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# Determination of Matrix Effects Occurred during the Analysis of Organochlorine Pesticides in Agricultural Products Using GC-ECD

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**Abstract** Matrix effects observed during the multiresidue analysis of seven organochlorine pesticides in six different agricultural products with GC-ECD were assessed. The presence of matrix coextractives, a major cause of observed matrix effects, directly and/or indirectly influenced the chromatographic responses of some pesticides. Two types of external calibrations, solvent calibration (SC) and matrix-matched calibration (MC), were used to assess matrix effects. Greater matrix effects were observed at the lower concentrations of each pesticide. The extent of matrix effects varied unpredictably with matrix type. Among the analyzed pesticides, iprodione, cyhalothrin, and cypermethrin exhibited greater matrix effects (>150%) for almost all matrices. The pesticide recovery rates obtained with MC were not statistically different from a 100% recovery rate in most samples, which indicates that MC may diminish the overestimates occurred due to matrix effects in GC analysis.

**Keywords:** GC-ECD, matrix effect, solvent calibration, matrix-matched calibration, recovery rate

## Introduction

The consumption of pesticide-contaminated products is regarded as a potential health threat to humans. Pesticide residues provoke serious food and environmental safety issues, as residues exceeding the tolerance of maximum residue levels may accumulate in the edible portions of vegetables. A large number of multiresidue extraction methods (MRMs) have been developed to simultaneously and accurately analyze various pesticide residues in commodities (1). These MRMs provide an effective means of quickly determining the levels of various pesticides in a sample, but it is practically impossible to obtain optimum results for all pesticides measured because of the different physicochemical properties of individual pesticides and the atypical characteristics of components (e.g., pigments, lipids, sterols *etc.*) coextracted from samples (2). The matrix components that coelute with pesticide residues during solvent extraction may increase the inaccuracy and uncertainty of results in multiresidue analytical methods (3). This phenomenon was first reported by Erney *et al*. (4) in 1993, and it was referred to as the "matrix-induced chromatographic response enhancement effect" or simply "matrix effect". Matrix effects during GC analysis of various kinds of pesticides have been reported for various matrices by several laboratories, but most of them were conducted with no clean-up processes in order to exclude the influences of purification on matrix effects (5-13). The factors influencing matrix effects and various methods of diminishing matrix effects were also proposed by several researchers (14-21). During pesticide analysis using GC, non-volatile matrix components coexisting with analytes in an injected sample usually accumulate in the GC inlet and/or in the front part of a column, masking active sites in the GC liner, and decreasing the loss of susceptible and thermolabile pesticides (18). Consequently, such masking may increase the transfer of target pesticides to the GC detector, and induce the enhancement of chromatographic response when compared to the analysis of matrix-free analytes dissolved in pure solvent (10). In most cases, unexpectedly high recovery rates exceeding 120% are usually due to this phenomenon, which has been known to be the main cause of erroneous results in instrumental quantification of pesticide residues (3,15).

Of the effective methods used to compensate for matrix effects, matrix-matched calibration (MC) was most commonly utilized despite the inconvenience of preparing a blank matrix extract (18). However, the US Environmental Protection Agency (EPA) and the Food and Drug Administration (FDA) prohibit the application of MC for pesticide analysis because of the possibilities of manipulating results (16). In contrast, the European Union (EU) usually recommends the use of MC for ensuring method validation in pesticide analysis (22), and the assessment of matrix effects is regarded as a core component of method validation.

It has been established that MRMs, including clean-up steps, cannot completely eliminate coextractives during pesticide residues analysis, and the response of chromatographic signal may be increased or decreased by the matrix components existing in a final sample preparation. The intensity and extent of matrix effects can be influenced by the type and concentration of a matrix, and matrix effects may also differ based on the analyte (2).

The objective of this study was to evaluate the extent of matrix effects in the multiresidue analysis of six agricultural products (broccoli, welsh onion, pepper, cucumber, leek, and rice) for seven organochlorine pesticides (chlorothalonil, chlorpyrifos, procymidone, chlorfenapyr, iprodione, cyhalothrin, and cypermethrin), which were the most frequently detected pesticides during monitoring experiment with GC-ECD. The recovery rates of the target pesticides were obtained by using calibration curves separately prepared in pure solvent and blank matrix extracts.

## Materials and Methods

**Commodities** All the agricultural products -broccoli, welsh onion, pepper, cucumber, leek, and rice- used in this experiment were obtained from retail markets located in the northern area of Seoul, Korea. All commodities with no pesticide residues were screened out using GC-ECD and GC-MSD. The selected samples were ground homogeneously using blender mixer (Robot-Coupe, Vincennes, France) and kept in a refrigerator at −20°C until use.

**Chemicals and materials** The pesticide analytical standards, chlorothalonil, chlorpyrifos, chlorfenapyr, procymidone, iprodione, cyhalothrin, and cypermethrin were purchased from Dr. Ehrensforfer GmbH (Augsburg, Germany), Chem Service (West Chester, PA, USA), and Sigma-Aldrich (St. Louis, MO, USA). The purity of all pesticide standards was higher than 98%, except for cypermethrin (91.5%). The organic solvents used were pesticide residue analysis grade. Acetonitrile was purchased from JT&Baker (Center Valley, PA, USA). Acetone and *n*-hexane were supplied from Kanto Chemical Co., Inc. (Tokyo, Japan). Anhydrous sodium chloride for phase separation was obtained from Merck (Darmstadt, Germany). An Omni Macro Homogenizer (Kennesaw, GA, USA) was used for extracting pesticide residues. The Florisil SPE cartridge (1GM, 6 cc) used for purifying samples was purchased from Agilent Technologies (Santa Clara, CA, USA). A SUPELCO VISIPREP™ vacuum manifold from Sigma-Aldrich was used to support the SPE cartridge. An N-EVAP™ 112 from Organomation Associates, Inc. (Berlin, MA, USA) was used for solvent evaporation.

