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Multiresidue analysis of 184 pesticides in high-fat fish feed using a new generic extraction method coupled with gas and liquid chromatography-tandem mass spectrometry

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Abstract

Animal feed is typically plant-based and can contain pesticide residues. Methods for testing food and feed samples, such as the Quick Easy Cheap Effective Rugged Safe (QuEChERS) method or the Swedish Ethyl Acetate (SweEt) method, successfully extract many pesticide residues. However, nonpolar pesticides, such as organochlorine pesticides, show poor recovery when extracted from lipid-rich samples. The previously developed water-acetonitrile-heptane-solid-phase-extraction (WAHSPE) method shows better recoveries for the nonpolar pesticides but requires two injections per sample and per instrument. Here, we present a modified version of the WAHSPE method for pesticides in fish feed using one injection per sample and per instrument. Of the 184 pesticides tested, 179 met the European Union Legislation's validation criteria at a spike level of 50 µg/kg, showing recoveries between 70 and 120% and a relative standard deviation (RSD) below 20%. Organochlorine pesticides accounted for 14 of the tested compounds.

Keywords: Multiresidue extraction method, Feed, Gas chromatography-tandem mass spectrometry, Lipid-rich sample, Liquid chromatography-tandem mass spectrometry, Organochlorine, Pesticide

Introduction

"Feed" is a general term describing any nourishment provided to animals, such as pigs, cows, and fish, and is mainly of plant origin [14]. Pesticides are used to ensure high yields and high quality crops. For food and environmental safety, the European Union (EU) established maximum residue limits (MRLs) for pesticide residues [13]. The MRLs established for food commodities also apply to crops intended for feed. Thus, all feed commodities also need to comply with the food laws.

In this study, it is crucial to monitor pesticide residues in feed samples. Common extraction procedures for pesticide analysis from feed samples include methods such as the Quick Easy Effective Rugged Safe (QuEChERS) method [1, 2, 5] and the Swedish ethyl acetate (SweEt) method [8]. Detection of compounds is typically performed by chromatography coupled to a mass spectrometer, such as gas chromatography-tandem mass spectrometry (GC-MS/MS) and liquid chromatography-tandem mass spectrometry (LC-MS/MS) [1, 2, 5, 10].

Although QuEChERS and SweEt are widely used methods and generally perform well, some analytes, such as organochlorine pesticides and other nonpolar pesticides, have low recoveries when extracted from lipid-rich samples [6]. We previously developed a method, "water-acetonitrile-heptane-solid-phase-extraction" (WAHSPE), that effectively addressed this problem [4]. However, for the analysis of pesticides in high-fat fish feed, the

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WAHSPE method requires multiple injections of each sample. Multiple injections are not optimal, because multiple injections mean lower overall sample throughput. Consequently, a modified version of the WAHSPE method was developed to reduce instrument time by requiring only one injection for each of the analytical techniques (GC-MS/MS or LC-MS/MS).

The modified method was validated for 184 pesticides, including 14 nonpolar organochlorine pesticides. The sample was a fish feed matrix with a high lipid content (23%). In our previous work we validated the initial WAHSPE method using matrix-matched standard calibration. Analyte recoveries were typically in the range of 70–120% with relative standard deviations below 20%. [4]. This article aims to further develop the WAHSPE method by minimizing the time from sample preparation to final result, while still obtaining good recovery and detection of highly polar and nonpolar pesticides in a lipid-rich matrix, thereby providing a more generic alternative to the QuEChERS and SweEt methods. This publication shows a streamlined workflow and its application for real fish feed samples.

Materials and methods

Chemicals

Acetonitrile (HPLC grade S) was obtained from Rathburn (Walkerburn, UK). Heptane and formic acid were purchased from Merck (Darmstadt, Germany). Water was obtained from a Millipore Milli-Q water purification system (Molsheim, France). Ammonium formate was purchased from Sigma Aldrich (Buchs, Switzerland).

The analytical pesticide standards included in the study (purity > 96%) were purchased from Dr. Ehrenstorfer (Augsburg, Germany) or Sigma Aldrich (Taufkirchen, Germany). The relevant pesticides are listed in the Additional file 1.

Sample material

The fish feed sample for the validation experiment, selected due to its high lipid content, was obtained from BioMar A/S (Brande, Denmark). The feed sample consisted of 2 mm pellets containing 22.8% crude fat and was called CPK 15 (brand name).

