

Comparison of QuEChERS and Solid Phase Extraction for Accurate Determination of Pesticide Residues in Kimchi Cabbage and Strawberry using Isotope Dilution Mass Spectrometry

Seonghee Ahn^{1*}, Kebede Gebeyehu Mekete^{1,2}, and Byungjoo Kim^{1,2}

¹Organic Metrology group, Division of Chemical and Biological Metrology, Korea Research Institute of Standards and Science, Daejeon 34113, Republic of Korea

²Department of Bio-Analytical Science, University of Science and Technology, Daejeon 34113, Republic of Korea

Received October 11, 2023, Revised December 12, 2023, Accepted December 15, 2023

First published on the web December 31, 2023; DOI: 10.5478/MSL.2023.14.4.178

Abstract : QuEChERS is used worldwide as a universal sample preparation method with many benefits, such as being quick, easy, cheap, effective, rugged and safe. This study examined whether QuEChERS can be employed in isotope dilution mass spectrometry (ID-MS) for accurate analysis of pesticides in food. The ratios of fortified values and measured values of malathion and fenitrothion using the QuEChERS method were compared with those using the solid phase extract (SPE) method which was previously used in this laboratory. The separations of the two pesticides on DB-5MS and VF-1701MS columns were compared. Malathion and fenitrothion were fortified into kimchi cabbage and pretreated with the QuEChERS method and the SPE method. The results obtained using the DB-5MS column varied according to the sample preparation method, column and pesticide level. Using the VF-1701 column, ratios were 98–102% by both QuEChERS and Carb/NH₂ SPE method for all fortification level. Malathion and fenitrothion were fortified into strawberry samples for comparison with kimchi cabbage. The results for the strawberry samples indicated that the ratios were not influenced by the sample preparation methods or GC column. The QuEChERS method could be acceptable in the ID-MS method for pesticide residue analysis in food, however other conditions should be carefully considered for accurate determination, such as the column, amount of analyte and food matrix.

Keywords : QuEChERS, Carb/NH₂ SPE, Isotope dilution mass spectrometry, Organophosphate pesticide

Introduction

Sample preparation is critical for the accurate determination of pesticide residues in food.^{1,2} A thorough clean-up process leads to a clean sample extract; however, analytes can be lost leading to low recoveries. In contrast, a simple clean-up process improves the recovery; however, it can result in severe matrix effects and reduced accuracy. Thus, balance between clean-up and recovery during sample preparation must be maintained. QuEChERS is a universal clean up method for the analysis of pesticide residues that is

quick, easy, cheap, effective, rugged and safe, which is the origin of its name.^{1,3-12} The ingredients used for QuEChERS have been modified for various types of samples such as fat-rich,^{13,14} pigment-rich,^{8,14,15} and biological samples.^{12,16,17} Previous studies have reported that pesticide analysis using the QuEChERS method can achieved limits of quantification (LOQ) below 0.01 mg/kg, and recoveries of 70-120% with a relative standard deviation (RSD) below 20 %, which satisfy the EU guidelines for the analysis of pesticide residues.¹⁸

The Korea Research Institute of Standards and Science (KRISS) as a national metrology institute in Korea has focused on the accuracy and reliability of experimental results. The method developed in this laboratory for the analysis of pesticides in food was optimized for reducing bias as far as possible, with less emphasis placed on ease, cost, effectiveness, and robustness. In addition, isotope dilution mass spectrometry (ID-MS) has been employed for the analysis of pesticide residues in food to obtain sufficient accuracy, repeatability and reproducibility to be used as a candidate reference method to establish the contents of certified reference materials.¹⁹⁻²²

In this study, the QuEChERS method was tested for use in ID-GC tandem MS for the accurate determination of pes-

Open Access

*Reprint requests to Seonghee Ahn

<https://orcid.org/0000-0002-4709-7968>

E-mail: sahn@kriss.re.kr

All the content in Mass Spectrometry Letters (MSL) is Open Access, meaning it is accessible online to everyone, without fee and authors' permission. All MSL content is published and distributed under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/3.0/>). Under this license, authors reserve the copyright for their content; however, they permit anyone to unrestrictedly use, distribute, and reproduce the content in any medium as far as the original authors and source are cited. For any reuse, redistribution, or reproduction of a work, users must clarify the license terms under which the work was produced.

pesticide residues in food. The results were compared with those of the solid phase extraction (SPE) method that has been previously used in this laboratory. The target analytes were malathion and fenitrothion which are synthetic organophosphorus pesticides that act as acetylcholinesterase inhibitors and endocrine disrupters.²³ Thus they are regulated by many nations and organizations and are expected to be the next candidate compounds for pesticide analysis reference materials at KRISS. Analysis was performed by obtaining the ratios of measured values and gravimetrically fortified values of malathion and fenitrothion into kimchi cabbage and strawberry. Kimchi cabbage is a leafy vegetable which is the most consumed vegetable in Korea. Strawberries are chosen to compare the effect of the food matrix on the results of sample prepared using two methods.