**Instruments and conditions of GC analysis** An HP 6890 gas chromatography (Agilent Technologies) equipped with a microelectron capture detector (μECD) and a 7683B autosampler was used. Samples were injected on splitless mode (25.3 mL/min, 0.75 min) using an injector equipped with a 10 μL syringe and a 4 mm i.d. tap GW liner (Agilent Technologies). The separation of pesticides was carried out with a HP-5 capillary column (30 m length, 0.32 mm i.d., 0.25 μm film thickness) containing a 5% phenyl methyl siloxane as stationary phase (Agilent Technologies). The GC-ECD operating conditions were as follows: injector temperature, 230°C; detector temperature, 280°C; initial oven temperature, 150°C for 1 min, then raised at 12°C/min to 240°C, held at 240°C for 2 min, then raised at 10°C/min to 280°C, and held at 280°C for 11 min. The total analysis time was 25.5 min. Nitrogen was used as a carrier gas at a flow rate of 1 mL/min.

**Extraction of pesticide residues** The target pesticides from various products were extracted using the multiclass pesticide multiresidue method provided by Korea Food & Drug Administration (KFDA) with slight modifications (23). A 50 g portion of homogeneously ground samples was extracted with 100 mL of acetonitrile in a glass bottle for 2 min at 2000 rpm using the Omni Macro Homogenizer. The homogenized samples were filtered using a qualitative filter paper with 18.5 cm diameter (Ahlstrom Filtration LLC, Mt. Holly Springs, PA, USA), and then the filtrates were vigorously shaken in a milk bottle containing 10 g of sodium chloride. For phase separation, the bottle was left stationary for 10 min. A 10 mL aliquot of the upper layer (acetonitrile layer) was then taken and evaporated to solid dryness in a water bath at 40°C.

**SPE clean-up** The SPE florisil cartridges were placed on a vacuum manifold and washed consecutively with 5 mL of *n*-hexane and acetone:*n*-hexane (2:8, v/v). The sample extracts dissolved with 5 mL of acetone:*n*-hexane (2:8, v/v) were loaded onto the top cartridge and collected into a glass conical tube at a flow rate of one or two drops per second. Repeatedly, 5 mL of acetone:*n*-hexane (2:8, v/v) was added to the cartridge and eluted into the same tube. The eluates were evaporated to solid dryness using a nitrogen evaporator at 40°C. The dried extracts were redissolved in 2 mL of acetone:*n*-hexane (2:8, v/v) and prepared as test solutions.

**Preparation of calibration curves** A stock solution of each standard was dissolved in acetone at a concentration range of 100-160 mg/L. These solutions were used to make a standard mixture containing all pesticides at 10 mg/L. In order to assess the influence of a sample matrix on chromatographic signals, two different calibration curves were prepared with concentrations of 0.1, 0.5, 1.0, and 2.0 mg/L, obtained by serial dilution of the standard mixture. The first calibration curve (solvent calibration, SC) was prepared in pure acetone:*n*-hexane (2:8, v/v) solvent using the above concentrations. For the second calibration curve, the matrix extracts obtained from each product were prepared using the following procedure. The dried extracts were dissolved in 2 mL of the standard mixture at the same concentration as for the SC, and used for the matrix-matched calibration (MC) curve. The concentration of matrix in the MC was adjusted to 2.5 g/mL.

**Assessment of matrix effects** With the objective of evaluating the influence of matrix coextractives on the chromatographic responses of the target pesticides, matrix effects were assessed by comparing the chromatographic responses (area) obtained from MC with those from SC at the above mentioned concentration using the following calculated formula. All experiments were performed in triplicate for each level.

$$\text{Matrix effect}(\%)=(CR_{MC}/CR_{SC})\text{x}100 \quad (1)$$

where $CR_{MC}$ and $CR_{SC}$ mean the average value of the chromatographic response (area) obtained with MC and SC at the same concentration, respectively.

**Recovery study** A 50 g sample of each produce that had been confirmed not to have pesticide residues was fortified with the standard mixture at 0.5 mg/L to perform the recovery study. The spiked samples were then treated by the previously described extraction method. The recovery experiments were performed in triplicate, and the recovery rates were determined using the following equations.

$$R_{SC}=C_{SC}/C_{added} \quad (2)$$

$$R_{MC}=C_{MC}/C_{added} \quad (3)$$

where $R_{SC}$ is the recovery rate obtained with SC; $R_{MC}$ is the recovery rate obtained with MC; $C_{SC}$ is the concentration of pesticide quantified with SC; $C_{MC}$ is the concentration of pesticide quantified with MC; $C_{added}$ is the concentration of pesticide spiked in samples.

**Statistical analysis** In order to statistically compare the recovery rates obtained using SC and MC with a 100% recovery rate, a *t*-test was applied. Using Eq. 4, a *t*-statistic was calculated, $t_{cal}$, and compared with a *t*-tabulated, $t_{tab}$, for a confidence level of 95% (24). Statistical significance exists if $t_{cal}$ is not less than $t_{tab}$, meaning that the calculated recovery rates are statistically different from the 100% recovery rate.

$$t_{cal}=\frac{\sqrt{n}\times|R-100|}{S_R} \quad (4)$$

where *n* is the number of data in each calibration; *R* is the recovery rate determined with each calibration; $S_R$ is the standard deviation of the recovery rate.

