Multiresidue Analysis of Pesticides in Bovine Milk by GC/MS/MS with Bond Elut QuEChERS EN Kits

Application Note

Food Testing and Agriculture

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Abstract

This application note describes the quantitative analysis of 60 pesticides and metabolites listed on the National Plan for Control of Residues and Contaminants (PNCRC) developed by the Ministry of Agriculture, Livestock, and Food Supply (MAPA) [1], and compounds with a maximum residue limit (MRL) listed in *Codex Alimentarius* for bovine milk [2]. We performed the extraction using an Agilent BondElut QuEChERS EN kit, and analyzed target pesticides by GC/MS/MS using an Agilent 7890A GC system and an Agilent 7000B Triple Quadrupole GC/MS system in a constant flow/midcolumn backflush configuration (Pesticide Analyzer 412) [3]. We validated the method in terms of recovery and reproducibility. The limits of detection (LOD) ranged between 0.0005 and 0.0369 mg/kg, and the limits of quantitation (LOQ) were between 0.004 and 0.1 mg/kg. Recoveries for all compounds were 70 to 120%, and relative standard deviations (RSDs) were below 20% for six replicates, except for dichlorvos, with 137% of recovery. LODs were calculated as three times the RSDs at LOQ levels. We applied the method to 14 brands of milk purchased at local supermarkets.

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Introduction

Milk is an important source of nutrients, and Brazil is the fourth largest producer in the world, with 34 billion liters in 2013 [4]. In general, the quality control of milk is checking for adulteration, fraud, and microbiological control of the product. However, many compounds, such as pesticides, can be secreted into the milk by contaminated feed consumption and parasite control drug application on the animals. Many countries monitor the presence of pesticide residues in cow milk, mainly for organochlorinated products. These compounds are highly liposoluble and stable, and residuals can accumulate in fat animal tissue and be detected in milk. In Brazil, legislators prohibited the use of organochlorinated compounds in the 1980s. Nevertheless, the compounds were used in some specific situations such as vector control. Moreover, few articles about monitoring pesticide residues in milk have been published in Brazil [5].

The most common milk found in supermarkets is of the ultra-heated treatment (UHT) type. This type of milk is heated to 130 to 150 °C for a minimum of two seconds and cooled down immediately to below 32 °C to eliminate the majority of the milk´s bacteria. This process can extend the shelf life up to nine months. We chose 14 brands of this type of milk for our study. All UHTs were described as homogenized, meaning they went through a mechanical process to break down fat molecules in the milk so that they resist separation. Without homogenization, fat molecules in milk rise to the top and form a layer of cream. Homogenizing milk prevents this separation from occurring by breaking the molecules down to such a small size that they remain suspended evenly throughout the milk instead of rising to the top [6].

Brazilian legislation requires that whole milk must contain at least 3% fat. The industry can remove the rest to produce cream and butter [7].

All samples purchased were whole milk with 3% fat content, making it possible to have enough sample cleanup using the Agilent Bond Elut QuEChERS SPE Dispersive Kit, which is recommended for up to this level of fat content.

Among the pesticides studied, acaricides for tick control are most likely to contaminate milk. They present derivatives of amidine, pyrethrin, avermectine, thiazolidine, and acid esters. The form of application as well as dosage on lactating cows depends on the product. Legislation allows dairy farmers to use acaricides, but they must follow the withdrawal period described on the drug's leaflet, which can range between hours to days, according to the substance after its pulverization, bath, or application. Contamination can occur when the producers do not follow these instructions [8].

Materials and Methods

The acetonitrile, isooctane, and acetone we used were pesticide-residue grade, and we used approximately 99% pure standards from AccuStandard to prepare stock solutions at 1,000 ng/µL, and working solutions that varied in concentration.

We performed the extractions using the Agilent QuEChERS Extraction Kit for EN method 15662EN (p/n 5982-5650CH), in which 10 g of bovine milk sample was extracted using premixed sachets of 4 g $MgSO_4$, 1 g NaCl, 1 g Na citrate, and 0.5 g disodium citrate sesquihydrate. Bovine milk commercialized in Brazil has about 3% fat, which can affect the chromatographic performance, requiring more maintenance. Therefore, we chose a subsequent dispersive cleanup designed to include fat removal (Agilent Bond ElutQuEChERS SPE Dispersive Kit Fruits and vegetables with fats and waxes, EN method, p/n 5982-5156CH). This included premixed sachets containing 150 mg PSA, 150 mg C18EC, and 900 mg $MgSO_4$.

