Application Note

Food Testing and Agriculture

Analysis of Multiclass Multiresidue Pesticides in Milk Using Agilent Captiva EMR—Lipid with LC/MS/MS and GC/MS/MS

Authors

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Abstract

This application note describes the analysis of multiclass, multiresidue pesticides in milk. The sample preparation method is based on Agilent QuEChERS extraction followed by Agilent Captiva EMR—Lipid cleanup and analysis. Two instrumental platforms were used: the Agilent 8890 gas chromatograph system coupled with the Agilent 7010B triple quadrupole mass spectrometry (GC/MS/MS) and the Agilent 1290 Infinity II LC system coupled with the Agilent 6470 triple quadrupole mass spectrometer (LC/MS/MS), respectively. The Captiva EMR—Lipid delivers highly efficient removal of matrix interferences in milk and allows detection of most pesticides down to 1 ng/mL. Results demonstrate the benefit of this workflow solution for multiresidue pesticide analysis in milk. For 171 pesticides studied, 98% of recoveries were within 60 to 120%, and over 95% achieve reproducibility of ≤10% RSD.

Introduction

Milk is an important food in the diet, especially for infants and children. The presence of any contamination in milk is a common food safety concern, and great strides have been taken throughout the dairy industry to ensure the safety of milk. One of the main classes of contaminants in milk is pesticides, which can come from animals ingesting contaminated feed or water.[1] The maximum residue limits for pesticides in milk are often much lower than for general fruits and vegetables.[2] Therefore, the analysis of pesticides in milk requires a sample preparation method for better matrix removal and analytical instrument methods for increased sensitivity. The aim of this study is to develop a simple and efficient workflow for determining a wide range of pesticides that are broadly controlled in milk worldwide.

Captiva EMR—Lipid, which is a lipid removal product, combines size exclusion and hydrophobic interaction to selectively capture lipid hydrocarbon chains without the loss of target analytes. Compared with the traditional QuEChERS dispersive cleanup, Captiva EMR—Lipid cleanup provides simplified pass-through workflow and highly selective and efficient lipid removal. In this application note, 171 pesticides and related metabolites were tested using a simple workflow with QuEChERS extraction followed with Captiva EMR—Lipid cleanup by both LC/MS/MS and GC/MS/MS analysis.

Experimental

Chemicals and reagents

All reagents and solvents were HPLC or analytical grade. Acetonitrile (ACN) was from Honeywell (Muskegon, MI, USA). Formic acid (FA) was from J&K Scientific Ltd. (Beijing, China). The pesticides and metabolites standards were purchased from Alta (Tianjin, China).

Solutions and standards

Individual pesticide stock solutions (100 µg/mL) in ACN were stored at –20 °C, and the mixed spiking solution (1 µg/mL) was prepared in ACN and stored at –20 °C. The 80/20 ACN/H_2O elution solvent was prepared and stored at room temperature.

Equipment and consumables

- Agilent Captiva EMR—Lipid, 6 mL cartridges, 600 mg (p/n 5190-1004)
- Agilent Vac Elut 20 manifold with collection rack for 13 × 100 mm test tubes (p/n 12234101)
- Agilent QuEChERS extraction kit EN 15662 method with 50 mL tubes with ceramic homogenizers (p/n 5982-5650CH)
- Agilent Bond Elut EMR—Lipid polish pouch, anhydrous $MgSO_4$ only (p/n 5982-0102)
- Agilent Bond Elut C18 cartridge, 500 mg, 6 mL, 40 µm (p/n 12102052)
- Agilent QuEChERS Dispersive Kit, fruits and vegetables with fats and waxes, AOAC method, 15 mL (p/n 5982-5158)
- SPEX SamplePrep 2010 Geno/Grinder (Metuchen, NJ, USA)
- Eppendorf Centrifuge 5810R (Hamburg, Germany)
- LC column and GC column, liner, etc.

Instrument conditions

Instrument detection was carried out using both LC/MS/MS and GC/MS/MS platforms. The LC/MS/MS detection was performed on an Agilent 1290 Infinity II LC System. This consisted of the Agilent 1290 Infinity II high speed pump (G7120A), the Agilent 1290 Infinity II multisampler (G7167B), and the Agilent 1290 Infinity II multicolumn thermostat (G7116B). These were coupled with an 6470A triple quadrupole LC/MS (G6470A) with an Agilent Jet Stream electrospray ion source. The GC/MS/MS detection was on an Agilent 8890 GC with the Agilent 7010 triple quadruple GC/MS. Agilent MassHunter workstation software was used for data acquisition and analysis.

Table 1 lists the GC/MS/MS method parameters for GC-amenable pesticides; Table 2 lists the LC/MS/MS method conditions for LC-amenable pesticides.

Table 1. GC/MS/MS method conditions.

GC/MS/MS Parameter	Setting
Column	Agilent HP-5ms UI, 30 m × 0.25 mm, 0.25 µm (p/n 19091S-433UI)
Carrier Gas	Helium, 1.019 mL/min, constant flow
Injection Volume	1 µL
Inlet Liner	Agilent Ultra Inert, splitless, single taper, glass wool (p/n 5190-2293)
Over Program	60 °C (1 min), 40 °C/min to 120 °C, then 5 °C/min to 310 °C
Inlet	Split/splitless; temperature: 280 °C Splitless mode, purge flow 30 mL/min at 0.75 min
Run Time	40.5 min
Transfer Line Temperature	280 °C
Collision Cell EPC	Quench Gas He, 2.25 mL/min ; Collision Gas N_2, 1.5 mL/min
Source Temperature (HES)	280 °C
Quadrupole Temperature	150 °C
Data Monitoring	dMRM
Gain Factor	10
Solvent Delay	3 min

The MRM transitions and settings are listed in the appendix. Figures 1 and 2 show a typical GC/MS/MS MRM chromatogram and LC/MS/MS chromatogram for milk samples fortified with pesticides at the level of 50 ng/mL

Table 2. LC/MS/MS method conditions.

LC/MS/MS Parameter	Setting
Column	Agilent ZORBAX Eclipse plus C18, 3.0 × 150 mm, 1.8 µm (p/n 959759-302)
Column Temperature	45 ℃
Autosampler Temperature	10 ℃
Injection Volume	2 µL
Mobile Phase	A) Water, containing 4.5 mM ammonium formate, 0.5 mM ammonium floride, 0.1% formic acid B) Methanol, containing 4.5 mM ammonium formate, 0.5 mM ammonium floride, 0.1% formic acid
Gradient	Time (min) %B Flow rate (mL/min) 0 2 0.45 0.5 2 0.45 1 50 0.45 4 65 0.45 16 100 0.45 18 100 0.45 18.1 2 0.45 20 2 0.45
Stop Time	20 min
Source Parameters	
Gas Temperature	250 °C
Gas Flow	11 L/min
Nebulizer	40 psi
Sheath Gas Temperature	350 °C
Sheath Gas Flow	12 L/min
Capillary Voltage	+3,500
Nozzle Voltage	+300
Time Segments	
Agilent 1290 Infinity II binary system	Start time (min) Scan type Div valve Delta EMV (+) 0 DMRM To Waste 0 2.1 DMRM To MS 400 18 DMRM To Waste 0

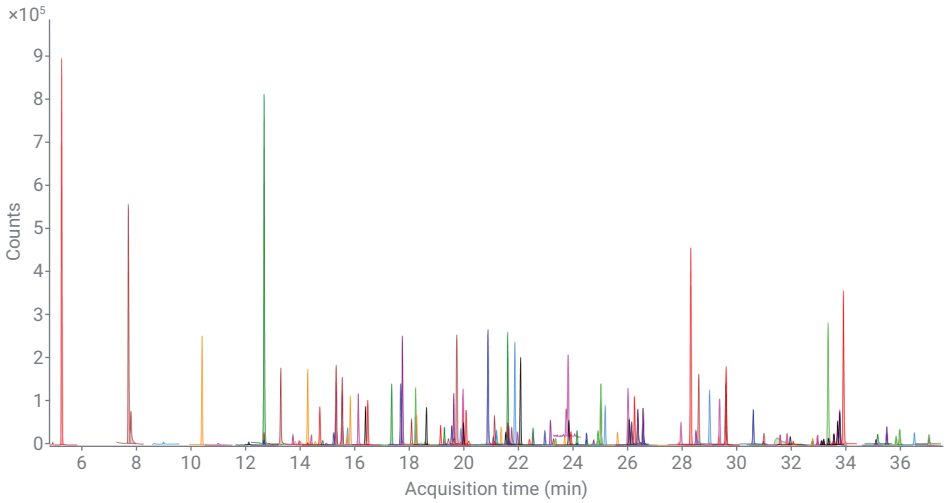

Figure 1. GC/MS/MS MRM chromatogram of pesticides in the fortified milk sample at the level of 50 ng/mL.

Sample preparation

Milk was purchased from a local grocery store and prepared using the developed sample preparation method. Figure 3 shows the step-by-step procedure, featuring three major parts: sample extraction using the QuEChERS extraction kit, sample extract cleanup using Captiva EMR—Lipid, and post treatment for water removal using anhydrous $MgSO_4$ salt partition specifically for GC/MS/MS analysis. The entire workflow introduced 3.125-fold and 2.5-fold dilution of the original sample concentration for LC/MS/MS and GC/MS/MS, respectively.