## Results and Discussion

**Calibration curves of SC and MC** To measure matrix effects and recovery rates for organochlorine pesticides in six agricultural products, SC and MC calibration curves were separately prepared. The calibration curves for all analyzed pesticides were linear for all matrices ($r^2$>0.99). The slopes of the calibration curves varied based on the type of pesticide and matrix. In almost all cases, the analytical curves prepared for MC exhibited steeper slopes than those prepared for SC. The differences in the slope of each calibration curve between SC and MC for cypermethrin are shown in Fig. 1. The slopes of the calibration curves for broccoli, leek, and rice differed significantly from those of the other products. Considering these results, it is evident that matrix effects may be greatly influenced by the matrix components in each sample.

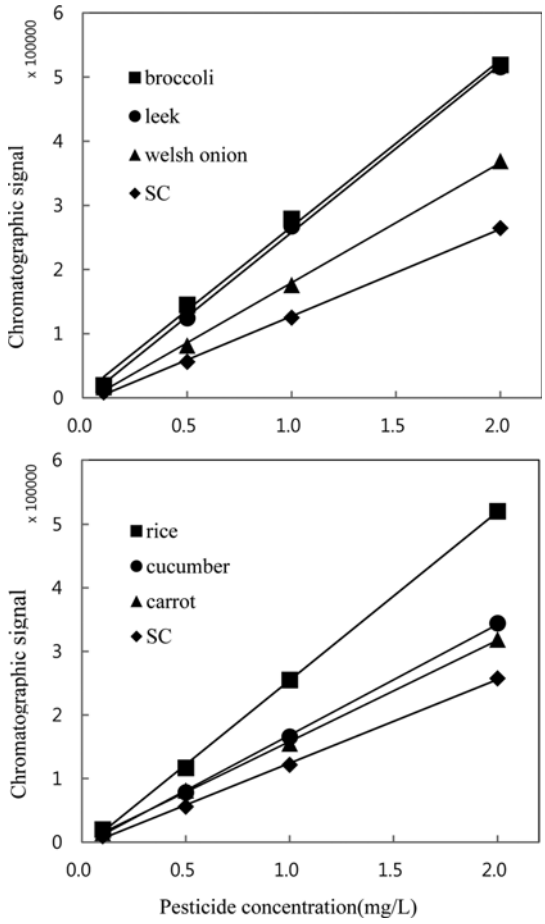


**Fig. 1.** Comparison of calibration curves between SC and MC prepared in agricultural product extracts for cypermethrin.

The disparities in the slopes of SC and MC calibration curves induce a proportional systematic error in GC chromatographic analysis, which are mainly caused by matrix components coextracted with analytes, and this error is generally attributed to the occurrence of matrix effects (25,26). Matrix effects can usually be expressed as positive (more than 100%) when the slope of MC is greater than that of SC. On the contrary, if the slope of MC is smaller than that of SC, matrix effects can be expressed as negative (less than 100%).

**Evaluation of matrix effects** Matrix blanks from broccoli, welsh onion, pepper, cucumber, leek, and rice, in which the absence of pesticide residues had previously been confirmed prior to the main experiment, were prepared by the previously described extraction method in order to assess matrix effects. The GC-ECD chromatograms

