Study on higher sensitivity for analysis of pesticide residues in foods by using GC-MS/MS (3)

Product used : Mass spectrometer (MS)

Introduction

The analysis of pesticide residues in foods requires the separation and detection of trace amounts of target pesticides present in complex matrices, and therefore, analytical instruments used for such measurements must have high performance. The GC-MS/MS method is effective for simultaneous analysis of multiple components in complex matrices, and is currently used by many analytical institutions as a general analytical method. Naturally, detection sensitivity can differ depending on the analytical instrument used, but various methods exist to increase the sensitivity of conventional analytical methods. In MSTips No. 413, an MMI was used to examine the effect of cold splitless injection on sensitivity, in contrast to conventional hot splitless injection. In MSTips No. 414, the effect of the EPIS on sensitivity was compared to a standard EI ion source. The results of each study showed a certain level of sensitivity improvement compared to the conventional method, but these methods can be applied simultaneously and further improvement in detection sensitivity can be expected due to an additive effect. In this study, the results of a comparison of the detection sensitivity enhancement effect by an analysis combining the cold splitless injection of an MMI as the GC sample injection method and the enhanced performance ion source (EPIS).

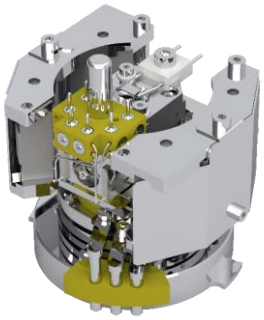
Experimental

1. Sample Conditions

Standard reagents : Pesticide Mixture Standard Solution PL-1,2,3,4,5,6,9,10,11,12,13 made by FUJIFILM Wako Pure Chemical Co.

Sample concentration : Pesticide mixed standard solutions were prepared at 0.1, 0.5, 1, 2, 5, 10, and 20 ppb

Sample volume : 2 µL (+ 0.2 µL co-injection of analyte protectants : SFA10mix made by Hayashi Pure Chemical Industry Co.)



EPIS

2. GC Conditions

Gas chromatograph : 8890GC (Agilent Technologies, Inc.)
Inlet mode : Cold splitless mode
Inlet temperature : 60 ° C (0.01 min) → 320 ° C (200 ° C / min, 10 min) → 60 ° C (200 ° C / min, 0 min)
Column: VF-5MS (length : 30 m, inner diameter : 0.25 mm, film thickness : 0.25 µm)
Oven temperature : 50 ° C (1 min) → 125 ° C (25 ° C / min, 0 min) → 300 ° C (10 ° C / min, 10 min)
Flow rate : 1.0 mL/min (constant flow)

3. MS Conditions

Mass spectrometer : JMS-TQ4000GC (JEOL Ltd.)
Ion source : EPIS
Measurement mode : SRM
SRM mode : High-sensitivity mode
Ion source temperature : 280 ° C
Interface temperature : 300 ° C
Ionization voltage : 70 eV

JMS-TQ4000GC

Results

Of the 292 analytes, a total of 283 analytes were detectable at 0.1 ppb using the conventional method (hot splitless mode + standard EI ion source) (see MSTips No. 413 for a list of compound names and retention times of all 283 detectable analytes). There were nine components that were difficult to detect at 0.1 ppb by conventional methods: procymidone, acetamiprid, halfenprox, imibenconazole, bifenox, flumiclorac pentyl, azoxystrobin, propaquizafop, and thiacloprid. Conversely, when cold splitless mode and the EPIS were applied simultaneously, all the components for measurement were detectable at 0.1 ppb, and a significant improvement in sensitivity due to the additive effect was observed compared to the results when each of the methods was applied alone (MSTips No. 413 and 414).