Materials and Methods

Chemicals and Reagents

Malathion, fenitrothion and their isotope analogues, malathion-*d*₁₀ and fenitrothion-*d*₆, were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). HPLC grade organic solvents including acetonitrile, toluene, and hexane were purchased from Honeywell-Burdick and Jackson (Muskegon, MI, USA). Magnesium sulfate and sodium chloride were obtained from Sigma-Aldrich (St. Louis, MO, USA).

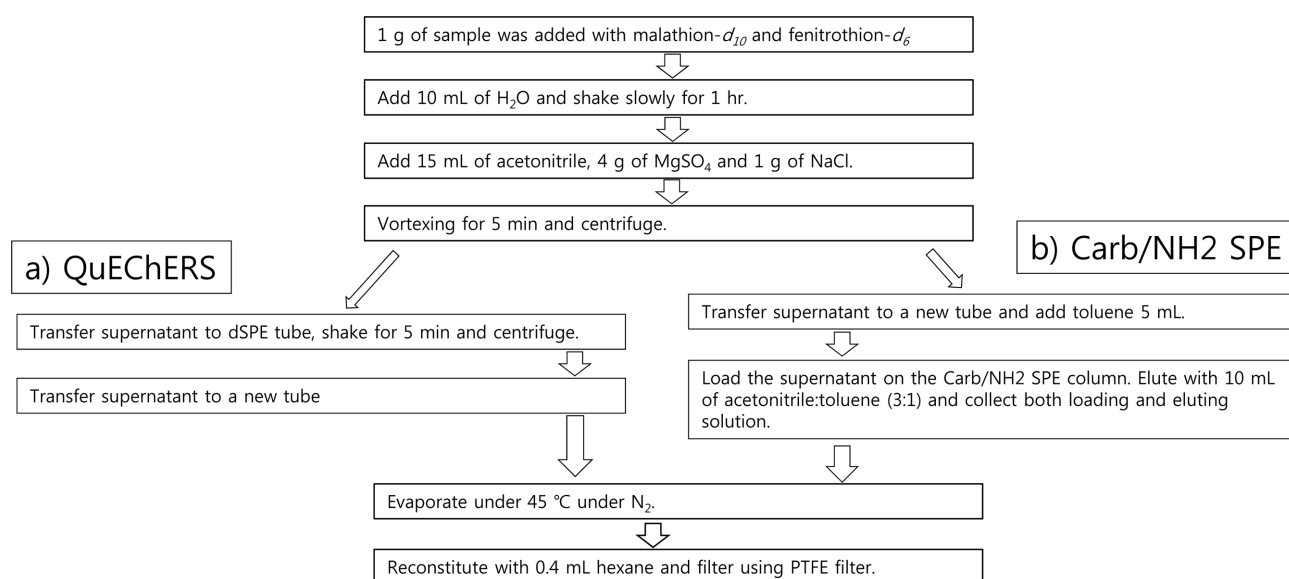
Stock solutions of malathion, fenitrothion, malathion-*d*₁₀ and fenitrothion-*d*₆ were prepared gravimetrically in hexane at approximately 5 mg/kg stored at -20°C in a freezer, and used for up to two months. The working solutions were prepared gravimetrically from the stock solutions, immediately prior to use on the day of the experiment. An isotope ratio standard solution was prepared gravimetrically by combin-

ing the standard solution and isotope standard solutions at an isotopic ratio of 1:1.

Sample preparation

QuEChERS

Kimchi cabbage powder was prepared as previously described in the literatures.^{19,20} Briefly, raw kimchi cabbage was obtained from a Korean farm, freeze-dried, and pulverized. Strawberries were purchased in powdered form product (FD Co., Jeollanam-do, Korea). Kimchi cabbage or strawberry powder samples (1 g) was placed into a 50 mL glass tube, and spiked with appropriate analyte concentrations of the working standard solutions and their corresponding isotope analogue solutions. Then, 10 mL of water was added to reconstitute as the raw material, and the mixture was slowly shaken for 1 hour using a Multi Reax shaker (Heidolph Instruments, Schwabach, Germany). For extraction, 15 mL of acetonitrile was added, and the mixture was vigorously shaken for 5 min. The extract solution was mixed with 4 g of magnesium sulphate and 1 g of sodium chloride (to separate the water and acetonitrile) and then centrifuged at 4500 rpm for 5 min (Beckman Coulter, Brea, CA, USA). The acetonitrile supernatant was transferred to a new conical tube containing the dispersive solid-phase extraction reagents (Q-sep, Restek, Bellefonte, PA, USA) for highly pigmented fruits and vegetables, namely 900 mg of MgSO₄, 300 mg of PSA, and 150 mg of graphitized carbon black. The tubes were then centrifuged again for 5 min at 5000 rpm. The acetonitrile layer was transferred to a new conical tube and evaporated at 45 °C under a stream of nitrogen gas generator (Goojung, Seoul, Korea). The remaining solid residue was reconstituted with 0.4 mL of hexane and filtered through a syringe filter (PTFE, 0.22 mm, 13 mm diameter, Whatman) for GC-MS/MS analysis.