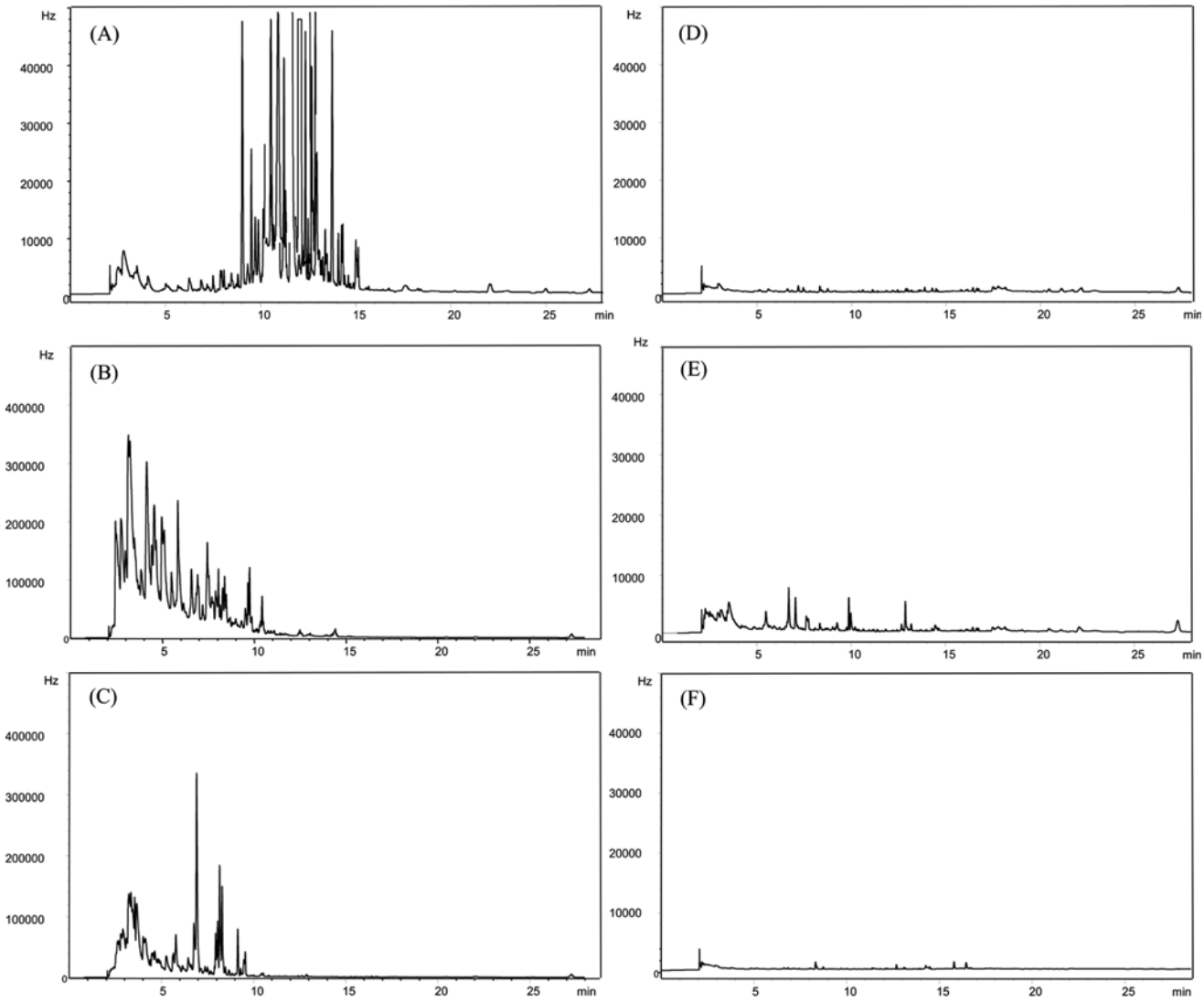


**Fig. 2.** GC-ECD chromatograms of blank sample extracts containing 2.5 g/mL of matrix concentration. (A) carrot; (B) welsh onion; (C) leek; (D) cucumber; (E) broccoli; (F) rice

of the matrix blanks are presented in Fig. 2. Each produce has a different composition of water, sugars, lipids, and colors, and these cannot be entirely eliminated in spite of cleanup steps in pesticide residue analysis (1,27). The matrix components present in an injected sample hinder the accurate analysis of pesticides and produce a peculiar chromatogram pattern for matrix blanks analyzed by GC. As shown in Fig. 2, the chromatograms of blank extracts from carrot, welsh onion, leek, and broccoli showed a lot of ghost (unknown) peaks, which are believed to originate from sulfur compounds and chlorophylls (27). Schenck *et al.* (28) reported that the ghost peaks in GC analysis were attributed to vegetables containing organic sulfur compounds (e.g., leek, onion, and welsh onion *etc.*) and suggested that the sulfur compounds could not be eliminated through the SPE cleanup process.

The mean values of matrix effects calculated using Eq. 1 at concentrations of 0.1, 0.5 1.0, and 2.0 mg/L in the six types of agricultural product extracts are presented in Table 1. It was observed that the matrix effect values for each pesticide were affected by the pesticide concentration and the matrix type. Generally, the greatest matrix effects were observed at the lowest concentration (0.1 mg/L) of each pesticide. These results were similar to previous results reported by Freita and Lancas (11) and Sousa *et al*. (12). This is because when a pesticide standard in pure solvent at low concentration is injected into a GC, a large amount of the pesticide interacts with the active sites in the liner and with the front parts of column, decreasing the chromatographic response. On the other hand, when a pesticide standard in a matrix extract at the same concentration is injected into a GC, the matrix components block the active sites of the liner, thus more amounts of the pesticide can get to the GC detector without interacting with the active sites, leading to increased chromatographic response (12). In addition, different values of matrix effects were acquired at the same concentration because of matrix diversity. The ranges of matrix effects observed from each produce were as follows: broccoli, 26.2-

