**BrJAC**

REVIEW

An Integrative Review on the Analysis of Pesticide Multiresidues in Sweet Pepper Samples using the QuEChERS Method and Chromatographic Techniques

Fabiane Ferraz Wisniewski [iD], Elisandra Carolina Martins* [iD] [✉]

Universidade Estadual do Paraná (UNESPAR), Praça Coronel Amazonas, s/n, Caixa Postal 57, União da Vitória, Paraná, 84600-185, Brazil

PESTICIDES RESIDUES IN SWEET PEPPER
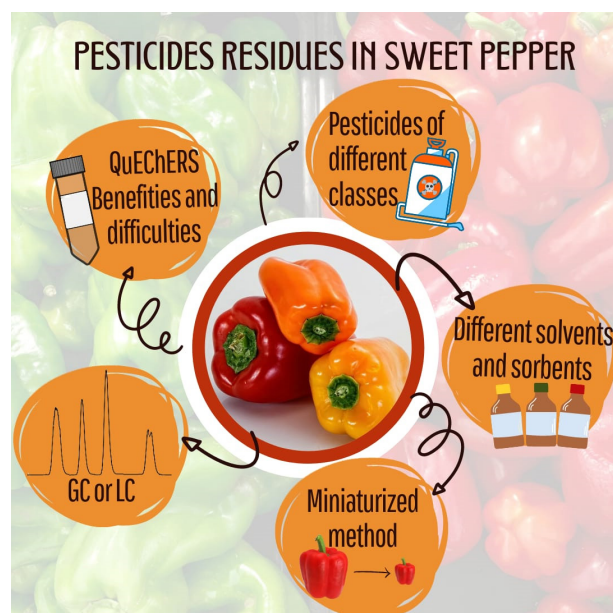
Since foods are complex matrices that contain pesticides of different classes, multiresidue sample preparation methods such as QuEChERS (Quick, Easy, Cheap, Effective, Rugged, Safe) are used and modified to obtain more accurate and sensitive results. This work was developed through an integrative review in the journal databases Capes, Science Direct, Scielo, and Scientia Chromatographica, from 2011 to 2021, to answer the following question: "What is the most efficient and advantageous sample preparation method for the determination of multiresidue pesticides of interest in sweet pepper samples, when chromatographic techniques are used for detection?" The sweet pepper was chosen because the Pesticide Residue Analysis in Food Program (PARA) suggests that it is the sample with the highest percentage of irregularities related to active ingredients not allowed or above the Maximum Residue Limit (MRL). A total of 391 articles were found, 11 of which met the inclusion criteria established. Several analyses were studied. The organophosphates were the most studied class of pesticide, with seven articles. In addition, there was a predominance of nonpolar analytes (log K_{ow} > 1). The use of different extracting solvents, such as methanol, acetonitrile, ethyl acetate, and acetone, was observed, with acetonitrile presenting the best analytical parameters in most cases. The use of different sorbents such as secondary and primary secondary amine (PSA), ocatadecyllane (C18), graphite carbon (GCB), and carbon black was noted, as well. The authors highlight the difficulties in the analysis when the matrix effect is significant (except for fensulfothion, tensulfothion, flonicamid, and its metabolite TFNA-AM) and the degradation of analytes through the analysis process

(flonicamid, captan, folpet, thiophanate methyl and benomyl). Finally, the statistical test Analysis of Variance (ANOVA) was used to identify if there was a significant difference between the different methods used for the same analysis or when the same method used for the different analytes.

Keywords: pesticides, multi-residue, sweet pepper, sample preparation, QuEChERS.

INTRODUCTION

Sweet pepper (*Capsicum annuum*) belongs to the *Solanaceae* family. It is rich in vitamin C when green and in vitamin A when ripe, while being a source of iron (Fe), potassium (K) and phosphorus (P).[1] According to the Brazilian Institute of Geography and Statistics (IBGE) it is estimated that, in 2017, Brazil produced 224,286 tons of sweet pepper, with São Paulo being the main producing state.[2]

The cultivation of sweet peppers has economic and social relevance, since a large part of the national production comes from family farming, as it allows quick economic return in addition to complementing the diet. However, the number of surveys and data on the crop are limited, making access to information about it difficult for those who produce or are interested in sweet pepper production. In addition, few pesticides are authorized for the crop,[3] which can make pest control difficult.

Pesticides are understood to be "products and agents of physical, chemical or biological processes, [...] whose purpose is to change the composition of flora or fauna, in order to preserve them from the harmful action of living beings considered harmful".[4] In the context of agricultural production, the use of pesticides from different agronomic classes (herbicides, fungicides, insecticides, etc.) and different chemical groups (organophosphates, triazines, pyrethroids, etc.) is commonplace, aiming to increase productivity by minimizing the occurrence of plant pests and diseases. However, the indiscriminate use of these substances can generate negative external effects, both for the environment, contaminating soil and water, and for human health, which can cause acute or chronic intoxication and bioaccumulation of some substances, due to the ingestion of waste that may be present in these foods. This is why Maximum Residue Limits (MRL) have been established, corresponding to the maximum amount of pesticide residues that can be found in food without being a concern to human health.[5]

According to the National Health Surveillance Agency (ANVISA), until the first quarter of 2021, 504 pesticides are authorized in Brazil for 154 crops. 57 of these pesticides are authorized for the sweet pepper crop[6] and are listed in Table I, together with their MRL, chemical group, and the agronomic class they belong to.

Table I. Pesticides allowed for the sweet pepper crop[6]

Authorized pesticide	MRL (mg kg⁻¹)	Chemical group	Agronomic class
Abamectin	0.040	Avermectins	Acaricide, insecticide, nematicide
Acetamiprid	0.700	Neonicotinoid	Insecticide
Alpha-cypermethrin	0.020	Pyrethroid	Insecticide
Azoxystrobin	0.500	Strobilurin	Fungicide
Bifenthrin	0.300	Pyrethroid	Insecticide, formicide and acaricide
Boscalida	0.500	Anilide	Fungicide
Buprofezin	0.500	Thiadiazinone	Fungicide
Kasugamycin	0.030	Antibiotic	Fungicide and bactericide

(continues on the next page)

Table I. Pesticides allowed for the sweet pepper crop[6] (continuation)

Authorized pesticide	MRL (mg kg⁻¹)	Chemical group	Agronomic class
Cyantraniliprole	0.150	Anthranilamide	Insecticide
Cymoxanil	0.100	Acetamide	Fungicide
Cletodim	0.500	Cyclohexanedione Oxime	Herbicide
Clomazone	0.050	Isoxazolidinone	Herbicide
Chlorantraniliprole	0.300	Anthranilamide	Insecticide
Chlorfenapyr	0.300	Pyrazole Analogue	Insecticide and acaricide
Chlorothalonil	5.000	Isophthalonitrin	Fungicide
Kresozym-Methyl	0.050	Strobilurin	Fungicide
Deltamethrin	0.060	Pyrethroid	Insecticide and formicide
Diafenthiuron	3.000	Phenylthiumea	Acaricide and insecticide
Difenoconazole	0.500	Triazole	Fungicide
Dimethomorph	0.200	Morpholine	Fungicide
Epinephrine	0.500	Spinosines	Insecticide
Spiromesifen	0.700	Ketoenol	Insecticide and acaricide
Ethofenproxy	0.700	Diphenyl Ether	Insecticide
Phenamidone	0.200	Imidazolinone	Fungicide
Fenpyroximate	0.100	Pyrazole	Acaricide
Phenpropatrine	0.200	Pyrethroid	Insecticide and acaricide
Fluazinam	0.070	Phenylpyridinylamine	Fungicide and acaricide
Fluensulfone	0.200	Heterocyclic Fluoroalkenyl Sulfone	Nematicide
Fluopicolide	0.200	Benzamide Pyridine	Fungicide
Flupiradifurone	0.600	Butenolide	Insecticide
Flutriafol	0.200	Triazole	Fungicide
Fluxapyroxad	0.100	Carboxamide	Fungicide
Formatanate	2.000	Phenyl Methylcarbamate	Insecticide and acaricide
Imidacloprid	0.500	Neonicotinoid	Insecticide
Indoxacarb	0.050	Oxadiazine	Insecticide, termite and formicide
Iprodione	4.000	Dicarboximide	Fungicide
Iprovalicarb	0.050	Carbamate	Fungicide
Lambda-Cyhalothrin	0.200	Pyrethroid	Insecticide

Table I. Pesticides allowed for the sweet pepper crop[6] (continuation)

Authorized pesticide	MRL (mg kg⁻¹)	Chemical group	Agronomic class
Mancozeb	3.000	Alkylenebis (Dithiocarbamate)	Fungicide and acaricide
Metconazole	0.100	Triazole	Fungicide
Methiocarb	0.050	Phenyl Methylcarbamate	Insecticide
Put In	3.000	Alkylenebis (Dithiocarbamate)	Fungicide
Pyraclostrobin	1.000	Strobilurin	Fungicide
Piridaben	0.500	Pyridazinone	Acaricide and insecticide
Pyrimethanil	1.000	Anilinopyrimidine	Fungicide
Pyriproxyfen	0.500	Pyridyloxyprophilic Ether	Insecticide
Propamocarb	2.000	Carbamate	Fungicide
Propineb	3.000	Alkylenebis (Dithiocarbamate)	Fungicide
Tebuconazole	0.200	Triazole	Fungicide
Teflubenzuron	0.150	Benzoylurea	Insecticide
Thiabendazole	2.000	Benzimidazole	Fungicide
Thiacloprid	0.200	Neonicotinoid	Insecticide
Thiamethoxam	0.200	Neonicotinoid	Insecticide
Thiophanate-Methyl	0.100	Benzimidazole (Precursor Of)	Fungicide
Trifloxystrobin	0.100	Strobilurin	Fungicide
Trifluralin	0.050	Dinitroaniline	Herbicide
Zoxamide	0.100	Benzamide	Fungicide

Source: ANVISA, 2021.[6]

In order to control and ensure safer food, regulatory bodies have carried out analyses to detect pesticides in food since 1960.[7] In Brazil, this monitoring has been carried out since 2001 by the Pesticide Residue Analysis in Food Program (PARA), coordinated by ANVISA. The program aims to identify whether the number of residues detected is in accordance with the MRL prescribed by legislation and whether they are authorized for cultivation.[8]

PARA prioritizes the most consumed foods according to the Family Budget Survey (POF), which is carried out by the IBGE (the Brazilian Institute of Geography and Statistics), as well as foods that are likely to present risk, according to previous reports of the program. Since PARAs was established, sweet pepper was the sample with the highest percentage of irregularities in the different sampling cycles regarding the presence of pesticide residues above the MRL established by the legislation and of pesticides not allowed for the crop.[8,9] The average percentage of irregularities during each sampling cycle is represented in Figure 1.
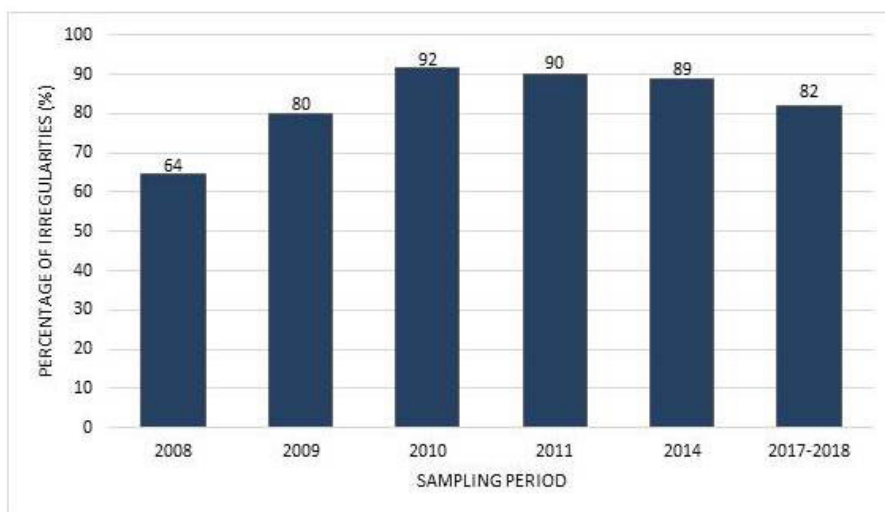
Figure 1. Mean percentage of irregularities in sweet pepper samples, according to PRAFP/
ANVISA. (Adapted from ANVISA 2009, 2010, 2011, 2013, 2016, 2019.[10-15])

Figure 1 shows that from 2008 to 2010 the number of irregularities has been growing, reaching 92% in 2010 (of a total of 146 analyzed samples). From then on, a decrease in irregularities has been observed, year after year. However, the percentage of irregularities in the last biannual sampling cycle (2017-2018) is still quite high, reaching 82% of a total of 326 analyzed samples.