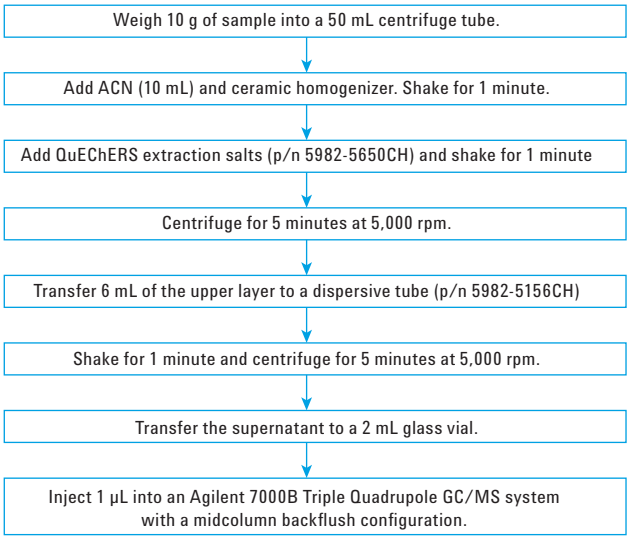

Figure 1. Sample preparation workflow showing QuEChERS extraction.

The GC/MS/MS triple quadrupole system was configured according to the Agilent Pesticide Analyzer 412 configuration, featuring two units of 15 m analytical column with midcolumn backflush.

Instrument conditions

GC conditions	
Columns:	Agilent J&W HP-5ms UI, 15 m × 0.25 mm, 0.25 µm (p/n 19091S-431UI) Two units
Inlet:	Split/splitless
Inlet liner:	Splitless, single taper, Ultra Inert liner with glass wool (p/n 5190-3167)
Carrier:	Helium
Inlet flow (column 1):	1 mL/min (constant flow mode) during run, 2 psi during backflush
PUU flow (column 2):	Column 1 flow + 0.2 mL/min
Inlet temp:	280 °C
Inj vol:	1 µL
Purge flow to split vent:	30 mL/min at 0.75 min
Gas saver:	On (20 mL/min at 2.0 min)
Oven temp:	60 °C (1 min), 40 °C/min to 170 °C (0 min), 10 °C/min to 310 °C (0 min), 16 °C/min to 280 °C (3 min)
Total run:	20.75 min
Capillary flow technology:	Purged Ultimate Union (p/n G3186) used for backflushing the column
Retention time (RT) locking:	Chlorpyrifos-methyl locked at 9.143 min
GC:	Agilent 7890A series (G3440A)
Autosampler:	Agilent 7693A injector and sample tray
MS conditions	
Spectrometer:	Agilent 7000B Triple Quadrupole GC/MS system
Mode:	Electron impact
Transfer line temp:	280 °C
Solvent delay:	2.3 min
Source temp:	300 °C
Quadrupole temp:	Q1 and Q2 = 180 °C

Results and Discussion

Performance evaluation, quantitative method

We spiked blank samples with concentrations of one maximum residue limit (MRL), and prepared calibration curves at six levels in the concentrations shown in Table 1. The table lists the MRL established by the Brazilian Ministry of Agriculture, Livestock, and Food Supply (MAPA) and *Codex Alimentarius*. We carried out the recovery study to determine method accuracy and precision, spiking blank matrix at one MRL level, which was determined as the limit of quantitation (LOQ) of the method.

Table 1. Pesticides analyzed with limits of detection (LOD), LOQ, relative standard deviation (RSD), and recovery (REC).

