Determination of 66 pesticide residues in livestock products using QuEChERS and GC–MS/MS

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Abstract Determinations of 66 pesticide residues in different matrices including beef, pork, chicken, eggs, and milk were conducted using GC–MS/MS combined with the quick easy cheap effective rugged safe (QuEChERS) method for sample extraction. A high linearity was achieved in the concentration range from 2.5 to 1000 μg/L ($R^2 \geq 0.99$), and the limit of quantification for multi-class pesticides ranged from 0.74 to 23.1 μg/kg. The recovery ranged from 70.0 to 120%, while the reproducibility of the measurements was between 0.23 and 19.9%. Monitoring was conducted for livestock products purchased from local markets. Chlorpyrifos and fenitrothion in beef and chlorpyrifos in pork were detected below the maximum residue limits for the respective samples. No detectable residues were found in the other samples. Due to its high efficiency, reproducibility, and simple analytical operation, the proposed method can be applied to the regular monitoring of multi-residue pesticides in livestock products.

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Introduction

The use of pesticides in modern agriculture has played a major role in boosting agricultural productivity; however, their misuse is a growing problem. Such misuse, including the application of pesticides to livestock and to improve the farm environment, can lead to the transfer of pesticide residues to livestock products (LeDoux, 2011). As such, pesticides are ubiquitous in the environment and are commonly found in livestock products, leading to their incorporation into the food chain. For example, in 2017 in Korea, the metabolites of fipronil, a pesticide used to control mites, were found to have contaminated chickens and eggs, resulting in the death of a cow that consumed contaminated rice straw feed (Ko et al., 2015; Rahman et al., 2016). The pathways by which livestock are exposed to pesticides include skin absorption, inhalation, and ingestion. The absorbed substances can then be metabolized or accumulate within the body and subsequently serve as an interim host for consumption by other animals (Covaci et al., 2004; Pagliuca et al., 2005). Due to such issues, the appropriate management of pesticide residues is crucial. Many countries therefore operate inspection programs to manage the pesticide residues present in livestock products, with examples including the National Residue Survey of the Australian Ministry of Agriculture and Fisheries, the National Chemical Residues Programme of the New Zealand Food Safety Agency, the National Chemical Residue Monitoring Program of the Canadian Food Inspection Agency, and the National Residue Program of the US Department of Agriculture (USDA, 2019).

In addition, Korea has a pesticide monitoring and management system through the National Residue Program for domestic and imported products. Since the maximum residue limits (MRLs) were established for 16 pesticides in livestock products in 1995, new standard limits have been continuously added by 2019 to become 99 pesticides (MFDS, 2019).

Currently, the majority of organochlorine pesticides are banned, but they are still found in the environment (Surma et al., 2014). For example, aldrin and dieldrin are known as persistent organic pollutants, as categorized by the UN Environment Programme. Although organophosphorus pesticides are degradable, they tend to be used in large quantities, and so continuous monitoring is required, and method development based on the use of mass spectrometry (MS) is necessary for the determination of low concentration multi-residue pesticides in livestock products. Indeed, the development and verification of analytical methods for pesticide residues in various foodstuffs are essential to ensure food safety. Such methods involve the monitoring of pesticide residues in livestock products according to changes in the pesticide residual acceptance criteria for different livestock products (Oh et al., 2009). Continued improvements to analytical methods are also required as the number of pesticides increases and the MRLs decrease. To date, pesticide residues have typically been analyzed by multi-component gas chromatography (GC) (Molina-Ruiz et al., 2015; Yang et al., 2011) and liquid chromatography (LC) (da Costa Morais et al., 2018; Stachniuk and Fornal, 2016), with various MS techniques also enabling the simultaneous analysis of hundreds of pesticides (Facco et al., 2015; He et al., 2015; Huang et al., 2010; Hunter et al., 2010; Samadi et al., 2012; Zhang et al., 2013). Although liquid–liquid extraction and solid-phase extraction are the most commonly used processes in terms of sample preparation for pesticide analysis, these processes are time-consuming, and the high volumes of solvent required can be detrimental to the environment (Bidari et al., 2011; Cho et al., 2008). Thus, the quick, easy, cheap, effective, rugged, and safe (QuEChERS) method is a popular alternative for the pre-treatment of pesticide analytical samples and veterinary drugs (Anastassiades et al., 2003; Qin et al., 2016; Xu et al., 2019). We therefore consider that the QuEChERS method could be applied to the analysis of pesticides in livestock products, especially for different matrices, such as meat, eggs, and milk. Several studies have been conducted to analyze pesticides in livestock products (Hercegová et al., 2007; Juhler, 1997; Rimkus et al., 1996). However, there are still complex steps and difficulties in extracting the fat compartment. In this study, we investigated methods of simultaneous analysis of multi-component pesticides in livestock products that contain a large amount of fat and a high level of interference such as proteins. Thus, we herein report the simultaneous analysis of 66 pesticides, including 24 insecticides, 15 fungicides, and 27 acaricides, in livestock products through the development of a combined QuEChERS and GC–MS/MS method to achieve simple and effective quantitation within the MRL criteria.

Materials and methods

Chemicals and reagents

Standards of the 66 pesticides were purchased from AccuStandard (New Haven, CT, USA), Chem Service (West Chester, PA, USA), Dr. Ehrenstorfer (Augsburg, Germany), Sigma-Aldrich (St. Louise, MO, USA), Toronto Research Chemicals (North York, ON, Canada), and Wako Pure Chemical Industries (Osaka, Japan). Acetonitrile, hexane, and acetone were purchased from Burdick & Jackson (Muskegon, MI, USA). All reagents were either of analytical or HPLC grade. Standard solutions were prepared by dilution of the stock solutions with acetone, and stored in amber bottles at 4 °C. Ultrapure water was obtained from a Milli-Q water purification system (Millipore, Bedford, MA, USA; resistivity $\geq$ 18.2 MΩ cm at 25 °C). A HyperSep^{TM} florisil solid phase extraction (SPE) cartridge (6 mL, 1 g, ThermoFisher Scientific, Waltham, MA, USA) was used for sample purification.

GC–MS/MS analysis

GC–MS/MS (TSQ EVO 8000, Thermo Scientific, Waltham, MA, USA) was used for analysis of the pesticides. Chromatographic separation was carried out using an HP-5MS capillary column (30 m × 0.25 mm ID, 0.25 μm film thickness). The GC oven temperature was programmed as follows: initial temperature of 70 °C, hold at 70 °C for 2 min, increase the temperature to 300 °C at a rate of 20 °C/min, hold at 300 °C for 8 min. The injection port temperature was set at 150 °C, and helium was used as the carrier gas at a flow rate of 1.0 mL/min. Splitless injection was used for trace analysis of the residual pesticides. For the MS measurements, the ion source and interface temperatures were 300 and 280 °C, respectively, and the electron impact voltage was 70 eV. MS was performed by measuring the retention time of the total ion chromatogram obtained in full scan mode (*m/z* 50–500) then selecting the retention times, precursor ions, and product ions of the 66 pesticides (Table 1). To increase the selectivity, two product ions were selected. Collision energy values were obtained and multiple reaction monitoring conditions were set.

