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REVIEWS

Extraction Procedures in Gas Chromatographic Determination of Pesticides[1]

Yang Farina[a], *, Pauzi Bin Abdullah[a], and Nusrat Bibi[b], **

[a] *Centre for Water Research and Analysis (ALIR) Faculty of Science and Technology, University Kebangsaan Malaysia 43600 Bangi, Malaysia*

[b] *Department of Chemistry Faculty of Science, Sardar Bahadur Khan Women University Quetta, Pakistan*

**e-mail: farina@ukm.edu.my*

***e-mail: nusratmunawarsbku@gmail.com*

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Abstract—Pesticides are necessary for increasing agricultural productivity; however, their enormous use contaminates air, water and food. Among various organic pesticides, organochlorine pesticides (**OCPs**) are most persistent; and though their use is banned, they are still used illegally. In contrast to OCPs, organophosphorous pesticides are less persistent and used most extensively, while synthetic pyrethroid pesticides are the least toxic and used as insecticides. Extensive use of these pesticides is vulnerable to the ecosystem. Various extraction methods are used worldwide both by the regulatory bodies and private laboratories for the determination of multi-residue pesticides in leafy vegetables. This mini review presents an update on extraction procedure in gas chromatographic methods of pesticides analysis in various samples with special emphasis on leafy vegetables. We have covered six years of work from 2008–2013, discussing various extraction methods and their applications.

Keywords: gas chromatography, pesticide, sextraction methods, vegetables

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Classification of pesticides and its effect on the environment and human beings. Green leafy vegetables are a good source of vitamins, minerals, and protein, and they are low in fat content [1]. Leafy vegetables are a source of nitrates that play an important role in human physiology by healing wounds, reducing blood pressure, hypertension, reducing the chances of cardiovascular diseases, and also act as antioxidants thus preventing radicals that act on such biomolecules as fats, deoxyribonucleic acids, and proteins [2, 3]. However, these vegetables are often contaminated by pesticides known to be the first generation pesticides including sulphur, arsenic, mercury, lead etc. Later on came the second generation of pesticides that includes organochlorine, organophosphate, pyrethroid and many other pesticides used for increasing crops and improve quality of products. More than 800 pesticides have been used belonging to more than 100 different classes in which United States is the main consumer followed by India and France; Europe accounts $30 billion of world market, i.e. one third, while Asia and North America share 25% of world market [4–6].

Pesticide is a general term that includes a variety of chemical and biological products used to kill or control pests such as rodents, insects, fungi and weeds [7]. In 2006 and 2008, the world used approximately 5.2 billion pounds of pesticides with herbicides constituting the majority of the world pesticide use, with 40% followed by insecticides and fungicides with totals of 17 and 10%, respectively. Pesticide exposure can cause a variety of adverse health effects [8]. These effects can range from simple irritation of the skin and eyes to more severe effects such as affecting the nervous system, mimicking hormones causing reproductive problems, and also causing cancer. Strong evidence also exists for other negative outcomes from pesticide exposure including neurological birth defects [9] and neuro-developmental disorder [10].

Pesticides are broadly classified into two groups: 1—chemical pesticides and 2—biopesticides. Chemical pesticides are conventionally synthetic materials that directly kill or inactivate the pest. These are further classified according to the type of organisms they act against, for example, i—herbicides, ii—insecticides, iii—fungicides, iv—rodenticides, v—nematicides [11–14]. In the following section, their main physicochemical properties and principal uses are briefly described.

Herbicides can be classified as soil- or foliage-applied compounds, which are normally absorbed by roots or leaf tissues, respectively. These compounds can be total or selective herbicides. Total herbicides

