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Application News

No. M279

GC/MS/MS

Study of a Method for Coping with Matrix Effects in Pesticide Residue Analysis Using GC/MS/MS

One of the issues cited in the analysis of pesticide residues in food using GC/MS/MS is the matrix effect that causes abnormal recovery rates. The matrix effect is a phenomenon where the matrix sample has a higher response for pesticide residues than the standard sample. It occurs because adsorption and decomposition occur at the active site with standard samples where there is no matrix, but in cases where there is a matrix the matrix coats the active site (Fig. 1).

The method of adding an analyte protectant (AP) is used as a countermeasure to reduce the matrix effect. Polyethylene glycol (PEG) 300 can be cited as a representative AP. K. Mastovska et al. have also reported a method where a sample of mixed ethylglycerol, sorbitol, and gulonolactone are used as a useful AP mixture. [1)]

In this article, we report on the results of studying a method for coping with matrix effects when PEG300, and a combination of AP, were used.

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■ Sample and Analysis Conditions

As the standard sample of pesticide for the spike and recovery test, we used a 312-component mixed standard solution, and as matrix samples we used spinach, orange, and brown rice respectively.

After extracting each matrix sample with acetonitrile, it was purified in a solid phase and the pesticide was added to bring the final concentration to 5 ppb.

When using PEG300 as an AP, acetone/ hexane solvents were used as the final solvent for both the standard sample and the matrix sample, and PEG300 was added so as to bring its final concentration to 200 µg/mL.

When using the combination of AP, acetonitrile solvent was used as the final solvent, and three kinds of analyte protectants were added to it. The composition and concentration of the AP mixture were prepared in accordance with the method reported by K. Matovska et al. (2005). For comparison, the same experiment was carried out with a sample consisting of the solvent only without adding an AP.

Table 1 shows the instruments used and the analysis conditions.

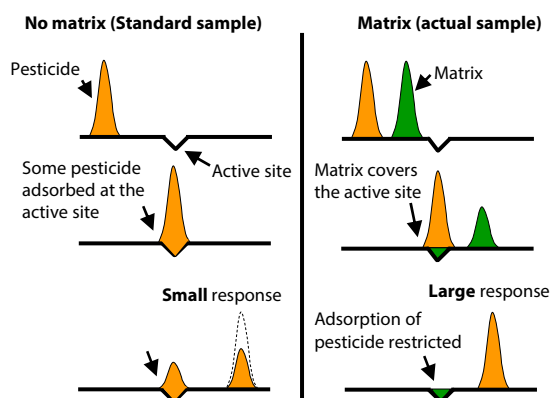The analysis method was created using Smart Pesticides Database™ Ver. 2.

No matrix (Standard sample)

Pesticide

Some pesticide adsorbed at the active site → Active site

Small response

Matrix (actual sample)

Matrix

Matrix covers the active site

Large response

Adsorption of pesticide restricted

Fig. 1 **Abnormal Area Value Due to Matrix Effect**

Table 1 **Instruments Used and Analysis Conditions**

Instrument used

GCMS	: GCMS-TQ™ 8050
Autosampler	: AOC-20i+s
Column	: SH-Rxi™-5Sil MS (L: 30 m, df: 0.25 µm, ID: 0.25 mm)
Pre-column	: SH-Rxi™ Guard Column (L: 1.5 m, ID: 0.25 mm)
Insert liner	: Topaz Liner, Splitless Single Taper w/Wool

GC conditions (PEG added)

Vaporizing chamber temperature	: 250 °C
Injection volume	: 2 µL
Injection mode	: Splitless
Carrier gas control	: Linear speed (47.2 cm/sec)
Column oven temperature	: 50 °C (1 min) → (25 °C/min) → 125 °C → (10 °C/min) → 300 °C (15 min)

GC conditions (AP added)