Table 1 Optimum conditions for multiple reaction monitoring of GC–MS/MS analysis

Pesticide	Retention time (min)	Precursor ion (*m/z*)	Product ion (*m/z*)	Collision energy (eV)
Dichlorvos	6.70	109/185/185	79/93/109	6/12/16
Methacrifos	8.45	125/208/180	79/93/165	8/14/6
Diphenyl0amine	9.23	168/169/167	167/168/166	14/12/18
Phorate	9.65	121/231/260	65/129/75	10/22/7
Dimethoate	9.85	87/93/125	86/63/79	6/8/8
BHC-gamma	10.09	181/183/217	145/147/181	14/12/8
Terbufos	10.11	153/231/231	97/129/175	10/22/12
Quintozene	10.18	142/212/237	107/177/119	24/12/20
Diazinon	10.19	137/179/304	84/137/179	12/16/8
Disulfoton	10.29	88/153/142	60/97/81	6/10/12
Etrimfos	10.36	181/292/292	153/181/153	8/6/18
Primicarb	10.47	238/166/166	166/86/71	8/14/24
Pentachloraniline	10.60	263/265/230	192/194/195	18/18/10
Chlorpyrifos-methyl	10.74	125/286/286	79/93/271	6/20/12
Vinclozolin	10.72	212/200/214	172/147/174	12/14/22
Heptachlor	10.87	272/270/235	237/235/141	12/12/24
Primiphos methyl	10.99	233/290/276	151/125/244	8/20/8
Fenitrothion	11.00	277/277/260	260/109/125	6/16/12
Pentachlorothioanisole	11.10	296/244/294	263/174/261	12/28/12
Fenthion	11.19	278/245/279	156/97/81	18/12/16
Chlorpyrifos	11.21	197/286/314	169/258/258	12/8/12
Aldrin	11.23	257/261/263	222/191/193	12/30/30
Triadimefon	11.25	208/181/208	111/127/127	20/6/14
Penconazole	11.58	159/248/186	123/206/115	18/12/30
Isofenphos	11.61	213/255/255	121/121/185	14/22/10
Chlorfenvinphos	11.62	267/323/295	159/267/267	14/12/8
Mecarbam	11.63	159/160/131	131/132/86	6/8/12
Oxychlordane	11.64	149/115/115	85/51/87	8/22/10
Triadimenol	11.66	168/128/128	70/65/100	8/18/12
Phenthoate	11.66	274/246/125	121/121/79	10/6/8
Heptachlor epoxide	11.67	217/217/353	147/182/263	28/18/12
Methidathion	11.82	145/85/93	85/58/63	6/6/8
Chinomethionat	11.85	234/206/116	206/148/89	8/12/12
Chlordane-trans	11.86	375/373/371	266/266/264	18/20/20
Endosulfan alpha	11.99	241/195/243	206/159/208	10/6/10
Chlordane-cis	12.01	264/373/264	194/264/229	34/18/22
Profenfos	12.10	139/337/339	97/267/269	6/12/12
p,p′-DDE	12.15	246/248/316	176/176/246	28/28/18
Myclobutanil	12.20	179/150/152	125/123/125	14/16/8
Kresoxim methyl	12.21	116/206/206	89/116/131	14/6/10
Flusilazole	12.22	233/206/206	165/151/137	16/14/18
Dieldrin	12.24	261/263/271	191/193/241	30/30/8
Endrin	12.46	261/245/263	191/173/193	28/24/28
Fensulfothion	12.49	292/293/140	156/97/81	15/20/25
Endosulfan beta	12.54	241/195/195	206/159/125	12/8/22
p,p′-DDD	12.55	235/200/199	165/165/163	22/10/30
Ethion	12.57	125/153/231	97/97/129	6/10/22
o,p-DDT	12.65	235/237/235	165/165/199	22/22/12

Table 1 continued

Pesticide	Retention time (min)	Precursor ion (*m/z*)	Product ion (*m/z*)	Collision energy (eV)
Trizaofos	12.69	161/161/257	134/106/162	8/12/6
Edifenphos	12.87	173/201/201	109/109/173	8/14/6
Propiconazole	12.90	173/259/259	145/173/69	4/14/10
Endosulfan sulfate	12.94	272/195/195	237/159/125	12/8/22
p,p′-DDT	12.94	235/165/199	165/164/163	20/24/28
Propagite	13.03	135/201/173	107/81/107	12/8/22
Bifenthrin	13.32	181/166/182	165/165/166	24/14/24
Phosmet	13.38	160/160/133	77/133/77	22/10/12
Fenpropathrin	13.41	181/265/125	152/210/97	22/8/6
keto Endrin	13.41	243/317/317	173/281/245	24/8/14
Phosalone	13.72	182/182/367	111/75/182	14/28/6
Pyriproxyfen	13.72	136/136/226	79/96/186	20/10/12
Fenarimol	14.00	139/219/251	111/107/139	14/10/12
Permethrin	14.34	183/183/163	168/153/91	10/10/12
Prochloraz	14.50	180/310/308	138/70/70	10/12/12
Fenbuconazole	14.70	129/198/125	102/129/89	14/8/14
Cypermethrin	14.95	127/181/163	91/152/91	8/22/12
Fenvalerate	15.70	167/125/225	125/89/119	8/18/16

Sample preparation

The homogenized sample (10 g) was transferred to a shaking bottle, a solution of acetonitrile containing 1% formic acid (50 mL) was added, and the resulting mixture was shaken for 30 min. After this time, anhydrous magnesium sulfate (4 g) and sodium chloride (1 g, to increase the ionic strength and distribution efficiency) were added, and the mixture was shaken for 10 min prior to centrifugation for 10 min at 4000 rpm. The supernatant (25 mL) was then added to acetone containing 2% diethylene glycol (0.2 mL) and the solvent was evaporated to dryness. The resulting extract was redissolved in a mixture of acetone/hexane (2:8, v/v, 4 mL), which was subsequently loaded onto an SPE-florisil cartridge that was activated with hexane (5 mL) and acetone/hexane (2:8, v/v, 5 mL) for sample purification. It should be noted that florisil cartridges are the most widely used adsorbents for pigments, maintenance, and removal, and are often used to remove the fats and residues present in livestock products (Chae et al., 2013). The extract was then filtered through the cartridge with the addition of acetonitrile/hexane (2:8, v/v, 5 mL). The obtained eluent was concentrated to dryness under a flow of nitrogen gas, and then redissolved in acetonitrile/hexane (2:8, v/v, 1 mL) for GC–MS/MS analysis.

Method validation

To verify the applicability of the developed method for the target pesticides, representative samples of beef, pork, chicken, eggs, and milk were used to determine the recovery rate. Five replicates were prepared by adding the standard solution mixture to each of the five representative food samples at three concentrations, 5, 10, and 100 µg/kg. Validation was determined by measurement of the linearity, limit of detection (LOD), limit of quantification (LOQ), recovery, and reproducibility, according to the standard procedure for the preparation of test methods, the Codex Alimentarius Guideline, CAC/GL 40 (2003). The method selectivity was confirmed using the total ion peak areas of the pesticide standards in the blank solution and in each matrix. The linearity was calculated using the correlation coefficient (R^2) of the calibration curves obtained using pesticide concentrations of 10, 20, 50, 100, 500, and 1000 µg/kg. The LOD and LOQ values were determined as 3 and 10 times the signal-to-noise ratio (S/N), respectively. The accuracy (recovery measurement) was calculated at three different pesticide concentrations (5, 10, and 100 µg/kg) for the five products (beef, pork, chicken, eggs, and milk) as the representative matrices. The precision was assessed using the relative standard deviation (RSD) of the recovery.