No.	Analyte	MAPA	CODEX	LOQ (mg/kg)	LOD (mg/kg)	Rec %	RSD %	RT (min)
1	Acephate	0.02	0.02	0.02	0.0041	94	7.3	5.72
2	Aldrin	0.004	0.006	0.004	0.0009	106	7.5	9.89
3	Amitraz		0.01	0.01	0.0045	125	11.7	14.75
4	Azinphos-ethyl	0.05		0.05	0.0101	105	6.4	15.21
5	Azinphos-methyl	0.05		0.05	0.0101	104	6.5	14.61
6	BHC-*alpha*	0.008		0.008	0.0015	107	5.9	7.66
7	BHC-*beta*	0.008		0.008	0.0017	108	6.5	8.05
8	BHC-*delta*	0.008		0.008	0.0019	105	7.5	8.53
9	BHC-*gamma*	0.004		0.004	0.0009	107	7.3	8.17
10	Carbaryl	0.02	0.05	0.02	0.0104	109	15.9	9.26
11	Carbofuran	0.1	0.05	0.1	0.0369	106	11.6	7.85
12	Chlorfenvinphos	0.01	0.01	0.01	0.0022	116	6.5	10.67
13	Chlorpyrifos	0.01	0.02	0.01	0.0022	111	6.7	9.96
14	Chlorpyrifos-methyl			0.01	0.0024	109	7.3	9.15
15	Cyfluthrin I	0.04	0.01	0.04	0.0102	112	7.7	16.16
16	Cyfluthrin II			0.04	0.0117	105	9.2	16.26
17	Cyfluthrin III			0.04	0.0178	93	15.0	16.34
18	Cyfluthrin IV			0.04	0.0126	111	9.0	16.34
19	Cyhalothrin (*lambda*)	0.025	0.2	0.2	0.0072	97	9.8	14.88
20	Cypermethrin I (*Zeta*)	0.1	0.05	0.1	0.0290	108	8.9	16.49
21	Cypermethrin II			0.1	0.0328	103	10.7	16.49
22	Cypermethrin IV			0.1	0.0234	107	7.2	16.70
23	DDD-*o,p´*	0.01		0.01	0.0017	106	5.3	11.79
24	DDD-*p,p´*	0.01		0.01	0.0023	111	6.8	12.37
25	DDE-*o,p´*	0.01		0.01	0.0018	120	5.0	11.08
26	DDE-*p,p´*	0.01		0.01	0.0020	104	6.3	11.63
27	DDT-*o,p´*	0.01	0.02	0.01	0.0016	108	5.0	12.37
28	DDT-*p,p´*	0.01	0.02	0.01	0.0017	100	5.7	13.03
29	Deltamethrin	0.03	0.05	0.03	0.0158	103	17.1	18.12
30	Diazinon	0.01	0.02	0.01	0.0021	113	6.0	8.30
31	Dichlorvos		0.01	0.01	0.0056	137	13.7	4.72
32	Dieldrin	0.004	0.006	0.004	0.0005	113	3.7	11.73
33	Dimethoate		0.05	0.01	0.0019	108	5.8	7.82

No.	Analyte	MAPA	CODEX	LOQ (mg/kg)	LOD (mg/kg)	Rec %	RSD %	RT (min)
34	Disulfoton		0.01	0.01	0.0021	108	6.4	8.44
35	DMF			0.01	0.0015	107	4.7	6.02
36	Endosulfan *alpha*		0.01	0.01	0.0028	105	9.0	11.27
37	Endosulfan *beta*		0.01	0.01	0.0023	115	6.5	12.28
38	Endosulfan sulfate		0.01	0.01	0.0021	110	6.4	13.03
39	Endrin	0.004	0.006	0.004	0.0011	119	7.7	12.07
40	Ethion			0.01	0.0024	113	7.1	12.43
41	Fenitrothion		0.01	0.01	0.0024	115	7.0	9.59
42	Fenpropathrin		0.1	0.1	0.0186	107	5.8	14.04
43	Fenvalerate I	0.04	0.1	0.04	0.0136	101	11.2	17.41
44	Fenvalerate II			0.04	0.0075	104	6.0	17.60
45	Flumetralin			0.01	0.0025	112	7.5	11.20
46	Heptachlor	0.004	0.006	0.004	0.0007	109	5.0	9.35
47	Heptachlor epoxido	0.004		0.004	0.0014	111	10.4	10.62
48	Hexachlorobenzene	0.008		0.008	0.0014	101	5.8	7.80
49	Methidathion	0.02	0.001	0.02	0.0046	114	6.8	11.01
50	Methoxychlor, *p,p´*-	0.004		0.004	0.0010	115	6.9	14.03
51	Mevinphos	0.05		0.05	0.0082	110	5.0	5.64
52	Mirex	0.004		0.004	0.0006	95	5.6	14.87
53	PCB #101	0.008		0.01	0.0015	110	4.6	11.13
54	PCB #138	0.008		0.01	0.0018	102	5.7	13.12
55	PCB #153	0.008		0.01	0.0019	102	6.3	12.62
56	PCB #180	0.008		0.01	0.0015	98	5.3	14.30
57	PCB #28	0.008		0.01	0.0017	115	4.8	9.06
58	PCB #52	0.008		0.01	0.0018	113	5.4	9.62
59	Pirimiphos-methyl	0.05	0.01	0.05	0.0089	116	5.1	9.60
60	Propoxur	0.05		0.05	0.0133	107	8.2	6.86

