Chapter 8

Sample Preparation Methods for Pesticide Analysis in Food Commodities, Biological and Environment Matrices

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Additional information is available at the end of the chapter

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Abstract

This chapter focuses on sample preparation procedures for pesticide analysis of food commodities, biological and environmental matrices. This will include pesticides with a broad range of polarity including those that are more amenable to gas chromatography-mass spectrometry (organochlorines, organophosphorus pesticides, and pyrethroids) and those commonly analyzed by liquid chromatography-mass spectrometry (carbamates, azole, and strobilurin fungicides, and phenylureas as well as organophosphorus pesticides). QuEChERS (quick, easy, cheap, effective, rugged, and safe) methods or QuEChERS methods with modifications to allow wetting of the dry sample matrix, buffering, changing extraction solvent from acetonitrile to ethyl acetate are examined. Subsequent cleanup using dispersive solid phase extraction or cartridge format solid phase extraction has also been completed to reduce matrix effects. Other solid matrices are frequently extracted with pressurized liquid extraction, microwave assisted extraction, or ultrasonic extraction combined with or followed by dispersive solid phase extraction or solid phase extraction. Particularly for chromatography-mass spectrometry, careful consideration of matrix effects needs to be made when considering the design of the sample preparation procedures. Selection of extraction solvent needs to consider both polarity of target analytes (and their solubility in selected solvents) as well as co-extracted matrix components.

Keywords: QuEChERS (quick, easy, cheap, effective, rugged, and safe) methods, solid phase extraction, gas chromatography-mass spectrometry (GC-MS), gas chromatography-tandem mass spectrometry (GC-MS/MS), liquid chromatography-tandem mass spectrometry (LC-MS/MS), azole fungicides, carbamates, organochlorines, organophosphorus pesticides (OPs), phenylureas, pyrethroids, strobilurin fungicides, metabolites, degradation products

1. Introduction

Gas chromatography-mass spectrometry (GC-MS), gas chromatography-tandem mass spectrometry (GC-MS/MS), and liquid chromatography-tandem mass spectrometry (LC-MS/MS) methods are used to analyze for azoles, carbamates, organophosphorus pesticides, pyrethroids, phenylureas, strobilurin fungicides, and other pesticides in a diverse range of sample matrices including food commodities, biological and environmental matrices. The chromatography-mass spectrometry choices for the analysis of these pesticides and others have been recently reviewed [1, 2]. Briefly, organochlorines (OCs), organophosphorus pesticides (OPs), and pyrethroids are frequently analyzed with GC-MS or GC-MS/MS methods. Analysis of azole fungicides, carbamates, neonicotinoids, phenylureas, and strobilurin fungicides is more often analyzed by LC-MS/MS methods. Use of liquid chromatography-electrospray ionization-mass spectrometry (LC-ESI^+-MS/MS) for analysis of OPs has also increased over the last 10 years [1]. This chapter will discuss selection choices for extraction and cleanup of sample extracts or preconcentration of target analytes prior to chemical analysis (chromatography-mass spectrometry methods) to minimize matrix enhancement or suppression observed in MS detection. The options for preconcentration or cleanup of sample extracts also depend upon whether the sample is a liquid or solid matrix, fat content, and water content. Modified QuEChERS and microwave and pressurized solvent extraction remain the most widely used extraction procedures with inclusion or subsequent cleanup using dispersive solid phase extraction (dSPE) or solid phase extraction (SPE) methods and will be the focus of discussions in this chapter.

2. Modified QuEChERS procedures and dispersive solid phase extraction

QuEChERS (quick, easy, cheap, effective, rugged, and safe) methods without buffer or with acetate or citrate buffer or other modified QuEChERS methods remain one of the most popular approaches to sample extraction and cleanup of food commodities (**Table 1**). This approach has also been applied to other solid sample matrices including bee products and soil as shown in **Table 1** [3–28]. **Figure 1** shows a comparison of the typical parameters used in various modified QuEChERS methods. Phase separation and partitioning of target analytes into the organic phase is generally achieved with addition of anhydrous $MgSO_4$ (subsequently noted as $MgSO_4$) and NaCl. Addition of NaCl improves the removal of acetonitrile from the aqueous phase and partitioning of polar analytes into acetonitrile [29]. The salt-out extraction is followed by cleanup of the extract with dispersive solid phase extraction (dSPE). Common dSPE sorbents include C18 or C8 for removal of lipids; florisil for removal of polar and low-fat co-extracts; graphitized carbon black (GCB) for removal of pigments and some fatty acids; primary secondary amine (PSA) for efficient removal of saccharides and organic acid as it is a weak anion exchanger; and Z-Sep (ZrO_2 bonded to silica) or Z-Sep+ (ZrO_2 and C18 both bonded to silica) for removal of lipids [15]. PSA has been reported to remove butanoic acid, decanoic acid, heptanoic acid, hexanoic acid, linoleic acid, and phytosterol (stigmasterol), while not effectively removing alkaloids (caffeine and theobromine) and γ-tocopherol [30]. The use of GCB with PSA, C18, and anhydrous $MgSO_4$ was found to improve recoveries for OPs and carbamates in egg matrix as compared to when GCB was not used [31].

QuEChERS (solvent, salts)	dSPE (solvent)	Sample matrix	Pesticides [recoveries]	Analysis method	Reference
ACN salt-out	PSA:C18:GCB (1:1:1) 50 or 125 mg (ACN followed by ACN/ toluene 3:1)	Pollen and single bumble pees	Neonicotinoids (acetamiprid, clothianidin, imidacloprid, thiacloprid, thiamethoxam) [81–87%, pollen; 88–96% bumble bee]; azoles (epoxiconazole, flusilazole, metconazole, tebuconazole, triticonazole) [81–102% pollen; 75–90% bumble bee]; strobilurin fungicides (fluoxastrobin, pyraclostrobin, trifloxystrobin) [71–87%, pollen; 74–82% bumble bee]; others (boscalid, carbendazim, carboxin, prochloraz, spiroxamine) [66–88%, pollen; 63–90% bumble bee].	LC-ESI$^+$-MS/MS	[3]
7.5 mL H_2O, 10 mL ACN, 6 g $MgSO_4$, 1 g NaCl	15 mg C18, 50 mg PSA, 50 mg $MgSO_4$ per mL of ACN extract	Honey bees	Azoles (imazalil, prochloraz, tebuconazole, thiabendazole) [77–96%]; Carbamates (carbendazim, carbofuran, methiocarb) [70–95%]; neonicotinoids (acetamiprid, imidacloprid, thiamethoxam) [80–92%]; OPs (azinphos ethyl, azinphos methyl, chlorfenvinphos, chlorpyrifos, coumaphos, diazinon, diclofenthion, dimethoate, ethion, fenitrothion, fenthion, malathion, omethoate, parathion-ethyl, parathion-methyl, triclofos-methyl) [70–95%]; phenylureas (diuron, isoproturon) [82–86%]; pyrethroids (flumethrin, fluvalinate) [84–93%]; triazines (atrazine, simazine, terbumeton, terbuthylazine) [80–91%]; Degradation products (atrazine-desethyl, atrazine-desisopropyl, carbofuran-3-hydroxyl, fenoxon-sulphone [70–75%],	LC-ESI$^+$-MS/MS	[4]

