Method validation for 243 pesticides and environmental contaminants in meats and poultry by tandem mass spectrometry coupled to low-pressure gas chromatography and ultrahigh-performance liquid chromatography

Lijun Han,^{a,b} Yelena Sapozhnikova,^{a,*} and Steven J. Lehotay^a

^a US Department of Agriculture, Agricultural Research Service; Eastern Regional Research Center; 600 East Mermaid Lane; Wyndmoor, PA 19038; USA

^b College of Science, China Agricultural University; No. 2 Yuanmingyuan West Road; Beijing 100193; P.R. China

* Corresponding author.

phone: 1-215-233-6655; fax: 1-215-233-6642; e-mail: Yelena.Sapozhnikova@ars.usda.gov

Disclaimer: Mention of brand or firm names does not constitute an endorsement by the U.S. Department of Agriculture above others of a similar nature not mentioned.

Abstract

An easy and reliable high-throughput analysis method was developed and validated for 192 diverse pesticides and 51 environmental contaminants (13 PCB congeners, 14 PAHs, 7 PBDE congeners, and 17 novel flame retardants) in cattle, swine, and poultry muscle. Sample preparation was based on the “quick, easy, cheap, effective, rugged and safe” (QuEChERS) approach using filter-vial dispersive solid-phase extraction (d-SPE) cleanup. Split final extracts were analyzed in parallel by low-pressure (vacuum outlet) GC-MS/MS and UHPLC-MS/MS (10 min each), providing an additional degree of confirmation for 55 overlapping LC- and GC-amenable pesticides. Analyte protectants were utilized to improve sensitivity and decrease matrix effects in GC analysis, and only filtration of initial extracts was enough to avoid ion suppression in UHPLC-MS/MS. The method was validated at three spiking levels (10, 25, and 100 ng/g) at or below established tolerance levels in the sample types. Satisfactory recoveries (70-120%) and RSDs $\leq 20\%$ were achieved for 200 analytes. The validated method was successfully applied to the analysis of real-world incurred meat samples, further demonstrating the utility of the method for implementation in regulatory and commercial laboratories.

Keywords: pesticides, environmental contaminants, meat, method validation, analysis, LPGC-MS/MS, UHPLC-MS/MS

1. Introduction

Worldwide meat production totaled 304 million tons in 2012, with an annual average estimated consumption of 42-76 kg per person. (Food Outlook. Biannual report on global food markets, 2014) Average meat consumption in the US consists of 55% beef and pork, followed by 37% poultry. (The United States Meat Industry at a Glance) Meat and poultry are important nutritional sources of proteins, essential amino acids, and bioavailable minerals and vitamins. (USDA National Nutrient Database) At the same time, many anthropogenic chemicals, particularly lipophilic pesticides and environmental contaminants, may bioaccumulate in meats resulting in human exposure during consumption. Food of animal origin was estimated to contribute >95% of the human exposure to lipophilic anthropogenic contaminants. (Boada, Sangil, Alvarez-Leon, Hernandez-Rodriguez, Henriquez-Hernandez, Camacho, et al., 2014) Because many pesticides have been shown to cause various health effects, maximum residue

levels (MRLs), called tolerances in the US, have been established to control their residues in meats and protect human health. Depending on toxicity, pesticide tolerances in meats range from 10 to 3,000 ng/g, with most set between 10-100 ng/g. (Global MRL database)

Environmental contaminants, including polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), polybrominated diphenyl ethers (PBDEs) and other flame retardants (FRs) represent another group of organic lipophilic chemicals that bioaccumulate in fatty biological tissues. Dioxin-like PCBs and some PBDE congeners are recognized by the Stockholm Convention as persistent organic pollutants (POPs) based on their high persistence, toxicity, and bio-magnification in the food chain. (The Stockholm Convention on Persistent Organic Pollutants. United Nations Environmental Programme)

Previous reports have shown that meat and poultry are the major dietary sources of PBDEs in the human diet, although the PBDE body burden has been decreasing (Huwe & West, 2011) since penta- and octa-PBDE congeners have been banned. Nevertheless, new organic flame retardants (organophosphorous, organochlorine, and organobromine compounds) have been introduced in the commerce to comply with fire safety regulations. These new chemicals also possess lipophilic properties, high log K_{ow} values, suggesting their ability to bioaccumulate in animal and human tissues and warranting their monitoring in foods.

Numerous food safety programs operate around the world to help ensure that food is safe for consumption and to reduce environmental impact. Fast, simple, efficient, and cost-effective analytical methods for pesticides and other contaminants are needed in food safety monitoring programs to provide high sample throughput and accurate results. In the USA, USDA Food Safety and Inspection Service (FSIS) conducts routine monitoring of meat (cattle, swine, poultry, sheep, goats) samples to enforce regulatory compliance. The current FSIS sample preparation method for pesticide screening is based on liquid extraction of meat samples with ethyl acetate, followed by freeze-out and solid phase extraction (SPE) clean-up to remove interfering compounds, and involves multiple evaporation steps. (US Department of Agriculture, Food Safety and Inspection Service. Screening for Pesticides by LC/MS/MS and GC/MS/MS. #CLG-PST5.06) Other commonly reported methods for extracting lipophilic pesticides and environmental contaminants from meats are based on pressurized liquid extraction (PLE) with nonpolar organic solvents (*e.g.* hexane, ethyl acetate, dichloromethane) usually followed by cleanup with gel-permeation chromatography (GPC) to remove lipids. (Munoz, Munoz, Pineda,

Serrahima, & Centrich, 2012; Wu, Bao, Zhao, Wu, Han, & Ye, 2011) These methods take much time, solvent, and labor and require specialized equipment.

We have previously developed a high-throughput analytical method for multi-class analysis of selected pesticides and environmental contaminants in fish and shrimp tissues based on QuEChERS extraction and dispersive solid phase extraction (d-SPE) clean-up (Sapozhnikova, 2014; Sapozhnikova & Lehotay, 2013) combined with in-vial filtration (Han, Sapozhnikova, & Lehotay, 2014) using low pressure (LP) gas chromatography (GC) with tandem mass spectrometry (MS/MS).

The goal of this study was to optimize and validate this approach to include FSIS-priority contaminants in FSIS-regulated foods (*e.g.* cattle, swine, and poultry) for transfer to FSIS regulatory field service laboratories for routine monitoring in their National Residue Program (NRP). We sought to develop and validate a simple and fast method for simultaneous determination of multi-class pesticides and diverse environmental contaminants (PCBs, PAHs, PBDEs and flame retardants) in food muscle tissues to provide better quality of results for more chemicals of concern in more samples at higher throughput, less labor, and lower costs.

2. Materials and methods

2.1. Chemicals and materials

Standards of PBDE congeners (#28, 47, 99, 100, 153, 154, and 183), PCB congeners (#77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 170, 180, and 189), and PAHs (acenaphthene, acenaphthylene, anthracene, benz(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(g,h,i)perylene, benzo(k)fluoranthene, chrysene, dibenz(a,h)anthracene, fluoranthene, fluorene, indeno(1,2,3-cd)pyrene, naphthalene, phenanthrene, and pyrene), flame retardants [dechlorane plus (mixture of syn- and anti-isomers), hexabromobenzene (HBB); hexachlorocyclopentadienyl-dibromocyclooctane (HCDBCO), 2,2',4,4',5,5'-hexabromobiphenyl (PBB 153), pentabromoethylbenzene (PBEB), pentabromotoluene (PBT), 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (TBB), 1,2,5,6-tetrabromocyclooctane (TBCO), 1,2-dibromo-4-(1,2-dibromoethyl)cyclohexane (TBECH), tribromoneopentyl alcohol (TBNPA), and tris(1,3-dichloro-2-propyl)phosphate (TDCPP)] were all purchased from AccuStandard (New Haven, CT; USA). Standards of 1,2,4,5-tetrabromo-3,6-dimethylbenzene (TBX), tris(2-chloroethyl)

phosphate (TCEP), tris(1-chloro-2-propyl)phosphate (TCPP), and triphenyl phosphate (TPP) were purchased from Sigma-Aldrich (St. Louis, MO; USA), and dechlorane 604 standard was from Santa Cruz Biotechnology (Santa Cruz, CA; USA). Pesticide standards were from the Environmental Protection Agency's National Pesticide Repository (Fort Meade, MD; USA) and ChemService (West Chester, PA; USA).

For use as internal standards (IS), $^{13}\text{C}_{12}$ -2,2,4,4,5,5-hexachlorobenzene ($^{13}\text{C}_{12}$ -PCB 153), and a PAH surrogate cocktail containing acenaphthylene- d_8 , benzo[a]pyrene- d_{12} , benzo[g,h,i]perylene- d_{12} , fluoranthene- d_{10} , naphthalene- d_8 , phenanthrene- d_{10} and pyrene- d_{10} , were purchased from Cambridge Isotope Laboratories (Andover, MA; USA). Atrazine- d_5 (ethyl- d_5) and fenthion- d_6 (o,o- dimethyl- d_6), were from C/D/N Isotopes (Pointe-Claire, Quebec; Canada). FBDE 126 (5-fluoro-2,3,4,4,5-pentabromodiphenyl ether) and *p*-terphenyl- d_{14} used as quality control (QC) standard (added just prior to injection) in GC were purchased from AccuStandard. Phenacetin-ethoxy-1- ^{13}C (^{13}C -phenacetin) used as a QC standard for LC was acquired from Sigma-Aldrich. All standards were $\geq 98\%$ purity.

HPLC-grade acetonitrile (MeCN) was from Fisher Scientific (Pittsburgh, PA; USA) and acetone was from Sigma-Aldrich. Deionized water of 18.2 M Ω -cm was obtained using an E-Pure system from Barnstead/Thermolyne (Dubuque, IA; USA). Formic acid (88% purity) was from Spectrum Quality Products (New Brunswick, NJ; USA). Ammonium formate (HCO_2NH_4) was from Sigma-Aldrich. Anhydrous magnesium sulfate (anh. MgSO_4), 99.5% purity, and primary secondary amine (PSA) were purchased from UCT (Bristol, PA; USA). C18 (40 μm) was purchased from Thomas Scientific (Swedesboro, NJ; USA), and zirconium-based Z-Sep sorbent was from Supelco (Bellefonte, PA; USA). Filter vials with 0.45 μm polyvinylidene fluoride (PVDF) filters were from Thomson Instrument Co. (Oceanside, CA; USA). Two types of filter vials were used: 1) for filter-vial d-SPE in GC, screw-cap vials with short plungers allowed room for sorbent in the bottom shell receptacles; and 2) for filtering-only in LC, slit-septa snap-cap filter vials had standard length plungers. A press tray for simultaneous filtering of up to 48 filter vials was provided by Thomson Instrument Co.

A working standard mixture of the environmental contaminants, containing a total of 51 PCBs, PBDEs, PAHs, and FRs and 192 pesticides was prepared at 2.5 ng/ μL in MeCN/acetone, except 10-fold lower PCB concentrations (0.25 ng/ μL). This mixture was used to prepare spiking and calibration standard solutions in MeCN. The IS solution in MeCN contained a mixture of

atrazine-*d*₅ and fenthion-*d*₆ at 5 ng/μL, FBDE at 2.5 ng/μL, isotopically-labeled IS for PAHs at 1
126 ng/μL, and ¹³C₁₂-PCB 153 at 0.1 ng/μL. Atrazine-*d*₅ was used as an IS for all pesticides, and
fenthion-*d*₆ served as a back-up IS.

128 A mixture of analyte protectants (APs) contained ethylglycerol at 10 μg/μL,
gulonolactone and D-sorbitol each at 1 μg/μL, and shikimic acid at 0.5 μg/μL was prepared in
130 4/1 (v/v) MeCN/water with 0.5% formic acid. Also, this solution contained the QC standard for
GC of 0.438 ng/μL *p*-terphenyl-*d*₁₄. A separate solution of ¹³C-phenacetin at 4 μg/mL was
132 prepared in MeCN for use as the QC standard in LC.

Ten ≈500 g samples each of cattle, pork, and poultry muscle tissue from different parts of
134 the animal (grown organically), were purchased from local grocery stores. For example, chicken
wings, breast, thigh, drumsticks, and whole cornish hens were used as poultry samples. All
136 samples were filleted into skinless and boneless pieces, frozen and comminuted with dry ice
using a Robot Coupe (Ridgeland, MS; USA) RSI 2Y1 chopper to produce a fine powder, which
138 were stored in glass jars at -18°C until analysis. A Glas-Col (Terre Haute, IN; USA) platform
pulsed-vortexing mixer was used for extraction, (Sapozhnikova & Lehotay, 2015) and a
140 ThermoFisher (Waltham, MA; USA) Sorvall Legend RT centrifuge was used for centrifugation.