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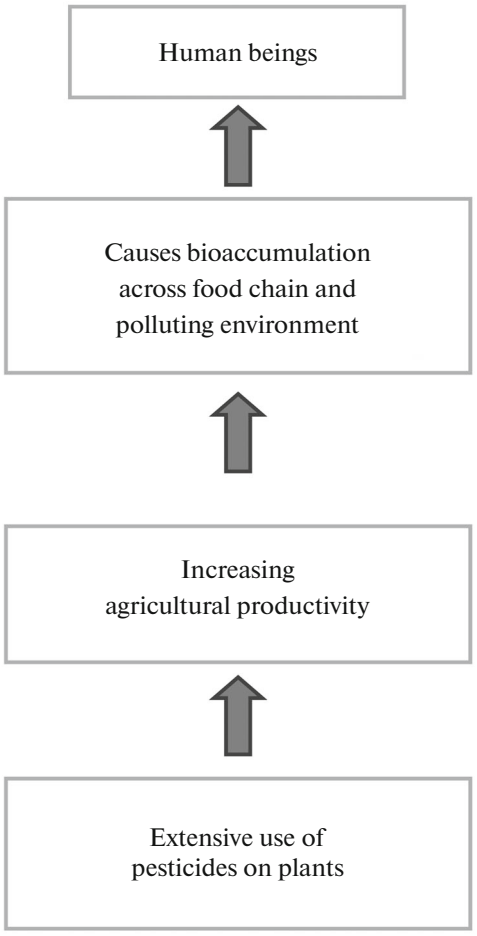

Percolation of pesticides from plants to human beings.

can kill all vegetation, whereas selective herbicides can control weeds without affecting the crop. These chemical substances (e.g. 2,4-D, 2,4,5-T), dinitrophenols like 2-methyl-4,6-dinitrophenol, bipyridyl compounds like paraquat, carbamate herbicides, substituted ureas, triazines and amide herbicides like alanine derivatives.

Insecticides are widely used to control pests in crops. These compounds may be applied to the soil to kill soil-borne pests, or to the aerial part of the plant. A major part of the applied insecticides reaches the soil either by direct application to the soil or indirectly by runoff from leaves and stems. Insecticides include organophosphates (TEPP, parathion, trimesters of phosphates and phosphoric acids), carbamates (aldicarb), organochlorines (dichlorodiphenyltrichloroethane, chlordane, aldrin, dielrin, lindane, endrin) and botanical insecticides (nicotine, rotenoids, pyrethrum).

Fungicides that are used in agriculture to control plant diseases belong to various chemical classes. A wide variation of physicochemical properties of these substances can be observed, according to the different chemical structures such as cap tan, folpet, pentachlorophenol, ziram, nambam etc. Fungicides containing mercury are known to cause nerve disorders. Rhodenticides are designed to kill rodents, mice, squirrels, gophers and other small animals. They vary from highly toxic ones with the ability to kill an organism with one-time dose or less toxic ones requiring repeated ingestion over a period of time.

Nematicides act against nematodes such as *Meloidogyne incognita, Criconemella xenoplax* etc.

Biopesticides fall into three major classes:

1—Microbial pesticides consist of microorganisms such as bacteria, fungi, viruses or protozoa as active ingredients. They can control many different kinds of pests, although each with separate active ingredient that is relatively specific for its target pest(s).

2—Plant-incorporated-protestants (PIPs) are pesticidal substances that are produced by genetically modified plants, for example, introduction of botulinus toxin gene in the cotton plants.

3—Biochemical pesticides are naturally occurring substances that control pests by non-toxic mechanisms (e.g., for insect sex pheromones that interfere with mating as well as various scented plant extracts).

Biopesticides are environmentally safe and non-toxic to plants and animals. However, their use is limited due to i—less social awareness, ii—comparatively lower crop yields, iii—need for frequent applications and iv—less worked research area. It is true that proper usage of these pesticides is beneficial for crops; however, improper usage might be hazardous for environment and human health [15], and it is also an ecological principle that whatever we dump in the environment returns back to us, as shown in the flow diagram (figure).

Effect of these pesticides depends upon their solubility in water, concentration and organic content of soil. The roots of plant up take the persistent pesticides [16]. Leafy vegetables have large surface area that allows their contamination through the cuticle of leaves. Secondly, they are cultivated close to ground, so volatile pesticides can deposit from soil on these leaves, as this is also one of the pathway of adsorption of these pesticides in plants [1]. Farmlands cultivating leafy vegetables should not be irrigated with waste water for long periods of time, as that might result in food-borne illnesses and microbiological contamination [17, 18].

