

Evaluation on Application of MS Imaging to Industrial Chemical Fields Using Dithranol Deposition Method

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User Benefits

- ◆ The dithranol deposition method with iMLayer can produce finer and more uniform crystals than the spray method.
- ◆ The dithranol deposition method with iMLayer has improved the quality of MS images of DVD dyes, compared to the spray method.
- ◆ The dithranol deposition method with iMLayer can reduce the effect of impurities in dithranol, compared to the spray method.



Fig. 1 iMLayer™



Fig. 2 DVD Used as a Sample

■ Introduction

Dithranol is one of the matrices indispensable for MALDI-MS measurements of polymeric materials and industrial chemicals since it is well-suited for ionization of non-polar polymers. However, commercially available dithranols are known to contain impurities, and it is therefore necessary to examine whether these impurities interfere with the ionization of analytes. Moreover, the spray method, a simple matrix coating method, has a drawback in that the matrix crystals are coarse and reduce the spatial resolution in MS imaging. In contrast, the vapor deposition method can produce uniform and fine matrix crystals, and thus maintain high spatial resolution.

The Shimadzu iMLayer matrix vapor deposition system (Fig. 1) has good reproducibility since it can control the amount of matrix applied by controlling the coating thickness. It can also set the heating temperature according to the matrix, and is therefore expected to reduce the contamination of impurities with higher sublimation temperatures. This article introduces an evaluation study aimed at suppressing impurity peaks of dithranol and improving its spatial resolution.

■ MS Imaging Analysis of the Dyes in Commercially Available DVD

A DVD (Fig. 2) is roughly composed of a protective layer made of materials such as polycarbonate, a reflective layer, a dye layer and so on. In this study, we analyzed the dye (m/z 587.4) that was peeled off along with the reflective layer of the DVD. Note that we extracted this dye beforehand and confirmed that it can be ionized by dithranol.

A DVD fragment (approx. 10 × 25 mm) with its reflective layer exposed was attached to an ITO glass slide with a conductive tape, and used as a sample.

As the deposition conditions for dithranol, the coating thickness was set to 0.8 μm by adapting the DHB conditions. The sample was coated by loading 170-180 mg of dithranol into the deposition boat where the matrix powder should be set. For the spray condition, 5 mL of 0.2% dithranol/THF was applied to almost the entire sample surface with an airbrush (H&S Infinity, 0.15 mm bore diameter), and the center area of the sample was analyzed. The measurement pitch for MALDI-TOF-MS analysis was 200 μm.

Fig. 3 shows a comparison of the matrix crystal structure on the surface of the samples made by the vapor deposition method and by the spray method, using a digital microscope. It can be observed that the vapor deposition method produces small and fine crystals (Fig. 3-a), while the spray method produces rough crystals with a diameter of about 50 μm on the sample surface (Fig. 3-b).

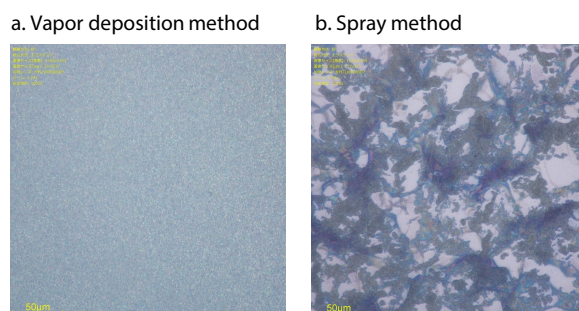


Fig. 3 Differences in Surface States of Matrix Crystals

Furthermore, it was also confirmed from the mass spectrum shown in Fig. 4 that the vapor deposition method was able to suppress dithranol brown (dianthrone), which is known as an impurity in dithranol (Fig. 4). Comparison of the mass imaging of the dye (m/z 587.4) (Figs. 5-a and 5-b) also confirmed the improvement in image quality, suggesting that MS imaging using the vapor deposition method is useful in the chemical industry field.