QuEChERS (solvent, salts)	dSPE (solvent)	Sample matrix	Pesticides [recoveries]	Analysis method	Reference
			fenoxon-sulfoxide, fenthion-sulfone, fenthion-sulfoxide [75–80%], terbumeton-desethyl, terbuthylazine-2-hydroxyl, terbuthylazine-desethyl [75–82%]) [80–94%].		
10 mL ACN, 3 mL hexane before salt addition		Honey bees Wetted (10 mL H_2O)	OPs (coumaphos, diazinon, dimethoate, heptenophos, methidathion, omethoate, oxydemeton-methyl, profenophos, pyrazophos, temephos) [70–93%]	LC-ESI$^+$-MS/MS	[5]
ACN, 4 g $MgSO_4$, 1 g NaCl, 1 g Na_3citrate dihydrate, 0.5 g Na_2Hcitrate sesquihydrate	PSA (25 mg), 150 mg $MgSO_4$ per mL extract	Pollen	Azole fungicides (bitertanol, bromuconazole, difenoconazole, diniconazole, epoxiconazole, fenbuconazole, flusilazole, flutriafol, hexaconazole, paclobutrazole, penconazole, prochloraz [70%], propiconazole, tetraconazole, etc.) [88–94%]; N-methylcarbamates (carbaryl, formetanate, methomyl, oxamyl, pirimicarb, propoxur) [93–96%]; Neonicotinoids (acetamiprid, clothianidin, imidacloprid, nitenpyram, thiacloprid, thiamethoxam) [average 96 and 107%]; OPs (azinphos methyl, demeton-s-methyl sulfone, diazinon, dicrotophos, dimethoate, ethio, ethoprophos, fenamiphos, fenthion degrades, malaoxon, methamidophos, phenofos, trichlorfon, etc.) [>70%]; Strobilurin fungicides (azoxystrobin, kresoxim-methyl, pyraclostrobin, trifloxystrobin) [77–107%]; Others (2,4-D, cyromazine, ethirimol, fipronil, pymetrozine) [35–66%].	LC-ESI$^+$-MS/MS	[6]
10 mL ACN +3 mL hexane (pollen); 10 mL			Neonicotinoids (acetamiprid, clothianidin,	LC-ESI$^+$-MS/MS	[7]

QuEChERS (solvent, salts)	dSPE (solvent)	Sample matrix	Pesticides [recoveries]	Analysis method	Reference
ACN for corn syrup with citrate buffer	50 mg PSA + 50 mg C18 + 150 mg $MgSO_4$	Pollen and high fructose corn syrup Wetted (1:4 dilution)	dinotefuran, flonicamid, imidacloprid, nitenpyram, thiacloprid, thiamethoxam) [>88–110%].		
ACN, 1% CH_3COOH, 6 g $MgSO_4$, 1.5 g NaOAc	0.6 g $MgSO_4$, 0.2 g PSA	Tomato	Azoles (bromuconazole, cyproconazole, difenconazole, diniconazole, epoxiconazole, flutriafol, hexaconazole, imazalil, myclobutanil, penconazole, propiconazole, thiaphanate methyl, triadimefon, triadimenol, triflumizole) [92–106%]; Carbamates (carbaryl, carbofuran, chlorpropham, cycloate, diethofencarb, ethiofencarb, fenoxycarb, methomyl, oxamyl, pirimicarb) [85–104%]; OPs (azinphos methyl, chlorpyrifos ethyl, chlorpyrifos methyl, diazinon, dimethoate, ethoprophos, fenthion, malathion, monocrotophos, omethoate, parathion methyl, pirimiphos methyl, prothiofos, thiometon) [83–109%]; strobilurin fungicides (azoxystrobin, kresoxim methyl, trifloxystrobin) [94–104%]; phenyl or benzoyl ureas (diuron; chlorfluazuron, hexaflumuron, lufenuron) [98–106%]; pyrethroids (bifenthrin, cypermethrin, deltamethrin, fenproprathrin) [93–112%]	LC-ESI^+-MS/MS	[8]
ACN, 4 g $MgSO_4$, 1 g NaCl	30 mg PSA, 150 mg $MgSO_4$	Leaf vegetable (pakchoi, rape, crown daisy, amaranth, spinach, lettuce)	Anilide fungicide (metalaxyl) [80–115%]; aryloxyphenoxypropionate herbicide (fluazifop-methyl) [83–119%]. OP (chlorpyrifos) [84–111%]; pyrethroid (Lambda-cyhalothrin) [81–117%].	LC-ESI^+-MS/MS GC-ECD	[9]
10 mL ACN, 4 g $MgSO_4$, 1 g NaCl	50 mg PSA, 100 mg $MgSO_4$	Fruits and vegetables (apple, cabbage, carrot, tomato)	Carbamates (aldicarb, baycarb, carbaryl, ethiofencarb, methiocarb); [88–120%]; OPs (azinphos-	LC-ESI^+-MS	[10]

QuEChERS (solvent, salts)	dSPE (solvent)	Sample matrix	Pesticides [recoveries]	Analysis method	Reference
			methyl, malathion, methidathion, pirimiphos-methyl [58–71%], etrimfos, pyraclofos, phosalone) [81–120%]; methiocarb-sulfone [72–87%]		
14 mL 1% CH_3COOH in ACN, 6 g $MgSO_4$, 1.4 g NaOAc, 4 g NaCl	All 900 mg $MgSO_4$ and 150 mg PSA >5% fat content also 150 mg C18 <5% colorless to pale extract color, no other sorbents <5% fat content with color (carotenoids/ chlorophyll content high) 45 mg GCB	Food commodities (citric fruits, vegetables, tree nuts, eggs, dairy products, meat, poultry, edible oils, chocolate, coffee, beverages)	OPs (acephate, azinphos-methyl, chlorpyrifos, chlorpyrifos-ethyl, diazinon, dimethoate, disulfoton, demeton-S, demeton-S methyl, ethion, fenamiphos, fenitrothion, fenthion, malathion, methamidophos, methidathion, mevinphos, monocrotophos, omethoate, formothion, parathion, parathion-methyl, phorate, phosalone, phosmet, phosphamidon, propetamphos, terbufos, tetrachlorvinphos, triazophos, trichlorfon, dicrotophos, edifenphos, fosthiazate, isofenphos-methyl, naled, phoxim profenofos, tolclofos-methyl, vamidothion, cadusafos, tribufos, coumaphos, dichlorvos, ethoprophos, isocarbophos, phenoate, quinalphos) PSA [84–107%]; PSA/C18 [83–111%]; PSA/GCB [83–110%] at 10 μg/kg; carbamates (aldicarb, benfuracarb, carbaryl carbofuran, EPTC, fenobucarb, formetanate HCl, isoprocarb, methiocarb, methomyl, molinate, oxamyl, pirimicarb, propamocarb, thiobencarb, thiocarb) PSA [83–106%]; PSA/C18 [85–111%]; PSA/GCB [87–110%] at 10 μg/kg; OP and carbamate degradates (sulfones, sulfoxides) and carbamate degrades (3-hydroxycarbofuran,	LC-ESI^+-MS/MS	[11]

QuEChERS (solvent, salts)	dSPE (solvent)	Sample matrix	Pesticides [recoveries]	Analysis method	Reference
			methiocarb) [92–114%] at 10 μg/kg		
(A) 10 mL 1% CH_3COOH in ACN, 4 g $MgSO_4$, 1 g NaCl, Method A, citrate buffer (1 g Na citrate dehydrate, 0.5 g Na_2H citrate sesquihydrate) (B) LLE with 1% HCOOH in acetone	SPE Oasis HLB	Milk (10 mL)	Azoles (azaconazole, epoxiconazole, fenbuconazole, paclobutrazol, thiabendazole, triflumizole) [(A) 82 to >130, (B) 35–114%]; carbamates (aldicarb, carbaryl, carbofuran, diethofencarb, iprovalicarb, methiocarb, methomyl, propamocarb, promecarb, thiophanate-methyl) [(A) <30 to >130%; (B) <30–138%]; neonicotinoids (acetamiprid, imidacloprid, thiacloprid) [(A) 67–123% (B) 83–124%]; benzoyl and phenylureas (diflubenzuron, isoproturon, linuron, metobromuron, metoxuron, monolinuron, pencycuron) [(A) 91 to >130%; (B) <30 to >130%]; sulfonyl ureas (chlorsulfuron, cinosulfuron, iodosulfuron methyl, triasulfuron, thifensulfuron methyl (A) <30–107%; (B) [<30–87%]; triazines (atrazine, metribuzin, propazine, sebuthylazine, simazine, terbuthylazine) [(A) 63 to >130%; (B) <30 to >130%].	LC-ESI^+-MS/MS	[12]
15 mL ACN with6.0 g $MgSO_4$ and 1.5 g NaCl	SPE Envicarb (GCB) + SPE Silica (pyrethroids) SPE C18 (pyrethroid degradates)	15 g (A) lettuce, pepper, onion, carrot, broccoli (B) Apple, grape, tomato, orange, banana	Pyrethroids (bifenthrin, cyfluthrin, cyhalothrin, cypermethrin, deltamethrin, esfenvalerate, permethrin) [(A) 49–11%; (B) 50–115%]; pyrethroid metabolites (3-PBA, DCCA, 4-F-3-PBA, DBCA, MPA [(A) 73–136%, (B) 61–121%])	LC-ESI^+-MS/MS	[13]
10 mL ACN rinse with 1 mL ACN, citrate buffer (4 g $MgSO_4$, 1 g NaCl, 0.5 g Na_2Hcitrate-	High fat (wheat flour, rolled oats, wheat germ):	Wheat flour and wheat germ shown %	OCs and other halogenated pesticides (aldrin, alachlor, benfluralin, dichlobenil, dieldrin (58–76%),	GC-EI-MS/MS	[14]

