SHIMADZU

Application Data Sheet

No.31

GCMS

Gas Chromatograph Mass Spectrometer

Analysis of Residual Pesticides in Foods Using Twin Line GC-MS

To obtain highly reliable data from analyzing residual pesticides in foods by GC requires confirmation tests using columns with different liquid phases. In contrast, with GC-MS, confirmation is possible by using not only retention times, but also m/z values. Therefore, normally only one type of column is used for tests. However, due to the increased number of pesticides and the diversification in substances subject to inspection, users are demanding higher reliability by using columns with different liquid phases, even for GC-MS analysis.
Therefore, a Twin Line MS Kit, which enables the installation of two types of columns with different liquid phases in one MS, without the use of splitters or flow restrictors, was used to analyze residual pesticides in food.

Experiment

Test Solution Preparation Method

To evaluate the effectiveness in analyzing actual samples, test solutions of six agricultural products: spinach, carrots, cabbage, brown short-grain rice, oranges, and apples, were prepared in accordance to the test method specified by the Japanese Ministry of Health, Labour, and Welfare – Method of Simultaneous Testing for Pesticides and Other Components (in Agricultural Products) [1]. Pesticides were then added to these test solutions to a concentration of 0.1 µg/mL.

Analytical Conditions for Twin Line GC-MS

The following analytical conditions were used to measure the test solutions. Columns 1 and 2 each had a dedicated sample vaporization chamber, each of which was used alternately for analysis.

GC-MS :GCMS-QP2010 Ultra (Twin Line MS kit)
Column1 :Rtx-5MS (30 mL. x 0.25 mmI.D., 0.25 µm)
Column2 :Rtx-OPPesticides2 (30 mL. x 0.25 mmI.D., 0.25 µm)

[GC]
Vaporization chamber temperature : 250℃
Column oven temperature: 50 ℃(1 min) -> (25 ℃ /min) -> 125 ℃ -> (25 ℃ /min) -> 300 ℃ (15 min)
Injection mode : : Splitless (Sampling time: 1 min)
High pressure injection: 250 kPa (1.5 min)
Carrier gas : Helium
Control mode :Linear velocity (47.2 cm/sec)
Injection quantity :2.0 µL

[MS]

Interface temperature	: 250℃	Ion source temperature	: 200℃
Measurement mode	: Scan	Mass range	: *m/z* 50-460
Event time	: 0.5 sec	Emission current	: 60 µA (normal)

＜Twin Line MS System＞
Connecting two different columns to the MS unit at the same time allows the smooth acquisition of application data with different columns, without shutting off the MS vacuum.
The outlets of the two columns were connected directly to the mass spectrometer interface, without using flow restrictors. Therefore, the same retention times and retention indices can be used as in methods for a single column. Due to the lack of losses for adsorption or other factors and due to the high-capacity differential vacuum system, the same sensitivity levels can be obtained as for a single column.

Results and Discussion

Column Selection

When two types of columns are used, elution patterns must be different. Therefore, it is reasonable to combine a low polarity column with a middle polarity column. In addition, since two columns are installed in the same column oven, the maximum operating temperature capacity must be at least 300 ° C for both columns (maximum temperature for heating parameters). Therefore, based on results previously reported [2], Rtx-5MS (330/350 ° C) and Rtx-OPPesticides 2 (310/330 ° C) columns were selected.

Overlap Between Added Pesticides and Impurities

Figures 1 and 2 show examples of how the overlap between pesticides and impurities differs for the two columns. In Figure 1 results for Rtx-OPPesticides2, Fenvalerate-2 is affected by impurities, but for Rtx-5MS, it is not affected by impurities.

In Figure 2 results for Rtx-5MS, Triadimenol-1 is affected by impurities, but for Rtx-OPPesticides2, it is not affected by impurities.