In addition, in Paraná, through the SESA Resolution Nº. 217/2011, the State Pesticide Residue Analysis in Food Program PARA/PR was established, coordinated by the Division of Food Sanitary Surveillance of the State Center for Sanitary Surveillance and by the Central Public Health Laboratory of Paraná (Lacen/PR).[16] In the state, samples are collected at Supply Centers (CEASA) units and schools in the state network. They are selected according to consumption data from the POF carried out by IBGE for the population of Paraná and the historical records of PARA residues maintained by ANVISA.[17]

In 2020, the first report from PARA/PR was released, in which twenty samples of sweet peppers collected at CEASA units were analyzed, with a total of 70% of unsatisfactory samples, including 17 pesticides not allowed for the crop and 6 others above the MRL. On the other hand, a sample collected from school meals showed no irregularities.[17]

The determination of pesticide residues in food is relevant in estimating human exposure to these compounds, due to the adverse effects that these substances can have. Since foods are complex matrices, samples must go through a previous preparation stage to extract and concentrate their analytes with subsequent sample clean-up. In this stage, it is common to use multiresidue methods, capable of simultaneously extracting large amounts of pesticides, since foods generally contain residues of different types of pesticides.[18]

Therefore, in order to comply with the strict MRLs prescribed by legislation and overcome the limitations of current methods, generating extracts that can be analyzed by Liquid Chromatography and Gas Chromatography-Tandem Mass Spectrometry (LC-MS/MS and GC-MS/MS), the QuEChERS (Quick, Easy, Cheap, Effective, Rugged, Safe), a multiresidue method was developed in 2003 by Anastassiades *et al.*[19] The main steps of the method are presented in Figure 2.
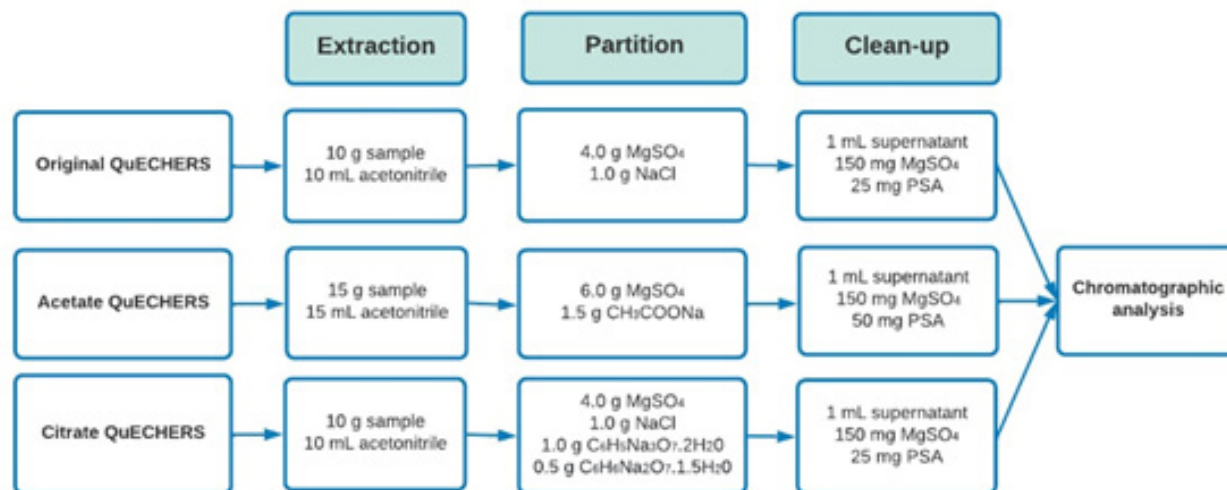
Figure 2. Original, Acetate and Citrate QuEChERS methods steps. [Adapted with permission from: (39) Zanella, R.; Prestes, O. D.; Adaime, M. B.; Martins, M. L. QuEChERS (Chapter 24). In: Borges, K. B.; Figueiredo, E. C.; Queiroz, M. E. C. *Preparo de amostras para análise de compostos orgânicos*. LTC, **2015**. License granted by LTC Publisher, GEN Group, on May 25, 2022.]

The original QuEChERS method consists of extracting the residue with acetonitrile, partitioning it through the addition of magnesium sulfate and sodium chloride, and clean-up using dispersive solid phase extraction (d-SPE).[19] Several modifications were studied in order to improve the analytical parameters, also increasing the percentage of recovery and the scope of analytes and samples. Two of these modifications stand out: acetate QuEChERS, where the medium is buffered at pH 4.8 after the socdium acetate is added, and citrate QuEChERS, which uses a mixture of sodium citrate dihydrate and hydrogen citrate sesquihydrate with a buffering effect at a pH from 5.0 to 5.5.[20]

In addition, different solvents can be used in the extraction step and different compounds can be used as sorbents in the clean-up step. The choice depends on the characteristics of the analyte and on the sample of interest. For example, methanol can be used as a solvent in the determination of polar analytes, while acetonitrile is used in the recovery of analytes with different polarities.[18] Regarding sorbents, the use of primary secondary amine (PSA) removes polar compounds, including pigments, sugars and fats, in addition to being indicated for the determination of nonpolar organophosphate pesticides.[21] In turn, graphite carbon black (GCB) removes pigments such as chlorophyll, while octadecyl (C18) removes nonpolar interference from the matrix and is indicated for a determination of polar analytes.[22]

Considering the above, correlating the characteristics of the analytes studied here with the analytical parameters, efficiency, and toxicity of the reagents used in the original QuEChERS method and its modifications would be extremely relevant for further research, as it would allow investigators to select the most appropriate methodology and/or experimental conditions for their studies, enabling them to identify which is the most efficient and/or advantageous sample preparation method to determine the pesticide multiresidues of interest in sweet pepper samples, using chromatographic techniques for detection.

METHODOLOGY

The integrative review is divided into six stages. The first step is the definition of the guiding question. Therefore, we determined that the question that should be answered was: "What is the most efficient and/or advantageous sample preparation method for the determination of multiresidue pesticides of interest in sweet pepper samples when chromatographic techniques are used for detection?"

In the second stage, the period from 2011 to 2021 was defined for the search of relevant data in the databases Scielo, Science Direct, Portal de Periódicos Capes, and Scientia Chromatographica, with

the following keywords: "QuEChERS and multiresidues" associated with "bell pepper, sweet pepper and *capsicum annuum,* and *pimentão*" (the latter being the Portuguese word for "sweet pepper"). At this stage, inclusion criteria were also defined:

i) Full text in Portuguese or English;
ii) Presence in the title or abstract of the terms "QuEChERS or multiresidues" associated with "bell pepper, sweet pepper, *pimentão*, or *capsicum annuum*";
iii) Articles must have used chromatographic techniques for detection;
iv) Articles must have presented an analytical validation for the sweet pepper sample.

Articles that did not meet one or more inclusion criteria were excluded. Review articles and duplicates were also excluded.

In the third step, we verified whether the articles met inclusion criterion *i.* Then, after reading the title and abstract, we included articles that met inclusion criteria *ii* and *iii.* The articles included in this stage were listed in a data collection table, including their titles, authors, years of publication, objectives, samples, analytes, and sample preparations used.

In the fourth step, duplicates were removed and the articles left were read in their entirety, to verify whether they met all inclusion criteria, especially the analytical validation for the sweet pepper sample (criterion *iv*). Then, a critical analysis of the articles included was carried out, showing similarities between the documents, and listing, on a table, data from the analytical validation of the proposed methods, which were: limit of detection (LOD), limit of quantification (LOQ), percentage of recovery, standard deviation, linearity and whether the method had a matrix effect.

In the fifth stage, the discussion of the results was carried out, seeking to identify possible shortcomings in the methods as well as to identify the advantages and disadvantages of each proposed modification.

Finally, the sixth stage of the integrative review consisted of concluding the study, comparing the efficiency of each method, the analytical parameters, as well as other advantages and disadvantages of each method, considering the characteristics of their respective analytes. The statistical test used to verify if there was a significant difference between the percentages of recovery was the Analysis of Variance (ANOVA), with a confidence level of 95%. In this step, the recovery values obtained for the same analyte were compared, from different sample preparation methodologies (original QuEChERS and its modifications) and to verify whether the recovery values in a given method were significantly different in different analytes. In cases where a significant difference was observed in ANOVA, the test of least significant difference (LSD) was performed, with 95% confidence, according to the equation represented in Figure 3.[23]

$$LSD = t \sqrt{\frac{2 \, X \, MSE}{N_g}}$$

Figure 3. Equation used to calculate LSD. (Source: Skoog, D. A.; Holler, F. H.; Crouch, S. R. *Fundamentos de química analítica.* Thompson, 2006.[23])

Where *MSE* corresponds to the mean squared error; *t* is the tabulated value with N-1 degrees of freedom and *Ng* is the number of replicas.[23]

Unfortunately, a statistical comparison for all analytes in the articles could not be carried out, and nor was it possible to compare all methods used for the same analyte, since the precision of the methods differs greatly depending on the analyte, and, consequently, the variance cannot be considered equal. Thus, only analytes that presented the smallest variances and could be considered statistically equal were compared.[23]

RESULTS AND DISCUSSION

Integrative reviews are the broadest form of review. It surveys current knowledge on a specific topic so the results of independent studies are identified, analyzed, and synthesized to contribute to the resolution of a specific question.[24] To start the integrative review protocol, the guiding question was determined, as mentioned in the previous section: "What is the most efficient and/or advantageous sample preparation method for the determination of multiresidue pesticides of interest in sweet pepper samples, when chromatographic techniques are used for detection?"