Calibration standards and quality control (QC) samples

Prespiked QC samples were fortified by spiking the appropriate standard spiking solution into milk and vortexing, then equilibrating for five minutes. Matrix-matched calibration standards were prepared by spiking standard solution into the matrix blank, which was processed using the developed sample preparation workflow. The calibration standards correspond to 1, 2, 5, 10, 20, 50, 100, 200, and 500 ng/mL in milk. Four levels of QC samples were quantified against calibration curves at low level (5 and/or 10 ng/mL), midlevel (50 ng/mL), and high level (100 ng/mL) in milk with four replicates. Analyte identification, confirmation, and quantitation were determined from the retention times and MRM transitions.

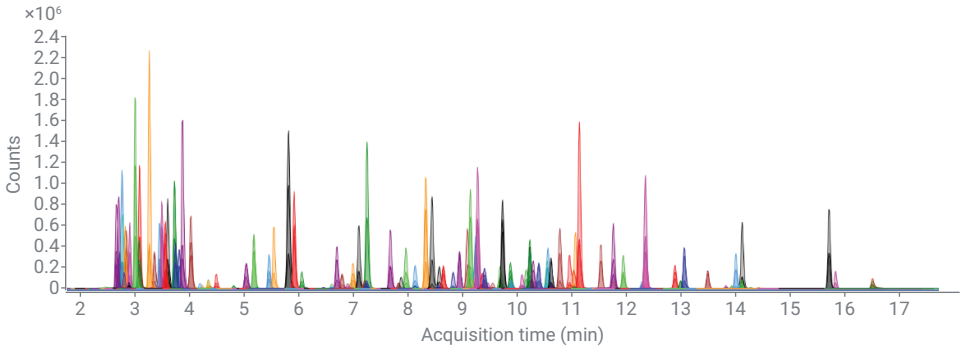

Figure 2. LC/MS/MS MRM chromatogram of pesticides in the fortified milk sample at the level of 50 ng/mL.

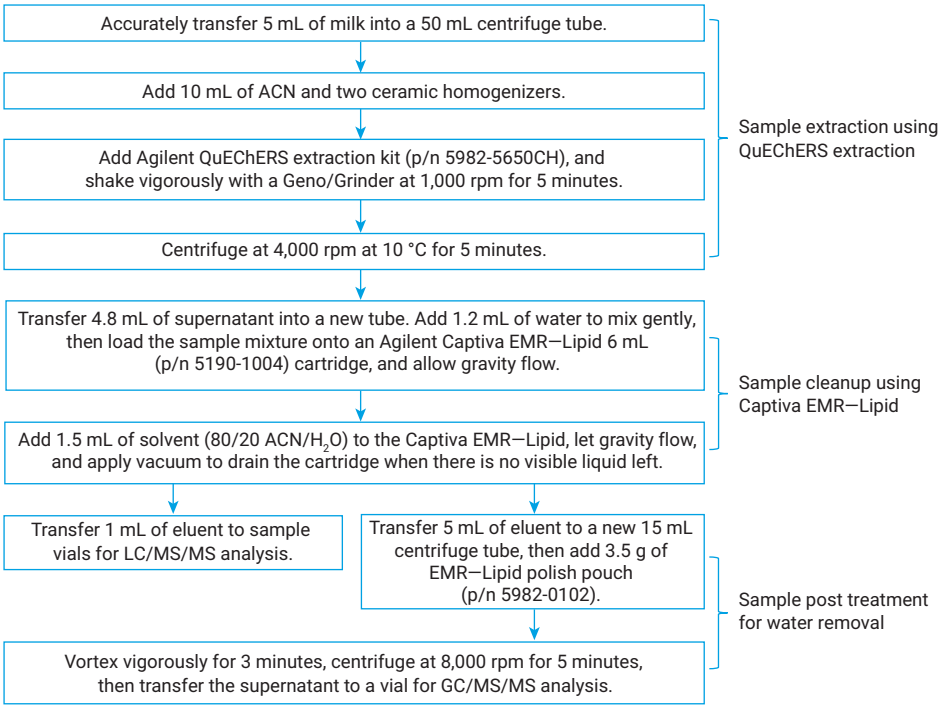

Figure 3. The step-by-step procedure for milk sample preparation.

Sample extraction and matrix removal investigation

The extraction method for a 5 mL milk sample was evaluated. First, a 15 mL ACN solvent extraction was compared to a QuEChERS extraction kit using 10 mL of ACN followed by the QuEChERS EN extraction. The cleanup step was also evaluated. The GC/MS full scan background profiles for sample extract without cleanup were compared to those for sample extract with the following cleanup techniques, including Captiva EMR—Lipid cleanup, Bond Elut C18 SPE cleanup, and Bond Elut QuEChERS dSPE cleanup.

Results and discussion

Sample preparation optimization

Two extraction methods were evaluated: solvent extraction with ACN and QuEChERS extraction using ACN. Nonacidified ACN was used because it was reported that acidified ACN can cause degradation of some pesticides such as amitraz and semiamitraz.[3] The results from QuEChERS extraction showed better recoveries for many hydrophobic pesticides than results from ACN extraction only. The QuEChERS extraction method was selected for the milk sample extraction.

Matrix removal was investigated with a GC/MS full scan background profile comparison for sample extract without cleanup and with various cleanups by Captiva EMR—Lipid, Bond Elut C18 cartridge, and the QuEChERS dSPE kit. The overlapped full scan chromatograms are shown in Figure 4. By comparing the total integration peak area within the entire retention window, Captiva EMR—Lipid cleanup was demonstrated for 99% of the matrix removal and significantly outperformed the other three cleanup methods. Cleanup with Captiva EMR—Lipid also removes late eluent interferences (as shown after 30 minutes), which are a significant contributor to instrument contamination.

The pesticide recoveries using various cleanup techniques were compared, and the results are shown in Figure 5. Results show that QuEChERS dispersive SPE cleanup caused significant loss of acidic pesticides, resulting from the use of basic sorbent PSA in the dispersive kit.

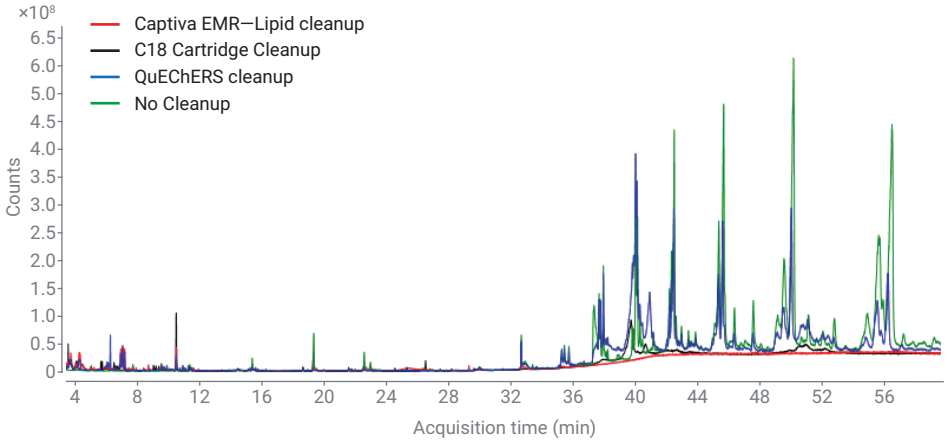

Figure 4. GC/MS full scan for the milk samples with different cleanup method.

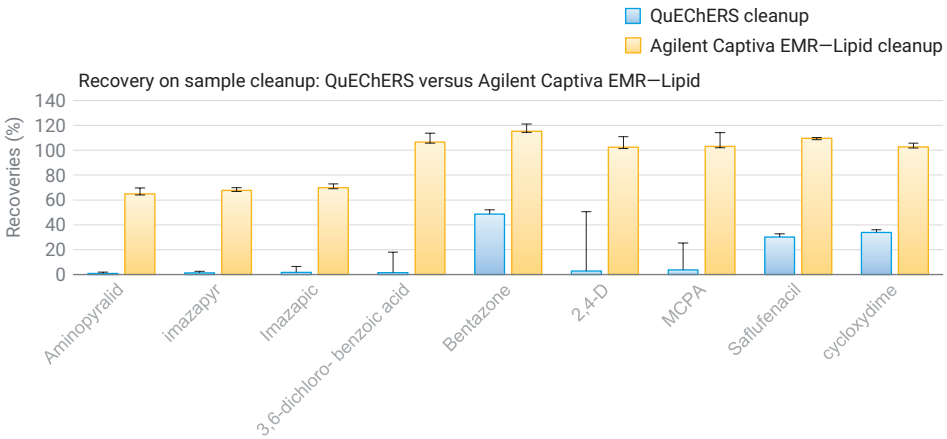

Figure 5. Comparison of the recoveries of acidic pesticides with Agilent QuEChERS dSPE cleanup and Agilent Captiva EMR—Lipid cleanup at 40 ng/mL spiking level by LC/MS/MS.

The recoveries for the Captiva EMR—Lipid cartridge cleanup step were subsequently studied for the total amount eluted with the two successive elution steps. From the box-and-whisker plot of the recovery data with and without 2nd elution in Figure 6, the middle line of the box represents the median recovery number, and the bottom and top lines of the box represent the median of the bottom half and top half recovery number, respectively. The whiskers (vertical lines) extend from the ends of the box to the minimum value and maximum value. Overall, the recoveries of the pesticides with 2nd elution were well improved. Therefore, a secondary elution with 1.5 mL of 80/20 ACN/water was applied after the initial 6 mL of sample mixture elution.

