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Method development, matrix effect, and risk assessment of 49 multiclass pesticides in kiwifruit using liquid chromatography coupled to tandem mass spectrometry

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ABSTRACT

In the present study, a liquid chromatography coupled with tandem mass spectrometry (LC-MS/MS) method with a minimal matrix effect (ME) was developed and validated for simultaneous determination of a diverse range of pesticides (49) in kiwifruit. Samples extracted by the quick, easy, cheap, effective, rugged, and safe (QuEChERS) citrate-buffered method were analyzed either without purification or following purification (with primary secondary amine (PSA) or PSA + graphitized carbon black (GCB)). With the addition of a clean-up step, the suppression of the ME decreased, with a higher number of pesticides determined by the application of PSA + GCB. The method exhibited good linearity with coefficients of determination (R^2) ≥ 0.9972 and satisfactory recoveries (70–120%) with a relative standard deviations (RSDs) < 10%. The limits of quantification (LOQ) were lower than the maximum residue limits (MRLs) set by the Korean Ministry of Food and Drug Safety (MFDS) and the CODEX Alimentarius. The developed method was applied to the real samples and the results indicated that the quantitated levels of all pesticides, except for pyraclostrobin and carbendazim, are lower than the MRLs set by the regulatory authorities. The percentage of the acceptable daily intake was < 20%, suggesting that there is no risk associated with the intake of residual pesticides through kiwifruit.

1. Introduction

Extreme climatic phenomena have been occurring worldwide because of global warming. The Korean peninsula, particularly Jeju Island, is currently experiencing a subtropical climate. Most of the tropical fruits distributed in the Republic of Korea are imported from Southeast Asia and other countries; however, recently, the production of subtropical fruits in the Korean peninsula has increased. In particular, the Halla Agricultural Cooperative of the Jeju Island Federation has succeeded in the mass production of "Kiwi pollen" for the first time. Hence, the substitution of Kiwi pollen for the imported kiwifruits is expected to affect hundreds of millions of Won each year. In addition, the Jeju Provincial Agricultural Technology Institute is promoting various Jeju varieties until 2018 to promote the competitiveness of the kiwi industry. Kiwi or "the king of fruits" constitutes a phytonutrient dense food, implying a high nutrient and low calorie content (70 kcal/100 g). The consumption of kiwis leads to health benefits, including the maintenance of a healthy skin tone and texture, lowering blood pressure, and prevention of heart disease and stroke [1]. Vitamin C is a typical nutrient present in kiwi, the content of which equals that of approximately three tangerines. In addition, the content of dietary fiber (e.g., pectin) is greater than that found in two bananas. High concentrations of vitamin E, which protects the skin and blood vessels, and potassium, are also present. Besides, kiwi contains folic acid, vitamin A, carotenoids, phenolics, chlorophyll, and flavonoids. Kiwi seeds contain alpha-linolenic acid and omega-3 fatty acids [2]. Currently, kiwifruit

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Table 1
Multiple reaction monitoring (MRM) transitions and instrument parameters for LC–MS/MS.