After the question was determined, the review protocol was developed in order to answer the guiding question. Sampling criteria must guarantee the representativeness of the sample as they are important indicators of the reliability of the results.[24] Figure 4 shows the number of articles selected and excluded in each stage.
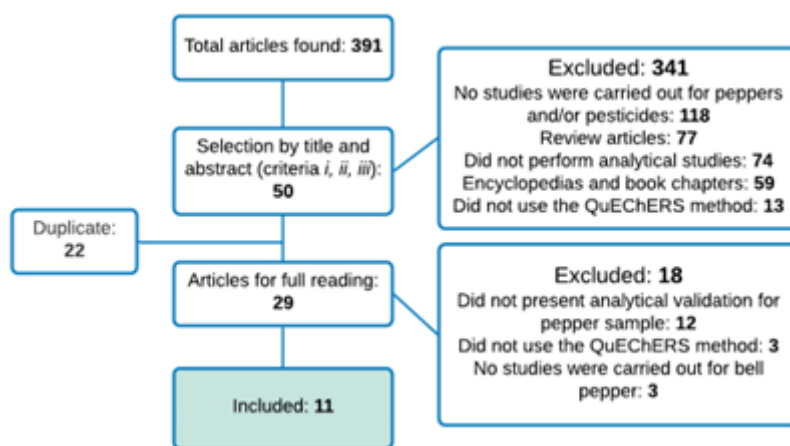
Figure 4. Diagram of identification and selection of integrative review articles. (Figure created by the authors.)

The selected articles were published in journals with an impact factor ranging from 0.68 to 7.51. Table II presents the QuEChERS method and the modifications used in the selected articles, the analysis technique, the samples, the number of analytes studied, the chemical group they belong to, and the impact factor of the journal in which they were published.

Table II. QuEChERS method and its modifications for the determination of pesticide multiresidues in sweet pepper samples

QuEChERS method	Analysis technique	Sample	Amount of Analytes	Chemical group	Impact factor
Original[25]*	GC-NPD	Sweet pepper	11	Organophosphate	0.68
Original without clean-up[22]*	UHPLC-Orbitrap-MS	Sweet pepper	5	Nicotinoid and organophosphate	3.06
Original without clean-up. Acetonitrile acidified with 1% formic acid. Optimization of grinding with addition of ascorbic acid.[26]*	SFC-MS/MS GC-MS/MS LC-MS/MS	Sweet pepper and tomato	2	Phthalimide and Dicarboximide	6.06

Table II. QuEChERS method and its modifications for the determination of pesticide multiresidues in sweet pepper samples (continuation)

QuEChERS method	Analysis technique	Sample	Amount of Analytes	Chemical group	Impact factor
Original with different sorbents (PSA, PSA + C18 and GCB)[27]*	UHPLC-MS/MS	Sweet pepper	81	Aryloxyphenoxypropionic acid, anilide, anilinopyrimidine, anthranilamide, benzimidazole, benzofuranyl, carbamate, carboxamide, chloroacetamide, strobilurin, phenylamide, phenylurea, phosphorothiolate, imidazole, isoxazolidinone, methylcarbamate, morphine, neonicotinoid, organophosphate, pyrazole, pyrethroid, pyridine, thiadiazinone, thiocarbamate, triazole, triazolopyrimidamine, urea	3.37
Citrate with solvent variation (acetonitrile, acetone, ethyl acetate and methanol), sorbent (use and non-use of PSA graphited carbon) and use of dry ice in the partition step[18]*	LC-MS/MS	Sweet pepper	21	Benzimidazole, carbamate, strobilurin, isoxazolidinone, neonicotinoid, organophosphate	7.51
Miniaturized citrate 3 g sample + 1.3 g MgSO$_4$ + 0.33 g NaCl + 0.16 sodium citrate sesquihydrate + 0.33 sodium citrate → 1 min shake → 5 min centrifugation. 1.5 mL supernatant + 50 mg PSA + 15 mg ENVI-Carb + 300 mg MgSO$_4$ → 30 s stirring → 5 min centrifugation[28]*	GC-QqQMS	Sweet pepper, tomato, cucumber and lettuce	88	Substituted benzene, cyclodiene, bridged diphenyl, phosphorothiolate, chlorinated hydrocarbon, organochlorine, organophosphate	4.76
Citrate and acetate with varying proportion of sorbents (MgSO$_4$, PSA, C18 and GCB)[29]*	LC-MS/MS	Sweet pepper, rice, soy, apple, tangerine and cabbage	3	Diamide	n. i.
Acetate with d-SPE and DLLME[30]*	LC-MS/MS	Sweet pepper, lettuce, garlic and ginger	8	Carbamate, phenylamide, neonicotinoid, organophosphate, thiocarbamate	0.83
Acetate[31]*	LC-MS/MS	Sweet pepper and tomato	3	Benzamide and Triazole	4.22
Acetate[21]*	HPLC-MS/MS	Sweet pepper, banana and papaya	11	organophosphates	0.96

(continues on the next page)

Table II. QuEChERS method and its modifications for the determination of pesticide multiresidues in sweet pepper samples (continuation)

QuEChERS method	Analysis technique	Sample	Amount of Analytes	Chemical group	Impact factor
Acetate[32]*	LC-MS/MS HPLC-PDA	Sweet pepper	2	Diamide	1.91

*Superscript numbers refer to the article reference. n. i. = not informed; GC-NPD: Gas Chromatography with Nitrogen-phosphorus Detector; UHPLC-Orbitrap-MS: Ultra High Performance Liquid Chromatographyhigh coupled to Orbitrap Mass Spectrometry; SFC-MS/MS: Supercritical Fluid Chromatography–Tandem Mass Spectrometry, Gas Chromatography–Tandem Mass Spectrometry; GC-MS/MS: Gas Chromatography–Tandem Mass Spectrometry; LC-MS/MS: Liquid Chromatography–Tandem Mass Spectrometry; UHPLC-MS/MS: Ultra High Performance Liquid Chromatography–; GC-QqQMS: Comprehensive two-dimensional Gas Chromatography with flow Modulation–Triple quadrupole Mass Spectrometry; HPLC-MS/MS: High-Performance Liquid Chromatography–Tandem Mass Spectrometry; HPLC-PDA: High-Performance Liquid Chromatography–Photo Diode Array.

The presence of analytes of different classes was noted in the articles, with organophosphates being the most observed, present in seven articles.[18,21,22,25,27,28,30] There was a predominance of nonpolar analytes (154 analytes with log k_{ow} > 1), when compared to polar analytes (22 analytes with log k_{ow} < 1), in addition to 51 analytes whose polarity was not specified.

Table II shows the predominance of acetate QuEChERS over citrate and original QuEChERS, as well as the predominance of original QuEChERS over citrate QuEChERS. In the 11 selected articles there have been different modifications aimed at minimizing the degradation of compounds,[26] minimizing the matrix effect and increasing extraction efficiency by combining different solvents and salts in different proportions,[29] as well the use of reduced samples, solvents and sorbents, in order to propose methods that are in accordance with green chemistry.[28]

The complete list of analytes studied in the selected articles (Table II), the class they belong to, their polarity, and recovery at the lowest concentration studied by the authors can be found in the supplementary material.

Original QuEChERS method

Four of the eleven articles selected used the original QuEChERS method,[22,25-27] to a total of ninety-nine analytes of different classes with different polarities. The ANOVA statistical treatment could only be performed for the articles of López-Ruiz *et al.* and Kemmerich *et al.*;[22, 27] the others did not present the exact standard deviation values. Table III shows parameters such as the percentage of recovery and log K_{ow} values, which can be related to polarity, and the higher the log K_{ow} value, the more hydrophobic the compound. The same parameters for all analytes studied by the authors selected in this work are found in the supplementary materials.

Table III. Analytical parameters for the analytes studied using the acetate QuEChERS method, except those whose variances were not small enough to be considered equal

QuEChERS	Analysis technique	Concentration µg kg^{-1}	Analytes	log k_{ow} [33]	Recovery (%)
Original without clean-up[22]	UHPLC-Orbitrap-MS	10	Flonicamid[a]	-0.24	88 ± 11
			TFNG[a]		89 ± 10
			TFNA[a]		NR
			TFNA-AM[a]		NR
		100	Flonicamid[a]	-0.24	91 ± 7
			TFNG[a]		84 ± 9
			TFNA[a]		88 ± 6
			TFNA-AM[a]		87 ± 9

(continues on the next page)

Table III. Analytical parameters for the analytes studied using the acetate QuEChERS method, except those whose variances were not small enough to be considered equal (continuation)

QuEChERS	Analysis technique	Concentration µg kg⁻¹	Analytes	log k_{ow}[33]	Recovery (%)
Original with variation of sorbents[27]	UHPLC-MS/MS	10	Thiacloprid[b]	1.26	85 ± 4
			Imazalil[a]	2.56	74 ± 4
			Pyrimethanil[c]	2.84	88 ± 4
			Methomyl[b]	0.09	82 ± 4
			Pyrifenoxa[a]	3.40	75 ± 5
			Thiabendazole[c]	2.39	90 ± 5
		50	Atrazine[a]	2.70	84 ± 3
			Pyrimethanil[a]	2.84	84 ± 3
			Pencicuron[b]	4.68	102 ± 3
		100	Thiabendazole[b]	2.39	78 ± 3
			Mephospholane[e]	1.04	90 ± 3
			Metobromuron[d]	2.48	85 ± 3
			Metalaxyl[c]	1.71	83 ± 3
			Ametrine[d]	2.36	85 ± 3
			Azaconazole[f]	2.36	99 ± 3
			Phenpropimorph[c]	4.50	81 ± 3
			Pyridafenthion[a]	3.20	73 ± 3
			Profenophos[d]	1.70	86 ± 3
			Atrazine[c]	2.70	80 ± 4
			Azoxystrobin[c]	2.50	82 ± 4
			Mevinphos[f]	0.12	96 ± 4
			Simazine[f]	2.10	96 ± 4

NR = not recovered. Superscript letters were used to indicate a significant difference.

As observed in Table III, from the original QuEChERS without clean-up, proposed by López-Ruiz *et al.*,[22] flonicamid and its metabolites showed recovery percentages between 87 and 91%, with no significant difference at 95% confidence. The method optimized by the authors is based on acidified QuEChERS, using acetonitrile containing 1% formic acid and a mixture of salts (magnesium sulfate and sodium chloride). Such results obtained by the authors, presented in Table III, refer to the optimized method, which added to the process a stirring with a PT2100 *polytron* (Kinematica AG, Littan/Luzern, Switzerland) and excluded the clean-up step with sorbents. The clean-up stage, using PSA and a mixture of PSA and graphited carbon, resulted in a decrease in the recovery percentage, with the use of 50 mg of PSA, the recoveries ranged from 65% for TFNG to 85% for flonicamid (polar), while the mixture of 50 mg of GCB with 50 mg of PSA provided recoveries of 60% for TFNA-AM and 80% for the flonicamid. The authors justified this by the fact that the analytes are retained in the binding sites of the sorbents, being an unnecessary step in matrices with high water content. The method studied was shown to have good sensitivity, with LOQ values lower than the MRL, for sweet pepper samples.[22] The use of sorbents (PSA, C18 and GCB) was also associated with a decrease in sorption percentage for two broflanilide metabolites, S (PFOH)-8007 (using PSA, C18 and GCB as sorbent) and DM-8007 (using GCB as sorbent).[29] However, the authors obtained excellent extraction of pigments from the samples, using a mixture of sorbents (MgSO$_4$, PSA and GCB).