Introduction of water residue can be detrimental to a GC instrument, so the water in the eluent after Captiva EMR—Lipid cleanup must be removed. There are different ways to remove water before GC/MS/MS analysis that have been applied in various Agilent solutions.[4,5] For large panel pesticide analysis with a broad range of different chemical physical feature on analytes, $MgSO_4$ salting out was usually recommended and proved to be the appropriate method for water removal.

Method validation

The quantitative method validation of GC/MS/MS and LC/MS/MS includes calibration curve linearity, analyte recovery, and precision at four spiking levels. The detailed quantitation results are shown in Tables 3 and 4, and the statistical summary results are shown in Figure 7. Acceptable recoveries (60% to 120%) were achieved for over 98% of analytes, and RSD values were less than 10% for over 95% of analytes. Of the 171 pesticides, 43 were verified with both GC/MS/MS and LC/MS/MS platform detection.

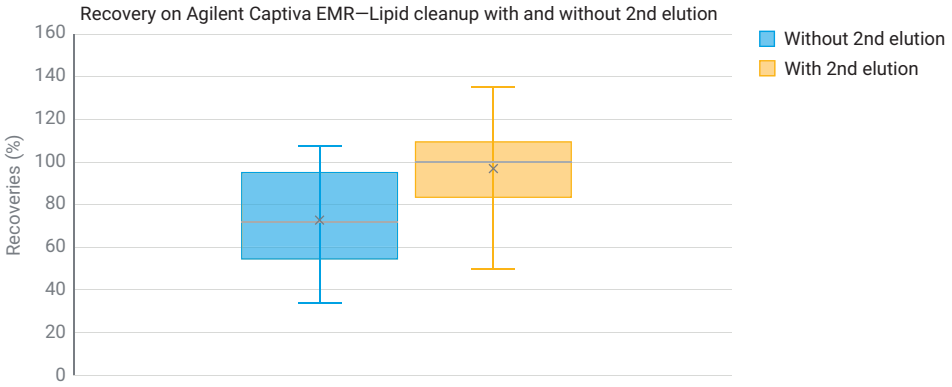

Figure 6. Comparison of with and without 2nd elution for the total pool of pesticides with LC/MS/MS and GC/MS/MS at 40 ppb spiking level in milk.

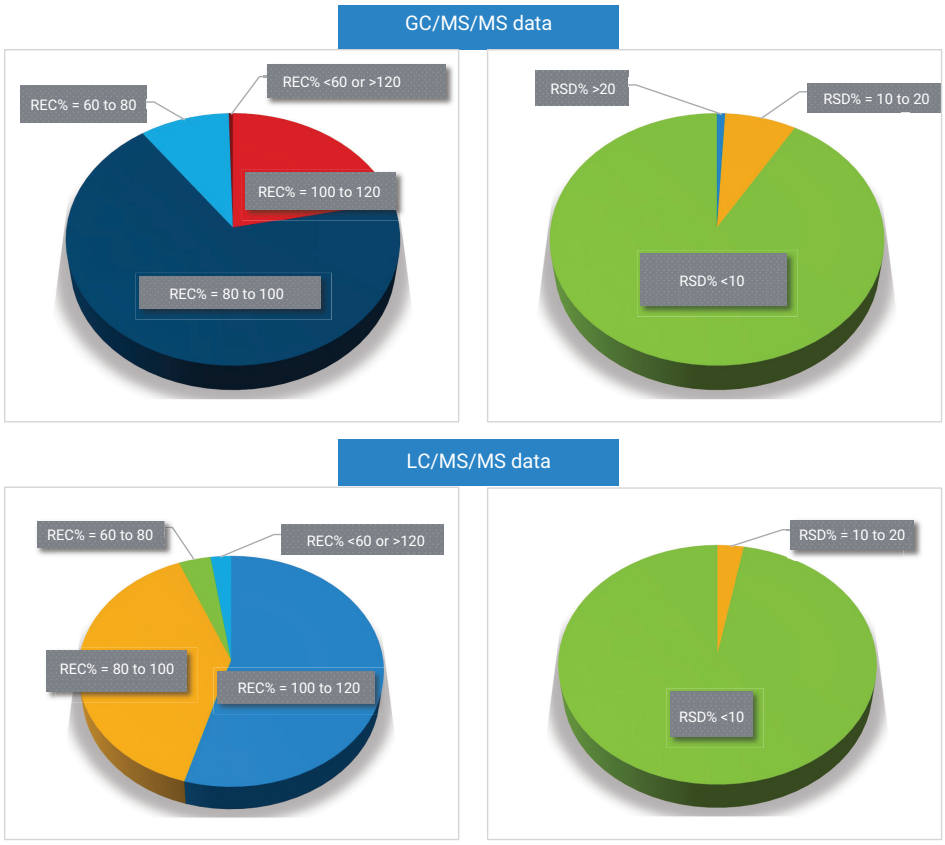

Figure 7. Statistical summary of the analysis of pesticides in milk method validation.

Table 3. Method quantitation results for 118 pesticides in milk with GC/MS/MS.

Pesticide	Linearity Range (ng/mL)	R^2	Low QC 5 ng/mL in Milk (n = 4)		Low QC 10 ng/mL in Milk (n = 4)		Mid QC 50 ng/mL in Milk (n = 4)		High QC 100 ng/mL in Milk (n = 4)	
			Mean Recovery %	RSD%	Mean Recovery %	RSD%	Mean Recovery %	RSD%	Mean Recovery %	RSD%
2,4,6-Trichlorophenol	1 to 500	0.998	98.5	5.2	101.2	2.9	94.8	7.2	92.0	5.5
Aldrin	1 to 500	0.998	80.7	6.2	78.4	4.7	74.9	5.6	71.2	2.5
Dichlorvos*	5 to 500	0.998	116.6	6.8	98.1	9.1	96.3	12.4	93.1	4.8
Phorate*	2 to 500	0.993	96.7	9.3	108.1	4.2	99.8	9.1	95.9	2.6
Methacrifos	1 to 500	0.998	99.7	5.3	110.1	5.3	102.4	8.1	97.8	1.3
Pentachloronitrobenzene	1 to 500	0.997	96.2	7.9	94.2	6.3	95.6	3.8	85.4	5.2
Endosulfan I (alpha isomer)	2 to 500	0.997	85.0	11.3	104.8	4.0	95.3	6.6	91.5	1.8
Acetamiprid*	5 to 500	0.995	73.3	20.7	69.8	5.1	78.5	4.1	83.6	2.0
Bentazone*	10 to 500	0.994	98.8	8.1	120.4	8.4	103.3	5.3	104.8	5.6
Chlorantraniliprole*	10 to 500	0.992	80.0	11.9	110.6	7.0	84.0	6.2	94.7	2.3
Cyromazine*	2 to 500	0.990	64.1	10.3	61.4	9.3	60.0	5.0	55.0	3.9
Famoxadone*	5 to 500	0.996	104.2	20.2	105.8	9.8	92.2	2.0	98.2	3.4
Methamidophos*	1 to 500	0.994	89.5	7.8	91.2	14.4	80.6	13.2	81.9	1.1
Spirodiclofen*	10 to 500	0.997	–	–	83.3	22.1	92.8	7.0	97.0	1.9
Oxamyl*	5 to 500	0.993	92.0	12.0	106.7	3.3	98.5	4.0	99.0	3.1
Prochloraz*	2 to 500	0.998	100.5	14.8	80.5	7.2	89.7	6.7	99.3	5.5
Azinphos-ethyl	1 to 500	0.993	98.4	8.8	96.6	2.1	85.4	5.1	94.6	0.7
Captan	50 to 500	0.999	–	–	–	–	70.4	14.4	72.2	5.6
Hexachlorobenzene	2 to 500	1.000	93.4	9.5	69.9	12.6	79.6	6.1	64.6	1.2
Fenamidone	1 to 500	0.991	83.4	10.8	86.2	4.2	79.9	1.3	87.8	3.3
Ethoprophos*	1 to 500	0.993	101.6	6.1	105.4	2.3	100.9	11.1	96.3	0.5
Azinphos-methyl	5 to 500	0.995	–	–	95.6	6.5	73.4	9.7	89.9	2.7
Phosmet	1 to 500	0.995	96.3	15.1	90.0	3.0	72.2	7.5	87.1	1.9
Azoxystrobin*	5 to 500	0.995	75.3	16.9	92.1	11.8	92.0	4.4	101.9	1.7
Bifenthrin*	1 to 500	0.990	73.2	12.6	76.8	5.1	70.3	2.8	71.4	3.5
Bitertanol*	5 to 500	0.998	89.4	4.6	90.6	9.5	90.5	8.2	94.5	1.2
Boscalid*	1 to 500	0.994	99.0	7.7	96.8	1.4	90.0	5.6	98.6	1.2
Buprofezin*	10 to 500	0.995	–	–	90.8	7.2	87.1	7.9	86.2	3.8
Carbaryl*	2 to 500	0.991	96.4	12.2	105.3	4.9	99.0	5.8	100.4	1.4
Chinomethionate (Oxythioquinox)	1 to 500	0.995	88.8	7.9	89.8	1.6	88.3	5.6	88.8	1.6
Chlordane-*cis*	1 to 500	0.998	87.4	7.7	90.4	1.8	88.6	5.1	86.6	1.5
Chlordane-oxy	1 to 500	0.998	88.9	4.8	93.4	3.3	93.0	5.2	88.1	2.1
Chlordane-trans	1 to 500	0.998	91.3	2.7	89.4	0.4	90.8	4.2	83.6	0.9
Chlorfenvinphos	1 to 500	0.994	88.5	14.3	91.5	4.4	80.7	10.9	94.3	2.5
Chlorpropham	1 to 500	1.000	104.8	3.2	105.7	3.5	105.9	3.7	99.0	3.5
Chlorpyrifos*	1 to 500	0.993	90.7	9.6	98.5	3.8	98.1	8.1	94.1	1.4
Chlorpyrifos-methyl*	1 to 500	0.990	94.3	5.9	97.6	4.2	98.4	6.1	96.9	2.1
Clofentezine*	1 to 500	1.000	111.5	1.8	106.4	5.1	107.7	1.4	107.8	1.4
Coumaphos	5 to 500	0.992	83.6	10.1	87.4	4.9	85.7	7.4	96.6	2.0
Cyfluthrin-1	2 to 500	0.998	101.9	5.0	89.1	6.8	83.0	5.2	88.8	3.4
Cyfluthrin-2	2 to 500	0.996	94.4	6.9	92.0	4.5	88.8	5.7	91.9	2.5
Cyfluthrin-3	5 to 500	0.998	94.5	7.8	88.3	6.4	85.4	5.0	93.8	1.4
Cyfluthrin-4	5 to 500	0.996	106.4	5.6	86.9	9.7	89.1	2.9	94.4	0.9
Cypermethrin-1	5 to 500	0.997	–	–	92.3	7.7	85.7	6.9	91.9	0.5