The 16 fish feed samples analyzed in this study were collected in 2017 by the National Reference Laboratories (NRL) within the EU. The samples originated from the following EU member states: Austria, Czech Republic, Denmark, Estonia, Germany, Greece, Hungary, Italy, Norway, Poland, Slovakia, and Spain.

Materials

Filter vials (0.2 µm pore size) were obtained from Whatman, GE Healthcare (Princeton, USA). The supelcleanTM SPE cartridge EZ-Pop NP was obtained from Supelco (St. Louis, USA). A Reax 2 shaker for end-over-end extraction was obtained from Heidolph (Schwabach, Germany). Primary secondary amine (PSA), $MgSO_4$, and C_{18} sorbent were obtained from Agilent (Santa Clara, USA), Merck (Darmstadt, Germany), and International Sorbent Technology Ltd (Hengoed, UK), respectively. Single-use 15 mL and 30 mL polypropylene extraction tubes were obtained from Sarstedt (Nümbrecht, Germany). A Multifuge X3 FR centrifuge was obtained from Thermo Scientific (Waltham, USA). An OLE DICH Z 216 MK microcentrifuge was purchased from Hermle Labortechnik GmbH (Wehingen, Germany). Glass tubes (16.0 × 0.8–1.0 mm) were obtained from VWR (Søborg, Denmark). A TurboVap LV Evaporator nitrogen degasser was obtained from Zymark (Hopkinton, USA). Micropipettes and 1.5 mL microcentrifuge tubes were obtained from Eppendorf (Hamburg, Germany).

Sample preparation procedure

Each sample (at least 100 g) was cryo-milled (using liquid nitrogen) on a mill from Retsch (Haan, Germany) using a 1.0 mm mesh sieve. An aliquot of the milled sample (5.0 g) was placed in a 50 mL tube, and 10.0 mL 5% formic acid in acetonitrile, 10 mL Milli-Q water, and 10 mL heptane were added before the mixture was shaken end-over-end for 1 h. A total of 5.0 g ammonium formate was added to induce phase separation, and the mixture was shaken manually for 1 min, followed by centrifugation for 10 min at 5000×*g* and 20 °C. Three phases (water, acetonitrile, and heptane) were formed, and the two organic phases were transferred to separate 15 mL tubes. A 1.0 mL aliquot of the acetonitrile phase was transferred to an Eppendorf vial containing 250 mg PSA, 150 mg $MgSO_4$, and 25 mg C_{18} for dispersive solid-phase extraction (dSPE) clean-up. The Eppendorf tube was shaken for 30 s and centrifuged at 10,000×*g* for 10 min. Approximately 350 µL of the supernatant was transferred to a filter vial (0.2 µm pore size). Then, 200 µL of the filtered supernatant was transferred to a glass vial with a glass insert and acidified by adding 10 µL of 1% formic acid in acetonitrile. A 1.0 mL aliquot of the heptane phase was transferred into a glass tube, and 1.0 mL of pure acetonitrile was added. A gentle stream of nitrogen (40 °C) was used to evaporate the heptane phase until only the acetonitrile and residual lipids remained. The acetonitrile and the residual lipids were cleaned-up using an EZ-Pop NP SPE column as follows: the column was pre-conditioned with 10 mL acetone and dried for 10 min by vacuum. The acetonitrile and the residual lipids were loaded onto

the column. The retained analytes were eluted into a 20 mL glass test tube using 15 mL acetonitrile. The eluate was evaporated using a nitrogen stream at 40 °C for approximately 2 h, until a sample of approximately 1 mL was obtained.

A 100 µL aliquot of the acetonitrile eluate (cleaned heptane phase) and 100 µL of the filtered and acidified acetonitrile extract were mixed in an Eppendorf vial. Then, 100 µL of this mixture was mixed with 100 µL TPP (triphenyl phosphate) solution (0.2 µg/mL TPP in acetonitrile) in an autosampler vial and analyzed by GC-MS/MS and LC-MS/MS.

Method validation

Spiking procedure

Cryo-milled and sieved fish feed samples (5.0 g) were spiked with a stock solution containing 184 pesticides at three different levels (5, 10, and 50 µg/kg), with six replicates for each level.

Recoveries

Quantitation was based on the quantifier ion peak area divided by the peak area of the internal standard (TPP) and compared to a procedural calibration curve, which was described by a best-fit line. Seven procedural calibration points for each pesticide were included, ranging from 5.0 to 267 µg/kg. The procedural standards were prepared by spiking, with calibration solutions, a milled and sieved blank fish feed sample and following the sample preparation procedure (see Section "Sample preparation procedure" after milling and sieving).