Scheme 1. Sample preparation processes for QuEChERS and Carb/NH₂ SPE.

Carb/NH₂ SPE cartridge

A kimchi cabbage or strawberry powder sample (1 g) was placed into a 50 mL glass tube and spiked with the working standard solutions and their isotope analogue solutions with appropriate analyte concentrations. The extraction process before clean-up with the SPE cartridge was the same as that of the QuEChERS method. The supernatant from the extract solution was transferred to a new conical tube, and 5 mL of toluene was added. A Carb/NH₂ SPE cartridge (Supelco, Bellefonte, PA, USA) pre-conditioned with 5 mL of acetonitrile and toluene mixture (3:1, v/v) was loaded with the sample extract and 10 mL of acetonitrile and toluene mixture (3:1, v/v) was used to elute the target analytes. The eluents of both the loading and eluting steps were collected and evaporated at 45 °C under a stream of nitrogen gas. For GC-MS/MS analysis, the remaining solid residue was reconstituted with 0.4 mL of hexane and filtered through a PTFE filter. The QuEChERS and Carb/NH₂ cartridge SPE procedures are shown in Scheme 1.

GC-MS/MS analysis

Malathion and fenitrothion were analyzed using an Agilent 7000D triple quadrupole with a 7890B GC system (GC-MS/MS; Agilent Technologies, Santa Clara, CA, USA). Chromatographic separation was carried out on an Agilent DB-5MS capillary column (60 m × 0.25 μm × 0.25 mm ID) with a 1 μL injection of 1000 mg/kg polyethylene glycol (PEG) 200 in methanol and on a VF-1701MS (30 m × 0.25 μm × 0.25 mm ID) capillary columns. The flow rate of the helium (purity 99.999%) as a carrier gas was set at 1.5 mL/min. The GC inlet was kept at 260 °C and lined with a liner without wool. The oven temperature was programmed as follows: started at 70 °C for 2 min, ramp to 200 °C at 30 °C/min and then to 300 °C at 10 °C/min (held for 10 min). The ion source and transfer line were both adjusted to 300 °C, and the ionization energy was set to 70 eV in electron ionization mode. 1 μL sample was injected into the GC-MS/MS system in splitless mode. Analytes were monitored in multiple reaction monitoring mode (MRM) at *m/z* 173 and *m/z* 277 for malathion and fenitrothion, and at *m/z* 183 and *m/z* 283 for malathion-*d*₁₀ and fenitrothion-*d*₆, respectively. The retention times, collision energies, and dwell times are listed in Table 1. The Agilent Mass Hunter Workstation software was used for data acquisition and analysis.

Table 1. GC conditions and MS/MS channels of malathion and fenitrothion.

Analytical parameters	Compound			
	Malathion	Malathion- <i>d</i> ₁₀	Fenitrothion	Fenitrothion- <i>d</i> ₆
Molecular formula	C ₁₀ H ₁₉ O ₆ PS ₂	C ₁₀ H ₉ D ₁₀ O ₆ PS ₂	C ₉ H ₁₂ O ₅ PS	C ₉ H ₆ D ₆ O ₅ PS
Precursor ion (<i>m/z</i>)	173	183	277	283
Product ion (<i>m/z</i>)	99	100	260	266
CE (eV)	15	15	5	5
Dwell time (ms)	10	10	10	10

Calculation

The concentrations of malathion and fenitrothion in kimchi cabbage and strawberry samples (*C*_{sample}) were calculated from the ID-GC-MS/MS analysis using Equation (1) as follows:

$$C_{\text{sample}} = \frac{M_{\text{is-sol,spiked}} \cdot AR_{\text{sample}} \cdot M_{\text{s-sol,std.mix.}} \cdot C_{\text{s-sol}}}{M_{\text{sample}} \cdot AR_{\text{std.mix.}} \cdot M_{\text{is-sol,std.mix.}}} \quad (1)$$

where *C*_{sample} is the measured concentrations of malathion or fenitrothion in the sample. *C*_{s-sol} is the concentration of the corresponding malathion and fenitrothion in the standard solution, *M*_{sample} is the mass of sample that has been analyzed, *M*_{is-sol,spiked} is the mass of malathion-*d*₁₀ and fenitrothion-*d*₆ was added to the sample, *AR*_{sample} is the measured the peak area ratio of the native and isotope-labeled analytes from GC-MS/MS analysis of the sample, *AR*_{std.mix} is the peak area of the mixed standard solution for isotopic ratio and *M*_{s-sol,std.mix} and *M*_{is-sol,std.mix} are the masses of the native standard solution and the isotope-labeled standard solution that are used for the preparation of the mixed standard solution of isotopic ratio, respectively.