Results and discussion

Verification of the GC–MS/MS conditions

The GC–MS/MS conditions for determination of the pesticide residues present in the various matrices were optimized using an HP5MS separation column. The total ion chromatogram of the 66 pesticides is shown in Fig. 1, where the concentrations of the standard pesticides in acetone were 100 μg/mL, and the various peaks were observed between 6 and 16 min. The peak numbers and corresponding retention times are presented in Table 1, along with the precursor ions (m/z), product ions (m/z), and collision energies of the quantification and confirmatory transitions for the 66 pesticides.

Specificity, LOD, and LOQ

To verify the specificity of the developed technique, the retention times and selected ions were confirmed. In terms of the pesticide retention times, only the selected precursor and product ions were detected in the samples to which the standard, blank, and mixed standard solutions were added. The lowest LODs were obtained as 0.4 μg/kg for beef and pork, and 0.2 μg/kg for chicken, eggs, and milk. The lowest LOQ was obtained as 0.74 μg/kg for the bifenthrin content in milk, and the highest LOQ was obtained as 23.1 μg/kg for the heptachlor epoxide content in pork

(Table 2). Manav et al. (2019) reported LODs for permethrin in milk and endosulfan sulfate in dairy products of 0.40 and 0.48 μg/kg, respectively using GC–MS and the QuEChERS method, which are similar to those determined in this study. In contrast, some studies have reported relatively high LODs (5.2–14 μg/kg) and LOQs (1.5–44 μg/kg) (Hamadamin and Hassan, 2020) and relatively low LOQs (less than 5 ng/g) (Sapozhnikova, 2018) compared with this study. As demonstrated by several studies, multiclass pesticide analysis using the QuEChERS method and MS is a simple, excellent approach, with low LODs and LOQs and high recoveries.

Linearity

The matrix-matched calibration curve was used to reduce the matrix effect of the method. During substance analysis, the intensity of the instrumental response should show a linearity that is quantitatively proportional to the amount of residue in the sample. This linearity can be confirmed using an internal standard material or by the addition of a standard to the matrix. In this study, the linearity of the calibration curve obtained by GC–MS/MS was observed at concentrations of 2.5, 10, 50, 100, 500, and 1000 μg/L with 5 replicates. Chromatograms of the pesticides in each time period contain the MS information of each ion; thus, a calibration curve can be produced using the MS intensity at each concentration. The correlation coefficients (R^2) for the
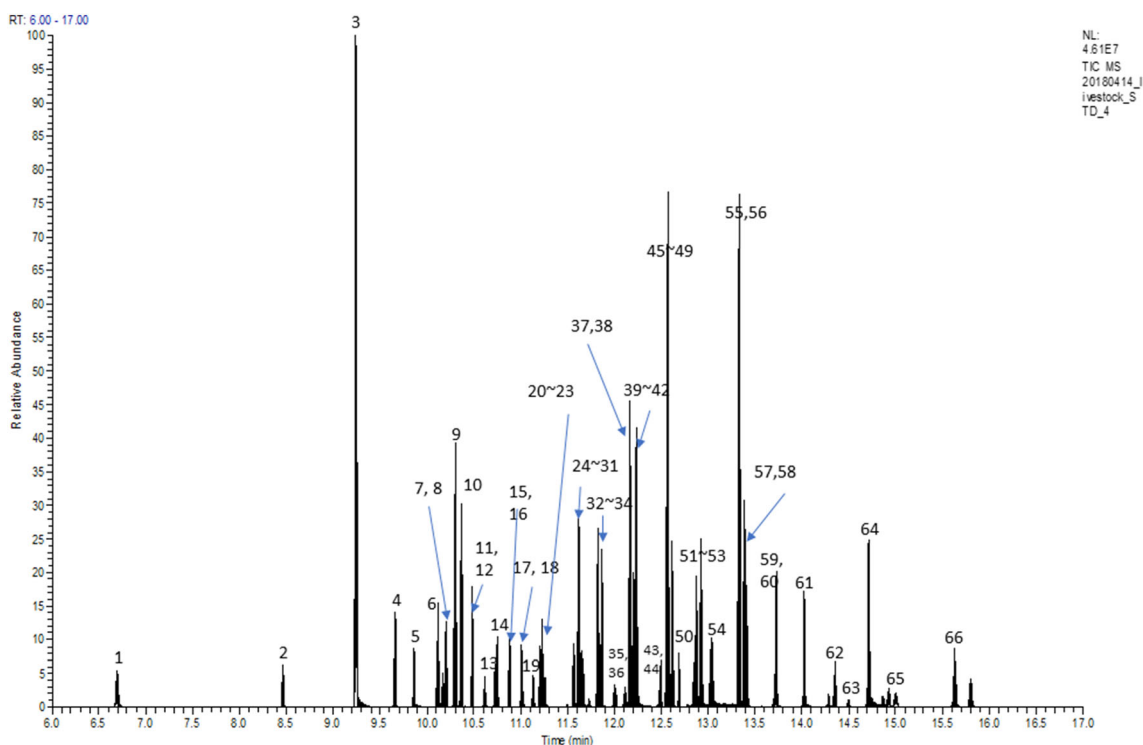
Fig. 1 Total ion chromatogram of 66 pesticides. The names of pesticides for the numbers indicated on the peaks are listed in Table 1

Table 2 Linearity, limit of detection (LOD) and limit of quantification (LOQ) in various matrices for 66 pesticides