142 2.2. Low-pressure gas chromatography tandem mass spectrometry (LPGC–MS/MS) analysis

A separation of 211 GC-amenable compounds (199 analytes, 11 IS, and 1 QC standard)
144 was performed on a 15 m × 0.53 mm × 1 μm film thickness DB-5ms GC column (Agilent; Santa
Clara, CA; USA) connected at the inlet to a 5 m × 0.18 mm non-coated restrictor/guard column
146 from Restek (Bellefonte, PA; USA). The connection between the two columns was secured by
Ultimate union connectors (Agilent) as previously described. (Koesukwiwat, Lehotay, &
148 Leepipatpiboon, 2011) The calculated virtual column length used for constant flow of 2 mL/min
helium carrier gas was 5.5 m × 0.18 mm i.d. (vacuum outlet). The instrument was an Agilent
150 7890A/7000B gas chromatograph/triple quadrupole tandem mass spectrometer (the GC was
upgraded to 220V to allow fast temperature ramps). The GC oven temperature program started at
152 70°C, where it was held for 1.5 min, followed by ramps of 80°C/min to 180°C, 40°C/min to
250°C, and 70°C/min to 320°C, where it was held for 3.4 min, totaling 10 min. Injection volume
154 was 2.5 μL into a Multi-Mode Inlet (MMI) from Agilent operated as a programmable
temperature vaporizer with solvent vent mode. The initial MMI temperature was held at 80°C for

0.31 min (at which point the vent was closed), then ramped to 320°C at 420°C/min, and held at 320°C until the end of the run. Rinsing solutions of water/MeCN/acetone/methanol (1/1/1/1, v/v) for Wash 1 and MeCN for Wash 2 were used to prevent the syringe from clogging when using sugary APs in the final extracts.

The MS transfer line was at 250°C and ion source was 320°C. Electron ionization (EI) at -70 eV was used in MS/MS after a 2 min solvent delay; quadrupole temperatures were 150°C, and collision gas (nitrogen) was at 1.5 mL/min and quench gas (helium) was 2.25 mL/min. Two multiple reaction monitoring (MRM) transitions were selected for each analyte, and the MRM method was divided into 29 time segments, each containing 62 MRM transitions with a dwell time of 2.5 ms and “wide” MS resolution for all transitions. In the process of method development, we observed some large interferences from matrix for some analytes, which resulted in our replacement of the original (and perhaps the most intense quantifier ions) with others not susceptible to matrix interferences. Quantifier and qualifier transitions, collision energy (CE), and average retention times (t_R) for LPGC-MS/MS analysis are presented in Table S1. MassHunter software was used for instrument control and data acquisition/processing.

2.3. Ultrahigh-performance liquid chromatography tandem mass spectrometry (UHPLC-MS/MS) analysis

A Waters (Milford, MA; USA) Acquity UPLC-TQD, controlled by MassLynx software was used for UHPLC-MS/MS of 98 pesticides (55 overlapping with LPGC-MS/MS). A Waters BEH C18 column, 100 mm × 2.1 mm i.d., 1.7 µm particles, integrated with a Waters VanGuard pre-column of 5 mm × 2.1 mm i.d., 1.7 µm BEH C18 particles, was used for separation at 40°C. The mobile phase consisted of: (A) 95/2.5/2.5 (v/v/v) H₂O/MeOH/MeCN and (B) 1/1 (v/v) MeOH/MeCN, both solutions containing a mixture of 20 mM ammonium formate and 0.1% formic acid. The gradient was 95% A for 0.25 min, then ramped to 99.8% B from 0.25 min to 7.75 min, followed by 1.00 min hold time, after which the column was re-equilibrated for 1.45 min, making the total run time 10.25 min. The flow rate was 0.45 mL/min, and the injection volume was 2 µL (autosampler tray at 18°C).

Electrospray positive ionization (ESI+) was used for the analysis of 100 LC-amenable compounds (98 pesticides, 1 IS and 1 QC standard) with 3 MRM transitions for all but a few analytes (Table S2). Fixed parameters included 2kV capillary voltage, 3 V extractor voltage,

120°C source temperature, 450°C desolvation temperature, 1000 L/hr desolvation gas flow, 50 L/hr cone gas flow. The gas cones were cleaned and changed between each long sequence of sample extracts.

One precursor and two product ions were selected, and identification was based on 3 ion transitions, their ratios, and t_R . MRM transitions were scheduled within ± 0.2 min for each analyte expected t_R with auto-dwell time automatically adjusted by the software. Table S2 lists t_R , selected ions, cone voltages, and optimized CEs for LC-amenable analytes.

2.3.1. Post-column infusion

To evaluate d-SPE cleanup efficiency and matrix effects (MEs) in UHPLC-MS/MS analysis, a post-column infusion approach (Stahnke, Reemtsma, & Alder, 2009) was employed for 5 selected pesticides. Blank reagents and matrix extracts with and without d-SPE cleanup were injected in the UHPLC method as usual and the different infused pesticides (25 ng/ μ L, 20 μ L/min) were monitored throughout the chromatogram in MS/MS. The acquired data were subjected to smoothing with a smooth factor = 2, window size = ± 5 scans, and applying a mean smoothing method in Smooth Tool of the MassLynx software, thus resulting in 508 smoothed data points for each MRM chromatogram for each sample matrix and treatment.

2.4. Sample preparation

The sample preparation procedure was based on the previously reported QuEChERS approach using filter-vial d-SPE with a few modifications (Han, Sapozhnikova, & Lehotay, 2014). For example, a sample test portion of 5 g rather than 10 g was used to save cost of reagents while still representing the bulk sample, in accordance with finding from a recent study. (Sapozhnikova & Lehotay, 2015)

Several experiments were conducted to re-assess and optimize the method for the new matrices. For example, the use of APs was evaluated and integrated into the final LPGC-MS/MS method. Also, different d-SPE sorbents and their combinations were tested in filter-vial d-SPE to evaluate recoveries of the selected contaminants. In this experiment, 4 mL H₂O (reagent blank) was fortified with the analytes 100 ng/mL, and extracted with 4 mL of MeCN using a Glas-Col shaker for 10 min at 80% setting with a maximum pulsing. Then, 2 g of HCO₂NH₄ was added, and the tubes were shaken for 1 min and centrifuged for 3 min at 4150 rpm (3711 rcf). Aliquots

(0.5 mL) of the extracts were placed into 0.45 μ m PVDF filter-vials for d-SPE cleanup as follows (each in triplicate): (1) 75 mg anh. MgSO_4 , (2) 75 mg anh. MgSO_4 + 25 mg of C18, (3) 75 mg anh. MgSO_4 + 25 mg of PSA, (4) 75 mg anh. MgSO_4 + 25 mg of Z-Sep, (5) 75 mg anh. MgSO_4 + 25 mg of each C18, PSA, and Z-Sep. The resulting extracts were analyzed by both LPGC-MS/MS and UHPLC-MS/MS.

Based on these experiments, the final sample preparation protocol was as follows: (1) 5 g test portion is weighed into a 50 mL polypropylene centrifuge tube (3.5 mL water served as reagent blank); (2) 100 μ L of IS solution is added (or spike solution including IS), and the tubes are briefly vortexed and 15 min is allowed for integration into the muscle tissue; (3) 5 mL of MeCN is added using a bottle dispenser, and the samples are extracted on the platform shaker for 10 min at 80% setting with a maximum pulsation; (4) 2.5 g of HCO_2NH_4 is added to induce phase separation, and the tubes are shaken as before for 1 min; and (5) the tubes are centrifuged at room temperature for 3 min at 4150 rpm (3711 rcf).

For UHPLC-MS/MS, 0.5 mL of this extract, 25 μ L of QC standard ^{13}C -phenacetin, and 71.4 μ L of MeCN (to compensate for calibration standard volumes) are transferred to the shell portion of the filter vial and filtered through 0.45 μ m PVDF (without d-SPE) by pressing the plunger portion of the vial into its shell.

For LPGC-MS/MS analysis, filter-vial d-SPE cleanup is performed as follows: (A) transfer 0.6 mL of extracts into a vial shells containing a 180 mg sorbent mixtures consisting of 90 mg anh. MgSO_4 + 30 mg each of PSA, C18, and Z-Sep; (B) place the plungers halfway into the shells in a tray, and shake the tray vigorously for 30 s; (C) use the press to fully depress the plungers to filter the extracts; (D) transfer 175 μ L of the cleaned/filtered extracts to an amber-glass autosampler vial containing a micro-vial insert, plus 40 μ L of the AP mixture containing *p*-terphenyl- d_{14} and 25 μ L of MeCN to match sample volumes with the calibration standards; (E) shake the vials end-to-end for 10 s (this is important because diffusion is initially slow).

2.5. Method validation

The three days validation procedure involved analysis of beef (day 1), chicken (day 2) and pork (day 3) samples. On each day, 4 replicate test portions of the 10 different comminuted beef/chicken/pork samples were weighed into 50 mL tubes. One portion was a matrix blank, and the others were spiked at 10, 25, and 100 ng/g, yielding 10 replicates for each matrix type at each

level. Equal parts of the 10 muscles of each kind of meat were mixed together to make an
“average” blank matrix, extracts of which were used in matrix-matched (MM) calibration
standards at 0, 5, 10, 25, 100, and 200 ng/g (10 times lower for PCBs). Also, a reagent blank was
included each day during the validation study. Reagent-only (RO) calibration standards were
prepared in MeCN at the same concentrations as MM standards.

3. Results and Discussion

3.1. Instrumental method

Diverse pesticides were selected to represent different classes of non-polar and relatively
polar pesticides (stable organochlorine, organophosphorous, pyrethroids, triazines, carbamates,
strobins, azoles, urea, etc.) totaling to 192 compounds. Among environmental contaminants, 14
PAHs were selected representing the US EPA priority PAHs, including carcinogenic ones; 13
PCB congeners identified by the World Health Organization (WHO), including dioxin-like
congeners; 7 common PBDE congeners, and 17 flame retardants representing large volume
production chemicals used to replace the banned PBDE flame retardants. Fast LPGC and
UHPLC were used in parallel (10 min each) for compounds separation and tandem triple
quadrupole mass spectrometry was used in both cases. Fifty-five pesticides were both GC- and
LC-amenable allowing an additional degree of confirmation with an orthogonal technique.

3.2. Sample preparation

3.2.1. Comparison of different sorbents in filter-vial d-SPE approach

The most common d-SPE sorbents used to remove interfering lipids and fats from
extracts are C18, PSA (Hou, Han, Dai, Yang, & Yi, 2013), and a recently introduced zirconium
dioxide based sorbent called Z-Sep. We have previously reported successful use of these
sorbents for cleaning fish extracts. In order to investigate retention properties of these sorbents
for the selected 243 analytes, we conducted a recovery experiment as described in section 2.4.
The recoveries of 243 analytes were calculated vs. representative IS using RO calibration curves.
Table S3 and Table S4 list calculated recoveries and standard deviations (SDs) of the analytes
with different d-SPE sorbents measured by LPGC-MS/MS and UHPLC-MS/MS, respectively.

Most of the contaminants were not retained by the tested sorbents and had satisfactory
recoveries above 70%. However, some analyte adsorption was observed for 16 pesticides

resulting in decreased recoveries as presented in Figure S1. Specifically, C18 retained trinexapac-ethyl (46% recovery), and spinosyn A and D isomers (38 and 37%, respectively), and PSA retained trinexapac-ethyl (20% recovery), flumetsulam and chlorsulfuron (6 and 8% recoveries, respectively). Imazaquin and imazethapyr were completely retained by all tested sorbents except for C18. Z-Sep retained 14 tested analytes (Figure S1): imazaquin, imazethapyr, and trinexapac ethyl (all 0% recovery), methamidophos (7-11%), cyromazine (30%), spinosyns A&D, oxydemeton-methyl, chlorpyrifos oxon (all 40% recoveries), acephate, flutriafol, omethoate, paraoxon-methyl (50%), and dichrotophos (60%). Our results for acephate, omethoate, methamidophos and dichrotophos recoveries with Z-Sep were practically identical to the results of a recent study by Morris and Schriener (Morris & Schriener, 2015) reporting pesticide recoveries in avocado after automated column SPE (c-SPE) cleanup with Z-Sep. Interestingly, the latter study used 30% more Z-Sep per mL of avocado extract compared to our study which used reagent blank samples (no matrix), and different cleanup format (c-SPE vs. filter-vial d-SPE). Another recent study (Rajski, Lozano, Ucles, Ferrer, & Fernandez-Alba, 2013) reported decreased recovery of cyromazine (50%) with Z-Sep d-SPE cleanup for avocado extracts, similar to our finding, where cyromazine recovery was only 30%. In this study, the amount of Z-Sep used per mL of extract was 30% less than in our study. Also, this study reported 80-100% recovery for methamidophos, flutriafol, and dichrotophos, which differed from our results (11-60%). Perhaps, decreased amount of Z-Sep sorbent per mL of extract in the latter study explains greater recoveries of these pesticides.

3.2.2. Matrix effects (MEs) in LPGC-MS/MS

Meat samples are very complex matrices, containing proteins, lipids, saturated and monounsaturated fatty acids (USDA National Nutrient Database) and even thorough cleaning of the extracts does not prevent matrix co-extractives in the final extracts. In order to estimate MEs caused by matrix components in the injected extracts, calibration standard solutions at 0, 5, 10, 50, 100, and 200 ng/g were prepared in MeCN (RO) and matrix-matched (MM) extracts. A mixture of muscle tissue samples containing equal parts of beef, chicken, and pork (by weight) was extracted and subjected to d-SPE cleanup as described above, and the aliquots of this extract were used to prepare MM calibration standards.