Pesticide	Linearity Range (ng/mL)	R^2	Low QC 5 ng/mL in Milk (n = 4)		Low QC 10 ng/mL in Milk (n = 4)		Mid QC 50 ng/mL in Milk (n = 4)		High QC 100 ng/mL in Milk (n = 4)	
			Mean Recovery %	RSD%	Mean Recovery %	RSD%	Mean Recovery %	RSD%	Mean Recovery %	RSD%
Cypermethrin-2	5 to 500	0.997	—	—	91.0	5.6	91.4	5.9	97.8	1.9
Cypermethrin-3	2 to 500	0.996	—	—	97.5	3.5	84.0	5.6	89.3	2.0
Cypermethrin-4	2 to 500	0.996	—	—	93.2	2.9	86.6	5.5	91.5	1.4
Cyprodinil*	1 to 500	0.993	87.8	6.4	93.2	2.3	89.5	7.2	93.7	1.1
DDD-*o,p'*	1 to 500	1.000	85.1	7.6	83.5	4.2	81.9	5.8	79.8	1.2
DDD-*p,p'*	1 to 500	1.000	81.9	7.9	78.9	3.3	80.3	7.9	77.8	2.2
DDE-*p,p'*	1 to 500	0.999	105.9	5.3	84.6	2.6	80.9	6.6	80.6	2.7
DDT-*o,p'*	1 to 500	0.997	80.0	7.4	76.5	2.9	75.3	5.8	73.0	1.6
DDT-*p,p'*	1 to 500	0.996	81.2	11.3	72.0	3.3	68.7	5.3	67.6	1.7
Deltamethrin	2 to 500	0.993	92.3	8.8	95.2	1.1	90.5	2.9	92.8	2.5
Demeton-S-methyl	5 to 500	0.991	95.0	11.6	111.0	7.6	90.5	11.0	94.4	3.3
Diazinon*	1 to 500	0.995	101.1	5.8	107.0	4.1	101.1	7.2	98.6	1.4
Dichlofenthion	1 to 500	0.993	99.7	5.8	105.3	2.8	98.2	7.0	95.8	1.5
Dichloran	1 to 500	0.995	105.9	5.2	106.9	4.4	101.0	5.9	99.3	0.9
Dieldrin	2 to 500	0.999	92.3	8.5	90.2	5.1	90.3	5.3	87.6	2.1
Difenoconazole I	1 to 500	0.994	100.5	12.7	99.4	6.4	92.8	4.5	97.2	1.2
Difenoconazole II	1 to 500	0.992	98.0	8.2	106.6	2.4	93.4	3.7	98.4	1.2
Dimethipin	1 to 500	0.997	95.9	4.7	105.1	4.1	108.3	3.8	103.6	0.7
Dimethoate*	2 to 500	0.996	101.9	7.4	104.0	2.5	90.1	9.7	99.0	2.1
Diphenylamine*	1 to 500	0.998	101.5	3.5	103.6	4.4	99.9	6.9	96.4	1.0
Endosulfan II (*beta* isomer)	1 to 500	0.997	93.0	4.1	91.0	3.7	92.3	4.5	95.2	0.7
Endosulfan sulfate	1 to 500	0.993	88.5	7.1	86.5	1.1	83.6	5.8	90.9	1.6
Endrin	2 to 500	0.993	89.3	9.2	91.3	2.6	86.1	8.1	88.2	2.0
Ethion	1 to 500	0.996	90.7	9.1	92.5	1.3	89.3	6.3	94.5	0.9
Ethofenprox	1 to 500	0.992	92.3	6.7	84.6	3.2	79.5	7.3	81.7	1.1
Fenamiphos sulfone*	10 to 500	0.992	77.9	16.2	83.9	2.1	74.6	10.1	82.0	2.6
Fenitrothion	1 to 500	0.996	101.7	7.6	101.9	3.1	97.7	7.4	102.3	0.5
Fenpropathrin	2 to 500	0.993	82.2	13.9	85.4	6.8	79.2	2.3	87.3	3.9
Fenpropimorph*	1 to 500	0.994	78.6	4.2	78.9	3.8	79.7	7.3	82.3	2.0
Fensulfothion	2 to 500	0.995	97.3	4.9	91.8	1.9	83.8	5.9	97.0	0.7
Fenthion	1 to 500	0.992	93.9	9.0	102.2	2.4	97.2	7.3	99.8	1.3
Fenvalerate I	1 to 500	0.994	102.5	6.4	92.8	3.2	87.3	7.0	90.0	1.5
Fenvalerate II	1 to 500	0.994	98.8	8.4	92.1	2.5	89.0	5.2	92.5	1.3
Fipronil*	1 to 500	0.994	103.5	5.6	101.8	2.4	97.5	4.2	101.8	1.5
Fipronil sulfide*	1 to 500	0.995	90.4	5.2	96.1	1.7	97.1	4.7	102.9	1.2
Fipronil sulfone	1 to 500	0.995	99.0	12.4	102.7	2.3	92.6	6.1	100.7	1.3
Flusilazole*	1 to 500	0.991	90.9	9.8	97.3	2.1	90.4	6.5	100.9	1.2
HCH-*alpha*	1 to 500	0.999	100.2	5.6	104.6	2.7	104.0	7.8	92.4	2.8
HCH-*beta*	1 to 500	0.999	102.2	6.4	104.9	4.2	106.1	4.8	97.3	1.1
HCH-*delta*	1 to 500	0.998	101.8	3.4	104.5	3.0	104.5	3.9	98.6	0.5
HCH-*gamma*	1 to 500	0.999	102.0	3.3	101.3	5.3	101.9	3.9	95.7	1.6
Heptachlor	1 to 500	0.996	93.7	2.2	95.4	5.7	94.3	4.6	93.6	0.9
Heptachlor exo-epoxide	2 to 500	0.994	92.7	8.3	91.8	4.0	93.5	7.0	88.1	1.9
Isopyrazam*	2 to 500	0.991	101.3	7.6	91.5	4.7	84.4	6.5	93.3	0.4
Malathion	1 to 500	0.995	92.1	1.6	98.0	2.9	94.5	7.2	99.2	1.8