QuEChERS (solvent, salts)	dSPE (solvent)	Sample matrix	Pesticides [recoveries]	Analysis method	Reference
1.5H_2O, 1 g Na_3citrate dihydrate	salt, PSA, C18 Rich in carotene and chlorophyll (red pepper): salt, PSA, GCB Others (fruits and vegetables) salt, PSA		heptachlor, HCHs, heptachlor epoxide, hexachlorobenzene (42–77%), endosulfan, endosulfan sulfate, iprodione, pendimethalin, trifluralin, triallate, vinclozolin) [most > 80–105% exceptions in brackets]; OPs (bromfenvinphos-methyl, bromophos-methyl, chlormephos, chlorpyrifos, coumaphos, diazinon, dichlorvos, heptenophos, ethoprophos, fenchlorphos, fenthion, fenitrothion, isofenphos, isofenphos-methyl, malathion, mevinphos, parathion, parathion-methyl, tolclofos-methyl) [>80%]; pyrethroids (λ-cyhalothrin, cypermethrin, deltamethrin, esfenvalerate, fenvalerate, flucythrinate, permethrin) [72–103%]		
EtOAc or ACN, 4 g $MgSO_4$, 1 g NaOAc	100 mg PSA, GCB, Zr-Sep+ or C18 or mix of all at 50 mg each	Soya-based nutraceutical–wetted	78–92% of pesticides in 70–120% with ethyl acetate; 3–28% with acetonitrile	GC-EI-MS/MS	[15]
15 mL 1% CH_3COOH in ACN, 6 g $MgSO_4$, 1.5 g NaOAc	200 mg PSA, 600 mg $MgSO_4$	Parsley, lettuce, spinach	Azoles (cyproconazole, difenoconazole, epoxiconazole, penconazole, propiconazole, tebuconazole, triadimefon, triadimenol, triflumizole) [90–100%]; carbamates (carbaryl, carbofuran, carbosulfan, ethiofencarb, fenoxycarb, methiocarb, oxamyl, pirimicarb) [78–111%]; OPs (chlorpyrifos, diazinon, dichlorvos, malathion, dimethoate, profenofos, prothiofos) [86–106%]; pyrethroids (bifenthrin, cypermethrin, deltamethrin, tau-fluvalinate) [98–102%];	LC-ESI^+-MS/MS	[16]

QuEChERS (solvent, salts)	dSPE (solvent)	Sample matrix	Pesticides [recoveries]	Analysis method	Reference
			neonicotinoids (acetamiprid, imidacloprid, kresoxim-methyl, thiamethoxam) [77–91%]; strobilurin fungicides (azoxystrobin, trifloxystrobin) [87–103%].		
15 mL EtOAc, 4 g $MgSO_4$, 1.5 g NaCl	Freeze-out, 100 mg Al2O3, 60 mg C18, 600 mg $MgSO_4$	(5 g) bovine liver and muscle	Azoles (tebuconazole, tebufenozide) [73–109%], Benzoylphenylurea (triflumuron) [77–91%]; neonicotinoids (thiacloprid, thiamethoxam) [71–85%]; strobilurin fungicide (trifloxystrobin) [82–94%], other (Spinosyn D) [70–78%]	LC-ESI^+-MS/MS and GC-EI-MS	[17]
ACN, 4 g $MgSO_4$, 1g NaCl, 0.6 g Na_2Hcitrate sesquihydrate, 1 g Na_3citrate dihydrate	Freeze-out followed by dSPE with 25 mg PSA and 150 mg $MgSO_4$	Wheat flour (wetted), fruits and vegetables	Organophosphorus pesticides (chlorpyrifos, chlorpyrifos-methyl, fenitrothion, malathion quinalphos) [wheat flour 99–104%]; pyrethroids (bifenthrin, λ-cyhalothrin) [wheat flour 93–99%]; strobilurin fungicides (azoxystrobin, trifloxystrobin) [wheat flour 103–106%] Azoles (difenconazole, tebuconazole) [88–96%]; carbamates (aminocarb, fenobucarb, prochloraz, propamocarb, thiobencarb) [73–108%]; neonicotinoids (acetamiprid, clothianidin, imidacloprid, nitenpyram, thiacloprid, thiamethoxam) [wheat flour 76–102%]; phenylureas (diflubenzuron, flufenoxuron, lufenuron, monolinuron) [wheat flour 86–98%]	GC-EI-MS/MS LC-ESI^+-MS/MS	[18]
10 mL ACN, 4 g MgSO4, 1 g NaCl	1 g EMR-Lipid, 1.6 g $MgSO_4$, 1 g NaCl	10 g olive oil or avocado	Azoles (difenoconazole, paclobutrazol, penconazole, tebuconazole, tetraconazole) [76–116%]; carbamates (carbaryl, carbendazim, carbofuran, methomyl) [77–117%]; OPs (acephate, azinphos-	LC-ESI^+-MS/MS	[19]

QuEChERS (solvent, salts)	dSPE (solvent)	Sample matrix	Pesticides [recoveries]	Analysis method	Reference
			methyl, chlorfenvinphos, chlorpyrifos [45–51%], chlorpyrifos-methyl [66%], diazinon [102–121%], dimethoate, fenamiphos, fenthion, malathion, methamidophos [60–67%], pirimiphos-methyl, quinalphos, trichlorfon) [71–103%]; neonicotinoids (acetamiprid, imidacloprid, kresoxim-methyl, thiacloprid, thiamethoxam) [82–102%]; phenylureas (chlorotoluron, diuron, flufenoxuron, isoproturon) [73–99%]; strobilurin fungicides (azoxystrobin) [92–96%]		
10 mL ACN with 0.68 mL HCOOH, 2.5 g NaCl	30 mg PSA, 100 mg C18, 60 mg GCB, 150 mg $MgSO_4$	pepper	Neonicotinoid (thiacloprid); spirotetramat and its metabolites [100; 76–89%] at 5 μg/kg	LC-ESI^+-MS/MS	[20]
1% CH_3COOH in ACN, 2 g $MgSO_4$ + 500 mg NaOAc	125 mg PSA and 375 mg $MgSO_4$	Bivalve Scrobicularia plana	OCs and related halogenated pesticides (alachlor, aldrin, cyhalofop-butyl, DDD, DDE, DDT, endosulfan, endosulfan sulfate, endrin, HCB, heptachlor, heptachlor epoxide, lindane, mirex, methoxychlor, metoachlor, trifluralin) [81–119%]; OPs (azinphos-methyl, chlorpyrifos, diazinon, dichlorvos, dimethoate, fenamiphos, fenitrothion, fonofos, malathion, methamidophos, parathion, parathion-methyl, phosmet, tetrachlorvinphos) [81–110%] Pyrethroids (cyfluthrin, cyhalothrin, cypermethrin (6%), deltamethrin)[94–114%]; triazines (atrazine, cyanazine, metribuzin, propazine, propyzamide, simazine, terbuthylazine) [85–105%].	GC-EI-MS/MS	[21]
10 mL ACN, 4 g $MgSO_4$, 1 g NaCl	200 mg $MgSO_4$, 200 mg C18	Parsley, basil, mint, thyme, salvia	Carbamates (aldicarb, asulam, benfuracarb, benomyl, benthiocarb,	LC-ESI^+-MS/MS	[22]