In LPGC-MS/MS, comparison of the sensitivities (slopes) for MeCN and MM calibration curves for environmental contaminants (PBDEs, PCBs, PAHs and FRs) and 69 pesticides showed very little differences, demonstrating low ($\leq 20\%$) MEs for these analytes (Figure S2). However, for the vast majority of pesticides, analyte responses were greater in MM calibration compared to MeCN-only (Figure S2), demonstrating matrix-induced response enhancement previously described (Erney, Gillespie, Gilvydis, & Poole, 1993; Erney, Pawlowski, & Poole, 1997). Indeed, hydrophilic compounds containing relatively polar functional groups are prone to interact with active sites of the inlet liner, column, and ion source when injected in RO solutions without matrix. When MM calibration is used, matrix components fill the active sites, causing increase in analyte responses compared to RO calibration.

AP solution was added to the final LPGC-MS/MS extracts before injection as described in section 2.4. Addition of APs had no effect on sensitivities of PBDEs, PCBs, PAHs, FRs and 69 pesticides that demonstrated $\leq 20\%$ MEs in MeCN vs. MM. However, APs significantly increased the signals of other pesticides, which had already exhibited higher MEs. As presented in Figure S2, the most polar and problematic pesticides gave greatly increased analyte responses upon the addition of APs, reducing loss of polar analytes on active sites. For example, acephate, propargite, and pyraclostrobin responses were 9-10 times greater after APs addition to MeCN calibration standards (Figure S2). Nevertheless, polar pesticides prone to adsorption on active sites of inlet liner, column, and ion source exhibited rather different behaviors. Figure S2 lists pesticides in order of retention times, which shows that earlier eluting analytes present a different pattern compared to late eluting analytes that give much greater responses in MM + APs solutions than in MeCN+APs. A similar phenomenon was reported previously indicating that APs could not fully compensate for MEs of those late-eluting pesticides (Mastovska, Lehotay, & Anastassiades, 2005). Therefore, we chose to use MM calibration standards with addition of APs for LPGC-MS/MS analysis.

In addition to APs leading to increased sensitivity, improved peak shapes and decreased peak tailing were observed in many cases. As exhibited in Figure S3, significant peak shape improvements were observed with introduction of APs, resulting in sharper, narrower, taller peaks, as well as reduced peak tailing for susceptible analytes.

3.2.3. Matrix effects in UHPLC-MS/MS

Post-column infusion of 5 selected pesticides with different physicochemical properties was performed to evaluate effectiveness of d-SPE cleanup *via* measuring MEs. It has been reported that thorough cleanup of complex biological extracts reduces amounts of co-extractives and helps to decrease MEs. Because our results showed that some relatively polar pesticides were retained by the sorbents employed in d-SPE cleanup (C18, PSA, and Z-Sep), that works well for GC-MS/MS analysis, we aimed to determine if the cleanup is indeed beneficial for LC-MS/MS analysis, too, which is generally more rugged. Our intention was to compare if ME profiles of RO and meat extracts after d-SPE cleanup were significantly different from the extracts without cleanup at all.

As reported by Stahnke *et al.* (Stahnke, Reemtsma, & Alder, 2009), MEs for pesticides in ESI+ are matrix-dependent (not analyte-dependent) with analytes exhibiting similar behavior independent of their properties. Similar findings were reported for veterinary drugs by Geis *et al.* (Geis-Asteggiante, Lehotay, Lightfield, Dutko, Ng, & Bluhm, 2012).

Figure S4 illustrates ME profiles of cyromazine, acetamiprid, paraoxon-ethyl and trifloxystrobin. The ME profile was also determined for fenazaquin, which was identical to trifloxystrobin's. Interestingly, only ~10% differences in MEs were observed for these pesticides with d-SPE cleanup *vs.* samples without cleanup. Based on these results, we decided not to use d-SPE cleanup for extracts subjected to LC-MS/MS analysis. A recent study analyzing pesticides in cocoa beans utilized the same approach where d-SPE was employed for GC extracts, and no clean-up was used for LC-MS/MS analysis. (Zainudin, Salleh, Mohamed, Yap, & Muhamad, 2015)

Similarly, the signal difference between RO, pork, chicken, and beef matrices (both with and without cleanup) was also only ~10% for 4 pesticides, and ~20% for paraoxon-ethyl. These findings are similar to the results of Stahnke *et al.* who reported that 80% out of 129 pesticides had a ME difference <10% for simple matrices like pears, and up to 26% differences for more difficult matrices like orange (Stahnke, Reemtsma, & Alder, 2009).

3.3. Method validation

3.3.1. Linearity, sensitivity and matrix effects (MEs)

In LPGC analysis, visual inspection of calibration curves (RO and MM) consisting of 6 points at 0, 5, 10, 25, 100, and 200 ng/g (10 times lower for PCBs) for each matrix demonstrated

linear regression coefficient values of (R^2) ≥ 0.99 . Lowest calibration levels (LCLs) for the majority of analytes were 5 ng/g (0.5 ng/g for PCBs), with exceptions of atrazine, atrazine-desethyl, dieldrin, endrin, endrin ketone, ethoprop, fenpropathrin, HCDBCO, hexazinone, *cis*- and *trans*-nonaclar, PBB 153, PBDE 153&154, PBEB, prochloraz, TDCPP, thiamethoxam (LCL=10 ng/g), azoxystrobin, dechlorane 604, α - and β -endosulfan, endosulfan sulfate, PBDE 183, TBB (LCL=25 ng/g), and HBB (LCL=100 ng/g) (See Table S1).

For UHPLC analysis, LCLs were ≤ 5 ng/g for all pesticides (Table S2), except for ethofumesate, hexythiazox, and paraoxon-methyl (10 ng/g); diflubenzuron, novaluron, resmethrin, and tolylfluanid (25 ng/g); and bifenthrin, τ -fluvalinate (100 ng/g), and permethrin (200 ng/g). We attempted to include pyrethroid pesticides (bifenthrin, cypermethrin, deltamethrin, τ -fluvalinate, resmethrin, and permethrin) in UHPLC-MS/MS analysis as previously reported by Mastovska *et al.* (Mastovska, Dorweiler, Lehotay, Wegscheid, & Szpylka, 2010). Different adducts ($[M+H]^+$, $[M+NH_4]^+$, and $[M+Na]^+$) were tested and compared in MS/MS experiments, and the most intense transitions were selected (see table S2). However, under the selected UHPLC-MS/MS conditions, the sensitivities of the selected pyrethroids was very low compared to their sensitivities in LPGC-MS/MS. Two other recent studies also reported greater LOQs for pyrethroid pesticides when analyzed by LC compared to the most of LC-amenable pesticides (Jabot, Fieu, Giroud, Bulete, Casabianca, & Vulliet, 2015; Kasiotis, Anagnostopoulos, Anastasiadou, & Machera, 2014). Nevertheless, this trial shows a potential for analysis of some pyrethroids by LC-MS/MS, albeit at much higher concentrations.

In terms of linearity of MM calibrations with UHPLC, all but one compound (diflubenzuron, $R^2=0.98$) had linear regression coefficients $R^2 \geq 0.99$ normalized to IS atrazine- d_5 .

Figure S5 demonstrates the difference between MEs in GC and LC analyses. Only a few analytes fall outside of the $\pm 20\%$ MEs box for LC-amenable compounds, despite using no cleanup. Co-extractive materials from meat samples do not contribute to MEs with ESI, and the results are rather homogenous, independent of the matrix. Since most LC-amenable pesticides are rather polar, with low $\log K_{ow}$ values, lipid co-extractives are not influencing their signal in ESI+ compared to EI in GC analysis. An interesting example of comparing MEs in GC and LC is omethoate that was analyzed by both techniques, and had MEs up to (-50%) in pork in GC vs. (-10%) in LC.

Conversely, the majority of GC-amenable analytes demonstrated rather high MEs (up to 100%) with a clear differences in MEs among different meat types. MEs in pork matrix were the lowest ($\pm 20\%$), and MEs for the majority of analytes in chicken and beef were 20-60%. Pork was the leanest matrix with 2-3 times lower fat content compared to chicken and beef, leading to practically non-existent MEs. This finding highlights the importance of MM calibrations in analysis of complex matrices to achieve accurate results.

3.3.2. Recoveries and reproducibilities

Method validation was conducted according to the FSIS protocol to evaluate recoveries and relative standard deviations (RSDs) of 243 analytes from pork, beef, and chicken samples ($n=10$ each) fortified at low (10 ng/g), medium (25 ng/g), and high (100 ng/g) levels. Overall, satisfactory recoveries (70-120%) and $RSD \leq 20\%$ were achieved for 200 analytes (82%) (see Figure 1). The recoveries were consistent across the spiking levels, but as expected, more analytes (91-95%) had $RSDs \leq 20\%$ for 100 ng/g spiking levels compared to 72-80% of analytes with $RSD \leq 20\%$ at the low 10 ng/g spiking level (10 and 1 ng/g levels for PCBs, respectively).

Most of the analytes with $<70\%$ recoveries were either retained by sorbents in d-SPE (see section 3.2.1) or their peak areas were not normalized to an IS. For example, tri-BDE (#28) and tetra-BDE (#47) and tetra- (#77 and 81), and penta-chlorobiphenyl (CB) congeners (#105, 114, 118, 123, and 126) showed $\approx 200\%$ recoveries when normalized to IS originally selected for PBDEs: FBDE 126 (penta-BDE) and PCBs: $^{13}\text{C}_{12}$ -PCB 153 (hexachlorobiphenyl). These IS had $\approx 50\%$ recoveries through the sample preparation process, resulting in inflated recoveries for low halogenated PBDE and PCB congeners. Otherwise, both IS worked well for higher brominated PBDE (penta-, hexa- and hepta-brominated congeners (#99, 100, 153, 154 and 183) and higher chlorinated PCB congeners: hexa- (#156, 157, 167, 169), and heptachlorobiphenyl (#170, 180, and 189), exhibiting similar behavior through the sample preparation process as a result of similar chemical structure and properties (in particular, $\log K_{ow}$ values). This emphasizes the importance of careful method validation and continuous QA/QC along each processed batch of samples, as the fact of inflated recoveries is obvious in the case of spiked samples, but may cause inaccurate results in the case of unknown concentrations.

In our previous studies using FBDE 126 and $^{13}\text{C}_{12}$ -PCB as IS for PCBs and PBDEs in fish and shrimp tissues (Han, Sapozhnikova, & Lehotay, 2014; Sapozhnikova & Lehotay, 2013),

the recoveries were satisfactory for all of the PBDE and PCB congeners, indicating matrix-dependent behavior of these IS. It is commonly known, that fish have higher concentrations of polyunsaturated fatty acids compared to meats, which contain more saturated fatty acids that interact with lipophilic PCBs and PBDEs in a different manner. Huwe and West (2011) conducted a study measuring PBDEs in meat and poultry utilizing 10^{13}C -labeled PBDE internal standards for quantification of 16 native PBDEs to cover the range of their properties (Huwe & West, 2011). Another recent study performed quantification of tri- and penta-BDEs using fluorinated BDE 69 (FBDE 69) and hexa- and nona-BDEs using FBDE 160 (Labunska, Harrad, Wang, Santillo, & Johnston, 2014). In the absence of a suitable IS for low halogenated PCBs and PBDEs, we resorted to calculating their “true” recoveries without normalizing to IS, which led to <70% recoveries.

Recoveries of environmental contaminants and GC-amenable pesticides are presented in Figure 2. Seventeen novel FR compounds in this study represented a diverse group of chlorinated, brominated, and organophosphate chemicals. For the majority of FRs, the recoveries and RSDs were satisfactory, however, a few brominated FRs (PBEB, PBT, TBX, and HBB) had low recoveries (26-63%). Dechlorane 604 and HBB had low sensitivity, and were only measurable at 100 ng/g spiking levels, with dechlorane 604 recoveries ranging from 82 to 103% and HBB recoveries reaching 43-63% at this spiking level.

Some pesticides showed a different pattern in recoveries depending on the meat type. For example, propachlor had relatively low recoveries (14-46%) in fortified beef samples compared to chicken (99-102%) and pork samples (89-96%). HCB's recoveries were lower in pork samples (46-56%) vs. recoveries in beef (78-112%) and chicken (67-86%).

Among 55 pesticides analyzed by both LC and GC techniques, the majority of compounds had similar recoveries. However, because some pesticides have been shown to adsorb on Z-Sep used in cleanup prior to GC, their recoveries were greater when analyzed by LC-MS/MS without d-SPE cleanup. These included acephate (11-49% recoveries in GC vs. 46-54% in LC), methamidophos (1-30% GC vs. 37-46% in LC), flutriafol (24-44% in GC vs. 92-128% in LC), omethoate (17-32% in GC vs. 60-80% in LC) and dicrotophos (40-101% in GC vs. 90-111% in LC).

In beef samples, 85% and 88% of analytes analyzed by GC and LC techniques, respectively, had 70-120% recoveries, and 2% of LC-amenable analytes had recoveries >120%.

For chicken, 89% (GC) and 87% (LC) of the analytes were recovered at 70-120%, and 1% (GC) and 6% (LC) of the analytes' recoveries were calculated to be >120%. During the last day of the validation study, recoveries from pork samples were 70-120% for 75% of GC-amenable and 68% of LC-amenable analytes, with 13% and 25% of the analytes' recoveries over 120% for GC and LC analyses, respectively. The trend of increasing recoveries was observed as the validation progressed, most clearly seen in the case of LC-amenable compounds (Figure 1). We hypothesize that the solvent evaporated in the spiking solution from day 1 to day 3, introducing a bias into calculated recoveries.