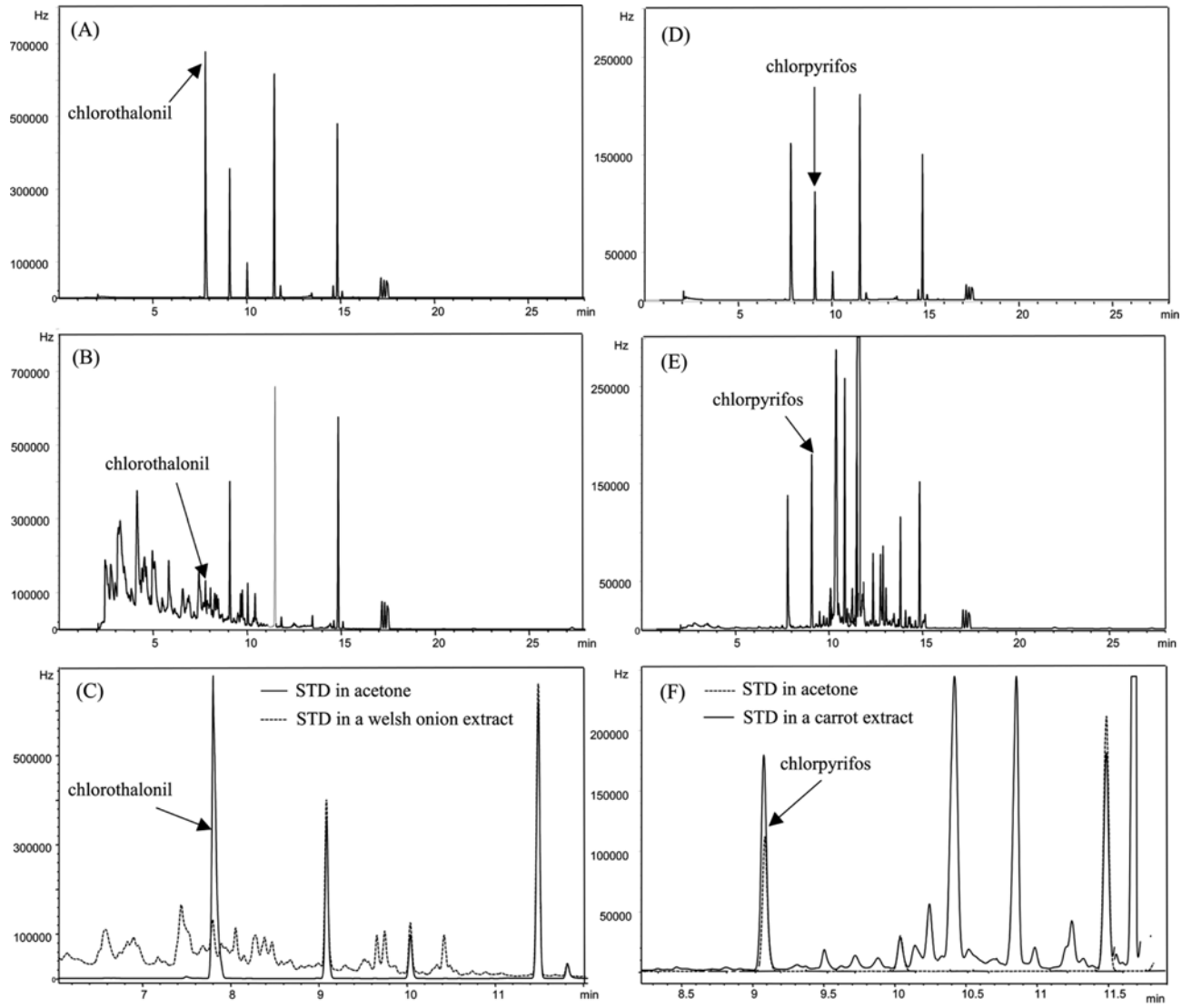


**Fig. 3.** GC-ECD chromatograms from standard mixture at 2.0 mg/L (A, B, C) and 0.5 mg/L (D, E, F). (A, D) STD in acetone; (B) STD in a blank welsh onion extract; (C) enlarged peak of chlorothalonil in overlaid chromatograms between (A) and (B); (E) STD in a blank carrot extract; (F) enlarged peak of chlorpyrifos in overlaid chromatograms between (D) and (E)

298.0%; welsh onion, 12.9-234.5%; carrot, 77.6-725.2%; cucumber, 106.8-205.4%; leek, 110.6-334.8%; rice, 104.6-248.4%.

The direct effect of the ghost peaks originating from matrix components on pesticide analysis are shown in Fig. 3. For chlorothalonil at 2.0 mg/L in welsh onion, the peak of chlorothalonil prepared in acetone was much bigger than that prepared in a blank welsh onion extract (Fig. 3C). Thus, the assessed matrix effects were in the range of ND-15.0% at all concentrations. The decrease in the chromatographic signal of chlorothalonil prepared in the blank welsh onion extract may be attributed to the matrix components of welsh onion, which possibly interact with chlorothalonil. As shown in Table 1, the values of matrix effects for chlorpyrifos in carrot were relatively large compared to those in other samples. As can be seen in Fig. 3E, a ghost peak with the exact retention time originating from a blank carrot extract overlapped with the chlorpyrifos peak, and enhanced the signal response of chlorpyrifos prepared in the blank carrot extract. When analyzing pesticide residues with GC, these effects are likely to result in analytical errors and inaccurate results.

The mean values of matrix effect for the analyzed pesticides in rice are presented in Fig. 4. Iprodione, cyhalothrin, and cypermethrin showed higher average values of matrix effects at 224.7, 157.4, and 208.7%, respectively. Meanwhile, chlorothalonil, chlorpyrifos, procymidone, and chlorfenapyr showed less matrix effects. Sugitate *et al*. (29) reported similar results, with matrix effects for cypermethrin and cyhalothrin in potato and brown rice using GC-MS of 319-353%. According to Fig. 4, a trend was observed in which some pesticides with longer retention times showed higher matrix effects. Sousa *et al*. (21) reported that similar results were observed in pesticides eluted at the end of a chromatographic run. Sanchez-Brunete *et al*. (17) suggested that the pyrethroid pesticides, such as cyhalothrin