We determined the LOQs for the pesticides based on the recovery and RSD results at the MRL level, meeting the requirement described in SANCO/12571/2013 [9], where recovery should be 70 to 120%, and RSD below 20%. All compounds attended this requirement for six replicates, except for dichlorvos, which was above 120%. The standard spiking mixture contained the listed compounds trichlorfon, chlordane, and cyromasine. However, those were eliminated from the method for not achieving a good detection at the MRL level. The MRL level for methamidofos, trichorfon, and cyromasine is 0.01 mg/kg and 0.004 mg/kg for chlordane. Since the standard spiking mixture contained trichlorfon, and its degradation generates dichlorvos, it could lead to higher recovery of this compound. We calculated the LODs as three times the RSD of the spiked samples at their assigned LOQ levels.

Table 2 lists the calibration curve linearity for each compound included in the final quantitative method. Multiple reaction monitors (MRMs) of the compounds were selected based on the Agilent Pesticide and Environmental Pollutants MRM Database (G9250AA) and Agilent Pesticide Analysis Reference Guide [10].

Table 2. Calibration curve and MRM transition for each compound.

No.	Analyte	Regression fit/ weight	R^2	Cal. range (mg/kg)	Quant	CE (V)	Qual	CE (V)
1	Acephate	Linear, 1/x	0.9860	0.0025–0.1	136.0 → 42.0	6	136.0 → 94.0	14
2	Aldrin	Linear, 1/x	0.9977	0.0005–0.02	262.9 → 192.9	35	261.0 → 191.0	30
							292.8 → 186.0	35
3	Amitraz	Linear, 1/x	0.9929	0.001–0.05	162.0 → 132.2	15	162.0 → 121.1	5
							132.1 → 117.1	5
4	Azinphos-ethyl	Linear, 1/x	0.9966	0.00625–0.25	132.0 → 77.1	15	160.0 → 132.1	20
							160.0 → 77.1	20
5	Azinphos-methyl	Linear, 1/x	0.9977	0.00625–0.25	160.0 → 77.1	20	160.0 → 132.1	0
							132.0 → 77.1	15
6	BHC-*alpha*	Linear, 1/x	0.9998	0.001–0.04	218.9 → 183.0	5	180.9 → 145.0	15
							218.8 → 145.0	20
7	BHC-*beta*	Linear, 1/x	0.9963	0.001–0.04	218.9 → 183.0	5	180.9 → 145.0	15
							218.8 → 145.0	20
8	BHC-*delta*	Linear, 1/x	0.9978	0.001–0.04	180.9 → 145.0	15	218.8 → 145.0	20
							218.9 → 183.0	5
9	BHC-*gamma*	Linear, 1/x	0.9992	0.0005–0.02	180.9 → 145.0	15	218.8 → 145.0	20
							218.9 → 183.0	5
10	Carbaryl	Linear, 1/x	0.9599	0.0025–0.1	144.0 → 115.1	20	144.0 → 116.1	10
							116.0 → 115.1	10
11	Carbofuran	Linear, 1/x	0.9836	0.0125–0.5	164.2 → 149.1	10	221.0 → 164.0	5
12	Chlorfenvinphos	Linear, 1/x	0.9981	0.001–0.05	266.9 → 159.1	15	268.9 → 161.0	15
							322.8 → 266.8	10
13	Chlorpyrifos	Linear, 1/x	0.9994	0.001–0.05	196.9 → 169.0	15	198.9 → 171.0	15
							313.8 → 257.8	15
14	Chlorpyrifos-methyl	Linear, 1/x	0.9993	0.001–0.05	124.9 → 47.0	15	124.9 → 78.9	5
							285.9 → 92.9	20
15	Cyfluthrin I	Linear, 1/x	0.9839	0.005–0.2	163.0 → 127.0	5	226.1 → 199.0	10
							226.1 → 206.1	10
16	Cyfluthrin II	Linear, 1/x	0.9930	0.005–0.2	163.0 → 127.0	5	226.1 → 199.0	10
							226.1 → 206.1	10
17	Cyfluthrin III	Linear, 1/x	0.9917	0.005–0.2	163.0 → 127.0	5	226.1 → 199.0	10
							226.1 → 206.1	10
18	Cyfluthrin IV	Linear, 1/x	0.9870	0.005–0.2	163.0 → 127.0	10	226.1 → 199.0	10
							226.1 → 206.1	10
19	Cyhalothrin (*lambda*)	Linear, 1/x	0.9983	0.00313–0.125	181.1 → 152.0	25	197.0 → 161.1	10
							197.0 → 141.1	10

