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Application News

Liquid Chromatograph Mass Spectrometer LCMS-9050/9030
Kit for Direct Probe Ionization Mass Spectrometer DPiMS™ QT

Analysis of Fungicide on the Peel Surface of Imported Oranges (1) —Identifying Substances by Simple Pretreatment and Accurate Mass Analysis—

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User Benefits

- The presence or absence of target substances on target surfaces can be determined easily.
- Using Q-TOF accurate mass analysis, substances can be identified with only simple pretreatment.

■ Introduction

Due to the long transport time of agricultural products imported to Japan from overseas, post-harvest pesticides are applied after agricultural products are harvested to prevent mold or decay during transport. However, Japan prohibits the importation, use, or sale of foods with unapproved post-harvest pesticides. Therefore, inspection technologies that require only simple pretreatment and operating steps to determine whether or not post-harvest pesticides were used are expected to achieve shorter inspection times and result in shorter overall transport times.

This article describes an example of using an LCMS-9050 quadrupole time-of-flight (Q-TOF) mass spectrometer in combination with a DPiMS QT kit for a direct probe ionization mass spectrometer. The equipment combination shows that it detects post-harvest fungicide residues on the peel surface of imported oranges with a simple sample pre-treatment.

Fig. 1 LCMS-9050 and DPiMS™ QT

■ Pretreating the Peel of Imported Oranges

Enilconazole is a type of post-harvest agricultural chemical that is sometimes applied to citrus fruits imported to Japan. In Japan, post-harvest pesticides are considered food additives with regulated residual concentration levels. Therefore, a simple inspection method that can determine whether or not post-harvest pesticides have been used would result in shorter inspection times.

This article describes an experiment to determine whether DPiMS QT and LCMS-9050 mass spectrometers (Fig. 1) can be used to detect enilconazole applied to imported oranges. The probe electrospray ionization (PESI) method used in the DPiMS QT system is ionization technology that ionizes a micro quantity of liquid removed by a probe from samples inserted in a sample plate. The ions generated by ionization are then injected into the MS unit to analyze their masses (Fig. 2). Using the PESI method in combination with an LCMS-9050 system enables accurate mass analysis without any complicated sample pretreatment.

For the example described, the process steps used to pretreat the peel of imported oranges before they are analyzed are shown in Fig. 3.

In DPiMS QT analysis, it is necessary to set two parameters for probe actuation and the mass spectrometer. The analytical conditions for this example are indicated in Tables 1 and 2.

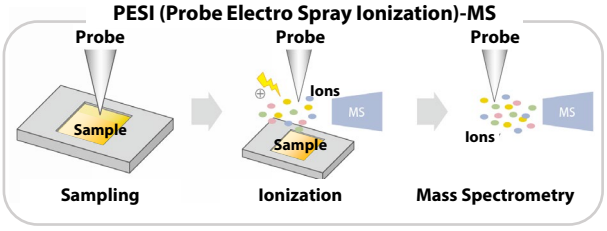
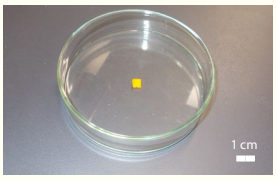
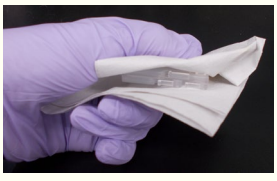


Fig. 2 Principle of Probe Electrospray Ionization (PESI)



1. An analysis sample was cut into a 5 × 5 mm square 1 to 2 mm thick.

2. Then the sample was placed with the surface to be analyzed facing upward in the circular indentation area indicated with an arrow on the biological sample plate.



3. The plate was closed by folding it in half.

4. 35 µL of solvent was added via a hole in the plate and then the sample was analyzed.

A video showing the pretreatment process is also available.
(Starts from 0:48.
The narration is in Japanese.)

Fig. 3 Imported Orange Peel Pretreatment Method Using Biological Sample Plate
The same method can also be used to analyze many other samples that can fit inside the folded plate.

■ Identifying Substances by Accurate Mass Analysis

Fig. 4 shows the results from integrating average chromatogram obtained from analyzing a standard sample. A peak consistent with the exact mass peak *m/z* 297.0555 of the protonated form of enilconazole was detected. The compound includes Cl, it shows a characteristic isotope distribution (indicated by ▼ marks in Fig. 4).

Next, the orange peel surface was pretreated by the method shown in Fig. 3 and analyzed. The mass spectrum in Fig. 5 shows that many substances were detected in the material extracted from the peel surface. An enlargement of part of the spectrum shows not only peaks that match the *m/z* for enilconazole standard sample, but also match the distribution of characteristic isotope peaks. Those results show that enilconazole is present on the orange peel surface.

Table 1 Probe Actuation Parameters

Ionization Position:	–37 mm
Ionization Stop Position:	160 msec
Sample Acquisition Position:	–46.0 mm
Sample Acquisition Stop Time:	30 msec
Probe Speed:	300 mm/s
Probe Acceleration:	0.86 G

■ Conclusion

This article describes using DPiMS QT and LCMS-9050 systems to determine the presence or absence of the post-harvest pesticide enilconazole, commonly applied to the peel surfaces of imported oranges, based on accurate mass measurement and the characteristic distribution of isotopes without any special pretreatment steps. The simple pretreatment method used for the DPiMS system in combination with the accurate mass measurement obtained from the Q-TOF system provides an extremely powerful tool for quickly identifying target substances. The technique described in this article can also be used to analyze all sorts of other samples that can fit inside the folded plate, which can be expected to be useful in a wide range of fields.