Results and discussion

ID-GC/MS/MS analysis

For MS/MS analysis, full scan mass spectra and product ion spectra of 5 mg/kg solutions of malathion, malathion-*d*₁₀, fenitrothion and fenitrothion-*d*₆ were collected. Initially, the DB-5MS column and a liner with glass wool were used in the GC system. The most abundant peak in the full scan spectra of malathion and malathion-*d*₁₀ was a fragment, [M - C₂H₆O₂PS₂]⁺ at *m/z* 173 and 183 respectively without a molecular ion peak. Thus, the peak of [M - C₂H₆O₂PS₂]⁺ was used as the precursor for malathion and malathion-*d*₁₀. Fenitrothion and fenitrothion-*d*₆ exhibited parent ion peaks, [M]⁺ at *m/z* 277 and 283, respectively, which were used as the precursors. The most abundant peaks of the product ion spectra were the [M-C₂H₆O₂PS₂-O(CH₂CH₃)₂]⁺ peak for malathion and malathion-*d*₁₀ and the [M-OH]⁺ peak for fenitrothion and fenitrothion-*d*₆. The channels for MS/MS and their corresponding conditions were listed in Table 1.

After optimizing the MS conditions, the isotope ratios of

the mixture of malathion, malathion- d_{10} , fenitrothion and fenitrothion- d_6 were examined. However, using the DB-5MS column and a liner with glass wool, relative the standard deviations (RSDs) of the isotope ratios and peak areas of the analytes were greater than 10% which was outside the acceptance criterion of this laboratory. An active site of the GC column can cause the adsorption and decomposition of pesticides and lead to abnormal recoveries.²⁴ An analyte protectant such as PEG series, can coat these active sites; therefore, 1 mL of a 1000 mg/kg solution of PEG 200 was injected once a day into the DB-5MS column before the analysis, and the liner was changed to one without wool. With these modifications, the RSDs of the isotopic ratios of malathion and fenitrothion were below 2%. The chromatograms of malathion, malathion- d_{10} , fenitrothion and fenitrothion- d_6 with the liner without wool, injection of PEG 200 and DB-5MS column are shown in Figure 1(a). The peaks of the two analytes and their corresponding isotopes were optimized; however, they were not well separated. The difference in the retention times of malathion and fenitrothion was only 0.02 min. Although these peaks were not well separated, quantitation of analytes is possible using the MRM mode of the GC-MS/MS. To better separate the peaks, a VF-1701 MS column which is more polar than the DB-5MS column was installed in the GC. The liner was one without wool and there was no injection of PEG 200. The chromatograms are shown in Figure 1(b). The difference in retention times between malathion and fenitrothion was 0.17 min, indicating baseline separation. The DB-5MS and VF-1701 columns are compared in Tables 2 and 3 for the analysis of malathion and fenitrothion. With the conditions of GC/MS/MS.

Comparison of QuEChERS and Carb/NH₂ cartridge

Table 2 lists the results of kimchi cabbage powder forti-

fied gravimetrically with malathion and fenitrothion at 10, 25, 100 and 250 $\mu\text{g}/\text{kg}$, analyzed using a DB-5MS column after PEG 200 injection. With the QuEChERS method, the ratios of fortified value and measured value were greater than 100% at all levels, indicating a positive bias. However, with the Carb/NH₂ SPE method, only the 10 $\mu\text{g}/\text{kg}$ fortification level exhibited the ratios greater than 100% for both malathion and fenitrothion. The QuEChERS products used in this experiment were intended for highly pigmented fruits and vegetables such as kimchi cabbage. However, after the QuEChERS clean-up step, the green chlorophyll pigment in the kimchi cabbage sample extract was not completely removed. After the Carb/NH₂ SPE clean-up method, the sample extract solutions were almost clear or slightly yellow, indicating the most of the chlorophyll had been removed. Thus, the pigment in the kimchi cabbage sample extract affected the determination of malathion and fenitrothion using the DB-5MS column.

Table 3 summarizes the malathion and fenitrothion results using the VF-1701 MS column; sample preparation and clean-up processes were the same as those in the previous experiments. The ratios at all malathion and fenitrothion fortification levels of with both QuEChERS and Carb/NH₂ SPE methods were 98%-102% without any noticeable trends or bias. The VF-1701 MS column was more polar than the DB-5MS column, and could separate malathion and fenitrothion from the pigment in the kimchi cabbage.

Comparison of kimchi cabbage and strawberry

Malathion and fenitrothion were fortified into strawberries which is a different food matrix from that of kimchi cabbage. The sample preparation and clean-up methods were same as those of the kimchi cabbage experiments.