No.	Analyte	Regression fit/ weight	R^2	Cal. range (mg/kg)	Quant	CE (V)	Qual	CE (V)
20	Cypermethrin I (*Zeta*)	Linear, 1/x	0.9957	0.0125–0.5	163.0 → 127.0	5	165.0 → 127.0	5
							181.0 → 127.0	30
							209.0 → 116.0	15
21	Cypermethrin II	Linear, 1/x	0.9914	0.0125–0.5	163.0 → 127.0	5	165.0 → 127.0	5
							181.0 → 127.0	30
							209.0 → 116.0	15
22	Cypermethrin IV	Linear, 1/x	0.9959	0.0125–0.5	163.0 → 127.0	5	165.0 → 127.0	5
							181.0 → 127.0	30
							209.0 → 116.0	15
23	DDD-*o,p′*	Linear, 1/x	0.9989	0.001–0.05	235.0 → 165.2	20	235.0 → 200.2	10
							237.0 → 165.2	20
24	DDD-*p,p′*	Linear, 1/x	0.9993	0.001-0.05	234.9 → 165.1	20	234.9 → 199.1	15
25	DDE-*o,p′*	Linear, 1/x	0.9879	0.001-0.05	246.0 → 176.2	30	248.0 → 176.2	30
							317.8 → 248.0	15
26	DDE-*p,p′*	Linear, 1/x	0.9986	0.001-0.05	246.1 → 176.2	30	315.8 → 246.0	15
							317.8 → 246.0	15
27	DDT-*o,p′*	Linear, 1/x	0.9989	0.001-0.05	235.0 → 165.2	20	235.0 → 199.1	15
							237.0 → 165.2	20
28	DDT-*p,p′*	Linear, 1/x	0.9987	0.001-0.05	235.0 → 165.2	20	235.0 → 199.2	15
							237.0 → 165.2	20
29	Deltamethrin	Linear, 1/x	0.9905	0.00375-0.15	250.7 → 172.0	15	252.9 → 93.0	25
30	Diazinon	Linear, 1/x	0.9995	0.001-0.05	137.1 → 84.0	10	137.1 → 54.0	20
							199.1 → 93.0	15
31	Dichlorvos	Linear, 1/x	0.9993	0.001-0.05	185.0 → 93.0	5	108.9 → 79.0	15
32	Dieldrin	Linear, 1/x	0.9949	0.0005-0.02	262.9 → 193.0	35	262.9 → 191.0	35
							277.0 → 241.0	5
33	Dimethoate	Linear, 1/x	0.9992	0.001-0.05	86.9 → 46.0	15	86.9 → 86.0	5
							92.9 → 63.0	10
34	Disulfoton	Linear, 1/x	0.9996	0.001-0.05	88.0 → 60.0	5	142.0 → 109.0	5
							153.0 → 96.9	10
35	DMF	Linear, 1/x	0.9927	0.001-0.05	120.0 → 77.0	25	149.0 → 120.0	15
							149.0 → 106.0	15
							120→77	25
36	Endosulfan *alpha*	Linear, 1/x	0.9979	0.001-0.05	241.0 → 206.0	15	241.0 → 136.0	40
							207.0 → 172.0	15
							239.0 → 204.0	15
							339.0 → 267.0	2
37	Endosulfan *beta*	Linear, 1/x	0.9980	0.001-0.05	207.0 → 172.0	15	239.0 → 204.0	15
							241.0 → 136.0	15
							241.0 → 206.0	15
							339.0 → 267.0	2
38	Endosulfan sulfate	Linear, 1/x	0.9967	0.001-0.05	271.9 → 237.0	15	273.8 → 236.9	15
							273.8 → 238.9	15
39	Endrin	Linear, 1/x	0.9848	0.0005-0.02	260.8 → 191.1	30	262.7 → 193.1	30
							278.8 → 242.8	7
							280.8 → 244.8	7

