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Determination of carbamates in edible vegetable oils by ultra-high performance liquid chromatography–tandem mass spectrometry using a new clean-up based on zirconia for QuEChERS methodology

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ABSTRACT

In this study a fast, selective and sensitive multiresidue method based on QuEChERS methodology has been evaluated and validated for the determination of carbamate pesticides, in edible vegetable oils by UHPLC–MS/MS. A new clean-up sorbent, Supel^{TM} QuE Z-Sep$^+$, has been successfully applied in vegetable oil extracts. Z-Sep$^+$ was compared with other sorbents (i.e. mixture of C18 and PSA) previously used for dispersive solid phase extraction of these matrices, reducing more effectively matrix effects without a significant decrease of analyte recoveries. Matrix effect was studied in different matrices (extra-virgin olive, sunflower, maize, linseed and sesame oil) being $\leq |30|$% for most of the studied pesticides. Under optimum conditions, recoveries ranged from 74% to 101%, with relative standard deviations lower than 10%. Limits of quantification ranged from 0.09 to 2.0 μg kg^{-1}, allowing their determination at the low concentration levels demanding by current legislation.

1. Introduction

Vegetable edible oils are products extracted from vegetable fruits or seeds by mechanical pressure or extraction with organic solvents. Within the group of vegetable edible oils, olive oil is most demanded by the European consumers, accounting for a market share of 21% [1]. Besides olive oil, European Union (EU) vegetable oil consumption also includes sunflower oil (20%), babassu oil (15%), maize oil (2%) and groundnut oil (1%) among others. In order to increase farming yield, pesticides are applied to crops at various stages of cultivation to provide protection against pests. However, the use of pesticides may generate residues which involve a risk for both the environment and human health. As they can persist up to the harvest stage, contamination of the raw material (olive fruits or oilseeds) and therefore of the final oil product is possible, especially when mechanical procedures are used for extraction [2,3]. Carbamate (CRB) pesticides are extensively used for agricultural activities. This kind of pesticides has an anticholinesterase activity, and its presence in foods could have adverse health effects [4,5]. Furthermore, most of the CRBs have been classified from category one (fatal if swallowed) to category 5 (maybe harmful if swallowed) by the Globally Harmonized System of Classification and Labelling of Chemicals (GHS), recommended by the World Health Organization (WHO) [6]. Therefore, the concentration of CRB residues in vegetable oils should be monitored strictly to ensure food safety. Several international organizations such as the EU [7] and the Codex Alimentarius Commission (Food and Agriculture Organization (FAO) and WHO) [8] have set up maximum residue limits (MRLs) in different vegetable oils that cover a large number of pesticides including some CRBs.

Abbreviations: (MeCN), acetonitrile; (ALD), aldicarb; (ALDSFN), aldicarbsulfone; (ALDSFX), aldicarbsulfoxide; (ASL), asulam; (BFU), benfurocarb; (BY), benomyl; (BTH), benthiocarb; (CAR), carbaryl; (CRB), carbamate; (CBZ), carbendazim; (CF), carbofuran; (CY), cymoxanil; (dSPE), dispersive solid phase extraction; (DETH), diethofencarb; (ESI), electrospray ionization; (ETH), ethiofencarb; (ETHSFN), ethiofencarbsulfone; (ETHSFX), ethiofencarbsulfoxide; (FEN), fenobucarb; (FNX), fenoxycarb; (FAO), Food and Agriculture Organization; (FURA), furathiocarb; (GC), gas chromatography; (GPC), gel permeation chromatography; (GHS), Globally Harmonized System of Classification and Labelling of Chemicals; (3-CF), 3-hidroxy carbofuran; (ISO), isoprocarb; (LOD), limit of detection; (LOQ), limit of quantification; (LC), liquid chromatography; (MS), mass spectrometry; (ME), matrix effect; (MRLs), maximum residue limits; (MeOH), methanol; (MTH), methiocarb; (MTHSFN), methiocarbsulfone; (MTHSFX), methiocarbsulfoxide; (MTY), methomyl; (METOL), metolcarb; (MRM), multiple reaction monitoring; (NP), napropamid; (OX), oxamyl; (PIR), pirimicarb; (PIRDES), pirimicarbdesmethyl; (Q), precursor ion; (PSA), primary secondary amine; (PR), promecarb; (PRM), propamocarb; (I), product ion; (PX), propoxur; (PY), pyraclostrobin; (QuEChERS), quick, easy, cheap, rugged, effective and safe; (S/N), signal to noise ratio; (SPE), solid phase extraction; (SPME), solid phase microextraction; (QqQ), triple quadrupole; (TH), thiodicarb; (UHPLC), ultra-high performance liquid chromatography; (WHO), World Health Organization