Pesticide	Linearity (R^2)	LOD (μg/kg)					LOQ (μg/kg)				
		Beef	Pork	Chicken	Eggs	Milk	Beef	Pork	Chicken	Eggs	Milk
Aldrin	0.9986	1.91	2.31	1.04	0.79	1.63	6.30	7.61	3.43	2.62	5.39
BHC-gamma	0.9989	1.42	1.14	0.52	0.85	0.38	4.70	3.75	1.71	2.80	1.25
Bifenthrin	0.9999	0.35	0.78	0.37	0.43	0.22	1.16	2.58	1.23	1.41	0.74
Chinomethionat	0.9999	2.29	0.87	0.51	0.43	0.87	7.55	2.88	1.68	1.43	2.87
Chlordane-cis	0.9982	2.15	5.01	2.82	2.31	2.60	7.08	16.5	9.32	7.62	8.56
Chlordane-trans	0.9986	1.89	1.46	0.60	0.81	1.20	6.22	4.81	1.97	2.69	3.96
Chlorfenvinphos	0.9992	3.68	1.30	0.57	0.68	0.94	12.1	4.29	1.89	2.25	3.09
Chlorpyrifos	0.9996	2.99	2.44	0.80	0.81	0.66	9.88	8.05	2.64	2.69	2.16
Chlorpyrifos-methyl	0.9997	3.92	5.07	0.88	1.27	2.31	12.9	16.7	2.91	4.20	7.62
Cypermethrin	0.9968	1.01	2.18	1.10	0.78	1.89	3.33	7.20	3.64	2.58	6.24
p,p′-DDD	0.9999	0.87	0.67	0.23	0.48	0.40	2.85	2.20	0.75	1.60	1.33
p,p′-DDE	1.0000	0.94	1.08	0.64	0.61	0.89	3.09	3.55	2.13	2.02	2.94
o,p-DDT	0.9978	0.79	1.80	0.60	0.84	0.91	2.60	5.95	1.97	2.77	2.99
p,p′-DDT	0.9973	1.67	0.76	0.73	0.59	0.34	5.50	2.50	2.42	1.93	1.13
Diazinon	0.9998	0.56	1.51	5.57	0.42	1.08	1.85	4.97	18.4	1.38	3.55
Dichlorvos	0.9999	0.77	1.87	1.16	0.86	1.90	2.55	6.16	3.81	2.85	6.25
Dieldrin	0.9976	3.36	4.34	2.41	1.38	2.77	11.1	14.3	7.95	4.55	9.14
Dimethoate	0.9989	2.56	2.77	1.09	0.62	0.52	8.45	9.14	3.61	2.05	1.71
Diphenylamine	0.9999	0.96	0.36	0.29	0.30	0.33	3.15	1.20	0.96	1.00	1.10
Disulfoton	0.9998	0.49	0.85	0.60	0.35	0.68	1.63	2.81	1.98	1.15	2.25
Edifenphos	0.9996	0.73	1.33	0.69	0.65	0.52	2.40	4.39	2.29	2.15	1.71
Endosulfan alpha	0.9951	2.13	2.02	2.12	1.80	0.86	7.04	6.67	7.00	5.92	2.84
Endosulfan beta	0.9969	1.91	3.49	2.57	2.55	3.11	6.31	11.5	8.47	8.42	10.25
Endosulfan sulfate	0.9991	5.77	3.88	1.01	4.17	0.89	19.0	12.8	3.33	13.8	2.95
Endrin	0.9995	2.42	3.38	1.05	0.75	2.91	8.00	11.1	3.45	2.49	9.60
Ethion	0.9851	1.22	4.29	2.43	0.56	3.08	4.01	14.1	8.01	1.83	10.2
Etrimfos	0.9998	0.57	1.26	0.43	0.33	0.80	1.89	4.16	1.43	1.09	2.62
Fenarimol	0.9997	0.23	0.60	0.43	0.53	0.88	0.75	1.99	1.43	1.74	2.91
Fenbuconazole	0.9999	0.30	0.55	0.34	0.24	0.27	0.98	1.82	1.12	0.78	0.88
Fenitrothion	0.9998	2.27	1.42	0.69	1.31	0.37	7.50	4.69	2.28	4.33	1.22
Fenpropathrin	0.9999	2.91	1.02	0.96	0.63	0.76	9.62	3.37	3.17	2.08	2.52
Fensulfothion	0.9944	3.45	4.99	2.58	2.21	2.48	11.4	16.5	8.50	7.28	8.20
Fenthion	0.9989	1.39	1.23	0.73	0.56	1.02	4.59	4.07	2.41	1.86	3.38
Fenvalerate	0.9998	0.93	4.43	0.37	0.90	2.32	3.08	14.6	1.23	2.96	7.65
Flusilazole	0.9996	0.88	0.57	0.79	0.33	0.85	2.90	1.89	2.62	1.10	2.80
Heptachlor	0.9995	1.96	2.02	0.57	1.07	1.20	6.46	6.68	1.88	3.51	3.96
Heptachlor epoxide	0.9974	1.93	5.82	3.10	1.21	1.11	6.37	19.2	10.2	3.99	3.69
Isofenphos	0.9994	0.80	1.27	0.76	0.70	0.51	2.64	4.18	2.52	2.32	1.67
keto Endrin	0.9984	3.25	3.09	1.17	1.18	1.34	10.7	10.2	3.87	3.90	4.43
Kresoxim methyl	0.9997	1.20	0.87	0.38	0.69	0.59	3.95	2.86	1.26	2.28	1.94
Mecarbam	0.9988	2.25	3.44	4.34	0.71	1.78	7.42	11.4	14.3	2.35	5.89
Methacrifos	1.0000	0.96	2.53	1.16	0.96	1.34	3.17	8.35	3.81	3.15	4.43
Methidathion	0.9978	1.89	1.32	0.69	0.58	0.79	6.22	4.37	2.29	1.91	2.60
Myclobutanil	0.9998	1.10	0.68	0.65	0.46	1.02	3.63	2.23	2.14	1.53	3.35
Oxychlordane	0.9994	0.96	1.72	1.55	1.08	1.73	3.18	5.66	5.10	3.56	5.71
Penconazole	0.9999	0.77	2.53	0.66	0.76	1.42	2.53	8.36	2.17	2.50	4.69
Pentachloraniline	0.9996	0.72	1.16	1.03	0.67	1.64	2.37	3.83	3.41	2.21	5.43

Table 2 continued

Pesticide	Linearity (R^2)	LOD (µg/kg)					LOQ (µg/kg)				
		Beef	Pork	Chicken	Eggs	Milk	Beef	Pork	Chicken	Eggs	Milk
Pentachlorothioanisole	0.9989	3.12	2.57	0.84	1.65	1.66	10.3	8.48	2.78	5.45	5.49
Permethrin	0.9999	1.88	1.98	2.30	2.31	0.63	6.20	6.53	7.58	7.62	2.08
Phenthoate	0.9980	1.10	0.94	1.05	0.53	0.74	3.64	3.11	3.46	1.74	2.46
Phorate	0.9998	0.86	0.46	0.39	0.44	0.95	2.83	1.53	1.28	1.46	3.14
Phosalone	0.9998	1.10	0.85	1.55	0.56	1.19	3.61	2.81	5.10	1.83	3.92
Phosmet	0.9999	3.48	1.62	0.70	0.45	0.49	11.5	5.36	2.29	1.47	1.61
Primicarb	0.9985	0.37	0.65	0.46	0.19	0.41	1.23	2.13	1.52	0.62	1.35
Primiphos methyl	0.9988	4.61	1.66	1.99	0.87	1.15	15.2	5.48	6.56	2.85	3.78
Prochloraz	0.9992	1.17	1.77	1.30	3.03	0.48	3.87	5.83	4.28	10.01	1.59
Profenphos	0.9926	0.68	2.20	2.68	1.38	0.62	2.25	7.26	8.8	4.57	2.03
Propagite	0.9972	2.14	3.20	3.21	2.33	4.91	7.05	10.6	10.6	7.70	16.2
Propiconazole	0.9959	3.89	7.01	1.78	2.19	0.79	12.9	23.1	5.87	7.21	2.60
Pyriproxyfen	0.9993	0.82	1.42	2.94	0.88	0.95	2.70	4.69	9.70	2.89	3.13
Quintozene	0.9979	3.25	3.87	2.16	1.02	1.08	10.7	12.8	7.11	3.36	3.57
Terbufos	0.9995	2.87	1.73	4.82	5.65	3.24	9.4	5.70	15.9	18.7	10.7
Triadimefon	0.9976	0.68	1.95	1.28	0.58	0.93	2.26	6.43	4.24	1.92	3.05
Triadimenol	0.9959	3.34	2.13	2.46	2.37	2.45	11.0	7.03	8.12	7.81	8.09
Trizaofos	0.9982	1.54	3.52	0.69	0.55	1.11	5.07	11.6	2.29	1.83	3.66
Vinclozolin	0.9982	0.91	1.26	0.95	1.07	1.19	3.00	4.15	3.14	3.54	3.94

66 substances reached 0.99–1.0 (Table 2), indicating a satisfactory agreement with the level ($R^2 > 0.99$) recommended by the International Commission on Food Standards (CAC/GL 40, 2003). These results indicate that the proposed method is suitable for the calculation of residual amounts of the examined pesticides in the samples of interest and over the concentration range employed herein.