No.	Analyte	Regression fit/ weight	R^2	Cal. range (mg/kg)	Quant	CE (V)	Qual	CE (V)
40	Ethion	Linear, 1/x	0.9982	0.001-0.05	152.9 → 96.9	10	124.9 → 96.9	5
							230.9 → 175.0	10
41	Fenitrothion	Linear, 1/x	0.9982	0.001-0.05	125.1 → 47.0	15	125.1 → 79.0	5
							277.0 → 260.1	5
42	Fenpropathrin	Linear, 1/x	0.9986	0.0125-0.5	181.1 → 152.1	25	125.0 → 55.1	10
							207.9 → 181.0	5
43	Fenvalerate I	Linear, 1/x	0.9953	0.005-0.2	167.0 → 125.1	5	181.0 → 152.1	20
							208.9 → 141.1	15
44	Fenvalerate II	Linear, 1/x	0.9988	0.005-0.2	167.0 → 125.1	5	181.0 → 152.1	20
							208.9 → 141.1	15
45	Flumetralin	Linear, 1/x	0.9979	0.001-0.05	143.0 → 107.1	20	143.0 → 117.0	20
							157.0 → 109.1	25
46	Heptachlor	Linear, 1/x	0.9971	0.0005-0.02	271.7 → 236.9	15	273.7 → 236.9	15
							273.7 → 238.9	15
47	Heptachlor epoxido	Linear, 1/x	0.9969	0.0005-0.02	352.8 → 262.9	10	354.8 → 264.9	15
							262.9 → 193.0	35
48	Hexachlorobenzene	Linear, 1/x	0.9852	0.001-0.04	283.8 → 213.9	30	283.8 → 248.8	15
49	Methidathion	Linear, 1/x	0.9989	0.0025-0.1	144.9 → 85.0	5	144.9 → 58.1	15
							85.0 → 58.0	5
50	Methoxychlor, *p,p′*-	Linear, 1/x	0.9973	0.0005-0.02	227.0 → 169.1	25	227.0 → 212.1	15
							227.0 → 141.1	40
51	Mevinphos	Linear, 1/x	0.9996	0.00625-0.25	127.0 → 109.0	10	192.0 → 127.0	10
52	Mirex	Linear, 1/x	0.9947	0.0005-0.02	271.8 → 236.8	15	273.8 → 236.8	15
							273.8 → 238.8	15
53	PCB #101	Linear, 1/x	0.9976	0.001-0.05	325.9 → 255.9	30	184.0 → 149.0	20
							327.9 → 292.9	15
54	PCB #138	Linear, 1/x	0.9960	0.001-0.05	359.9 → 289.9	30	218.0 → 183.0	20
							361.9 → 326.8	15
55	PCB #153	Linear, 1/x	0.9944	0.001-0.05	359.9 → 289.9	25	324.8 → 289.8	10
							361.9 → 326.8	15
56	PCB #180	Linear, 1/x	0.9906	0.001-0.05	393.8 → 323.8	30	251.9 → 181.9	30
							323.8 → 288.8	25
57	PCB #28	Linear, 1/x	0.9960	0.001-0.05	256.0 → 186.0	25	186.0 → 151.0	25
							258.0 → 186.0	25
58	PCB #52	Linear, 1/x	0.9973	0.001-0.05	289.9 → 219.9	25	184.0 → 149.0	15
							222.0 → 187.0	25
59	Pirimiphos-methyl	Linear, 1/x	0.9994	0.00625-0.25	290.0 → 125.0	20	232.9 → 125.0	5
							232.9 → 151.0	5
60	Propoxur	Linear, 1/x	0.9945	0.00625-0.25	110.0 → 63.0	25	110.0 → 64.0	15
							152.0 → 110.0	10