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As high selectivity is required for the identification of pesticides in samples with high fat content, gas chromatography (GC) and liquid chromatography (LC) coupled with mass spectrometry (MS), or tandem mass spectrometry (MS/MS) detection are widely used for the determination of pesticides in vegetable oils [9]. Thus, several methods have been published for the determination of pesticides in vegetable oils, including CRBs, using mainly GC–MS [10], GC–MS/MS [11–14], LC–MS [15] or LC–MS/MS [2,14,16]. On the other hand, the well-known advantages of ultra-high performance LC (UHPLC) make it a good alternative to conventional LC, and it has also been proposed for CRB determination [17–19].

The main components of vegetable oils are lipids, pigments and a high percentage of monounsaturated and saturated fatty acids [20]. Thus, the determination of pesticide residues in vegetable oils is still a challenge, as these matrices are highly complex. Sample treatment of oil samples, before the determination of pesticides by chromatography, should allow the complete removal of the high molecular-mass fat from the sample, in order to maintain the chromatographic system in working conditions [9]. With this purpose, different approaches have been proposed for the clean-up step in different vegetable oils such as solid-phase extraction (SPE) [10,12,21], solid-phase microextraction (SPME) [22], gel permeation chromatography (GPC) [13] and liquid–liquid extraction [10,15].

Over the last decade, quick, easy, cheap, rugged, effective and safe (QuEChERS) sample preparation approach, firstly established by Anastassiades et al. [23], has grown in popularity among pesticide residue determination, mainly for fruit and vegetable samples [24,25]. Nevertheless, the use of this methodology has been poorly explored for the analysis of vegetable oils, with the exception of the analysis of olives and olive oils [2,16,26]. The evaluation of different combinations of sorbents, such as PSA, C18 and CGB, for the dispersive SPE (dSPE) step of QuEChERS procedure has been reported [16]. However, a new clean-up sorbent, Supel™ QuE Z-Sep$^+$, consisting of both C18 and zirconia bound to the same silica particles, has been recently developed [27]. The C18 binds fats through hydrophobic interaction, while the zirconia acts as a Lewis acid, attracting compounds with electron donating groups. This material has been recently proposed for cleaning-up extracts of highly fatty vegetable commodities, such as avocado and almond, before the determination of pesticide residues [28]. It has proved to retain lipids and pigments much more effectively than the usually used C18 sorbent.

In this work, MS/MS combined with UHPLC was investigated for the determination of 31 CRB pesticide residues in edible vegetable oils. Moreover, the use of a new lipid-removal sorbent (Z-Sep$^+$) has been evaluated. To the best of our knowledge, no applications of this sorbent for cleaning vegetable oil extracts before the determination of CRB pesticides have been reported before. The sample treatment was developed to be easy, economic and with sufficient clean-up capacity to remove both fatty component and pigments which may cause matrix effect (ME). The proposed method has been validated according to EU guidelines [29] for five different edible vegetal oil matrices: extra-virgin olive, sunflower, maize, linseed and sesame oil. The results show the suitability of this procedure for monitoring CRBs in these products in a single run.

2. Material and methods

2.1. Chemicals and reagents

Methanol (MeOH) (LC–MS grade) and acetonitrile (MeCN) (LC grade) were supplied from VWR International (Darmstadt, Germany). Formic acid was obtained from Sigma-Aldrich (St. Louis, MO, USA) and acetic acid was supplied from Merck (Darmstadt, Germany). Ultrapure water (Milli-Q plus system, Millipore, Bedford, MA, USA) was used throughout the work.

