

Simultaneous Analysis of 477 Residual Pesticides in Agricultural Crops Using GC-MS/MS

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1: Introduction

GC-MS/MS systems can measure more than 400 residual pesticides in foods. However, analyzing more than 400 pesticides simultaneously requires a short dwell time (data loading time) during MRM measurements, which results in problems with inadequate sensitivity and the tedious process of creating MRM measurement programs. Consequently, several different methods are used for target pesticides and the same sample is measured multiple times to analyze all components. That can decrease productivity, due to the time required for analyzing all the components involved in the large number of pesticides being inspected. This Application Data Sheet describes a solution to these problems with the creation of a method for simultaneously analyzing 477 components and evaluating the resulting sensitivity and accuracy.

2: Experiment

2-1: Sample Preparation

Matrix solutions were prepared by processing soy bean, orange, brown rice, and spinach samples according to a pretreatment procedure for residual pesticide analysis, and then purifying them using the GPC Cleanup System (from Shimadzu Corporation).¹⁾ Measurement sample solutions (1 g/mL sample concentration) were then prepared by spiking the prepared matrix solutions with 477 components (including internal standard substances) to a concentration of 5 ppb (or 200 ppb for the internal standard substances). 19 kinds* of surrogate pesticides were used as the internal standard substances.

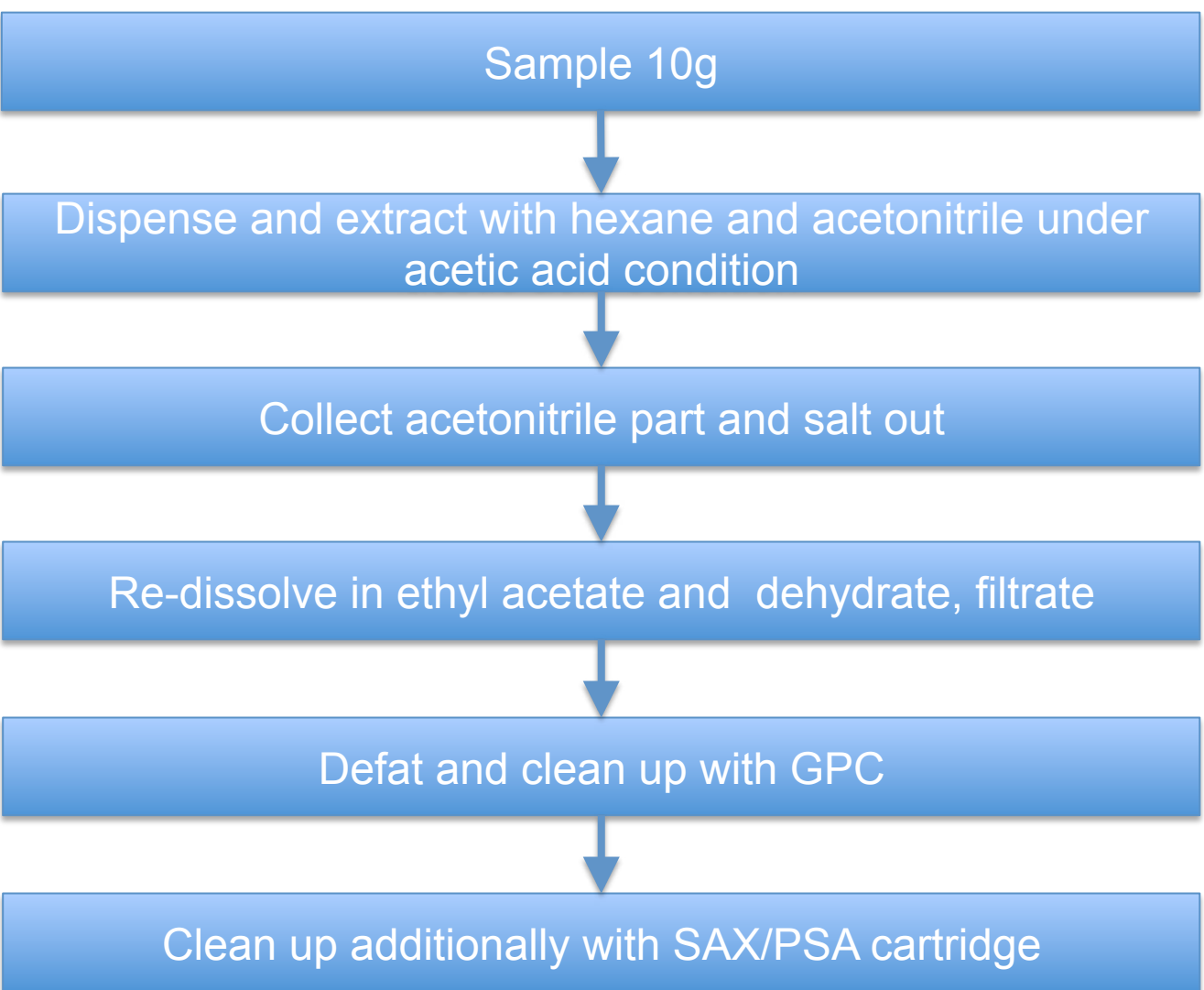


Fig. 1: Procedure of sample preparation

2-1: Analysis Conditions

The GCMS-TQ8040 combined with the Twin Line MS System was used to measure samples based on the following analytical conditions. Two transitions were specified for each component, one for quantitation and the other for confirmation, and Smart MRM was used to automatically create a measurement program.

Fig. 2: Analytical Program created by Smart MRM for column 1



Figure in parentheses is dwell time for 1 ch

2-1: Analysis Conditions, continued

[Instrument]
GC-MS: GCMS-TQ8040 (Twin Line MS System, Shimadzu)
SH-Rxi-5Sil MS (Length 30 m, 0.25 mm I.D., df=0.25 µm, Shimadzu)
SH-Rtx-200MS (Length 30 m, 0.25 mm I.D., df=0.25 µm, Shimadzu)
Liner: Sky Liner, Splitless Single Taper Gooseneck w/Wool (Restek)
Software: GCMSsolution Ver. 4.2 (Shimadzu)

[GC]
Injection Temp.: 250 °C
Column Oven Temp: 60 °C (1 min), 25 °C/min to 160 °C, 4 °C/min to 240 °C, 10 °C/min to 290 °C (11 min)
Injection Mode: Splitless (High Pressure Injection 250 kPa, 1.5 min)
Carrier Gas Control: Linear Velocity (40.0 cm/sec)
Injection Volume: 2 µL

[MS]
Interface Temp.: 300 °C
Ion Source Temp.: 200 °C
Measurement Mode: MRM
Loop Time: 0.4 sec
Processing Time: 0.3 min



3: Results

3-1. Consideration of Analysis Method

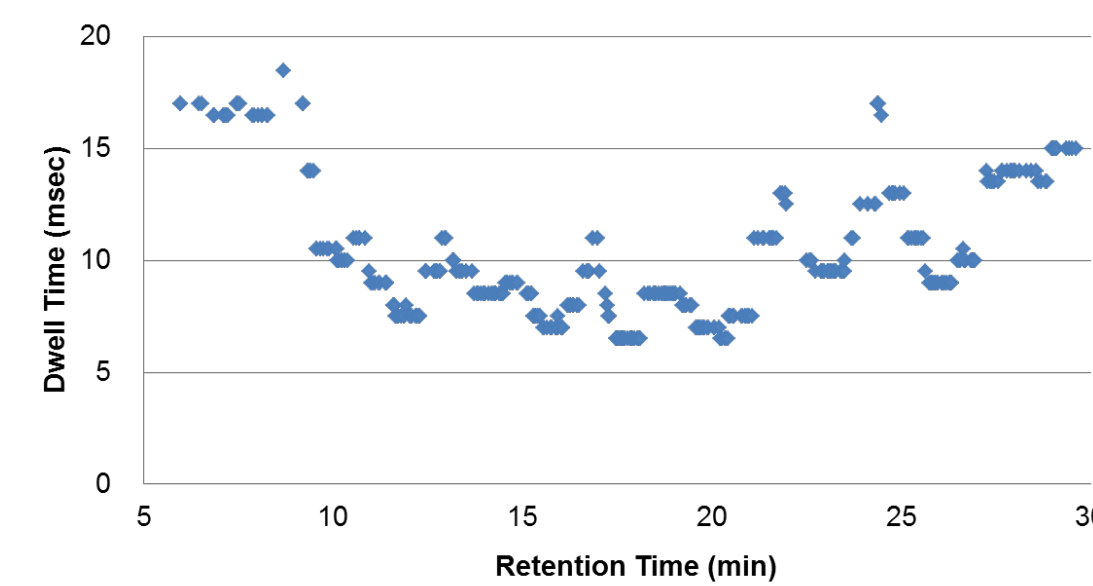


Fig. 3: Relationship Between Retention Time and Dwell Time (for retention times from 5 to 30 minutes)

The average dwell time for all components was 12.3 msec, with over 6.5 msec provided even for retention time bands where a high number of pesticides were eluted by Smart MRM.

