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ONE-STEP EXTRACTION VERSUS QuEChERS FOR PESTICIDE ANALYSIS IN SELECTED FRUITS AND VEGETABLES

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This research was focused on the performance evaluation of a simple sample preparation involving acetonitrile extraction followed by liquid chromatography/mass spectrometry (LC/MS) analysis. Simplified method validation parameters, along with several other features, were compared to those of the citrate QuEChERS for 19 pesticides analyzed in four representative fruits and vegetables. The results showed comparable performances of the two methods for 5 of the 6 investigated validation parameters. The simplified method had better performance regarding the selectivity, since three analytes experienced a selectivity issue in one of four QuEChERS-treated matrices. Overall, results lead to an assumption that acetonitrile extraction could be reasonably implemented in certain cases of pesticide analysis, as an efficient and economical alternative to the official method. Since the research provides an insight into acetonitrile extraction capabilities in the domain of pesticide analysis in complex matrices, scientists, researchers or analytical practitioners can determine which method is most beneficial for a particular analysis.

Keywords: acetonitrile; EN 15662; HPLC; sample preparation

ЕКСТРАКЦИЈА ВО ЕДЕН ЧЕКОР НАСПРОТИ QuEChERS ЗА АНАЛИЗА НА ПЕСТИЦИДИ ВО ИЗБРАНО ОВОШЈЕ И ЗЕЛЕНЧУК

Ова истражување беше фокусирано на евалуација на перформансите на едноставна подготовка на примерок која вклучува екстракција со ацетонитрил проследена со анализа со течна хроматографија/масена спектрометрија (LC/MS). Параметрите за валидација на поедноставениот метод, заедно со неколку други карактеристики, беа споредени со оние на цитратно пуфериран QuEChERS за 19 пестициди анализирани во четири репрезентативни видови овошје и зеленчук. Резултатите покажаа споредливи перформанси на двата метода за 5 од 6-те параметри истражени за валидација. Поедноставениот метод имаше подобри перформанси во однос на селективноста, бидејќи три аналити покажаа проблем со селективноста во една од четирите матрици третирани со QuEChERS. Општо земено, резултатите водат до претпоставка дека екстракцијата со ацетонитрил може разумно да се спроведе во одредени случаи на анализа на пестициди, како ефикасна и економична алтернатива на официјалниот метод. Бидејќи истражувањето дава увид во способностите за екстракција со ацетонитрил во доменот на анализа на пестициди во сложени матрици, научниците, истражувачите односно аналитичките практичари можат да одредат кој метод е најкорисен за одредена анализа.

Клучни зборови: ацетонитрил; EN 15662; HPLC; подготовка на примероци

1. INTRODUCTION

The diversity and complexity of fruit and vegetable contents remain the main challenge in pesticide monitoring in these matrices. Consequently, various sample preparation methods have been developed, each one with the same goal, to generate consistent high-quality results of multiresidue analysis in many plant matrices at the lowest possible pesticide concentrations. At this point, the established sample preparation method is QuEChERS. Owing to the simple steps, QuEChERS is time effective and less prone to errors, thus it represents a streamlined approach to assess multiple pesticide residues in food.

A recent literature overview shows that the established QuEChERS method and its versions are dominantly employed for pesticide analysis in fruits and vegetables.[1-4] The non-QuEChERS sample preparation methods,[5,6] simple solvent extraction methods[7,8] and methods comprising minimal sample preparation[9-12] are less frequently reviewed. A gas-liquid microextraction technique (GLME), based on the distinctive boiling points between the analytes and the interferences to achieve effective separation, has been coupled to a dispersive solid-phase extraction (*d*SPE) in a one-step sample pretreatment approach by Jin and co-workers.[6] The main feature of such a method is that the integrated extraction and clean-up can be performed in several minutes. This method was evaluated for 35 pesticides in apple, leek, orange and honey matrices. Guo and co-workers[5] implemented the reverse approach, involving carbamate pesticide extraction from tomato and apple samples onto column-packed covalent organic frameworks with acrylamide sites, eluted with acetonitrile and subjected to the liquid chromatography/ultraviolet-visible analysis (LC/UV-Vis). Solid-liquid extraction with acetonitrile was employed for the analysis of chlorpyrifos and acetamiprid in tomato peel.[7,8]

