SHIMADZU
Excellence in Science

Application News

No. B115

DPiMS-2020

Analysis of Antifungal Agent on Surface of Imported Orange

The transportation of agricultural products imported into Japan from overseas requires considerable time. In such a case, some agricultural products are sprayed with postharvest agricultural chemicals to prevent mold and decay in the transportation process after harvesting. As Japan prohibits the importation, use, and sale of food products in which undesignated postharvest agricultural chemicals have been used, a technology that makes it possible to conduct inspections to identify postharvest agricultural chemicals by a simple sample preparation and testing procedure can shorten the inspection time, and as a result, is expected to lead to a shorter transportation time.

This article introduces an example of detection of an antifungal agent, which is used as a postharvest agricultural chemical, on the surface of an imported orange with simple sample preparation by using a DPiMS™-2020 direct probe ionization mass spectrometer and a biological sample plate.

K. Waki, H. Saiki

Sample Preparation of Imported Orange Skin

The antifungal agent enilconazole (Fig. 1), which is one type of postharvest agricultural chemical, is sometimes used on citrus fruits imported into Japan. In Japan, postharvest agricultural chemicals are treated as food additives, and their residual concentrations are regulated. Therefore, a simple inspection method for determining whether postharvest agricultural chemicals have been used or not would lead to a shorter inspection time.

In this experiment, enilconazole sprayed on an imported orange was detected by using a DPiMS-2020 direct probe ionization mass spectrometer (Fig. 2). The probe electro spray ionization (PESI) method is a technology in which a probe is used to extract and ionize a trace amount of a liquid from a sample deposited on a sample plate, the formed ions are introduced into the mass spectrometry section, and a mass spectrometry analysis is conducted (Fig. 2). Therefore, it is possible to carry out an MS analysis with only simple sample preparation. Fig. 3 shows the workflow of sample preparation of the skin of the imported orange used in this analysis.

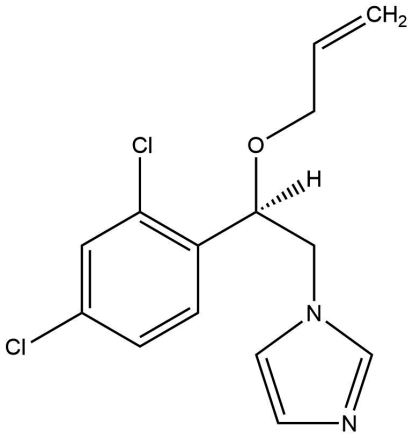


Fig. 1 Structural Formula of Enilconazole

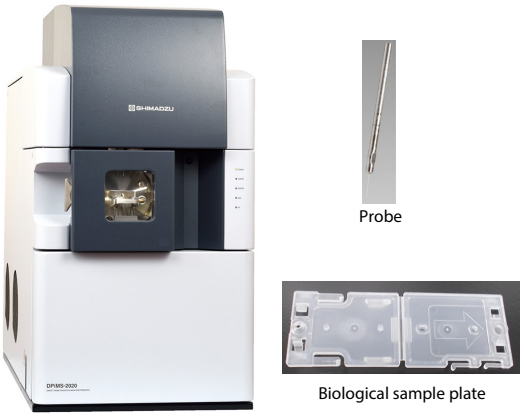
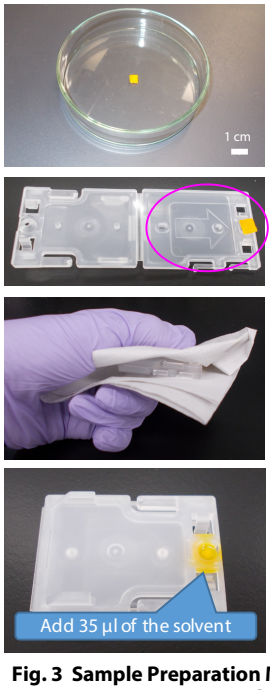


Fig. 2 Appearance of DPiMS™-2020 and Principle of Probe Electro Spray Ionization Method
The probe is inserted into the sample on the sample plate, and the sample molecules are ionized by applying a voltage to the sample adhering to the probe surface.



1. Cut the sample to a 5 mm square shape with a thickness of 1 to 2 mm.
2. Set the sample in the circular hollow with the arrow on the biological sample plate so that the sample surface which is to be analyzed is facing upwards.
3. Fold the plate in two and close.
4. Add 35 µL of the solvent to the hole in the plate, and then analyze.

Fig. 3 Sample Preparation Method of Skin of Imported Orange Using Biological Sample Plate
If the sample is inserted between the plates, analysis is possible by the same method.

Analysis by DPiMS-2020

In the analysis by the DPiMS-2020, the probe operation conditions and the mass spectrometry conditions are set. In this experiment, the analysis was conducted under the conditions shown in Table 1 and Table 2. Fig. 4 A shows the result of integration of the average of chromatograms obtained by analysis of the standard sample. The isotopic ion at *m/z* 297, which is specific to enilconazole, could be confirmed by analysis by the DPiMS-2020 (Fig. 4 A'). Next, the skin of one orange was sampled from two points, sample preparation was carried out by the method shown in Fig. 3, and the respective samples were analyzed. Enilconazole was detected from the skin at one location (Fig. 4 C), but was not detected at the other location (Fig. 4 B), and the isotopic ion of enilconazole was also detected (Fig. 4 C). It is thought that the difference in the results depending on the sampling position of the skin of this imported orange derives from uneven spraying of the enilconazole on the imported orange.