The data of European Union of pesticides action network of 2008 showed that some 350 different pesticides in food were produced in European Union and about 5% of these exceeded the maximum permitted limits [19]. Pesticides such as organophosphates, organochlorine and pyrethroid come under the synthetic organic pesticides have many toxic effects on both human beings and the environment. Organochlorine pesticides that come under the persistent organic pollutants biomagnify across the food web

causing cancer, birth defects, immune system disruption, it disables the learning abilities, effects the reproductive system and causes neurological disorder in human beings and animals. OCPs are also responsible for the thinning of egg shells and reducing the level of hormone in female birds for laying eggs [10, 20–22]. Organophosphorous pesticides (**OPPs**) having low persistence and high effectiveness—make their use as insecticides—are acetyl cholinesterase inhibitors. OPPs cause diarrhea, headache, respiratory problems effecting children memory and also responsible for Parkinson disease [23, 24]. Pyrethroid pesticides are similar in function as OCPs but less toxic and persistent and are respiratory allergens causing asthma, breast cancer, skin itching, nausea sneezing and paralysis if ingested orally [24].

Sample preparation. Analytical process in gas chromatography (**GC**) relies on strategy beginning with representative sample collection, sample handling protocols and appropriate guidelines to achieve the goals of analysis. Sample preparation consists of homogenization, extraction and cleanup steps. In food samples, homogenization needs special precautions to decrease pesticides losses [25]. The addition of dry ice, the quality of chopper and the use of an appropriate sample size are also important in achieving complete homogenization. Extraction is then applied to separate the analytes from the matrix and bring it in a form that can be analyzed. Extraction strategies are aimed at exhaustive extraction and dividing the analytes into different classes by means of several group extractions with extractants of different polarity. The choice of solvents in this regard determines the selectivity of extraction. There are a variety of techniques to be used for extraction [26]. For multiresidues analysis, the most common solvents are acetone, acetonitrile, ethyl acetate and methanol. A novel approach is selective solid phase extraction (**SPE**) [27]. Once a liquid extract has been obtained, it is subsequently subjected to a purification step (namely cleanup), which is usually performed by SPE or liquid–liquid extraction. In some cases, extraction and cleanup procedures can be performed in a unique step (i.e., SPE with selective sorbents), which enormously simplifies the sample preparation procedure.

Gas chromatography is the most frequently used instrument for pesticide analysis. Its high resolving power by column, sensitivity and specificity of its detectors and the ability to connect to mass-spectrometry (**MS**) allows the detection of pesticide residues up to 0.1 μg/L [28]. GC was initially used with different detectors that gave response on the basis of heteroatoms present in analyte such as electron capture detector (**ECD**), nitrogen–phosphorus detector (**NPD**) or thermionic specific detector (TSD), flame photometric detector (**FPD**), thermal conductivity detector (TCD), flame ionization detector (FID). However, with the arrival of GC–MS, the determination of multi-residues of pesticides became easy and more reliable for confirmation and identification. The analyte could be identified on the basis of fragmentation pattern of its mass spectrum, either in full scan mode (FSM), selective ion monitoring (SIM) or selective reaction monitoring (SRM). The use of GC–MS was initiated in 1990 for multi-residue pesticide analysis and is now a standard method for quantification and identification of analytes in complex matrices [29].

GC–MS has the ability to analyze hundreds of pesticides mixture without using high resolution mass analysis. Numerous detectors have been used with the GC and among all the important detector is accurate mass MS. The accurate mass MS provides empirical formula for molecular and fragment ions that helps in absolute identification [30]. The selectivity and sensitivity of the determination of pesticides has improved by multidimensional MS (MS/MS). GC procedure has been modified to improve the sensitivity and selectivity by introducing concurrent solvent recondensation (CRC) using large volume injections [31]. GC–GC is also very popular in reducing the matrix coextractives in making identification of analysis more accurate in complex matrices [32].