Methods comprising minimal sample preparation depend on the technique used for instrumental analysis. A minimal sample preparation was utilized in the screening of 6 pesticides on lemon surface by the paper-spray ionization mass spectrometry.[9] Pesticide detection can be achieved by rubbing the fruit surface with some tool, then exposing it to the mass spectrometer inlet. Another technique involving minimal sample preparation is the surface-enhanced Raman spectroscopy (SERS), an optimized version of Raman spectroscopy, that involves an application of gold- and/or silver-based nanoparticles onto the analytical surface to enhance the Raman signal. The technique was developed for the analysis of thiram in apples,[11] triazophos in apples and cherry tomatoes,[10] and chlorpyrifos on tomato and grape surfaces.[12]

The objective of this study was to evaluate the performance of solvent extraction as the simplest possible sample preparation method. Evaluation included 19 pesticides, acetonitrile as an extraction solvent and four commodities (cucumber, lettuce, tomato and lemon) chosen for diverse texture, pigmentation and acidity.

The performances of pesticide analysis in the selected fruits and vegetables were compared to those of the citrate-buffered QuEChERS followed by dispersive solid phase extraction (*d*SPE) with PSA. Contrary to the practice of analysis in multiple reaction monitoring (MRM) mode, analytes were detected and quantified in the full scan MS^1 mode. Since the goal was to evaluate and compare the performances of the two methods, the simplification in mass analysis was intentionally implemented. Furthermore, if the screening itself is a purpose, recording a sample's spectrum in full scan mode will offer a possibility for the retroactive analysis of some other analytes, not covered by the current plan of analysis.

2. MATERIALS AND METHODS

2.1. *Chemicals and consumables*

Formic acid (FA) (98 %) and high purity pesticide standards (acetamiprid, azoxystrobin, boscalid, buprofezin, chlorpyrifos, cyprodinil, difenoconazole, fenhexamid, imidacloprid, kresoxim-methyl, metsulfuron-methyl, propiconazole, pyraclostrobin, pyrimethanil, pyriproxyfen, tebuconazole, thiacloprid, thiamethoxam, trifloxystrobin) were produced by Sigma-Aldrich® (St. Louis, Missouri, USA). Ammonium formate (AMF) (98 %), deionized water and high-performance liquid chromatography (HPLC) grade ethanol were produced by Carlo Erba (Emmendingen, Germany). HPLC grade methanol (MeOH) and HPLC grade acetonitrile (AcN) were produced by J.T. Baker, Thermo Fisher Scientific (Waltham, Massachusetts, USA). For the sample preparation, procedure prepacked Hillium QuEChERS extraction pouches (1 g of NaCl, 4 g of $MgSO_4$, 1 g of trisodium citrate dihydrate and 0.5 g disodium hydrogen citrate) and Hillium QuEChERS dispersion kits (25 mg PSA and 150 mg $MgSO_4$) were used. Syringe microfilters (Nylon Hydrophilic 0.22 µm) were produced by Membrane Solutions (Auburn, Washington, USA).

Fresh fruits and vegetables (tomato, cucumber, lettuce, and lemon) were purchased in a local supermarket.

2.2. *Instruments and instrumental parameters*

Appliances. For high purity standards weighing procedures, the analytical balance Sartorius BP110S (Göttingen, Germany) was used. The sample preparation procedure used the following appliances: blender 0.9 l BL142A by TEFAL (Rumilly, Haute-Savoie, France); balance (acc. ± 0.01 g) KB 2000-2N by KERN & SOHN GmbH (Balingen, Germany); and centrifuge Jouan C4i by Thermo Fisher Scientific. To facilitate the extraction, Digital Vortex-Genie 2 by Scientific Industries (Bohemia, New York, USA) was used. Nitrogen (99 %) was supplied by a nitrogen generator by PEAK Scientific (Glasgow, Scotland, UK).

Analytical instruments. Instrumental analysis was performed on an LC/MS system including a Surveyor autosampler by Thermo Finnigan LLC (San Jose, California, USA), and an Accela MS pump and LTQ XL mass spectrometer with linear ion trap analyzer by Thermo Fischer Scientific. Analytes were separated on a Hypersil GOLD column (C_{18}, 150 mm × 2.1 mm, particle size 3 µm), ionized in ESI+ ionization mode and monitored in MS^1 full scan mode (scan range *m*/*z* 150–600). Data was acquired and analyzed by Thermo Xcalibur™ software, version 2.1.0, SP1.1160.