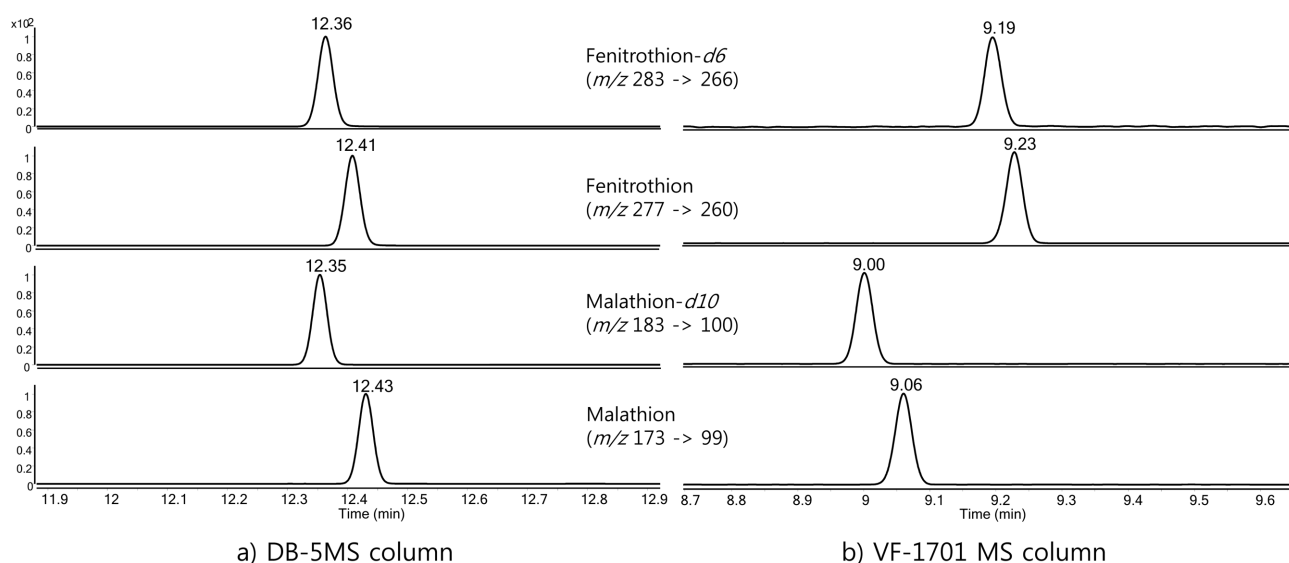


Figure 1. Comparison of chromatograms for malathion and fenitrothion with DB-5MS and VF-1701MS columns using ID-GC-MS/MS.

Table 2. Measurement results of malathion and fenitrothion in gravimetrically fortified kimchi cabbage powder samples by the ID-GC-MS/MS method with the DB-5MS column with PEG 200.

Analyte	Malathion			Fenitrothion		
Methods	Fortified value (µg/kg)	Measured value (µg/kg)	Ratio (%) ^a	Fortified value (µg/kg)	Measured value (µg/kg)	Ratio (%)
QuEChERS	12.35 ± 0.002 ^b	13.16 ± 0.36 ^c	106	12.16 ± 0.002	12.67 ± 0.36	104
	12.30 ± 0.002	13.18 ± 0.37	107	12.24 ± 0.002	12.56 ± 0.34	103
	12.51 ± 0.002	13.21 ± 0.35	105	12.48 ± 0.002	12.70 ± 0.54	102
	12.82 ± 0.002	13.68 ± 0.34	106	12.59 ± 0.002	13.33 ± 0.37	106
	25.20 ± 0.002	25.74 ± 0.32	102	24.17 ± 0.002	23.81 ± 0.41	98
	25.20 ± 0.002	25.84 ± 0.30	103	24.04 ± 0.002	23.80 ± 0.31	99
	25.22 ± 0.002	25.74 ± 0.32	102	24.40 ± 0.002	24.25 ± 0.29	99
	25.24 ± 0.002	25.85 ± 0.31	102	24.46 ± 0.002	24.15 ± 0.32	99
	99.77 ± 0.002	99.80 ± 0.88	102	98.6 ± 0.002	100.4 ± 1.3	102
	97.04 ± 0.002	99.29 ± 0.85	102	98.3 ± 0.002	101.0 ± 1.2	103
	98.09 ± 0.002	100.3 ± 1.0	102	98.7 ± 0.002	100.8 ± 1.5	102
	99.35 ± 0.002	101.49 ± 0.81	102	98.7 ± 0.002	101.0 ± 1.3	102
	236.3 ± 0.002	239.1 ± 1.8	101	238.3 ± 0.002	243.0 ± 2.8	102
	236.0 ± 0.002	240.5 ± 1.6	102	236.3 ± 0.002	239.7 ± 2.6	101
	233.0 ± 0.002	236.6 ± 1.9	102	236.0 ± 0.002	238.1 ± 2.5	101
	237.0 ± 0.002	241.0 ± 1.7	102	240.2 ± 0.002	244.3 ± 2.5	102
Carb/NH ₂	12.40 ± 0.002	12.58 ± 0.21	101	12.15 ± 0.002	12.41 ± 0.29	102
	12.44 ± 0.002	12.68 ± 0.24	102	12.21 ± 0.002	12.46 ± 0.29	102
	12.55 ± 0.002	12.92 ± 0.22	103	12.37 ± 0.002	12.69 ± 0.25	102
	12.55 ± 0.002	12.85 ± 0.29	102	12.54 ± 0.002	12.50 ± 0.33	100
	24.48 ± 0.002	24.40 ± 0.45	100	24.87 ± 0.002	24.30 ± 0.50	99
	24.36 ± 0.002	23.90 ± 0.46	98	24.36 ± 0.002	23.81 ± 0.54	99
	24.08 ± 0.002	24.10 ± 0.32	100	24.78 ± 0.002	24.21 ± 0.55	99
	24.25 ± 0.002	24.16 ± 0.40	100	24.85 ± 0.002	23.84 ± 0.46	97
	93.49 ± 0.002	92.64 ± 1.22	99	96.00 ± 0.002	95.51 ± 0.88	99
	95.09 ± 0.002	94.09 ± 1.11	99	94.42 ± 0.002	93.88 ± 1.01	99
	95.00 ± 0.002	94.75 ± 0.93	100	94.46 ± 0.002	94.58 ± 0.95	100
	95.29 ± 0.002	94.02 ± 0.95	99	94.20 ± 0.002	94.90 ± 1.47	101
	237.0 ± 0.002	235.9 ± 1.7	100	227.8 ± 0.002	229.6 ± 2.5	101
	240.6 ± 0.002	237.2 ± 1.9	99	226.5 ± 0.002	230.5 ± 2.6	102
	224.9 ± 0.002	221.0 ± 2.3	98	224.1 ± 0.002	226.8 ± 2.5	101
	227.8 ± 0.002	223.9 ± 1.7	98	227.4 ± 0.002	228.5 ± 3.0	100