Vaporizing chamber temperature	: 250 °C
Injection volume	: 2 µL
Injection mode	: Splitless
Carrier gas control	: Linear speed (44.1 cm/sec)
Column oven temperature	: 105 °C (3 min) → (10 °C/min) → 130 °C → (4 °C/min) → 200 °C → (8 °C/min) → 290 °C (6 min)

MS Conditions

Interface temperature	: 250 °C
Ion source temperature	: 230 °C
Ionization method	: EI
Measurement mode	: MRM
Event time	: 0.3 sec
Loop time	: 0.5 sec

■ Effect of Pseudo-Matrix Addition

It was found that the addition of PEG300 or AP mixture leads to coating of the active site in the line, improving the response when compared with cases where no AP is added. Fig. 2 shows a comparison of mass chromatograms for standard samples, 5 ppb, of Esprocarb and Pyriproxyfen with and without an AP.

For standard samples with no matrix, the calibration curve becomes curved due to the major influence of adsorption and decomposition of the pesticide at the active site at low pesticide concentrations, which is an issue. The addition of an AP prevents the adsorption and decomposition of the pesticide and improves the linearity of the calibration curve. Fig. 3 shows a comparison of the calibration curves for Fosthiazate and Edifenphos that resulted on analysis of standard pesticide samples with no AP added, with PEG300 added, and with AP mixture added. The linearity of the calibration curve was improved by adding an AP.
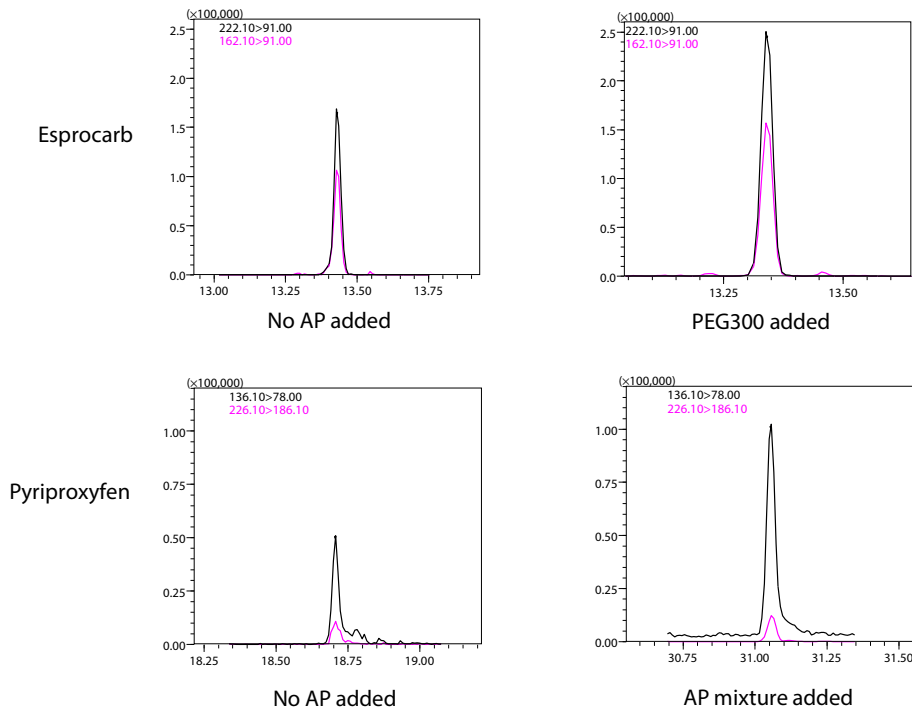
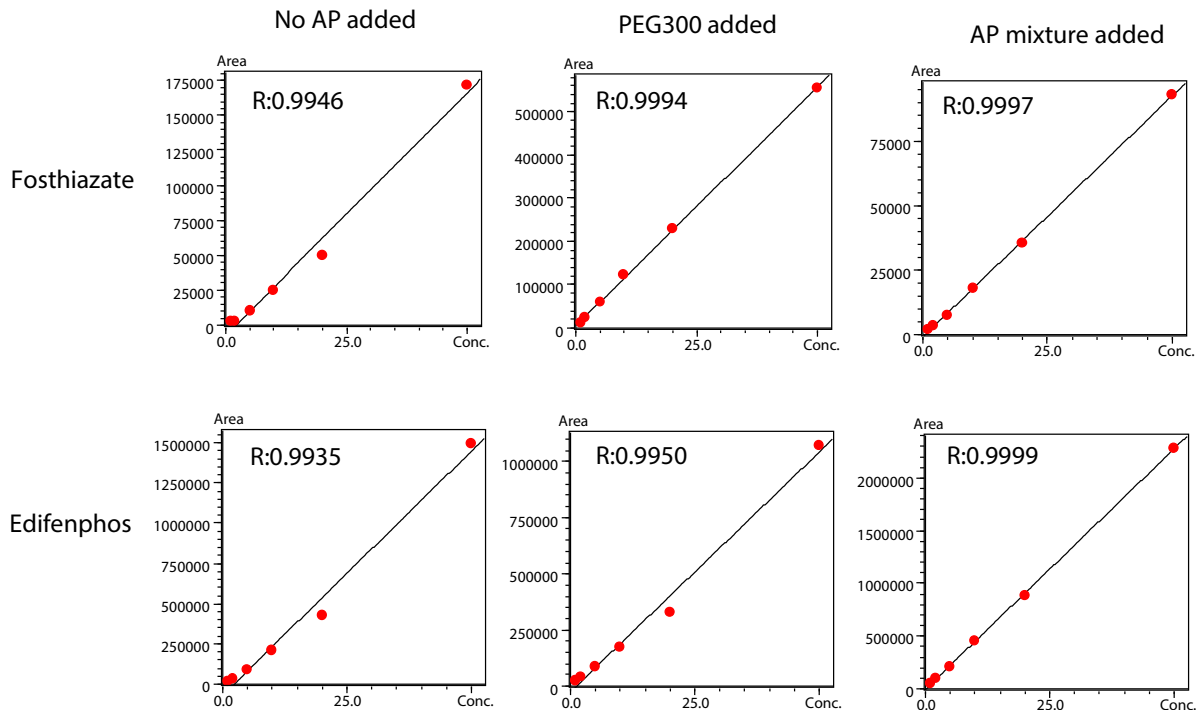Fig. 2 **Comparison of Mass Chromatograms of Standard Samples, 5 ppb, With and Without an AP**