In addition, it is easy to switch between DPiMS QT and LC/MS analysis. Therefore, the approach can also be used to reduce the number of samples tested by using the DPiMS system to initially screen samples by qualitative analysis before LC/MS quantitative analysis.

Table 2 MS Analytical Conditions

DL Temp.:	250 °C
Heat Block Temp.:	50 °C
Interface Voltage:	+2.50 kV (ESI – positive mode)
Scan Range:	*m/z* 50 to 1000
Measurement Time:	0.5 min

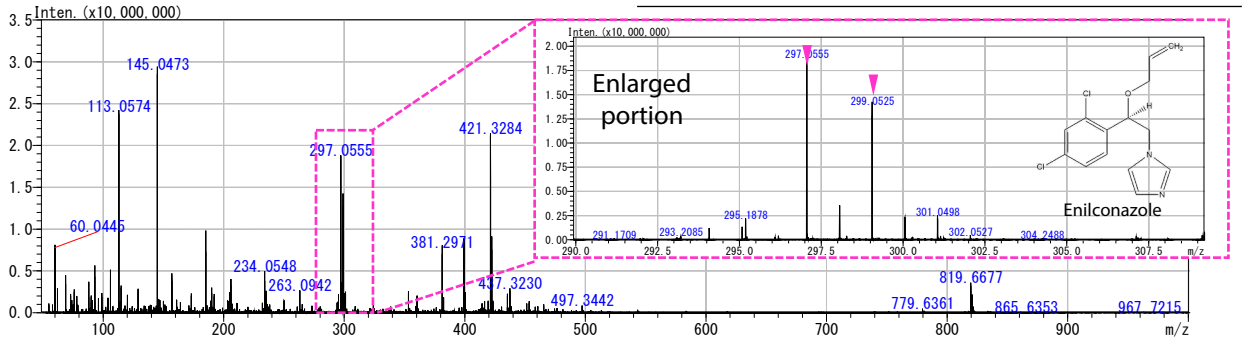


Fig. 4 Mass Spectrum of 0.1 ppm Enilconazole Standard Sample
▼ : Peak from enilconazole

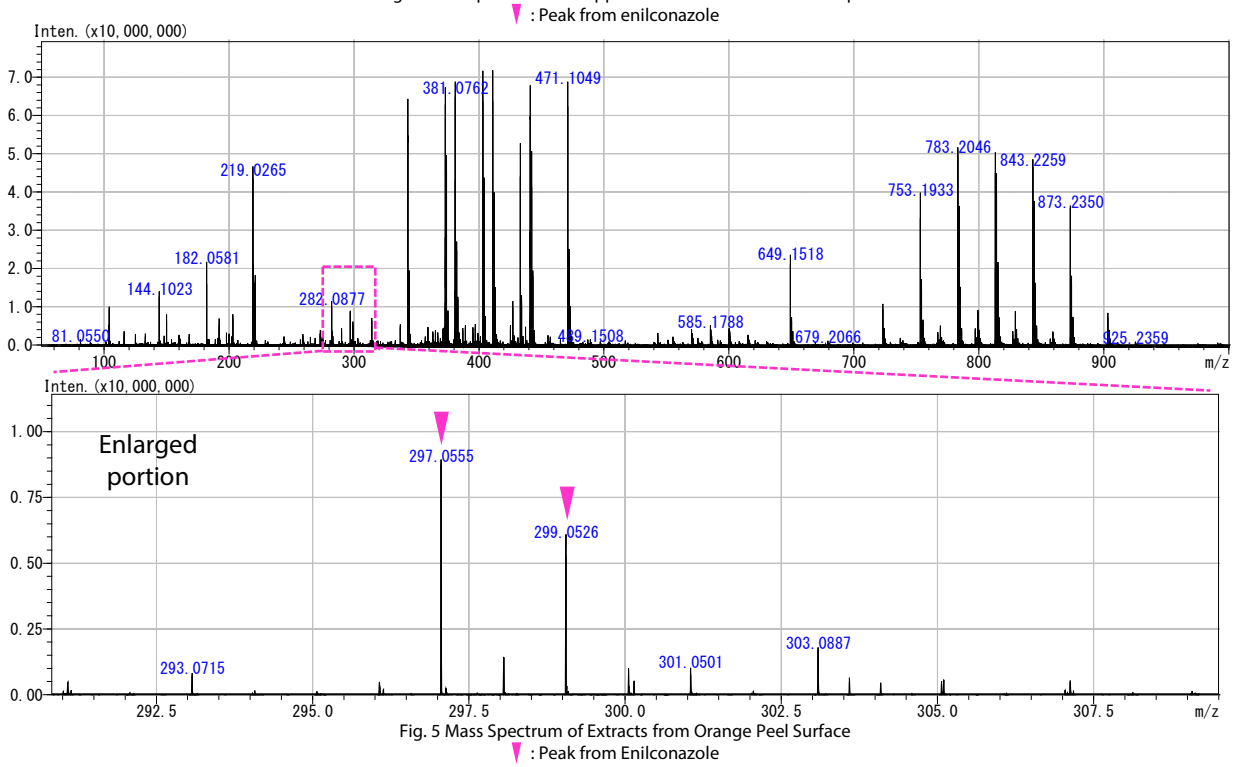


Fig. 5 Mass Spectrum of Extracts from Orange Peel Surface
▼ : Peak from Enilconazole

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