^a The % values are the ratios of the measured values and the gravimetrically fortified values.

^b The values after '±' is the expanded uncertainties of the fortified values at a confidence level of 95 %. The uncertainties are mostly from weighing blank samples and the spiked calibration standard solutions.

^c The values after '±' is the expanded uncertainties of the fortified values at a confidence level of 95 %. The uncertainties are combined with measurement uncertainties of calibration standard solutions and samples.

Other QuEChERS products and SPE cartridges exist for strawberry samples; however, in this experiments the same QuEChERS products and Carb/NH₂ SPE used for the kimchi cabbage samples were used for the strawberries as a comparison. The results are listed in Table S1 and S2. With

the DB-5MS column, the results were no difference between QuEChERS and Carb/NH₂ methods but the ratios for malathion were low at the level of 10 mg/kg. With the VF-1701 column, ratios of malathion and fenitrothion were 98-102% and there was no difference between the QuECh-

Table 3. Measurement results of malathion and fenitrothion in gravimetrically fortified kimchi cabbage powder samples by the ID-GC/MS/MS method with the VF-1701MS column.

Analyte	Malathion			Fenitrothion		
Methods	Fortified value (µg/kg)	Measured value (µg/kg)	Ratio (%) ^a	Fortified value (µg/kg)	Measured value (µg/kg)	Ratio (%)
QuEChERS	13.16 ± 0.002 ^b	13.30 ± 0.35 ^c	101	12.96 ± 0.002 ^a	12.81 ± 0.32	99
	12.47 ± 0.002	12.76 ± 0.33	102	12.32 ± 0.002	12.25 ± 0.46	99
	12.56 ± 0.002	12.77 ± 0.30	102	12.57 ± 0.002	12.40 ± 0.38	99
	13.20 ± 0.002	13.44 ± 0.30	102	13.07 ± 0.002	12.77 ± 0.32	98
	25.43 ± 0.002	25.10 ± 0.51	99	25.92 ± 0.002	25.50 ± 0.49	99
	25.19 ± 0.002	25.12 ± 0.51	100	25.58 ± 0.002	25.05 ± 0.42	99
	25.44 ± 0.002	25.56 ± 0.54	99	25.94 ± 0.002	25.39 ± 0.56	98
	25.25 ± 0.002	24.96 ± 0.60	100	25.58 ± 0.002	25.35 ± 0.57	98
	96.8 ± 0.002	97.95 ± 1.7	101	94.2 ± 0.002	95.1 ± 3.5	101
	100.1 ± 0.002	101.8 ± 1.7	102	97.4 ± 0.002	96.4 ± 3.5	99
	99.6 ± 0.002	101.3 ± 1.8	102	97.4 ± 0.002	95.6 ± 3.4	98
	100.6 ± 0.002	101.5 ± 1.7	101	97.0 ± 0.002	97.9 ± 3.6	101
	248.7 ± 0.002	247.7 ± 2.1	100	259.7 ± 0.002	257.5 ± 2.1	99
	220.9 ± 0.002	219.6 ± 1.8	99	263.0 ± 0.002	261.3 ± 1.5	99
	242.5 ± 0.002	240.1 ± 1.8	99	263.2 ± 0.002	261.8 ± 1.5	99
	257.9 ± 0.002	257.2 ± 2.0	100	262.2 ± 0.002	259.2 ± 1.5	99
Carb/NH ₂	16.02 ± 0.002	16.09 ± 0.44	100	16.72 ± 0.002	16.80 ± 0.47	100
	15.82 ± 0.002	15.52 ± 0.50	98	16.51 ± 0.002	16.87 ± 0.36	102
	15.96 ± 0.002	15.75 ± 0.42	99	16.66 ± 0.002	16.52 ± 0.34	99
	15.72 ± 0.002	15.35 ± 0.33	98	16.40 ± 0.002	16.34 ± 0.46	100
	22.84 ± 0.002	22.92 ± 0.28	100	22.35 ± 0.002	22.49 ± 0.45	101
	23.91 ± 0.002	23.34 ± 0.32	98	23.39 ± 0.002	23.41 ± 0.53	101
	24.14 ± 0.002	23.94 ± 0.34	99	23.61 ± 0.002	23.58 ± 0.56	100
	24.02 ± 0.002	24.30 ± 0.24	101	23.50 ± 0.002	23.29 ± 0.54	99
	97.8 ± 0.002	97.1 ± 1.2	99	95.7 ± 0.002	96.3 ± 2.0	101
	96.6 ± 0.002	96.1 ± 0.8	99	94.5 ± 0.002	94.4 ± 2.3	100
	95.0 ± 0.002	95.4 ± 1.8	100	92.9 ± 0.002	91.2 ± 1.9	98
	87.3 ± 0.002	87.5 ± 1.1	100	85.4 ± 0.002	84.3 ± 1.6	99
	246.2 ± 0.002	251.6 ± 4.3	102	251.0 ± 0.002	248.7 ± 4.2	99
	247.7 ± 0.002	250.8 ± 4.2	101	264.5 ± 0.002	262.4 ± 3.7	99
	251.70 ± 0.002	254.6 ± 4.3	101	256.8 ± 0.002	257.2 ± 2.9	100
	253.8 ± 0.002	255.7 ± 4.5	101	259.0 ± 0.002	258.4 ± 4.2	100