Instrumental parameters. Ten microliters of sample were loaded on to a column in a partial loop injection mode and eluted with a mixture containing eluent *A* (buffer solution –0.1 % of FA and 0.03 % of AMF in water) and eluent *B* (MeOH), following the gradient: 0 min (90 % A), 0–2 min (90 % A), 2–7 min (30 % A), 7–30 min (30 % A), 30–35 min (90 % A) and 35–40 min (90 % A) with a flow rate equal to 300 µl min^{-1}. The chromatographic column was kept at thermostatic conditions at 25 °C. ESI source parameters were: sheath gas = 21 arbitrary units; auxiliary gas = 18 arb; *I* (spray voltage) = 5 kV; capillary *T* = 275 °C. Protonated molecular ions of tested analytes cover the *m*/*z* range from 200 to 409 (Table S1), therefore, the ion optics were optimized according to the pesticides' ions from the lower, middle and higher part of the *m*/*z* range, that is, according to the ions of pyrimethanil, buprofezin and trifloxystrobin. Tuned parameters meeting optimal detectability for all analytes were chosen.

2.3. *Procedures*

Stock preparation. Single-pesticide stock solutions (1 mg ml^{-1} each) were prepared by dissolving high purity pesticide standards in ethanol. Multi-pesticide solutions were prepared by mixing and diluting single stocks in ethanol.

Sample homogenization. Lemon, tomato, cucumber and lettuce, one kilogram of each, were cut and homogenized by blending for 5 min. All parts (flesh and peel) of the tomato, lettuce and cucumber were included in analysis. For lemon samples, only the flesh was used.

Sample preparation – extraction with AcN. Ten grams of homogenate were extracted with 10 ml of AcN. Extracts were centrifuged (10 min/3000 rpm) and supernatants were microfiltered prior to instrumental analysis. In the case of procedural standards preparation, the homogenate portion was spiked prior to the solvent extraction.

Sample preparation – citrate-buffered QuEChERS (EN 15662). Ten grams of homogenate were extracted with 10 ml of AcN, after which an extraction pouch was added. The mixture was immediately vortexed for one minute and centrifugated (10 min/3000 rpm). A supernatant aliquot was subjected to a dispersive extraction by the addition of one dispersion kit per ml of supernatant. The mixture was vortexed for one minute and centrifugated (10 min/3000 rpm). Supernatant was microfiltered prior to instrumental analysis. In the case of procedural standards preparation, the homogenate portion was spiked prior to the solvent extraction.

Validation study. Samples obtained from the market were initially screened for tested pesticides residues. Since none of the targeted pesticides was detected, the samples were considered blank samples and used for validation procedures. The matrix effect (ME) was evaluated by comparing the slopes of the calibration curves (0.01–15.00 µg ml^{-1}) of solvent-based and matrix-based multi-pesticide standards. The linear range of methods was evaluated with 7 procedural standards in the concentration range 0.00–15.00 mg kg^{-1}. Chromatographic repeatability was evaluated from the successive injections of ten procedural-based (5.00 mg kg^{-1}) and ten solvent-based standards (5.00 µg ml^{-1}). Trueness and precision were evaluated at three concentration levels (0.50, 5.00 and 15.00 mg kg^{-1}), each level at 5 replicates. Detection limits (DLs) were evaluated by the S/N criterion. The concentration of spiked sample that produced an analyte peak with *S/N* = 3 is established as the method's DL. In cases where the spiked samples produced an *S/N* ratio other than 3, the DL was estimated by a proportion involving the procedural standard with S/N ratio closest to 3.

3. RESULTS AND DISCUSSION

A prerequisite for a successful analysis is chromatographic or mass separation of analytes. Among the targeted analytes, boscalid and propiconazole would express a selectivity issue if they were not chromatographically separated, due to the closeness of MH^+ *m*/*z* values (Table S1).