Accuracy and precision

To verify the efficiency and reliability of the proposed analytical method, the recovery was used to determine the accuracy, while the RSD was used to obtain the precision. The standard pesticide solutions were added to each matrix at concentrations of 5, 10, and 100 µg/kg for five replicates to determine recovery and RSD. A high-concentration standard (100 µg/kg) was included to validate the method for pesticides with high Korean MRLs in livestock products such as endrin (1.0 mg/kg for poultry meat, 0.1 mg/kg for pig muscle), DDT (0.3 mg/kg for poultry meat, 0.1 mg/kg for eggs), chlorfenvinphos (0.2 mg/kg for cattle meat), and permethrin (0.1 mg/kg for milk). The results presented in Table 3 indicate that the pesticides showed similar tendencies for all samples, and the various pesticides were successfully recovered in all cases, likely due to the inclusion of 1% formic acid in the acetonitrile extraction solvent, i.e., the recovery was improved by the auxiliary

role of the acid (AOAC, 2010; Codex, 2003; USFDA, 1999). In addition, a previous study showed that the recovery increased upon increasing the concentration from 5 to 10 µg/kg and then to 100 µg/kg due to a smaller matrix effect (Mastovska et al., 2005); however, no significant differences were observed herein when different concentrations were employed. The recoveries ranged from 70.1 to 118% for beef, 70.1 to 116% for pork, 70.0 to 120% for chicken, 70.1 to 120% for eggs, and 70.1 to 105% for milk, giving an overall recovery range of 70.0–120%. Figure 2 shows the distribution of the average recovery ranges of the pesticides for each product. The main recovery distribution was located differently for each product. Of the tested pesticides, 88% had recoveries of 70–80% for beef and 35% had recoveries of 81–90% for pork. The highest recovery rates were 91–100% for chicken, 101–110% for eggs, and 111–120% for milk, but the distribution rates were not significantly different.

The method precision was then obtained by calculating the RSD of the pesticide recoveries from the beef, pork, chicken, egg, and milk samples. The RSD ranged from 1.56 to 19.7% for beef, 1.71 to 19.9% for pork, 0.57 to 19.9% for chicken, 0.23 to 19.8% for eggs, and 1.22 to 19.7% for milk (Table 3). These results confirm that for all samples, the RSD satisfied the CAC/GL 40 criteria of < 20% at concentrations of > 0.01 mg/kg and ≤ 0.1 mg/kg.

Table 3 Recovery and relative standard deviation (RSD) at three concentrations of pesticides in livestock products

Pesticide	Fortified Concentration (mg/kg)	Beef		Pork		Chicken		Eggs		Milk	
		Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
Aldrin	0.005	71.6	10.1	70.8	8.79	76.7	13.2	87.6	10.0	85.7	11.4
	0.01	72.3	3.73	70.9	6.57	85.5	6.65	85.6	16.3	95.5	8.05
	0.1	70.4	6.42	70.1	4.45	90.2	12.3	90.0	11.7	93.7	2.93
BHC-gamma	0.005	72.7	16.7	70.6	6.99	75.4	15.9	95.1	1.26	92.2	8.69
	0.01	72.0	3.90	70.5	6.30	77.8	9.09	85.0	11.0	88.7	4.31
	0.1	72.5	9.80	74.4	6.64	73.2	18.6	90.0	8.45	88.9	3.98
Bifenthrin	0.005	75.1	8.26	82.3	4.83	89.4	4.96	116	4.68	90.6	5.76
	0.01	79.9	5.88	76.2	6.57	90.0	3.90	111	13.1	86.1	3.81
	0.1	75.8	6.87	85.9	3.60	116	3.08	120	10.7	84.2	2.99
Chinomethionat	0.005	71.2	8.44	72.0	10.0	103	7.86	73.0	3.61	95.1	9.34
	0.01	75.8	4.85	70.1	9.41	105	6.90	71.1	6.43	95.3	3.67
	0.1	74.5	7.12	74.3	12.4	114	9.62	70.6	14.7	90.9	3.67
Chlordane-cis	0.005	102	9.12	77.8	15.1	81.1	17.2	110	12.7	100	11.7
	0.01	92.4	5.30	73.9	12.9	86.9	12.6	97.7	15.9	97.4	3.35
	0.1	71.4	6.16	74.3	17.1	105	7.18	77.1	19.5	94.7	5.90
Chlordane-trans	0.005	74.6	10.8	78.2	14.1	85.9	14.2	74.9	2.43	73.3	12.3
	0.01	72.5	5.31	77.3	12.1	89.2	9.88	71.5	11.4	76.9	12.2
	0.1	70.5	10.0	83.2	7.13	116	8.81	71.0	11.9	91.1	8.42
Chlorfenvinphos	0.005	76.6	12.7	83.4	6.44	85.3	9.43	78.4	13.7	92.9	7.21
	0.01	81.0	5.37	74.2	6.73	85.9	4.65	84.3	8.16	84.2	3.65
	0.1	70.6	8.56	86.8	3.78	85.4	8.56	87.5	13.3	95.9	3.10
Chlorpyrifos	0.005	73.4	10.8	86.5	9.52	86.7	7.38	116	6.27	95.2	9.80
	0.01	78.9	1.56	72.2	7.30	91.8	8.62	104	12.0	95.4	4.60
	0.1	74.7	19.1	81.5	2.76	103	5.07	111	10.9	97.2	3.34
Chlorpyrifos-methyl	0.005	81.4	12.8	95.3	6.84	81.9	13.2	91.7	15.2	81.9	10.6
	0.01	92.6	5.47	80.0	4.25	84.0	4.21	92.8	16.4	87.9	8.33
	0.1	75.0	9.02	97.8	2.79	86.7	14.7	99.1	8.36	95.8	1.81
Cypermethrin	0.005	88.6	3.04	104	8.01	86.9	5.25	109	10.4	89.7	4.64
	0.01	93.8	4.66	93.5	7.78	90.6	3.58	119	16.2	84.6	2.38
	0.1	77.9	7.29	101	3.91	109	4.99	120	9.76	92.2	5.20
p,p′-DDD	0.005	72.7	14.3	81.2	3.91	87.3	9.25	114	2.93	93.5	5.96
	0.01	71.4	5.03	74.7	7.19	89.2	8.52	114	13.4	89.1	3.77
	0.1	70.3	11.6	89.1	4.52	112	5.24	118	12.1	95.2	4.31
p,p′-DDE	0.005	70.5	8.81	71.8	8.35	88.9	6.90	108	0.44	89.6	4.63
	0.01	70.3	4.25	70.9	7.94	93.0	5.77	91.7	16.1	85.5	2.70
	0.1	70.2	6.96	71.1	13.9	118	3.81	94.9	13.0	72.6	3.73
o, p-DDT	0.005	113	11.3	74.1	3.75	85.5	5.17	82.4	9.18	80.4	7.57
	0.01	71.3	18.1	75.7	6.71	83.8	9.56	75.8	15.8	90.1	2.73
	0.1	70.2	16.3	77.1	7.66	103	1.55	74.9	8.90	79.2	3.72
p,p′-DDT	0.005	70.7	14.7	75.7	5.15	73.8	6.02	102	19.2	74.9	5.57
	0.01	75.9	8.64	78.6	6.60	71.3	3.25	106	4.92	70.1	5.01
	0.1	72.2	13.1	75.9	5.39	89.4	8.10	88.6	12.2	72.6	3.73
Diazinon	0.005	72.0	12.7	71.3	7.86	72.0	12.7	99.4	3.99	71.3	15.4
	0.01	76.6	2.41	70.6	8.41	76.6	2.41	88.2	10.8	73.4	5.54
	0.1	74.6	7.84	77.9	5.71	74.6	7.84	94.4	12.4	70.5	6.99