Pestanal grade analytical standards of propamocarb (PRM), asulam (ASL), aldicarb sulfoxide (ALDSFX), aldicarb sulfone (ALDSFN), oxamyl (OX), methomyl (MTY), carbendazim (CBZ), benomyl (BY), ethiofencarb sulfone (ETHSFN), pirimicarb desmethyl (PIRDES), ethiofencarb sulfoxide (ETHSFX), methiocarb sulfoxide (MTHSFX), 3-hidroxy carbofuran (3-CF), methiocarb sulfone (MTHSFN), cymoxanil (CY), aldicarb (ALD), metolcarb (METOL), pirimicarb (PIR), propoxur (PX), carbofuran (CF), carbaryl (CAR), ethiofencarb (ETH), thiodicarb (TH), isoprocarb (ISO), fenobucarb (FEN), diethofencarb (DETH), methiocarb (MTH), promecarb (PR), napropamid (NP), fenoxycarb (FNX), pyraclostrobin (PY), benthiocarb (BTH), benfurocarb (BFU) and furathiocarb (FURA) were supplied by Fluka Analytical (Steinheim, Germany). Individual stock standard solutions of each compound were prepared by dissolving accurately weighed amounts in MeOH and were stored in the dark at 4 °C. They were stable for at least 4 months. Working standard solutions containing all the CRBs were freshly prepared by proper dilution of the stock standard solutions with MeOH.

QuEChERS extraction tubes were prepared in the lab. They consisted of a 50-mL tube with 4 g $MgSO_4$ and 1 g NaCl (Panreac Química, Barcelona, Spain) for extraction, and a 15-mL dSPE tube with different quantities of bulk C18, PSA, $MgSO_4$ (Agilent Technologies, Waldbron, Germany) and Z-Sep$^+$ (Supelco, Bellafonte, PA, USA): 150 mg C18+150 mg PSA+150 mg $MgSO_4$; or 150 mg $MgSO_4$+Z-Sep$^+$ (from 100 to 300 mg, with increments of 25 mg).

Nylon syringe filters, 0.2-μm × 13-mm (Bonna-Agela Technologies Inc., Wilmington, USA) were used for filtration of sample extracts prior to the injection into the UHPLC system.

2.2. Instrumentation

Separation was performed on an Agilent 1290 Infinity LC using a C18 column (Zorbax Eclipse plus RRHD 50 mm × 2.1 mm, 1.8 μm) supplied by Agilent Technologies. The mass-spectrometer measurements were performed on a triple quadrupole (QqQ) mass spectrometer API 3200 (AB Sciex, Darmstadt, Germany) with electrospray ionization (ESI). The instrumental data were collected using the Analyst® Software version 1.5 with Schedule MRM™ Algorithm (AB Sciex).

A centrifuge (Universal 320 model from Hettich, Leipzig, Germany), a mechanical shaker (model 384 from Vibromatic, Noblesville, USA), a nitrogen evaporator (System EVA-EC from VLM GmbH, Bielefeld, Germany) and a vortex (Genie 2 model from Scientific Industries, Bohemia, NY, USA) were also used throughout the sample preparation procedure.

2.3. Extraction procedure

Extra-virgin olive, sunflower, maize, linseed and sesame oils were collected in retail shops or department stores from Granada (Spain). The QuEChERS procedure was as follows: 3 g of sample was placed in a 50-mL falcon tube. Subsequently, 7 mL of water and 10 mL of MeCN were simultaneously added to the tube, and it was mechanically shaken for 10 min. QuEChERS extraction salts (4 g $MgSO_4$, 1 g NaCl) were added to the tube and it was shaken again for another 10 min. After that, the sample was centrifuged at 5000 rpm for 5 min. Then, 3 mL of the supernatant was transferred to the dispersive tube containing 150 mg of Z-Sep$^+$ and 150 mg of $MgSO_4$, stirred in vortex for 2 min and centrifuged (5000 rpm for 5 min). An aliquot of 2 mL of the MeCN extract was transferred to a vial, dried under a gentle N_2 stream and the final residue was re-dissolved with 500 μL of H_2O:MeOH (80:20 v/v),

shaken by vortex for 2 min, filtered through syringe filters and injected into the UHPLC–MS/MS system.

