of headspace solidphase microextraction for the determination of pesticide residues in vegetables and fruits //The Malaysian Journal of Analytical Sciences. – 2008. – Vol. 24. – P. 273-276.

68 Chai X., Jia J., Sun T., Wang Y. Suitability of a novel circulating cooling spme for analysis of organophosphorous pesticides in tomatoes // Chromatographia. – 2008. – Vol.67. – P.309-313.

69 Menezes F. A., dos Santos F. N., de Paula Pereira P. A. Development, validation and application of a methodology based on solid-phase micro extraction followed by gas chromatography coupled to mass spectrometry (SPME/GC-MS) for the determination of pesticide residues in mangoes //Talanta. –2010. –Vol. 81. –P. 346-354.

70 Guillet V., Fave C., Montury M. Microwave SPME method to quantify pesticide residues in tomato fruits //Journal of Environmental Science and Health. – 2009. – Vol. 44. – P. 145-122.

71 Tomasz Rejczak, Tomasz Tuzimski A review of recent developments and trends in the QuEChERS sample preparation approach // Open Chemistry. – 2015. – Vol. 13. – P. 980-1010.

72 Kaewsuya P., Brewer W.E., Wong J., Morgan S.L., Automated QuEChERS tips for analysis of pesticide residues in fruits and vegetables by GC-MS //Journal of Agricultural and Food Chemistry. – 2013. – Vol. 61. – P. 2299- 2314.

73 Bar-Helgouach C. Quality control of cereals and pulses: Practical Guide. – France, Arvalis, 2012 – P. 268. – ISBN: 2-86492-618-0.

74 Alimzhanova, M., Nurzhanova, Y. Screening of endocrine disruptors in water samples by SPME-GC/MS //International Multidisciplinary Scientific GeoConference Surveying Geology and Mining Ecology Management. – Bulgaria, 2015. – Vol. 2. – P. 441-446.

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ДӘНДІ ДАҚЫЛДАРДАҒЫ ПЕСТИЦИДТЕРДІ ТАЛДАУДЫҢ ЖАСЫЛ ӘДІСТЕРІ: ШОЛУ

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Пестицидтер XX ғасырдың ортасынан бастап бүкіл әлемде, ауыл шаруашылығында дәнді-дақылдарды және олардың туындыларын өндіру үшін пайдаланылуда. Көптеген пестицидтер, әсіресе фунгицидтер мен инсектицидтер әр түрлі аурулардың алдын алу және пісу кезінде өнімділікті арттыру үшін қолданылады. Пестицидтердің қоршаған ортаға шығарылуы химиялық ластаушы заттардың жалпы санының бір пайызын құрайды, бірақ бұл қосылыстар организмдердің белгілі бір топтарын, пестицидтер мен олардың трансформация өнімдерін басуға бағытталғанын ескере отырып, олар биотаның әр түрлі түрлеріне және ағзаға көкөністер мен жемістер арқылы еніп, оның ішінде олар нашар жуылған болса адам денсаулығына улы әсер етеді. Сонымен қатар, олар дәнді дақылдардан топырақтан сіңіп кету арқылы енеді. Қазіргі таңда, қауіпсіз пестицидтер жоқ, тіпті аз мөлшерде қолданған кезде де олар әртүрлі аллергиялық реакциялар мен улануды тудыруы мүмкін. Ауылшаруашылық өнімдерін өндіруде мақұлданған пестицидтер қолданылады, бірақ бұл препаратты ұзақ уақыт қолданудың жағымсыз салдары болуы мүмкін екендігін жоққа шығармайды. Демек, осы өнімдердегі пестицидтердің қалдықтарын үнемі бақылау адам денсаулығы мен қоршаған ортаға қауіпті азайтады. Сондықтан пестицидтердің қалдықтарын анықтаудың тиімді, жылдам және үнемді әдістері қажет. Мақалада дәнді дақылдардағы пестицидтерді талдауға сынама дайындау әдістері, сондай-ақ сынамаларды дайындауда экологиялық, жасыл химия әдістерінің бірі болып табылатын қатты фазалы микроэкстракция әдісінің ерекшеліктері көрсетілген.

Түйінді сөздер: дәнді-дақылдар, пестицидтер, сынаманы дайындау әдістері, қатты фазалы микроэкстракция әдісі, хроматография

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ЗЕЛЕНЫЕ МЕТОДИКИ АНАЛИЗА ПЕСТИЦИДОВ В ЗЕРНОВЫХ КУЛЬТУРАХ: ОБЗОР

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Пестициды используются во всем мире, начиная с середины XX века, для производства зерновых культур и их производных в сельском хозяйстве. Многие пестициды, особенно фунгициды и инсектициды, используются для предотвращения различных заболеваний и повышения урожайности во время созревания. Поступление пестицидов в окружающую среду составляет долю одного процента от общего количества химических загрязнителей, но, учитывая, что эти соединения нацелены на подавление определенных групп организмов, пестициды и продукты их трансформации оказывают токсическое воздействие на здоровье человека, попадая в организм с овощами и фруктами, в том числе с их поверхности, если плоды плохо вымыты и на различные формы биоты. А также, из злаков, так как они могут всасываться в них из почвы. Безопасных пестицидов не существует, даже при использовании в малых количествах они могут вызывать различные аллергические реакции и отравления. При производстве сельскохозяйственной продукции используются одобренные пестициды, но это не отменяет того факта, что у длительного использования препарата могут быть негативные последствия. Следовательно, постоянный мониторинг остаточного количества пестицидов в этих продуктах снижает риск для здоровья человека и окружающей среды. Поэтому необходимы эффективные, экспрессные и экономически выгодные методики определения остаточных количеств пестицидов. В статье отражены методы подготовки проб при анализе пестицидов в зерновых культурах, а также особенности метода твердофазной микроэкстракции одной из методов экологической, зеленой химии при подготовке проб.

Ключевые слова: злаки, пестициды, методы пробоподготовки, метод твердофазной микроэкстракции, хроматография.