Real-world sample analysis, quantitative method

We purchased 14 brands of UHT bovine milk at local groceries in the middle of the year, and we purchased the same brands again at the end of the year to see if there was a difference between the production batches. We analyzed a total of 28 samples with our proposed method, verifying the presence of chlorpyrifos in four samples and cypermethrin in one sample, all below the LOQ but above the LOD.

Samples detected with chlorpyrifos, the concentrations were 0.0022, 0.003, 0.0033, and 0.0026 mg/kg in which the LOD was 0.002 mg/kg and the LOQ was 0.01 mg/kg for this compound. For cypermethrin the LOQ is 0.1 and the LOD is 0.0290 mg/kg. The concentration detected in the sample was 0.0370 mg/kg.

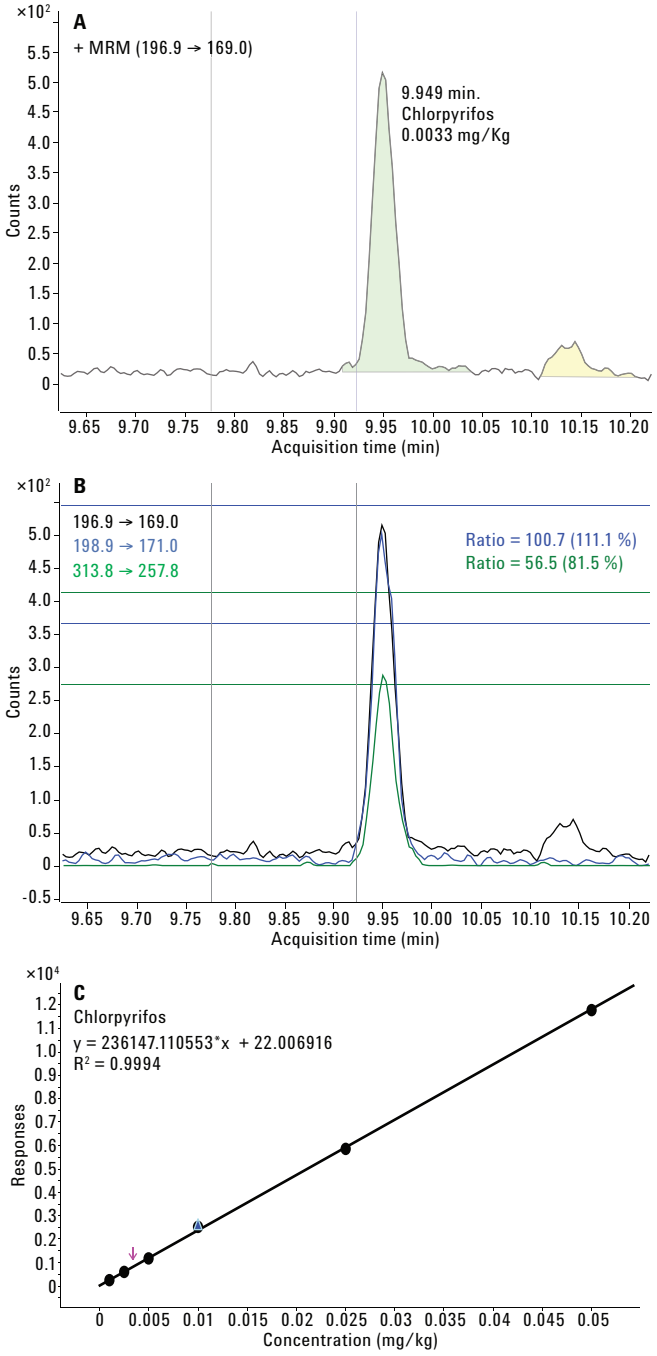

Figure 2. A) Quantifier ion of chlorpyrifos detected in the milk sample purchased at São Paulo supermarket. B) Overlay of qualifier and quantifier ions. C) Calibration curve for chlorpyrifos 0.001–0.05 mg/kg.