QuEChERS (solvent, salts)	dSPE (solvent)	Sample matrix	Pesticides [recoveries]	Analysis method	Reference
			carbaryl, carbendazim, diethofencarb, ethiofencarb, fenobucarb, fenoxycarb, isoprocarb, oxamyl, methiocarb, pirimicarb, propamocarb, promecarb, propoxur) [72–98%] at 2 μg/kg		
10 mL ACN	150 mg Z-Sep+ and 150 mg $MgSO_4$	Edible oils (olive, sunflower, maize, linseed and sesame oils) (3:7 dilution with water)	Carbamates (aldicarb, asulam, benomyl, benthiocarb, carbaryl, carbendazim, carbofuran, diethocarb, ethiofencarb, fenobucarb, fenoxycarb, isoprocarb, oxamyl, methomyl, methiocarb, metolcarb, napropamid, pirimicarb, promecarb, propamocarb, propoxur, thiodicarb) [71–104%]	LC-ESI^+-MS/MS	[23]
10 mL ACN, followed by freeze-out (−20°C for fat precipitation)	150 mg PSA, 40 mg activated charcoal sorbent, 300 mg $MgSO_4$	Edible oils (rice bran and nut oil)	OCs (aldrin, chlordane, dieldrin, DDD, DDE, DDT, endosulfan, endrin, HCHs, heptachlor) [70–103%]; OPs (dichlorvos, chlorpyrifos, diazinon, fenitrothion, malathion, parathion, parathion methyl, phorate, quinalphos, profenofos, phosmet, phosalone) [67–96%]; Pyrethroids (allethrin, cyfluthrin, cypermethrin, deltamethrin, flumethrin) [68–88%] at 20 ng/g	GC-NCI-MS/MS	[24]
1% CH_3COOH in 10 mL ACN, 4 g $MgSO_4$, 1.7 g NaOAc	40 mg PSA, 150 mg $MgSO_4$	Orange juice	Azoles (bromuconazole, difenoconazole, epoxiconazole, penconazole, propiconazole, tebuconazole, tebufenozide, tetraconazole, thiabendazole) [89–117%]; carbamates (carbaryl, carbofuran, carboxin, mecarbam, thiobencarb) [81–101%]; neonicotinoids (acetamiprid, thiacloprid) [101–106%]; OPs (diazinon, dicrotophos, dimethoate, ethoprophos, fenamiphos,	LC-ESI^+-MS/MS	[25]

QuEChERS (solvent, salts)	dSPE (solvent)	Sample matrix	Pesticides [recoveries]	Analysis method	Reference
			monocrotophos, o-methoate, triazophos) [82–113%]; Phenylureas (diuron, linuron, monolinuron) [90–101%]; strobilurin fungicides (azoxystrobin, dimoxystrobin, picoxystrobin) [84–112%].		
1% CH_3COOH in 10 mL ACN, 4 g $MgSO_4$, 1.7 g CH_3COONa	100 mg PSA, 500 mg C18, 600 mg $MgSO_4$ per 4 mL extract	Coconut water and pulp	Azole carbendazim (59% in water), cyproconazole, difenoconazole, thiabendazole, thiophanate-methyl (172% in water) [72–94%]; carbamate (carbofuran) [115 water and 78% pulp]; neonicotinoid (thiamethoxam) [100% water and 96% pulp].	LC-ESI^+-MS/MS	[26]
10 mL ACN with 4 g $MgSO_4$ and 1 g NaCl	50 mg PSA, 100 mg C18, 100 mg $MgSO_4$	Meats (high proteins and fats)	Pyraclostrobin, propiconazole, isopyrazam [76–94%] at 5 μg/kg	LC-ESI^+ -MS/MS	[27]
10 mL ACN with 4 g $MgSO_4$ and 1 g NaCl	25 mg PSA +150 mg $MgSO_4$	Soil (wetting by diluted 1:1 with H_2O)	Neonicotinoids (acetamiprid, clothianidin, imidacloprid, thiacloprid, thiamethoxam) [94–105%]	LC-ESI^+-MS/MS	[28]

Table 1. Modified QuEChERS methods for pesticides.

The selection of dSPE sorbent also depends on the target list of pesticides. The use of GCB can reduce recoveries of some pesticides including planar pesticides such as carbendazim, coumaphos, and other pesticides including prochloraz, boscalid, and pyraclostrobin due to strong absorption onto GCB [14]. The use of 25% toluene solution (v/v) can desorb planar pesticides and improve recoveries. The mass of dSPE sorbent is also optimized with reduction of mass improving recoveries for strobilurin fungicides and neonicotinoids along with other problematic pesticides [3]. The original QuEChERS method used 25 mg PSA per mL of extract, but others have increased PSA to 50 mg per mL of acetonitrile extract to obtain recoveries >77% [8].

The original QuEChERS version included no pH control, while current methods use acetate of citrate buffer for pH control to address pesticides that are partially ionized or those that degrade particularly at basic pH conditions such as observed for captan, folpet, dichlofluanid, and tolylfluanid [25, 26]. The buffers are selected as they allow for buffering to pH 4–5.5 for acid sensitive pesticides with minimal loss of base-sensitive pesticides. Some food commodities such as coconut water and pulp also see reduced co-extracts with use of acetate buffer [26]. Comparison of different QuEChERS including the original (salt only), CEN EN 15662 Standard Method (citrate buffer), and AOAC method (acetate buffer) show that recoveries ≥80% can be

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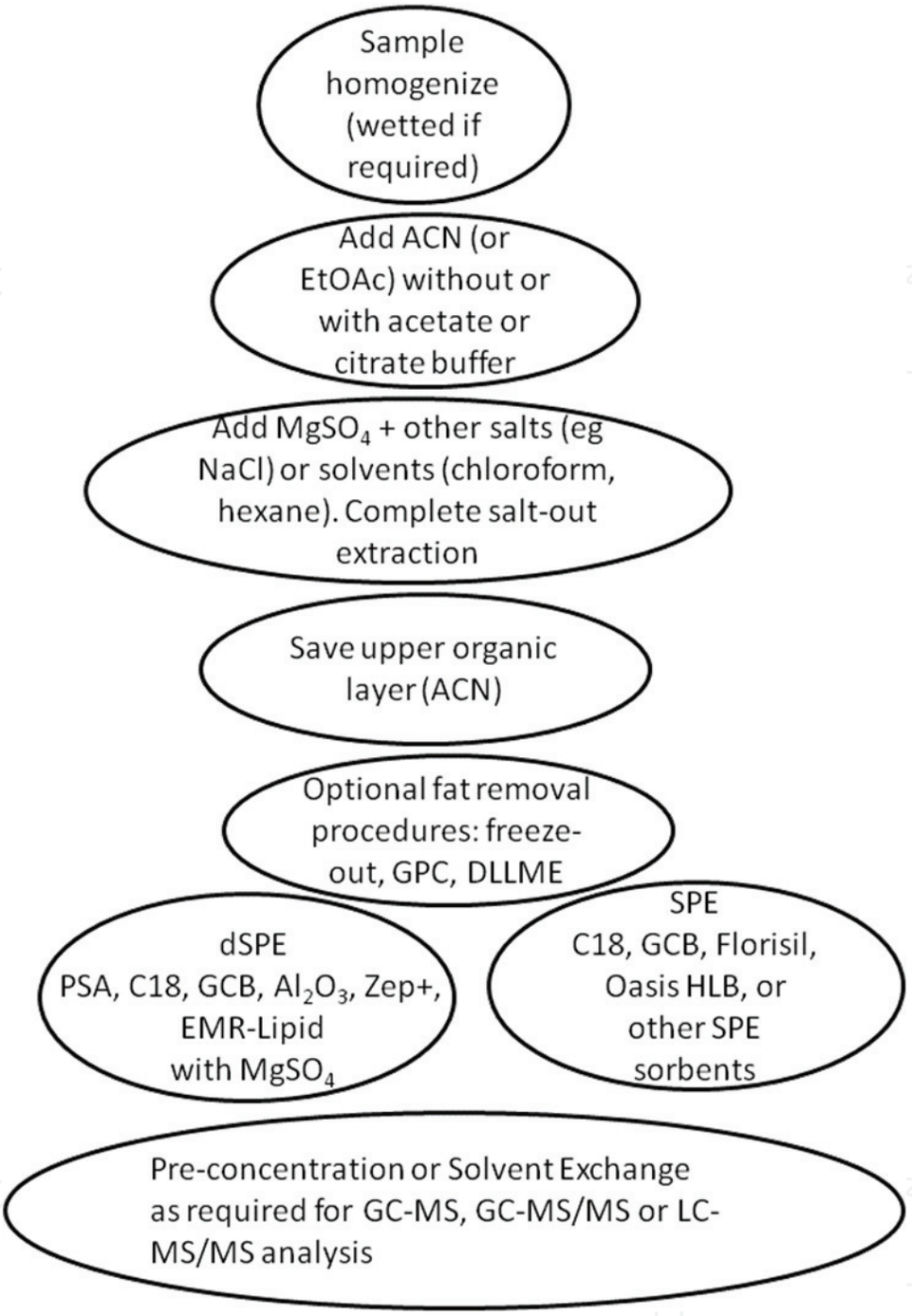