JEOL Ltd.
3-1-2 Musashino Akishima Tokyo 196-8558 Japan Sales Division Tel. +81-3-6262-3560 Fax. +81-3-6262-3577
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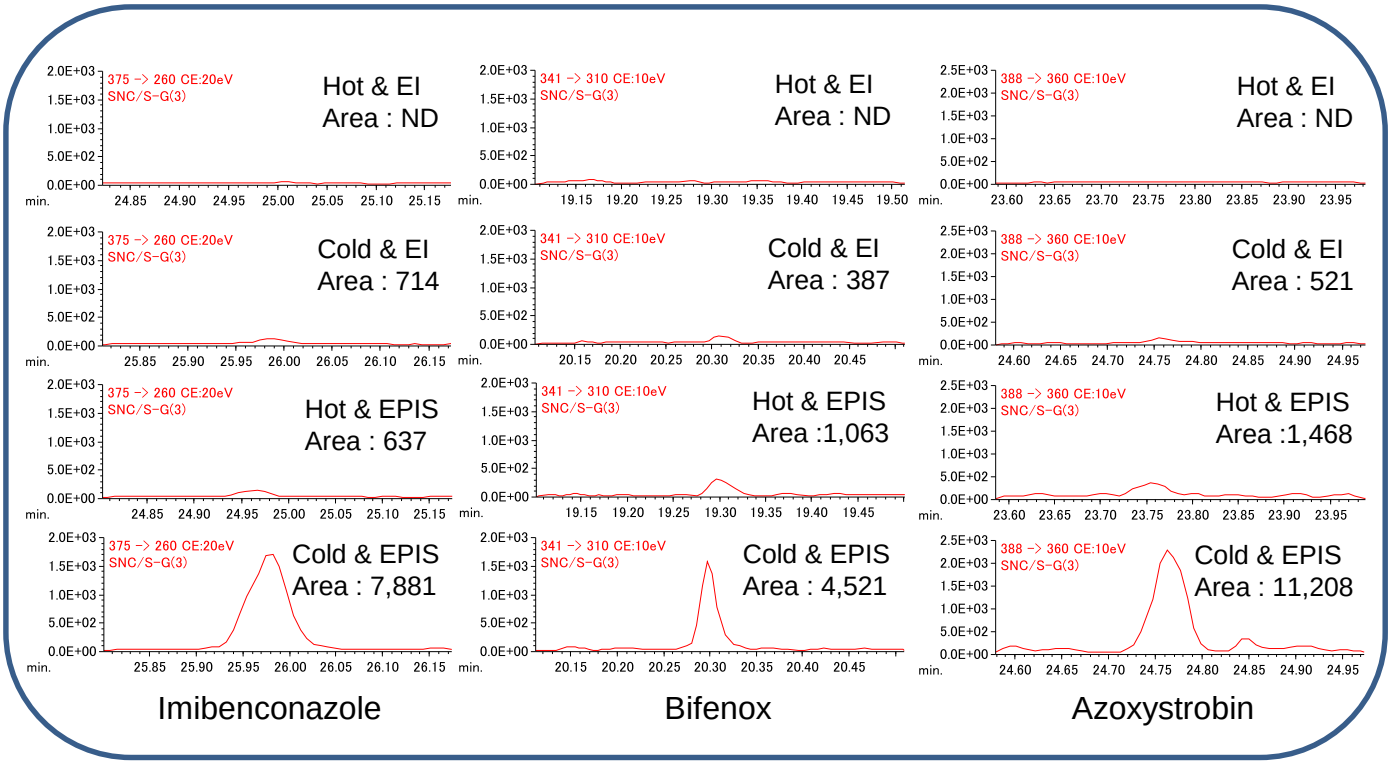
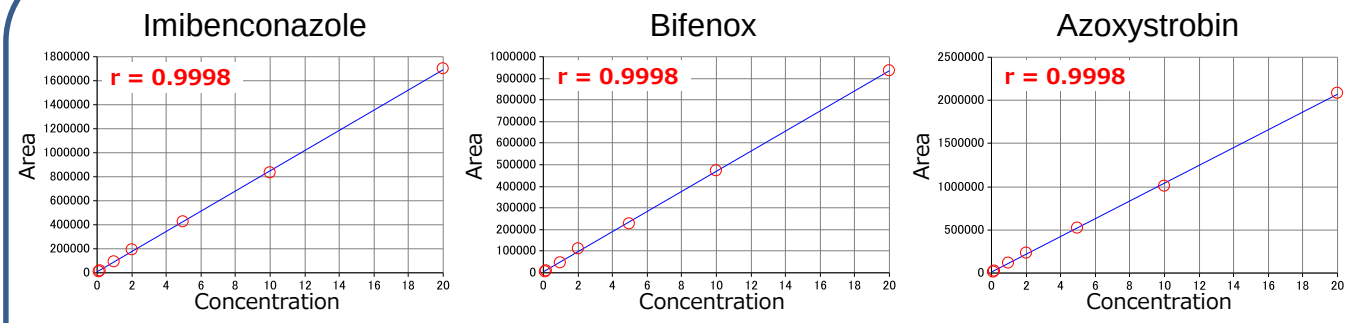