3.4. Application of the method for analysis of meat samples from the market

The validated method was applied to determine pesticides and environmental contaminants in nine different species of meat samples supplied by USDA FSIS, including samples of beef (1), chicken (1), goat (1), lamb (1), horse (1), pork (2), and catfish (2) muscles. Each sample was prepared and analyzed in triplicate, and reagent blank and matrix spike samples for chicken, pork, beef, and catfish were used for quality control.

Residues of tetraconazole (5.7 ng/g), α -BHC (1.5 ng/g), and *p,p'*-DDE (0.8 ng/g) were measured in the lamb sample (Table 3). Both α -BHC and *p,p'*-DDE are stable organochlorine pesticides that have been banned for decades, however, due to their persistence, their residues are still detected. Tetraconazole is a fungicide with an established tolerance of 10 ng/g. DDT pesticides were also measured in one of the catfish samples: *p,p'*-DDT (0.9 ng/g), *o,p'*-DDD (1.1 ng/g), *o,p'*-DDT + *p,p'*-DDD (9.3 ng/g), and *p,p'*-DDE (24 ng/g). DDT's reported half-life is approximately 30 years; it degrades into DDD and DDE. This explains the higher DDE amount measured in the catfish, and points to an old source of contamination. We have also previously reported measured DDT residues in catfish samples from the market (Sapozhnikova, 2014). A residual amount of an herbicide, metolachlor (0.7 ng/g), was also measured in the catfish, which was significantly below the tolerance (20 ng/g). Piperonyl butoxide (PBO) was also determined in one of the pork samples at 49 ng/g, which was below the established tolerance of 100 ng/g. PBO is a synergist added to pyrethroid pesticide formulations to increase their potency.

4. Conclusions

A multi-class, multiresidue method for analysis of 243 pesticides and environmental
contaminants (PCBs, PAHs, PBDEs, and FRs) was developed and validated in swine, cattle, and
poultry muscle. The method is based on QuEChERS sample preparation with filter-vial d-SPE
prior to LPGC-MS/MS and filtration-only for UHPLC-MS/MS of 10 min analyses each. APs
were used in GC analysis to improve peak shapes, sensitivities, and reduce relative MEs. The
method was validated at three spiking levels (10, 25, and 100 ng/g). Satisfactory recoveries (70-
120%) and precision (RSDs $\leq$ 20%) were demonstrated for 200 (82%) of the targeted analytes.
LCLs were $\leq$ 5 ng/g for 90% of the analytes allowing their determination at or below established
tolerance levels. The final method was simple, fast, and inexpensive, and the overlapping
UHPLC-MS/MS and LPGC-MS/MS coverage of 55 pesticides allowed confirmation of the
analytes in the extracts using orthogonal techniques. The validated method was used for analysis
of 9 incurred meat samples from the market.

5. Acknowledgments

Technical assistance of Alan Lightfield, Tawana Simons, and Robyn Moten are greatly
appreciated. Lijun Han's sabbatical funding was provided by the China Scholarship Council. We
thank Sam Ellis of Thomson Scientific for providing a press tray apparatus. Thanks to Catalina
Yee of USDA-FSIS for providing incurred meat samples.

References:

- Boada, L. D., Sangil, M., Alvarez-Leon, E. E., Hernandez-Rodriguez, G., Henriquez-Hernandez, L. A., Camacho, M., Zumbado, M., Serra-Majem, L., & Luzardo, O. P. (2014). Consumption of foods of animal origin as determinant of contamination by organochlorine pesticides and polychlorobiphenyls: Results from a population-based study in Spain *Chemosphere*, 114, 121-128.
- Erney, D. R., Gillespie, A. M., Gilvydis, D. M., & Poole, C. F. (1993). Explanation of the matrix-induced chromatographic response enhancement of organophosphorus pesticides during open-tubular column gas-chromatography with splitless or hot on-column injection and flame photometric detection *J. Chromatogr.*, 638(1), 57-63.
- Erney, D. R., Pawlowski, T. M., & Poole, C. F. (1997). Matrix-induced peak enhancement of pesticides in gas chromatography: Is there a solution? *HRC J. High Resolut. Chromatogr.*, 20(7), 375-378.
- Food Outlook. Biannual report on global food markets. (2014). Available at: <http://www.fao.org/3/a-i4136e.pdf>
- Geis-Asteggianti, L., Lehotay, S. J., Lightfield, A. R., Dutko, T., Ng, C., & Bluhm, L. (2012). Ruggedness testing and validation of a practical analytical method for > 100 veterinary drug residues in bovine muscle by ultrahigh performance liquid chromatography-tandem mass spectrometry *J. Chromatogr. A*, 1258, 43-54.
- Global MRL database. Available at: <https://www.globalmrl.com>
- Han, L., Sapozhnikova, Y., & Lehotay, S. J. (2014). Streamlined sample cleanup using combined dispersive solid-phase extraction and in-vial filtration for analysis of pesticides and environmental pollutants in shrimp *Anal. Chim. Acta*, 827(0), 40-46.
- Hou, X., Han, M., Dai, X. H., Yang, X. F., & Yi, S. G. (2013). A multi-residue method for the determination of 124 pesticides in rice by modified QuEChERS extraction and gas chromatography-tandem mass spectrometry *Food Chem.*, 138(2-3), 1198-1205.
- Huwe, J. K., & West, M. (2011). Polybrominated diphenyl ethers in US meat and poultry from two statistically designed surveys showing trends and levels from 2002 to 2008 *J. Agric. Food. Chem.*, 59(10), 5428-5434.
- Jabot, C., Fieu, M., Giroud, B., Bulete, A., Casabianca, H., & Vulliet, E. (2015). Trace-level determination of pyrethroid, neonicotinoid and carboxamide pesticides in beeswax using dispersive solid-phase extraction followed by ultra-high-performance liquid chromatography-tandem mass spectrometry *Int. J. Environ. Anal. Chem.*, 95(3), 240-257.
- Kasiotis, K. M., Anagnostopoulos, C., Anastasiadou, P., & Machera, K. (2014). Pesticide residues in honeybees, honey and bee pollen by LC-MS/MS screening: Reported death incidents in honeybees *Sci. Total Environ.*, 485-486, 633-642.
- Koesukwiwat, U., Lehotay, S. J., & Leepipatpiboon, N. (2011). Fast, low-pressure gas chromatography triple quadrupole tandem mass spectrometry for analysis of 150 pesticide residues in fruits and vegetables *J. Chromatogr. A*, 1218(39), 7039-7050.
- Labunska, I., Harrad, S., Wang, M. J., Santillo, D., & Johnston, P. (2014). Human dietary exposure to PBDEs around e-Waste recycling sites in Eastern China *Environ. Sci. Technol.*, 48(10), 5555-5564.
- Mastovska, K., Dorweiler, K. J., Lehotay, S. J., Wegscheid, J. S., & Szpylka, K. A. (2010). Pesticide multiresidue analysis in cereal grains using modified QuEChERS method

- combined with automated direct sample introduction GC-TOFMS and UPLC-MS/MS techniques *J. Agric. Food. Chem.*, 58(10), 5959-5972.
- Mastovska, K., Lehotay, S. J., & Anastassiades, M. (2005). Combination of analyte protectants to overcome matrix effects in routine GC analysis of pesticide residues in food matrixes *Anal. Chem.*, 77(24), 8129-8137.
- Morris, B. D., & Schriner, R. B. (2015). Development of an automated column solid-phase extraction cleanup of QuEChERS extracts, using a zirconia-based sorbent, for pesticide residue analyses by LC-MS/MS *J. Agric. Food. Chem.*, 63(21), 5107-5119.
- Munoz, E., Munoz, G., Pineda, L., Serrahima, E., & Centrich, F. (2012). Multiresidue method for pesticide residue analysis in food of animal and plant origin based on GC or LC and MS or MS/MS *J. AOAC Int.*, 95(6), 1777-1796.
- Rajski, L., Lozano, A., Ucles, A., Ferrer, C., & Fernandez-Alba, A. R. (2013). Determination of pesticide residues in high oil vegetal commodities by using various multi-residue methods and clean-ups followed by liquid chromatography tandem mass spectrometry *J. Chromatogr. A*, 1304, 109-120.
- Sapozhnikova, Y. (2014). Evaluation of low-pressure gas chromatography–tandem mass spectrometry method for the analysis of >140 pesticides in fish *J. Agric. Food. Chem.*, 62(17), 3684-3689.
- Sapozhnikova, Y., & Lehotay, S. J. (2013). Multi-class, multi-residue analysis of pesticides, polychlorinated biphenyls, polycyclic aromatic hydrocarbons, polybrominated diphenyl ethers and novel flame retardants in fish using fast, low-pressure gas chromatography–tandem mass spectrometry *Anal. Chim. Acta*, 758(0), 80-92.
- Sapozhnikova, Y., & Lehotay, S. J. (2015). Evaluation of different parameters in the extraction of incurred pesticides and environmental contaminants in fish *J. Agric. Food. Chem.*, 63(21), 5163-5168.
- Stahnke, H., Reemtsma, T., & Alder, L. (2009). Compensation of matrix effects by postcolumn infusion of a monitor substance in multiresidue analysis with LC-MS/MS *Anal. Chem.*, 81(6), 2185-2192.
- The Stockholm Convention on Persistent Organic Pollutants. United Nations Environmental Programme. Available at: <http://chm.pops.int/Convention/tabid/54/Default.aspx>
- The United States Meat Industry at a Glance. Availavle at: <https://www.meatinstitute.org>
- US Department of Agriculture, Food Safety and Inspection Service. Screening for Pesticides by LC/MS/MS and GC/MS/MS. # CLG-PST5.06 Available at: www.fsis.usda.gov/shared/PDF/CLG-PST5.pdf.
- USDA National Nutrient Database. Available at: <http://ndb.nal.usda.gov/ndb/>
- Wu, G., Bao, X. X., Zhao, S. H., Wu, J. J., Han, A. L., & Ye, Q. F. (2011). Analysis of multi-pesticide residues in the foods of animal origin by GC-MS coupled with accelerated solvent extraction and gel permeation chromatography cleanup *Food Chem.*, 126(2), 646-654.
- Zainudin, B. H., Salleh, S., Mohamed, R., Yap, K. C., & Muhamad, H. (2015). Development, validation and determination of multiclass pesticide residues in cocoa beans using gas chromatography and liquid chromatography tandem mass spectrometry *Food Chem.*, 172, 585-595.

Figure 1. Recoveries and relative standard deviations (RSDs) of 243 analytes using LPGC-MS/MS and UHPLC-MS/MS analysis

Figure 2. Average recoveries of environmental contaminants (PCBs, PBDEs, PAHs and flame retardants (FRs)) and pesticides from meat samples fortified at 10 (low), 25 (mid) and 100 ng/g (high) by LPGC-MS/MS. Error bars represent standard deviations (n=10 samples).

Table 1. Average %recoveries $\pm$ standard deviation (SD), n=10 each level and matrix, in method validation of 199 pesticides and environmental contaminants in cattle, pork, and chicken muscle tissues at three spiking levels using LPGC-MS/MS for analysis.