Figure 1. QuEChERS and modified QuEChERS approaches.

obtained for all methods for most pesticides (chemical classes including azoles, carbamates, organophosphorus pesticides, and strobilurin fungicide) in fruit and vegetable matrices analyzed by both GC and LC-MS/MS methods [32]. Acetate buffer pH 4.8 and citrate buffer 5.0–5.5 are used for low pH susceptible compounds such as thiabendazole and imazalil [25]. Low pH samples such as orange juice (pH~3.5) also need pH adjustment during extraction to efficiently extract pesticides of a range of polarities [25]. C18 cleanup decreased the differences in recoveries

of the acetate and citrate buffer QuEChERS approaches and was generally found to further improve recoveries [32]. Target analytes with the lowest recoveries included folpet (63–69%) and tolylfluanid (63–71%) analyzed by GC and pymetrozine (31–82%) and tolylfluanid (60–76%) analyzed by LC methods [32]. Ethyl acetate instead of acetonitrile (extraction solvent) has also been used particularly for GC-amenable pesticides [15, 17, 31, 33], but the dSPE is generally more effective with acetonitrile and in some matrices such as peas, the co-extractives may increase significantly when ethyl acetate is used as the extraction solvent [32]. Others have found that the number of GC-amenable pesticides increases with the use of ethyl acetate rather than acetonitrile and good recoveries were obtained with dSPE using a mixture of PSA, GCB, PSA, and Zr-Sep$^+$ [15]. Recoveries improved for cleanup of extracts for analysis of OPs and carbamates by LC-MS/MS (egg products) when acetonitrile, rather than ethyl acetate, was used, and when ethyl acetate was used, recoveries >120% were reported even when followed by dSPE [31]. The use of freezing-out after ethyl acetate salt-out extraction can remove the high lipid content in the co-extracted matrix and if this is followed by C18 and Al_2O_3 addition for removal of lipophilic compounds, fatty acids, sugars, and other acidic compounds (along with $MgSO_4$ to handle water content and high protein content of extracts) it provides better recoveries than when only dSPE with PSA, C18, and Al_2O_3 combinations was used [17]. Buffering of the ethyl acetate extraction can also improve recoveries particularly when the sample matrix is acidic, but care should be taken to minimize ionization of the acidic pesticides (which subsequently increases their solubility in the aqueous phase) [33].

Acetone is a poor extraction solvent and has been found to poorly recover polar analytes such as acephate and cyromazine [31]. Addition of hexane to acetonitrile prior to salt-out has been used to improve recoveries of OPs for bee samples that contain co-extracted beeswax with exception of diazinon and coumaphos that observed a drop in recoveries of 22 and 12%, respectively [5]. Recoveries of neonicotinoids from pollen also improved with addition of hexane to acetonitrile due to the high wax content [7]. Chloroform has also been added to acetonitrile to reduce the amount of acetonitrile remaining in the aqueous phase after phase separations and to further improve the partitioning of polar OPs (methamidophos and acephate) into acetonitrile [29].

For food commodities, the recoveries of analytes analyzed by LC-MS/MS (OPs, azoles, sulfonylureas) increased with dSPE following the salt-out acetonitrile extraction, while for analytes (OCs, OPs, pyrethroids) analyzed by GC-MS/MS, recoveries often decrease into an acceptable range of 70–120% [30]. PSA can bind some analytes strongly such as cinosulfuron that observed 20% decrease in recoveries [30]. Some OPs may exhibit better recoveries with GC-MS/MS rather than LC-MS/MS methods as observed for acephate and methidathion [30]. GC-amenable pesticides tend to include the more lipophilic pesticides, particularly OCs and pyrethroids that have a higher tendency to be extracted with the fatty acid matrix components. If the sample has a low water content, a wetting step is often used; however, if the sample matrix has a high fat content such as wheat flour (5 mg/mL extract) and wheat germ (45 mg/mL) then removing this wetting step (using the Ultra Turrax) will avoid the potential for target analytes such as OCs and pyrethroids to partition into the fatty layer that can form when water is present [14]. QuEChERS method has also been used with a freeze-out step prior to dSPE with PSA for sample matrices with higher levels of co-extracts including lipids (or waxes and sugars)

such as wheat flour and citrus extracts [18]. This step can minimize the need for use of other dSPE sorbents. PSA with C18 has improved the recoveries of neonicotinoids from pollen and high fructose corn syrup when the sample is diluted in water (1:4 or 1:8) prior to extraction with acetonitrile (neonicotinoids would be protonated under acidic conditions such that buffers are not used during the salt-out extraction) [7]. Extracts from soil samples also had better recoveries for neonicotinoids when extracted without buffering of acetonitrile (along with salt-out with $MgSO_4$ and NaCl) [28]. C18 (200 mg) alone was used for extract cleanup for analysis of carbamates by LC-MS/MS and found to be better than other dSPE sorbents [22]. The addition of 200 mg of $MgSO_4$ was also used to improve the removal of water so that the evaporation of organic solvent was quicker. QuEChERS with acetate buffer observed low recoveries for PSA + C18 when larger amounts of sorbent were used such that it is often preferred to use only 50 mg C18 [27]. PSA without C18 or GCB was found to provide better recoveries and precision for neonicotinoids in soil [28]. C18 can result in poor recoveries of some more nonpolar GC-amenable analytes (recoveries <70 or >120%) when the sample matrix has a high fat content and, under these situations, Zr-Sep+ has been used to remove lipids [15]. Zr-Sep+ was also used for cleanup of extracts from high fat content edible oil samples reducing matrix effects better than observed with PSA and C18 [23]. Activated charcoal with PSA has also been used for edible oils [24]. A new material called enhanced matrix removal (EMR)-Lipid was also found to perform similar or better than Zr-Sep+ or PSA+C18 for high fat content vegetable matrices with good recoveries for azoles, OPs, neonicotinoids, and phenylureas [19].

The addition of protectants including 3-ethoxy-1,2-propanediol and D-sorbitol prior to GC-MS/MS analysis can also minimize strong interactions of target analytes and matrix with the injector liner or GC column [14, 15, 21]. Re-acidifying extracts after cleanup with acetic or formic acid have also been used to improve peak shapes and response for GC-MS or LC-MS/MS methods and protect analytes that are sensitive to degradation at high pH [18].

QuEChERS approach does not always provide adequate recoveries at low concentrations and issues with large matrix peaks can still be observed in some separations of difficult matrix samples. Consequently, QuEChERS method has been modified to use cartridge SPE cleanup rather than dispersive SPE (**Figure 1**) [12, 13, 34]. Recoveries of pyrethroids and their metabolites improved with the use of cartridge SPE rather than dSPE with 42% of recoveries ≥90%, 70% were ≥80%, 90% were ≥70%, although a range in recoveries was still observed [13]. Metabolites 3-PBA and 4-F-3-PBA did not elute from GCB such that C18 SPE was selected and for some food commodity matrices, a second SPE step with silica or C18 was required [13]. A tandem GCB and PSA cartridge has been used for the cleanup of soil extracts after salt-out acetonitrile extraction for the analysis of range of pesticide classes including azoles, Ops, and pyrethroids [34]. For a wide range of chemical classes of varying polarity, Oasis® HLB (hydrophilic liquid balance) (SPE) was used after the acetonitrile with citrate buffer salt-out extraction to remove additional co-extract matrix components [12]. Although C18 can also provide good recoveries, it is more prone to clogging problems from turbid extracts (in food matrices extract may contain lipids and proteins) such that Oasis HLB is often preferred (**Table 2**) [12].