Fig.1 Comparison of EICs at 0.1ppb (Hot / Cold splitless and EI / EPIS)



Conc. [ppb]	Area
0.1	7,881
0.2	19,985
1.0	92,937
2.0	194,468
5.0	423,286
10.0	833,118
20.0	1,702,296

Conc. [ppb]	Area
0.1	4,521
0.2	10,996
1.0	47,886
2.0	109,935
5.0	228,466
10.0	471,275
20.0	937,454

Conc. [ppb]	Area
0.1	11,208
0.2	26,804
1.0	113,165
2.0	232,951
5.0	523,004
10.0	1,010,108
20.0	2,089,063

Fig.2 Calibration curves by using Cold splitless and EPIS

As an example, Fig. 1 shows an EIC comparison at 0.1 ppb for imibenconazole, bifenox, and azoxystrobin, and Fig. 2 shows calibration curves and a list of area values calculated from the data obtained using cold injection and the EPIS. In addition, in order to compare the effect of this method on sensitivity improvement, peak area ratios were calculated for the 283 components that could be detected at 0.1 ppb by the conventional method, and a scatter diagram arranged in retention time order is shown in Fig. 3. At the same time, the measurement results of MSTips No. 413 and 414 are also shown as a summary of the results of a series of studies on sensitivity improvement.