Unfortunately, the unspiked blank sample contained low amounts of the pesticides fenpropidin, permethrin, pirimiphos-methyl, and propargite. Thus, the blank sample peak areas were subtracted from all spiked sample peaks for these pesticides. The content in the blank sample was also subtracted from the content in the calibration samples before preparation of the calibration curves.

LC-MS/MS analysis

For LC-MS/MS analysis, a Sciex Q-TRAP 6500 MSMS system linked to a Waters Acquity LC-system (degasser, pump, autosampler, and column compartment) was used. The column oven temperature was 40 °C, and the injection volume was 10 µL. For separation, a Sielc Obelisc R HPLC column (5 µm particle size, 2.1 × 150 mm) was used. The mobile phase consisted of Eluent A (water with 0.4% formic acid and 20 mM ammonium formate) and Eluent B (acetonitrile). The mobile phase gradient was as follows: linear gradient from 20 to 80% B (0–4 min), isocratic at 80% B (4–12 min), linear gradient to 20% B (12–12.5 min), and isocratic 20% B for 7.5 min (12.5–20 min) to prepare the column for the next injection. Electrospray ionization (ESI) source parameters were as follows: curtain gas, 40 L/h; collision gas, medium; ion spray voltage, 3000 V; source temperature, 500 °C; ion source gas 1, 40 L/h; ion source gas 2, 60 L/h. The dwell time was 10 ms, and the entrance potential (EP) was 10 V. The mass spectrometer was operating in multiple reaction monitoring (MRM) mode. To identify the pesticides, retention time and at least two product ions were acquired. MRM transitions are listed in Additional file 2: Table S1. One product ion was used for quantitation (quantifier ion), and the other product ion was used for identification (qualifier ion). Quantitation was based on the quantifier ion peak area divided by the peak area of the internal standard (TPP) and compared to the procedural calibration curve.

GC-MS/MS analysis

GC-MS/MS analysis was performed on a TSQ 8000 Evo Triple Quadrupole Mass Spectrometer paired with a TRACE 1310 GC and a Thermo Scientific TriPlus RSH autosampler. For chromatographic separation, a DB5-MS column was employed. The instrument was operating in MRM mode. Electron energy was 70 eV, the source temperature was 180 °C, and the transfer line temperature was 250 °C. The injection volume was 5 µL. For each pesticide, two sets of precursor and product ions were determined. One ion was for quantification and at least one ion was for qualification. MRM transitions are listed in Additional file 2: Table S1. The temperature program was as follows: 60 °C steady for 0.8 min, a gradient of 30 °C/min until 180 °C, a gradient of 5 °C/min until 280 °C, a gradient of 40 °C/min until 300 °C, a gradient of 120 °C/min until 310 °C. Quantitation was based on the quantifier ion peak area divided by the peak area of the internal standard (TPP) and compared to the procedural calibration curve.

Availability of data and materials

The datasets used and analyzed during the current study are available from the corresponding author upon reasonable request.

Results and discussion

Method development

The method that was developed was based on the method reported in Eyring et al., but improvements were made by decreasing preparation and instrument time [4]. The decrease in instrument time was achieved by decreasing the number of injections for each extract from

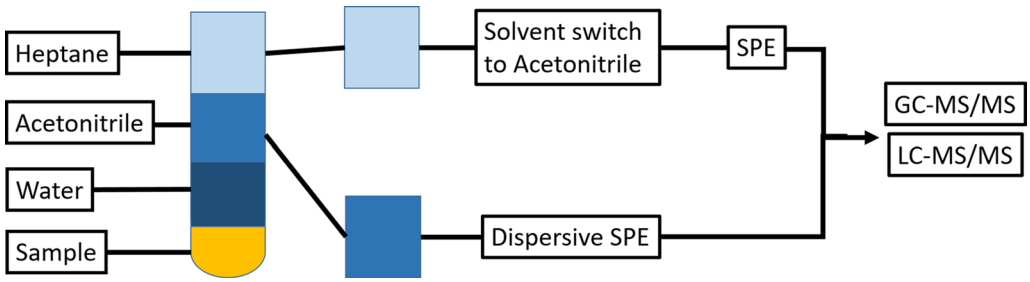

Fig. 1 Modified WAHSPE extraction method using one injection

two to one. The sample was extracted with three solvents (water, acetonitrile, and heptane) in the new method. A solvent shift to acetonitrile was done before the clean-up of the heptane phase. After the clean-up, the two acetonitrile extracts for each sample were mixed and analyzed (see Fig. 1).