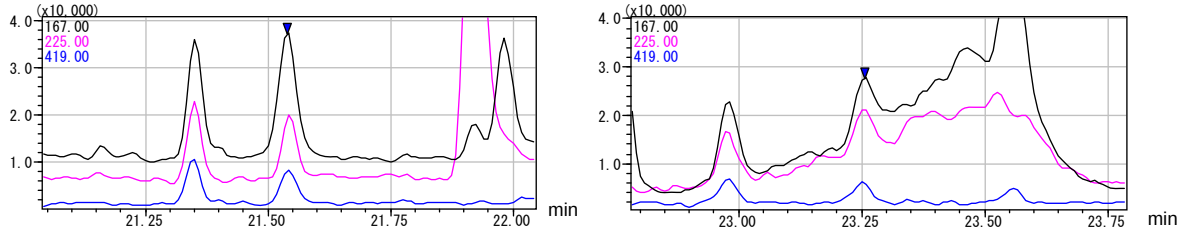

Fig. 1: Mass Chromatogram of Orange Extract Spiked with Fenvalerate-2 (left: Rtx-5MS; right: Rtx-OPPesticides2)

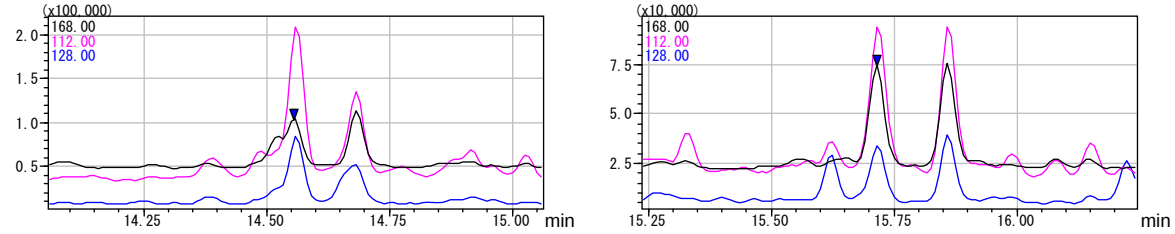

Fig. 2: Mass Chromatogram of Brown Rice Extract Spiked with Triadimenol-1 (left: Rtx-5MS; right: Rtx-OPPesticides2)

Verifying Detection of Pesticides in Actual Samples

For Rtx-5MS, an impurity peak coexists at the retention time for captan, as shown in Figure 3, which makes it difficult to determine whether or not captan is present. However, for Rtx-OPPesticides2, there are no impurity peaks coexisting at the retention time for captan, which makes it easy to determine that the pesticide was not detected.

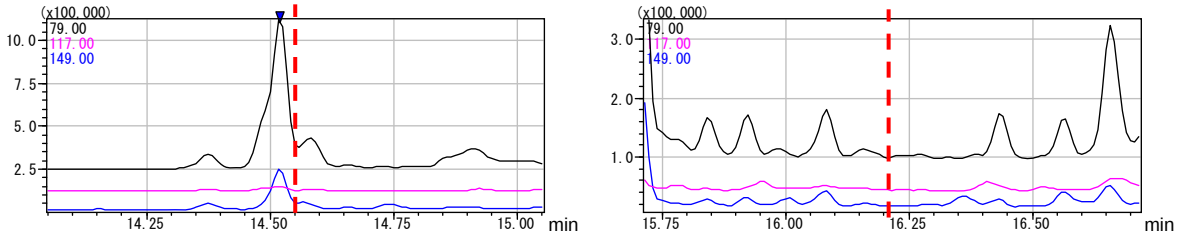

Fig. 3: Mass Chromatogram of Brown Rice Extract at the Retention Time for Captan (left: Rtx-5MS; right: Rtx-OPPesticides2)

References
[1] Test method specified by Japanese Ministry of Health, Labour, and Welfare;
http://www.mhlw.go.jp/topics/bukyoku/iyaku/syoku-anzen/zanryu3/3-001.html
[2] By Ueno, Ohshima, Saito, Matsumoto; Journal of the Food Hygienic Society of Japan 41, 385-393(2001)

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