^a The % values are the ratios of the measured values and the gravimetrically fortified values.

^b The values after '±' is the expanded uncertainties of the fortified values at a confidence level of 95 %. The uncertainties are mostly from weighing blank samples and the spiked calibration standard solutions.

^c The values after '±' is the expanded uncertainties of the fortified values at a confidence level of 95 %. The uncertainties are combined with measurement uncertainties of calibration standard solutions and samples.

ERS and Carb/NH₂ SPE methods. The ratios of measured values and fortified values of malathion and fenitrothion from strawberries did not vary with the sample preparation method.

Conclusion

For the accurate determination of pesticide residues in kimchi cabbage and strawberry, QuEChERS and Carb/NH₂ SPE were compared using ID-GC-MS/MS. For malathion

and fenitrothion in kimchi cabbage using a DB-5MS column, the ratios of fortified values and measured values had a positive bias with the QuEChERS method at most fortification levels, but those with the Carb/NH₂ SPE method were acceptable except at 10 µg/kg. Using a VF-1701MS column, the ratios at all fortified levels were satisfactory using both QuEChERS and Carb/NH₂ SPE methods. Although QuEChERS included graphitized carbon black for the removal of chlorophyll, this pigment was not completely removed and affected the analysis of malathion and fenitrothion with the DB-5MS column. The VF-1701MS, a more polar column, separated malathion and fenitrothion better than the DB-5MS column. In addition, the VF-1701MS column could separate malathion and fenitrothion from chlorophyll eluted kimchi cabbage, thus the ratios were not affected by the clean-up methods using GC column. The ratios of malathion and fenitrothion fortified into strawberries did not vary with two sample preparation methods, QuEChERS and Carb/NH₂ SPE, and two columns, DB-5 MS and VF-1701MS. The ratios of malathion from the strawberry samples fortified at 10 µg/kg exhibited a negative bias in both the QuEChERS and Carb/NH₂ methods with the DB-5MS column, indicating that further research on negative bias is required. Therefore, the QuEChERS method can be successfully applied to ID-MS for the accurate determination of pesticide residues in food, although at lower fortification levels, the food matrix effect required additional study.

Funding

This study was supported by Korea Research Institute of Standards and Science under the project “Establishing measurement standards for organic analysis” (Grant no. 23011071). The funding source had no further detailed involvement in this study.

Notes

Electronic Supplementary Information (ESI) is available [Table S1 and Table S2]. See DOI: 10.5478/MSL.2023.14.4.178