2.4. UHPLC–MS/MS analysis

The chromatographic method for the determination of CRBs was previously developed in our laboratory [19]. UHPLC separations were performed on a C18 column using a mobile phase consisting of 0.01% aqueous formic acid solution (solvent A) and MeOH with the same percentage of acid (solvent B) at a flow rate of 0.5 mL min^{-1}. The gradient profile was 0% B at the beginning; 20% B from 0.7 to 1.2 min; 50% B from 2.5 to 3 min; 95% B from 6.5 to 7.0 min; and finally in order to come back to the initial conditions, 0% B at 7.5 min, equilibrating for 3 min. Under optimum conditions, all the analytes were eluted for 6 min, while the run time for each injection was 9.5 min. The temperature of the column was 25 °C and the injection volume was 10 μL. The mass-spectrometer was working with ESI in positive mode under the multiple reaction monitoring (MRM) conditions shown in supplementary data (Table SD1). The ionization source parameters were: source temperature 400 °C; curtain gas (nitrogen) 30 psi; ion spray voltage 5000 V; and GAS 1 and GAS 2 (both of them nitrogen) were set to 50 psi.

3. Results and discussion

3.1. Optimization of QuEChERS

QuEChERS methodology was selected in order to achieve a quick and effective extraction. The optimization of QuEChERS was carried out with 3 mL aliquots of extra-virgin olive oil spiked at 50 μg kg^{-1} of each CRB. The recovery was used to evaluate the extraction efficiency.

The first extraction step of CRBs was based on the non-buffered QuEChERS method with MeCN extraction [26]. The use of MeCN as an extraction solvent allowed the simultaneous extraction of non-polar and relatively polar analytes in one extraction step, but a lot of interfering substances were co-extracted as well. It is well-known that ME is a key point for the determination of pesticides in fat matrices. We found necessary to optimize a dSPE clean-up step in order have cleaner extracts and avoid ME negative impact.

In order to compare the performance of the Z-Sep$^+$ sorbent material with those previously reported for dSPE of oil extracts [16], two combinations of sorbents were tested: (a) 150 mg C18 + 150 mg PSA + 150 mg $MgSO_4$; and (b) 150 mg Z-Sep$^+$ + 150 mg $MgSO_4$. The best results in terms of both average recoveries and ME were obtained when 150 mg Z-Sep$^+$ + 150 mg $MgSO_4$ were used. Fig. 1 shows the ME with these combinations, calculated as 100 × [(signal of spiked extract − signal of standard solution)/signal of standard solution]. As can be observed, for most of the 34 CRBs the decrease of ME employing this new sorbent was quite relevant, showing that Z-Sep$^+$ sorbent removes more efficiently lipids from the oil samples. The results clearly show that less residue remains in cleaned extracts and Z-Sep$^+$ sorbent removes more matrix than the combination of PSA and C18.

Finally, different amounts of Z-Sep$^+$ were weighted in the dSPE tube and tested (from 100 to 300 mg, with increments of 25 mg); the best results were obtained with 150 mg, as higher amounts did not reduce the ME and the recoveries of some of the target analytes, such as PRM for instance, were lower. However, even at the optimum conditions MEs for BTH, BFU and FURA were above ± 60% (see Fig. 1) without any improvement. Thus, it could be concluded that non-polar matrix compounds co-elute at the same retention time than these analytes. Therefore the method could not be validated for these three CRBs, and they were not considered for the rest of the study.

On the other hand, CBZ and BY were determined as the sum of both, as it is well known that BY is easily degraded to CBZ and butyl isocyanate [30]. Finally, at optimum conditions, 31 CRBs could be evaluated.

3.2. Method validation

In order to test the suitability of the method for the determination of CRBs in vegetable oils, it was characterized in terms of linear dynamic ranges, limits of detection (LODs) and limits of quantification (LOQs), ME, precision, trueness and selectivity.