Analyte	CATTLE			CHICKEN			PORK		
	10 ng/g	25 ng/g	100 ng/g	10 ng/g	25 ng/g	100 ng/g	10 ng/g	25 ng/g	100 ng/g
acenaphthene	102 $\pm$ 6	100 $\pm$ 6	90 $\pm$ 8	95 $\pm$ 7	96 $\pm$ 4	103 $\pm$ 3	109 $\pm$ 8	106 $\pm$ 3	103 $\pm$ 6
acenaphthylene	107 $\pm$ 6	106 $\pm$ 5	97 $\pm$ 8	103 $\pm$ 3	103 $\pm$ 3	108 $\pm$ 3	113 $\pm$ 5	115 $\pm$ 4	114 $\pm$ 5
acephate	13 $\pm$ 3	11 $\pm$ 1	12 $\pm$ 2	18 $\pm$ 4	17 $\pm$ 3	14 $\pm$ 2	49 $\pm$ 3	29 $\pm$ 2	19 $\pm$ 1
alachlor	93 $\pm$ 17	111 $\pm$ 7	108 $\pm$ 7	110 $\pm$ 8	105 $\pm$ 3	109 $\pm$ 5	118 $\pm$ 8	119 $\pm$ 6	118 $\pm$ 7
aldrin	58 $\pm$ 17	80 $\pm$ 13	77 $\pm$ 10	80 $\pm$ 10	81 $\pm$ 9	83 $\pm$ 8	86 $\pm$ 9	78 $\pm$ 15	70 $\pm$ 12
ametryn	100 $\pm$ 8	100 $\pm$ 6	93 $\pm$ 7	102 $\pm$ 9	98 $\pm$ 3	102 $\pm$ 4	110 $\pm$ 7	114 $\pm$ 5	108 $\pm$ 6
anthracene	99 $\pm$ 6	103 $\pm$ 4	95 $\pm$ 8	94 $\pm$ 9	99 $\pm$ 2	103 $\pm$ 5	90 $\pm$ 6	107 $\pm$ 1	105 $\pm$ 4
atrazine	101 $\pm$ 9	107 $\pm$ 9	96 $\pm$ 8	100 $\pm$ 13	102 $\pm$ 7	104 $\pm$ 5	106 $\pm$ 10	113 $\pm$ 5	109 $\pm$ 7
atrazine-desethyl	91 $\pm$ 12	107 $\pm$ 18	99 $\pm$ 9	124 $\pm$ 15	108 $\pm$ 7	105 $\pm$ 4	108 $\pm$ 18	112 $\pm$ 13	109 $\pm$ 8
azinphos-ethyl	118 $\pm$ 9	100 $\pm$ 2	92 $\pm$ 8	111 $\pm$ 13	104 $\pm$ 4	100 $\pm$ 6	127 $\pm$ 3	114 $\pm$ 5	103 $\pm$ 7
azinphos-methyl	127 $\pm$ 25	106 $\pm$ 15	91 $\pm$ 18	108 $\pm$ 19	100 $\pm$ 13	87 $\pm$ 9	119 $\pm$ 7	87 $\pm$ 6	75 $\pm$ 6
azoxystrobin	98 $\pm$ 17	78 $\pm$ 6	72 $\pm$ 7	0 $\pm$ 0	86 $\pm$ 12	80 $\pm$ 13	128 $\pm$ 25	103 $\pm$ 16	88 $\pm$ 10
benoxacor	89 $\pm$ 17	110 $\pm$ 7	110 $\pm$ 7	110 $\pm$ 5	105 $\pm$ 4	110 $\pm$ 4	116 $\pm$ 6	120 $\pm$ 7	115 $\pm$ 6
benz(a)anthracene+chrysene ^a	102 $\pm$ 8	96 $\pm$ 2	84 $\pm$ 7	96 $\pm$ 4	99 $\pm$ 4	102 $\pm$ 4	99 $\pm$ 4	99 $\pm$ 4	98 $\pm$ 4
benzo(a)pyrene	108 $\pm$ 4	112 $\pm$ 2	105 $\pm$ 8	101 $\pm$ 8	106 $\pm$ 4	113 $\pm$ 4	117 $\pm$ 10	124 $\pm$ 8	125 $\pm$ 7
benzo(b+k)fluoranthene	96 $\pm$ 6	102 $\pm$ 2	94 $\pm$ 7	94 $\pm$ 4	99 $\pm$ 5	105 $\pm$ 6	102 $\pm$ 4	111 $\pm$ 5	112 $\pm$ 7
benzo(g,h,i)perylene	104 $\pm$ 7	104 $\pm$ 5	94 $\pm$ 5	74 $\pm$ 5	94 $\pm$ 3	111 $\pm$ 5	100 $\pm$ 11	102 $\pm$ 20	104 $\pm$ 10
α -BHC (α -HCH)	78 $\pm$ 19	101 $\pm$ 9	105 $\pm$ 8	103 $\pm$ 6	109 $\pm$ 5	109 $\pm$ 6	102 $\pm$ 11	105 $\pm$ 13	105 $\pm$ 10
β -BHC (β -HCH)	95 $\pm$ 8	108 $\pm$ 7	103 $\pm$ 8	105 $\pm$ 7	103 $\pm$ 4	108 $\pm$ 4	103 $\pm$ 8	113 $\pm$ 12	111 $\pm$ 10
γ -BHC (γ -HCH), lindane	85 $\pm$ 20	111 $\pm$ 7	116 $\pm$ 9	101 $\pm$ 10	106 $\pm$ 6	107 $\pm$ 5	105 $\pm$ 10	107 $\pm$ 11	106 $\pm$ 9
δ -BHC (δ -HCH)	89 $\pm$ 8	103 $\pm$ 5	101 $\pm$ 7	101 $\pm$ 7	101 $\pm$ 4	106 $\pm$ 5	101 $\pm$ 10	109 $\pm$ 11	107 $\pm$ 10
bifenthrin	85 $\pm$ 14	84 $\pm$ 6	76 $\pm$ 9	88 $\pm$ 7	89 $\pm$ 6	93 $\pm$ 5	80 $\pm$ 10	81 $\pm$ 13	78 $\pm$ 10

bitertanol	85 ± 10	78 ± 4	72 ± 9	79 ± 14	79 ± 6	72 ± 7	112 ± 5	102 ± 6	85 ± 5
bromophos	82 ± 10	97 ± 5	94 ± 8	93 ± 7	93 ± 4	100 ± 4	104 ± 9	101 ± 12	96 ± 10
bromopropylate	76 ± 7	76 ± 4	73 ± 7	81 ± 10	81 ± 6	79 ± 6	86 ± 9	86 ± 13	82 ± 9
bupirimate	119 ± 8	106 ± 3	97 ± 7	100 ± 7	104 ± 7	106 ± 3	102 ± 9	99 ± 6	95 ± 5
buprofezin	84 ± 9	99 ± 8	94 ± 9	101 ± 11	95 ± 4	102 ± 6	93 ± 10	102 ± 14	99 ± 10
cadusafos	80 ± 15	114 ± 8	119 ± 8	99 ± 4	103 ± 4	107 ± 4	113 ± 6	116 ± 6	114 ± 7
carbofuran	100 ± 9	109 ± 5	104 ± 7	105 ± 5	105 ± 3	111 ± 4	143 ± 8	134 ± 5	122 ± 6
carbophenothion	91 ± 17	94 ± 7	90 ± 10	100 ± 11	95 ± 5	101 ± 5	105 ± 10	97 ± 15	89 ± 10
carboxin	90 ± 7	89 ± 5	83 ± 7	89 ± 7	89 ± 6	90 ± 6	111 ± 4	114 ± 6	106 ± 5
carfentrazone-ethyl	100 ± 14	107 ± 8	99 ± 6	97 ± 9	104 ± 11	107 ± 5	118 ± 11	119 ± 5	115 ± 5
<i>cis</i> -chlordane	83 ± 11	88 ± 7	84 ± 9	92 ± 10	85 ± 7	89 ± 7	87 ± 15	87 ± 17	83 ± 12
<i>trans</i> -chlordane	76 ± 13	89 ± 5	84 ± 11	93 ± 13	86 ± 9	87 ± 7	73 ± 17	88 ± 16	99 ± 15
chlorfenvinphos	96 ± 4	95 ± 3	91 ± 8	97 ± 4	97 ± 4	97 ± 4	116 ± 2	115 ± 5	109 ± 6
chloroneb	50 ± 24	118 ± 20	141 ± 12	77 ± 11	112 ± 9	116 ± 11	108 ± 21	115 ± 14	113 ± 8
chlorothalonil	1 ± 1	3 ± 3	10 ± 5	18 ± 3	6 ± 1	2 ± 0	25 ± 1	10 ± 0	3 ± 0
chlorpropham	103 ± 14	107 ± 6	101 ± 8	104 ± 7	103 ± 4	107 ± 5	114 ± 6	114 ± 6	110 ± 8
chlorpyrifos	95 ± 9	109 ± 4	103 ± 8	107 ± 7	102 ± 6	106 ± 4	103 ± 12	105 ± 14	102 ± 11
chlorpyrifos-methyl	83 ± 10	108 ± 5	109 ± 10	100 ± 5	100 ± 5	107 ± 4	108 ± 8	109 ± 10	106 ± 9
clofentezine	126 ± 11	100 ± 5	89 ± 8	119 ± 20	100 ± 18	100 ± 16	133 ± 9	106 ± 12	101 ± 9
coumaphos	117 ± 12	108 ± 8	95 ± 8	98 ± 17	107 ± 6	103 ± 7	113 ± 4	113 ± 13	107 ± 8
cyfluthrin	97 ± 28	99 ± 12	95 ± 12	68 ± 32	100 ± 13	90 ± 7	65 ± 41	79 ± 24	93 ± 12
λ-cyhalothrin	86 ± 14	95 ± 13	88 ± 12	96 ± 13	99 ± 13	91 ± 5	118 ± 10	114 ± 14	96 ± 9
cypermethrin	107 ± 13	102 ± 4	90 ± 8	105 ± 11	100 ± 5	92 ± 8	105 ± 8	100 ± 14	93 ± 10
cyprodinil	94 ± 10	98 ± 8	91 ± 7	85 ± 12	87 ± 6	97 ± 5	106 ± 14	102 ± 11	95 ± 9
<i>o,p'</i> -DDD	85 ± 9	93 ± 6	88 ± 9	93 ± 6	93 ± 5	96 ± 5	97 ± 11	94 ± 13	88 ± 12
<i>o,p'</i> -DDE	72 ± 11	81 ± 8	78 ± 9	99 ± 13	89 ± 7	89 ± 6	76 ± 20	99 ± 21	105 ± 17
<i>p,p'</i> -DDE	64 ± 13	65 ± 24	67 ± 8	83 ± 6	71 ± 24	82 ± 7	67 ± 11	67 ± 11	66 ± 10
<i>o,p'</i> -DDT + <i>p,p'</i> -DDD ^a	81 ± 9	84 ± 6	78 ± 8	88 ± 7	85 ± 5	91 ± 6	80 ± 10	80 ± 14	79 ± 12
<i>p,p'</i> -DDT	83 ± 11	79 ± 7	73 ± 8	84 ± 7	82 ± 6	88 ± 6	75 ± 12	73 ± 14	71 ± 11

dechlorane 604	< LCL	< LCL	82 ± 23	< LCL	< LCL	103 ± 15	< LCL	83 ± 27	89 ± 14
dechlorane plus, anti ^b	97 ± 13	104 ± 15	97 ± 14	90 ± 45	104 ± 11	122 ± 13	117 ± 17	112 ± 24	113 ± 12
dechlorane plus, syn ^c	66 ± 16	91 ± 11	93 ± 14	109 ± 38	104 ± 13	109 ± 11	84 ± 16	98 ± 16	107 ± 10
deltamethrin	99 ± 10	92 ± 7	87 ± 8	107 ± 27	99 ± 8	95 ± 11	108 ± 9	98 ± 14	88 ± 10
dibenz(a,h)anthracene	110 ± 9	110 ± 9	92 ± 13	89 ± 12	93 ± 8	104 ± 11	98 ± 12	82 ± 43	99 ± 32
dicloran	95 ± 8	100 ± 3	99 ± 6	102 ± 7	95 ± 5	102 ± 5	130 ± 5	115 ± 5	106 ± 6
dicrotophos	63 ± 11	46 ± 4	40 ± 5	82 ± 30	52 ± 9	43 ± 4	101 ± 13	70 ± 5	54 ± 2
dieldrin	78 ± 10	92 ± 8	87 ± 10	97 ± 12	90 ± 6	93 ± 5	87 ± 12	89 ± 11	84 ± 14
difenoconazole	103 ± 10	95 ± 5	86 ± 7	87 ± 27	90 ± 5	93 ± 10	119 ± 6	108 ± 6	102 ± 6
2,6-diisopropyl naphthalene	74 ± 17	96 ± 14	92 ± 12	75 ± 6	78 ± 7	83 ± 7	62 ± 12	67 ± 15	68 ± 11
dimethoate	100 ± 9	107 ± 5	98 ± 10	97 ± 7	97 ± 6	91 ± 29	126 ± 11	109 ± 7	103 ± 7
diphenylamine	87 ± 13	108 ± 5	109 ± 9	105 ± 4	101 ± 4	104 ± 5	110 ± 6	112 ± 7	108 ± 9
diuron	133 ± 16	99 ± 13	70 ± 14	128 ± 15	86 ± 9	101 ± 14	122 ± 25	91 ± 20	68 ± 6
α-endosulfan	73 ± 18	94 ± 13	90 ± 10	98 ± 5	89 ± 11	94 ± 5	83 ± 20	87 ± 16	85 ± 11
β-endosulfan	102 ± 19	107 ± 9	104 ± 9	108 ± 6	110 ± 5	109 ± 7	109 ± 19	116 ± 9	112 ± 6
endosulfan sulfate	89 ± 37	104 ± 17	105 ± 12	106 ± 44	102 ± 18	109 ± 16	108 ± 28	123 ± 18	115 ± 7
endrin	83 ± 16	95 ± 9	91 ± 9	95 ± 7	89 ± 4	94 ± 7	95 ± 15	94 ± 15	89 ± 11
endrin ketone	107 ± 8	100 ± 7	99 ± 11	115 ± 18	100 ± 12	105 ± 9	100 ± 12	118 ± 8	106 ± 10
ethalfluralin	67 ± 24	104 ± 15	115 ± 11	109 ± 10	116 ± 7	113 ± 6	111 ± 18	116 ± 16	107 ± 9
ethofumesate	100 ± 10	111 ± 4	106 ± 8	107 ± 7	107 ± 5	111 ± 5	127 ± 11	135 ± 8	122 ± 7
ethoprop	82 ± 18	105 ± 18	113 ± 10	93 ± 14	91 ± 6	96 ± 7	118 ± 14	107 ± 7	112 ± 5
ethoxyquin	62 ± 8	74 ± 8	85 ± 13	88 ± 19	70 ± 9	91 ± 10	58 ± 8	75 ± 15	95 ± 9
fenarimol	78 ± 18	74 ± 5	70 ± 10	75 ± 11	77 ± 6	69 ± 6	118 ± 5	102 ± 8	77 ± 4
fenazaquin	85 ± 12	81 ± 5	73 ± 7	81 ± 10	80 ± 7	78 ± 4	91 ± 10	89 ± 13	73 ± 10
fenobucarb	94 ± 13	114 ± 7	115 ± 8	107 ± 6	107 ± 4	110 ± 3	127 ± 7	125 ± 4	120 ± 6
fenpropathrin	97 ± 16	96 ± 5	88 ± 10	111 ± 14	101 ± 7	94 ± 4	96 ± 9	100 ± 11	96 ± 10
fensulfothion	110 ± 6	94 ± 5	85 ± 8	91 ± 14	92 ± 4	99 ± 7	120 ± 6	110 ± 8	99 ± 6
fenthion	94 ± 4	105 ± 4	102 ± 8	103 ± 6	105 ± 3	111 ± 5	118 ± 5	118 ± 6	112 ± 6
fenvalerate + esfenvalerate ^a	101 ± 12	94 ± 5	87 ± 7	103 ± 21	96 ± 6	95 ± 10	101 ± 10	97 ± 13	94 ± 11