For some basic analytes, such as pymetrozine which is highly polar, QuEChERS gives poor recoveries as the analyte remains in the aqueous phase as a protonated molecule and adjusting

SPE sorbent (mg)	Elution solvent (volume mL)	Sample type	Pesticide chemical classes [average recoveries %]	Analysis method	Reference
C18 SEP-PAK (500)	DCM (5)	Urine (diluted 1:1 with H2O)	Azoles, OCs, OPs, selected neonicotinoids (kresoxim methyl), pyrethroids [62–109%] Azoles, carbamates, neonicotinoids, phenylureas, strobilurin fungicides [61–101%]	GC-EI-MS/MS LC-ESI$^+$-MS/MS	[36]
C18 Empore extraction disks	ACN (20)	Water	OP (temephos and its degradation products)	LC-ESI$^+$-MS	[37]
C18 (200)	ACN (5.5)	Water	Carbamates [90–99%]	LC-ESI$^+$-MS	[38]
C18, top,+ aminopropyl, bottom	Not specified	Dust (ultrasonic ext with methylene chloride)	Pyrethroids and metabolites [51–101%, resmethrin 23%]	GC-EI-MS/MS	[39]
C18 (500)	MeOH (3)	Urine	Pyrethroid metabolites [90–98%]	GC-EI-MS	[40]
C18 (500)	EtOAc (5)	Air sorbents (filters, polyurethane foam, XAD-2, Tenax-TA), PSE EtOAc	OCs and OPs [80–110%]	GC-NCI-MS	[41]
C18 (500) followed by DLLME	MeOH (1.5)	Water	OCs, OPs, pyrethroids, selected carbamates (carbaryl, pirimicarb) [79–94%]	GC-EI-MS	[42]
ProElut C18 (200)	DCM:MeOH (9:1)	Blood serum	OPs [90–118%] 2.7 ng/mL	GC-EI-MS/MS	[43]
OMICs C18 TIP, μSPE	ACN (0.05)	Wheat (ACN pH 5 ext.)	OPs	LC-ESI$^+$-MS/MS	[44]
Activated carbon μSPE, (100)	EtOAc (2.5)	Vegetables and fruits (microwave ext. with hexane)	OPs [92–105%]	GC-EI-MS	[45]
CleanInert TPT (three materials) (remove pigments, alkaloids, polyphenols)	ACN:toluene 3:1 (20)	teaTea	Carbamates, OCs, OPs, pyrethroids and selected others [88–101%] 5 μg/kg	GC-EI-MS/MS	[46]
GPC + Florisil	Hexane:DCM 5:95 (8)	Milk	OCs	GC-EI-MS	[47]
Sep-Pak C18 (500)	MeOH (10)	Water	Azoles [92–122%], carbamates [OPs [0–108%], strobilurin fungicide [60%], triazine [123–127%] 20 ng/mL	LC-ESI$^+$-MS/MS	[48]
GCB (300)	MeOH (1) + DCM:MeOH 80:20 (5)	Water (pH 2)	Carbamates [83–100%], OPs [78–97%], phenylureas [91–99%], sulfonylureas [90–102%] Protocol 2	LC-ESI$^+$-MS/MS	[49]

SPE sorbent (mg)	Elution solvent (volume mL)	Sample type	Pesticide chemical classes [average recoveries %]	Analysis method	Reference
Oasis HLB (150)	MeOH or ethanol (4)	Tap water (pH 3)	Chlorinated pesticides (alachlor, pentachlorophenol), OP (chlorfenvinphos), triazine (atrazine, simazine), phenylurea (isoproturon) [>80%]	LC-ESI$^+$-MS/MS	[50]
Oasis HLB (150)	MeOH (5), ACN (5)	Water (tap, surface, etc.)	OCs (metolachlor, metazachlor) [76–88%], phenylureas (isoproturon, chlorotoluron, diuron) [86–91%], triazines (atrazine, deethylatrazine, simazine, terbuthylazine) [77–85%]	LC-ESI$^+$-MS/MS	[51]
Oasis HLB (200)	EtOAc (6)	Water	OCs [85–116%], OPs [91–112%], pyrethroids [92–113%], triazines [92–112%]	GC-EI-MS and GC-EI-MS/MS	[52]
Oasis HLB (60)	DCM (1) + MeOH (1)	Water pH 2.5	OCs [55–91%], OPs [35–102%], pyrethroids [74–92%] Azoles [78–91], carbamates [86–90%], strobilurin fungicides [77–92%], phenylureas [88–98%]	GC-EI-MS LC-ESI+-MS/MS	[53]
Envir-carb+NH_2-LC	ACN:toluene 3:1 (25)	Berries (ACN salt-out ext.)	OCs, OPs, selected azoles, and other GC-amenable pesticides	GC-EI-MS	[54]
Oasis HLB (60) or Strata®-X (200)	MeOH (1)	Water (NH_4Ac addition prior to SPE)	Neonicotinoids [85–104%]	LC-ESI+-MS/MS	[55]
Oasis HLB (500)	ACN (5)	ChesnutChestnut, shallot, ginger diluted with water (LLE with ACN)	Neonicotinoids [82–95%] at 0.01 mg/kg	LC-ESI+-MS/MS	[56]
C18 (1000)	MeOH (5)	Atmospheric particles collected on filters	Neonicotinoids and strobilurin fungicides [92–101%]	LC-ESI+-MS/MS	[57]
dSPE: SBA-15-NH_2 (polyphenols removal)	ACN:MeOH 7:3	teaTea	Neonicotinoids [73–85%]	LC-ESI$^+$-MS/MS	[58]
Florisil (500)	MeOH (5)	Honey (1 g diluted 3 mL water:MeOH)	Neonicotinoid (thiamethoxam) +fipronil and degradation products [90–102%]	LC-ESI ($^+$or $^-$) – MS/MS	[59]
Oasis HLB (225)	MeOH (5)	Apple-based infant foods (LLE with ACN)	Carbamates and degradates, azole (thiabendazole) [71–95%]	LC-ESI$^+$-MS/MS	[60]
Oasis HLB (10)	ACN (1)	Rice powder (microwave ext – aqueous extract)	Carbamates (aldicarb, carbaryl, carbofuran, isoprocarb, methomyl, metolcarb, propoxur), phenylurea (diuron) [67–103%] at 10 ng/g	LC-ESI$^+$-MS/MS	[61]