3.2.1. Calibration curves and analytical performance characteristics

Calibration curves were established at five different concentration levels for each analyte (5, 10, 50, 100 and 250 μg kg^{-1}) by spiking blank samples of oil before the extraction process.

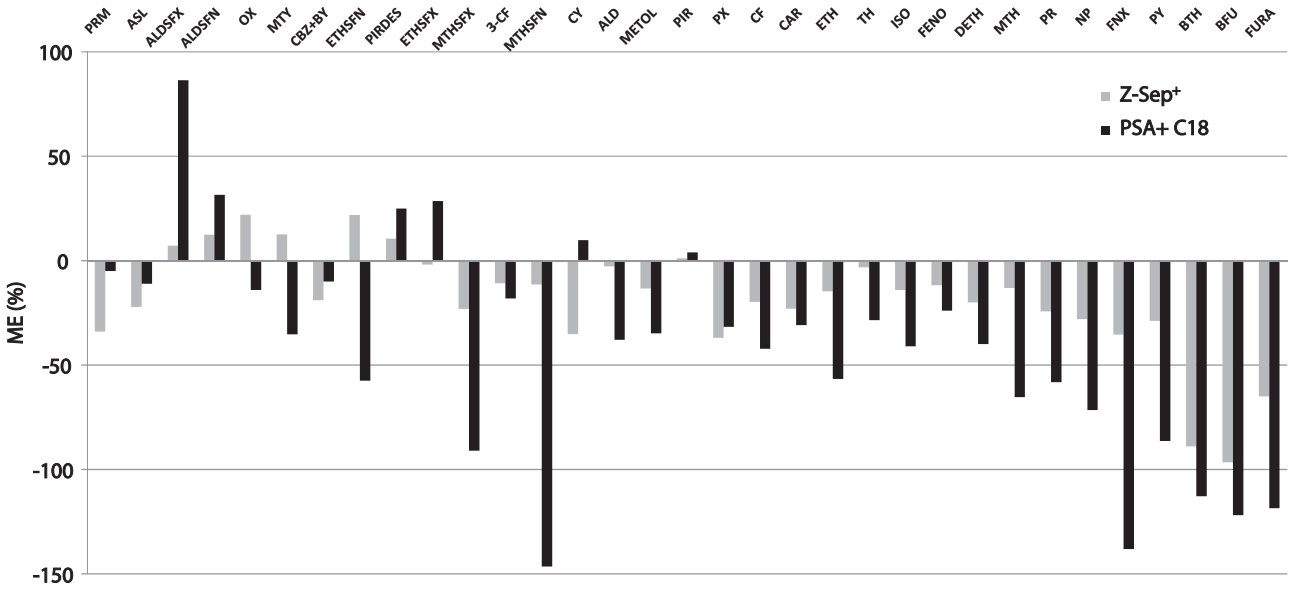

Fig. 1. Matrix effect (%) using two different sorbent combinations for dSPE (black: 150 mg C18 + 150 mg PSA + 150 mg $MgSO_4$; and gray: 150 mg Z-Sep$^+$ + 150 mg $MgSO_4$) (3 mL aliquots of extra-virgin olive oil spiked at 50 μg kg^{-1} of each CRB).

Using these calibration curves for routine analysis would allow overcoming not only ME, but also possible systematic errors that may occur during the sample treatment procedure. Each concentration level was processed following the proposed QuEChERS method and analyzed in triplicate in MRM mode, selecting the two highest precursor ions (*Q*)/product ion (*I*) transitions, which, together with retention times, were used to ensure adequate analyte identification according to SANCO guideline [29].

Performance characteristics of the method are summarized in Table 1 (complete information can be found in supplementary data, Tables SD2–SD6). LODs and LOQs were provided by the software analyst, as 3 × S/N and 10 × S/N, respectively. LOQ values were experimentally checked by analyzing three blank olive oil samples spiked at the LOQ concentration level for each CRB in triplicate. Good analytical signal with RSD ranging from 4% to 10% was obtained. As already commented in the introduction, MRLs have been established in vegetable oils only for some CRBs [8], so in supplementary data the MRLs for seeds, as reference values, are included [7]. As can be seen LOQs were always lower than the reference MRL. Therefore, the proposed method is adequate for the determination of very low levels of these compounds in the selected matrices.