No.	Pesticide	Precursor ion (*m*/*z*)	Quantifier (MRM1)	Qualifier (MRM2)	Collision energy (CE)	Rt (min)	Ionization mode
1	Dinotefuran	203	157	129	5	4.334	Positive
2	Oxamyl	237	90	72	5	4.675	Positive
3	Carbendazim	192	160	132	20	4.733	Positive
4	Thiamethoxam	292	211	132	10	5.199	Positive
5	Imidacloprid	256	209	175	30/15	5.710	Positive
6	Clothianidin	250	169	132	10	5.886	Positive
7	Acetamiprid	223	126	90	30	6.099	Positive
8	Sulfoxaflor	278	174	154	10/20	6.372	Positive
9	Imazalil	297	159	69	7	6.959	Positive
10	Pirimicarb	239	182	72	20	7.155	Positive
11	Ethiofencarb	226	164	107	5	7.700	Positive
12	Forchlorfenuron	248	155	129	15	7.906	Positive
13	Chlorantraniliprole	484	453	286	15	7.943	Positive
14	Azoxystrobin	404	372	344	10/20	8.008	Positive
15	Diethofencarb	268	226	180	10	8.177	Positive
16	Boscalid	343	307	240	20	8.283	Positive
17	Dimethomorph	388	301	165	20/30	8.313	Positive
18	Fludioxonil	229	185	158	20	8.387	Positive
19	Malathion	331	285	127	5	8.427	Positive
20	Myclobutanil	289	125	70	15	8.480	Positive
21	Spirotetramat	374	302	216	15/20	8.490	Positive
22	Fluopyram	397	208	173	15/30	8.551	Positive
23	Fenhexamid	302	97	55	25	8.591	Positive
24	Cyazofamid	325	261	108	10	8.683	Positive
25	Iprodione	330	288	245	10	8.699	Positive
26	Flubendiamide	408	274	71	20	8.710	Positive
27	Fenamiphos	304	217	202	10/20	8.719	Positive
28	Tebufenozide	297	133	105	10/20	8.737	Positive
29	Phenthoate	321	247	163	5	8.797	Positive
30	Cyprodinil	226	108	93	35	8.804	Positive
31	Pyraclostrobin	388	194	163	20	8.856	Positive
32	Fenthion	279	247	169	10	8.898	Positive
33	Prochloraz	376	308	266	5/15	8.969	Positive
34	Clofentezine	303	138	102	20	9.007	Positive
35	Diazinon	305	169	153	20	9.022	Positive
36	Difenoconazole	406	337	251	20	9.095	Positive
37	Metconazole	320	125	70	30/25	9.101	Positive
38	Pirimiphos-methyl	306	164	108	20	9.102	Positive
39	Novaluron	493	158	141	5/15	9.108	Positive
40	Trifloxystrobin	409	186	111	20	9.141	Positive
41	Cadusafos	271	159	97	10/20	9.282	Positive
42	Sethoxydim	328	282	178	10	9.593	Positive
43	Buprofezin	306	201	116	5	9.612	Positive
44	Chlorpyrifos	352	200	97	20	9.780	Positive
45	Deltamethrin	523	506	281	5/15	10.253	Positive
46	Pyridaben	365	309	147	10	10.515	Positive
47	Permethrin	183	165	155	10	10.914	Positive
48	Etofenprox	394	359	177	10	11.316	Positive
49	Bifenthrin	440	181	166	15/30	11.902	Positive

Rt: Retention time.

diseases are gradually increasing. Botrytis fruit rot, which causes mature kiwifruit to become soft and shriveled with a gray growth that mostly appears at the stem end, and bleeding canker, which is a rusty canker on branches, are the most common disease of kiwis [3]. Therefore, the application of pesticides is an extremely crucial task to control such kind of diseases in kiwifruits. The pesticides used on kiwifruit are categorized into various classes, and their use depends on the geographic area.

Liquid–liquid extraction (LLE) and solid-phase extraction (SPE) have been typically employed as sample preparation methods [4]. However, these methods are generally time-consuming and require considerable solvents [5]. Besides, the number of pesticides is increasing (such as azimsulfuron, fluxapyroxad, and spirotetramat). Hence, it is crucial to develop modern approaches focusing on rapid, environmentally friendly techniques, which utilize lesser solvents and smaller sample sizes [6]. The quick, easy, cheap, effective, rugged, and safe (QuEChERS) method is suitable for the analysis of pesticide multiresidues. The QuEChERS method can save time without additional preconcentration step and is eco-friendly (less use of organic solvents). In addition, it can complement the disadvantages of the existing methods [7]. Simultaneous multicomponent analysis using liquid chromatography coupled with tandem mass spectrometry (LC–MS/MS) and QuEChERS has been widely recognized because these methods are simple and rapid. However, a previous study has reported that quantitative analysis with electrospray ionization (ESI) can be substantially affected by the matrix effect (ME) [8]. MEs occur because of the competition between nonvolatile matrix components and analyte ions for access to the droplet surface in order to transfer to the gas phase. Components originating from the sample matrix that co-elute with the target compounds can interfere with the ionization in the mass spectrometer. Depending on the environment in which ionization and ion evaporation occur, this competition may effectively decrease (ion suppression) or increase (ion enhancement) the formation efficiency of the desired analyte ion. This phenomenon is commonly referred as the “ME,” which represents one of the major issues in pesticide residue analysis. ME can adversely affect the reproducibility, linearity, and