Examples of other works that used PSA and/or GCB as sorbents are the studies of Lemos *et al.*[21] and Figueiredo *et al.*[25] for nonpolar organophosphates and mevinphos and methamidophos (polar organophosphates), Morais, Collins and Jardim for analytes with different polarities,[18] and Figueiredo *et al.* for nonpolar analytes and for methamidophos.[25] Matadha *et al.* used a mixture of PSA and C18 was as sorbent in studies with apolar analytes. However, the authors did not perform comparative studies without the use of sorbents. And so, it is not possible to relate the results obtained with the use of sorbents.[31]

On the other hand, the use of original QuEChERS with varying sorbents, using UHPLC-MS/MS,[27] in studies with several classes of pesticides and original QuEChERS, using GC-NPD in studies with organophosphates,[25] obtained satisfactory results using the clean-up step with PSA. And of eleven analytes studied by Figueiredo *et al.*,[25] the use of sorbent was not efficient only for pirimiphos, obtaining a recovery of only 60%.

The use of original QuEChERS with varying sorbents by Kemmerich *et al.*[27] was validated for seventy-nine of the eighty-one analytes studied by the authors. The method could not be validated for two analytes of the benzimidazole class, benomyl (log K_{ow} = 1.4) and thiophanate methyl (log K_{ow} = 1.4), because they showed low percentages of recovery and determination coefficient lower than 0.99. The low percentages of recovery were associed whith degrading the analytes in carbendazin. Thus, benomyl and thiphanate methyl are calculated as carbendazim.

Among the analytes presented in Table III, for the initial concentration of 10 µg kg^{-1}, the method QuEChERS original with variation of sorbents presented by Kemmerich *et al.*[27] showed lower recoveries for imazalil (log k_{ow} = 2.56) and pyrifenox (log k_{ow} = 3.40), and greater recovery for thiabendazole (log k_{ow} = 2.39), in relation to the other analytes. For the concentration of 50 µg kg^{-1}, pencycuron (log k_{ow} = 4.68), a very nonpolar phenylurea, showed a higher percentage of recovery (102%), and for the initial concentration of 100 µg kg^{-1}, the lowest recovery was observed for pyridafenthione (log k_{ow} = 3.20), and the highest for azaconazole (log k_{ow} = 2.36), a nonpolar triazole.

In general, there was a significant difference between most analytes in study, but unfortunately it was not possible to establish a relationship between the recovery percentages and the log K_{ow}. The method showed higher LOD and LOQ for analytes with log K_{ow} greater than 2.9.

Furthermore, in the four articles that used original QuEChERS with and without modifications, a pronounced matrix effect was observed for the analytes, with the exception of captan, folpet,[26] and flonicamid and its metabolite TFNA-AM.[22] Another problem reported was the degradation of analytes such as captan (log K_{ow} = 2.5) and folpet (log K_{ow} = 3.02), which can be minimized using techniques and proper conditions. Supercritical fluid chromatography-tandem mass spectrometry (SFC-MS/MS) is a good alternative for the determination of folpet and captan, which tend to degrade during injection by GC-MS/MS and LC-MS/MS.[26] The addition of ascorbic acid (3%) and dry ice in the milling step, allowed recoveries between 94 and 99%, respectively. Without the use of dry ice, captan and folpet could not be detected even at the highest concentrations. The use of ascorbic acid and dry ice inhibits hydrolysis and oxidation, common degradation processes during milling. These processes may occur due to the presence of pectinase enzymes, which cause the hydrolysis of pectin, present in peppers, being a matrix-dependent process.[26]

It was also observed that the use of sodium chloride (NaCl), in the partition step, had a positive influence on the recovery of polar compounds, such as acetamiprid (log K_{ow} = 0.8) and chlorotianidin (log K_{ow} = 0.905), since the NaCl added to the system makes the phase separation more complete. By varying the amount of NaCl added to the extract, the polarity range (selectivity) and the degree of cleanliness in the partition stage can be controlled.[19] In addition, the use of acetonitrile proved to be efficient for providing the recovery of analytes with different polarities, in addition to reducing the number of lipophilic co-extractives and matrix pigments.[27]

Citrate QuEChERS method

The use of QuEChERS citrate was observed in articles by Morais, Collins and Jardim,[18] Ferracane *et al.*[28] and Noh *et al.*,[29] which together totaled one hundred and four analytes of different classes and polarities. Table IV presents log K_{ow} and recovery percentages for some analytes studied by the authors

— the complete list can be found in the supplementary materials. For the articles by Morais, Collins and Jardim[18] and Noh *et al.*[29] it was not possible to perform statistical treatments because they did not present numerical standard deviation values, only estimates, based on graphs.

Table IV. Analytical parameters for the analytes studied using the acetate QuEChERS method, except those whose variances were not small enough to be considered equal

QuEChERS	Analysis technique	Concentration (µg kg⁻¹)	Analytes	Log K_{ow} [33]	Recovery (%)
Miniaturized citrate[28]	GC-QqQMS	10	4.4-DDD[a]		63 ± 2
			Chlorfenson[a]	4.21	66 ± 2
			Fention[b]	4.84	70 ± 2
			Methyl tolclofos[b]		71 ± 3
			Pentachlorothianisol[b]		78 ± 2
			Sulfotep[c]	3.99	108 ± 2
			4,4-Dichlorobenzophenone[d]		109 ± 2
			Terbufos[e]	4.51	117 ± 2
		50	Trans-chlordane[a]	2.78	88 ± 2
			Ethion[b]	5.07	93 ± 2
			Chlorbenside[b]	5.59	95 ± 2
			Methoxychlorine[b]		95 ± 4
			2,4-DDE [b]		96 ± 2
			Pyrimiphos-methyl[c]	4.20	99 ± 2
			4,4-DDD[c]		99 ± 2
			Tolclofos-methyl[c]	3.80	101 ± 2
			Endrin[c]	3.20	101 ± 2
			Bromophos-ethyl[d]	6.15	106 ± 2
Miniaturized citrate[28]	GC-QqQMS	100	Piperonyl[a]	4.51	95 ± 2
			4,4 methoxychloro[a] olefina[a]		96 ± 2
			Terbufos[a]	4.51	96 ± 2
			Dieldrin[a]	3.70	96 ± 2
			Hexachlorobenzene[a,b]	3.93	97 ± 2
			Sulfotep[a,b]	3.99	98 ± 2
			Chlorbenside[b]	5.59	100 ± 2
			Pentachlorobenzene[b,c]		101 ± 2
			Pirimiphos-methyl[b,c]	4.20	102 ± 2
			Chlorpyrifos[c,d]	4.70	104 ± 2
			Paration[d]		105 ± 2
			Quinalphos[d]	4.44	107 ± 2

Superscript letters were used to indicate a significant difference.

As seen in Table IV, there is a significant difference between most analytes studied, demonstrating that despite being a multi-residue method, its efficiency varies according with the analyte. At the initial concentration of 10 µg kg^{-1} the recoveries obtained for the 4,4-DDD (63 ± 2% and log K_{ow} = 6.02) and chlorfenson (66 ± 2% and log K_{ow} = 4.21) are significantly lower than those obtained for the other analytes, while terbufos (log K_{ow} = 4.61) recovery was the highest (117 ± 2%), even though both are quite nonpolar analytes.

For the concentration of 50 µg kg^{-1}, among the ten analytes compared, a significantly lower recovery was observed for trans-chlorinated (88 ± 2%), which is a nonpolar organochlorine (log K_{ow} = 2.78), and the highest recovery was obtained for bromophosethyl (106 ± 2%), which is a very nonpolar organophosphate (log K_{ow} = 6.15).

Among the twelve analytes presented in Table IV, for the concentration of 100 µg kg^{-1}, the percentage of recovery for piperonyl (95 ± 2), 4,4'-methoxychlor-olefin (96 ± 2), terbufos (96 ± 2 and log K_{ow} = 4.51), dieldrin (96 ± 2 and log K_{ow} = 3.70), and hexachlorobenzene (97 ± 2 and log K_{ow} = 3.93) are statistically equivalent.

Observing the recoveries obtained for the eighty-eight analytes investigated from the use of miniaturized QuEChERS citrate, it can be noted that the method was efficient in most cases, with recoveries greater than 70%. Furthermore, it was observed that the smallest variances and, consequently, the greatest precision, were obtained for the most nonpolar analytes.

The matrix effect was pronounced for all analytes investigated in the articles by Morais, Collins and Jardim, Ferracane *et al.* and Noh *et al.*,[18,28,29] being more pronounced for the more polar analytes (log K_{ow} < 1), such as methamidophos, acephate, thiamethoxam, methomyl, and imidacloprid.[18] Alternatively, the matrix effect can be minimized by preparing the analytical curve in the sample matrix,[21] by dilution and purification, which are basic methods for the removal of impurities and, consequently, tend to minimize the matrix effect.[34] However, Noh *et al.* it was observed that when the matrix effect is not high, there is no significant improvement when diluting or purifying the sample.[29] In a comparative study between citrate QuEChERS and acetate QuEChERS, it was observed that the lowest matrix effect was found performing the extraction by the citrate buffer method, followed by purification with d-SPE, using 25 mg of PSA.[29]

Furthermore, different sorbents were evaluated in citrate QuEChERS, such as the use and non-use of GCB, which did not present a significant difference in the chromatographic responses for most of the analytes investigated. Positively, the use of graphite carbon helped to clean the samples, reducing the matrix effect. It was also observed that the use of methanol solubilizes the clean-up salts and results in extracts with a cloudy appearance. In addition, ethyl acetate, as it is less polar than acetonitrile and acetone, tends to cause a significant decrease (<70%) in the recovery of polar compounds, such as acephate (log K_{ow} = -0.85) and methamidophos (log K_{ow} = -0.79). On the other hand, acetone caused increased recovery of methamidophos and acephate, but a decrease in recoveries of other analytes. Acetone also resulted in greener extracts, due to the extraction of a greater number of pigments, which causes a greater matrix effect, compared to acetonitrile or methanol.[18]

Finally, it can be said that the miniaturized citrate QuEChERS method is the most eco-friendly and cheapest method proposed. It enabled the validation of sixty-eight analytes out of the eighty-eight studied, with recoveries ranging between 70 and 120%. However, it did not allow the detection of thirteen analytes, namely: endrin aldehyde, azinphos-methyl, bromfenvinphos, bromfenvinphos-methyl, edifenphos, ethylene, endrin ketone, phosalone, fenamiphos, leptophos, pyraclophos, prothiophos, profenophos. The lack of detection for these compounds may be associated with the use of GCB, which causes elution problems for aromatic pesticides, such as leptophos (log K_{ow} = 6.31), which bind strongly during the clean-up step. However, this can be overcome by adding a larger amount of solvents, such as toluene or acetonitrile. In addition, the method achieved low recoveries for: triazophos (60 ± 4% and log K_{ow} = 3.55), 4.4-DDD (63 ± 2%), chlorfenson (66 ± 2% and log K_{ow} = 4.21) and chloroneb (56 ± 5% and log K_{ow} = 3.58).[28]

Acetate QuEChERS Method

The use of acetate QuEChERS was observed in five articles,[21,29,30-32] totaling twenty analytes of different classes. The use of acetate QuEChERS without modifications was observed for the articles by Lemos *et al.*, Matadha *et al.* and Buddidathi *et al.*[21,31,32] Noh *et al.* included the use of different sorbents (PSA, C18, GCB),[29] and Lawal and Low the use of additional steps in d-SPE and dispersive liquid-liquid microextraction (DLLME).[30]

Table V presents analytical parameters such as log K_{ow} and percentages of recovery for the analytes that could be compared using ANOVA. For the article of Noh *et al.*[29] it was not possible to perform the statistical treatment because it did not present standard deviation values.