Multi-residue analysis of pesticides basically covers the wide range of residues through multiresidue methods (MRM), the first step is to make a homogenized sample followed by extraction of pesticides from sample matrix, removal of co-extracted water from the sample matrix, cleanup by SPE and finally determination by GC and liquid chromatographic techniques [33]. Then most common organic solvents used for extraction of pesticides from vegetables are acetone, acetonitrile and ethyl acetate [34]. Table illustrates the extraction methods used in gas chromatographic determination of pesticides.

Pesticides have no doubt played a huge role in increasing the crop yield. However, they could be dangerous for human beings and other animals if used extensively exceeding the maximum residue limit, as this is a pathway through which these toxic compounds transfer through a food chain. The toxicity of pesticides is highest at the top of trophic level that is the consumer's level. Therefore, it is important to determine the residue concentration in the vegetables to prevent the risk associated with it to the consumers. This review is basically to summarize various types of extraction methods for the determination of multiresidue of pesticides in leafy plants by using GC technique.

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Extraction methods in gas chromatographic for the determination of pesticides

Sample matrix	Analyte	Extraction method	Technique	LOD	LOQ	Reference
Lettuce, cucumber, tomato etc.	Multi-residue class	15 g sample + 10 mL acetonitrile + centrifuged for 1 min + 6 g anhydrous $MgSO_4$ + 1.5 NaCl + 1.5 g trisodium citrate + vortexed for 1 min + centrifuged for 5 min + upper layer centrifuged containing PSA + anhydrous $MgSO_4$ + shaken for 30 s by hand + centrifuged for 5 min	GC–MS	NR	0.001–0.003 mg/kg	[4]
Lettuce, cabbage, onion cucumber etc.	Multi-residue class	20 g sample + 40 mL ethylacetate + 5 g $NaHCO_3$ + 20 g anhydrous Na_2SO_4 + centrifuged (5 min) at 3000 rpm + supertanat cleaned by florisil and eluted with 10 mL ethyl acetate and concentrated and redissolved in 1 mL ethyl acetate	GC–ECD	0.001 mg/kg	NR	[15]
Spinach, lettuce, cabbage and tomato etc.	Organophosphates pesticides	20 g sample + anhydrous Na_2SO_4 shaken + 40 mL ethyl acetate + 5 g $NaHCO_3$ + Na_2SO_4 shaken for 1 h + filtered centrifuged at 1800 rpm for 5 min than 1 : 1 mixture ethyl acetate–hexane was added to organic layer + cleaned with activated silica gel topped up with anhydrous Na_2SO_4 + eluted with 2 mL of hexane thrice	GC–ECD, GC–MS	NR	NR	[16]
Spinach, lettuce, cabbage, mustard etc	Organochlorine insecticides	20 g sample + 20 g anhydrous Na_2SO_4 + Soxhlet extracted with 200 mL hexane–acetone for 48 h + concentrated + 10 mL hexane added and concentrated to 2 mL cleaned by C18 cartridge with 70 mL acetone–dichloromethane (7 : 3) + concentrated to 0.2 mL redissolved in 1 mL *n*-hexane	GC–MS	NR	NR	[17]
Lettuce, Swiss chard, spinach	Multi-residue class	10 g sample + 30 mL acetonitrile homogenized in ultrasound bath (10 min) + shaked with $MaSO_4$ + NaCl (5 min) concentrated cleaned with ENVI-Carb/PSA eluted with 20 mL acetone–toluene (3 : 1, v/v) + concentrated and reconstituted with 0.5 mL of acetone + protectant added homogenized	GC–MS	Less than 0.01 mg/kg	Less than 0.01 mg/kg	[34]
Lettuce, squash, cabbage, green pepper etc.	Multi-residue class	10 g sample + 20 mL acetone blended (2 min) + centrifuged (3000 rpm for 5 min) + cleaned by PS-DVB and DEA columns eluted with ethyl acetate–acetone (90 : 10, v/v), concentrated to 1 mL and reconstituted to 2 mL of acetone	GC–MS	0.002–0.01 mg/kg	0.006–0.02 mg/kg	[35]

Table. (Contd.)