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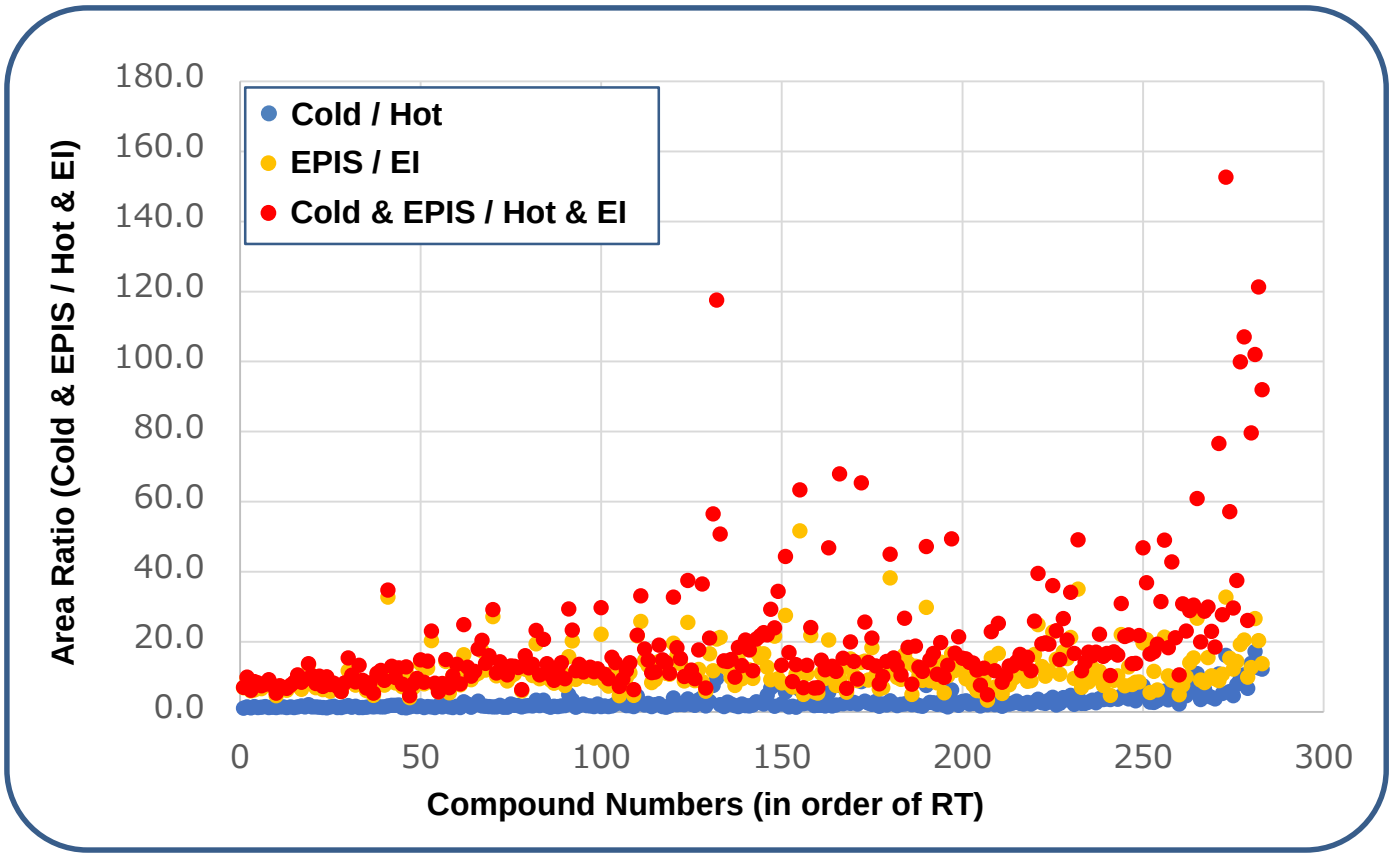

Fig.3 Scatter diagram of each compound and area ratio (Cold & EPIS / Hot & EI)

It has already been reported (MSTips No. 413, 414) that the application of cold splitless mode or EPIS enables peak detection even for components that were not detected using convention methods. When cold splitless mode was applied, area ratios tended to increase more for later-eluting compounds (MSTips No. 413), and when EPIS was applied, area ratios increased over the entire measurement time (MSTips No. 414). Each technique alone resulted in sensitivity improvement up to 50 times greater for some compounds compared to data obtained using conventional methods; however, using both techniques in the same analysis resulted in area ratio increases over 100X for later-eluting compounds.

The application of both techniques simultaneously suppresses the decomposition and adsorption of the target component in the GC injector and increases the amount of ions generated in the MS ion source chamber, resulting in a significant increase in the amount of ions reaching the detector compared to the conventional method. Because of the excellent dynamic range of the instrument, calibration curves generated under the present measurement conditions exhibit good linearity and correlation (Fig. 2). Increasing the amount of ions not only improves detection sensitivity, but also improves the reproducibility of the detected peak area, making this method particularly effective for simultaneous analysis of multiple components at extremely low concentrations, as in this study.

Conclusion

As part of a study on increasing sensitivity in the analysis of pesticide residues using GC-MS/MS, the detection sensitivity of hot splitless injection, which is the most common injection method for GC, was compared to cold splitless injection using MMI. In addition, the performance of the standard EI ion source and the EPIS were also compared, as well as a comparison of the detection sensitivity when both EPIS and cold-splitless injection are used in combination. When both methods were applied simultaneously, area ratio increases of over 100X were observed, and could be a very effective method for stable measurement of trace analytes. In the future studies, the effect of changing the GC carrier gas to an alternative carrier gas will be investigated.

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