Both one-step solvent extraction and the QuEChERS method expressed similar performances in terms of analyte recovery. Recoveries of the targeted analytes from tomato and lemon treated with the QuEChERS were within the limits (70–120 %) (Figs. S1 and S4). In lettuce and cucumber (Figs S2 and S3), at 0.50 mg kg^{-1} spike level, the recovery of imidacloprid was much below 70 %. Recoveries of the targeted analytes from each matrix treated with the simplified method (AcN extraction) were within the limits (70–120 %) (Figs. S1–S4). Considering the average recovery, both methods demonstrated satisfactory performance for each analyte (Fig. 1). The average recovery of thiamethoxam, after AcN extraction from lemon samples was less than 70 % (Fig. 1), however, out-of-limits recovery was 68 %. According to SANTE/11312/2021,[13] recoveries out of the 70–120 % range are acceptable if they are consistent (RSD < 20 %), but the mean recovery must not be lower than 30 % or higher than 140 %.

The detection limits of the two methods were comparable, and in most cases below or equal to the pesticide maximum residue limit (MRL) (Fig. 1). In three cases, the DLs were higher than the MRLs. The DLs of both methods were slightly higher than fenhexamid MRL in lemon; the DL of the QuEChERS was higher than cyprodinil MRL in lemon (Fig. 1).