fipronil	104 ± 9	109 ± 3	104 ± 9	111 ± 17	105 ± 8	102 ± 10	134 ± 7	131 ± 8	118 ± 7
fipronil sulfide	116 ± 14	117 ± 8	104 ± 8	112 ± 14	111 ± 7	112 ± 3	114 ± 11	117 ± 6	118 ± 5
fludioxonil	113 ± 9	106 ± 7	96 ± 7	105 ± 9	106 ± 4	104 ± 5	123 ± 8	109 ± 36	113 ± 6
fluopyram	104 ± 11	110 ± 5	100 ± 8	108 ± 8	104 ± 7	110 ± 5	128 ± 9	124 ± 4	115 ± 5
fluoranthene	105 ± 2	104 ± 3	96 ± 7	100 ± 3	100 ± 2	105 ± 2	111 ± 5	113 ± 2	111 ± 4
fluorene	112 ± 11	105 ± 6	96 ± 11	111 ± 6	90 ± 3	97 ± 9	131 ± 18	109 ± 12	96 ± 5
fluridone	111 ± 9	104 ± 6	92 ± 8	89 ± 25	97 ± 9	101 ± 12	116 ± 6	115 ± 9	108 ± 7
flutriafol	24 ± 4	22 ± 1	25 ± 4	26 ± 10	28 ± 5	26 ± 4	44 ± 6	37 ± 4	37 ± 3
τ-fluvalinate	100 ± 11	93 ± 5	87 ± 8	103 ± 24	96 ± 6	95 ± 10	104 ± 9	99 ± 14	94 ± 10
HCDBCO	104 ± 25	92 ± 12	90 ± 8	76 ± 35	114 ± 34	114 ± 12	122 ± 14	119 ± 11	115 ± 5
heptachlor	69 ± 21	87 ± 12	87 ± 9	85 ± 9	94 ± 6	92 ± 8	71 ± 10	79 ± 16	80 ± 13
heptachlor epoxide	88 ± 15	100 ± 9	97 ± 8	107 ± 16	98 ± 7	100 ± 5	85 ± 18	95 ± 13	95 ± 11
heptenophos	18 ± 7	35 ± 5	46 ± 7	49 ± 5	49 ± 5	45 ± 6	81 ± 6	72 ± 3	67 ± 4
hexabromobenzene (HBB)	<LCL	<LCL	43 ± 17	<LCL	<LCL	63 ± 14	<LCL	33 ± 30	63 ± 29
hexachlorobenzene (HCB)	78 ± 22	111 ± 20	112 ± 19	67 ± 11	86 ± 9	85 ± 13	46 ± 10	53 ± 15	56 ± 11
hexazinone	102 ± 6	94 ± 6	88 ± 7	96 ± 10	97 ± 5	97 ± 6	101 ± 9	110 ± 7	112 ± 6
imazalil	77 ± 5	73 ± 5	65 ± 7	31 ± 9	59 ± 6	61 ± 8	90 ± 4	77 ± 4	69 ± 3
indeno(1,2,3-c,d)pyrene	91 ± 9	96 ± 5	85 ± 7	80 ± 8	89 ± 5	103 ± 8	90 ± 6	93 ± 9	96 ± 4
indoxacarb	106 ± 12	103 ± 8	99 ± 9	92 ± 26	101 ± 11	102 ± 11	123 ± 5	130 ± 13	119 ± 7
iprodione	106 ± 11	98 ± 7	88 ± 9	114 ± 13	100 ± 10	90 ± 13	144 ± 11	117 ± 13	100 ± 5
kresoxim-methyl	108 ± 8	108 ± 4	101 ± 8	108 ± 3	108 ± 4	111 ± 4	125 ± 6	121 ± 2	116 ± 5
malathion	101 ± 6	110 ± 5	107 ± 8	105 ± 3	105 ± 4	111 ± 4	125 ± 3	124 ± 4	115 ± 4
metalaxyl	95 ± 16	105 ± 5	103 ± 8	101 ± 11	99 ± 9	108 ± 6	126 ± 24	127 ± 8	116 ± 6
methamidophos	23 ± 7	10 ± 1	1 ± 0	13 ± 2	6 ± 1	3 ± 1	30 ± 8	12 ± 3	4 ± 1
methidathion	106 ± 5	108 ± 4	101 ± 8	108 ± 8	106 ± 3	111 ± 3	118 ± 2	122 ± 4	116 ± 6
methiocarb	89 ± 7	100 ± 5	99 ± 7	108 ± 5	102 ± 3	107 ± 4	106 ± 4	117 ± 5	113 ± 6
methoxychlor	101 ± 8	96 ± 4	90 ± 8	100 ± 6	100 ± 4	102 ± 6	104 ± 10	102 ± 11	98 ± 9
metolachlor	94 ± 8	109 ± 4	106 ± 8	105 ± 5	103 ± 4	108 ± 4	120 ± 4	123 ± 5	118 ± 6
metribuzin	94 ± 5	101 ± 3	97 ± 7	103 ± 6	100 ± 6	105 ± 4	118 ± 6	118 ± 5	107 ± 6

mirex	38 ± 11	54 ± 8	50 ± 7	66 ± 8	62 ± 7	64 ± 7	50 ± 10	53 ± 12	52 ± 10
myclobutanil	98 ± 8	104 ± 4	100 ± 7	103 ± 6	105 ± 4	106 ± 4	117 ± 4	120 ± 5	114 ± 5
naphthalene	114 ± 8	103 ± 7	100 ± 16	103 ± 6	105 ± 8	116 ± 6	102 ± 17	121 ± 7	120 ± 7
napropamide	103 ± 7	106 ± 5	98 ± 7	105 ± 3	104 ± 3	107 ± 4	132 ± 12	115 ± 7	113 ± 5
<i>cis</i> -nonachlor	72 ± 22	79 ± 12	82 ± 11	79 ± 18	83 ± 10	85 ± 7	58 ± 30	80 ± 18	79 ± 14
<i>trans</i> -nonachlor	72 ± 17	86 ± 11	80 ± 10	80 ± 20	89 ± 10	90 ± 6	84 ± 19	82 ± 14	78 ± 12
omethoate	22 ± 10	17 ± 2	19 ± 4	27 ± 7	17 ± 4	20 ± 3	32 ± 13	29 ± 9	26 ± 3
oxadixyl	101 ± 8	101 ± 6	92 ± 10	103 ± 11	103 ± 6	99 ± 5	121 ± 6	121 ± 5	106 ± 6
oxyfluorfen	112 ± 14	99 ± 4	92 ± 6	110 ± 13	108 ± 6	111 ± 5	112 ± 8	109 ± 11	105 ± 8
parathion-methyl	99 ± 17	97 ± 8	100 ± 12	100 ± 15	102 ± 9	103 ± 8	105 ± 15	112 ± 12	109 ± 9
PBB 153	78 ± 19	90 ± 10	81 ± 14	86 ± 14	86 ± 16	85 ± 10	69 ± 14	93 ± 18	91 ± 15
PBDE 28	38 ± 5	57 ± 12	61 ± 8	53 ± 11	60 ± 9	73 ± 8	40 ± 9	50 ± 15	56 ± 12
PBDE 47	44 ± 9	51 ± 12	56 ± 9	77 ± 10	66 ± 6	69 ± 7	52 ± 11	56 ± 13	53 ± 10
PBDE 99	96 ± 18	107 ± 13	106 ± 13	106 ± 23	108 ± 8	112 ± 12	120 ± 19	117 ± 19	106 ± 11
PBDE 100	111 ± 16	116 ± 18	108 ± 16	122 ± 20	117 ± 12	117 ± 15	91 ± 23	118 ± 22	121 ± 19
PBDE 153	83 ± 25	95 ± 18	94 ± 12	85 ± 24	92 ± 9	95 ± 15	87 ± 24	95 ± 18	96 ± 10
PBDE 154	95 ± 24	95 ± 13	89 ± 10	98 ± 19	92 ± 17	93 ± 12	78 ± 32	95 ± 17	102 ± 15
PBDE 183	< LCL	< LCL	94 ± 24	< LCL	< LCL	88 ± 14	< LCL	86 ± 18	93 ± 20
PBEB	43 ± 17	41 ± 12	39 ± 7	0 ± 0	36 ± 9	47 ± 8	28 ± 13	35 ± 13	36 ± 9
PBT	38 ± 16	48 ± 9	44 ± 5	52 ± 12	47 ± 6	50 ± 6	33 ± 13	39 ± 12	40 ± 11
PCB 77	26 ± 5	51 ± 10	56 ± 7	49 ± 13	64 ± 10	76 ± 9	42 ± 13	52 ± 14	58 ± 12
PCB 81	23 ± 7	45 ± 11	54 ± 8	43 ± 7	55 ± 9	74 ± 7	32 ± 10	51 ± 14	56 ± 12
PCB 105	26 ± 8	43 ± 16	50 ± 8	47 ± 13	61 ± 13	70 ± 11	54 ± 14	53 ± 14	55 ± 13
PCB 114	31 ± 12	47 ± 11	48 ± 15	33 ± 8	54 ± 11	73 ± 9	44 ± 8	47 ± 15	55 ± 12
PCB 123+118 ^d	25 ± 8	44 ± 12	45 ± 6	23 ± 8	49 ± 10	65 ± 7	29 ± 9	43 ± 11	49 ± 11
PCB 126	26 ± 6	43 ± 11	48 ± 8	31 ± 7	53 ± 10	65 ± 8	31 ± 9	49 ± 13	51 ± 12
PCB 156+157 ^d	106 ± 31	102 ± 17	80 ± 10	104 ± 19	98 ± 20	116 ± 23	109 ± 20	135 ± 26	119 ± 17
PCB 167	82 ± 20	99 ± 29	75 ± 12	96 ± 18	87 ± 28	99 ± 24	109 ± 26	114 ± 28	111 ± 18
PCB 170	100 ± 18	96 ± 18	75 ± 6	88 ± 24	94 ± 14	113 ± 19	92 ± 36	130 ± 29	130 ± 39

PCB 180	105 ± 28	100 ± 26	69 ± 9	98 ± 23	95 ± 19	101 ± 15	97 ± 35	113 ± 28	122 ± 30
PCB 189	97 ± 20	98 ± 20	73 ± 9	85 ± 13	87 ± 21	96 ± 15	89 ± 16	112 ± 30	106 ± 29
penconazole	91 ± 5	97 ± 4	92 ± 7	100 ± 3	95 ± 4	100 ± 4	117 ± 2	114 ± 4	105 ± 6
pendimethalin	88 ± 10	97 ± 5	96 ± 9	99 ± 6	94 ± 5	100 ± 6	112 ± 11	100 ± 13	93 ± 10
penthiopyrad	113 ± 10	110 ± 5	99 ± 7	108 ± 13	107 ± 5	110 ± 5	119 ± 5	119 ± 6	116 ± 5
permethrin (<i>cis+trans</i>)	90 ± 14	85 ± 5	76 ± 7	88 ± 9	90 ± 6	87 ± 7	82 ± 10	83 ± 14	79 ± 12
phenanthrene	105 ± 4	108 ± 4	99 ± 6	105 ± 3	102 ± 3	103 ± 8	125 ± 9	119 ± 3	106 ± 4
<i>o</i> -phenylphenol	83 ± 17	92 ± 11	92 ± 7	93 ± 15	88 ± 5	89 ± 5	105 ± 9	107 ± 8	98 ± 5
phorate	74 ± 21	119 ± 15	137 ± 11	103 ± 6	110 ± 6	111 ± 6	106 ± 14	110 ± 14	110 ± 7
phosmet	117 ± 12	96 ± 5	88 ± 11	104 ± 8	96 ± 5	93 ± 6	107 ± 5	90 ± 7	85 ± 6
phosmet oxon	47 ± 18	70 ± 10	78 ± 7	81 ± 11	91 ± 10	95 ± 11	100 ± 10	140 ± 16	119 ± 5
piperonyl butoxide	105 ± 9	100 ± 4	92 ± 7	101 ± 11	103 ± 4	106 ± 4	107 ± 5	109 ± 8	106 ± 8
pirimiphos-methyl	93 ± 7	107 ± 3	106 ± 7	105 ± 5	101 ± 4	108 ± 4	109 ± 6	112 ± 6	111 ± 8
prochloraz	95 ± 16	83 ± 7	79 ± 8	93 ± 23	91 ± 7	84 ± 6	124 ± 7	112 ± 8	96 ± 5
procymidone	106 ± 13	104 ± 7	100 ± 8	104 ± 15	107 ± 10	112 ± 5	113 ± 10	120 ± 6	113 ± 6
profenophos	37 ± 5	37 ± 2	36 ± 6	43 ± 6	43 ± 7	44 ± 6	70 ± 6	63 ± 9	58 ± 5
promecarb	100 ± 9	112 ± 5	108 ± 8	106 ± 6	105 ± 4	112 ± 4	135 ± 5	133 ± 5	124 ± 6
prometryn	95 ± 9	102 ± 6	96 ± 7	94 ± 8	98 ± 5	103 ± 4	114 ± 8	113 ± 8	106 ± 7
propachlor	14 ± 9	33 ± 12	46 ± 10	102 ± 8	100 ± 5	99 ± 6	96 ± 11	91 ± 6	89 ± 9
propanil	97 ± 12	97 ± 4	91 ± 8	98 ± 4	96 ± 5	102 ± 4	111 ± 3	108 ± 6	102 ± 5
propargite	101 ± 12	113 ± 4	100 ± 8	92 ± 6	108 ± 4	111 ± 4	99 ± 9	111 ± 11	113 ± 8
propazine	98 ± 5	102 ± 4	99 ± 8	102 ± 7	101 ± 4	107 ± 4	118 ± 6	113 ± 7	109 ± 6
propetamphos	130 ± 15	120 ± 6	107 ± 7	127 ± 27	111 ± 5	114 ± 5	137 ± 21	124 ± 8	117 ± 5
propham	81 ± 19	123 ± 11	131 ± 10	103 ± 6	111 ± 5	110 ± 5	122 ± 8	124 ± 9	117 ± 5
propiconazole	91 ± 12	96 ± 4	90 ± 8	99 ± 8	94 ± 5	97 ± 3	109 ± 6	111 ± 5	108 ± 6
propyzamide	101 ± 5	109 ± 3	104 ± 7	108 ± 4	106 ± 4	108 ± 5	118 ± 4	119 ± 2	111 ± 6
pyraclostrobin	99 ± 13	103 ± 6	99 ± 9	94 ± 26	105 ± 7	110 ± 13	115 ± 9	112 ± 11	114 ± 8
pyrene	104 ± 3	112 ± 2	103 ± 8	106 ± 3	107 ± 4	112 ± 4	118 ± 6	119 ± 3	115 ± 3
pyridaben	100 ± 9	93 ± 4	85 ± 7	94 ± 13	94 ± 5	92 ± 7	102 ± 27	99 ± 14	89 ± 11