Fig. 3 **Calibration Curve Results for Fosthiazate and Edifenphos on Analysis Using Standard Pesticide Samples**

■ **Spike and Recovery Tests**

Fig. 4 shows the recovery rates for each matrix sample (brown rice, orange, spinach) with no AP added, with PEG300 added, and with AP mixture added. Also, as an example, Table 2 shows a comparison of the recovery rates for Dimethametryn and fenitrothion. When no AP was added, many pesticides had a recovery rate exceeding 120 %, and around 15 % of compounds had a recovery rate of 70 % to 120 %. On the other hand, when PEG300 and AP mixture were added, the 70 % to 120 % recovery rate of pesticides was improved to around 70 % and around 90 % of compounds respectively. This shows that adding an AP can improve the recovery rate with many pesticides.
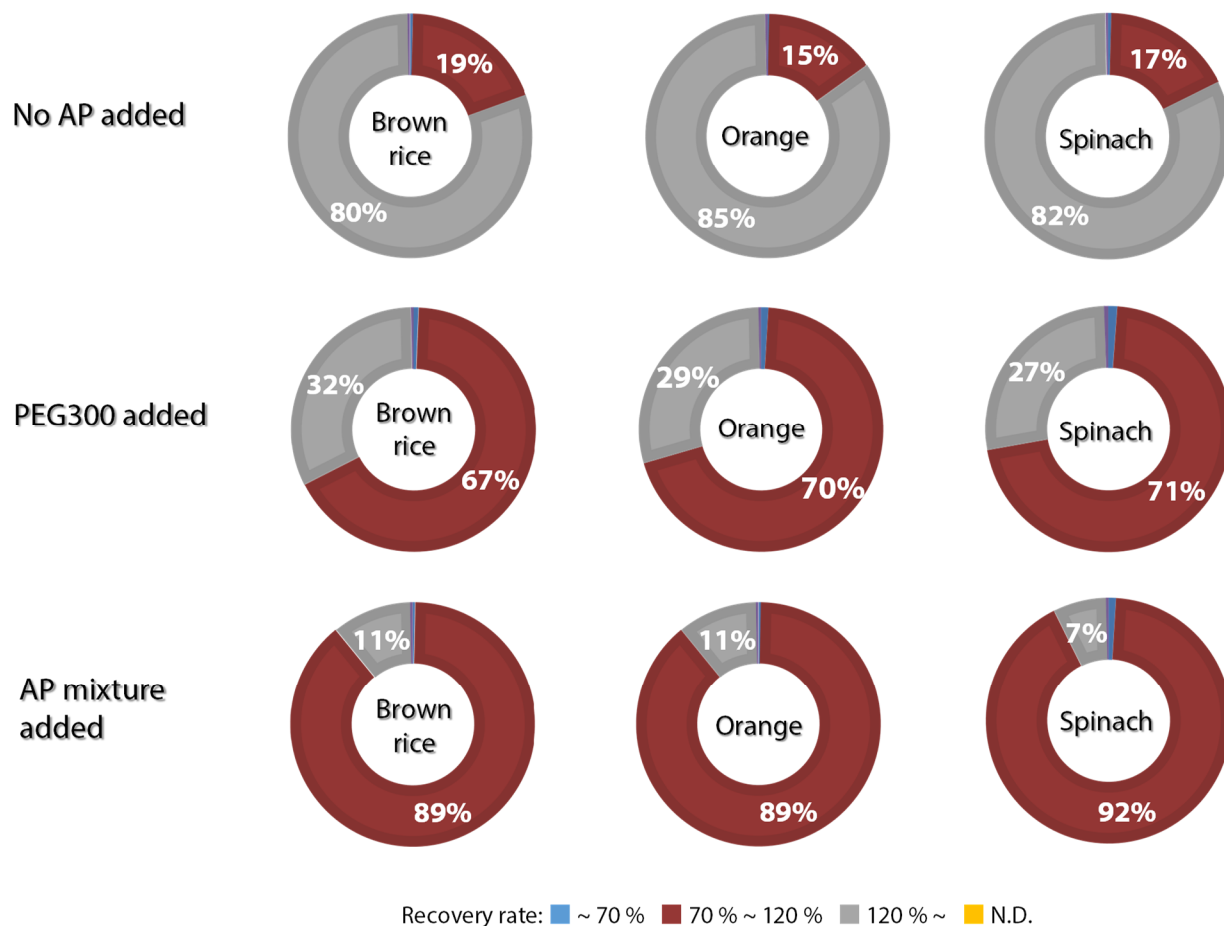

Recovery rate: ■ ~ 70 %   ■ 70 % ~ 120 %   ■ 120 % ~   ■ N.D.