Table V. Analytical parameters for the analytes studied using the acetate QuEChERS method, except those whose variances were not small enough to be considered equal

QuEChERS	Analysis technique	Concentration	Analytes	Log K_{ow}[33]	Recovery (%)
Acetate with *d-SPE* and DLLME[30]	LC-MS/MS	5 µg kg^{-1}	Thiobencarb[a]	4.23	91 ± 3
			Baycard[b]		102 ± 2
		100 µg kg^{-1}	Diazinon[a]	3.69	99 ± 3
			Thiamethoxam[a]	-0.13	99 ± 3
			Baycard[a]		100 ± 4
			Thiobencarb[a]	4.23	101 ± 3
		500 µg kg^{-1}	Thiobencarb[a]	4.23	98 ± 3
			Diazinon[a]	3.69	99 ± 4
			Propamocarb[a]	0.84	100 ± 3
			Baycard[a]		100 ± 4
Acetate[31]	LC-MS/MS	0.0005 mg kg^{-1}	Tebuconazole[a]	3.70	78 ± 6
			Fluopyram[a]	3.30	80 ± 7
			Fluopyram[a] benzamide[a]		84 ± 8
		0.01 mg kg^{-1}	Tebuconazole[a]	3.70	80 ± 6
			Fluopyram[a]	3.30	83 ± 7
			benzamed[a] Fluopyram[a]		85 ± 6
		0.025 mg kg^{-1}	Tebuconazole[a]	3.70	81 ± 5
			Fluopyram[a]	3.30	84 ± 5
			benzamine[a] Fluopyram[a]		88 ± 5
		0.05 mg kg^{-1}	Tebuconazole[a]	3.70	86 ± 4
			Fluopyram[a]	3.30	88 ± 4
			Fluopyram[a] benzamide[a]		91 ± 5
		0.1 mg kg^{-1}	Fluopyram[a] benzamide[a]		92 ± 4
			Fluopyram[a]	3.30	92 ± 3
Acetate[21]	HPLC-MS/MS	0.00625 mg kg^{-1}	Fensulfotion[a]	2.23	94 ± 7
			Mevinphos[a]	0.127	98 ± 7
			Diazinon[a,b]	3.69	102 ± 8
			Coumaphos[b]		106 ± 9

(continues on the next page)

Table V. Analytical parameters for the analytes studied using the acetate QuEChERS method, except those whose variances were not small enough to be considered equal (continuation)

QuEChERS	Analysis technique	Concentration	Analytes	Log K_{ow} [33]	Recovery (%)
Acetate[21]	HPLC-MS/MS	0.125 mg kg^{-1}	Fenthion[a]	4.84	84 ± 2
			Diazinon[b]	3.69	94 ± 3
		0.1 mg kg^{-1}	Azinphos-methyl[a]	2.96	99 ± 2
			Dichlorvos[a]	1.90	100 ± 2
			Fenthion[b]	4.84	103 ± 2
Acetate[32]	LC-MS/MS HPLC-PDA	0.05 mg kg^{-1}	Flubendiamide[a]	4.14	96 ± 8
			de-iodine Flubendiamide[a]		97 ± 6
		0.1 mg kg^{-1}	Flubendiamide[a]	4.14	98 ± 6
			de-iodine Flubendiamide[a]		100 ± 6
		1.00 mg kg^{-1}	Flubendiamide[a]	4.14	100 ± 4
			de-iodine Flubendiamide[a]		104 ± 5

Superscript letters were used to indicate a significant difference.

The use of acetate QuEChERS with d-SPE and DLLME by Lawal and Low[30] showed a significant difference between thiobencarb (log K_{ow} = 4.23) and baycarb at the lowest concentration studied, 5 µg kg^{-1}. Furthermore, the quantification of polar and nonpolar analytes did not show differences in the percentage of recovery.

On the other hand, the use of QuEChERS acetate by Matadha *et al*.[31] for the determination of tebuconazole (log K_{ow} = 3.70), fluopyram (log K_{ow} = 3.30) and fluopyram benzamide (both nonpolar analytes)[31] showed no significant difference, with 95% confidence, in any of the concentrations studied by the authors.

Furthermore, in acetate QuEChERS proposed for Lemos *et al*.[21] it was observed that the method presented recoveries in the range from 79 ± 4% (mevinphos at 0.1 mg kg^{-1}) to 112 ± 12% (azinphos-methyl at 0.00625 mg kg^{-1}), data available in the supplementary material. Therefore, it was noted that the only polar analyte analyzed by the author showed the lowest recovery; however, this fact was not observed for the other concentrations, and it cannot be said that the method is less efficient for polar analytes.

In the next article by Buddidathi *et al*.[32] which also used QuEChERS acetate, the determination of flubendiamide and its de-iodine metabolite flubendiamide was studied. Flubendiamide is a nonpolar diamide (log K_{ow} = 4.14) that tends to degrade in the field, forming de-iodine flubendiamide, with a half-life of 4.3 to 4.6 days in sweet pepper fruits produced in the open field, and from 5.7 to 6.6 days in sweet peppers produced in greenhouses. Thus, the detection of flubendiamide takes into account the presence of its metabolite to express the actual concentration of the substance. Both analytes studied by the authors showed no significant difference in their recovery percentages.

Furthermore, the matrix effect was pronounced for most analytes studied by the authors, with the exception of fensulfothion,[21] which showed neither suppression nor decrease in the chromatographic signal.

Comparison between the different methods used for the same analytes

The comparison of analyses of the same analyte using different QuEChERS sample preparation methods and the same range of enrichment was possible only for 2.65% of the analytes studied by the different authors, which corresponds six of 227, distributed in eleven articles. Table VI presents the concentration and analytical parameters for the analytes that could be compared.

Table VI. Analytical parameters for the analytes studied by different authors whose analysis could be compared, according with statistical treatment

QuEChERS	Analysis technique	Analyte	log k_{ow}[33]	Polarity	Concentration µg kg^{-1}	Recovery (%)	Significant difference
Miniaturized citrate[28]	GC-QqQMS					96 ± 4	
Acetate with d-SPE and DLLME[30]	LC-MS/MS	Diazinon	3.69	Nonpolar	100	99 ± 3	No
Miniaturized citrate[28]	GC-QqQMS					110 ± 9	
Original with different sorbents[27]	UHPLC-MS/MS	Mevinphos	0.127	Polar	10	76 ± 7	Yes
Miniaturized citrate[28]	GC-QqQMS					110 ± 10	
Original with diferente sorbents[27]	UHPLC-MS/MS	Pyridafenthion	3.20	Nonpolar	10	84 ± 3	Yes
Miniaturized citrate[28]	GC-QqQMS	Sulprophos	5.48	Nonpolar	100	97 ± 4	Yes
Acetate[21]	HPLC-MS/MS					81 ± 4	
Miniaturized citrate[28]	GC-QqQMS					117 ± 2	
Original with diferente sorbents[27]	UHPLC-MS/MS	Terbufos	4.51	Nonpolar	10	117 ± 2	No
Miniaturized citrate[28]	GC-QqQMS					121 ± 7	
Original with diferente sorbents[27]	UHPLC-MS/MS	Triazophos	3.55	Nonpolar	50	86 ± 9	Yes

From Table VI, it is possible to observe that diazinon was the only one to show no significant difference (comparison between the miniaturized citrate QuEChERS method and acetate QuEChERS with d-SPE and DLLME) and terbufos (comparison between the miniaturized QuEChERS citrate method and original QuEChERS with varying sorbents). For the determination of mevinphos, miniaturized citrate QuEChERS by Ferracane *et al.*[28] showed better recovery and lower accuracy, i.e., the standard deviation was higher compared to original QuEChERS with varying sorbents proposed by Kemmerich *et al.*[27] For the determination of pyridafenthione, miniaturized citrate QuEChERS of Ferracane *et al.*[28] showed high recovery with a higher standard deviation than the results found using the original QuEChERS with varying sorbents, which obtained lower recovery, but good accuracy, as indicated by a low standard deviation.[27] For the determination of sulprophos, miniaturized citrate QuEChERS[28] was shown to be more efficient when compared to acetate QuEChERS proposed by Lemos *et al.*[21] Finally, for the determination of triazophos, miniaturized citrate QuEChERS[28] showed recovery above the acceptable level of 70-120%, while the use of original QuEChERS with varying sorbents[27] showed recovery within the established range.

Methods currently used for sample preparation to determine pesticide multiresidues in food

Determining the amount of pesticide multiresidues in complex matrices, such as food, remains a challenge for the scientific community, due to the different properties of the analytes, as well as the interferences in the matrix. Therefore, the scientific community continually develops and improves sample preparation methods for the extraction of different pesticides from different matrices.

In addition to QuEChERS, other methods can be used for the extraction of pesticides from food matrices, such as gas-liquid microextraction (GLME) integrated with d-SPE, validated to determine residues of forty-seven pesticides, of different classes, in samples of apples, oranges, honey, and leek. The author reported that the method presented an equivalent or smaller matrix effect, compared to the QuEChERS method, which is commonly used.[35] Another method used as an alternative to QuEChERS is binary solvent liquid-phase microextraction (BS-LPME) for the determination of seventeen pesticides of different classes in red and rosé wines, which are a challenge for chemical analysis.[36]

Even with the use of different sample preparation methods for the determination of pesticide multiresidues in food, QuEChERS is still among the most used. According to the *Portal de Periódicos Capes*, until January 2022, QuEChERS was used as an extraction method in 6549 articles and in the Science Direct database, the method is found in 4194 articles, and the number of articles using it has been growing year after year.

There was a report on the use of the original QuEChERS method with an extra step of d-SPE for a better clean-up of extracts and reduction of the matrix effect for the extraction of triazole compounds from orange, grape and strawberry samples;[37] acetate QuEChERS was used for the determination of pesticides in samples of onion, watermelon, tomato, sweet pepper, cabbage, carrot, amaranth, cabbage, eggplant, beans, and okra.[38] Also, original and modified QuEChERS were used to determine different analytes in sweet pepper samples.[26,28,30]

CONCLUSIONS

The use of the QuEChERS method, with or without modifications proposed by the literature, showed good analytical parameters for most analytes investigated. However, even being a multiresidue method, its efficiency varies according to the analyte. In addition, miniaturized citrate QuEChERS by Ferracane *et al.*[28] stands out as the most eco-friendly method as it uses less reagents and, consequently, has a lower cost than methods for determining pesticide multiresidues in sweet pepper samples.