pyrimethanil	91 ± 8	99 ± 3	93 ± 7	100 ± 4	98 ± 5	101 ± 5	107 ± 4	106 ± 8	101 ± 7
pyriproxyfen	99 ± 11	93 ± 4	85 ± 8	89 ± 9	96 ± 5	101 ± 6	94 ± 10	93 ± 12	90 ± 11
quintozene (PCNB)	53 ± 24	101 ± 18	116 ± 12	89 ± 12	95 ± 8	94 ± 10	83 ± 15	88 ± 15	83 ± 14
resmethrin	106 ± 12	92 ± 10	82 ± 9	88 ± 8	95 ± 8	98 ± 5	95 ± 12	95 ± 14	87 ± 10
TBB	101 ± 19	96 ± 12	90 ± 12	92 ± 20	97 ± 13	93 ± 10	81 ± 23	102 ± 21	99 ± 11
TBCO	85 ± 15	92 ± 9	93 ± 9	92 ± 10	90 ± 6	91 ± 6	91 ± 16	78 ± 16	85 ± 14
TBECH	61 ± 13	91 ± 10	92 ± 10	90 ± 11	88 ± 8	89 ± 6	84 ± 18	98 ± 15	84 ± 14
TBNPA	88 ± 14	104 ± 7	104 ± 8	89 ± 9	100 ± 8	101 ± 4	117 ± 11	113 ± 5	107 ± 6
TBX	26 ± 13	43 ± 9	43 ± 6	53 ± 11	50 ± 9	51 ± 7	38 ± 12	40 ± 11	37 ± 9
TCEP	103 ± 7	109 ± 7	102 ± 8	108 ± 7	106 ± 8	108 ± 4	132 ± 9	122 ± 3	117 ± 4
TCPP	106 ± 16	114 ± 9	106 ± 8	69 ± 13	100 ± 26	112 ± 6	135 ± 13	131 ± 5	125 ± 6
TDCPP	98 ± 14	109 ± 8	103 ± 8	100 ± 20	99 ± 7	106 ± 5	111 ± 15	112 ± 8	115 ± 5
tebuconazole	48 ± 11	45 ± 5	47 ± 8	56 ± 13	51 ± 6	48 ± 6	64 ± 18	66 ± 7	65 ± 5
terbufos	88 ± 15	105 ± 8	105 ± 7	101 ± 8	104 ± 4	109 ± 5	103 ± 12	107 ± 11	106 ± 10
terbutylazine	96 ± 5	106 ± 3	99 ± 6	96 ± 6	101 ± 5	105 ± 4	118 ± 8	115 ± 8	110 ± 7
tetrachlorvinphos	62 ± 5	64 ± 2	65 ± 7	72 ± 7	71 ± 6	69 ± 4	120 ± 4	111 ± 5	96 ± 5
tetraconazole	97 ± 11	104 ± 6	101 ± 9	104 ± 11	108 ± 10	109 ± 4	108 ± 6	117 ± 4	121 ± 7
thiamethoxam	108 ± 18	86 ± 17	83 ± 13	69 ± 35	74 ± 16	96 ± 9	122 ± 8	88 ± 10	77 ± 5
thiobencarb	94 ± 6	101 ± 4	94 ± 6	100 ± 4	99 ± 3	105 ± 4	108 ± 9	109 ± 9	103 ± 9
tolclofos-methyl	84 ± 9	108 ± 5	110 ± 8	103 ± 5	101 ± 3	105 ± 3	106 ± 9	113 ± 10	110 ± 9
triadimefon	98 ± 7	107 ± 5	101 ± 8	109 ± 5	106 ± 3	108 ± 4	125 ± 7	121 ± 5	117 ± 5
tribufos	75 ± 10	72 ± 6	69 ± 7	82 ± 11	79 ± 7	78 ± 5	88 ± 9	86 ± 14	80 ± 9
trifloxystrobin	106 ± 9	107 ± 4	98 ± 8	114 ± 7	110 ± 4	112 ± 5	116 ± 4	119 ± 4	115 ± 4
triflumizole	100 ± 7	98 ± 4	94 ± 7	109 ± 8	103 ± 6	103 ± 5	124 ± 6	132 ± 7	127 ± 7
trifluralin	66 ± 29	121 ± 14	144 ± 14	112 ± 12	108 ± 4	108 ± 7	106 ± 10	105 ± 16	103 ± 10
triphenyl phosphate (TPP)	94 ± 7	90 ± 7	87 ± 6	84 ± 21	92 ± 7	105 ± 8	92 ± 7	112 ± 11	112 ± 7
vinclozolin	92 ± 14	110 ± 7	106 ± 6	100 ± 14	105 ± 7	112 ± 4	123 ± 9	122 ± 6	117 ± 8

PCB spiking levels: 1, 2.5, 10 ng/g; ^a – spiking levels: 20, 50, 200 ng/g; ^b - spiking levels: 7.5, 18.75, 75 ng/g; ^c - spiking levels: 2.5, 6.25, 25 ng/g; ^d - spiking levels: 2, 5, 20 ng/g. Bold values show recoveries and SD that are outside of the accepted quality control criteria of 70-120% for recoveries and >20% for SD.

Table 2. Average %recoveries $\pm$ standard deviations (SD), n=10 each level and matrix, in method validation of the 98 pesticide analytes in cattle, pork, and chicken muscle tissues at three spiking levels using UHPLC-MS/MS for analysis.

Analyte	CATTLE			CHICKEN			PORK		
	10 ng/g	25 ng/g	100 ng/g	10 ng/g	25 ng/g	100 ng/g	10 ng/g	25 ng/g	100 ng/g
acephate	46 $\pm$ 4	47 $\pm$ 2	46 $\pm$ 5	47 $\pm$ 3	46 $\pm$ 4	49 $\pm$ 4	51 $\pm$ 6	54 $\pm$ 9	50 $\pm$ 5
acetamiprid	103 $\pm$ 12	99 $\pm$ 6	95 $\pm$ 12	112 $\pm$ 8	97 $\pm$ 10	105 $\pm$ 9	115 $\pm$ 14	122 $\pm$ 20	113 $\pm$ 10
aldicarb sulfone	99 $\pm$ 9	102 $\pm$ 5	100 $\pm$ 11	101 $\pm$ 6	98 $\pm$ 10	103 $\pm$ 11	108 $\pm$ 14	121 $\pm$ 19	114 $\pm$ 12
aldicarb sulfoxide	70 $\pm$ 7	68 $\pm$ 3	68 $\pm$ 7	71 $\pm$ 5	71 $\pm$ 6	75 $\pm$ 6	84 $\pm$ 12	87 $\pm$ 14	81 $\pm$ 8
aldicarb	96 $\pm$ 10	101 $\pm$ 5	96 $\pm$ 11	99 $\pm$ 10	96 $\pm$ 9	106 $\pm$ 11	106 $\pm$ 15	120 $\pm$ 11	120 $\pm$ 11
ametryn	98 $\pm$ 7	100 $\pm$ 8	91 $\pm$ 12	102 $\pm$ 11	97 $\pm$ 5	104 $\pm$ 8	113 $\pm$ 15	121 $\pm$ 16	116 $\pm$ 12
atrazine	102 $\pm$ 11	106 $\pm$ 9	95 $\pm$ 15	108 $\pm$ 17	105 $\pm$ 18	111 $\pm$ 8	115 $\pm$ 19	118 $\pm$ 18	116 $\pm$ 13
atrazine-desethyl	97 $\pm$ 13	106 $\pm$ 9	97 $\pm$ 13	94 $\pm$ 16	85 $\pm$ 14	92 $\pm$ 12	102 $\pm$ 19	112 $\pm$ 19	105 $\pm$ 12
azinphos-ethyl	96 $\pm$ 18	102 $\pm$ 13	108 $\pm$ 10	115 $\pm$ 21	108 $\pm$ 22	111 $\pm$ 18	115 $\pm$ 20	117 $\pm$ 13	121 $\pm$ 13
azinphos-methyl	96 $\pm$ 9	114 $\pm$ 18	114 $\pm$ 17	95 $\pm$ 16	109 $\pm$ 23	107 $\pm$ 13	78 $\pm$ 10	109 $\pm$ 11	121 $\pm$ 16
azoxystrobin	106 $\pm$ 15	103 $\pm$ 21	102 $\pm$ 13	115 $\pm$ 7	109 $\pm$ 7	115 $\pm$ 13	113 $\pm$ 16	127 $\pm$ 12	128 $\pm$ 13
bifenthrin	< LCL	< LCL	82 $\pm$ 24	< LCL	< LCL	113 $\pm$ 36	< LCL	< LCL	93 $\pm$ 43
buprofezin	100 $\pm$ 6	100 $\pm$ 5	94 $\pm$ 12	97 $\pm$ 6	94 $\pm$ 6	102 $\pm$ 9	101 $\pm$ 17	106 $\pm$ 17	101 $\pm$ 12
cadusafos	102 $\pm$ 8	103 $\pm$ 6	97 $\pm$ 13	107 $\pm$ 9	106 $\pm$ 9	108 $\pm$ 9	119 $\pm$ 12	121 $\pm$ 9	120 $\pm$ 12
carbaryl	107 $\pm$ 11	109 $\pm$ 6	103 $\pm$ 14	109 $\pm$ 12	103 $\pm$ 7	111 $\pm$ 10	120 $\pm$ 13	126 $\pm$ 16	120 $\pm$ 14
carbendazim	82 $\pm$ 5	81 $\pm$ 5	77 $\pm$ 9	86 $\pm$ 8	80 $\pm$ 7	85 $\pm$ 10	98 $\pm$ 13	102 $\pm$ 18	94 $\pm$ 11
carbofuran	100 $\pm$ 10	103 $\pm$ 7	99 $\pm$ 10	106 $\pm$ 8	103 $\pm$ 8	109 $\pm$ 9	121 $\pm$ 12	123 $\pm$ 10	123 $\pm$ 14
carboxin	95 $\pm$ 8	95 $\pm$ 5	88 $\pm$ 12	110 $\pm$ 10	107 $\pm$ 13	113 $\pm$ 10	119 $\pm$ 13	126 $\pm$ 20	119 $\pm$ 10
carfentrazone-ethyl	112 $\pm$ 25	109 $\pm$ 17	101 $\pm$ 24	108 $\pm$ 26	108 $\pm$ 23	113 $\pm$ 24	105 $\pm$ 23	128 $\pm$ 23	119 $\pm$ 18