Table 3 continued

Pesticide	Fortified Concentration (mg/kg)	Beef		Pork		Chicken		Eggs		Milk	
		Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
Dichlorvos	0.005	103	13.1	76.5	19.8	73.9	3.04	77.5	11.9	73.5	13.1
	0.01	110	4.92	74.4	11.8	72.1	8.02	70.9	9.74	71.9	5.19
	0.1	113	5.22	77.7	14.5	70.2	3.38	71.5	19.6	70.6	7.90
Dieldrin	0.005	77.9	15.2	116	7.41	83.9	11.0	98.2	2.59	86.6	7.09
	0.01	72.4	8.69	70.9	10.8	87.6	10.6	81.7	8.80	88.1	3.72
	0.1	76.2	7.99	74.8	7.28	102	3.75	85.1	10.6	81.4	3.17
Dimethoate	0.005	79.5	15.0	87.4	8.86	90.3	7.16	91.5	15.2	76.8	8.85
	0.01	90.4	5.61	86.8	6.90	82.9	11.2	104	13.7	70.9	6.08
	0.1	81.7	11.3	104	1.86	116	5.65	96.8	8.09	82.4	3.54
Diphenylamine	0.005	113	11.5	70.5	17.7	107	13.1	84.3	3.41	80.9	11.8
	0.01	111	3.33	112	9.94	114	11.4	75.7	4.71	94.5	10.9
	0.1	88.7	6.54	97.8	11.0	107	5.25	72.4	6.48	93.8	9.91
Disulfoton	0.005	96.7	13.1	91.9	4.07	71.4	11.4	99.5	2.16	81.0	7.38
	0.01	102	8.19	105	13.5	79.9	5.16	89.9	11.7	78.9	4.22
	0.1	86.8	8.09	79.7	13.2	73.3	8.91	77.1	9.07	77.2	5.68
Edifenphos	0.005	73.0	15.3	84.3	8.68	75.1	4.58	77.1	9.02	75.5	6.40
	0.01	82.0	4.13	75.9	13.1	75.8	6.13	70.5	10.6	71.9	3.86
	0.1	74.9	12.4	99.6	10.3	97.9	5.57	79.6	15.3	71.3	5.40
Endosulfan alpha	0.005	70.9	15.8	77.2	18.5	91.6	9.83	102	3.44	97.8	10.5
	0.01	72.8	12.0	72.5	12.7	97.7	13.4	98.0	12.3	96.3	3.49
	0.1	71.7	14.6	75.5	14.9	107	9.28	71.0	8.24	94.3	2.34
Endosulfan beta	0.005	108	10.7	77.4	16.2	83.6	12.4	114	2.22	95.9	12.7
	0.01	71.2	19.7	70.6	5.92	90.4	12.4	95.2	15.8	83.4	6.16
	0.1	71.6	10.7	79.4	2.83	109	2.94	114	8.18	95.5	4.54
Endosulfan sulfate	0.005	74.4	12.3	84.1	6.82	71.7	4.12	73.8	8.69	99.9	10.9
	0.01	70.5	6.40	77.6	10.1	80.5	4.23	86.5	18.1	91.7	4.17
	0.1	70.6	12.2	87.8	8.92	114	6.35	84.9	9.86	92.1	2.88
Endrin	0.005	70.7	15.7	75.9	11.3	84.3	15.1	93.8	15.7	92.2	7.15
	0.01	77.0	8.13	70.8	5.34	86.7	6.96	86.5	18.1	79.9	5.68
	0.1	71.7	12.9	77.0	5.69	99.2	4.27	84.9	9.86	79.5	2.71
Ethion	0.005	89.8	11.7	74.3	19.9	76.2	10.6	115	0.23	92.9	11.5
	0.01	78.1	11.9	71.5	17.8	77.8	12.0	110	0.52	84.1	5.41
	0.1	90.0	3.44	91.2	19.1	99.3	4.18	115	6.29	96.2	2.07
Etrimfos	0.005	70.1	11.9	76.8	5.42	70.6	17.7	97.5	0.24	76.7	8.09
	0.01	73.2	3.05	77.4	5.79	70.5	2.28	83.5	9.61	76.7	6.27
	0.1	72.5	9.04	74.8	4.10	70.2	7.20	88.0	6.32	76.3	4.67
Fenarimol	0.005	75.6	10.8	85.4	7.38	80.6	14.2	111	11.9	93.4	4.09
	0.01	84.3	6.30	81.3	6.91	88.0	2.07	111	12.0	94.9	2.10
	0.1	71.6	7.77	89.4	5.12	102	8.56	119	10.0	96.3	3.28
Fenbuconazole	0.005	84.2	9.81	88.5	7.16	82.2	14.7	119	15.4	85.3	9.05
	0.01	90.2	6.05	86.2	6.99	82.0	2.72	119	9.62	80.2	2.77
	0.1	76.8	6.88	95.0	4.22	108	9.73	117	12.3	87.2	1.55
Fenitrothion	0.005	72.6	13.4	70.8	4.83	80.0	8.37	111	2.40	83.2	9.77
	0.01	80.5	4.89	80.1	5.49	87.3	9.80	95.1	8.32	86.0	4.91
	0.1	71.0	11.4	90.7	6.26	100	8.56	72.4	18.0	85.4	5.59