Pesticide	Linearity Range (ng/mL)	R^2	Low QC 5 ng/mL in Milk (n = 4)		Low QC 10 ng/mL in Milk (n = 4)		Mid QC 50 ng/mL in Milk (n = 4)		High QC 100 ng/mL in Milk (n = 4)	
			Mean Recovery %	RSD%	Mean Recovery %	RSD%	Mean Recovery %	RSD%	Mean Recovery %	RSD%
Mecarbam	5 to 500	0.996	103.6	8.3	96.8	7.5	94.2	7.4	98.7	2.5
Methidathion*	1 to 500	0.991	99.7	11.2	98.9	2.2	90.8	6.9	98.8	2.0
Metrafenone*	5 to 500	0.994	95.7	9.3	92.8	2.9	85.4	6.4	94.1	0.6
Dicrotofos	5 to 500	0.997	86.2	11.0	96.3	9.5	69.3	22.0	85.2	5.1
Parathion	1 to 500	0.990	103.4	8.6	102.3	1.0	101.5	7.3	100.3	1.0
Permethrin, (1R)-*cis*-	5 to 500	0.996	83.5	7.1	82.0	5.2	77.9	6.3	77.5	1.7
Permethrin, (1R)-*trans*-	5 to 500	0.995	92.3	9.0	82.0	4.2	80.2	8.8	80.2	2.6
Phenthoate	1 to 500	0.996	90.9	2.4	98.1	3.6	95.6	6.1	98.3	1.9
Phorate sulfone*	2 to 500	0.992	106.5	7.1	94.1	2.8	96.3	8.0	103.0	5.0
Phosalone	1 to 500	0.991	91.0	9.9	91.6	2.2	83.9	3.6	93.4	1.6
Pirimicarb	1 to 500	0.993	102.8	6.8	103.9	2.1	100.1	7.3	99.8	0.8
Pirimiphos-methyl*	1 to 500	0.994	84.7	12.1	98.8	4.1	93.7	7.7	94.6	2.8
Profenofos*	1 to 500	0.993	82.9	13.1	83.7	4.6	73.6	9.9	82.2	2.9
Propanil	1 to 500	0.994	94.7	5.5	105.9	2.5	98.0	6.3	102.6	1.0
Propiconazole I	5 to 500	0.995	113.5	11.1	101.5	2.3	88.6	6.7	88.7	4.0
Prothiofos	1 to 500	0.991	82.8	7.2	83.2	2.6	80.5	6.5	79.4	1.9
Pyraclostrobin*	10 to 500	0.991	—	—	92.8	12.4	87.1	5.0	101.5	1.3
Pyrimethanil*	1 to 500	0.996	101.4	4.9	104.4	2.9	100.9	7.1	98.6	1.3
Pyriproxyfen	1 to 500	0.997	80.9	12.2	81.1	4.3	74.2	5.0	83.5	2.1
Quinalphos	1 to 500	0.995	93.9	7.6	94.1	2.3	94.9	7.0	97.3	1.3
Quinoxyfen*	1 to 500	0.992	87.0	7.1	88.9	1.0	83.8	5.1	89.6	1.1
Ronnel	1 to 500	0.991	94.5	8.0	101.5	3.1	95.1	7.6	94.3	0.5
Sulfoxaflor*	2 to 500	0.998	102.6	4.0	105.8	6.5	105.3	5.2	100.7	2.4
Terbufos	1 to 500	0.995	103.5	9.0	104.8	1.0	98.0	8.4	100.0	1.2
Terbufos sulfone*	1 to 500	0.996	98.7	5.8	104.2	4.9	96.9	7.3	95.6	3.0
Tetradifon	1 to 500	0.997	93.1	8.2	93.3	4.0	85.1	2.1	89.3	2.5
Thiabendazole*	1 to 500	0.994	85.5	6.5	96.8	3.1	88.3	6.8	95.8	1.1
Triadimefon*	1 to 500	0.993	94.2	5.7	104.8	2.7	100.0	7.2	100.9	1.7
Triazophos	2 to 500	0.990	93.6	8.3	97.3	0.5	87.4	6.3	97.6	0.5

* Pesticides validated with two instrumental platforms of GC/MS/MS and LC/MS/MS.

Table 4. Method quantitation results for 95 pesticides in milk with LC/MS/MS.

Name	Linearity Range (ng/mL)	R^2	Low QC 5 ng/mL in Milk (n = 4)		Low QC 10 ng/mL in Milk (n = 4)		Mid QC 50 ng/mL in Milk (n = 4)		High QC 100 ng/mL in Milk (n = 4)	
			Mean Recovery %	RSD%	Mean Recovery %	RSD%	Mean Recovery %	RSD%	Mean Recovery %	RSD%
2,4-D	1 to 500	0.999	83.1	10.8	87.1	16.0	94.7	2.5	100.3	3.1
2-Chlorobenzoic acid	20 to 500	0.995	–	–	–	–	98.0	14.5	109.7	14.1
3,6-dichloro- benzoic acid	1 to 500	0.996	92.2	9.6	96.6	4.7	103.7	2.4	105.3	1.9
4-Hydroxy chlorothalonil	1 to 500	0.998	97.2	16.2	102.0	7.8	95.0	5.6	99.6	1.9
Acetamiprid*	1 to 200	0.998	103.8	7.3	108.5	3.0	113.2	0.7	110.3	0.8
Aldicarb	1 to 200	0.999	96.3	5.1	102.3	4.9	114.4	2.2	115.0	1.8
Aldicarb-sulfone (Aldoxycarb)	1 to 200	0.999	105.1	2.8	104.6	4.7	110.7	3.6	110.5	2.5
Aldicarb-sulfoxide	1 to 500	1.000	92.6	5.2	98.3	3.2	102.9	1.1	105.7	0.7
Aminopyralid	1 to 100	0.994	69.7	10.5	85.1	6.2	87.2	1.7	82.9	1.9
Amitraz	1 to 500	0.997	69.7	9.8	66.0	3.0	64.2	3.5	63.7	1.9
Azoxystrobin*	1 to 500	0.999	95.4	4.6	97.7	1.2	99.7	2.1	102.4	1.9
Bentazone*	1 to 500	1.000	91.0	8.6	93.1	6.7	103.2	2.7	105.6	3.0
benzovindiflupyr	1 to 500	0.995	101.6	8.9	107.2	4.4	119.2	3.1	121.7	1.5
Bifenazate	1 to 200	0.999	99.2	5.9	104.9	2.5	110.7	0.4	110.9	1.0
Bifenazate metabolite B	1 to 200	0.998	91.2	6.9	91.5	2.8	96.0	1.6	101.3	0.5
Bifenthrin*	1 to 500	1.000	71.9	8.5	81.1	2.3	84.1	4.7	80.2	7.1
Bitertanol*	1 to 500	0.997	101.9	5.3	106.8	2.4	115.6	0.7	116.2	1.6
Boscalid*	1 to 500	0.994	102.5	7.2	109.7	1.6	117.8	1.6	117.1	0.4
Buprofezin*	1 to 500	0.998	89.7	7.3	94.3	3.3	98.6	1.3	102.3	0.2
Carbaryl*	1 to 500	0.999	96.5	5.1	102.3	4.1	107.8	1.2	108.3	1.3
Carbendazim	1 to 200	0.999	94.3	6.5	94.9	1.7	100.1	1.4	106.9	0.3
Chlorantraniliprole*	1 to 500	0.997	97.3	8.2	103.1	4.4	113.7	0.8	116.0	1.5
Chlorpyrifos*	1 to 500	0.999	85.3	2.7	91.1	5.6	95.9	1.6	99.1	0.5
Chlorpyrifos-methyl*	2 to 500	0.998	89.7	8.0	98.7	7.2	102.9	2.5	105.8	2.8
Clofentezine*	1 to 500	0.999	94.8	9.9	98.2	2.6	104.5	1.7	106.6	1.2
Clothianidin	1 to 500	0.994	103.8	5.2	116.7	3.5	120.1	0.7	111.5	1.4
Cycloxydime	1 to 500	1.000	88.9	7.1	89.5	3.0	94.5	0.4	96.7	2.6
Cyhalothrin	1 to 200	0.998	91.1	7.2	103.1	5.2	125.9	1.4	126.3	1.6
Cypermethrin	1 to 500	0.995	89.8	4.8	100.6	2.6	110.1	3.3	110.3	1.4
Cyprodinil*	1 to 500	0.998	89.5	6.7	95.7	2.0	107.9	2.6	107.6	1.6
Cyromazine*	1 to 500	0.999	55.9	9.7	58.1	5.4	64.1	1.7	64.9	1.2
Diazinon*	1 to 500	1.000	92.5	3.9	97.7	3.6	103.5	2.7	105.1	0.4
Dicamba	5 to 500	0.997	–	–	85.3	9.0	82.9	10.7	90.0	11.1
Dichlorvos*	5 to 500	0.999	–	–	101.4	8.5	112.0	2.6	115.2	3.6
Difenoconazole	1 to 500	0.999	93.0	5.1	98.4	4.0	106.5	1.1	107.9	1.6
Diflubenzuron	1 to 200	0.996	100.2	8.4	107.6	2.7	114.8	1.7	111.3	0.8
Dimethoate*	1 to 500	0.998	98.4	5.9	100.9	3.1	107.3	1.3	110.4	0.9
Dinotefuran	1 to 500	0.998	96.5	4.1	101.9	4.1	111.0	2.2	110.3	1.3
Dinotefuran metabolite UF	1 to 200	1.000	88.2	4.6	91.4	2.9	96.4	1.2	98.8	0.3
Diphenylamine*	20 to 500	0.999	–	–	–	–	108.2	7.5	123.6	2.5
Ethoprophos*	1 to 500	0.998	98.3	5.9	104.5	3.7	111.8	2.0	112.6	1.2
Etofenprox	1 to 500	0.998	75.1	3.0	85.9	3.1	85.8	3.6	78.8	13.1
Famoxadone*	1 to 200	0.995	102.1	7.3	114.0	5.5	125.6	3.0	118.1	2.5