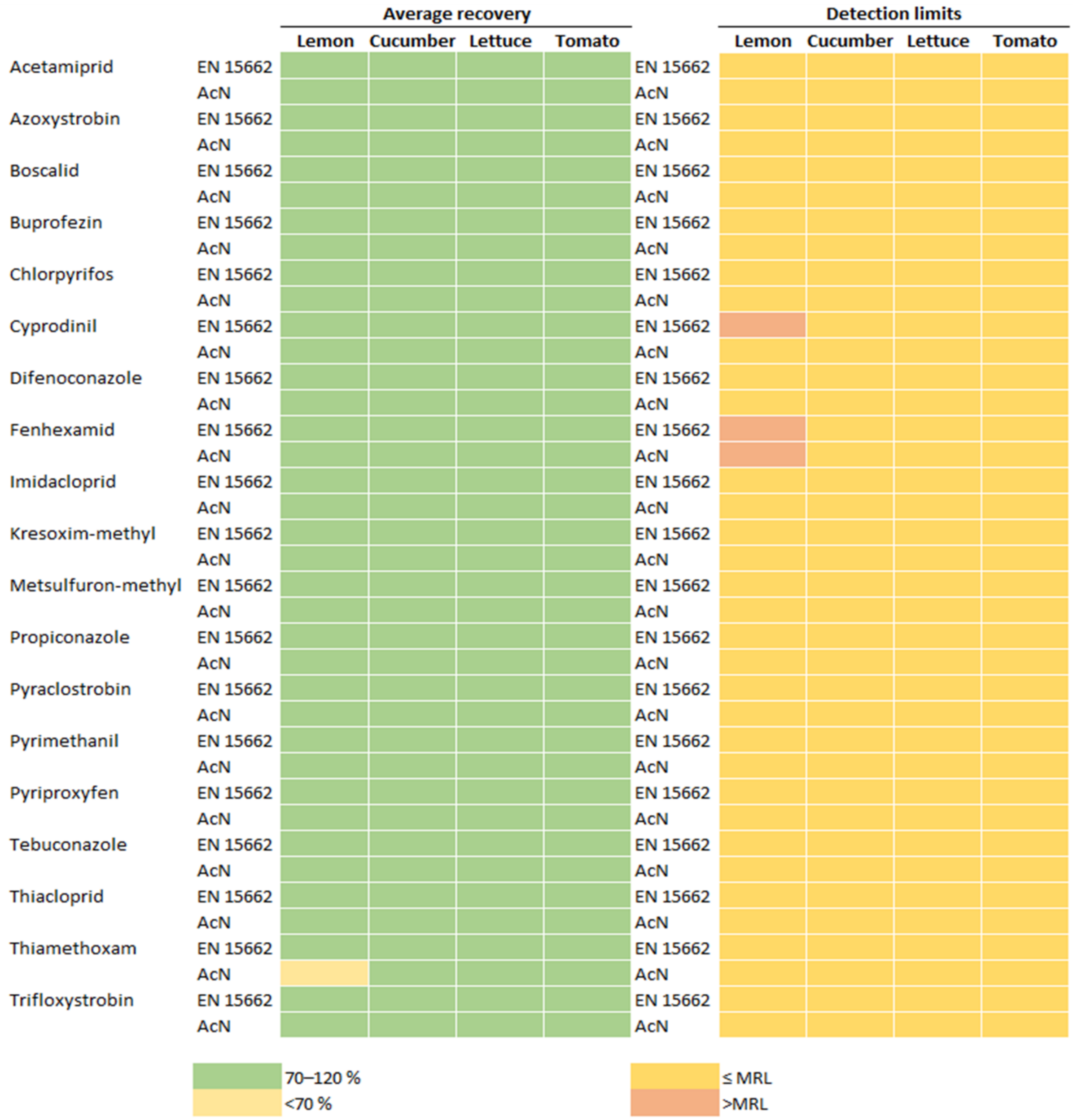

Fig. 1. Main performances overview of two methods for the targeted pesticide analysis in selected fruits and vegetables

Both methods demonstrated similar performances regarding the matrix effect and linearity range. Strong signal suppression was observed for each analyte in each tested matrix, regardless of the sample preparation procedure (Figures S1-S4). Analyte signals were suppressed by at least 37 %. Methods were linear in the tested analytical range (0.00 – 15.00 mg kg^{-1}), with back-calculated concentration deviations < 20 % and correlation coefficients > 0.90 (Table 1).

Significant pesticide retention time shifts were observed in sample extracts, regardless of the sample preparation procedure (Figure S5). The shift ranged from 0.12 to 1.11 min. The tolerable limit of ± 0.10 min was exceeded by 8 analytes in tomato, 4 in lettuce and cucumber and 12 analytes in lemon, all treated with the QuEChERS. The exceedance rate in samples treated with the simplified method was similar i.e., the retention time shift of 3 analytes in tomato, 5 in lettuce, 12 in cucumber and 11 in lemon exceeded the limits. The strongest shift was noticed in the lemon matrix, which stands out with the lowest pH value of the final extracts.

In terms of method selectivity, lemon was identified as a difficult matrix. A selectivity issue was observed for pyraclostrobin, tebuconazole and fenhexamid in the QuEChERS-treated lemon (Figure S6) and for fenhexamid in AcN-treated lemon (Figure S7). The issue for pyraclostrobin and fenhexamid was related to the overlay of analyte chromatographic peaks with the peaks of interferences. The issue for tebuconazole was related to the overlay of its peak with the peak of buprofezin, due to the heavy retention time shift of tebuconazole in lemon. Interestingly, the selectivity issue for pyraclostrobin and tebuconazole could be exclusively observed in the QuEChERS extracts.

Analytical data for herein investigated methods and for similar methods found in the literature are generally in mutual agreement. Melton and Taylor[4] implemented the same QuEChERS procedure for the analysis of buprofezin and chlorpyrifos in lemon by gas chromatography/mass spectrometry (GC/MS), which resulted in more than 94 % of recovered analytes and a DL of 0.01 mg kg^{-1}. Martinez Bueno et al.[3] also implemented the citrate QuEChERS for multi-pesticide LC/MS analysis in lettuce, but the *d*SPE step was performed with C_{18}. Percentages of recovered analytes ranged from 77 for azoxystrobin to 91 for thiacloprid. Another variation of the citrate QuEChERS followed by the *d*SPE with PSA and ENVI-Carb was implemented by Fearracane et al.[1] for the analysis of chlorpyrifos in tomatoes, cucumbers and lettuce by flow-modulated GC/MS. The recovery of chlorpyrifos was higher than 99 % in each matrix. The lowest DL of 1.8 µg kg^{-1} was established for cucumbers. Mahdavi et al.[2] implemented the dispersive solid-phase extraction with primary-secondary amine (PSA) for pesticide LC/MS analysis in cucumbers, but as a part of the acetate-buffered QuEChERS. Ten of more than 50 investigated pesticides matched our study. The recovery ranged from 74 % for kresoxim-methyl to 107 % for propiconazole. The lowest and the highest DL of 0.002 and 0.01 mg kg^{-1} were established for kresoxim-methyl and imidacloprid, respectively. Çatak and Tiryaki[14] implemented the same acetate-buffered QuEChERS for GC/MS analysis of chlorpyrifos and acetamiprid in cucumbers. A recovery higher than 80 % and LOQs of 2 and 10 µg kg^{-1} for acetamiprid and chlorpyrifos, respectively, were established. Dashtbozorgi et al.[15] applied a dispersive liquid–liquid microextraction technique for the extraction and pre-concentration of acetamiprid, imidacloprid, azoxystrobin and 17 other pesticide residues from QuEChERS extracts of tomato and cucumber. This combined procedure resulted in recovery of around 100 % and DLs ranging from 3.9 to 9.4 µg kg^{-1}.