Due to the flexibility of the QuEChERS method, which is apt to be modified, different solvents and sorbents could be investigated by different authors. Acetonitrile proved to be the solvent with the best analytical parameters for analytes with different polarities,[18,27] while methanol is better for polar analytes.[18] On the other hand, among the sorbent extractors used, the use of PSA tends to remove polar compounds from the matrix, including pigments, sugars and fats, and is indicated for the determination of nonpolar pesticides.[21] In turn, C18 removes nonpolar compounds from the matrix and is indicated for the determination of polar analytes.[29] In addition, for flonicamide and its metabolites, the clean-up step (d-SPE), using PSA and GCB as sorbents, lowers the percentage of recovery, possibly because, in aqueous matrices (such as peppers), flonicamide and its metabolites are retained in PSA and GBC sites.[22] Therefore, the choice of solvent and/or sorbent for the optimization of the method depends on the characteristics of the analyte and the sample of interest.

Furthermore, other modifications can be used to improve efficiency or decrease matrix effects. Examples include the modified QuEChERS-dSPE Ionic Liquid-based DLLME method by Lawal and Low[30] and the optimization of the sample milling step through the addition of ascorbic acid and/or dry ice, allowing better recoveries for captan and folpet, which prevents hydrolysis and oxidation of analytes during milling.[26] Furthermore, the determination of captan and folpet by GC-MS/MS is problematic, due to the tendency of these analytes to degrade during the injection. Thus, other techniques should be investigated to this end, such as SFC-MS/MS.[26]

Although the instrumentation used for the detection of analytes is costly (GC-MS/MS, LC-MS/MS, UHPLC-MS/MS, among other chromatographic techniques), the ability to detect numerous analytes

simultaneously makes the investment in chromatographic systems worthwhile. We expect this study encourages future investigations regarding the determination of pesticide multiresidues in sweet peppers to provide cheaper, eco-friendly methods with good analytical parameters, in compliance with the strict international legislation.

Conflicts of interest

The authors declare no conflicts of interest.

REFERENCES

(1) Empresa Brasileira de Pesquisa Agropecuária (Embrapa)*.* https://embrapa.br/hortalica-nao-e-so-salada/pimentao (accessed 2021-11-17).

(2) Instituto Brasileiro de Geografia e Estatística (IBGE). https://www.ibge.gov.br/explica/producao-agropecuaria/pimentao/br (accessed 2021-11-17).

(3) Centro de Estudos Avançados em Economia Aplicada, Escola Superior de Agricultura Luiz de Queiroz, Universidade de São Paulo (Cepea-Esalq/USP). "Pequenos mercados, grandes oportunidades: Boas opções para diversificar a produção." *Hortifruti Brasil* **2017**. https://www.hfbrasil.org.br/br/revista/acessar/completo/pequenos-mercados-grandes-oportunidades.aspx (accessed 2021-11-20).

(4) Presidência da República. Law nº 7.802, 1989-07-11, **1989**. http://www.planalto.gov.br/ccivil_03/Leis/L7802.htm (accessed 2021-12-29).

(5) Tosetto, E. E.; Andrioli, A. I.; Christoffoli, P. I. Análises das causas das subnotificações das intoxicações por agrotóxicos na rede de saúde em município no Sul do Brasil. *Ciência & Saúde Coletiva* **2021**, *26* (2), 6037-6047. https://doi.org/10.1590/1413-812320212612.15182021

(6) Agencia Nacional de Vigilância Sanitária (ANVISA). https://www.gov.br/anvisa/pt-br/acessoainformacao/dadosabertos/informacoes-analiticas/monografias-de-agrotoxicos?fbclid=IwAR14dJAc9BAOZsg_wqINGDGIfCSQgxsewyzGduRs2GcPldxUKfJYmvvbPN0 (accessed 2021-12-19).

(7) Souza, R. C. S. Revisão sistemática aplicada à determinação de resíduos de agrotóxicos em alimentos: técnicas de análise e práticas de validação intralaboratorial. Master's dissertation, Federal University of Minas Gerais, Belo Horizonte, **2018**. http://hdl.handle.net/1843/BUOS-B57JHS

(8) Agencia Nacional de Vigilância Sanitária, Programa de Análise de Resíduos de Agrotóxicos em Alimentos (ANVISA/PARA). https://www.gov.br/anvisa/pt-br/assuntos/agrotoxicos/programa-de-analise-de-residuos-em-alimentos (accessed 2021-11-17).

(9) Lopes, C. V. A.; Albuquerque, G. S. C. Agrotóxicos e seus impactos na saúde humana e ambiental: uma revisão sistemática. *Saúde em Debate* **2018**, *42* (117), 518–534. https://doi.org/10.1590/0103-1104201811714

(10) Agencia Nacional de Vigilância Sanitária, Programa de Análise de Resíduos de Agrotóxicos em Alimentos (ANVISA/PARA). *Nota Técnica para divulgação dos resultados do PARA de 2008*. ANVISA **2009**. https://www.gov.br/anvisa/pt-br/assuntos/agrotoxicos/programa-de-analise-de-residuos-em-alimentos/arquivos/3811json-file-1 (accessed 2021-05-02).

(11) Agencia Nacional de Vigilância Sanitária, Programa de Análise de Resíduos de Agrotóxicos em Alimentos (ANVISA/PARA). *Relatório de atividades de 2009*. ANVISA **2010**. https://www.gov.br/anvisa/pt-br/assuntos/agrotoxicos/programa-de-analise-de-residuos-em-alimentos/arquivos/3803json-file-1?fbclid=IwAR1QcrZC8LwOWANRBQIaHT25vRQYqYVAYk919nXLjedFlWRWxU8apvwkA6g (accessed 2021-05-02).

(12) Agencia Nacional de Vigilância Sanitária, Programa de Análise de Resíduos de Agrotóxicos em Alimentos (ANVISA/PARA) *Relatório de atividades de 2010*. ANVISA **2011**. https://www.gov.br/anvisa/pt-br/assuntos/agrotoxicos/programa-de-analise-de-residuos-em-alimentos/arquivos/3799json-file-1 (accessed 2021-05-03).

(13) Agencia Nacional de Vigilância Sanitária, Programa de Análise de Resíduos de Agrotóxicos em Alimentos (ANVISA/PARA). *Relatórios de atividades de 2011 e 2012*. ANVISA **2013**. https://www.gov.br/anvisa/pt-br/assuntos/agrotoxicos/programa-de-analise-de-residuos-em-alimentos/arquivos/3791json-file-1 (accessed 2021-05-03).

(14) Agencia Nacional de Vigilância Sanitária/Programa de Análise de Resíduos de Agrotóxicos em Alimentos (ANVISA/PARA). *Relatório de atividades 2013–2015*. ANVISA **2016**. https://www.gov.br/anvisa/pt-br/assuntos/agrotoxicos/programa-de-analise-de-residuos-em-alimentos/arquivos/3778json-file-1?fbclid=IwAR1zSgnV5bWUYu5FuMsFTBHHzZf4EuUlJNdBbqzMibDZCU8S6u8puqWM7Yk (accessed 2021-05-04).

(15) Agencia Nacional de Vigilância Sanitária, Programa de Análise de Resíduos de Agrotóxicos em Alimentos (ANVISA/PARA). *Relatório das amostras analisadas no período 2017–2018 e primeiro ciclo do plano plurianual 2017–2020*. ANVISA **2019**. https://www.gov.br/anvisa/pt-br/assuntos/agrotoxicos/programa-de-analise-de-residuos-em-alimentos/arquivos/3770json-file-1 (accessed 2021-05-05).

(16) Secretaria da Saúde do Paraná. http://saude.pr.gov.br/Pagina/Programa-de-Analise-de-Residuos-de-Agrotoxicos-em-Alimentos-PARA (accessed 2021-12-01).

(17) Agencia Nacional de Vigilância Sanitária, Programa de Análise de Resíduos de Agrotóxicos em Alimentos (ANVISA/PARA). *Relatório PARA/PR: Ciclo 2018-2019*. ANVISA **2020**. https://www.documentador.pr.gov.br/documentador/pub.do?action=d&uuid=@gtf-escriba-sesa@409a2f59-6330-4db8-9cf4-eee5b664d7d2&emPg=true (accessed 2021-12-01).

(18) Morais, E. H. C.; Collins, C. H.; Jardim, I. C. S. F. Pesticide determination in sweet peppers using QuEChERS and LC-MS/MS. *Food Chem.* **2018**, *249*, 77-83. https://doi.org/10.1016/j.foodchem.2017.12.092

(19) Anastassiades, M.; Lehotay, S. J.; Stajnbaher, D.; Schenck, F. J. Fast and Easy Multiresidue Method Employing Acetonitrile Extraction/Partitioning and "Dispersive Solid-Phase Extraction" for the Determination of Pesticide Residues in Produce. *J. AOAC Int.* **2003**, *86* (2) 412-434. https://doi.org/10.1093/jaoac/86.2.412

(20) Perestrelo, R.; Silva, P.; Figueira, P. P.; Pereira, J.; Silva, C.; Medina, S.; Câmara, J. QuEChERS – Fundamentals, relevant improvements, applications and future trends. *Anal. Chim. Acta*. **2019**, *1070*, 1-28. https://doi.org/10.1016/j.aca.2019.02.036

(21) Lemos, F. M.; Lemos, M. F.; Pacheco, L. H. P.; Scherer, R. Monitoring of organophosphorous pesticide resdues in samples of banana, papaya, and bell pepper. *Quim. Nova*. **2015**, *38* (2), 268-273. http://dx.doi.org/10.5935/0100-4042.2015005

(22) López-Ruiz, R.; Romero-González, R.; Vidal, J. L. M.; Frenich, A. G. Determination of flonicamid and its metabolites in bell pepper using ultra-high-performance liquid chromatography coupled to high-resolution mass spectrometry (Orbitrap). *Food Addit. Contam. Part A* **2016**, 1-9. https://doi.org/10.1080/19440049.2016.1232865

(23) Skoog, D. A.; Holler, F. H.; Crouch, S. R. *Fundamentos de química analítica*. Thompson, **2006**.