Name	Linearity Range (ng/mL)	R^2	Low QC 5 ng/mL in Milk (n = 4)		Low QC 10 ng/mL in Milk (n = 4)		Mid QC 50 ng/mL in Milk (n = 4)		High QC 100 ng/mL in Milk (n = 4)	
			Mean Recovery %	RSD%	Mean Recovery %	RSD%	Mean Recovery %	RSD%	Mean Recovery %	RSD%
Fenamiphos	1 to 500	0.994	96.1	4.2	103.8	1.9	110.2	2.0	114.8	1.1
Fenamiphos sulfone*	1 to 200	0.998	105.9	3.6	110.9	3.8	115.3	1.1	111.4	1.2
Fenamiphos sulfoxide	1 to 500	0.998	101.4	4.1	108.4	2.4	117.9	1.2	114.7	1.1
Fenpropimorph*	1 to 500	0.999	77.6	0.7	79.8	2.8	86.1	3.8	85.7	0.7
Fenvalerate	1 to 500	0.997	89.9	10.1	107.0	5.5	108.4	3.3	108.5	2.4
Fipronil Desulfinyl	1 to 500	1.000	90.9	7.8	94.8	3.2	100.9	1.6	105.6	0.9
Fipronil*	1 to 500	0.999	93.2	2.4	98.2	5.9	104.0	1.9	107.6	1.8
Fipronil sulfide*	1 to 500	0.999	89.9	8.5	89.1	5.6	101.4	2.4	106.9	1.0
Fipronil-sulfone	1 to 500	1.000	89.8	2.6	96.2	9.4	101.3	3.7	107.3	2.0
Flubendiamide	1 to 500	0.998	91.3	2.3	90.0	6.0	97.4	2.6	100.2	2.9
Fluopicolide	1 to 500	0.995	104.6	5.1	109.8	3.7	117.9	2.2	118.4	2.1
Flusilazole*	1 to 500	0.995	98.0	9.4	107.1	4.2	115.1	2.4	114.6	2.4
Hexythiazox	1 to 500	1.000	91.5	5.1	93.5	2.7	99.5	1.1	99.2	1.3
Imazapyr	1 to 500	0.999	76.0	5.5	81.9	3.0	89.2	2.1	88.7	1.1
Imidacloprid	1 to 200	0.998	98.4	6.4	103.5	3.6	107.1	0.9	108.1	0.9
Isopyrazam*	1 to 500	1.000	94.2	7.8	96.9	1.5	102.3	0.7	104.9	1.0
Kresoxim-methyl acid	1 to 200	0.994	94.2	6.2	103.7	6.4	112.2	3.1	110.7	0.7
MCPA	1 to 500	0.999	82.9	9.1	90.5	6.8	98.0	3.8	101.6	2.6
Metaflumizone	1 to 200	0.996	100.8	6.7	112.7	6.2	122.5	2.4	113.8	1.7
Methamidophos*	1 to 500	0.998	92.9	5.4	98.3	2.7	104.4	1.1	106.3	0.5
Methidathion*	1 to 500	0.999	98.0	3.8	103.2	2.1	108.5	1.1	109.0	1.8
Metrafenone*	1 to 500	1.000	92.6	6.0	93.4	4.0	99.6	2.1	101.5	0.6
Novaluron	1 to 500	0.998	101.1	6.7	104.7	1.3	111.9	1.4	113.5	1.0
Oxamyl*	1 to 500	1.000	99.2	5.2	103.7	3.1	108.3	0.5	108.7	1.3
Penthiopyrad	1 to 500	0.998	94.3	4.8	98.5	3.4	105.1	2.0	107.8	0.9
Penthiopyrad metabolite (3-(Trifluoromethyl)-1-methyl-1H-pyrazole-4-carboxamide)	1 to 200	0.999	94.9	5.2	97.9	2.9	102.6	1.3	108.5	0.6
Phorate*	1 to 500	0.999	89.5	11.8	97.3	1.8	107.1	1.1	109.0	1.6
Phorate Sulfone*	1 to 500	0.996	95.3	2.6	102.8	2.2	111.7	1.4	113.2	0.5
Phorate Sulfoxide	1 to 500	0.999	96.8	5.0	99.8	3.0	106.0	2.1	109.1	1.3
Pirimiphos-methyl*	1 to 500	0.999	92.9	4.4	95.8	2.3	100.7	2.6	101.8	1.1
Prochloraz*	1 to 500	1.000	92.2	8.5	94.0	2.7	100.8	1.6	102.5	1.0
Profenofos*	1 to 500	0.998	94.6	6.8	101.2	1.1	108.0	1.5	108.7	0.4
Propargite	1 to 500	1.000	93.5	9.6	98.5	2.7	107.7	2.9	107.4	1.5
Propiconazole	1 to 500	0.997	99.5	6.1	102.8	3.5	113.4	3.9	113.2	0.8
Prothioconazole-desthio	1 to 500	0.999	95.1	6.8	96.6	2.7	99.0	1.6	100.5	1.1
Pyraclostrobin*	1 to 500	1.000	94.8	6.6	98.4	2.5	104.0	1.4	105.3	1.1
Pyrimethanil*	1 to 500	0.999	95.2	6.1	99.9	4.1	108.8	1.1	109.8	0.9
Quinoxyfen*	1 to 500	0.999	83.1	9.5	85.9	1.6	90.2	1.6	92.1	0.8
Saflufenacil	1 to 200	0.998	104.2	3.5	110.8	2.1	118.1	1.3	114.7	1.6
Semiamitraz	1 to 500	0.996	73.7	9.8	87.6	5.3	95.9	2.3	97.4	2.1
Spirodiclofen*	1 to 500	1.000	89.2	5.4	92.9	3.1	96.9	1.8	98.8	0.7
Spirotetramat	1 to 500	0.994	91.7	7.0	107.9	4.1	112.3	3.7	112.2	3.2

Name	Linearity Range (ng/mL)	R^2	Low QC 5 ng/mL in Milk (n = 4)		Low QC 10 ng/mL in Milk (n = 4)		Mid QC 50 ng/mL in Milk (n = 4)		High QC 100 ng/mL in Milk (n = 4)	
			Mean Recovery %	RSD%	Mean Recovery %	RSD%	Mean Recovery %	RSD%	Mean Recovery %	RSD%
Spirotetramet metabolite BYI08330-cis-enol	1 to 200	1.000	95.9	5.6	100.6	3.2	109.2	0.9	109.5	0.6
Sulfoxaflor*	1 to 500	0.998	100.2	5.2	105.5	3.9	112.0	0.7	113.4	1.0
Tebufenozide	1 to 500	0.998	102.4	8.4	109.3	5.9	116.2	6.2	115.3	1.9
Terbufos Sulfone*	1 to 500	1.000	90.5	3.0	95.9	0.9	102.4	2.3	106.6	1.1
Terbufos-sulfoxide	1 to 500	0.993	95.4	6.9	100.8	2.5	107.8	1.6	113.6	0.3
Thiabendazole*	1 to 500	0.996	96.0	6.7	104.6	4.9	112.8	1.4	113.1	2.3
Thiacloprid	1 to 200	1.000	97.9	5.5	101.1	4.0	105.6	1.2	109.0	1.5
Thiamethoxam	1 to 200	0.999	99.8	6.4	108.7	3.6	116.1	0.9	117.9	1.7
Triadimefon*	1 to 200	0.999	96.6	2.3	102.9	3.4	109.8	1.5	108.3	0.7
Triadimenol	1 to 500	0.999	99.9	7.0	104.4	3.0	108.2	0.6	108.0	1.2
Triforine	1 to 200	0.999	92.7	5.2	102.9	3.8	114.6	2.4	112.6	1.3

* Pesticides validated with two instrumental platforms of GC/MS/MS and LC/MS/MS.

Conclusion

A rapid, reliable, and robust workflow using QuEChERS extraction followed by Agilent Captiva EMR—Lipid cartridge cleanup was developed and verified for the analysis of 171 pesticide multiresidues in milk using LC/MS/MS and GC/MS/MS. The sample preparation procedure was investigated and optimized for extraction method, matrix removal, elution efficiency, and water removal. Captiva EMR—Lipid cleanup provides the best matrix removal efficiency and the least instrumental contamination. The total workflow delivers satisfactory quantitation results, and demonstrates an efficient solution for the analysis of multiclass multiresidue pesticides in milk.