SPE sorbent (mg)	Elution solvent (volume mL)	Sample type	Pesticide chemical classes [average recoveries %]	Analysis method	Reference
Zorbax C18 (500)	MeOH: ACN 1:1 (3)	Water	Carbamates [74–93%]	LC-ESI$^+$-MS	[62]
Graphene (30)	Acetone (5)	Water	Carbamates [55–95%]	LC-ESI$^+$-MS/MS	[63]
Graphene (50)	EtOAc (20)	Apple juice	OPs [94–105%]	LC-ESI$^+$-MS/MS	[64]
C18 (1000)	EtOAc (5)	Air sorbents XAD-2, Tenax-TA, polyurethane foam, PSE EtOAc	OPs, Opoxons, and other OP degradation products [70–100%]	LC-ESI$^+$-MS/MS	[65]
C18 (1000)	0.1% HCOOH in EtOAc-2-Propanol-ACN, 10:55:35, (0.425)	Air sorbents XAD-2, Tenax-TA, polyurethane foam, PSE EtOAc	Azole fungicides [80–108%]	LC-ESI$^+$-MS/MS	[66]
CN-SPE (500)	DCM:MeOH 98:2 v:v	Potato, tomato, orange (LLE)	Carbamate (aldicarb and aldicarb sulfone and sulfoxide) [68–89%]	LC-APCI$^+$-MS	[67]
Oasis HLB (60)	MeOH (3)	wastewaterWastewater	Metabolites of triazines, OPs, pyrethroids	LC-ESI ($^+$ or $^-$)-MS/MS	[68]
Bond Elut SAX + Strata-X	Not specified	Meconium samples from babies	Carbamate (propoxur), OPs, OP metabolites (dialkylphosphates), pyrethroids and metabolites, triazoles	LC-ESI ($^+$ or $^-$)-MS/MS	[69]
Strata X-AW	Parent pesticides EtOAc (5); degradates MeOH:HCOOH 90:10 v/v (3)	Meconium samples from babies	OPs (chlorpyrifos, diazinon, malathion), OP degradates, pyrethroids and degradate, carbamates, phenylurea and metabolite, phenoxyacid herbicide	LC-ESI ($^+$ or $^-$)-MS/MS	[70]
Oasis HLB 96 well plate format (30)	Acetone (0.75)	Urine	Metabolites of OPs [51–92%] and pyrethroids [86–97%]	LC-ESI ($^+$ or $^-$)-MS/MS	[71]
Silica SPE (1000) 1.ISOLUTE ENV+ (200) 2.Bond Elut PPL (200)	MeOH (10) 1. DCM/EtOac 1:1 v:v (6) 2. DCM/EtOAc 1:1 v:v (6)	Urine LLE EtOAc Urine diluted with NH_4Ac buffer (25:10)	Oxy-pyrimidine metabolites of diazinon [LLE +SPE 95:106; SPE only 83–114%]	GC-EI/MS LC-ESI$^+$-MS/MS	[72]
Carbograph (100)	Toluene (8)	Honey	Pyrethroid (tau-fluvalinate), OP (coumaphos), Others: amitraz, fipronil, bromopropylate [99–106%]	GC-PTV-EI-MS	[73]
Oasis HLB (200)	MeOH (8)	wastewaterWastewater	Diazinon, IMP, pharmaceuticals	LC-ESI$^+$-QTOF/MS	[74]
Sep-Pak Plus PS -2, C18 (665) or Oasis HLB (225)	ACN (5), followed by EtOAc (3)	Surface water	OPs, triazines, and selected others [76–99%]	LC-ESI$^+$-MS/MS	[75]

SPE sorbent (mg)	Elution solvent (volume mL)	Sample type	Pesticide chemical classes [average recoveries %]	Analysis method	Reference
Oasis HLB (200)	MeOH (5) followed by EtOAc (5)	Surface water	OCs [45–101%], pyrethroids [45–91%] Azoles [84–133%], carbamates [84–140%], neonicotinoids [104–119%], OPs [68–102], triazines [95–164%]	GC-EI-MS/MS LC-ESI$^+$-MS/MS	[76]
Bond Elut Nexus (polymeric)	MeOH + DCM (1)	Water and wastewater (acidified pH 3)	OCs and OPs [70–120%] some selected OPs and OCs outside of range	GC-EI-MS/MS	[77]

Table 2. Solid phase extraction (SPE) methods for pesticides.

the pH of the extraction leads to problems with recoveries of other acidic or basic analytes. Liquid extraction with acetonitrile (without phase separation using salt) can provide better recoveries than QuEChERS for these analytes, as it does not discriminate basic analytes [35].

3. Solid phase extraction for preconcentration or extract cleanup

Figure 2 illustrates the application of solid phase extraction for different sample matrix types. Solid phase extraction is widely used for the preparation of liquid sample matrices including food beverages, biological fluids, and water samples (drinking water, surface water, ground water). It is also widely used as a cleanup step following prior extraction steps for solid samples such as bee products, air sampling sorbent materials, and soil samples (**Table 2**) [36–77]. For solid sample matrices, popular initial extraction approaches include pressurized liquid extraction (PLE), microwave extraction (MAE), ultrasonic extraction, or liquid-solid extraction [41, 45, 57, 61, 66, 78–96]. Often an organic solvent is selected for the initial extraction of pesticides from the solid materials such that the SPE procedure must be adapted to accommodate the organic content of the sample extract to ensure adequate sorption of target analytes or the sample is diluted with water if feasible prior to SPE.

Table 2 shows common SPE sorbents used along with sample matrix type and target chemical classes of pesticides. SPE sorbents include bonded silica phases such as C18 (or less commonly selected C8); polymeric phases with an aromatic moiety to give stronger retention for more aromatic pesticides through π-interactions; Oasis HLB which is made of a copolymer consisting of divinylbenzene and N-vinylpyrrolidone; carbon based sorbents including graphene for removal of pigments; and NH_2-based sorbents for removal of polar matrix components such as sugars and proteins. N-vinylpyrrolidone acts as a hydrophilic group to give the Oasis HLB sorbent a mixed mode of retention and can improve the retention of more polar pesticides that are weakly retained on C18 sorbents. New generation molecularly imprinted polymers have also been used for cleanup of extracts for analysis of OCs [97]. Both the retention of target analytes and matrix co-extracts must be considered when optimizing an SPE procedure with sample pH and volume during loading, type of SPE sorbent, and extraction solvent and volume optimized.

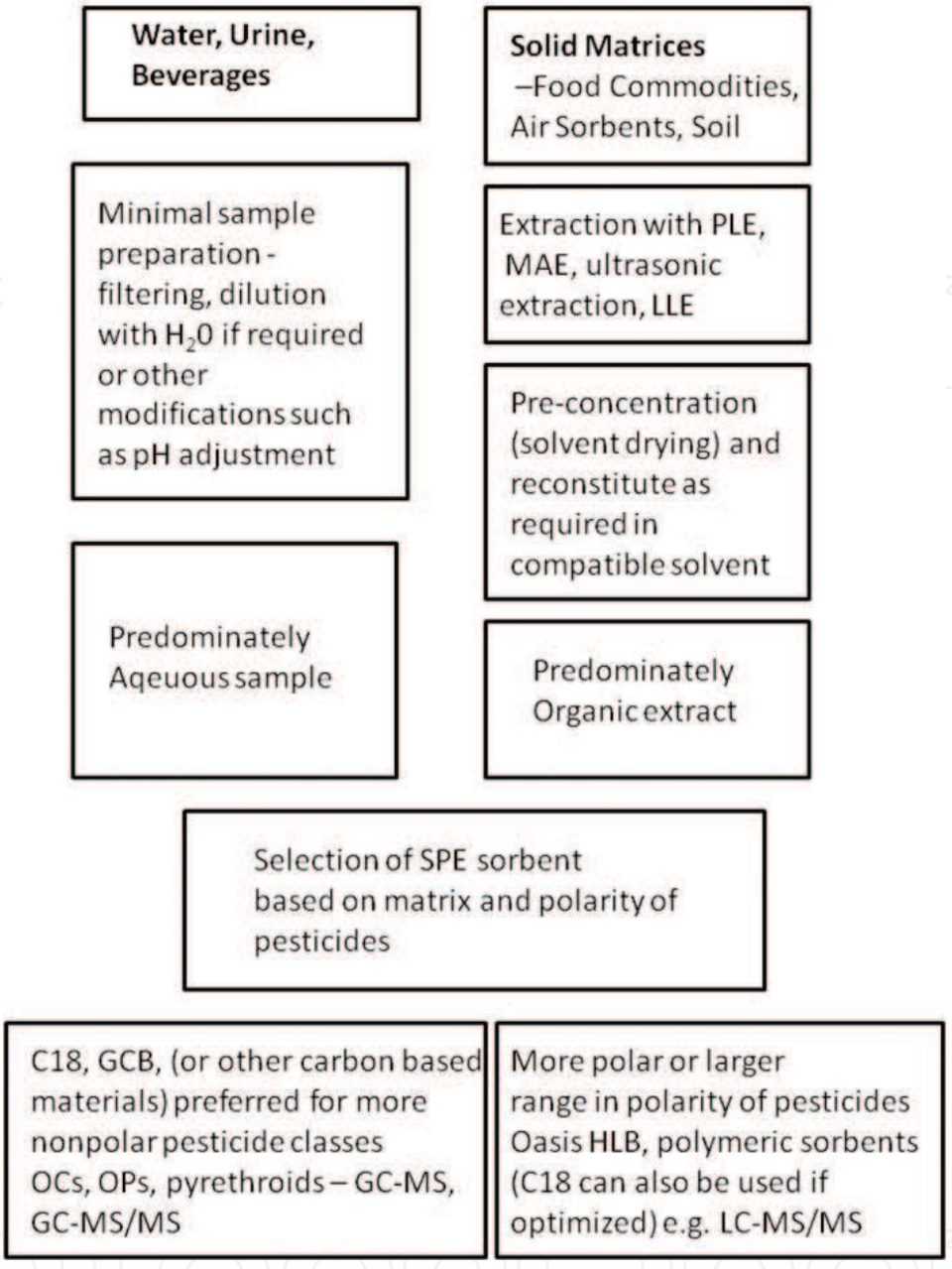

Figure 2. Strategies for extraction utilizing solid phase extract for preconcentration or extract cleanup.