**Table 1.** Matrix effects of organochlorine pesticides with different concentrations in agricultural product extracts

| Pesticide conc. (mg/L) | Matrix effect±SD (%)[1)] | | | | | |
|---|---|---|---|---|---|---|
| | Broccoli | Welsh onion | Carrot | Cucumber | Leek | Rice |
| Chlorothalonil | | | | | | |
| 0.1 | 26.2±9.2 | ND[2)] | 103.0±4.6 | 161.5±7.0 | 118.8±7.2 | 123.5±6.1 |
| 0.5 | 45.6±8.3 | 15.0±2.6 | 103.8±4.4 | 117.8±6.5 | 113.6±7.3 | 110.5±5.2 |
| 1.0 | 56.4±6.3 | 14.4±3.1 | 101.5±4.1 | 115.7±6.3 | 113.4±6.0 | 109.8±5.5 |
| 2.0 | 61.4±6.0 | 12.9±2.6 | 101.3±3.8 | 114.7±5.3 | 110.6±6.1 | 100.7±4.3 |
| Chlorpyrifos | | | | | | |
| 0.1 | 117.5±6.1 | 76.5±11.1 | 367.3±7.2 | 135.3±5.9 | 135.8±5.2 | 112.3±5.2 |
| 0.5 | 108.6±5.2 | 100.4±5.3 | 234.5±8.1 | 125.9±5.6 | 127.6±6.3 | 112.7±4.2 |
| 1.0 | 102.5±5.1 | 102.7±5.8 | 163.7±8.3 | 124.8±4.7 | 121.4±5.0 | 110.4±3.9 |
| 2.0 | 101.6±5.4 | 101.7±3.3 | 147.5±7.3 | 121.8±4.5 | 121.1±4.8 | 109.7±4.1 |
| Procymidone | | | | | | |
| 0.1 | 126.6±6.2 | 86.2±5.9 | 77.6±7.4 | 112.5±6.1 | 141.3±5.2 | 111.3±4.9 |
| 0.5 | 108.4±3.0 | 105.3±4.1 | 96.1±6.0 | 106.8±5.7 | 132.7±5.4 | 109.8±4.2 |
| 1.0 | 107.5±2.2 | 110.0±2.5 | 96.5±6.3 | 107.5±5.1 | 128.1±4.4 | 105.4±3.2 |
| 2.0 | 107.8±2.4 | 116.7±2.1 | 96.7±4.2 | 107.1±5.1 | 126.8±4.2 | 104.6±3.1 |
| Chlorfenapyr | | | | | | |
| 0.1 | 136.2±5.5 | 103.3±6.2 | 116.9±5.5 | 133.5±5.0 | 111.6±6.1 | 120.5±6.3 |
| 0.5 | 131.7±6.1 | 105.2±4.6 | 101.0±4.6 | 118.6±5.0 | 113.0±5.5 | 120.7±5.3 |
| 1.0 | 126.3±5.8 | 104.1±4.9 | 101.5±6.0 | 111.2±3.8 | 113.4±5.3 | 118.5±5.1 |
| 2.0 | 120.7±5.3 | 103.5±4.1 | 98.3±3.2 | 111.5±3.1 | 114.5±5.1 | 117.6±3.9 |
| Iprodione-1 | | | | | | |
| 0.1 | 202.5±11.0 | 104.2±6.8 | 725.2±19.9 | 176.5±9.1 | 175.3±8.0 | 248.4±11.0 |
| 0.5 | 193.6±9.3 | 94.6±5.1 | 591.8±13.5 | 133.5±7.1 | 173.7±7.9 | 207.2±8.8 |
| 1.0 | 190.4±9.1 | 83.2±5.1 | 407.4±12.4 | 130.8±6.1 | 171.9±7.3 | 202.7±7.2 |
| 2.0 | 184.9±7.5 | 79.5±5.2 | 300.3±10.9 | 124.5±5.1 | 166.1±6.8 | 190.4±6.1 |
| Iprodione-2 | | | | | | |
| 0.1 | 298.0±7.7 | 234.5±10.2 | 371.9±17.6 | 205.4±8.0 | 334.8±10.2 | 247.4±11.3 |
| 0.5 | 285.9±8.3 | 229.8±10.2 | 337.4±12.0 | 195.4±8.1 | 343.7±10.1 | 237.6±9.1 |
| 1.0 | 269.5±7.3 | 219.7±8.1 | 313.7±10.0 | 196.4±5.1 | 344.6±8.7 | 233.1±6.5 |
| 2.0 | 245.5±7.1 | 198.7±8.3 | 304.7±9.1 | 194.1±5.9 | 344.4±9.3 | 230.4±6.1 |
| Cyhalothrin-1 | | | | | | |
| 0.1 | 172.7±7.0 | 149.5±3.9 | 151.2±6.0 | 165.9±7.7 | 158.0±6.4 | 155.6±9.1 |
| 0.5 | 169.0±7.3 | 126.9±4.5 | 128.2±5.8 | 142.7±6.3 | 156.4±7.2 | 150.5±8.2 |
| 1.0 | 159.6±6.1 | 125.4±2.9 | 121.8±6.2 | 137.1±6.9 | 146.3±6.8 | 145.6±8.2 |
| 2.0 | 156.5±6.3 | 125.9±2.5 | 115.9±5.7 | 135.4±5.2 | 144.8±6.2 | 144.6±6.8 |
| Cyhalothrin-2 | | | | | | |
| 0.1 | 165.5±7.1 | 124.3±7.9 | ND | 135.3±6.9 | 132.1±6.5 | 171.2±8.9 |
| 0.5 | 159.3±5.7 | 115.4±5.8 | 124.0±6.3 | 129.0±5.6 | 122.8±6.2 | 166.0±8.8 |
| 1.0 | 158.5±5.1 | 112.4±6.9 | 118.7±6.1 | 129.3±6.2 | 122.5±5.0 | 164.5±8.3 |
| 2.0 | 157.1±4.9 | 110.5±6.3 | 110.6±5.1 | 128.1±4.8 | 119.4±4.5 | 160.8±7.0 |
| Cypermethrin | | | | | | |
| 0.1 | 231.8±9.1 | 194.3±6.1 | 157.2±7.0 | 167.1±6.9 | 225.4±9.8 | 213.4±9.4 |
| 0.5 | 220. ±6.5 | 145.6±5.3 | 145.5±6.3 | 140.3±6.7 | 210.9±9.8 | 209.4±9.1 |
| 1.0 | 214.4±6.0 | 140.5±6.3 | 127.4±5.2 | 136.4±6.2 | 204.1±7.8 | 209.7±8.1 |
| 2.0 | 196.7±6.3 | 139.5±5.3 | 123.7±5.3 | 133.6±6.1 | 195.5±7.2 | 202.1±6.6 |

[1)]Mean values±standard deviation (SD) as repeatability ($n$=3)
[2)]ND, not detectable

and cypermethrin, have a high molar mass (over 400 g/mol), which make them remain at the GC inlet longer and delay their volatilization when injected into the GC. Owing to this phenomenon, the pesticides may have a longer time to interact with the active sites of the GC inlet, thus much higher matrix effects can be obtained.