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Appendix

MRM parameters setting of GC/MS/MS and LC/MS/MS

Compound Name	GC/MS/MS MRM Setting		
	RT (min)	Quant Transition	Qualifier Transition
2,4,6-Trichlorophenol	7.73	131.8 -> 97.0	96.9 -> 62.0
Acetamiprid	27.87	126.0 -> 73.0	152.0 -> 116.1
Aldrin	19.57	262.9 -> 192.9	254.9 -> 220.0
Azinphos-ethyl	30.62	132.0 -> 77.1	160.0 -> 77.1
Azinphos-methyl	29.35	160.0 -> 77.0	160.0 -> 132.1
Azoxystrobin	37.06	344.1 -> 329.0	344.1 -> 171.9
Bentazone	20.36	119.0 -> 92.0	198.0 -> 119.0
Bifenthrin	28.33	181.2 -> 165.2	181.2 -> 166.2
Bitertanol	31.51	170.1 -> 141.1	170.1 -> 115.0
Boscalid	33.36	140.0 -> 112.0	140.0 -> 76.0
Buprofezin	23.76	104.0 -> 51.0	104.0 -> 77.0
Captan	21.42	151.0 -> 80.0	149.0 -> 79.1
Carbaryl	18.25	144.1 -> 116.1	144.1 -> 89.0
Chinomethionate (Oxythioquinox)	21.89	233.9 -> 206.1	206.0 -> 148.1
Chlorantraniliprole	28.34	277.8 -> 215.0	277.8 -> 248.8
Chlordane-cis	22.55	271.8 -> 236.9	372.8 -> 265.9
Chlordane-oxy	21.14	114.9 -> 51.1	114.9 -> 87.0
Chlordane-trans	21.99	271.7 -> 236.9	372.8 -> 265.8
Chlorfenvinphos	21.55	266.9 -> 159.1	322.8 -> 266.8
Chlorpropham	13.31	153.0 -> 90.0	153.0 -> 125.1
Chlorpyrifos	19.99	198.9 -> 171.0	196.9 -> 169.0
Chlorpyrifos-methyl	18.10	285.9 -> 93.0	287.9 -> 92.9
Clofentezine	5.28	136.7 -> 102.0	138.7 -> 102.0
Coumaphos	31.97	210.0 -> 182.0	361.9 -> 109.0
Cyfluthrin-1	32.79	226.0 -> 206.0	198.9 -> 170.1
Cyfluthrin-2	32.97	226.0 -> 206.0	198.9 -> 170.1
Cyfluthrin-3	33.12	226.0 -> 206.0	198.9 -> 170.1
Cyfluthrin-4	33.20	226.0 -> 206.0	198.9 -> 170.1
Cypermethrin-1	33.11	163.0 -> 91.0	163.0 -> 127.0
Cypermethrin-2	33.20	163.0 -> 91.0	163.0 -> 127.0
Cypermethrin-3	33.37	163.0 -> 127.0	163.0 -> 91.0
Cypermethrin-4	33.56	163.0 -> 91.0	163.0 -> 127.0
Cyprodinil	20.90	225.2 -> 224.3	224.2 -> 208.2
Cyromazine	15.47	151.0 -> 109.0	165.9 -> 151.0
DDD-*o,p'*	23.72	235.0 -> 165.2	237.0 -> 165.2
DDD-*p,p'*	24.93	234.9 -> 165.1	236.9 -> 165.2
DDE-*p,p'*	23.42	246.1 -> 176.2	315.8 -> 246.0
DDT-*o,p'*	25.04	235.0 -> 165.2	237.0 -> 165.2
DDT-*p,p'*	26.27	235.0 -> 165.2	237.0 -> 165.2
Deltamethrin	36.52	252.9 -> 93.0	250.7 -> 172.0
Demeton-S-methyl	12.70	88.0 -> 60.0	142.0 -> 78.9
Diazinon	16.42	137.1 -> 84.0	137.1 -> 54.0

Compound Name	GC/MS/MS MRM Setting		
	RT (min)	Quant Transition	Qualifier Transition
Dichlofenthion	17.76	278.9 -> 222.9	222.9 -> 204.9
Dichloran	14.74	206.1 -> 176.0	160.1 -> 124.1
Dichlorvos	6.13	109.0 -> 79.0	184.9 -> 93.0
Dicrotofos	13.75	127.0 -> 109.0	127.0 -> 95.0
Dieldrin	23.38	262.9 -> 193.0	277.0 -> 241.0
Difenoconazole I	35.85	322.8 -> 264.8	264.9 -> 202.0
Difenoconazole II	35.98	322.8 -> 264.8	264.9 -> 202.0
Dimethipin	15.25	118.0 -> 58.0	124.0 -> 76.0
Dimethoate	14.85	87.0 -> 46.0	142.9 -> 111.0
Diphenylamine	12.70	169.0 -> 168.2	168.0 -> 167.2
Endosulfan I (*alpha* isomer)	22.42	194.9 -> 159.0	194.9 -> 125.0
Endosulfan II (*beta* isomer)	24.51	206.9 -> 172.0	194.9 -> 124.9
Endosulfan sulfate	26.03	271.9 -> 237.0	273.8 -> 238.9
Endrin	24.16	262.8 -> 193.0	244.8 -> 173.0
Ethion	25.19	230.9 -> 129.0	230.9 -> 175.0
Ethofenprox	33.92	163.0 -> 107.1	163.0 -> 135.1
Ethoprophos	12.99	157.9 -> 97.0	157.9 -> 114.0
Famoxadone	37.06	197.0 -> 115.0	223.9 -> 196.2
Fenamidone	28.62	238.0 -> 237.2	268.0 -> 180.2
Fenamiphos sulfone	27.89	319.8 -> 292.0	171.0 -> 107.0
Fenitrothion	19.17	277.0 -> 260.1	277.0 -> 109.0
Fenpropathrin	28.52	181.1 -> 152.1	207.9 -> 181.0
Fenpropimorph	19.98	128.1 -> 70.1	128.1 -> 110.1
Fensulfothion	24.77	291.8 -> 156.0	291.8 -> 108.8
Fenthion	19.90	278.0 -> 109.0	278.0 -> 169.0
Fenvalerate I	35.11	167.0 -> 125.1	224.9 -> 119.0
Fenvalerate II	35.51	167.0 -> 125.1	224.9 -> 119.0
Fipronil	21.64	366.8 -> 212.8	368.8 -> 214.8
Fipronil sulfide	21.38	351.0 -> 254.9	420.0 -> 350.9
Fipronil sulfone	23.96	382.8 -> 254.9	384.8 -> 256.8
Flusilazole	23.86	233.0 -> 165.1	233.0 -> 91.0
HCH-*alpha*	14.30	216.9 -> 181.0	218.9 -> 183.0
HCH-*beta*	15.34	181.0 -> 145.0	216.9 -> 181.1
HCH-*delta*	16.50	181.1 -> 145.1	217.0 -> 181.1
HCH-*gamma*	15.56	181.0 -> 145.0	216.9 -> 181.0
Heptachlor	18.28	271.7 -> 236.9	273.7 -> 238.9
Heptachlor exo-epoxide	21.10	352.8 -> 262.9	354.8 -> 264.9
Hexachlorobenzene	14.56	283.8 -> 213.9	283.8 -> 248.8
Isopyrazam	31.01	159.0 -> 42.1	159.0 -> 139.0
Malathion	19.65	126.9 -> 99.0	172.9 -> 99.0
Mecarbam	21.63	158.9 -> 131.0	130.9 -> 74.0

Compound Name	GC/MS/MS MRM Setting		
	RT (min)	Quant Transition	Qualifier Transition
Methacrifos	10.43	207.9 -> 180.1	207.9 -> 93.0
Methamidophos	5.84	141.0 -> 95.0	141.0 -> 79.0
Methidathion	22.09	144.9 -> 85.0	144.9 -> 58.1
Metrafenone	30.98	208.9 -> 166.0	394.8 -> 364.8
Oxamyl	11.02	162.0 -> 114.9	98.0 -> 58.0
Parathion	20.01	139.0 -> 109.0	290.9 -> 109.0
Pentachloronitrobenzene	15.76	295.0 -> 237.0	236.9 -> 142.9
Permethrin, (1R)-*cis*-	31.61	183.1 -> 168.1	183.1 -> 153.0
Permethrin, (1R)-*trans*-	31.85	183.1 -> 168.1	183.1 -> 153.0
Phenthoate	21.66	273.7 -> 121.0	273.7 -> 124.9
Phorate	14.20	260.0 -> 75.0	230.9 -> 128.9
Phorate sulfone	19.76	124.9 -> 96.9	153.0 -> 97.0
Phosalone	29.38	182.0 -> 111.0	182.0 -> 102.1
Phosmet	27.97	160.0 -> 77.1	160.0 -> 133.1
Pirimicarb	17.37	166.0 -> 55.1	238.0 -> 166.2
Pirimiphos-methyl	19.30	290.0 -> 125.0	232.9 -> 151.0
Prochloraz	32.09	195.9 -> 96.9	180.0 -> 138.0

Compound Name	GC/MS/MS MRM Setting		
	RT (min)	Quant Transition	Qualifier Transition
Profenofos	23.30	207.9 -> 63.0	338.8 -> 268.7
Propanil	17.70	161.0 -> 99.0	161.0 -> 90.0
Propiconazole I	26.16	172.9 -> 145.0	172.9 -> 74.0
Prothiofos	23.19	266.9 -> 239.0	308.9 -> 238.9
Pyraclostrobin	35.18	132.0 -> 104.0	132.0 -> 77.1
Pyrimethanil	16.15	198.0 -> 118.1	198.0 -> 183.1
Pyriproxyfen	29.61	136.1 -> 78.1	136.1 -> 96.0
Quinalphos	21.63	146.0 -> 118.0	146.0 -> 91.0
Quinoxyfen	26.03	271.9 -> 237.1	237.0 -> 208.1
Ronnel	18.64	285.0 -> 269.9	286.9 -> 272.0
Spirodiclofen	31.55	109.1 -> 81.1	109.1 -> 79.1
Sulfoxaflor	12.70	173.7 -> 104.1	173.7 -> 154.0
Terbufos	15.86	230.9 -> 175.0	230.9 -> 129.0
Terbufos sulfone	21.22	153.0 -> 97.0	198.9 -> 96.9
Tetradifon	29.02	158.9 -> 131.0	226.9 -> 199.0
Thiabendazole	21.22	201.0 -> 174.0	201.9 -> 175.0
Triadimefon	20.10	208.0 -> 181.1	208.0 -> 111.0
Triazophos	25.64	161.2 -> 134.2	161.2 -> 106.1