References

- Lambropoulou, D.A.; Albanis, T.A. *Anal Bioanal Chem* **2007**, 389, 1663. <https://doi.org/10.1007/s00216-007-1348-2>.
- Zhang, L.; Liu, S.; Cui, X.; Pan, C.; Zhang, A.; Chen, F. *Central European Journal of Chemistry* **2012**, 10, 900. <https://doi.org/https://doi.org/10.2478/s11532-012-0034-1>.
- González-Curbelo, M.Á.; Socas-Rodríguez, B.; Herrera-Herrera, A.V.; González-Sálamo, J.; Hernández-Borges, J.; Rodríguez-Delgado, M.Á. *TrAC Trends in Analytical Chemistry* **2015**, 71, 169. <https://doi.org/10.1016/j.trac.2015.04.012>.
- Hakme, E.; Lozano, A.; Ucles, S.; Gomez-Ramos, M.M.; Fernandez-Alba, A.R. *J Chromatogr A* **2018**, 1573, 28. <https://doi.org/10.1016/j.chroma.2018.08.046>.
- Lee, J.; Kim, L.; Shin, Y.; Lee, J.; Lee, J.; Kim, E.; Moon, J.K.; Kim, J.H. *J Agric Food Chem* **2017**, 65, 3387. <https://doi.org/10.1021/acs.jafc.7b00576>.
- Lehotay, S.J.; Maštovská, K.; Lightfield, A.R. *Journal of AOAC International* **2005**, 88, 615. <https://doi.org/https://doi.org/10.1093/jaoac/88.2.615>.
- Perestrelo, R.; Silva, P.; Porto-Figueira, P.; Pereira, J.A.M.; Silva, C.; Medina, S.; Camara, J.S. *Anal Chim Acta* **2019**, 1070, 1. <https://doi.org/10.1016/j.aca.2019.02.036>.
- Pszczolinska, K.; Kociolek, B. *J Sep Sci* **2022**, 45, 149. <https://doi.org/10.1002/jssc.202100304>.
- Santana-Mayor, Á.; Socas-Rodríguez, B.; Herrera-Herrera, A.V.; Rodríguez-Delgado, M.Á. *TrAC Trends in Analytical Chemistry* **2019**, 116, 214. <https://doi.org/10.1016/j.trac.2019.04.018>.
- Varela-Martínez, D.A.; González-Curbelo, M.Á.; González-Sálamo, J.; Hernández-Borges, J. *Food chemistry* **2019**, 297, 124961. <https://doi.org/https://doi.org/10.1016/j.foodchem.2019.124961>.
- Walorczyk, S.; Drożdżyński, D.; Kierzek, R. *Journal of Chromatography A* **2015**, 1412, 22. <https://doi.org/https://doi.org/10.1016/j.chroma.2015.08.022>.
- Zhang, C.; Deng, Y.; Zheng, J.; Zhang, Y.; Yang, L.; Liao, C.; Su, L.; Zhou, Y.; Gong, D.; Chen, L.; Luo, A. *TrAC Trends in Analytical Chemistry* **2019**, 118, 517. <https://doi.org/10.1016/j.trac.2019.06.012>.
- Theurillat, X.; Dubois, M.; Huertas-Perez, J.F. *Food Chem* **2021**, 353, 129039. <https://doi.org/10.1016/j.foodchem.2021.129039>.
- Wilkowska, A.; Biziuk, M. *Food Chemistry* **2011**, 125, 803. <https://doi.org/10.1016/j.foodchem.2010.09.094>.
- Tuzimski, T.; Rejczak, T.; Pieniazek, D.; Buszewicz, G.; Teresinski, G. *J AOAC Int* **2016**, 99, 1436. <https://doi.org/10.5740/jaoacint.16-0277>.
- Daljit Vuldathala, M.C.; Lisa Murphy. *Journal of Analytical Toxicology* **2010**, 34, 273. <https://doi.org/https://doi.org/10.1093/jat/34.5.273>.
- Townsend, R.; Keulen, G.; Desbrow, C.; Godfrey, A.R. *Analytical Science Advances* **2020**, 1, 152. <https://doi.org/10.1002/ansa.202000018>.
- European Commission, **2021**. Main changes introduced in Document No. SANTE/11312/2021 with respect to the previous version.
- Ahn, S.; Lee, J.-Y.; Kim, B. *Chromatographia* **2020**, 84, 27. <https://doi.org/10.1007/s10337-020-03976-y>.
- Ahn, S.; Son, S.; Kim, B.; Choi, K. *Journal of Analytical Science and Technology* **2022**, 13. <https://doi.org/10.1186/s40543-022-00319-4>.
- Bdeson, P. *Guidelines for Achieving High Accuracy in Isotope Dilution Mass Spectrometry (IDMS)*, Royal Society of Chemistry, Place, **2002**.

22. Yarita, T.; Otake, T.; Aoyagi, Y.; Kuroda, Y.; Numata, M.; Iwata, H.; Watai, M.; Mitsuda, H.; Fujikawa, T.; Ota, H. *Talanta* **2014**, 119, 255. <https://doi.org/10.1016/j.talanta.2013.11.011>.
23. Sidhu, G.K.; Singh, S.; Kumar, V.; Dhanjal, D.S.; Datta, S.; Singh, J. *Critical Reviews in Environmental Science and Technology* **2019**, 49, 1135. <https://doi.org/10.1080/10643389.2019.1565554>.
24. Maštovská, K.; Lehotay, S.J.; Anastassiades, M. *Analytical Chemistry* **2005**, 77, 8129. <https://doi.org/10.1021/ac0515576>.