Table 3 continued

Pesticide	Fortified Concentration (mg/kg)	Beef		Pork		Chicken		Eggs		Milk	
		Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
Fenpropathrin	0.005	79.0	7.11	82.3	4.42	89.0	5.91	110	8.43	90.2	3.95
	0.01	83.8	4.76	79.4	7.48	88.9	7.12	113	11.2	88.4	3.41
	0.1	73.6	7.61	90.3	3.24	115	0.57	119	9.94	92.7	4.01
Fensulfothion	0.005	73.7	8.67	72.3	18.7	75.7	9.16	73.8	12.2	72.4	16.6
	0.01	71.3	11.7	71.3	7.77	82.8	10.7	78.5	5.63	75.9	11.5
	0.1	70.8	10.5	72.4	10.9	103	11.8	70.4	10.3	71.1	14.7
Fenthion	0.005	72.8	10.3	72.0	7.33	76.6	6.90	108	2.52	93.0	9.64
	0.01	72.6	4.02	71.1	4.74	76.6	9.12	87.4	12.1	83.6	4.05
	0.1	72.2	8.18	71.9	8.97	79.1	12.7	93.9	9.45	90.3	4.73
Fenvalerate	0.005	87.2	8.51	99.4	2.76	88.1	6.90	111	15.6	98.4	5.29
	0.01	89.9	5.29	91.9	7.08	87.6	5.19	107	14.5	91.8	2.92
	0.1	76.3	7.14	100	3.69	109	6.90	113	9.61	82.0	3.78
Flusilazole	0.005	76.3	11.0	74.6	8.31	87.1	10.6	114	6.34	91.0	6.69
	0.01	82.5	3.87	78.2	6.36	86.7	6.50	107	13.8	82.0	4.72
	0.1	70.2	9.68	80.3	4.51	116	6.50	113	11.9	89.0	1.92
Heptachlor	0.005	71.9	15.0	74.5	6.95	73.3	1.73	92.6	2.55	89.4	9.89
	0.01	72.1	3.70	75.5	7.26	77.9	8.80	80.7	10.4	83.6	9.75
	0.1	70.5	7.83	72.1	10.3	97.6	3.22	78.7	7.59	93.2	6.93
Heptachlor epoxide	0.005	73.5	16.3	75.5	15.4	80.0	12.0	85.3	1.95	95.0	12.3
	0.01	70.6	10.4	71.0	9.65	95.8	11.3	87.9	5.46	95.6	3.71
	0.1	72.0	6.90	79.3	3.61	102	8.02	101	7.50	94.6	1.22
Isofenphos	0.005	76.0	6.87	80.2	6.66	85.0	9.72	96.0	3.46	93.6	7.31
	0.01	77.1	4.21	72.6	7.13	83.9	6.18	87.6	11.0	89.8	4.43
	0.1	75.3	9.32	81.3	2.13	86.4	10.5	99.1	10.2	90.7	2.54
keto Endrin	0.005	97.6	17.0	70.2	9.77	78.7	11.5	107	5.14	89.7	7.45
	0.01	70.6	15.2	70.2	6.71	80.2	8.10	91.3	14.3	97.9	4.85
	0.1	71.3	10.9	71.8	14.4	109	2.07	97.2	11.3	95.4	3.43
Kresoxim methyl	0.005	71.1	9.98	81.1	6.46	82.4	15.2	118	4.51	90.9	6.34
	0.01	70.7	4.17	72.4	7.14	86.5	11.2	112	15.3	72.4	6.73
	0.1	70.8	7.64	72.7	11.4	106	9.76	113	15.7	87.8	5.70
Mecarbam	0.005	81.0	9.76	94.1	15.7	89.8	6.61	112	3.00	98.7	11.7
	0.01	76.0	2.82	82.5	19.9	85.3	14.8	110	2.88	93.0	6.21
	0.1	71.7	9.78	81.5	3.76	113	6.41	106	9.67	89.4	3.20
Methacrifos	0.005	110	12.0	70.4	17.9	81.0	9.76	81.9	2.93	70.2	12.0
	0.01	72.5	19.4	71.3	4.74	76.0	2.82	85.8	12.2	70.4	9.82
	0.1	72.5	19.1	76.5	8.05	71.7	9.78	84.7	5.89	73.2	11.1
Methidathion	0.005	71.8	10.0	71.1	10.8	105	8.20	70.1	12.4	94.4	6.69
	0.01	71.4	4.93	70.4	7.06	101	4.92	71.1	10.7	91.5	3.27
	0.1	75.7	7.83	71.8	7.90	120	9.98	71.5	13.7	88.0	2.56
Myclobutanil	0.005	75.3	9.05	77.1	9.11	83.0	18.2	117	15.8	86.8	7.09
	0.01	71.1	5.68	70.5	7.01	85.8	8.41	118	16.2	86.9	5.77
	0.1	71.2	7.40	77.6	8.19	112	8.03	115	13.4	92.3	4.62
Oxychlordane	0.005	72.3	11.6	73.8	8.78	93.5	9.65	102	6.83	92.5	11.6
	0.01	72.0	8.33	72.0	10.8	90.0	4.28	93.5	6.20	93.9	4.21
	0.1	72.3	9.81	75.5	5.06	102	10.4	105	10.5	91.2	3.77

Table 3 continued

Pesticide	Fortified Concentration (mg/kg)	Beef		Pork		Chicken		Eggs		Milk	
		Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
Penconazole	0.005	79.8	8.54	92.4	10.6	97.5	6.41	109	3.16	93.8	8.93
	0.01	81.4	7.29	82.5	8.07	91.7	8.28	101	10.5	95.4	3.09
	0.1	72.7	7.94	93.2	3.12	118	4.12	110	10.3	88.5	3.03
Pentachloraniline	0.005	71.3	9.68	75.9	4.57	82.6	13.7	84.0	0.33	89.1	11.5
	0.01	70.2	2.78	71.6	8.05	86.5	2.78	81.3	10.6	76.7	4.73
	0.1	71.6	5.47	80.1	3.16	87.8	11.7	83.9	9.23	84.7	11.7
Pentachlorothioanisole	0.005	70.1	19.2	72.1	3.15	85.2	2.55	90.8	9.53	82.4	5.68
	0.01	70.6	11.7	71.4	4.40	87.0	5.37	83.6	14.0	92.0	5.98
	0.1	71.9	12.9	78.1	4.55	97.5	17.5	86.5	9.59	99.0	6.30
Permethrin	0.005	77.2	4.96	72.8	4.09	94.4	4.56	117	7.87	81.9	9.70
	0.01	73.2	6.01	72.2	8.39	93.7	9.63	111	11.2	76.1	2.05
	0.1	75.4	6.93	94.2	4.17	110	6.54	116	10.1	80.4	3.53
Phenthoate	0.005	73.2	10.6	80.3	7.18	90.4	8.99	100	2.26	94.0	6.86
	0.01	78.6	4.52	70.1	7.04	90.2	7.38	93.7	11.7	86.8	5.46
	0.1	75.4	7.54	79.4	1.94	88.4	7.84	94.6	10.8	91.5	4.74
Phorate	0.005	86.8	17.3	70.3	10.8	88.4	15.8	93.8	2.75	86.6	8.16
	0.01	110	5.27	84.9	3.96	118	7.47	87.3	11.8	80.9	6.75
	0.1	92.3	5.20	74.3	4.28	116	5.69	90.4	6.63	80.6	4.99
Phosalone	0.005	79.6	13.4	91.3	3.28	83.7	11.8	105	11.0	83.1	4.47
	0.01	84.6	4.40	83.2	7.35	88.5	6.03	93.4	12.0	90.7	6.96
	0.1	71.0	9.27	92.4	3.11	107	3.90	101	10.7	96.4	5.71
Phosmet	0.005	75.3	13.2	87.6	6.97	73.4	9.46	93.2	19.8	90.1	2.91
	0.01	82.8	7.43	84.1	8.68	74.4	5.84	83.7	10.6	85.2	3.14
	0.1	72.6	10.8	99.4	3.45	99.9	5.64	87.2	14.2	87.0	3.19
Primicarb	0.005	72.4	10.5	76.9	9.61	76.1	15.4	101	9.37	73.3	12.6
	0.01	76.2	3.87	71.1	6.77	72.0	1.69	92.0	8.83	71.3	7.73
	0.1	81.5	6.87	79.6	3.54	86.1	11.7	95.6	7.88	74.3	6.11
Primiphos methyl	0.005	70.1	18.3	74.4	11.3	72.5	12.0	72.4	8.62	74.9	15.5
	0.01	77.4	4.18	74.8	9.06	78.9	6.27	74.1	6.52	71.3	6.11
	0.1	72.4	11.6	83.6	5.50	85.8	10.2	72.7	16.6	72.5	3.74
Prochloraz	0.005	77.1	10.0	81.7	7.64	80.1	12.8	115	9.44	79.5	9.51
	0.01	82.9	6.66	79.0	8.18	77.8	5.30	96.3	11.8	74.0	6.81
	0.1	70.2	8.38	88.0	5.25	97.0	8.77	98.3	13.6	77.3	2.69
Profenphos	0.005	118	9.12	92.4	15.9	118	9.12	80.2	10.6	71.1	19.7
	0.01	94.9	6.01	76.0	16.9	94.9	6.01	91.2	11.2	71.0	13.7
	0.1	70.3	14.8	72.7	17.0	70.3	14.5	85.3	12.3	90.0	4.71
Propagite	0.005	104	16.3	74.2	19.4	70.2	1.78	70.1	3.05	74.3	8.53
	0.01	75.2	15.2	70.6	14.5	70.5	3.67	74.2	4.77	75.1	6.94
	0.1	72.6	6.96	73.3	4.24	70.0	4.60	71.2	2.98	77.2	3.16
Propiconazole	0.005	71.6	16.1	85.9	19.9	71.6	16.1	107	14.8	92.8	10.9
	0.01	109	6.59	77.8	15.4	109	6.59	84.2	15.2	70.9	5.02
	0.1	71.7	7.38	71.0	3.22	71.7	7.38	73.0	14.5	73.9	3.13
Pyriproxyfen	0.005	84.9	10.2	86.7	5.13	74.1	15.1	112	17.1	87.9	8.26
	0.01	85.2	7.02	80.1	6.85	83.7	6.06	113	14.5	91.6	5.18
	0.1	71.8	7.75	88.0	3.61	114	4.91	119	9.96	89.9	6.26