ME is normally the combined effect of all components of the sample other than the analytes on the measurement [31]. The ME can be attributed to many sources, and normally in LC–MS it is due to the ion suppression/enhancement [32]. In order to check any possible difference among the five selected vegetable oils, ME was estimated for each CRB in the different matrices, by comparing the slopes of matrix-matched calibration curves (obtained by adding CRB standards to an extract of a blank sample) with the slopes of external standard calibration curves, both obtained with the same final concentrations levels (considering the proposed QuEChERS method). The following equation was used [33]:

$$\mathrm{ME}(\%) = \left(\left(\frac{\text{Slope of matrix}-\text{matched}}{\text{Slope of standard solution}}\right) - 1\right) \times 100$$

Table 1 shows the ME range values (lower ME and higher ME, considered in absolute values) for each CRB determined in the different oil samples by QuEChERS–UHPLC–MS/MS method (complete information for all CRB in each oil sample can be found in supplementary data, Tables SD2–SD6). As can be observed, all MEs were lower than ± 45%.

Table 1
Ranges of LODs, LOQs and ME (%) of the QuEChERS–UHPLC–MS/MS method for the determination of CRBs in vegetable oils (from the lowest value to the highest value obtained in all samples; for classification, ME has been considered in absolute value).

	LOD (μg kg^{-1})	LOQ (μg kg^{-1})	Matrix effect	
			Lowest %	Highest %
PRM	0.07–0.19	0.23–0.63	−6	−34
ASL	0.18–0.34	0.62–1.13	−22	−45
ALDSFX	0.08–0.27	0.26–0.37	12	−43
ALDSFN	0.04–0.13	0.13–0.95	15	−21
OX	0.08–0.57	0.26–1.90	22	−30
MTY	0.04–0.12	0.15–0.41	−2	19
CBZ+BY	0.13–0.30	0.43–0.98	−13	−35
ETHSFN	0.04–0.24	0.16–0.81	−3	22
PIRDES	0.06–0.29	0.19–0.98	11	−16
ETHSFX	0.05–0.28	0.18–0.95	−2	−19
MTHSFX	0.16–0.25	0.54–0.83	−12	−24
3-CF	0.06–0.29	0.19–0.99	−11	−22
MTHSFN	0.18–0.29	0.63–0.99	−8	−20
CY	0.28–0.46	0.92–1.50	−25	−35
ALD	0.05–0.15	0.16–0.49	−1	−21
METOL	0.03–0.17	0.09–0.58	−8	−31
PIR	0.16–0.29	0.54–0.98	−6	−21
PX	0.16–0.29	0.53–0.98	−12	−37
CF	0.04–0.25	0.13–0.84	−8	−40
CAR	0.08–0.48	0.28–1.60	−10	−23
ETH	0.04–0.26	0.13–0.86	−15	−25
TH	0.04–0.18	0.13–0.60	−3	−18
ISO	0.07–0.29	0.24–0.96	−14	−30
FENO	0.05–0.22	0.18–0.72	−12	−29
DETH	0.06–0.27	0.21–0.91	−7	−21
MTH	0.05–0.31	0.18–1.02	7	−30
PR	0.10–0.27	0.32–0.91	−17	−30
NP	0.08–0.25	0.27–0.84	−28	−35
FNX	0.09–0.60	0.30–2.00	−17	−39
PY	0.08–0.60	0.28–2.00	−24	−32

3.2.2. Precision study

The precision of the method was evaluated in terms of repeatability (intraday precision) and intermediate precision (interday precision) by application of the proposed QuEChERS–UHPLC–MS/MS method to extra-virgin olive oil samples spiked at three different concentration levels of CRBs. Repeatability was evaluated over three

Table 2
Intraday ($n=9$) and interday precision ($n=15$) expressed as %RSD of peak areas for spiked extra-virgin olive oil samples (level 1 = 10 μg kg^{-1}, level 2 = 50 μg kg^{-1} and level 3 = 100 μg kg^{-1}).