In addition to our study, acetonitrile-based solvent extractions were implemented by Moura et al.[8] and Hegazy et al.[7] for the analysis of chlorpyrifos and acetamiprid in tomatoes. The detection techniques, however, were the paper-spray ionization mass spectrometry (chlorpyrifos) and the LC/UV-Vis (acetamiprid), providing the DL of 0.01 ppm and 0.03 µg ml^{-1}, respectively. In each case, pesticide recovery was higher than 94 %. A different solvent extraction procedure was implemented by Mohamed et al.[16] for the analysis of chlorpyrifos and five other pesticides in tomatoes and cucumbers by gas chromatography/flame ionization detection (GC/FID). Pesticides were extracted from samples in a successive extraction with acetone and dichloromethane, after which the extract was cleaned-up on a Florisil® stationary phase. Achieved DLs ranged from 0.001 (chlorpyrifos) to 0.20 mg kg^{-1} (profenofos).

T a b l e 1

Linear regression parameters (y = ax + b, conc. range 0.00 – 15.00 mg kg^{-1}, 7 points) for EN 15662 and AcN method

		Tomato			Cucumber			Lettuce			Lemon		
	Method	*a*	*b*	R^2	*a*	*b*	R^2	*a*	*b*	R^2	*a*	*b*	R^2
Thiame-toxam	EN 15662	49,942	607	0.9999	39,064	4,578	0.9971	45,668	–5,647	0.9990	23,806	8,495	0.9938
	AcN	29,397	–4,759	0.9989	22,034	–1,084	0.9998	25,274	4,890	0.9843	21,210	7,403	0.9964
Acetam-iprid	EN 15662	486,466	248,738	0.9834	379,027	278,482	0.9817	425,279	587,260	0.9815	165,015	165,897	0.9536
	AcN	312,583	237,557	0.9952	223,458	133,826	0.9859	272,525	150,852	0.9876	145,965	21,718	0.9984
Thiaclo-prid	EN 15662	122,297	33,645	0.9952	87,546	36,645	0.9910	116,744	30,588	0.9952	51,924	20,519	0.9931
	AcN	76,465	9,992	0.9995	49,158	16,813	0.9958	63,079	11,697	0.9959	29,673	11,311	0.9969
Im-idaclo-prid	EN 15662	21,500	29,936	0.9881	12,056	7,919	0.9907	14,559	18,370	0.9850	7,042	6,694	0.9992
	AcN	12,383	11,748	0.9976	7,176	4,941	0.9940	13,209	27,382	0.9178	5,332	2,489	0.9965
Metsulfu-ron me-thyl	EN 15662	38,308	147,477	0.9114	22,447	99,689	0.9482	22,974	123,848	0.9070	15,644	63,143	0.9595
	AcN	25,804	103,910	0.9797	18,556	70,425	0.9556	17,295	175,560	0.9320	9,075	83,970	0.9958
Pyrime-thanil	EN 15662	1,170,566	926,818	0.9901	742,540	756,042	0.9911	993,453	223,656	0.9996	403,327	23,229	0.9999
	AcN	667,633	73,335	0.9998	353,311	73,690	0.9992	527,774	136,482	0.9989	273,318	38,903	0.9998
Azoxystr obin	EN 15662	1,576,230	1,241,236	0.9660	982,868	754,357	0.9697	1,303,263	2,373,800	0.9810	624,781	509,640	0.9753
	AcN	1,047,786	641,847	0.9850	642,729	403,148	0.9765	926,415	668,696	0.9763	596,502	380,286	0.9771
Cyprodi-nil	EN 15662	2,944,760	1,610,905	0.9914	1,826,160	1,099,191	0.9907	2,753,017	1,483,388	0.9919	1,347,705	578,017	0.9892
	AcN	1,912,974	1,081,959	0.9928	1,101,383	945,764	0.9923	1,601,024	1,045,906	0.9885	857,576	927,468	0.9801
Boscalid	EN 15662	164,078	568,662	0.9492	105,761	509,623	0.9449	158,072	417,802	0.9592	73,347	301,370	0.9799
	AcN	102,244	526,804	0.9516	47,261	672,624	0.9691	74,009	595,158	0.9763	37,466	584,884	0.9662