3-2. Analytical Accuracy

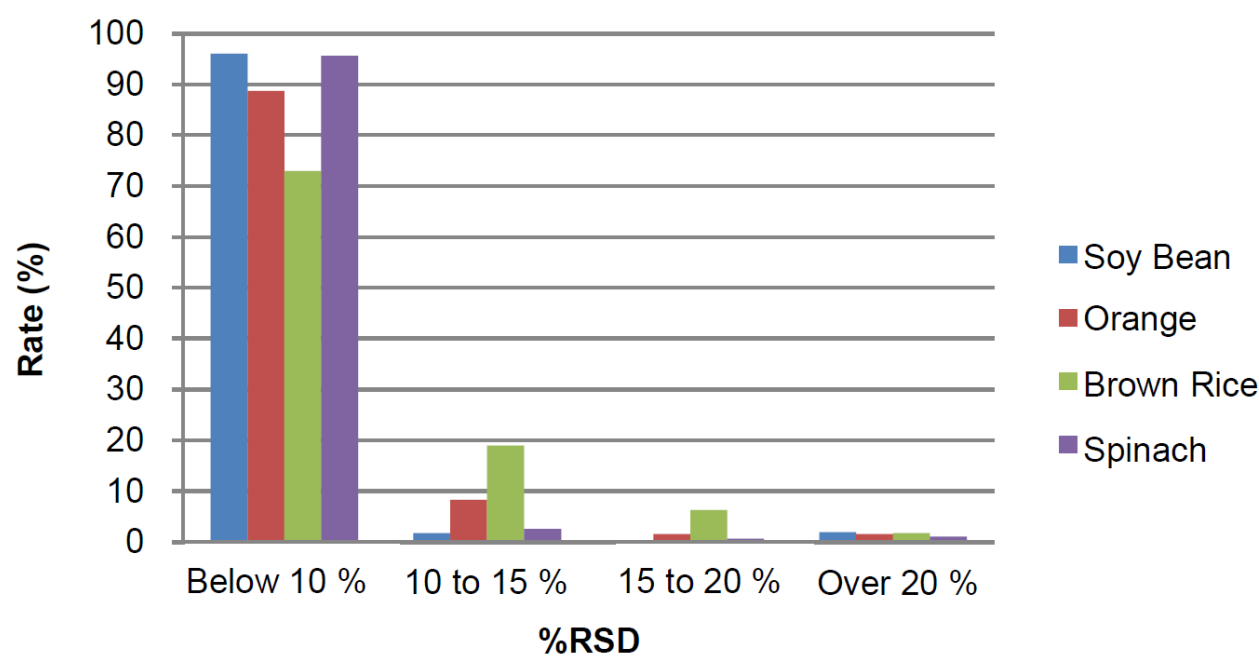


Fig. 4: %RSD Distribution for Each Matrix

This shows that %RSD (n = 5) was 10 % or less for 88 % of targets (1618 of the 1832 components in four types of matrix), which indicates that high analytical accuracy was achieved when analyzing as many as 477 components simultaneously.

Due to matrix interference, some pesticide peaks cannot be detected properly with column 1, but using column 2 allows separation of the matrix and results in accurate detection. Furthermore, high-precision analytical results can be obtained even when using column 2.