chlorfenvinphos	110 ± 9	114 ± 8	103 ± 12	109 ± 12	104 ± 5	110 ± 7	119 ± 13	120 ± 6	119 ± 11
chlorpyrifos oxon	63 ± 18	76 ± 11	96 ± 10	62 ± 14	64 ± 10	86 ± 15	80 ± 22	95 ± 11	107 ± 21
chlorsulfuron	41 ± 8	36 ± 5	37 ± 6	38 ± 10	33 ± 7	34 ± 7	41 ± 12	43 ± 7	39 ± 6
coumaphos oxon	113 ± 13	120 ± 11	114 ± 17	101 ± 12	108 ± 13	114 ± 15	88 ± 21	125 ± 15	136 ± 12
cyprodinil	83 ± 18	92 ± 8	90 ± 10	105 ± 15	92 ± 10	100 ± 10	100 ± 23	102 ± 18	99 ± 13
cyromazine	33 ± 2	14 ± 5	15 ± 4	67 ± 5	29 ± 13	24 ± 7	< LCL	16 ± 4	19 ± 2
dicotophos	97 ± 8	95 ± 5	90 ± 16	90 ± 6	93 ± 9	96 ± 7	105 ± 11	111 ± 15	105 ± 11
diflubenzuron	<LCL	<LCL	77 ± 35	<LCL	<LCL	<LCL	<LCL	<LCL	136 ± 37
dimethoate	98 ± 12	97 ± 8	95 ± 10	100 ± 8	101 ± 7	102 ± 7	116 ± 16	120 ± 19	114 ± 12
diuron	108 ± 16	95 ± 13	102 ± 16	94 ± 33	94 ± 15	106 ± 20	117 ± 24	116 ± 17	118 ± 18
ethofumesate	102 ± 45	109 ± 39	129 ± 19	<LCL	<LCL	121 ± 26	101 ± 30	128 ± 27	124 ± 32
ethoprop	108 ± 13	109 ± 5	98 ± 11	112 ± 15	108 ± 10	112 ± 10	89 ± 11	119 ± 8	124 ± 10
fenazaquin	94 ± 13	97 ± 6	90 ± 13	111 ± 18	99 ± 14	89 ± 11	69 ± 33	87 ± 14	93 ± 15
fenobucarb	101 ± 11	102 ± 10	98 ± 13	105 ± 8	101 ± 10	110 ± 11	119 ± 12	128 ± 23	126 ± 15
fensulfothion	99 ± 13	104 ± 9	95 ± 11	108 ± 21	100 ± 12	104 ± 15	112 ± 16	122 ± 20	129 ± 14
flumetsulam	55 ± 6	51 ± 7	48 ± 7	57 ± 10	53 ± 9	57 ± 8	69 ± 10	70 ± 9	65 ± 6
fluopyram	99 ± 8	101 ± 11	97 ± 12	108 ± 15	95 ± 9	100 ± 10	101 ± 20	120 ± 11	124 ± 11
fluroxypyr-methylheptyl ester	128 ± 26	105 ± 30	106 ± 25	< LCL	<LCL	121 ± 33	116 ± 31	111 ± 20	115 ± 22
flutriafol	92 ± 13	96 ± 8	96 ± 16	101 ± 16	97 ± 11	108 ± 12	124 ± 15	128 ± 15	115 ± 11
τ-fluvalinate	<LCL	<LCL	132 ± 36	< LCL	< LCL	126 ± 35	< LCL	<LCL	<LCL
fluxapyroxad	115 ± 20	101 ± 28	107 ± 26	108 ± 42	99 ± 24	110 ± 26	117 ± 35	127 ± 27	118 ± 21
heptenophos	99 ± 14	103 ± 7	100 ± 14	108 ± 17	104 ± 10	114 ± 11	119 ± 16	124 ± 10	120 ± 13
hexythiazox	<LCL	99 ± 19	115 ± 27	<LCL	77 ± 26	73 ± 13	<LCL	86 ± 24	89 ± 14
3-hydroxycarbofuran	99 ± 12	106 ± 6	102 ± 10	105 ± 9	91 ± 5	105 ± 11	114 ± 16	124 ± 21	116 ± 11
imazalil	84 ± 10	92 ± 8	89 ± 10	105 ± 19	93 ± 11	107 ± 9	119 ± 16	119 ± 22	112 ± 14
imazaquin	11 ± 5	8 ± 4	9 ± 1	12 ± 5	5 ± 3	9 ± 2	< LCL	10 ± 5	10 ± 2
imazethapyr	7 ± 2	8 ± 1	8 ± 1	8 ± 4	6 ± 1	7 ± 2	6 ± 2	9 ± 3	9 ± 2
imidacloprid	73 ± 15	97 ± 9	87 ± 9	80 ± 14	79 ± 16	82 ± 15	119 ± 13	115 ± 19	121 ± 14

indoxacarb	98 ± 17	104 ± 20	100 ± 20	86 ± 41	107 ± 18	106 ± 31	116 ± 25	123 ± 34	128 ± 15
linuron	91 ± 29	103 ± 16	95 ± 22	71 ± 35	76 ± 32	88 ± 23	90 ± 25	114 ± 19	119 ± 14
malathion	97 ± 14	103 ± 14	105 ± 17	107 ± 12	105 ± 14	109 ± 14	107 ± 9	125 ± 9	126 ± 14
metalaxyl	100 ± 10	106 ± 6	100 ± 11	107 ± 13	107 ± 11	111 ± 7	110 ± 13	120 ± 22	119 ± 14
methamidophos	37 ± 4	41 ± 2	39 ± 4	42 ± 5	40 ± 3	44 ± 4	46 ± 7	46 ± 7	44 ± 4
methiocarb	117 ± 15	110 ± 12	106 ± 19	117 ± 17	107 ± 12	114 ± 8	115 ± 10	127 ± 18	124 ± 15
methomyl	90 ± 9	96 ± 6	96 ± 12	99 ± 7	92 ± 7	101 ± 9	120 ± 13	118 ± 20	111 ± 13
methoprene	87 ± 9	95 ± 11	87 ± 11	93 ± 18	103 ± 18	109 ± 9	87 ± 20	98 ± 25	93 ± 19
methoxyfenozide	103 ± 15	102 ± 17	109 ± 14	106 ± 9	104 ± 15	105 ± 11	123 ± 9	126 ± 9	126 ± 14
metolachlor	99 ± 8	100 ± 7	92 ± 14	102 ± 10	102 ± 5	103 ± 13	106 ± 11	118 ± 9	121 ± 7
monocrotophos	79 ± 6	80 ± 6	80 ± 8	87 ± 8	85 ± 8	90 ± 7	104 ± 10	108 ± 17	101 ± 11
norflurazon	93 ± 25	95 ± 14	98 ± 10	116 ± 20	92 ± 18	111 ± 13	124 ± 20	124 ± 22	123 ± 18
novaluron	<LCL	<LCL	120 ± 22	<LCL	<LCL	<LCL	<LCL	<LCL	123 ± 26
omethoate	62 ± 3	64 ± 3	60 ± 7	65 ± 7	61 ± 5	64 ± 5	79 ± 9	80 ± 13	73 ± 8
oxadixyl	103 ± 8	108 ± 6	100 ± 12	104 ± 11	103 ± 9	107 ± 7	115 ± 10	125 ± 21	118 ± 11
oxamyl	98 ± 8	99 ± 5	97 ± 11	98 ± 12	94 ± 11	99 ± 9	112 ± 15	117 ± 14	110 ± 9
oxydemeton-methyl	71 ± 8	77 ± 7	70 ± 10	78 ± 12	72 ± 9	79 ± 9	91 ± 14	100 ± 12	91 ± 8
paraoxon-ethyl	107 ± 18	92 ± 24	92 ± 24	85 ± 37	82 ± 16	97 ± 18	107 ± 25	122 ± 21	124 ± 19
paraoxon-methyl	91 ± 28	106 ± 14	95 ± 11	101 ± 6	71 ± 13	101 ± 16	110 ± 23	96 ± 17	111 ± 18
penconazole	99 ± 8	97 ± 10	93 ± 12	119 ± 25	111 ± 13	121 ± 16	111 ± 5	128 ± 19	117 ± 10
penthiopyrad	113 ± 13	111 ± 8	103 ± 16	131 ± 14	120 ± 14	119 ± 12	120 ± 14	120 ± 15	119 ± 16
permethrin	<LCL	<LCL	<LCL	<LCL	<LCL	<LCL	<LCL	<LCL	<LCL
phosmet	101 ± 27	89 ± 17	100 ± 35	113 ± 33	109 ± 28	150 ± 26	94 ± 31	119 ± 25	140 ± 33
phosmet oxon	99 ± 9	100 ± 4	96 ± 10	107 ± 13	99 ± 9	111 ± 7	121 ± 11	120 ± 9	116 ± 15
pirimiphos-methyl	102 ± 9	103 ± 4	98 ± 13	101 ± 8	96 ± 8	101 ± 8	110 ± 17	115 ± 18	111 ± 11
profenofos	97 ± 12	94 ± 13	93 ± 16	99 ± 17	80 ± 13	90 ± 11	96 ± 22	107 ± 16	108 ± 17
promecarb	110 ± 8	106 ± 16	103 ± 13	102 ± 11	104 ± 11	107 ± 9	119 ± 15	125 ± 17	121 ± 11
promethryn	102 ± 10	92 ± 20	95 ± 14	106 ± 9	97 ± 7	105 ± 9	110 ± 12	119 ± 16	114 ± 11
propanil	<LCL	75 ± 12	78 ± 16	<LCL	99 ± 19	111 ± 17	<LCL	129 ± 28	134 ± 20

propazine	91 ± 11	104 ± 10	97 ± 13	107 ± 13	98 ± 11	111 ± 11	121 ± 19	128 ± 32	117 ± 13
propiconazole	102 ± 9	99 ± 7	97 ± 9	106 ± 16	96 ± 10	102 ± 13	106 ± 14	116 ± 10	120 ± 13
propoxur	102 ± 8	106 ± 4	102 ± 12	104 ± 10	101 ± 9	109 ± 9	115 ± 12	120 ± 17	117 ± 11
pymetrozine	47 ± 4	48 ± 4	46 ± 6	47 ± 5	44 ± 4	49 ± 5	53 ± 7	53 ± 8	51 ± 6
pyraclostrobin	103 ± 8	103 ± 8	102 ± 13	107 ± 10	99 ± 7	106 ± 10	120 ± 11	125 ± 16	119 ± 11
pyridaben	88 ± 7	85 ± 7	82 ± 12	102 ± 10	94 ± 8	104 ± 8	92 ± 15	95 ± 17	94 ± 12
pyrimethanil	98 ± 10	102 ± 5	95 ± 9	104 ± 14	94 ± 8	102 ± 10	121 ± 14	116 ± 14	111 ± 11
quizalofop-ethyl	98 ± 16	100 ± 17	93 ± 18	111 ± 29	108 ± 32	115 ± 23	101 ± 15	110 ± 18	112 ± 11
resmethrin	104 ± 26	119 ± 37	93 ± 31	<LCL	<LCL	101 ± 21	93 ± 20	88 ± 34	92 ± 14
spinosyn A ^a	105 ± 11	106 ± 8	104 ± 12	110 ± 8	102 ± 10	111 ± 10	120 ± 7	123 ± 10	122 ± 12
spinosyn D ^b	99 ± 7	102 ± 7	101 ± 12	108 ± 9	98 ± 5	108 ± 8	114 ± 13	125 ± 21	117 ± 12
tebuconazole	107 ± 15	111 ± 12	105 ± 13	109 ± 27	93 ± 15	106 ± 10	124 ± 17	125 ± 27	121 ± 14
tebufenozide	102 ± 12	102 ± 7	101 ± 14	113 ± 11	108 ± 12	109 ± 10	114 ± 17	120 ± 11	125 ± 15
temephos	111 ± 24	100 ± 14	98 ± 14	97 ± 34	94 ± 27	113 ± 17	99 ± 11	117 ± 9	119 ± 11
tetrachlorvinphos	117 ± 23	115 ± 12	105 ± 11	128 ± 18	98 ± 24	105 ± 16	113 ± 11	127 ± 25	123 ± 15
tetraconazole	99 ± 15	109 ± 13	106 ± 14	105 ± 37	135 ± 36	124 ± 32	122 ± 26	128 ± 14	120 ± 20
thiabendazole	89 ± 7	87 ± 4	82 ± 9	91 ± 7	87 ± 10	94 ± 8	104 ± 11	103 ± 15	97 ± 11
thiamethoxam	89 ± 7	93 ± 7	84 ± 8	95 ± 9	97 ± 11	98 ± 9	109 ± 10	118 ± 22	107 ± 13
tolyfluanid	11 ± 0	5 ± 3	8 ± 4	< LCL	<LCL	<LCL	< LCL	<LCL	<LCL
triadimefon	105 ± 12	98 ± 24	105 ± 16	94 ± 49	107 ± 37	119 ± 24	121 ± 26	119 ± 17	123 ± 16
trifloxystrobin	99 ± 12	97 ± 11	97 ± 14	114 ± 13	102 ± 15	108 ± 11	120 ± 7	122 ± 7	120 ± 9
trinexapac-ethyl	108 ± 29	104 ± 25	84 ± 15	<LCL	78 ± 34	90 ± 33	113 ± 31	114 ± 35	112 ± 24

^a – spiking levels: 8.5, 21.25, 85 ng/g; ^b – spiking levels: 1.5, 3.75, 15 ng/g. Bold values show recoveries and SD that are outside of the accepted quality control criteria of 70-120% for recoveries and >20% for SD.

Table 3. Analytes determined in samples from the market.

Muscle Sample	Analyte	Concentration (ng/g)	Tolerance (ng/g)
Lamb	<i>p,p'</i> -DDE	0.8*	
	α -BHC	1.5	
	tetraconazole	5.7	10
Catfish	<i>p,p'</i> -DDE	24	
	<i>o,p'</i> -DDD	1.1	
	<i>o,p'</i> -DDT + <i>p,p'</i> -DDD	9.3	
	<i>p,p'</i> -DDT	0.9*	
	metolachlor	0.7*	20
Pork	piperonyl butoxide	49	100

* < LCL of 1 ng/g