Fenhex-amid	EN 15662	332,842	55,619	0.9984	200,520	29,784	0.9989	288,272	27,730	0.9997	61,730	8,002	1.0000
	AcN	201,886	–2,966	0.9995	108,899	12,473	0.9993	157,094	31,708	0.9980	106,134	16,633	0.9996
Kresoxim methyl	EN 15662	115,839	26,132	0.9975	81,169	7,792	0.9974	112,297	–35,606	0.9992	55,463	3,860	0.9997
	AcN	67,531	–9,810	0.9992	44,782	-5,484	0.9992	55,713	–1,362	0.9967	44,333	27,402	0.9965
Tebucon-azole	EN 15662	456,056	44,800	0.9995	335,944	46,944	0.9995	405,717	15,865	0.9999	49,270	4,971	0.9996
	AcN	264,252	–15,632	0.9993	180,366	4,045	0.9999	212,257	42,837	0.9981	161,520	349	0.9999
Pro-picona-zole	EN 15662	506,139	55,230	0.9995	359,105	39,303	0.9996	462,719	25,161	0.9999	249,045	24,293	0.9997
	AcN	298,162	–2,832	0.9997	198,263	9,269	0.9999	241,819	108,716	0.9930	178,305	68,814	0.9955
Pyra-clostrobin	EN 15662	386,406	200,652	0.9895	240,437	81,509	0.9952	353,274	170,541	0.9972	112,019	53,701	0.9926
	AcN	230,295	45,069	0.9978	140,144	32,557	0.9978	183,003	105,754	0.9951	92,956	61,009	0.9786
Bu-profezin	EN 15662	2,104,004	1,128,657	0.9826	1,408,629	621,707	0.9893	2,017,341	702,916	0.9921	881,980	275,503	0.9949
	AcN	1,295,527	361,312	0.9966	860,423	232,692	0.9949	1,186,921	410,927	0.9912	705,379	256,715	0.9914
Difeno-conazole	EN 15662	706,205	–43,422	0.9982	504,815	–75,625	0.9992	664,133	–216,835	0.9993	329,484	9,350	1.0000
	AcN	408,421	–135,632	0.9986	266,223	–110,243	0.9999	323,682	282,868	0.9522	213,260	–24,047	0.9988
Tri-floxystro bin	EN 15662	1,675,420	366,819	0.9973	1,132,714	311,321	0.9987	1,584,188	265,710	0.9993	802,219	166,187	0.9999
	AcN	1,015,259	65,089	0.9999	590,471	255,918	0.9987	822,058	314,827	0.9967	541,449	159,258	0.9968
Pyriproxy fen	EN 15662	1,716,352	539,341	0.9937	1,117,834	303,442	0.9973	1,574,590	351,082	0.9986	767,966	110,028	0.9997
	AcN	1,019,948	69,890	0.9998	616,235	106,065	0.9981	852,834	232,179	0.9953	546,597	134,723	0.9962
Chorpyri-fos	EN 15662	370,699	13,928	0.9967	234,163	34,077	0.9989	310,092	91,233	0.9941	178,660	–1,059	0.9999
	AcN	182,143	11,644	0.9933	114,122	32,707	0.9945	142,877	63,797	0.9891	114,403	17,945	0.9984

4. CONCLUSION

Performances of the first step of the QuEChERS sample preparation procedure, which is the acetonitrile extraction, were evaluated for 19 pesticides in four representatives of fruits and vegetables and were compared to the performances of the citrate-buffered QuEChERS. Both methods expressed comparable performances regarding most of the validated parameters, including the matrix effect, chromatographic repeatability, recovery, detection limits and linearity. Better performances regarding the selectivity were expressed in the acetonitrile extraction method, since 3 analytes experienced a selectivity issue in QuEChERS-treated lemon. In the end, the comparable performances of the simplified method and QuEChERS reasonably qualify the simplified method for implementation in certain cases of pesticide analysis, as an efficient and economical alternative to the official method.

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