Compound Name	LC/MS/MS MRM Setting					
	RT (min)	Precursor Ion	Product Ion	Fragmentor	Collision Energy	Polarity
2,4-D	5.79	219.0	161.0	90	15	–
		221.0	163.0		15	
2-Chlorobenzoic acid	4.19	155.0	111.0	65	4	–
		155.0	35.1		10	
3,6-Dichloro- benzoic acid	4.03	204.9	160.9	80	10	–
		204.9	125.0		22	
4-Hydroxy chlorothalonil	4.89	244.9	181.9	146	34	–
		244.9	174.9		30	
Acetamiprid	3.60	223.0	126.1	80	18	–
		223.0	99.0		44	
Aldicarb	4.52	208.0	116.0	65	6	+
		208.0	89.1		10	
Aldicarb-sulfone (Aldoxycarb)	2.92	223.1	86.1	80	8	+
		223.1	76.0		0	
Aldicarb-sulfoxide	2.85	207.1	131.9	65	2	+
		207.1	105.2		4	
Aminopyralid	2.77	207.0	161.0	90	20	+
		207.0	134.0		32	
Amitraz	14.30	294.2	163.0	90	12	+
		294.2	122.0		32	
Azoxystrobin	7.11	404.0	372.2	105	10	+
		404.0	344.0		24	
Bentazone	4.66	239.0	197.0	105	17	–
		239.0	132.0		25	
Benzovindiflupyr	9.48	398.1	378.0	90	14	+
		398.1	342.1		18	

Compound Name	LC/MS/MS MRM Setting					
	RT (min)	Precursor Ion	Product Ion	Fragmentor	Collision Energy	Polarity
Bifenazate	8.32	301.1	198.2	90	5	+
		301.1	170.1		18	
Bifenazate metabolite B	10.78	299.1	213.0	85	10	+
		299.1	197.0		18	
Bifenthrin	15.90	440.2	198.2	100	4	+
		440.2	181.0		14	
Bitertanol	10.55	338.1	269.2	70	2	+
		338.1	251.2		6	
Boscalid	7.65	343.2	307.2	140	20	+
		343.2	271.0		35	
Buprofezin	12.42	306.1	201.2	105	9	+
		306.1	116.0		15	
Carbaryl	5.42	202.0	145.0	65	2	+
		202.0	127.1		28	
Carbendazim	3.40	192.1	160.1	105	16	+
		192.1	132.1		32	
Chlorantraniliprole	6.76	483.9	452.9	105	16	+
		483.9	286.0		12	
Chlorpyrifos	13.05	351.9	199.9	100	15	+
		349.9	197.9		22	
Chlorpyrifos-methyl	11.08	322.0	290.0	110	10	+
		322.0	125.0		25	
Clofentezine	10.55	303.0	138.0	80	15	+
		303.0	102.1	110	40	
Clothianidin	3.42	250.0	169.0	90	8	+
		250.0	131.9		8	
Cycloxydime	11.33	326.2	280.1	90	14	+
		326.2	180.0		22	
Cyhalothrin	13.99	467.1	450.1	90	4	+
		467.1	225.0		12	
Cypermethrin	14.18	435.1	193.0	100	10	+
		433.1	191.0		12	
Cyprodinil	9.51	226.1	108.1	140	24	+
		226.1	93.1		40	
Cyromazine	2.64	167.0	125.0	120	20	+
		167.0	108.0		15	
Diazinon	10.37	305.1	169.0	105	26	+
		305.1	153.1		24	
Dicamba	4.20	221.0	177.0	60	2	–
		219.0	175.0		2	
Dichlorvos	5.04	221.0	109.0	100	12	+
		221.0	95.1		32	
Difenoconazole	11.08	406.0	251.1	120	25	+
		406.0	188.1		46	
Diflubenzuron	9.09	311.0	158.0	80	18	+
		311.0	141.0		46	
Dimethoate	3.70	230.0	199.0	70	4	+
		230.0	171.0		12	

Compound Name	LC/MS/MS MRM Setting					
	RT (min)	Precursor Ion	Product Ion	Fragmentor	Collision Energy	Polarity
Dinotefuran	2.82	203.1	157.0	85	2	+
		203.1	129.0		6	
Dinotefuran metabolite UF	2.83	159.1	102.1	85	10	+
		159.1	67.1		22	
Diphenylamine	8.42	170.1	93.1	115	32	+
		170.1	92.6		24	
Ethoprophos	9.02	243.0	173.1	90	12	+
		243.0	131.0		16	
Etofenprox	15.79	394.2	359.2	100	12	+
		394.2	177.2		13	
Famoxadone	10.14	392.0	331.1	75	6	+
		392.0	238.1		18	
Fenamiphos	9.30	304.1	234.0	120	16	+
		304.1	217.1		20	
Fenamiphos sulfone	5.15	336.1	308.0	110	12	+
		336.1	266.0		16	
Fenamiphos sulfoxide	5.02	320.1	233.0	115	20	+
		320.1	171.1		16	
Fenpropimorph	6.99	304.0	147.0	120	30	+
		304.0	130.0		30	
Fenvalerate	14.80	437.2	181.0	90	38	+
		437.2	167.0		14	
Fipronil Desulfinyl	8.80	387.0	351.0	90	14	–
		387.0	331.0		34	
Fipronil	9.24	435.0	330.0	70	12	–
		435.0	250.0		28	
Fipronil sulfide	9.50	419.2	383.2	80	18	–
		419.2	262.0		13	
Fipronil-sulfone	9.92	450.9	415.0	100	9	–
		450.9	282.0		25	
Flubendiamide	9.61	681.0	274.0	101	14	–
		681.0	271.9		14	
Fluopicolide	8.02	385.0	147.0	112	60	+
		382.9	172.9	110	32	
Flusilazole	9.26	316.0	247.2	120	15	+
		316.0	219.1		26	
Hexythiazox	13.11	353.0	228.1	90	12	+
		353.0	194.1		24	
Imazapyr	3.47	262.1	217.0	121	22	+
		262.1	69.2		30	
Imidacloprid	3.36	256.0	209.1	80	12	+
		256.0	175.1		22	
Isopyrazam	11.17	360.0	320.0	75	10	+
		360.0	244.1		20	
Kresoxim-methyl acid	7.44	300.1	253.0	85	2	+
		300.1	222.0		10	
MCPA	6.10	201.0	143.0	100	15	–
		199.0	141.0		15	

Compound Name	LC/MS/MS MRM Setting					
	RT (min)	Precursor Ion	Product Ion	Fragmentor	Collision Energy	Polarity
Metaflumizone	12.29	507.0	287.1	150	20	+
		507.0	267.0		40	
Methamidophos	2.75	142.0	125.0	85	10	+
		142.0	94.1		12	
Methidathion	6.71	302.9	145.0	55	6	+
		302.9	85.1		20	
Metrafenone	10.38	409.1	226.9	106	22	+
		409.1	209.0		14	
Novaluron	11.55	493.1	310.0	90	16	+
		493.1	158.1		18	
Oxamyl	2.94	237.1	220.0	50	2	+
		237.1	90.0		2	
Penthiopyrad	9.36	360.1	276.0	90	14	+
		360.1	256.0		22	
Penthiopyrad metabolite	3.05	194.1	174.0	80	6	+
		194.1	154.0		14	
Phorate	10.69	261.0	199.0	60	2	+
		261.0	75.1		6	
Phorate Sulfone	6.07	293.0	171.0	80	6	+
		293.0	143.0		15	
Phorate Sulfoxide	5.92	277.0	199.0	80	5	+
		277.0	171.0		12	
Pirimiphos-methyl	10.72	306.0	164.2	130	24	+
		306.0	136.1		32	
Prochloraz	10.42	376.0	308.0	70	4	+
		376.0	265.9		12	
Profenofos	11.99	374.9	347.0	120	9	+
		373.0	344.9		10	
Propargite	13.55	368.1	81.0	82	44	+
		368.0	231.1		1	
Propiconazole	10.29	342.0	158.9	115	36	+
		342.0	123.1		56	
Prothioconazole-desthio	9.10	312.1	125.0	111	46	+
		312.1	70.0		26	
Pyraclostrobin	10.44	388.0	194.1	95	6	+
		388.0	163.1		20	
Pyrimethanil	7.57	200.1	167.9	120	28	+
		200.1	107.1		20	
Quinoxyfen	12.89	308.0	214.1	120	40	+
		308.0	197.0		36	
Saflufenacil	7.00	501.1	459.0	160	8	+
		501.1	349.0		24	
Semiamitraz	3.14	163.1	122.0	116	10	+
		163.1	107.0		18	
Spirodiclofen	14.10	411.1	313.0	110	6	+
		411.1	213.1		36	
Spirotetramat	8.69	374.1	330.3	117	10	+
		374.1	302.2		14	

Compound Name	LC/MS/MS MRM Setting					
	RT (min)	Precursor Ion	Product Ion	Fragmentor	Collision Energy	Polarity
Spirotetramat metabolite	5.65	302.2	270.1	131	22	+
		302.2	216.0		34	
Sulfoxaflor	3.81	278.2	174.1	95	8	+
		278.2	154.1		32	
Tebufenozide	9.40	353.0	297.2	95	5	+
		353.0	133.1		15	
Terbufos Sulfone	7.20	321.0	171.0	80	5	+
		321.0	142.9		20	
Terbufos-sulfoxide	7.30	305.1	186.9	50	10	+
		305.1	96.9		50	
Thiabendazole	3.68	202.0	175.1	151	22	+
		202.0	131.1		30	
Thiacloprid	3.86	253.0	126.0	100	20	+
		253.0	99.1		44	
Thiamethoxam	3.11	292.0	211.1	85	10	+
		292.0	181.1		28	
Triadimefon	8.13	294.1	225.0	111	2	+
		294.1	197.0		6	
Triadimenol	8.50	298.1	70.1	70	10	+
		296.1	227.2		6	
Triforine	6.76	434.9	389.9	110	12	+
		434.9	214.9		28	

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