Table 3 continued

Pesticide	Fortified Concentration (mg/kg)	Beef		Pork		Chicken		Eggs		Milk	
		Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
Quintozene	0.005	102	14.2	74.0	6.62	77.2	15.2	81.4	2.16	88.0	7.68
	0.01	99.2	4.33	75.5	7.47	79.6	5.55	77.0	13.6	87.4	5.60
	0.1	82.3	4.98	90.6	1.71	102	1.30	77.0	6.53	86.8	3.41
Terbufos	0.005	79.3	15.0	112	10.1	79.3	15.0	81.4	18.4	82.2	11.4
	0.01	77.3	18.2	83.0	5.20	77.3	18.2	104	7.62	105	11.2
	0.1	76.1	11.2	87.0	3.49	76.1	11.2	89.2	8.83	85.1	5.02
Triadimefon	0.005	78.1	13.0	79.9	10.2	86.6	12.6	109	6.78	82.9	13.0
	0.01	79.6	9.36	72.0	7.33	86.2	2.41	99.4	8.45	76.5	6.35
	0.1	71.2	7.80	84.1	4.13	109	7.23	106	10.7	87.3	3.08
Triadimenol	0.005	83.3	15.1	99.7	11.9	86.7	5.41	105	6.69	72.2	4.37
	0.01	73.9	1.79	71.7	10.9	72.6	12.5	115	4.99	73.1	4.31
	0.1	76.2	6.03	73.5	8.46	104	12.3	117	9.98	75.1	3.10
Trizaofos	0.005	81.0	7.93	83.3	7.49	74.1	9.60	118	9.84	89.7	7.13
	0.01	84.6	5.43	78.9	6.17	81.7	12.7	115	11.1	83.9	4.77
	0.1	71.4	6.89	88.1	3.71	101	7.41	118	10.9	93.7	4.27
Vinclozolin	0.005	90.6	8.08	82.2	2.74	83.8	14.3	100	1.92	95.1	7.07
	0.01	92.8	4.24	82.9	8.53	86.0	5.35	97.9	10.1	89.1	4.20
	0.1	79.9	8.10	95.2	1.94	96.3	6.47	99.2	9.03	85.3	3.04

Fig. 2 Distribution of the average recovery of pesticides in beef, pork, chicken, eggs, and milk
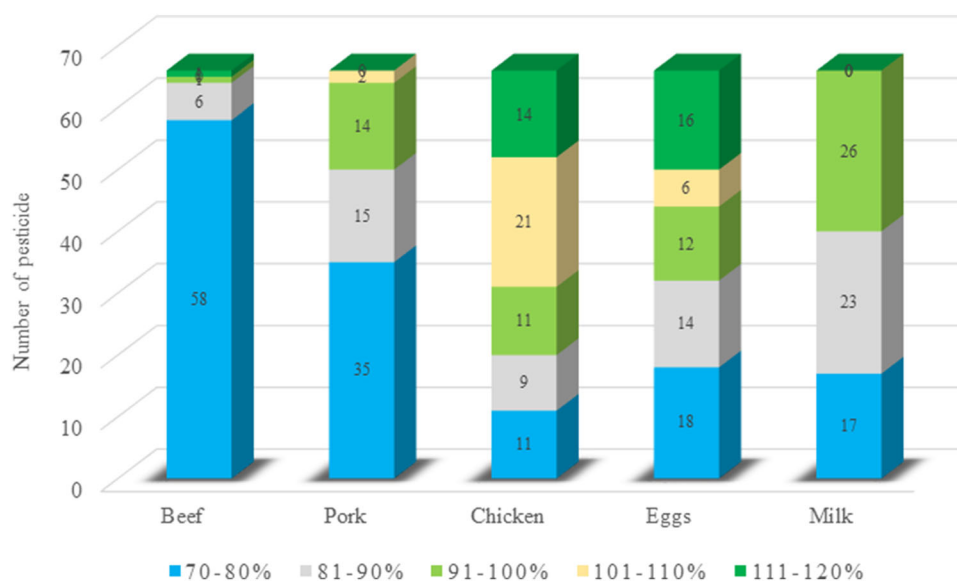
Monitoring of market samples

Monitoring was conducted for a total of 89 samples (14 beef, 15 pork, 15 chicken, 15 eggs, and 15 milk) collected from Seoul, Busan, and Incheon markets in Korea, and the contents of the 66 pesticides in these samples were simultaneously analyzed. Chlorpyrifos and fenitrothion in beef and chlorpyrifos in pork were detected at levels lower than the respective MRLs (chlorpyrifos: 1.0 mg/kg in cattle

fat; 0.02 mg/kg in pig fat; fenitrothion 0.05 mg/kg in mammal fat). No other pesticides were found in any of the samples. In addition, 15 samples of lamb, the consumption of which has increased in Korea were also collected for monitoring; however, none of the 66 target pesticides were detected. These results were compared with Surma et al. (2014), who found organochlorine pesticides, DDT, BHC and its isomers in ham. Additionally, Rejczak and Tuzimski (2017) reported that low (ng/mL) levels of monuron,

methabenzthiazuron, buturon, linuron, aziprotryne, bitertanol, and clofentezine were detected in natural milk samples. However, no pesticides were found in milk in this study. Since pesticides are ubiquitous in the environment and are commonly found as residues in livestock products, continuous pesticide monitoring is required, as is the development of improved methods to allow for the determination of low–concentration multi-residue pesticides in these matrices.

In conclusion, the simultaneous analysis of pesticides presented in this study indicated the potential of the method for the rapid monitoring of residual pesticides in livestock products, due to its short run time, inexpensive nature, simple procedure, and high efficiency. An efficient extraction method was developed using a florisil cartridge as an adsorbent to simultaneously analyze 66 pesticides, including organic phosphorus and chlorine, in a single experiment. The experimental steps were simple and resulted in low LODs and LOQs. The highly sensitive method satisfies the Codex's criteria and is environmentally friendly with less solvent and waste than conventional approaches. The results of this study will help in establishing a continuous, precise and reliable monitoring system for livestock products in a fast and efficient manner. Expanding the simultaneous analysis of pesticide residues in livestock products will continue to receive focus in our future studies.

Compliance with ethical standards

Conflict of interest No potential conflicts of interest are reported by the authors.

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