Conditioning solvents for the SPE sorbents are also an important consideration, particularly for liquid extracts that contain an organic solvent from a prior extraction step.

C18 sorbents are more effective at retaining nonpolar pesticides than Oasis HLB with solvent used for extraction often more nonpolar to improve solubility of the target analytes [36]. Selection of elution solvent should also consider a need to dry or evaporate the solvent after SPE either as a preconcentration step or for solvent exchange compatibility for GC-MS or LC-MS/MS analysis. Nonpolar solvents often have higher volatility with ethyl acetate, dichloromethane or mixtures of dichloromethane with methanol commonly selected [36].

For a range of polarity of pesticides (covering both GC- and LC-amenable pesticides), dichloromethane was better at recovering more pesticides (70 and 90 pesticides) compared to methanol (10 and 30 pesticides for LC- and GC-amenable pesticides) [36]. For triazines and phenylureas at acidic sample, pH recoveries were better with Oasis HLB compared to polymeric sorbents (two different nonfunctionalized styrene divinylbenzene (SDVB), hydroxylated SDVB) [51]. Oasis HLB and Strata-X gave good recoveries of neonicotinoids with a lower sample water volume and sorbent amount (60 mg) for Oasis HLB allowing for a small solvent elution volume (1 mL), thereby removing the need for a drying step [55]. Dinotefuran (most polar) and thiacloprid (least polar) had low recoveries due to matrix effects with recoveries improving to 60% with Oasis HLB with a washing step with 5% methanol [55]. For carbamates, better recoveries were observed with Oasis HLB when acetonitrile rather than methanol or ethanol was used as the elution solvent (the lowest recovery observed for methomyl with all solvents) [61]. Oasis HLB, Strata-X, and Strata-C18 were also shown to provide recoveries between 70 and 120% for more pesticides when water samples were acidified to pH 2.5 for both GC- and LC-amenable pesticide classes [53]. Under the optimized method, more pesticides had acceptable recoveries with Oasis HLB as expected from this mixed-mode sorbent [53]; however, recoveries for OCs and OPs varied (**Table 2**), so care should be taken if more nonpolar pesticides are of greatest interest. Under neutral pH conditions, recoveries for OCs and pyrethroids were also more variable when Oasis HLB was used [76]. A larger number of OPs and OCs gave acceptable recoveries with a polymeric sorbent with acidified water samples (Bond Elut Nexus) [77]. Chlorpyrifos and pendimethalin observed low recoveries with Sep-Pak plus PS-2 (C-18) with 5 mL acetonitrile as an elution solvent, but recoveries were improved to >76% with a second elution with 3 mL of ethyl acetate [75]. Carbamates gave good recoveries with C18, while other sorbents including Oasis HLB and carbon-graphitized cartridges gave good recoveries for these carbamates except for pirimicarb and carbofuran [62]. Hydroxylated polystyrene-divinylbenzene copolymer also gave poor recoveries for pirimicarb. Poor recoveries were observed for acephate, chlorpyrifos, and methamidophos in water with C18 SPE, although other OPs observed acceptable recoveries [48]. Graphene is a new SPE sorbent and performs slightly better than C18 or GCB for carbamates except for carbaryl which has lowest recovery of ~55% attributed to stronger π-π interactions with graphene than other sorbents [98]. PRS performed the worst for carbamates of all sorbents tested [98]. Carbon-based sorbents are often selected to remove pigments with the elution solvent selected as toluene or toluene:acetonitrile rather than dichloromethane or ethyl acetate as nonpolar analytes that can bind more strongly to this sorbent material [73, 54]. For extraction of OPs with graphene, ethyl acetate was found to provide better recoveries than dichloromethane or acetonitrile as the elution solvent [99]. Graphene sheets with covalently bonded Fe_3O_4 have also been used for magnetic solid phase extraction (MSPE) of organochlorines in orange juice [100]. Other modified MSPE with Fe_3O_4 including coated carbon nanotubes has been utilized for water or fruit juice extraction of GC-amenable pesticides [99, 101]. Zirconia nanoparticle-decorated calcium alginate hydrogel fibers have been used for extraction of OPs from water and fruit juices [102].

For added selectivity, a molecularly imprinted polymer has been used for SPE sorbent for the analysis of OCs in water, soil, rice, and tea leaves [97]. Micro-SPE has also been used in combination or after extraction methods for recovery of OPs [44–45]. On-line SPE coupled

with LC-MS/MS has been used with many of the same sorbents materials described for off-line methods with C18 or C8 and PLRP-s (styrene divinyl-benzene copolymer sorbent) as popular choices [103–106].

4. Other considerations

Solid matrices including soil, sediment, food commodities, and air sampling solid sorbent materials (filter, polyurethane foam, solid sorbents (XAD-2, XAD-4, Tenax-TA)) are extracted prior to an SPE (or dSPE) cleanup step with a variety of approaches including microwave extraction, pressurized liquid extraction (as referred commonly as pressurized solvent extraction), ultrasonic extraction, and traditional solid-liquid extractions [41, 45, 57, 61, 66, 78–96]. These approaches are not selective and the polarity of the organic solvents and choices of additives in these extraction procedures will impact the co-extractive matrix, which necessitate the subsequent SPE or dSPE cleanup choices. In addition, for SPE, aqueous extracts are easier to optimize SPE loading, washing, and elution steps as extracts of organic solvents need careful consideration to ensure adequate retention of target analytes on sorbent materials to prevent washout. The most common solvent choices for pressurized liquid extraction and microwave extraction of solid matrices were acetonitrile, ethyl acetate, acetone, hexane, or combinations of these solvents [81–96]. With microwave extraction, acetone has been added to hexane (2:1) to improve the recoveries for polar OPs, while use of hexane can reduce matrix co-extractives [81]. Ethyl acetate and acetone have been used for microwave extraction of azoles [82]. Reduction in co-extracts has also been reported with acetonitrile rather than methanol or acetone (with microwave extraction) and good recoveries have been reported for OCs and neonicotinoids [83, 84]. Hexane, dichloromethane, ethyl acetate, acetone, and acetonitrile have also been commonly used for pressurized solvent extraction of a large range of polarity of pesticides [41, 57, 65, 66, 85–96].

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Abbreviations

ACN	Acetonitrile
APCI	Atmospheric pressure chemical ionization
dSPE	Dispersive solid phase extraction
EI	Electron ionization
EMR-Lipid	Enhanced matrix removal-lipid
ESI	Electrospray ionization

EtOAc	Ethyl acetate
GCB	Graphitized carbon black
GC-MS	Gas chromatography-mass spectrometry
GC-MS/MS	Gas chromatography-tandem mass spectrometry
LC-MS/MS	Liquid chromatography-tandem mass spectrometry
MSPE	Magnetic solid phase extraction
MAE	Microwave assisted extraction
$MgSO_4$	Anhydrous magnesium sulfate
OCs	Organochlorines
Ops	Organophosphorus pesticides
PLE	Pressurized liquid extraction
PSA	Primary secondary amine
QuEChERS	Quick, easy, cheap, effective, rugged, safe
SPE	Solid phase extraction

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