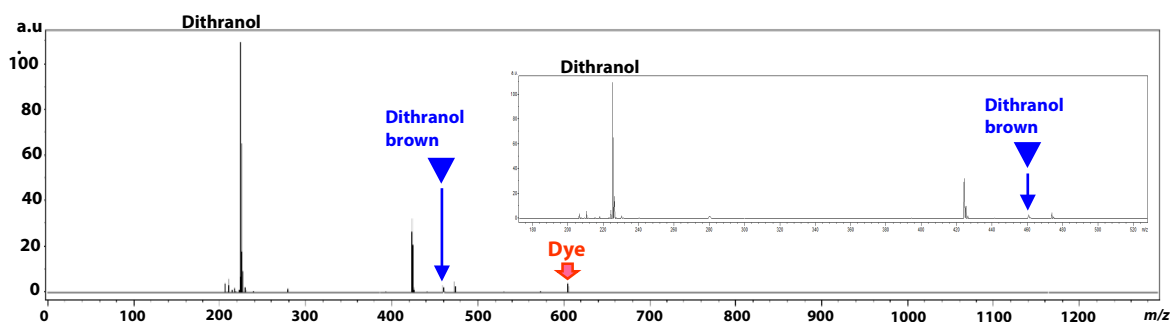
Conclusion

In this study, it was confirmed that the effect of impurities on dithranol was reduced by the vapor deposition method, and also the intensity of the dye peak was increased, resulting in improved contrast of the MS image. Since the effectiveness of the vapor deposition method was confirmed for dithranol, we will consider adding a new deposition method of dithranol to the three standard methods: CHCA, DHB, and 9-AA, already implemented in iMLayer.

<Acknowledgment>

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a. Vapor deposition method (matrix coating with iMLayer): Coating thickness of 0.8 μm



b. Spray method (matrix coating with airbrush): Spraying 5 ml of 0.2 % dithranol/THF

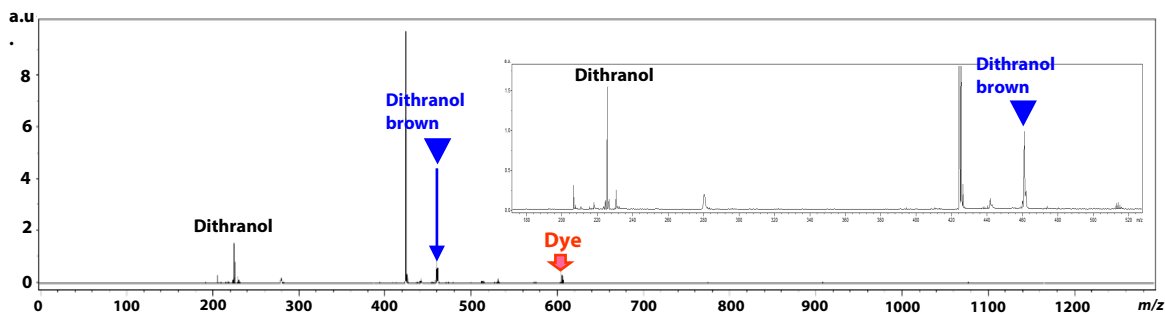


Fig. 4 Mass Spectra

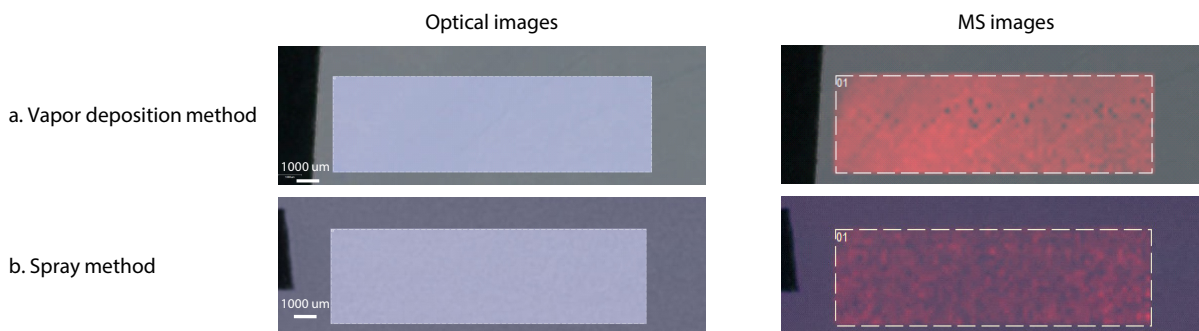


Fig. 5 Optical Images of the MS Analysis Region and MS Images of the Dye (m/z 587.4)

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