Method validation

A validation study for 184 pesticides in fish feed with 23% lipid content was carried out to determine the performance of the modified WAHSPE method. The validation study involved extraction and analysis of the pesticides from fish feed samples spiked at three levels (5, 10, and 50 µg/kg) with six replicates at each level.

The validation parameters for the developed method were linearity, selectivity, limit of quantitation (LOQ), repeatability, accuracy, and precision. Matrix effects were taken into account using a calibration curve of procedural standards.

Linearity was tested by injecting seven different concentrations of each pesticide, plotting calibration curves, and calculating the correlation coefficients (R^2) for a linear fit. Selectivity was assessed by detecting the quantifier ion and at least one qualifier ion for each pesticide. The LOQ was determined by injecting six replicates of blank samples that were spiked at concentrations of 5, 10, and 50 µg/kg. The lowest of these concentrations that met the acceptance criteria (recovery of 70–120% and relative standard deviation (RSD) below 20%) was defined as the LOQ. Recoveries below 70% were accepted if the RSD was below 20%, but the concentrations found in these cases were corrected for the low recovery as described in SANTE/12682/2019 [3].

The repeatability was tested by performing six replicates within one day (intra-day variability) for each concentration. Repeatability was evaluated by measuring the RSDs of recovery replicates studied for each pesticide. The accuracy was determined from the recoveries from the spiked blank samples. The precision of the method for each pesticide was evaluated by determining the RSDs on the recoveries for the replicates.

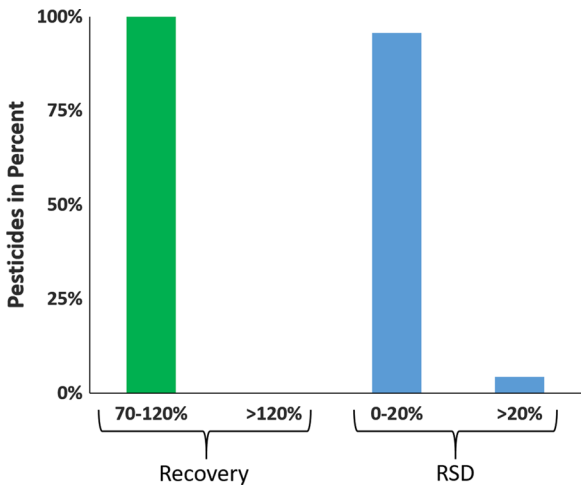

Fig. 2 Percent of the 184 pesticides achieving 70–120% or > 120% recovery (blue) and 0–20% or 20–40% RSD (green) when spiked into fish feed samples at 50 µg/kg

All analytes showed good linearity, since all calculated R^2 values were ≥ 0.98. The LOQs for the 184 pesticides were between 5 and 50 µg/kg (see Additional file 3: Table S2). An LOQ of 50 µg/kg was achieved for 179 pesticides (see Fig. 2). There were no pesticides with recoveries above 120%, but some recoveries were not possible to validate due to RSD values higher than

Table 1 Recoveries and repeatability values (RSDs in parentheses) for the analysis of organochlorine pesticides at a 50 µg/kg spike level

Compound	Percent total recovery (RSD)
Dieldrin	93 (29)
Chlordane alpha-cis	87 (15)
Chlordane gamma-trans	94 (12)
DDD pp	91 (13)
DDE pp	94 (16)
DDT op	97 (20)
DDT pp	97 (17)
Endosulfan sulfate	98 (16)
Endosulfan alpha	91 (11)
Endrin	88 (16)
HCH, alpha	88 (11)
HCH, beta	88 (17)
Heptachlor	93 (19)
Heptachlor epoxide	92 (15)

20%. These pesticides were dichlorvos, dieldrin, hexaconazole, profenofos, and propargite. A possible reason for these high RSDs may be interfering compounds, which co-elute with the analytes [9, 11, 12].