In this method, it is possible to identify the positions where a target chemical exists because the measurements are conducted by sampling a small region of the target.

Conclusion

As described in this article, the presence or absence of the postharvest agricultural chemical enilconazole sprayed on the skin of an imported orange could be confirmed without special sample preparation by using the DPiMS-2020 direct probe ionization mass spectrometer. This technique can be used as a simple screening technique for target substances, and can also be expanded to quantitative analysis by use in combination with an LC-MS/MS. This method can be applied to various types of samples if the sample is enclosed between the plates of the biological sample plate, and is useful in cases where it is necessary to determine quickly whether a target substance exists in a sample or not. Use as a screening technique for target compounds for subsequent quantitative analysis by LC-MS/MS is also expected.

Table 1 PESI (Probe) Drive Conditions

Ionization position	: -37 mm
Ionization stop time	: 200 msec
Sampling position	: -44.5 mm
Sampling stop time	: 50 msec
Probe speed	: 250 mm/s
Probe acceleration	: 0.63 G

Table 2 Mass Spectrometer Analysis Conditions

DL temperature	: 250 °C
Heating block temperature	: 50 °C
Interface voltage	: +2.45 kV (ESI – Positive mode)
Sampling stop time	: 50 msec
Scan speed	: 5000 µ/s

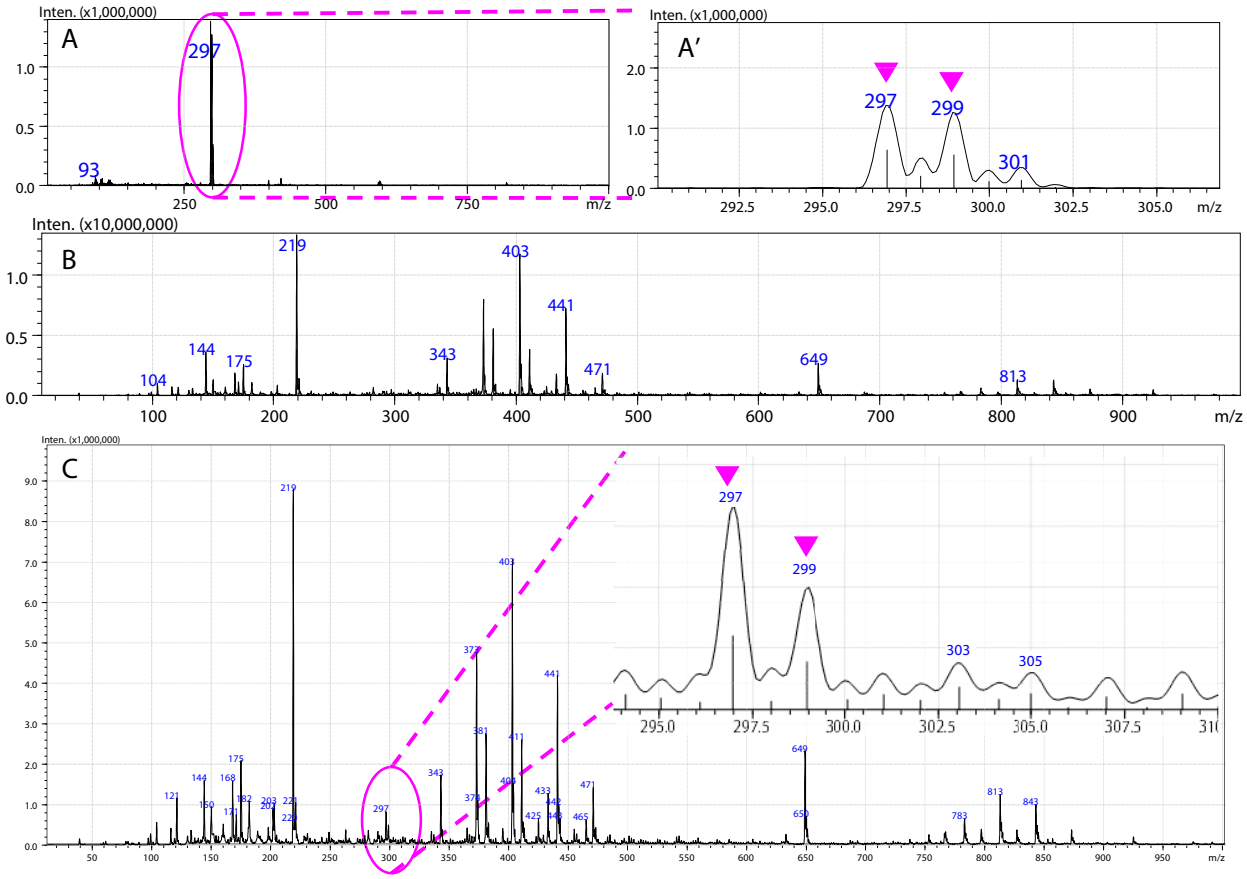


Fig. 4 Mass Spectra of Enilconazole in Samples
A: Enilconazole standard sample; A': Enlarged view of area around *m/z* 297 in A;
B, C: Mass spectra obtained by analysis of skin surface of a Minneola tangelo

First Edition: Feb. 2021

Shimadzu Corporation
www.shimadzu.com/an/