	Intraday precision			Interday precision		
	Level 1	Level 2	Level 3	Level 1	Level 2	Level 3
PRM	6	4	3	7	7	7
ASL	6	6	5	8	8	7
ALDSFX	5	4	4	6	5	5
ALDSFN	6	5	5	8	7	6
OX	5	5	5	8	6	6
MTY	6	6	5	9	7	7
CBZ+BY	5	4	3	5	5	5
ETHSFN	4	3	2	6	5	5
PIRDES	3	3	2	6	4	4
ETHSFX	5	4	4	7	7	6
MTHSFX	4	4	4	8	7	6
3-CF	4	2	2	6	5	5
MTHSFN	4	3	3	6	6	6
CY	6	4	4	7	8	6
ALD	5	3	4	7	6	5
METOL	3	3	3	6	5	4
PIR	5	5	4	7	6	6
PX	5	4	4	7	6	5
CF	4	4	3	5	5	4
CAR	6	5	5	7	5	5
ETH	5	5	4	8	8	7
TH	6	5	4	8	7	7
ISO	6	5	5	8	8	7
FENO	4	4	3	6	6	6
DETH	6	4	4	6	6	5
MTH	7	5	4	9	8	8
PR	7	6	5	9	8	7
NP	4	4	4	7	7	6
FNX	5	3	3	6	5	6
PY	4	3	3	6	5	5

Table 3
Ranges of recoveries and RSD for different spiked oil samples ($n=9$; level 1 = 10 μg kg^{-1}, level 2 = 50 μg kg^{-1} and level 3 = 100 μg kg^{-1}).

	Level 1		Level 2		Level 3	
	R (%)	RSD (%)	*R* (%)	RSD (%)	*R* (%)	RSD (%)
Extra virgin olive oil	72–110	3–7	78–102	2–6	79–99	2–5
Sunflower oil	76–102	4–9	78–100	4–9	80–99	4–8
Maize oil	71–103	3–7	75–105	2–6	88–103	2–4
Linseed oil	74–101	4–10	75–99	4–8	80–99	3–7
Sesame oil	83–104	4–8	83–100	3–8	87–97	2–8