Sample matrix	Analyte	Extraction method	Technique	LOD	LOQ	Reference
Spinach, cauliflower, green chilies, tomato etc.	Multi-residue class	15 g sample + 30 mL dichloromethane homogenized for 2–3 min + 30 g anhydrous Na_2SO_4 rested for 3 min in ultrasound bath at 40°C + filtered in presence of anhydrous Na_2SO_4, concentrated and redissolved in 10 mL of cyclohexane	GC–MS	0.01–0.07 mg/kg	0.08–0.26 mg/kg	[36]
Spinach, cauliflower, cabbage, cucumber etc.	Lindane and HCH isomers	5 g of sample blended with different sorbent materials C8, C18, ENVI Carb, florisil and alumina for 5 min + 1 g $MgSO_4$ and 0.5 g NaCl + grounded and mixed for 5 min + alumina column deactivated with 3% acetone + anhydrous Na_2SO_4 different solvents were used for elution and concentrated, redissolved with 1 mL *n*-hexane	GC–ECD	3–6 ng/g	NR	[37]
Celery, rice, mung bean and snake bean	Organophosphates	5 g of sample added 15 mL acetone in centrifuge tube shaken in ultrasonic vibration for 30 min + again centrifuged at 4000 rpm for 10 min + supernatant concentrated under stream of N_2 and cleaned by GCB/PSA, eluting with 10 mL acetone–dichloromethane (1 : 1, v/v) and redissolved in 120 μL hexane	GC–FPD	8.8–13.6 μg/L	NR	[38]
Spinach, lettuce, green bean, broccoli etc.	Organochlorine	100 mg homogenized sample + 2 mL acetone followed by ultrasonication + centrifuged at 4000 rpm for 5 min + supernatant undergoes stir bar sorptive extraction after dilution with 30 ml of water at 1000 rpm for 180 min + stir bars dried desorption of analytes takes place by sonication for 15 min after immersing it in 1.5 mL of acetonitrile + concentrated and redissolved in 120 μL of hexane.	GC–MS	NR	0.001–44.5 μg/kg	[39]
Spinach, reddish, pumpkin, potato bean etc.	HCH isomers and DDT	10 g homogenized sample + anhydrous Na_2SO_4 Soxhlet extracted in 120 mL of acetone–dichloromethane (2 : 1, v/v) for 48 h + concentrated at 40°C up to 2 mL + transferred to separatory funnel with solvent *n*-hexane and 3 mL H_2SO_4 + cleaned by alumina:silica gel (1 : 2, v/v) eluted 3 times with 30 mL dichloromethane–hexane + concentrated	GC–ECD	NR	NR	[40]

Table. (Contd.)

Sample matrix	Analyte	Extraction method	Technique	LOD	LOQ	Reference
Spinach, lettuce, celery, green vegetables etc.	Multi-residue class	50 g sample + 100 mL acetonitrile added oscillated in vortex mixer followed by 2 min oscillation + 5 g NaCl + centrifuged at 3000 rpm for 5 min + concentrated to 1 mL + cleaned by ENVI Carb/NH_2 eluted with 5 ml acetone–methylbenzene (1 : 1, v/v) + concentrated redissolved in acetonitrile again concentrated up to 0.5 mL finally eluent redissolved to 1 mL	GC–ECD, GC–FPD	NR	0.0003–0.0008 mg/kg	[41]
Spinach, cabbage and shangai green	Organochlorine pesticides	10 g sample + 15 g anhydrous Na_2SO_4 + 20 g ethyl acetate centrifuged than blended at 3000 rpm for 2 min than shaked over water bath for 30 min at 25°C + supernatant filtered and centrifuged with by adding 0.05–0.1 g acidified activated carbon followed by shaking and filtering again + concentrated + cleaned with SPE eluted with hexane + concentrated	GC–NPD	NR	NR	[42]
Spinach, lettuce, swiss chards	Multi-residue class	10 g sample + 30 mL acetonitrile homogenized in ultrasound bath for 10 min + NaCl + anhydrous sodium magnesium sulphate + shaking and phase partitioning for 5 and 10 min + organic layer concentrated + cleaned with ENVI Carb/PSA + eluted with 20 mL acetonitrile–toluene (3 : 1, v/v) + concentrated + redissolved in 0.5 mL acetone, analyte protectant added	GC–MS	<0.01 mg/kg	<0.01 mg/kg	[43]
Lettuce, cabbage and leek	Organophosphates pesticides	10 g sample +10 mL acetonitrile shaken vigorously for 5 min by quecher method + 0.5 g disodium hydrogen citrate + 1 g trisodium citrate anhydrate + 4 g anhydrous $MgSO_4$ + 1 g of NaCl and hand shaken for 1 min followed by centrifugation at 4500 rpm for 2 min + extract transferred into a centrifuge tube containing 150 mg anhydrous $MgSO_4$, 12.5 GCB and 25 mg PSA than vortexed for 2 min at 4500 rpm + 1.5 mL supernatant acidified with 5% 50 μL formic acid + concentrated and redissolved in toluene	GC–MS	0.005-0.07 mg/kg	NR	[44]