When analyzing the combined heptane and acetonitrile phases, more interfering matrix compounds may have been present than when the heptane and acetonitrile phases were analyzed separately. Different clean-up sorbents could be applied to reduce the amount of interfering matrix compounds, though the benefit compared to the higher effort should always be considered. The interfering matrix level was found to be acceptable overall for the clean-up method presented here. Thirteen of the 14 organochlorine pesticides were successfully validated at the spike level of 50 µg/kg (see Table 1). The QuEChERS method typically results in low recoveries for organochlorine pesticides from lipid-rich samples [6]. Generally, the SweEt method performs well when used to analyze pesticides in fruits and vegetables that have a low lipid content [8]. The SweEt method was tested, in a modified version, on samples with a high lipid content. Cyclohexane was used as the extraction solvent and gel permeation chromatography was added as a clean-up step [7]. Unfortunately, this additional step made the method very time-consuming.

The WAHSPE method used in the present study in general showed good performance for the analysis of nonpolar analytes and pesticides in lipid-rich matrices. Therefore, the modified WAHSPE method excels exactly where QuEChERS and SweEt fall short. Furthermore, the improvement of the WAHSPE procedure from our previous work [4] allows for increased sample throughput.

Application of the method to real samples and achieved benefits

The validated method was applied to the analysis of 16 real-world fish feed samples. This analysis was intended to demonstrate the applicability of the method to real-world samples and the potential for implementation of the method in routine monitoring of pesticides. Of the 16 samples, eight contained pesticides above the respective LOQs (see Table 2). Bromuconazole was found in four samples, difenoconazole and fludioxonil were each found in two samples, and 2-phenyl-phenol, cypermethrin, deltamethrin, diphenylamine, and fenazaquin were each found in one sample. Even though fish feed represents a complex sample for which it is difficult to obtain acceptable pesticide multi-residue analysis results, especially for nonpolar pesticides such as organochlorines, the present study showed that a modified WAHSPE method, combined with GC-MS/MS and LC-MS/MS analysis, is an excellent tool for analyzing pesticides of a wide polarity range in lipid-rich matrices. Compared to other extraction methods, such as QuEChERS and SweEt, the proposed method demonstrates improved recoveries of nonpolar organochlorine pesticides and provides acceptable recoveries for other pesticides at the same time. Furthermore, this modified version of the WAHSPE method requires fewer injections than the initial version, thus matching the SweEt and QuEChERS methods regarding efficiency. Acceptable values for precision, LOQs, and accuracy were obtained, showing that the method is suitable for regulatory and routine pesticide multi-residue analysis in lipid-rich matrices.

Table 2 Results for analyzed fish feed samples. Results are depicted in µg/kg

Name	K17-120	K17-121	K17-122	K17-123	K17-124	K17-125	K17-126	K17-129	K17-130	K17-131	K17-132	K17-133	K17-134	K17-135	K17-136	K17-137	Instrument
2-Phenylphenol	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	14.8	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	GC-MSMS
Bromuconazole	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	5.0	< LOQ	< LOQ	5.4	< LOQ	< LOQ	5.3	5.4	GC-MSMS
Chlorpropham	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	GC-MSMS
Cypermethrin	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	35.9	< LOQ	< LOQ	< LOQ	< LOQ	LC-MSMS
Deltamethrin	< LOQ	59.7	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	GC-MSMS
Difenoconazole	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	23.9	< LOQ	< LOQ	< LOQ	< LOQ	119.6	GC-MSMS
Diphenylamine	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	5.4	< LOQ	GC-MSMS
Fenazaquin	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	16.7	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	LC-MSMS
Fenvalerate	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	GC-MSMS
Fludioxonil	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	35.4	< LOQ	< LOQ	< LOQ	< LOQ	177.3	GC-MSMS
Phosalone	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	GC-MSMS
Pirimicarb desmetyl	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	GC-MSMS
Prothiofos	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	GC-MSMS

Supplementary Information

The online version contains supplementary material available at https://doi.org/10.1186/s13765-021-00610-9.

Additional file 1: Pesticide standards used in this work.

Additional file 2: Table S1. MRM and retention times of 184 pesticides.

Additional file 3: Table S2. Validation results and LOQs.

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Authors' contributions
PE: planning experiments, executing experiments, data analysis, data evaluation; SSH: planning experiments, support and advice in LC-MS/MS data analysis, support in result evaluation; MEP: planning experiments, support and advice in GC-MS/MS data analysis, support in result evaluation. All authors read and approved the final manuscript.

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Availability of data and materials
The datasets used and/or analysed during the current study are available from the corresponding author on reasonable request.

Declarations

Competing interests
The authors of the paper do not declare a competitive fiscal gain.

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