(24) Souza, M. T.; Silva, M. D.; Carvalho, R. Revisão integrativa: o que é e como fazer. *Einstein* **2010**, *8* (1),102-106. https://doi.org/10.1590/S1679-45082010RW1134

(25) Figueiredo, V. O.; Miranda, J. A. T.; Colares, L. G. T.; Carvalho, J. L. V.; Castro, I. M.; Carvalho, L. M. J. Organophosphorus pesticides residues in cooked *Capsicum annum*. *Chem. Eng. Trans.* **2015**, *44*, 241-246. https://doi.org/10.3303/CET1544041

(26) Cutillas, V.; Jesús, F.; Ferrer, C.; Fernández-Alba, A. R. Overcoming difficulties in the evaluation of captan and folpet residues by supercritical fluid chromatography coupled to mass spectrometry. *Talanta* **2021**, *223*, 1-7. https://doi.org/10.1016/j.talanta.2020.121714

(27) Kemmerich, M.; Rizzetti, T. M.; Martins, M. L.; Prestes, O. D.; Adaime, M. B.; Zanella, R. Optimization by central composite design of a modified QuEChERS method for extraction of pesticide multiresidue in sweet pepper and analysis by ultra-high-performance liquid chromatography – tandem mass spectrometry. *Food Anal. Methods* **2014**, 1-12. https://doi.org/10.1007/s12161-014-9951-2

(28) Ferracane, A.; Zoccali, M.; Cacciola, F.; Salerno, T. M. G.; Tranchida, P. Q.; Mondello, L. Determination of multi-pesticide residues in vegetable products using a "reduced-scale" Quechers method and flow-modulated comprehensive two-dimensional gas chromatography-triple quadrupole mass spectrometry. *J. Chromatogr. A* **2021**, *1645*, 1-11. https://doi.org/10.1016/j.chroma.2021.462126

(29) Noh, H. H.; Kim, C. J.; Kwon, H.; Jin, D.; Moon, B. C.; Baek, S.; Oh, M.; Kyung, K. S. Optimized residue analysis method for broflanilide and its metabolites in agricultural produce using the QuEChERS method and LC-MS/MS. *Plos One* **2020**, *15* (10), 1-12. https://doi.org/10.1371/journal.pone.0235526

(30) Lawal, A.; Low, K. H. Residual determination of multiple pesticides in vegetables samples by LC-MS/MS coupled with modified QuEChERS-dSPE ionic liquid-based DLLME method. *J. Turkish Chem. Soc. Sect. A Chem.* **2021**, *8* (2), 693-704. https://doi.org/10.18596/jotcsa.845578

(31) Matadha, N. Y.; Mohapatra, S.; Siddamallaiah, L.; Udupi, V. R.; Gadigeppa, S.; Raja, D. P. Uptake and distribution of fluopiram and tebuconazole residues in tomato and bell pepper plant tissues. *Environ. Sci. Pollut. Res.* **2019**, 1-12. https://doi.org/10.1007/s11356-018-04071-4

(32) Buddidathi, R.; Mohapatra, S.; Siddamallaiah, L.; Gourishankar, M.; Hebbar, S. S. Dissipation pattern of flubendiamide residues on capsicum fruit (*Capsicum annuum L.)* undes field and controlled environmental conditions. *J. Environ. Sci. Heal. - Part B Pestic. Food Contam. Agric. Wastes* **2016**, *51* (1), 44-51. https://doi.org/10.1080/03601234.2015.1080496

(33) *PPDB: Pesticide Properties DataBase.* University of Hertfordshire. http://sitem.herts.ac.uk/aeru/ppdb/en/atoz.htm#E (accessed 2021-10-30).

(34) Guo, J.; Tong, M.; Tang, J.; Bian, H.; Wan, X.; He, L.; Hou, R. Analysis of multiple pesticide residues in polyphenol-rich agricultural products by UPLC-MS/MS using a modified QuEChERS extraction and dilution method. *Food Chem.* **2019**, *274*, 452-549. https://doi.org/10.1016/j.foodchem.2018.08.134

(35) Jin, X.; Kaw, H. Y.; Liu, Y.; Zhao, J.; Piao, X.; Jin, D.; He, M.; Yan, X. P.; Zhou, J. L.; Li, D. One-step integrated sample pretreatment technique by gas-liquid microextraction (GLME) to determine multi-class pesticide residues in plant-derived foods. *Food Chem.* **2022**, *367*, 1-9. https://doi.org/10.1016/j.foodchem.2021.130774

(36) Santiago, M. A. P. A.; Anjos, J. P.; Nascimento, M. M.; Rocha, G. O.; Andrade, J. B. A miniaturized simple binary solvente liquid phase microextraction (BS-LPME) procedure for pesticides multiresidues determination in red and rosé wines. *Michochemical J.* **2021**, *167*, 1-9. https://doi.org/10.1016/j.microc.2021.106306

(37) Hergueta-Castillo, M. H.; López-Rodríguez, E.; López-Ruiz, R.; Romero-González, R.; Frenich, A. G. Targeted and untargeted analysis of triazole fungicides and their metabolites in fruits and vegetables by UHPLS-Orbitrap-MS. *Food Chem.* **2022**, *368*, 1-9. https://doi.org/10.1016/j.foodchem.2021.130860

(38) Kapeleka, J. Á.; Sauli, E.; Sadik, O.; Ndakidemi, P. A. Co-exposure risks of pesticides residues and bacterial contamination in fresh fruits and vegetables under smallholder horticultural production systems in Tanzania. *Plos one.* **2020**, *15* (7), 1-13. https://doi.org/10.1371/journal.pone.0235345

(39) Zanella, R.; Prestes, O. D.; Adaime, M. B.; Martins, M. L. Chapter 24: QuEChERS. In: Borges, K. B.; Figueiredo, E. C.; Queiroz, M. E. C. *Preparo de amostras para análise de compostos orgânicos*. Publisher: LTC, **2015**.

SUPPLEMENTARY MATERIAL

Table 1. Analytes studied using quEChERS, by different authors

Ref.	Analytes	Class[33]	Polarity	log K_{ow}[33]	Recovery (%)	Standard deviation
(25)	Chlorpyrifos	organophosphate	nonpolar	4.7	74.2	It did not present standard deviation values.
	ethion	organophosphate	nonpolar	5.1	70.0	
	phentoate	organophosphate	-	-	93.0	
	phorate	organophosphate	-	-	101.1	
	Melation	organophosphate	nonpolar	2.8	76.6	
	methamidophos	organophosphate	Polar	-0.8	86.6	
	paration	organophosphate	-	-	77.7	
	Pyrazophos	phosphorothiolate	nonpolar	3.8	77.4	
	Pyrimifos	organophosphate	-	-	60.0	
	terbufos	organophosphate	nonpolar	4.5	87.9	
	Triazophos	organophosphate	nonpolar	3.6	74.6	
(22)	Flonicamid	nicotinoid	Polar	-0.2	88.0	11.0
	TFNA	organophosphate	-	-	NR	NR
	TFNA-AM	organophosphorus	-	-	NR	NR
	TFNG	organophosphorus	-	-	89.0	10.0
(26)	capture	Phthalimide	nonpolar	2.5	96.0	It did not present standard deviation values.
	folpet	Dicarboximide	nonpolar	3.0	89.0	
(27)	3-hydroxy carbofuran	carbamate	-	-	88.0	14.0
	acetamiprid	neonicotinoid	Polar	0.8	98.0	9.0
	ametrine	triazine	nonpolar	2.6	90.0	6.0
	atrazine	triazine	nonpolar	2.7	101.0	12.0
	azaconazole	triazole	nonpolar	2.4	91.0	7.0
	azoxystrobin	strobilurin	nonpolar	2.5	83.0	12.0
	benomyl	benzimidazole	nonpolar	1.4	NR	NR
	Boscalida	carboxamide	nonpolar	3.0	82.0	13.0
	bromuconazole	triazole	nonpolar	3.2	91.0	16.0
	buprofezin	Thiadiazinone	nonpolar	4.9	88.0	7.0
	carbaryl	carbamate	nonpolar	2.4	79.0	11.0

Table 1. Analytes studied using quEChERS, by different authors (continuation)

Ref.	Analytes	Class[33]	Polarity	log K$_{ow}$[33]	Recovery (%)	Standard deviation
(27)	Carbendazine	benzimidazole	nonpolar	1.5	105.0	12.0
	carbofuran	benzofuranil	nonpolar	1.8	110.0	8.0
	cyanazine	triazine	nonpolar	2.1	85.0	12.0
	cyproconazole	triazole	nonpolar	3.1	72.0	11.0
	Clomazone	isoxazolidinone	nonpolar	2.6	96.0	15.0
	Chloranthraniliprole	anthranilamide	nonpolar	2.9	85.0	12.0
	chlorbromuron	Urea	nonpolar	3.1	80.0	12.0
	Chlorpyrifos	organophosphate	nonpolar	4.7	75.0	11.0
	Clothianidin	neonicotinoid	Polar	0.9	106.0	18.0
	diazinon	organophosphate	nonpolar	3.7	92.0	14.0
	difenoconazole	triazole	nonpolar	4.4	96.0	17.0
	Dimethoate	organophosphate	Polar	0.8	93.0	9.0
	dimoxystrobin	strobilurin	nonpolar	3.6	95.0	11.0
	diuron	Urea	nonpolar	2.9	89.0	12.0
	dodemorph	Morphine	nonpolar	4.6	96.0	13.0
	epoxiconazole	triazole	nonpolar	3.3	117.0	22.0
	Ethiofencarb sulfone	methylcarbamate	-	-	73.0	11.0
	ethiofencarb sulfoxide	methylcarbamate	-	-	94.0	17.0
	ethoprophos	organophosphate	nonpolar	3.0	89.0	16.0
	fembuconazole	triazole	nonpolar	3.8	73.0	15.0
	Fempropatrin	pyrethroid	nonpolar	6.0	105.0	18.0
	phenpropimorph	Morphine	nonpolar	4.5	80.0	14.0
	Fluazifop-p-butyl	Aryloxyphenoxypropionic acid	nonpolar	4.5	89.0	12.0
	flusilazole	triazole	nonpolar	3.9	96.0	17.0
	flutolanil	carboxamide	nonpolar	3.2	101.0	14.0
	flutriafol	triazole	nonpolar	2.3	78.0	14.0
	furathiocarb	carbamate	nonpolar	4.6	99.0	16.0
	imazalil	imidazole	nonpolar	2.6	74.0	4.0
	iprovalicarb	carbamate	nonpolar	3.2	99.0	16.0
	linuron	Urea	nonpolar	3.0	80.0	15.0

Table 1. Analytes studied using quEChERS, by different authors (continuation)

Ref.	Analytes	Class[33]	Polarity	log K_{ow}[33]	Recovery (%)	Standard deviation
(27)	Linuron-d6 S	Urea	nonpolar	3.0	86.0	8.0
	Mephospholan	organophosphate	nonpolar	1.0	93.0	10.0
	Metalaxyl-M	phenylamide	nonpolar	1.7	92.0	9.0
	Metobrumuron	Urea	nonpolar	2.5	89.0	9.0
	metolachlor	Chloroacetamide	nonpolar	2.9	83.0	14.0
	mepronil	benzanilide	nonpolar	3.7	82.0	17.0
	metosulam	triazolopyrimidamine	Polar	0.2	95.0	8.0
	Mevinphos	organophosphate	Polar	0.1	76.0	8.0
	monocrotophos	organophosphate	Polar	-0.2	91.0	13.0
	monolinuron	Urea	nonpolar	2.2	84.0	12.0
	omethoate	organophosphate	Polar	-0.9	73.0	10.0
	ethyl paraoxon	organophosphate	-	-	85.0	7.0
	pencicuron	Phenylurea	nonpolar	4.7	93.0	10.0
	penconazole	triazole	nonpolar	3.7	88.0	9.0
	Picoxystrobin	strobilurin	nonpolar	3.6	86.0	15.0
	pyraclostrobin	strobilurin	nonpolar	4.0	97.0	17.0
	Pyrazophos	phosphorothiolate	nonpolar	3.8	79.0	9.0
	pyridafenthion	organophosphate	nonpolar	3.2	84.0	8.0
	pyrifenox	pyridine	nonpolar	3.4	75.0	5.0
	pyrimethanil	anilinopyrimidine	nonpolar	2.84	88.0	4.0
	ethyl pirimiphos	organophosphate	nonpolar	4.8	96.0	15.0
	methyl pyrimiphos	organophosphate	nonpolar	4.2	106.0	16.0
	Profenophos	organophosphate	nonpolar	1.7	94.0	16.0
	propanil	anilide	nonpolar	2.3	108.0	13.0
	propiconazole	triazole	nonpolar	3.7	102.0	9.0
	simazine	triazine	nonpolar	2.1	98.0	15.0
	tebuconazole	triazole	nonpolar	3.7	77.0	13.0
	tebufempyrade	pyrazole	nonpolar	4.9	94.0	15.0
	terbufos	organophosphate	nonpolar	4.5	117.0	2.0
	terbuthylazine	triazine	nonpolar	3.4	95.0	14.0
	tetraconazole	triazole	nonpolar	3.6	95.0	19.0