Fig. 4 **Comparison of Recovery Rates for Actual Samples According to the Type of AP Added**

Table 2 **Comparison of the Recovery Rates of Dimethametryn and Fenitrothion in Actual Samples According to the Type of Matrix Added**

Dimethametryn	Brown rice		Orange		Spinach	
	Recovery rate	%RSD	Recovery rate	%RSD	Recovery rate	%RSD
No AP added	130	2.53	134	3.46	126	7.43
PEG300 added	106	1.24	108	2.90	103	4.32
AP mixture added	103	2.22	106	2.42	102	4.46

Fenitrothion	Brown rice		Orange		Spinach	
	Recovery rate	%RSD	Recovery rate	%RSD	Recovery rate	%RSD
No AP added	153	9.41	158	3.09	134	8.08
PEG300 added	111	6.80	118	3.84	117	4.75
AP mixture added	105	2.01	108	2.07	105	2.56

■ Notes on AP Addition

We were able to confirm the reduction of matrix effects as a result of adding PEG300 and AP mixture. However, addition of PEG300 and AP mixture promoted the decomposition with some pesticides and increased the background level with other pesticides. Fig. 5 shows chromatograms for iprodione, whose decomposition has been promoted by the addition of PEG300, and Demeton-S-methyl, whose background level have been increased by the addition of AP mixture.
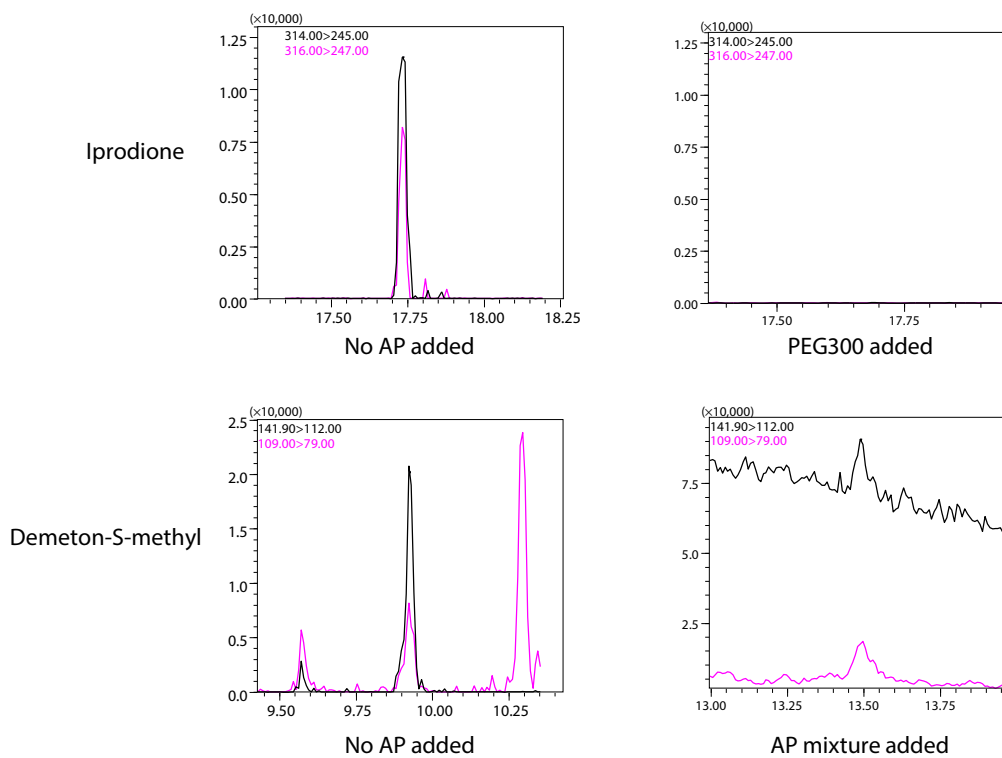

Fig. 5 **Pesticides Whose Peak Shape has been Affected by Adding a Pseudo-Matrix**

■ Conclusion

We investigated the effect of addition of PEG300 and AP mixture as a countermeasure to reduce the matrix effect in the analysis of pesticide residues using GC/MS/MS. The result was that it was possible to greatly improve abnormal recovery rates due to matrix effects by adding PEG300 and AP mixture. In addition, it is considered that the AP mixture is more effective than PEG300.

References
1) K. Matovska, S.J. Lehotay, M. Anastassiades, Anal. Chem. 77 (2005) 8129-8137

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