**Comparison of recovery rates** A study of recovery rates obtained with SC and MC separately was performed for pesticides spiked into agricultural products at 0.5 mg/L, and the results are presented in Table 2. Each recovery rate was calculated using Eq. 2 and 3, and then the calculated recovery rates were statistically compared with

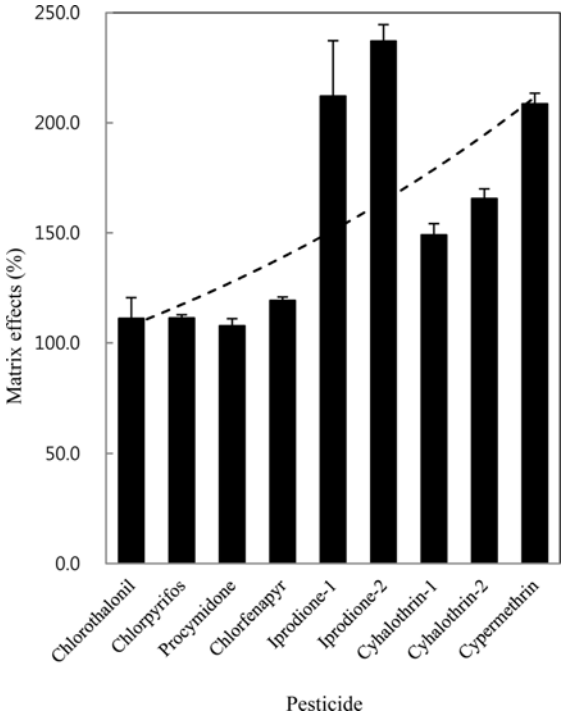


**Fig. 4.** Mean values of matrix effects for the analyzed pesticides in rice.

theoretical 100% recovery rate using a statistical paired *t*-test. A statistic *t* value, *t*-calculated, was obtained using Eq. 4.

Hill *et al*. (30) suggested that the matrix effect should be determined if a matrix effect is observed in the analytical range of pesticides, and the recovery rate of analyzed pesticides should be evaluated to validate an analytical method. The matrix effect has been known to be one of several factors that induce a higher recovery rate. In order to compensate the higher recovery rate, MC has been used as a validation tool. Generally, a recovery rate in the range of 70-110%, with a standard deviation of less than 20% is accepted as a reliable validation result (22).

As shown in Table 2, it was observed that the recovery rates obtained with SC were higher for iprodione-1 (83.0-506.8%), iprodione-2 (189.3-334.4%), cyhalothrin-1 (114.8-158.8%), cyhalothrin-2 (109.6-150.8%), and cypermethrin (125.5-201.0%) for almost all matrices. This suggests that the higher recovery rates are influenced by matrix effects. Erney *et al*. (4) proposed that some pesticides exhibiting greater matrix effects also showed higher recovery rates, which was consistent with our results. Menkissoglu-Spiroudi *et al*. (2) reported that pyrethroid pesticides showed higher recovery rates, with a range of 135-320%, in tomato and pepper. Hajslova *et al*. (7) also reported a range of recovery rates for cypermethrin and iprodione in

**Table 2.** Comparison between recovery rates obtained using SC and those using MC of organochlorine pesticides spiked in agricultural product extracts at 0.5 mg/L