Table. (Contd.)

Sample matrix	Analyte	Extraction method	Technique	LOD	LOQ	Reference
Spinach, cabbage, potato, onion etc.	Multi-residue class	10 g sample + 10 mL ethyl acetate + 4 g anhydrous $MgSO_4$ + 1 g NaCl + shaken at 50 rpm for 10 min + extract centrifuged at 10000 rpm for 10 min + cleaned by PSA, anhydrous $MgSO_4$ and activated charcoal + extract again shaken at 50 rpm for 10 min followed by centrifugation at 10000 rpm for 10 min + supernatant mixed with 5 μL acidified ethyl acetate	GC–ECD, GC–NPD	NR	0.001–0.009 mg/kg	[45]
Lettuce, spinach, orange, strawberry and plum	Multi-residue class	Quecher method applied	GC–MS	0.52–291.35 mg/kg	0.01–0.05 mg/kg	[46]
Lettuce, potato, strawberry, orange and tomato	Multi-residue class	15 g sample + 15 mL acetonitrile in centrifuge tube (unbuffered version) or add 1% methanol in 15 mL acetonitrile (buffered version) + shake for 30 s in hand + pour extracts in tube containing 6 g anhydrous $MgSO_4$ + 1.5 g NaCl (unbuffered) or 6 g anhydrous $MgSO_4$ + 1.5 g CH_3COONa (buffered version) + shake two versions for 1 min in hand and than at 3000 rcf for 2 min + if d-SPE used than transfer extract into it containing 150 mg anhydrous $MgSO_4$ + 50 mg C18 and 7.5 mg GCB vortex for 30 s + centrifuge at 3000 rcf for 2min + dissolve in acidified 50 uL acetonitrile or if disposable pipette extraction is used than also same procedure, centrifuge and dissolve in 50 μL acidified acetonitrile reduce extract to 0.5 mL	GC–MS	NR	10–25 ng/g	[47]
Spinach, celery, rape and scallion	Multi-residue class	20 g sample + 40 mL acetonitrile in centrifuge tube + blended at 15000 rpm for 1 min + 5 g NaCl + homogenized at 4200 rpm for 5 min + concentrated to 1 mL on rotary evaporator + cleaned by elut carbon/NH_2 eluted with 20 mL acetonitrile–toluene (3 : 1, v/v) + concentrated to 0.5 mL redissolved in 10 ml of hexane	GC–MS	NR	Below 10 ppb	[48]
Spinach, celery, lettuce, cabbage etc.	Multi-residue class	200 g sample + 100 mL ethyl acetate + 75 g anhydrous Na_2SO_4 + blended for 5 min + filtered through 20 g anhydrous Na_2SO_4 + residues washed with 50 mL ethyl acetate + concentrated + redissolved in 10 mL ethyl acetate	GC–ECD	NR	NR	[49]

Table. (Contd.)