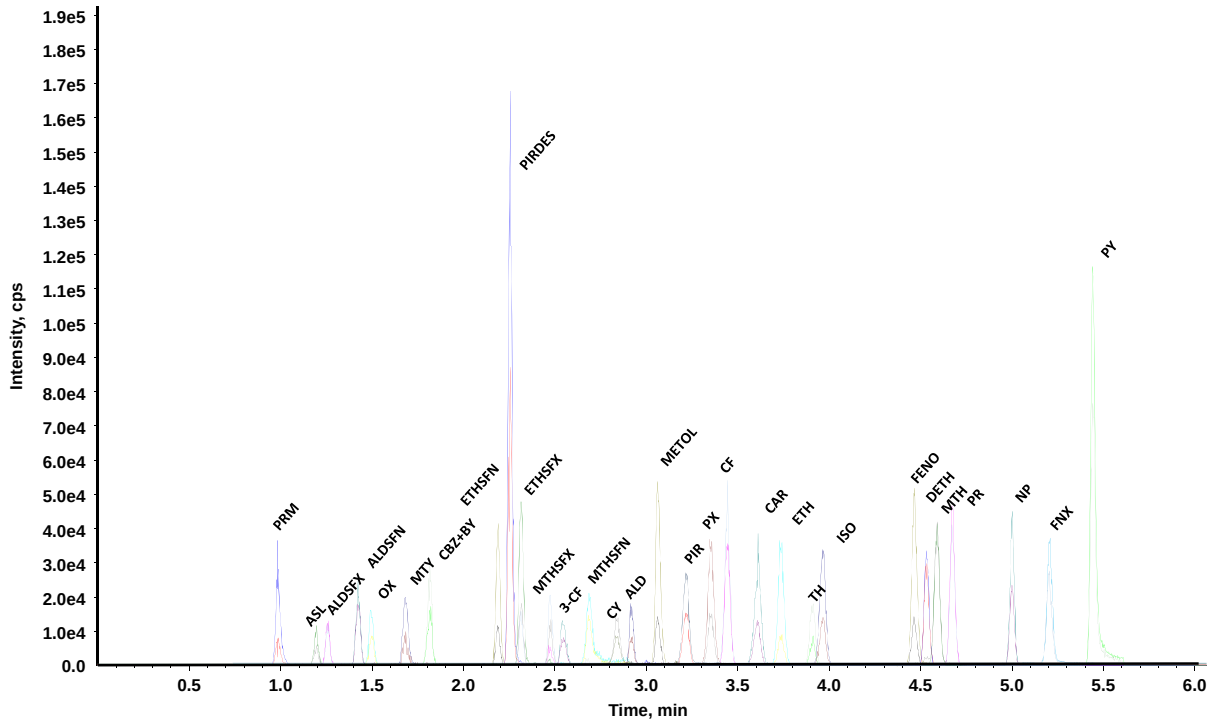

Fig. 2. Extracted ion chromatogram of a spiked extra-virgin olive oil sample applying the proposed method (5 μg kg^{-1} for each CRB).

samples prepared and injected in triplicate on the same day, under the same conditions. Intermediate precision was evaluated with a similar procedure, but the samples were analyzed in five consecutive days. The results, expressed as %RSD of peak areas, are summarized in Table 2. Good precision (RSD lower than 9%) was obtained in all cases. These results can be considered in agreement with the current demand [29,34].

3.2.3. *Trueness assessment*

In order to check the trueness of the proposed methodology, recovery experiments were carried out in different types of vegetable oil matrices, spiked at three different concentration levels of CRBs (10, 50 and 100 μg kg^{-1} for each CRB). For this study, quantification was carried out using matrix-matched calibration (obtained by adding CRB standards to an extract of a blank sample). Thus only ME was compensated and systematic errors of the sample treatment procedure (extraction efficiency plus losses during the procedure) were taken into account. In all the cases, samples were previously analyzed to check and prove the absence of target compounds; none of them gave a positive result above the LODs of the method.

The results are summarized in Table 3 (complete information can be found in supplementary data, Tables SD7–SD11). Recoveries between 71% and 110% were obtained, with satisfactory precisions (RSD $\leq$ 10%, n=9), fulfilling current legislation [29,34].

A typical UHPLC chromatogram corresponding to extra-virgin olive oil spiked with 5 μg kg^{-1} of each CRB and analyzed by the proposed QuEChERS–UHPLC–MS/MS method is shown in Fig. 2.

3.2.4. *Selectivity*

The confirmation of the identification of CRBs was carried out according to European guidelines for pesticides' determination [29,34], which establishes a tolerance level for the relative intensity between Q and I MRM transitions in real samples. This tolerance value depends on the Q/I value obtained from a standard solution. As can be seen in supplementary data (Table SD12), the Q/I ratios obtained from a spiked extra-virgin olive oil sample (5 μg kg^{-1} for each CRB), and from a standard solution (6 μg L^{-1} for each CRB) were within the tolerance range indicated in the above mentioned European guidelines [29,34]. Similar results were obtained for the rest of the matrices included in this study. Thus, considering these results along with the values obtained in the ME evaluation, it can be concluded that the method is selective for these pesticides and no significant interferences from the studied matrices affected the analytical response.

4. Conclusions

A simple and fast analytical method for simultaneous determination of CRB pesticides in five different edible vegetable oils (extra-virgin olive, sunflower, maize, linseed and sesame) has been developed and validated. The use of Z-Sep^{+} clean-up for the dSPE step of QuEChERS methodology provided a significant removal of co-extractive interferences and excellent recoveries with good RSD for 31 CRBs in such a complex matrix. The method is applicable for the determination of these contaminants at trace concentrations. The results in terms of analysis time, sensitivity, selectivity, precision, cleanliness of extracts and ME showed the suitability of this procedure for the monitoring of CRB residues in different kinds of vegetable oils in a single run.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2014.04.045.

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