| Pesticide | Commodity | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Broccoli | | Welsh onion | | Carrot | | Cucumber | | Leek | | Rice | |
| | $\overline{R}_{SC}\pm S_R$ [1] | $t_{cal\_SC}$ [3] | $\overline{R}_{SC}\pm S_R$ | $t_{cal\_SC}$ | $\overline{R}_{SC}\pm S_R$ | $t_{cal\_SC}$ | $\overline{R}_{SC}\pm S_R$ | $t_{cal\_SC}$ | $\overline{R}_{SC}\pm S_R$ | $t_{cal\_SC}$ | $\overline{R}_{SC}\pm S_R$ | $t_{cal\_SC}$ |
| | $\overline{R}_{MC}\pm S_R$ [2] | $t_{cal\_MC}$ [4] | $\overline{R}_{MC}\pm S_R$ | $t_{cal\_MC}$ | $\overline{R}_{MC}\pm S_R$ | $t_{cal\_MC}$ | $\overline{R}_{MC}\pm S_R$ | $t_{cal\_MC}$ | $\overline{R}_{MC}\pm S_R$ | $t_{cal\_MC}$ | $\overline{R}_{MC}\pm S_R$ | $t_{cal\_MC}$ |
| Chlorothalonil | 64.2±7.9 | 15.7 | 16.2±3.6 | 80.6 | 88.0±4.1 | 10.1 | 87.0±6.2 | 7.3 | 103.8±6.3 | 2.1 | 97.0±4.5 | 2.3 |
| | 101.9±5.1 | 1.1 | 101.6±2.8 | 2.0 | 102.4±3.8 | 2.2 | 101.6±5.7 | 1.0 | 97.8±5.8 | 1.3 | 99.7±4.1 | 0.2 |
| Chlorpyrifos | 100.4±5.1 | 0.3 | 99.0±6.7 | 0.5 | 211.3±7.1 | 54.3 | 85.0±5.2 | 10.0 | 115.6±5.7 | 9.5 | 104.8±3.7 | 4.5 |
| | 102.4±4.2 | 2.0 | 102.1±5.8 | 1.4 | 102.8±7.4 | 1.1 | 102.1±4.8 | 1.5 | 102.9±5.4 | 1.9 | 101.3±3.8 | 1.1 |
| Procymidone | 112.4±3.2 | 13.4 | 103.2±4.6 | 2.4 | 90.2±5.4 | 6.3 | 97.6±5.2 | 1.6 | 125.4±4.6 | 19.1 | 105.2±4.3 | 4.2 |
| | 100.5±2.7 | 0.6 | 102.6±5.2 | 1.7 | 102.6±4.8 | 1.9 | 101.0±4.5 | 0.7 | 100.7±4.1 | 0.6 | 102.3±4.4 | 1.8 |
| Chlorfenapyr | 114.4±5.5 | 9.1 | 101.4±5.2 | 0.9 | 95.0±4.2 | 4.1 | 102.8±4.5 | 2.2 | 110.2±5.1 | 6.9 | 116.8±4.8 | 12.1 |
| | 101.4±4.3 | 1.1 | 102.6±4.6 | 2.0 | 101.2±4.1 | 0.9 | 101.2±3.3 | 1.0 | 102.4±4.2 | 2.0 | 101.3±4.1 | 1.1 |
| Iprodione-1 | 190.3±9.2 | 34.0 | 83.0±12.4 | 4.7 | 506.8±11.3 | 124.7 | 90.8±6.5 | 4.9 | 156.4±7.4 | 26.4 | 181.6±8.1 | 34.9 |
| | 98.6±6.4 | 0.8 | 104.5±11.5 | 1.3 | 104.2±10.4 | 1.4 | 96.3±6.7 | 1.9 | 102.7±6.5 | 1.4 | 97.2±6.4 | 1.5 |
| Iprodione-2 | 263.6±8.2 | 69.1 | 201.2±11.2 | 31.3 | 334.4±10.5 | 77.3 | 189.3±7.8 | 39.7 | 322.1±9.4 | 81.8 | 216.8±7.8 | 51.9 |
| | 101.4±5.4 | 0.9 | 102.8±10.4 | 0.9 | 103.6±10.1 | 1.2 | 102.8±7.1 | 1.4 | 103.1±7.5 | 1.4 | 97.8±6.6 | 1.2 |
| Cyhalothrin-1 | 158.8±7.1 | 28.7 | 120.6±5.6 | 12.7 | 114.8±5.1 | 10.1 | 116.0±6.2 | 8.9 | 148.4±6.3 | 26.6 | 142.8±8.1 | 18.3 |
| | 102.3±5.3 | 1.5 | 102.7±5.9 | 1.6 | 104.8±4.6 | 3.6 | 102.6±5.6 | 1.6 | 102.7±6.1 | 1.5 | 97.4±7.5 | 1.2 |
| Cyhalothrin-2 | 150.8±5.5 | 32.0 | 116.8±6.6 | 8.8 | 113.0±5.7 | 7.9 | 109.6±5.2 | 6.4 | 114.4±6.1 | 8.2 | 147.7±8.2 | 20.1 |
| | 99.2±4.6 | 0.6 | 97.2±5.8 | 1.7 | 97.2±6.2 | 1.6 | 102.8±5.6 | 1.8 | 102.8±5.3 | 1.8 | 96.8±7.2 | 1.5 |
| Cypermethrin | 201.0±6.1 | 57.4 | 136.8±6.2 | 20.6 | 132.4±6.2 | 18.1 | 125.5±6.2 | 14.2 | 183.1±8.8 | 32.7 | 190.8±8.8 | 35.7 |
| | 102.0±5.7 | 1.2 | 102.5±6.6 | 1.3 | 101.6±5.1 | 1.1 | 103.4±6.1 | 2.0 | 102.9±7.5 | 1.3 | 98.8±7.4 | 0.6 |

[1] $\overline{R}_{SC}$, The mean value of recovery rates of the spiked sample quantified with SC; $S_R$, Standard deviation of recovery rates ($n$=3)
[2] $\overline{R}_{MC}$, The mean value of recovery rates of the spiked sample quantified with MC
[3] $t_{cal\_SC}$, The value of $t$ calculated applying recovery rates quantified with SC
[4] $t_{cal\_MC}$, The value of $t$ calculated applying recovery rates quantified with MC
$t_{tab}$=2.2, The value of $t$ tabulated for degree of freedom f=11 at 95% confidence level

various vegetables of 151-319% and 118-204%, respectively.

As shown in Table 2, the values of $t_{cal\_SC}$ were greater than $t_{tab}$=2.2 in most cases except for chlorothalonil in leek ($t_{cal\_SC}$=2.1), chloropyrifos in broccoli ($t_{cal\_SC}$=0.3) and welsh onion ($t_{cal\_SC}$=0.5), procymidone in cucumber ($t_{cal\_SC}$=1.6), and chlorfenapyr in welsh onion ($t_{cal\_SC}$=0.9) and cucumber ($t_{cal\_SC}$=2.2), which meant that the recovery rates obtained with SC statistically differed from a 100% recovery rate in most matrices. On the other hand, the recovery rates obtained with MC showed different results, and are also presented in Table 2. The recovery rates quantified with MC were in the range of 96.3-104.8%, indicating that the values of $t_{cal\_MC}$ were less than $t_{tab}$ in almost all matrices except for cyhalothrin-1 in carrot ($t_{cal\_MC}$=3.6), which meant that the recovery rates quantified with MC did not statistically differ from a 100% recovery rate.

In conclusion, matrix effects due to the presence of matrix coextractives from six different agricultural products have been determined during the analysis of pesticide residues with GC-ECD. The standard mixture was dissolved in pure solvent and blank matrix extracts to prepare two calibration curves, SC and MC, which were utilized to calculate matrix effects. It was confirmed that the intensity and variability of matrix effects are dependent on the matrix type and the concentration of pesticides studied. The recovery rates quantified with MC were not statistically different from a 100% recovery rate, meaning that the overestimation and/or underestimation of recovery rates were largely due to matrix effects. The application of MC to overcome matrix effects in pesticide multiresidue analysis using GC-ECD may be a useful tool to acquire more accurate results.

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