Sample matrix	Analyte	Extraction method	Technique	LOD	LOQ	Reference
Spinach, raspberry, reddish sprouts, cereals etc.	Multi-residue class	Sample + acetonitrile + followed by salting with $MgSO_4$ + NaCl + cleanup by d-SPE, primary secondary amine and graphitized carbon black and primary secondary amine and octadecyl	GC–MS	NR	NR	[50]
Celery, lettuce, cabbage, cauliflower etc.	Multi-residue class	20 g sample + 50 mL acetonitrile + blended 2 min + filtered and shaken vigorously for 1 min with 5–7 g NaCl + rest for 10 min + 10 mL acetonitrile phase concentrated finally dissolved in 2 mL acetone for OPPs, and for pyrethroid cleaned with florisil eluted with hexane + concentrated and redissoved in 10 mL, 5% acetone–hexane	GC–FPD, GC–ECD	NR	NR	[51]
Lettuce, onion, green onion etc.	Organophosphates	4 g sample + 10 mL ethyl acetate–acetone (90 : 10, v/v) + 5 g anhydrous $MgSO_4$ + stirred for 10 min and allowed to rest for 10 min + concentrated	GC–NPD	NR	0.0027–0.008 mg/kg	[52]
Spinach, orange, nectarine etc.	Multi-residue class	10 g sample + ethyl acetate placed in accelerated solvent extraction cell of at 70°C and 10.34 MPa the static and preheating time was 3–4 min, time of contact with solvent was 5 min and flush volume 60% with 2 cycles + concentrated + anhydrous Na_2SO_4 added and redissolved 0.5 mL ethyl acetate but in case of spinach cleaned by gel permeation chromatography eluted with ethyl acetate–hexane (1 : 1, v/v) + concentrated and redissolved in ethyl acetate	GC–MS	0.01 mg/kg	0.0001–0.01 mg/kg	[53]
Spinach, cabbage, orange and grape	Multi-residue class	10 g sample + 10 mL acetonitrile + shaken vigorously for 1 min + 1 g anhydrous $NaSO_4$ + 4 g $MgSO_4$ + centrifugation at 3800 rpm for 5 min + 1 mL supernatant introduced in 2 mL microcentrifuge tube containing 10 g multi-walled carbon nano tubes + 150 g $MgSO_4$ + shaken for 1 min + centrifuged at 10000 rpm for 3 min + filtered for comparison PSA was also used for cleaning up	GC–MS	0.001–0.02 mg/kg	0.003–0.05 mg/kg	[54]
Spinach, lettuce, crown daisy, amaranth etc.	Chloripyrifos and cyhalothrin	10 g sample + 10 mL acetonitrile + centrifuged for 1 min + 4 g anhydrous $MgSO_4$ + 1 g NaCl + shaken vigorously for 1 min at 3800 rpm for 5 min + 1 mL supernatant + 20 mg PSA + 150 mg anhydrous $MgSO_4$ + shaken for 1 min + centrifuged at 10000 rpm for 3 min	GC–ECD	0.001–.01 mg/kg	NR	[55]

Table. (Contd.)