Conclusions

In this study, we developed a quantitative method to detect 60 pesticides and metabolites in bovine milk with good recovery and detection limits. The sample preparation was simple and fast, and the detection of the compounds using MRM proved to be much better than using an electron capture detector. With this method, we were able to detect very low concentrations, enabling us to verify traces of pesticides even in milk that had passed through processes such as pasteurization and homogenization. Although the quantities we found in our samples were low, we believe it is important to continue monitoring pesticide residues due to the large consumption of this product, mainly by infants, whose small size makes them more vulnerable to toxicity than adults.

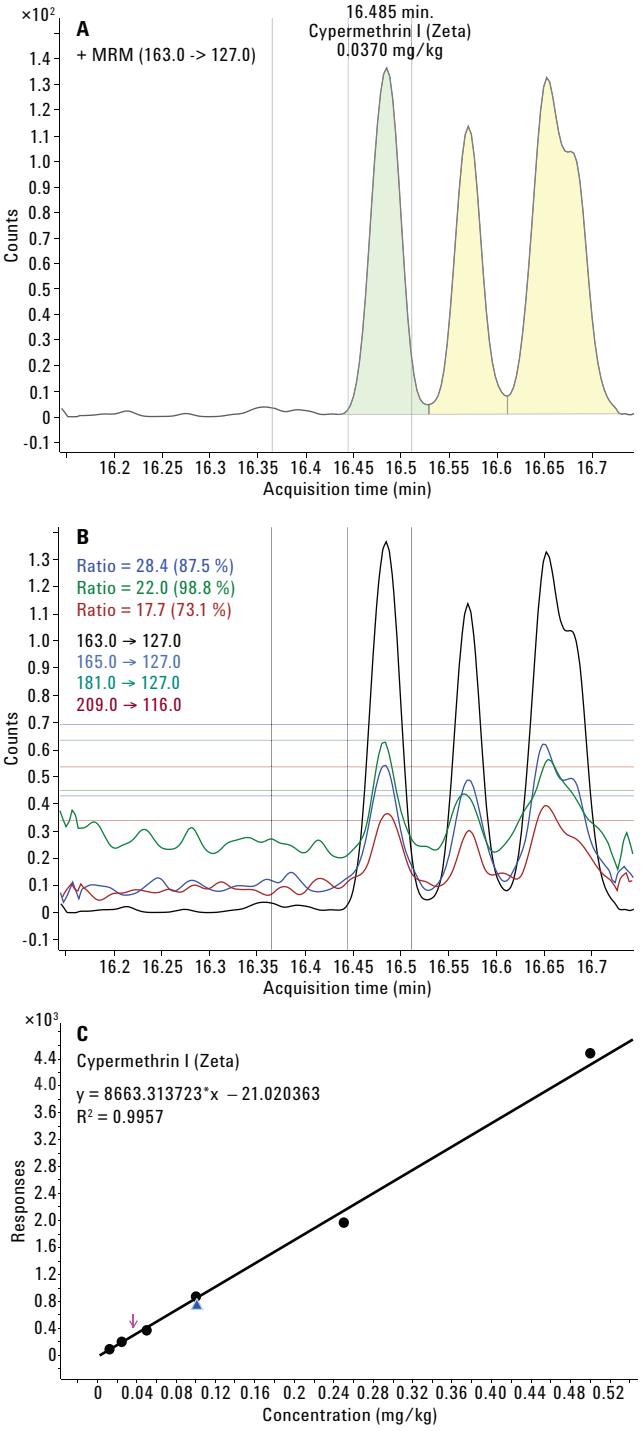

Figure 3. A) Quantifier ion of cypermethrin detected in the milk sample purchased at São Paulo supermarket. B) Overlay of qualifiers and quantifiers ions. C) Calibration curve for cypermethrin 0.0125–0.5 mg/kg.

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