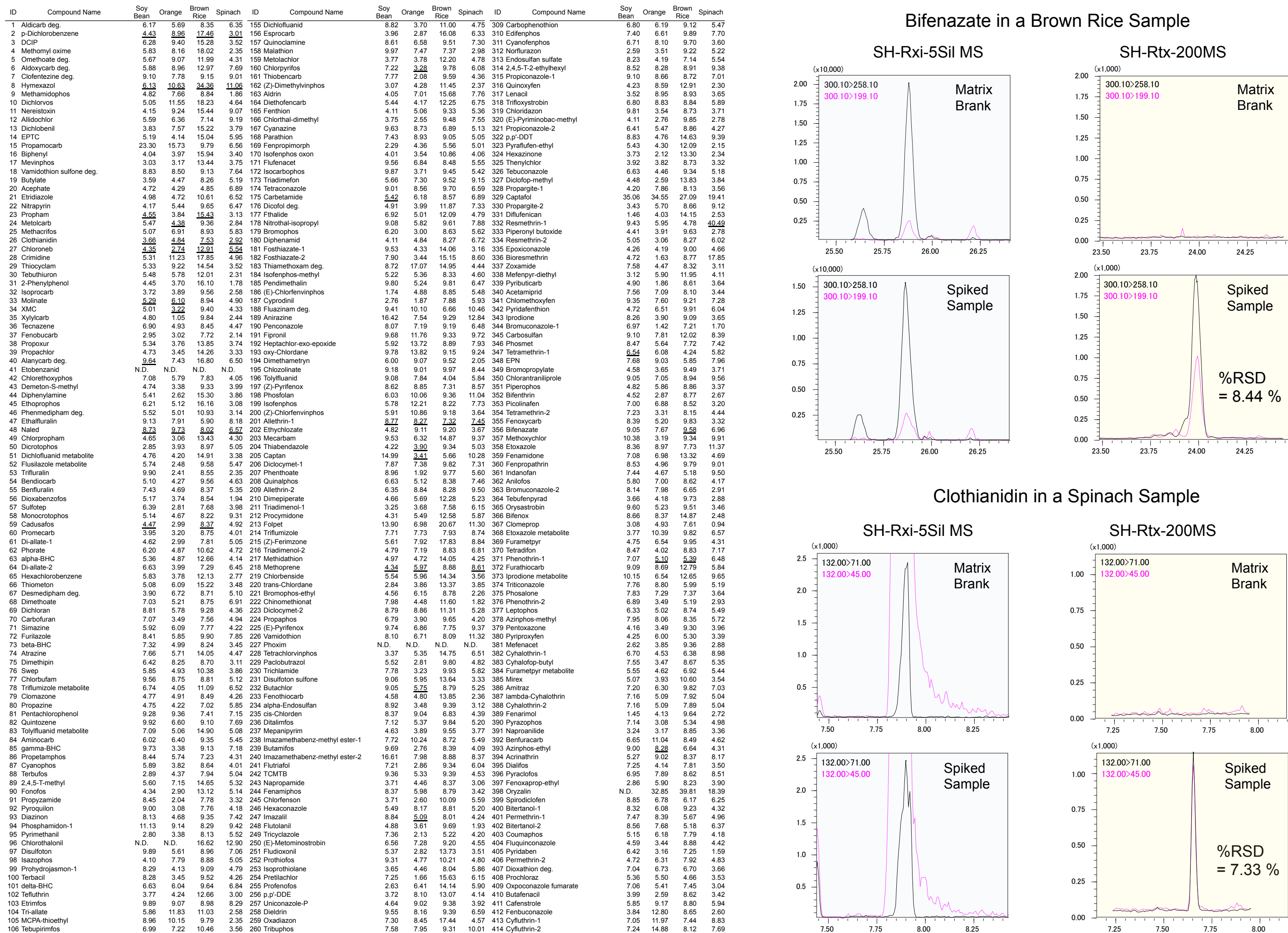


Fig. 5 Matrix Separation by Twin Line MS System

4. Conclusion

- High analytical accuracy was achieved when analyzing as many as 477 components simultaneously.
- By eliminating the need to split the analysis using multiple methods, the number of injections is reduced and productivity increased. This also allows maintenance frequency and costs to be minimized

5. References

1) E. Ueno, et al., *J. AOAC INT.* **87**, (2004) 1003–1015

*Dichlorvos=*d*₆, Acephate=*d*₆, Diazinon=*d*₁₀, Iprobenfos=*d*₇, Carbaryl=*d*₇, Fenitrothion=*d*₈, Linuron=*d*₆, Metolachlor=*d*₆, Chlorpyrifos=*d*₁₀, Diethofencarb=*d*₇, Fosthiazate=*d*₅, Pendimethalin=*d*₅, Thiabendazole=¹³C₆, Imazalil=*d*₆, Isoprothiolane=*d*₆, Isoxathion=*d*₁₀, EPN=*d*₆, Etofenprox=*d*₆, and Esfenvalerate=*d*₇

Table 1 %RSD (n = 5) of Samples Spiked with Pesticides (5 ppb)

Items determined to have 20 % or more overlap (area values) between pesticide-spiked and blank samples are underlined (reference data). Excludes the 19 internal standard substances.