Sample matrix	Analyte	Extraction method	Technique	LOD	LOQ	Reference
Spinach, coriander leaves, cabbage etc.	Multi-residue class	10 g sample + 15 mL acetone–acetonitrile (50 : 50) + 0.1 mL acetic acid + sonicated + microwaved at 2 min ramp from 100–300 W (2 min hold), 2 min ramp from 300–100 W (2 min hold) + filtered through $NaSO_4$ + filtrate cleaned by PSA (100 mg) + $MgSO_4$ + vortexed + supernatant concentrated and redissolved in 0.5 mL ethyl acetate in case of high chlorophyll content vegetables like spinach, coriander etc. 200 mg PSA + graphitized carbon black was used for cleanup	GC–MS	0.025–0.1 mg/kg	0.002–0.02 mg/kg	[56]
Spinach, apple, orange, rice	Multi-residue class	15 g sample + 15 mL acetonitrile containing 1% glacial acetic acid + shaken for 30 s + 6 g anhydrous $MgSO_4$ + 1.5 g anhydrous sodium acetate + shaken for 1 min + centrifuged for 2 min at 3250 rcf + 8 mL extract transferred into d-SPE containing 0.4 g PSA + 0.4 g C18 + 0.06 g GCB + vortexed for 30 s and centrifuge at 3250 rcf for 2 min add 20 μL analyte protectant	GC–MS	NR	NR	[57]
Lettuce, cabbage, peach apple etc.	Multi-residue class	50 g sample containing higher water content and water was added to make the volume of total water up to 100 g, calculated by formula, $M(w) = 100 - M(s.\ x)/100$ + 100 mL acetone + homogenized for 2 min + 17.5 g NaCl + 50 mL mixture of cyclohexane–ethyl acetate (1 : 1, v/v) + homogenized for 2 min + 100 mL organic phase filtered through $NaSO_4$ (50 g) + rinsed by 10 mL ethylacetate–hexane + filtrate concentrated + redissolved in 7.5 mL ethyl acetate + salt mix 2.5 g anhydrous $NaSO_4$–NaCl (1 : 1) added + cleaned by GPC eluted with ethyl acetate–hexane(1 : 1, v/v), samples having less water content pH was adjusted to 7 + $NaHCO_3$ added and same procedure applied as above	GC–MS	NR	NR	[58]
Lettuce, orange, apple	Multi-residue class	20 g sample + 40 mL acetone extracted on polytron at 9500–9700 rpm + 40 mL dichloromethane + 40 mL crude petroleum, again processed on polytron at same speed + centrifuged at 2000 rpm for 5 min + 5 mL organic layer added to decane in light petroleum + 0.1 μg triphenylphosphate + dithalimphos + concentrated and redissolved in isoketone–toluene (9 : 1, v/v)	GC–MS	NR	0.02–0.1 mg/kg	[59]

Table. (Contd.)

Sample matrix	Analyte	Extraction method	Technique	LOD	LOQ	Reference
Spinach, broccoli, tomato etc	Multi-residue class	15 g sample + 15 mL acetonitrile + 6 g $MgSO_4$ + 1.5 g NaCl + shaken in hand for 2 min + centrifuged at 4500 rpm + supernatant transferred to centrifuge tube containing 50 mg C18 + 1.2 g anhydrous $MgSO_4$ + shaken for 1 min + centrifuged at 4500 rpm for 5 min + again 9 mL extract transferred to another centrifuge tube containing 400 mg PSA + 200 mg GCB containing +1.2 g anhydrous $MgSO_4$ + vortexed for 15 s + 3 mL toluene + vigorously shaken for 2 min + centrifuged at 4500 rpm for 5 min + concentrated + 1 mL toluene + 50 mg anhydrous $MgSO_4$ + vortexed at 1500 rpm	GC–MS	NR	NR	[60]
Spinach, orange, tomato etc.	Organophosphates	15 g sample + 15 mL acetonitrile + shaken for 1 min + 1.5 g NaCl + 6 g $MgSO_4$ + shaken vigorously for 2 min + centrifuged for 3 min at 3000 rpm + supernatant cleaned by PSA + GCB + $MgSO_4$ + 3 mL toluene added and vortexed for 30 s + centrifuged + supernatant evaporated to 0.2 mL and redissolved in toluene to make up volume up to 1 mL	GC–FPD	NR	NR	[61]
Spinach and ginseng	Multi-residue class	10 g sample +15 mL acetonitrile + 4 g $MgSO_4$ + 1 g NaCl + shaken vigorously for 1 min in geogrinder at 1000 strokes/min + centrifuged at 4500 rpm for 5 min + cleaned by GCB/PSA eluted with 12 mL acetone–toluene (75 : 25, v/v) + concentrated to 0.2 mL and redissolved to makeup volume 1 mL by internal standards	GC–MS	NR	NR	[62]
Spinach	Multiresi-due class	10 g sample +15 mL acetonitrile + shaked for 30 s + vortexed for 1 min + cooled on ice bath + 6 g anhydrous $MgSO_4$ + 1.5 g sodium acetate + shaked and vortexed for 1 min + centrifuged for 5 min at 4000 rpm + supernatant cleaned with PSA + anhydrous $MgSO_4$ (150 mg) vortexed for 1 min + centrifuged for 2 min + filtered	GC–MS	50–250 μg/kg	NR	[63]

Notations: LOD – limit of detection, LOQ – limit of quantification, NR – not reported.

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