(continues on the next page)

Table 1. Analytes studied using quEChERS, by different authors (continuation)

Ref.	Analytes	Class[33]	Polarity	log K_{ow}[33]	Recovery (%)	Standard deviation
(27)	Thiabendazole	benzimidazole	nonpolar	2.4	90.0	5.0
	Thiacloprid	neonicotinoid	nonpolar	1.3	85.0	4.0
	Thiamethoxam	neonicotinoid	Polar	-0.1	99.0	12.0
	Thiobencarb	Thiocarbamate	nonpolar	4.2	99.0	15.0
	methyl thiophanate	benzimidazole	nonpolar	1.4	50.0	0.5
	Triazophos	organophosphate	nonpolar	3.6	103.0	18.0
	trifloxystrobin	strobilurin	nonpolar	4.5	99.0	12.0
	Triflumizole	imidazole	nonpolar	4.8	108.0	14.0
(18)	Acephate	organophosphate	Polar	-0.8	It did not show recovery values.	It did not present standard deviation values.
	azoxystrobin	strobilurin	nonpolar	2.5		
	carbaryl	carbamate	nonpolar	2.4		
	carbendazim	benzimidazole	nonpolar	1.5		
	carbofuran	carbamate	nonpolar	1.8		
	Clomazone	isoxazolidinone	nonpolar	2.6		
	Imidacloprid	neonicotinoid	Polar	0.6		
	methamidophos	organophosphate	Polar	-0.8		
	methiocarb	carbamate	nonpolar	3.2		
	Methomyl	carbamate	Polar	0.1		
	Thiabendazole	benzimidazole	nonpolar	2.4		
	Thiacloprid	neonicotinoid	nonpolar	1.3		
	Thiamethoxam	neonicotinoid	Polar	-0.1		
(28)	2.4-DDD	organochlorine	nonpolar	6.0	112.0	8.0
	2.4-DDE	-	-	-	122.0	7.0
	2,4-DDT	-	-	-	70.0	7.0
	2,4-Methoxychlor	-	-	-	97.0	7.0
	4,4,-methoxychloro olefin	-	-	-	124.0	6.0
	4.4-DDD	-	-	-	63.0	2.0
	4.4-DDE	-	-	-	117.0	8.0
	4,4-DDT	-	-	-	118.0	14.0
	4,4-Dichlorobenzophenone	-	-	-	109.0	2.0
	Aldrin	organochlorine	nonpolar	6.5	98.0	6.0

(continues on the next page)

Table 1. Analytes studied using quEChERS, by different authors (continuation)

Ref.	Analytes	Class[33]	Polarity	log K_{ow}[33]	Recovery (%)	Standard deviation
(28)	Alpha- BHC	-	-	-	110.0	6.6
	alpha-endosulfan	organochlorine	nonpolar	4.7	101.0	10.0
	azinphos-ethyl	organophosphate	nonpolar	3.2	NR	NR
	azinphos-methyl	organophosphate	nonpolar	3.0	NR	NR
	Beta-BHC	-	-	-	115.0	6.0
	beta-endosulfan	organochlorine	nonpolar	3.8	70.0	8.0
	bromfenvinphos	organophosphate	-	-	NR	NR
	bromfenvinphos-methyl	-	-	-	NR	NR
	bromophosethyl	organophosphate	nonpolar	6.2	86.0	4.0
	bromophos-methyl	organophosphate	nonpolar	5.2	96.0	5.0
	piperonyl butoxide	-	-	-	126.0	5.0
	carbophenion	organophosphate	nonpolar	4.8	74.0	4.0
	cis-chlordane	organochlorine	nonpolar	2.8	76.0	8.0
	cis-nanochlor	-	-	-	102.0	4.0
	chlorbenside	organochlorine	nonpolar	5.6	110.0	7.0
	chlorfenson	bridged diphenyl	nonpolar	4.2	66.0	2.0
	chlorfenvinphos	organophosphate	nonpolar	3.8	83.0	6.0
	chloroneb	substituted benzene	nonpolar	3.6	56.0	5.0
	Chlorpyrifos	organophosphate	nonpolar	4.7	102.0	3.0
	chlorpyrifos-methyl	organophosphate	nonpolar	4.0	107.0	5.0
	Chlorthiophos	-	-	-	102.0	3.0
	Coumaphos	-	-	-	152.0	15.0
	diazinon	organophosphate	nonpolar	3.7	120.0	4.0
	dieldrin	chlorinated hydrocarbon	nonpolar	3.7	120.0	6.0
	disulfoton	organophosphate	nonpolar	4.0	119.0	6.0
	Edifenphos	organophosphate	nonpolar	3.8	NR	NR
	endrin aldehyde	-	-	-	NR	NR
	endrin ketone	-	-	-	NR	NR
	endrina	organochlorine	nonpolar	3.2	78.0	5.0
	EPN	organophosphate	nonpolar	5.0	86.0	4.0
	heptachlor epoxide	-	-	-	57.0	4.0

Table 1. Analytes studied using quEChERS, by different authors (continuation)

Ref.	Analytes	Class[33]	Polarity	log K_{ow}[33]	Recovery (%)	Standard deviation
(28)	endosulfan ether	organochlorine	nonpolar	4.8	81.0	13.0
	ethion	organophosphate	nonpolar	5.1	84.0	5.0
	ethyl	-	-	-	NR	NR
	Phenamiphos	organophosphate	nonpolar	3.3	NR	NR
	Fenchlorphos	organophosphate	nonpolar	4.9	104.0	4.0
	Phenitrothion	organophosphate	nonpolar	3.3	108.0	11.0
	Fenson	organochlorine	nonpolar	3.6	107.0	4.0
	fenthion	organophosphate	nonpolar	4.8	70.0	2.0
	Phonofos	organophosphate	nonpolar	3.9	120.0	5.0
	phorate	organophosphate	nonpolar	3.86	111.0	4.0
	fosalone	organophosphate	nonpolar	4.0	NR	NR
	Gamma-BHC	-	-	-	117.0	10.0
	heptachlor	organochlorine	nonpolar	5.4	94.0	6.0
	hexachlorobenzene	chlorinated hydrocarbon	nonpolar	3.9	107.0	8.0
	iodofenphos	organophosphate	nonpolar	5.5	105.0	15.0
	isazophos	organophosphate	nonpolar	3.1	110.0	10.0
	isodrin	cyclodiene	nonpolar	6.8	112.0	6.0
	leptophos	organophosphate	nonpolar	6.3	NR	NR
	Lindane	organochlorine	nonpolar	3.5	118.0	11.0
	malathion	organophosphate	nonpolar	2.8	110.0	11.0
	Metacrypha	organophosphate	nonpolar	1.5	101.0	8.0
	Mevinphos	organophosphate	Polar	0.1	110.0	9.0
	mirex	organochlorine	nonpolar	5.3	106.0	6.0
	parathion	organophosphate	-	-	92.0	8.0
	Parathion-Methyl	organophosphate	nonpolar	3.0	109.0	14.0
	pentachloroanisole	-	-	-	119.0	5.0
	pentachlorobenzene	-	-	-	75.0	1.0
	pentachlorothioanisole	-	-	-	78.0	2.0
	pyraclophos	organophosphate	nonpolar	3.8	NR	NR
	Pyrazophos	phosphorothiolate	nonpolar	3.8	129.0	5.0
	pyridafenthion	organophosphate	nonpolar	3.2	110.0	10.0

Table 1. Analytes studied using quEChERS, by different authors (continuation)

Ref.	Analytes	Class[33]	Polarity	log K$_{ow}$[33]	Recovery (%)	Standard deviation
(28)	pyrimiphos-ethyl	organophosphate	nonpolar	4.8	113.0	4.0
	pyrimiphos-methyl	organophosphate	nonpolar	4.2	90.0	4.0
	Profenophos	organophosphate	nonpolar	1.7	NR	NR
	prothiophos	organophosphate	nonpolar	5.7	NR	NR
	Quinalphos	organophosphate	nonpolar	4.4	79.0	3.0
	endosulfan sulfate	organochlorine	-	-	111.0	3.0
	sulfotepp	organophosphate	nonpolar	4.0	108.0	2.0
	sulprophos	organophosphate	nonpolar	5.5	108.0	4.0
	terbufos	organophosphate	nonpolar	4.5	117.0	2.0
	tetrachlorvinphos	organophosphate	nonpolar	3.5	148.0	27
	Tetradiphon	organochlorine	nonpolar	4.6	108.0	4.0
	Tolclofos-methyl	organophosphate	nonpolar	3.8	71.0	3.0
	trans-chlordane	organochlorine	nonpolar	2.8	84.0	7.0
	trans-nanachlor	organochlorine		--	147.0	21.0
	Triazophos	organophosphate	nonpolar	3.6	60.0	4.0
(29)	broflanilide	Diamide	nonpolar	5.2	It did not show recovery values.	It did not show recovery values.
	DM-8007	-	-	-		
	S (PFH-OH)-8007	-	-	-		
(30)	baycarb	-	-	-	102.0	2.0
	carbaryl	carbamate	nonpolar	2.4	98.0	3.0
	diazinon	organophosphate	nonpolar	3.7	105.0	4.0
	Durban	organophosphate	-	-	108.0	6.0
	Metalaxyl	phenylamide	nonpolar	1.8	101.0	10.0
	propamocarb	carbamate	Polar	0.8	92.0	5.0
	Thiamethoxam	neonicotinoid	Polar	-0.1	91.0	4.0
	Thiobencarb	Thiocarbamate	nonpolar	4.2	91.0	3.0
(31)	fluopyram	benzamide	nonpolar	3.3	80.3	7.3
	Fluopyram benzamide	-	-	-	83.5	7.7
	tebuconazole	triazole	nonpolar	3.7	78.5	6.5

(continues on the next page)

Table 1. Analytes studied using quEChERS, by different authors (continuation)

Ref.	Analytes	Class[33]	Polarity	log K_{ow}[33]	Recovery (%)	Standard deviation
(32)	de-iodine fluobendiamide	-	-	-	97.2	6.4
	flubendiamide	Diamide	nonpolar	4.1	96.4	7.5
(21)	azinphos-methyl	organophosphate	nonpolar	3.0	111.5	10.0
	Coumaphos	organophosphate	-	-	106.0	8.1
	Demeton-S-methyl sulfone	organophosphate	-	-	118.0	10.1
	diazinon	organophosphate	nonpolar	3.7	102.2	7.9
	dichlorvos	organophosphate	nonpolar	1.9	92.7	0.7
	ethoprophs	organophosphate	nonpolar	3.0	87.2	11.4
	Fensulfotion	organophosphate	nonpolar	2.2	94.2	7.7
	fenthion	organophosphate	nonpolar	4.8	94.5	12.0
	Mevinphos	organophosphate	Polar	0.1	98.3	6.9
	sulprophos	organophosphate	nonpolar	5.5	101.8	12.7
	tetrachlorvinphos	organophosphate	nonpolar	3.5	99.5	3.4